RHODIUM-CATALYZED AND UNCATALYZED SYNTHESIS OF BORONATE ESTERS AND THEIR SUBSEQUENT UTILITY IN THE SUZUKI REALM

Submitted in fulfilment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

By

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THESIS DECLARATION

I hereby certify that this research is a result of my own investigation, which has not already been accepted in substance for any degree and is not being submitted in candidature for any other degree.

Signed…….....

Siphamandla Wiseman Hadebe (Candidate)

I hereby certify that this statement is correct

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My sincere gratitude and appreciation must extend to a number of people, without whose help and encouragements this Doctoral Thesis would never have been achieved.

- A special thanks to my parents, Mr and Mrs Hadebe for their infinite patience, love and support. Mr and Mrs Hlubi, Mr A. S. Hadebe (my son), Ms A. K. Hadebe (my daughter), Ms M. E. Litedu and my entire family for their love and support for the duration of this work.

Ngibonga uMvelinqangi nani bo-Bhungane, oSigoloza nabanye, ngakhokonke eningenzele kona.

ABSTRACT

This study has shown that alkythioboranes 1,3,2-dithiaborolane and 1,3,2-dithiaborinane, disproportionated significantly during their synthesis. Their interaction with 1-octene has been investigated, and the rate constants, enthalpies and entropies of the hydroboration process, have been determined. The thermodynamic and kinetic parameters obtained have shown that the hydroboration reaction is sluggish and proceeded *via* an associative mechanism.

The observed hydroboration and disproportionation reactions have been corroborated using the ground state density functional theory (DFT) at B3LYP/3-21+G and 6-31+G(d) levels, which has shown that although hydroboration reactions require slightly higher activation energies than disproportionation, but, yielded thermodynamically more stable products. This study has also demonstrated that these heterocyclic compounds have enough kinetic and thermal energy to undergo disproportionation at room temperature. A systematic study of aromatic derivatives has shown that the reactivity of substituted boranes is determined by the availability of the empty p_z orbital of the boron atom. Thermodynamic data including the activation energies, activation enthalpies, Gibbs free energy of activation and the entropy of activation for the hydroboration reaction of propene with aliphatic, cyclic and aromatic derivatives of oxygen-, sulfur-, and nitrogen-based hydroborating agents were determined using DFT.

The use of Wilkinson's catalyst in conjunction with microwave irradiation and the oxidized Wilkinson's catalyst have been shown to provide a convenient and rapid route to the terminal pinacolboronate ester from *trans*-4-octene and pinacolborane. Our study has also shown that the sulfur- and nitrogen analogues are significantly less prone to disproportionation than catecholborane during rhodium-catalyzed transformations. Their use resulted in enhanced yields of the desired compounds.

It has also been shown that nitrogen-based boronate esters are suitable coupling partners in Suzuki type chemistry, and furnish excellent yields upon the use of microwave irradiation in solvent free reaction conditions.

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PUBLICATION DECLARATION

The experimental and computational work discussed in the publications as well as the writing of the publications was performed by me and was carried out within the School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg, under the supervision of Dr Ross S. Robinson. I was the primary author for the publications 1 to 7 and minor grammatical changes were performed at a later stage by me under the suggestion of my research supervisor. Titles and full literature references for these publications are as follows.

1. *A mechanistic study of hydroboration of 1-octene with 1,3,2-dithiaborolane and 1,3,2-dithiaborinane,* **Part 1**, Hadebe, S. W.; Robinson, R. S. *S. Afr. J. Chem.* **2008**, MS 683, accepted for publication.

2. *A mechanistic study of hydroboration of 1-octene with 1,3,2-dithiaborolane and 1,3,2-dithiaborinane,* **Part 2**, Hadebe, S. W.; Robinson; H. G. Kruger, R. S. *S. Afr. J. Chem.* **2008**, MS 684, accepted for publication.

3. *Microwave mediated rhodium-catalyzed hydroboration of trans-4-octene with pinacolborane*, Hadebe, S. W.; Robinson, R. S. *Tetrahedron Letters* **2006**, *47*, 1299–1302.

4. *Rhodium-catalyzed hydroboration reactions with sulfur and nitrogen analogues of catecholborane*, Hadebe, S. W.; Robinson, R. S. *Eur. J. Org. Chem* **2006**, *21*, 4898–4904.

5. *Solvent-Free, Microwave-Assisted Suzuki-Miyaura Coupling of B-Alkyl-benzo-1,3,2-diazaborolanes*, Hadebe, S. W.; Robinson, R. S. *Org. Lett.* **2008**, article in preparation.

The writing of publication 6 below was performed by me under the guidance of Professor Orde Q. Munro who at a later stage assisted on editing, structural refinements, grammatical changes and software manipulations. Publication 7 was written by me and at a later stage, minor grammatical changes and software manipulations were conducted by me under the guidance of Professor Hendrik G. Kruger of the University of KwaZulu-Natal, Westville. Part of my research results constituted a section in publication 8 below,

written by Dr Arno de Klerk of Sasol Technology in collaboration with our research team at the University of KwaZulu-Natal, Pietermaritzburg. I was involved in writing the section that related to my research, and assisted in proof reading the entire paper. Titles and full literature references for these publications are as follows.

6. *A bis(benzenedithiolate)-bridged dinuclear Rh^{III} complex with capping triphenylphosphine ligands and an Rh_2S_2 core*, Hadebe, S. W.; Robinson, R. S.; Munro, O. Q. *Acta Cryst.* **2007**, *E63*, m175–m177.

7. *A DFT study of the hydroboration reaction with oxygen-, sulfur-, and nitrogen-based boranes*, Hadebe, S. W.; Kruger, H. G.; Robinson, R. S. *Theochem* **2008**, article in prepartion.

8. *Linear α-olefins from linear internal olefins by a boron-based continuous double-bond isomerization process*, der Klark, A.; Hadebe, S. W.; Robinson, R. S.; Govender, J.; Jaganyi, D.; Mzinyathi, A.; Xaba, N. *Ind. Eng. Chem. Res.* **2006**, 400– 410.

All publications declared above have been included in the text of this thesis as per faculty guidelines, and these studies represent original work by the author and have not otherwise been submitted in candidature for any other degree.

I hereby certify that this statement is correct

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December 2008

1.1 OVERALL PROJECT OBJECTIVES

The project is aimed at investigating the synthesis and ^{11}B NMR spectroscopic analysis of a range of sulfur, nitrogen and oxygen heterocycles (Figure 1.1), which in turn are to be evaluated in terms of their reactivity towards selected alkenes. The study was expected to shed light on the suitability of these reagents to mediate isomerisation and final displacement of the borolane to form the anticipated linear α-olefin.

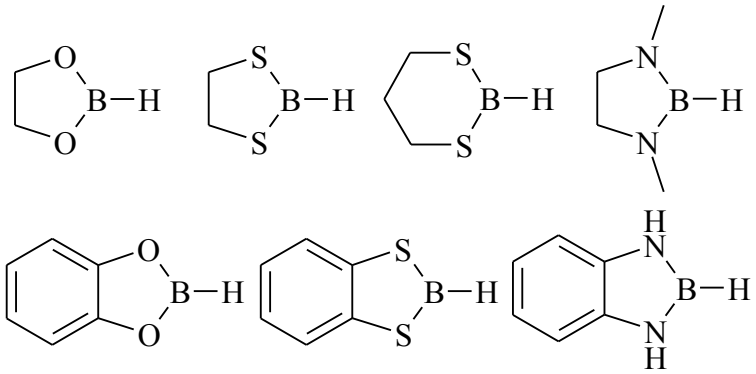


Figure 1.1

These results would ultimately assist in the potential evaluation of such electron deficient borolanes as possible reagents in an industrial process for the commercial production of linear α-olefins. The second part of the study was aimed towards the use of computational molecular modeling, with the intention to rationalise the hydroboration trends observed experimentally and lastly to investigate the utility of transition metal catalysis in hydroboration reactions and lastly the utility of the synthesized boronate esters in organic synthesis *via* the Suzuki-Miyaura cross coupling reaction.

1.2 IMPORTANCE OF LINEAR α-OLEFINS

Linear α-olefins are defined as straight chain hydrocarbons containing a double bond at the terminal or α-position. Alpha-olefins are commercially more valuable than the internal olefins; thus much interest has been focused towards the production of these compounds. Their chain lengths vary from C_4 (1-butene) to C_{30+}.[1] About 33% of α-

olefins are used in the polymer industry as polyethylene comonomers; 22% are used in detergent alcohols; 21% in synthetic lubricants and lube oil additives including polyalpha-olefins (PAOs); 10% in plasticizer alcohols; 3% in alkyldimethylamine and dialkylmethylamines; 2% are used in surfactants including linear α-olefin sulfonates and linear alkylbenzene; 2% in fatty acids and 7% in miscellaneous uses, including the production of mercaptans and alkenylsuccinic anhydrides (ASA).[2]

C.A. Houston & Associates, Inc. (CAHA)[3] studied the world market for α-olefins, and their study revealed that the consumption of LAOs (linear α-olefins) in direct end uses totalled 2.5 million tons in 2000 and forecast growth at an average rate of 6.6% per year to 2010. The study also indicated that the production capacity for α-olefins has increased from 2.4 million ton/year in 1997 to 3.2 million tons/year by year-end 2001, and was expected to reach 4.2 million tons/year by 2005, including both confirmed and potential new plants and expansions.[3]

CAHA, Inc.[3] also reported that the α-olefins market is facing a complex array of developments, including major new plants and expansions coming on stream in the 2000 - 2004 time frame. Currently, seven companies manufacture a range of α-olefins *via* the most important method for LAO production, that is, ethylene oligomerization and one company produces specific chain lengths from coal-derived synthesis gas.[3]

The new expansions included CpChem's new plant which started operating in 2000 in Texas;[2,3] BP brought a new plant on stream in Canada in 2001; and Shell's new plant was also commissioned in Louisiana in early 2002. There are also other new plants which were under consideration for the 2003 – 2005 time frame and these were proposed to be located in the Middle East, Asia and Africa.[3]

The latest report by CAHA[4] showed that the global market of alpha olefins has faced some challenges due to the closure of Ineo's Pasadena, Texas α-olefin plant at the end of 2005, that produced 505,000 ton/year which accounted for 14 % of the global capacity.[4] To date, CPChem, Shell and Ineo are still the three major companies that dominate the

global market. Idimitsu, Mitsubish and Nizhnekamskneftekhim produce LAO in smaller capacities. all six companies manufacture α-olefins *via* ethylene oligomerization.[4]

Further expansions have been underway in order to satisfy the demand for α-olefins. SABIC started up a new 150,000 ton/year plant in Saudi Arabia. Sasol was expected to double its capacity of 1-octene with a 100,000 ton/year plant, which was expected to be operational in 2007. CPChem jointly with Qatar Petroleum is expected to launch a new 350,000 ton/year plant producing a full range of LAO in 2008.[4]

Most of the linear α-olefin producers rely on ethylene oligomerization as a synthetic route, while other synthetic methods for α-olefin production are not considered to be economical routes and include alcohol dehydration, paraffin wax cracking, and internal olefin isomerization.[1]

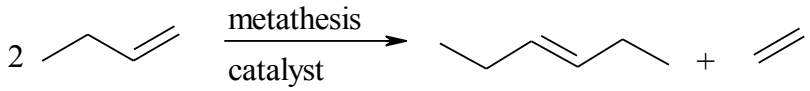
In South Africa, Sasol recovers both odd and even numbered α-olefins ranging from C_5 to C_8 from raw petrol streams produced in the Fischer-Tropsch process. Sasol is the sole commercial producer of 1-pentene in the world.[1]

1.3 **IMPORTANCE OF ISOMERIZATION TO SASOL**

It has been stated in the above section that about seven producers of α-olefins manufacture their product *via* ethylene oligomerization. At Sasol, the situation is very different as there are enormous quantities of internal olefins produced *via* metathesis and or linear dimerization of 1-butene and 1-pentene. This availability of internal olefin feed-stock is the driving force for the development of an internal olefin isomerization process.

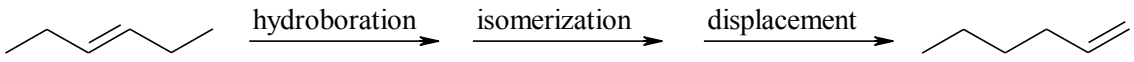
From a report by Grubbs *et al.,*[5] it has been shown that 1-alkene metathesis results in the cleavage of an olefinic carbon-carbon double bond of an alkene yielding the corresponding internal alkene and ethylene after reorganization of the fragments (Scheme 1.1). Sasol has excessive amounts of 1-pentene and 1-butene which undergo metathesis

as reported by Grubbs *et al*. to produce internal isomers, 4-octene and 3-hexene (Scheme 1.1) respectively.



Scheme 1.1

In the mid 1960s Brown and Batt showed that internal trialkylboranes can be isomerized and displaced at elevated temperatures to afford the corresponding 1-alkenes.[6] The key step in this process is hydroboration yielding the desired alkylborane. This is followed by isomerization and the final displacement (Scheme 1.2). However, the suitable hydroborating agents are not available commercially, and consequently these should be synthesized prior to hydroboration. The main objectives of this project are the synthesis of hydroborating agents, the investigation of their reactivity towards olefins including catalyzed transformations, and the computational search of transition states associated with the hydroboration reactions as well as the investigation of the suitability of boronate esters in coupling reactions.



Scheme 1.2

1.4 **REFERENCES**

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[2] http://www.the-innovation-group.com/ChemProfiles/Alpha%20Olefins%20(linear).htm [Date of access: 26 November 2008].

[3] C. A. Houston & Associates, Inc., *Alpha-Olefins-World Markets, 2000 – 2010 and Alpha-Olefin Market Intelligence Database*, web: http://www.caharesearch.com/ao/Alpha-Olefin_prospectus.pdf

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[4] C. A. Houston & Associates, Inc., *Alpha-Olefins-World Markets, 2005–2015*, web: http://www.colin-houston.com/files/Alpha-Olefin%20-%20World%20Markets,%202005-2015.pdf [Date of access: 26 November 2008].

[5] Grubbs, R. H; Pine, S. H.; Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, **1991**, *5*, chapter 9.3, 1115.

[6] Brown, H.C.; Batt, M. V. *J. Am. Chem. Soc.*, **1966**, *88*, 1440.

PREFACE

The demand and widespread applicability of α-olefins motivated the investigation into the possibility of employing hydroboration, isomerization and displacement to produce α-olefins. Other members of our research team have investigated hydroboration reactions using BH_3:SMe_2, haloboranes, borane dimers and boranes coordinated to different Lewis bases, with the intention of obtaining kinetic and thermodynamic data for this process.[1] The primary aim of this chapter was to investigate the use of hetero atom containing hydroborating agents in order to evaluate the role of hetero atoms in hydroboration reactions.

[1] (a) A. B. Mzinyati, *Thermal Transformations of Trialkylboranes and Hydroboration Kinetics of Functionalzed Alkenes*, M Sc Thesis, University of Natal, Pietermaritzburg, 2003. (b) J. R. Govender, *Mechanistic and Kinetic Study of the Hydroboration of 1-and 4-octene by Dialkylborane dimers*, M Sc Thesis, University of Natal, Pietermaritzburg, 2003. (c) N. Xaba, *Kinetic and Mechanistic Study of the Hydroboration Reactions of Selected Organic Compounds with HBBr2:SMe2 and H2BBr:SMe2 complexes: A comparison of the GC and 11B NMR Spectroscopy Techniques*, M Sc Thesis University of kwaZulu Natal, Pietermaritzburg, 2004.

2.1 **INTRODUCTION**

2.1.1 **HYDROBORATION REACTIONS**

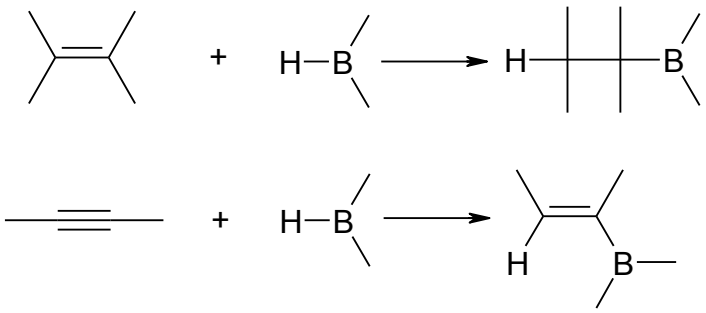
In 1956, the first examples of the hydroboration reactions were reported by Brown and Subba Rao.[i] These initial investigations showed that unsaturated organic compounds are rapidly converted into organoboranes when treated with diborane or diborane precursors in ethereal solvents providing new convenient routes to valuable organoborane derivatives (Scheme 2.1).[i,ii] Prior to these reports, the only practical synthetic route to organoboranes was the use of organozinc[iii] or organomagnesium[iv] compounds with the borohalide or ester.

$$9\ RCH{=}CH_2 + 3\ NaBH_4 + AlCl_3 \xrightarrow{DG} 3\ (RCH_2CH_2)_3B + 3\ NaCl + AlH_3$$

$$12\ RCH{=}CH_2 + 3\ NaBH_4 + 4BF_3 \xrightarrow{THF} 4\ (RCH_2CH_2)_3B + 3\ NaBF_4$$

Scheme 2.1

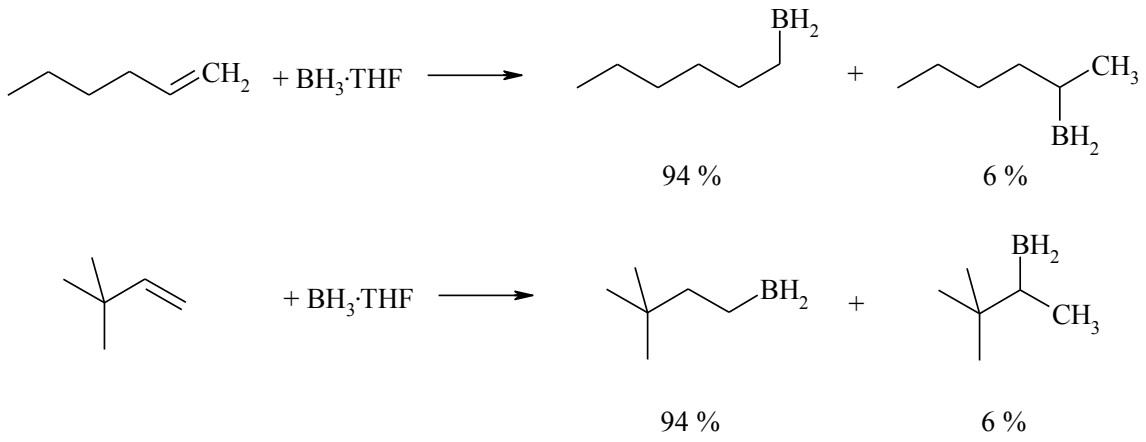
The hydroboration reaction involves a rapid and quantitative addition of the boron – hydrogen bond to the carbon – carbon double bonds of alkenes and carbon – carbon triple bond of alkynes (Scheme 2.2).[v]



Scheme 2.2

2.1.2 **REGIOSELECTIVITY IN HYDROBORATION**

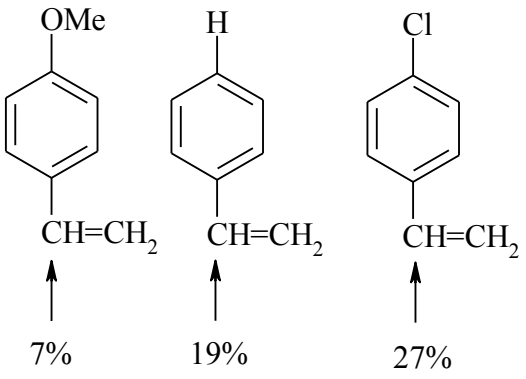
Brown and Zweifel[vi] showed that for simple 1-alkenes such as 1-hexene, the hydroboration reaction results in the placement of 94% of the boron atom on the terminal position and only 6% at the 2-position. This distribution is not affected significantly by branching of the alkyl group (Scheme 2.3).[vi]



Scheme 2.3

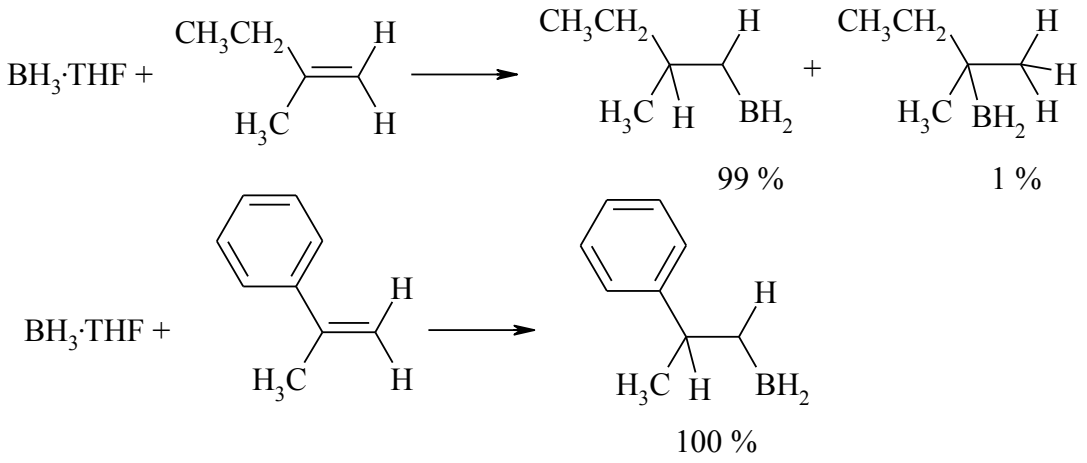
Their study also showed that the presence of aryl groups caused increased placement of the boron atom on the non-terminal position.[vi] However, this distribution is significantly changed by substituents on the aromatic ring. Alkoxy groups donate electrons into the benzene ring by resonance, leading to decreased placement of the boron at the non-

terminal position, compared with the halogens, which withdraw electrons inductively from the ring, leading to an increase in the placement of the boron atom in the non-terminal position (Scheme 2.4, shows the percentage distribution of the boron atom, from the reaction of BH_3·THF with the corresponding styrene).[vi]

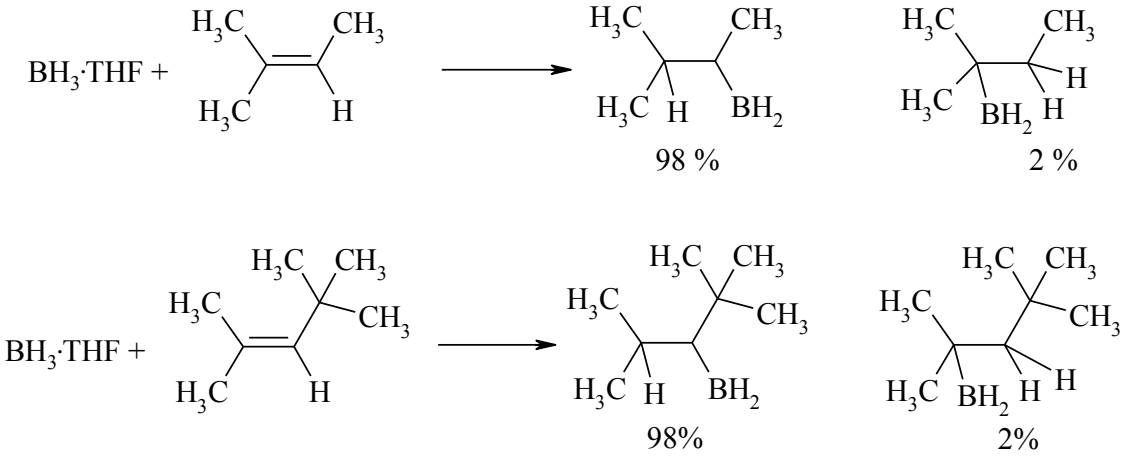


Scheme 2.4

Alkyl substituted alkenes were investigated with the intention to determine the effect of steric hindrance. It has been shown that an alkyl substituent present on the 2-position of the alkene enhances attachment of the boron atom to the terminal position as a result of steric hindrance (Scheme 2.5),[vi] Preference for the less substituted position is also exhibited in internal olefins (Scheme 2.6).[vi]



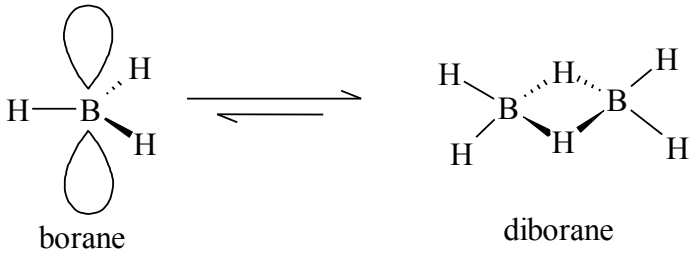
Scheme 2.5



Scheme 2.6

2.1.3 **MECHANISM OF HYDROBORATION**

The simplest boron hydride is borane, BH_3, where the boron atom is sp^2 hybridized with a vacant *p*-orbital which lies perpendicular to the plane of the three hydrogen bonds. As a result, borane is an electrophile, and reacting readily with electron-rich molecules.[vii] If the vacant *p*-orbital is not involved in any interaction with nucleophiles, the borane dimerizes to diborane B_2H_6 in an equilibrium that favours diborane (Scheme 2.7).[vii]



Scheme 2.7

In the 1960's Brown proposed the initial mechanism of hydroboration that involved a concerted four-centre transition state, between the olefinic double bond and the dissociated molecule of borane (Figure 2.1 **A**).[v] In the 1970's Fehlner's[viii] gas phase kinetic studies disputed Brown's mechanism. A year later, Jones[ix] studied the

hydroboration mechanism based on symmetry considerations, with the aim to rationalize the mechanism. However, results obtained showed that the proposed four-centre transition state (Figure 2.1 **A**) has significant symmetry barriers and suggested a three-centre electron-deficient bond implied by π-complex formalism (Figure 2.1 **B**).

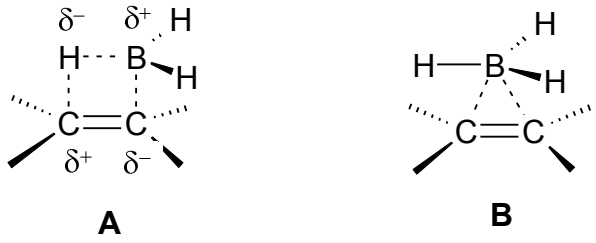
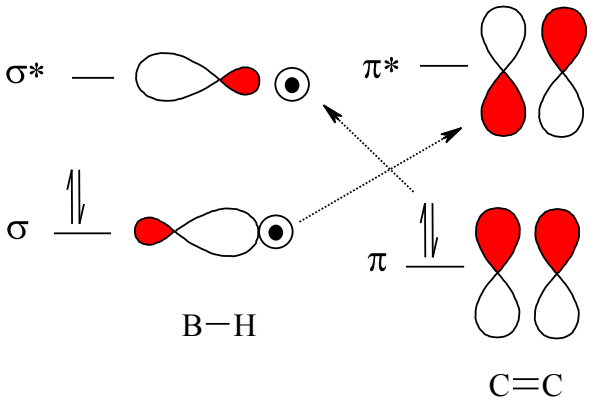


Figure 2.1

The mechanism proposed for the traditional 4-centre transition state complex is expected to go through a concerted flow of electrons from the π orbital of the alkene to the σ* orbital of the B-H bond, and from the σ B-H orbital to the π* orbital of the alkene (Scheme 2.8).[ix]

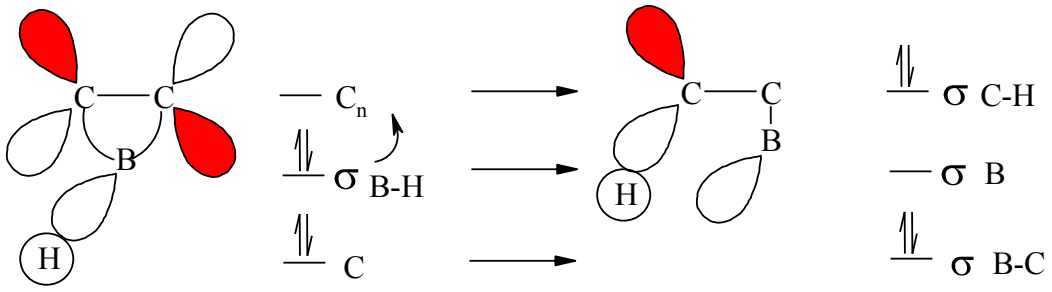


Scheme 2.8

This results in a very small net overlap between the pairs of orbitals, thus resulting in a symmetry restriction.[ix] The alternative π complex proposed by Jones (Figure 2.1 **B**), is formed through the interaction of π electrons from the olefinic double bond with a vacant

boron orbital,[ix] as is the case in the gas-phase reaction of borane with ethylene[viii] and this is a symmetry allowed process.

Arguments against the π complex intermediate (three-centre intermediate) are based on the assumption that the π complex must rearrange to a σ complex during the later stages of the reaction.[ix] The conversion is achieved through the electron flow from the σ system of the moiety involved in the π complex (boron in this case) to the C_n three-centre molecular orbital.[ix] A σ bond is formed between carbon and hydrogen as the C_n orbital is occupied, finally the carbon three centre bonding orbital of the complex becomes a boron-carbon σ bond (Scheme 2.9).[ix]

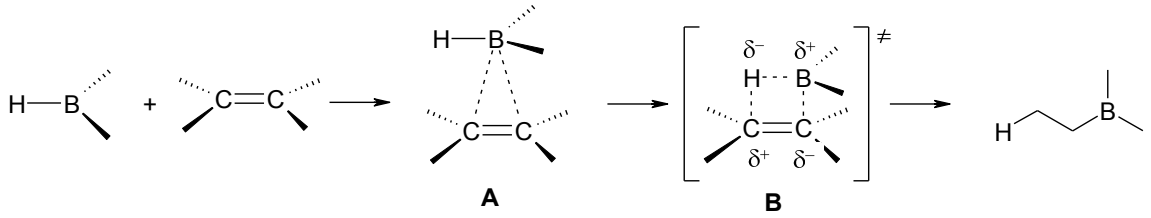


Scheme 2.9

Subsequent computational studies have been employed to further elucidate the hydroboration mechanism. A CNDO/2 study by Dasgupta *et al.*[x] supported the 3-centre π-complex. Dewer *et al.*,[xi] showed that the concerted [$_{\pi}2_s + {}_{\sigma}2_s$] addition of borane to an alkene is not a forbidden reaction because the vacant p-orbital on boron takes part in the process and removes symmetry restrictions. Electrons from the π orbital of an alkene are donated to the empty boron orbital and there is also a back-donation from the B-H bond to the π*-orbital and this process accounts for a concerted addition.

More advanced studies by Sunberg *et al.*,[xii] revealed a different perspective, this study reported a donation and back-donation mechanism resulting in a 3-centre π-complex **A** leading to the formation of a 4-centre transition state **B** (Scheme 2.10). This type of mechanism was supported by Nagase *et al.*[xiii] whose report proposed a two step process,

firstly the formation of a loose 3-centre π-complex in the early stage without any energy barrier. Secondly, the transformation of this complex into product *via* a 4-centre transition state takes place and it is this step that determines the reaction rate.[xiii]



Scheme 2.10

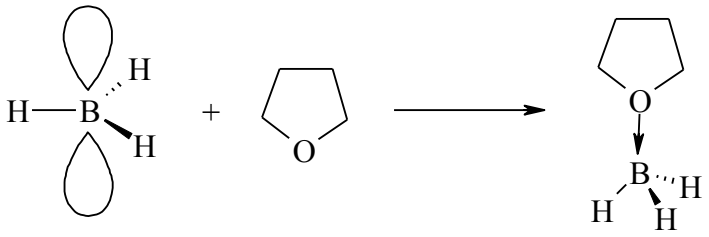
A range of alkenes were studied by Wang *et al*.,[xiv] whose findings also agreed with the presence of a 3-centre π-complex (precomplex) and then the 4-centre transition state. The question of solvent molecule participation in the transition state was addressed by Clark *et al*.[xv] through an *Ab initio* study of the reaction of ethylene with $BH_3 \cdot OH_2$ complex. This study concluded that the solvent played no role in the transition state, which agrees with Wang's report.[xvi] The finding of Clark *et al*. showed that the use of the reaction of BH_3 with olefins in the gas phase is in fact a reasonable model for hydroborations in solutions.[xv]

2.1.4 **PREPARATION OF HYDROBORATING AGENTS**

2.1.4.1 **UNSUBSTITUTED BORANES**

The electrophilicity of the boron atom in borane makes this compound combine readily with electron rich species, such as the solvent tetrahydrofuran (Scheme 2.11).[vii] The addition compound derived from dissolving diborane (B_2H_6) in THF is known as *Borane-tetrahydrofuran complex* ($BH_3 \cdot THF$).[xvii,xviii] It is the most stable of the ether complexes, the stability trend observed is $BH_3 \cdot THF > BH_3 \cdot OMe_2 > BH_3 \cdot OEt_2$.[xviii] Borane THF

complex is the most frequently used hydroborating agent, since it reacts very fast with a wide range of alkenes and alkynes at 0 ºC and below with predictable regiochemistry.



Scheme 2.11

Borane-dimethyl sulfide complex ($BH_3{\cdot}SMe_2$), and its derivatives show higher stability than the corresponding ether complexes. The following stability trend has been reported: $BH_3{\cdot}SMe_2 \geq BH_3{\cdot}SEt_2 > BH_3{\cdot}S(CH_2)_4$,[xix] borane-dimethyl sulfide complex is a better hydroborating agent than $BH_3{\cdot}THF$ due to its stability at room temperature and it can be obtained in concentrations 10 times that of commercial borane-THF solution.[xix] Excellent reactivity in a range of solvents, including hydrocarbons has also been observed.[xix] It is widely used in hydroboration and in the synthesis of a range of hydroborating agents.[xx,xxi]

Borane-1,4-oxathiane complex is a stable liquid at room temperature, and is readily synthesized by passing gaseous diborane directly into 1,4-oxathiane at 25 ºC to saturation.[xxii] The interaction with the *p*-orbital is through the sulfur heteroatom of 1,4-oxathiane. It hydroborates significantly faster than $BH_3{\cdot}SMe_2$.[xxii]

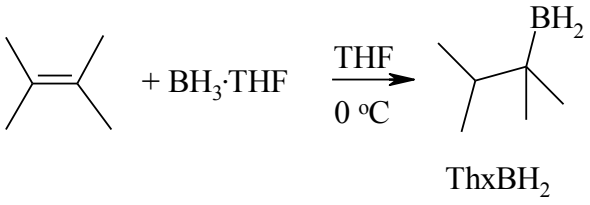
Borane-amine complexes. A wide range of amine-boranes can be achieved from the reaction of diborane with a desired amine in ethereal solvent.[xxiii] These compounds are very stable liquids or solids and are generally air stable. In addition, they are also soluble in a wide range of solvents, including water. The reactivity of these compounds can be modified by changing the structure of the amine molecule.[xxiii]

2.1.4.2 **ALKYL SUBSTITUTED BORANES**

A wide range of alkenes are transformed into trialkylboranes through hydroboration. However, the trifunctional nature of borane and its trialkyborane products causes limitations on its usefulness in organic synthesis. Trialkylboranes are useful in many synthetic reactions, but in reactions that require the formation of mono- or disubstituted boranes, the formation of trialkyborane reduces the products significantly.[vii] The use of monoalkylborane and dialkylborane surmounts this problem. Commonly used hydroborating agents are thexylborane, disiamyborane, 9-BBN, dicyclohexylborane, diisopinacampheylborane, dilongifolylborane, to name but a few.[vii]

2.1.4.2.1 **THEXYLBORANE**

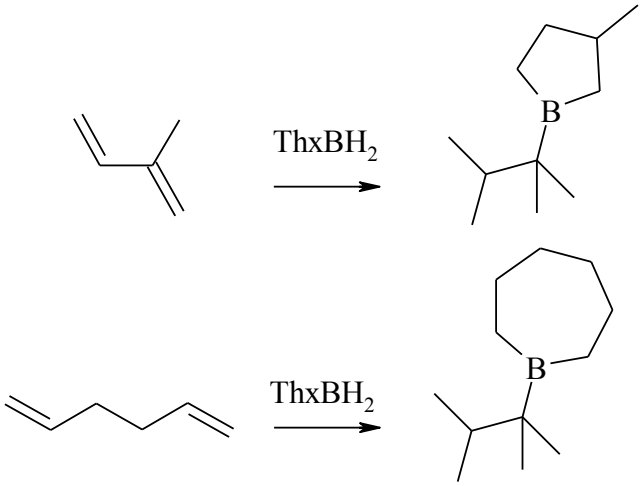
The hydroboration of 2,3-dimethyl-2-butene yields a monoalkylborane compound known as 1,1,2-trimethylpropylborane (thexylborane) (Scheme 2.12).[xxiv]



Scheme 2.12

This compound is prepared and used directly without storage, because the tertiary alkyl group has been reported to isomerize slowly to a primary alkyl group on standing at room temperature.[vii] It exists as a monomer in THF solutions due to the large steric interactions exerted by the thexyl group.[xxv] It is the most readily available of the monoalkyboranes and has been shown to be valuable for the cyclic hydroboration of dienes and numerous other uses.[xxvi] It has also proven to be valuable in achieving the union of two different alkenes to boron and simplified the synthesis of cyclic derivatives. In contrast to

diborane, which forms polymeric organoboranes, thexylborane yields β-thexylboraheterocycles in very good yields (Scheme 2.13).[xxvii]

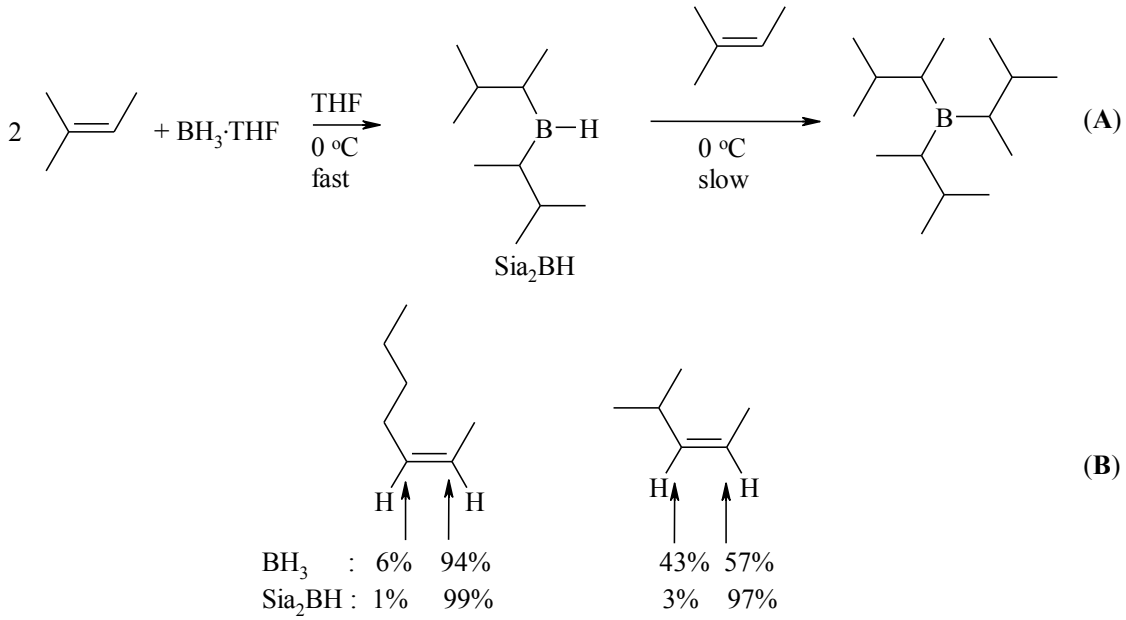


Scheme 2.13

2.1.4.2.2 **DISIAMYLBORANE**

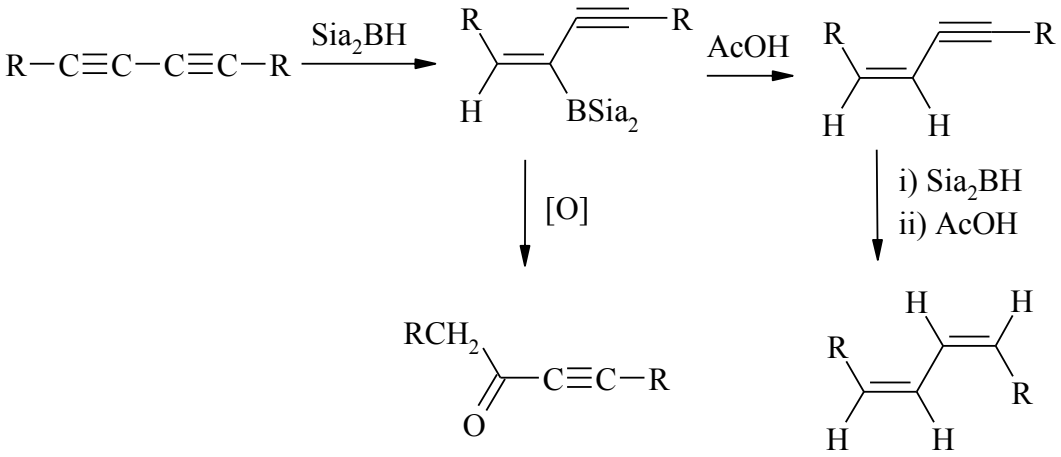
The hydroboration of 2-methyl-2-butene can be controlled to achieve the synthesis of a dialkylborane called disiamylborane (Sia_2BH) (Scheme 2.14 **A**)

Brown and Zweifel showed that Sia_2BH possesses enhanced selectivity compared to borane (Scheme 2.14 **B**).[xxviii] Sia_2BH exhibits the desired stereoselectivity for the less hindered position of a double bond. The results showed that Sia_2BH is highly sensitive to the structure of the alkene to be hydroborated, thus terminal alkenes such as 1-hexene and 2-methyl-1-pentene are more rapidly hydroborated than internal alkenes.[xxviii]



Scheme 2.14

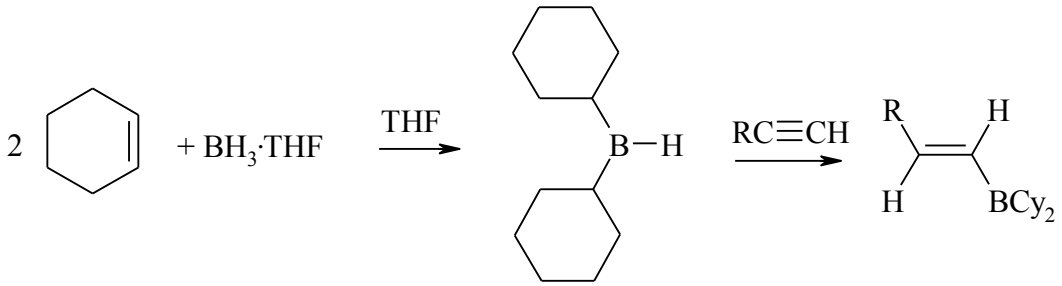
Further investigations by Brown *et al*.[xxix] demonstrated that Sia_2BH has much higher reactivity towards alkynes than alkenes, it has proved to be useful in the synthesis of (*Z,Z*)-conjugated and propargylic ketones from the same precursor (Scheme 2.15).[xxix]



Scheme 2.15

2.1.4.2.3 **DICYCLOHEXYLBORANE**

In the early 1970's Brown and Larock[xxx] reported the preparation of dicyclohexylborane from the the controlled hydroboration of cyclohexene with borane tetrahydrofuran complex. It is advantageous to use this reagent on occasions where less hindered moieties are desired (Scheme 2.16).[xxx]

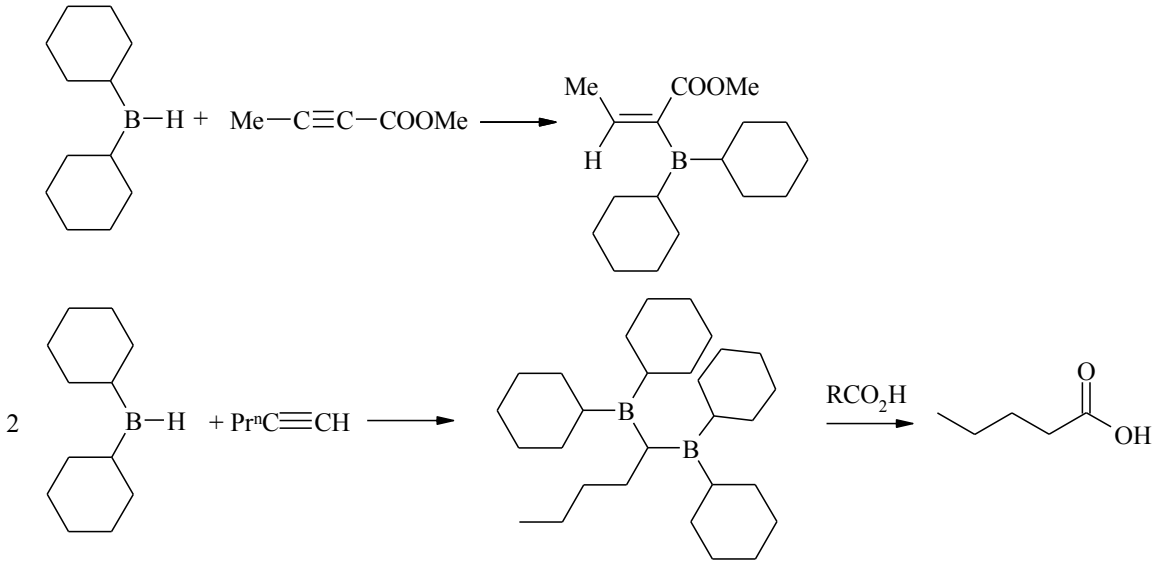


Cy_2BH

Scheme 2.16

In addition, it is reported that if Cy_2BH is used instead of disiamylborane, better yields are achieved and product isolation is also facilitated.[xxxi] Cy_2BH is superior to disiamylborane in applications such as hydroboration of alkynes and thermal isomerization of organoboranes.[xxxi] Moreover Cy_2BH shows an increased thermal stability, which allows it to be used during reactions requiring elevated temperatures. Unlike Sia_2BH, where at high temperatures, the boron atom migrates (within the reagent) to the terminal position.[xxxi]

The reduced steric requirements of Cy_2BH, permit more potential dihydroboration of alkynes, unlike that of Sia_2BH which is more hindered. Consequently, hydroboration of terminal alkynes can be controlled to yield either vinylboranes or *gem*-dibora derivatives (Scheme 2.17).[xxxii]

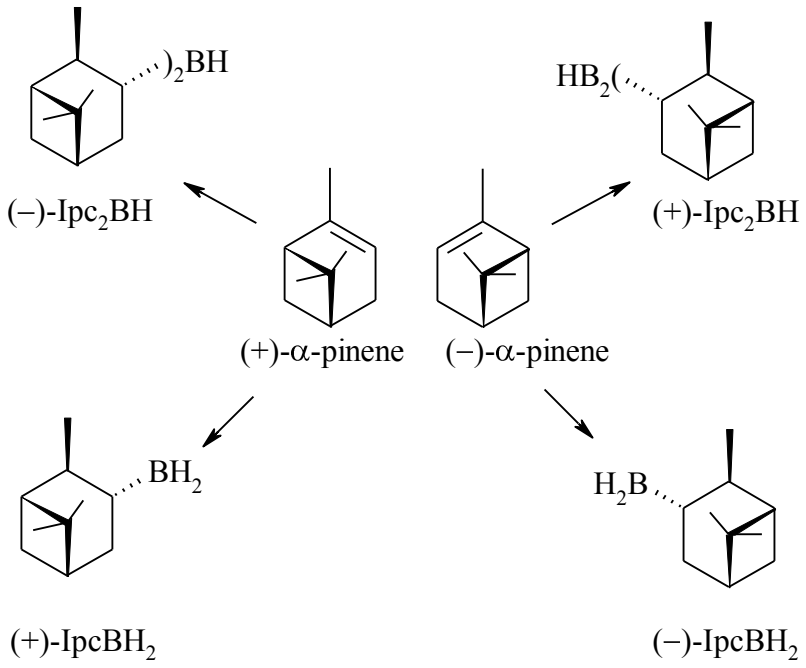


Scheme 2.17

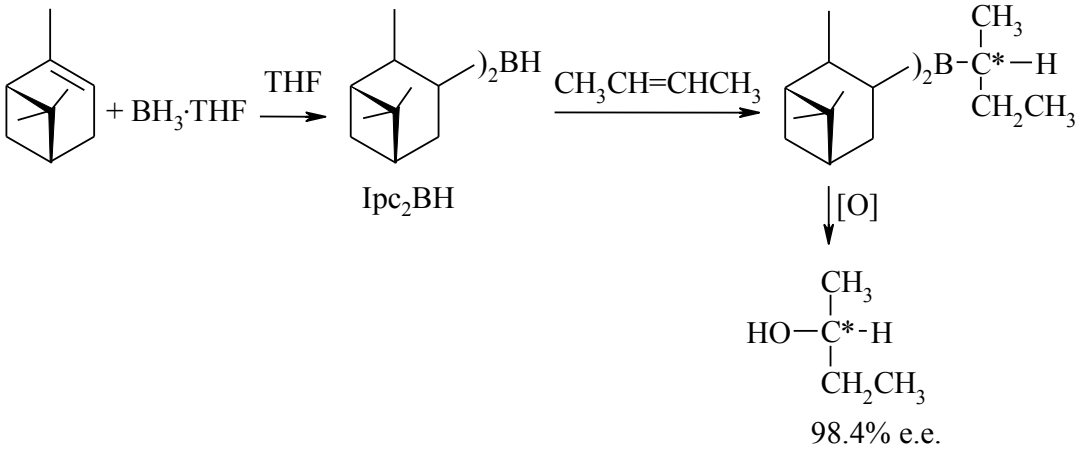
2.1.4.2.4 **DIISOPINOCAMPHEYLBORANE**

Hydroboration of α-pinene with borane proceeds readily to the formation of either monoisopinocampheylborane $IpcBH_2$ or diisopinocampheylborane Ipc_2BH, depending on the reaction conditions employed.[vii] These hydroborating reagents can be afforded in both optically active forms, (+) and (–) because α -pinene is available from natural sources in both optically active stereo isomers (Scheme 2.18).[vii]

These homochiral hydroborating agents are widely utilized in asymmetric hydroboraton of prochiral alkenes,[xxxiii] such as the reaction of *cis*-2-butene with Ipc_2BH in its enantiomerically pure form, resulting in the formation of an organoborane which, upon oxidation with alkaline hydrogen peroxide, yields (–)-2-butanol, [α $^{20}_{D}$ = –11.8° in an enantiomeric excess of > 98.4% (Scheme 2.19).[xxxiv]



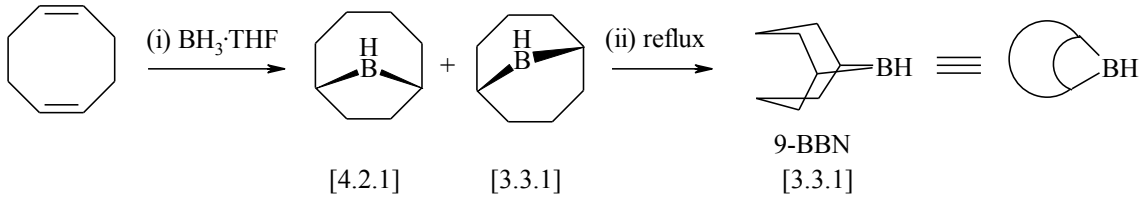
Scheme 2.18



Scheme 2.19

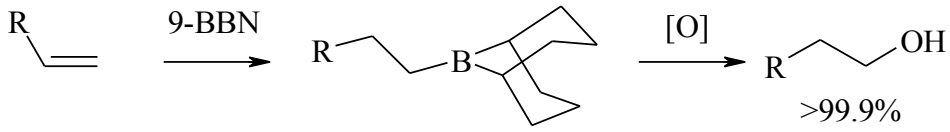
2.1.4.2.5 **9-BORABICYCLO[3.3.1]NONANE**

The controlled hydroboration of 1,5-cyclooctadiene with BH_3·THF produces a mixture of 9-borabicyclo[3.3.1]nonane, termed 9-BBN for convenience, and 9-borabicyclo[4.2.1]nonane.[vii] The [4.2.1] compound is isomerized to the thermodynacally more stable [3.3.1] compound upon heating (Scheme 2.20).[vii]

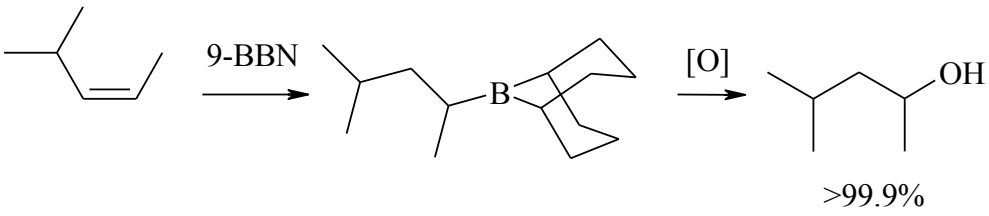


Scheme 2.20

It also exhibits remarkable regioselectivities, even greater than those of disiamylborane, due to its greater steric demand.[vii] The hydroboration reaction of terminal olefins with this reagent leads to the placement of the boron atom at the terminal position with a selectivity of at least 99.9% (Scheme 2.21).[xxxv] Interestingly, the regioselectivity exhibited on hydroboration of cis-4-methyl-2-pentene is essentially exclusive for the secondary carbon (Scheme 2.22).[xxxv]

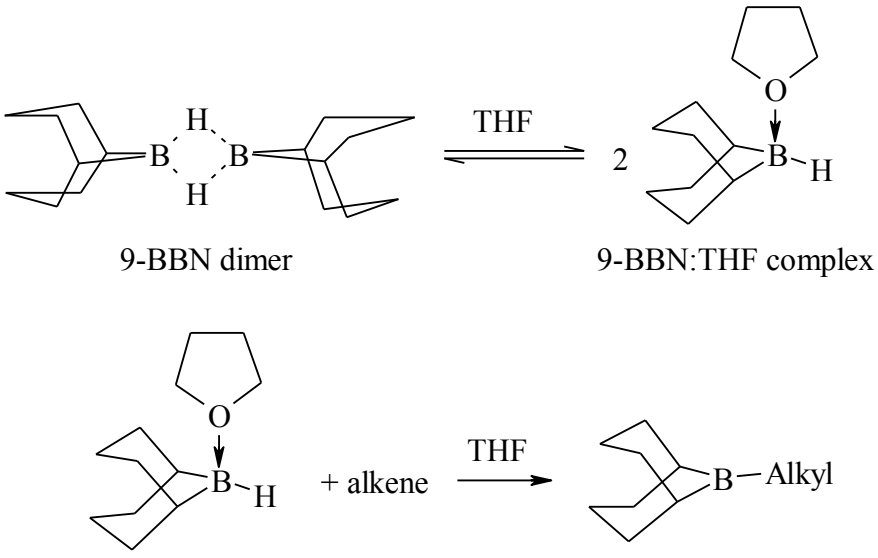


Scheme 2.21



Scheme 2.22

Crystallographic analysis by Kruger and Brauer showed that 9-BBN exists as a dimer in the solid state.[xxxvi] Those results supported the initial report that was based on the spectral properties[xxxv] (Scheme 2.23). Interestingly, it also exists exclusively as a dimer in certain solvents, for example tetrachloromethane, cyclohexane, benzene and diethyl ether.[xix] Nevertheless, dissolution of the dimmer in coordinating solvents such as THF or SMe_2 has been reported to dissociate the dimer, forming an equilibrium between $(9\text{-BBN})_2$ and a solvent complex 9-BBN monomer. The monomer has been shown by kinetic studies to be the active hydroborating species (Scheme 2.23).[xix]



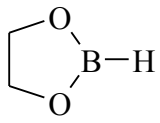
Scheme 2.23

Hydroboration of internal alkenes is attained at 60 – 80 ºC, this showed reduced reactivity towards alkenes compared to disiamylborane,[xix] However, its thermal stability permits

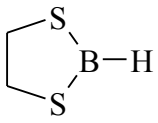
reactions to be conducted at elevated temperatures. This reagent also hydroborates tetrasubstituted double bonds which fail to react with Sia_2BH.[xxxvii] 9-BBN has two other applications in organic synthesis beside hydroboration: it is used in the reduction of carbonyl groups of α,β-unsaturated aldehydes and ketones with 100% selectivity, yielding allylic alcohols in high yields.[xxxviii] Secondly, its pyridine complex is used in the selective reduction of aldehydes in the presence of ketones.[xxxix]

2.1.4.3 **HETERO SUBSTITUTED BORANES**

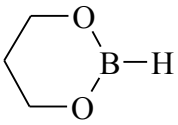
Heterosubstituted boranes, are defined as borane compounds containing the heteroatom bonded directly to the borane, hereteroatoms such as oxygen, sulfur, nitrogen and halogens are widely used. These compounds include a family of heterosubstituted borolanes (a five membered ring with a single boron atom) and borinanes (a six membered ring with a single boron atom). All these reagents show reduced reactivity if compared to BH_3 or dialkylborane due to the bonding between oxygen or sulfur and boron, which lowers the Lewis acidity of the boron atom.[xix] A few examples are listed below (Figure 2.2), some of which have been well precedented, and are discussed below.



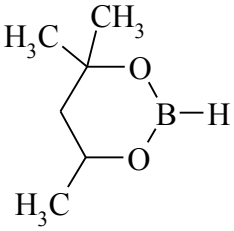
1,3,2-dioxaborolane



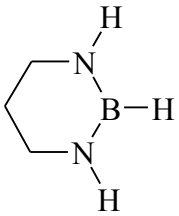
1,3,2-dithiaborolane



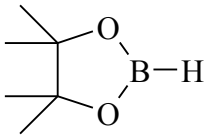
1,3,2-dioxaborinane



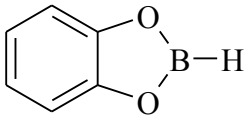
4,4,6-trimethyl-1,3,2-dioxaborinane



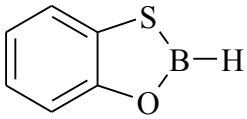
1,3,2-diazaborinane



4,4,5,5-tetramethyl-1,3,2-dioxaborolane
(pinacholborane)



benzo-1,3,2-dioxaborolane
(catecholborane)

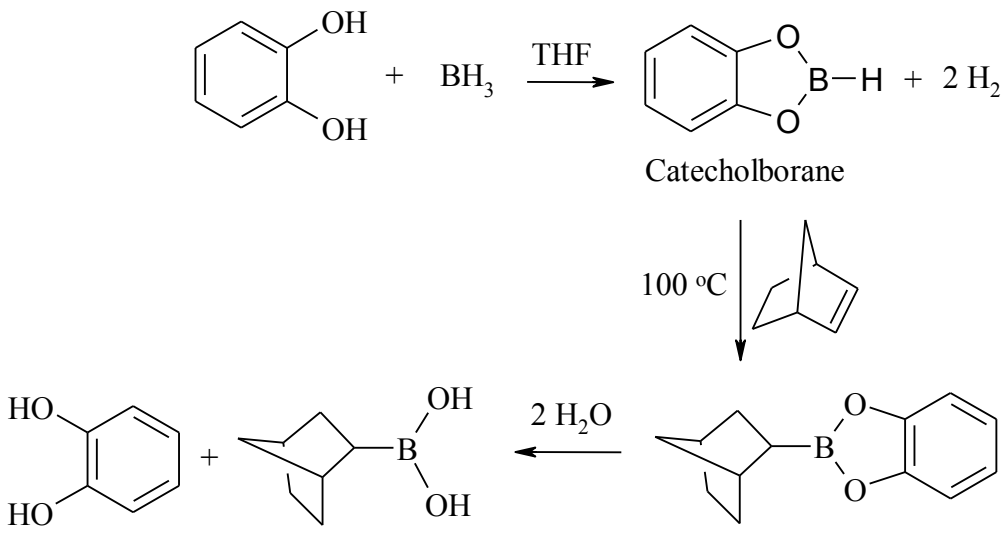


1,3,2-Benzooxathiaborolane

Figure 2.2

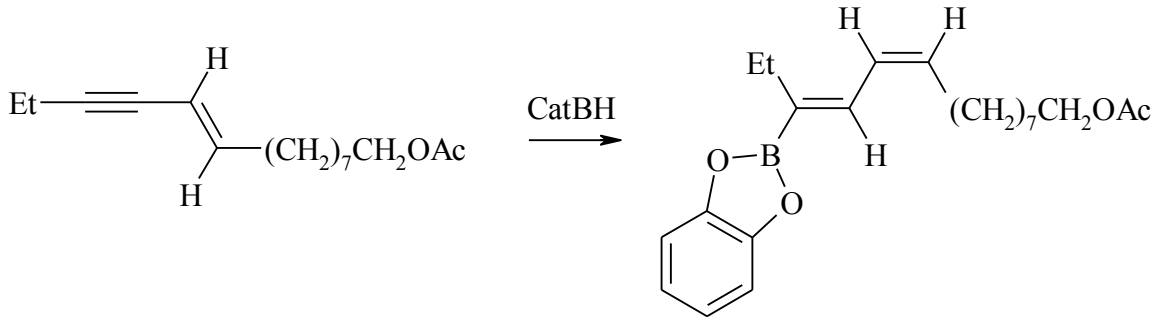
2.1.4.3.1 **CATECHOLBORANE**

In the early 1970's, Brown and Gupta[xl] reported the preparation of benzo-1,3,2-dioxaborolane termed "catecholborane" from the reaction of 1,2-benzenediol (catechol) with borane in THF. This reagent is a considerably better hydroborating agent than other alkoxy derivatives. Olefins are readily hydroborated at 100 °C using this reagent (Scheme 2.23).[xl] Since its discovery, a number of research groups have utilized this reagent in a wide spectrum of organic transformations.[xli]



Scheme 2.23

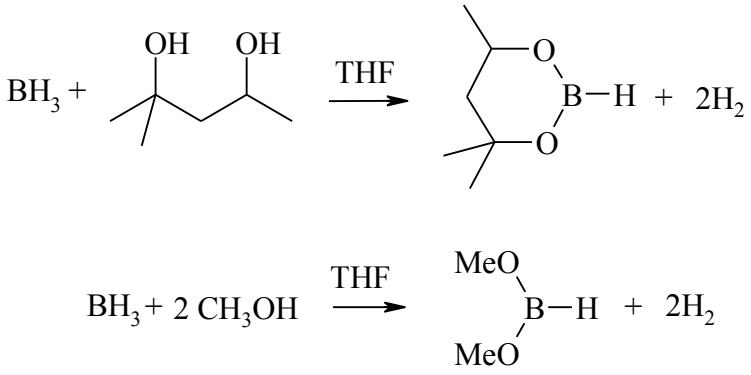
Hydrolysis of the hydroboration products produces the corresponding boronic acids (Scheme 2.23), which have been used in coupling reactions such as the Suzuki-Miyaura cross coupling reaction.[xlii] It is therefore advantageous to use catecholborane over other dialkylboranes. The disadvantage of using this compound is that it has a reduced reactivity in the hydroboration process, requiring elevated reaction temperatures for alkenes and alkynes to undergo hydroboration. However, interestingly, triple bonds are selectively hydroborated in the presence of double bonds (Scheme 2.24).[xli]



Scheme 2.24

2.1.4.3.2 **4,4,6-TRIMETHYL-1,3,2-DIOXABOROLANE**

Glycols and alcohols like catechol (as discussed above) react with borane to produce disubstituted boranes (Scheme 2.25).[xliii] These derivatives are poor hydroborating agents due to the fact that the oxygen substituents supply electron density to the boron atom thus greatly decreasing the electrophilic character of the reagent.



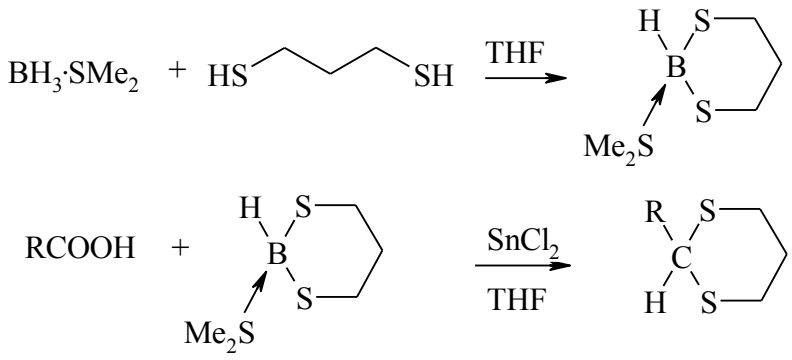
Scheme 2.25

The new hydroborating agent, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, also known as pinacolborane, made its first appearance in the early 1990's from the report by Tucker *et al*.[xliv] Pinacolborane prepared from the reaction of pinacol with $BH_3{\cdot}SMe_2$ in CH_2Cl_2 afforded a significantly greater level of regio- and stereoselectivity when compared to catecholborane.

1,3,2-Dioxaborinane and 1,3,2-dioxaborolane (Figure 2.2) undergo disproportionation.[xliii,xlv] The two aromatic ring systems, catecholborane and 1,3,2-benzooxathiaborole, are free from such problems due to the conjugation of the aromatic ring with the lone pair of oxygen or sulfur. Very little information is available on 1,3,2-benzooxathiaborole as a hydroborating agent. It has been reported that 1,3,2-benzooxathiaborole hydroborates cyclohexene at 83 °C in 3 hours.[xlvi]

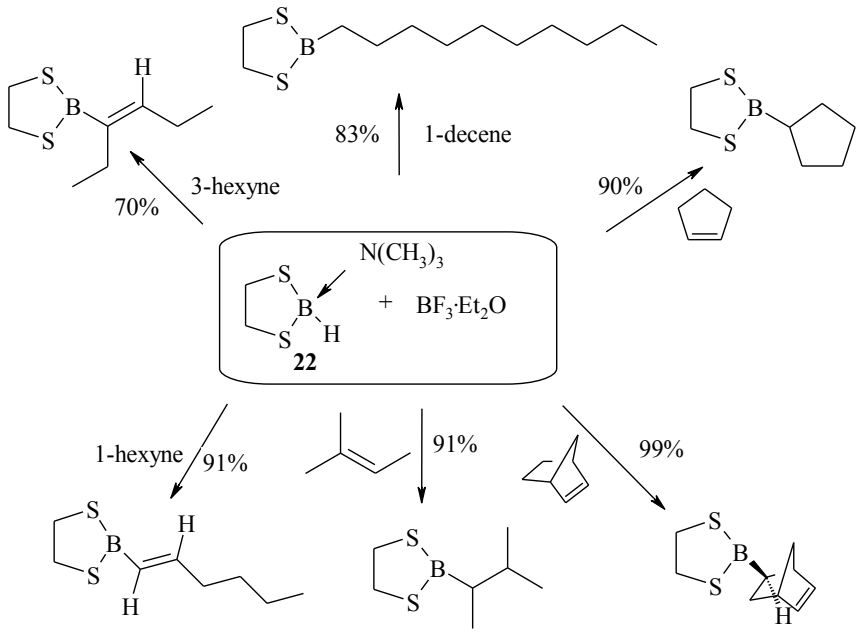
2.1.4.3.3 **SULFUR-SUBSTITUTED BORANES**

Niedenzu *et al*. reported the synthesis of 1,3,2-dithiaborinane from the reaction of borane-methyl sulfide complex with an equimolar amount of 1,3-propanedithiol .[xlvii] O'Neill *et al.*[xlviii] reported its use as an efficient reagent for direct conversion of carboxylic acids to 1,3 -dithianes in the presence of stannous chloride (Scheme 2.25).



Scheme 2.25

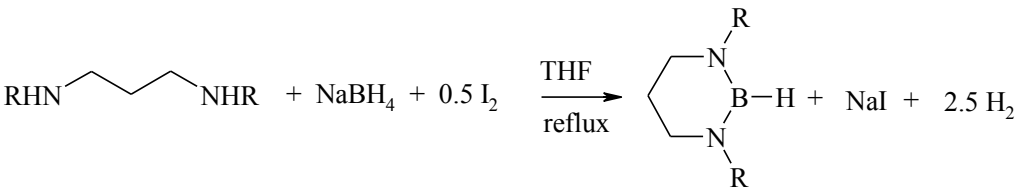
Very little information is available on these dithiaboranes as hydroborating agents. Of all these dithiaboranes, 1,3,2-dithiaborolane trimethyl amine complex has been reported as an effective hydroborating agent when treated with $BF_3{\cdot}OEt_2$ in boiling benzene, hydroboration of a representative group of alkenes and alkynes into alkyl- and alkenyl-1,3,2-dithiaborolanes was achieved (Scheme 2.26).[xlv]



Scheme 2.26

2.1.4.3.4 **NITROGEN-SUBSTITUTED BORANES**

Azaborocycloalkanes such as 2-alkyl substituted-1,3,2-diazaborolane have been known for some time, with previous work focused mostly on the β-alkyl and -aryl derivatives of these heterocycles.[xlix] All β-halo derivatives of this compound have been described.[l] 2-Hydrido-1,3,2-diazaborinane can be synthesized from the reaction of sodium borohydride with the corresponding diamine, in the presence of iodine (Scheme 2.27).[li]



Scheme 2.27

The use of trimethylamine borane complex as an alternative route has been reported to serve equally well as the source of borane.[li] In this method, trimethylamine is produced as a by-product and thus assists the purification of the desired heterocycles.

2.1.4.3.5 **HALOGEN-SUBSTITUTED BORANES**

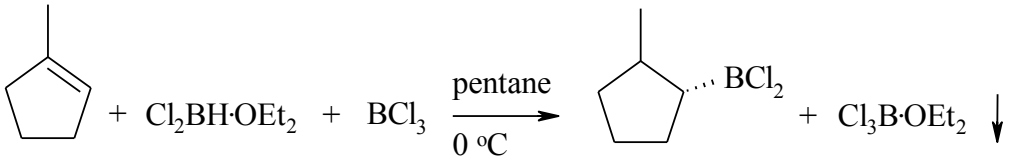
Dichloro- and monochloroborane-etherates are prepared readily from the reaction of borontrichloride with diboranes in ethereal solvents. These chloroborane derivatives are unstable species and they disproportionate to diborane and boron trichloride. The use of ethereal solvents slows this disproportionation by forming the corresponding ether complexes (Scheme 2.28).[lii] Alternatively, chloroborane-etherate complexes are prepared through the reaction of hydrogen chloride with borane-tetrahydrofuran.[liii]

$$B_2H_6 + 4\ Cl_3B{\cdot}OEt_2 + 2OEt_2 \xrightarrow{\text{ethyl ether}} 6\ Cl_2BH{\cdot}OEt_2$$

$$B_2H_6 + Cl_3B{\cdot}OEt_2 + 2OEt_2 \xrightarrow{\text{ethyl ether}} 3\ ClBH_2{\cdot}OEt_2$$

Scheme 2.28

Hydroboration of terminal alkenes with monochloroborane-diethyl etherate was reported to proceed readily at 0 °C. Regioselectivity of > 99.5 % for terminal hydroboration was achieved.[liv] The exhibited regioselectivity is much greater than that of borane itself, and is comparable to 9-BBN in many instances.[liv] Whereas, dichloroborane-diethyl etherate is a much less reactive hydroborating agent, it fails to react spontaneously with olefins. This compound hydroborates alkenes and alkynes with the aid of one molar equivalent of boron trichloride, which facilitates precipitation of boron trichloride-diethyl etherate and yields a rapid hydroboration process (Scheme 2.29).[lv]

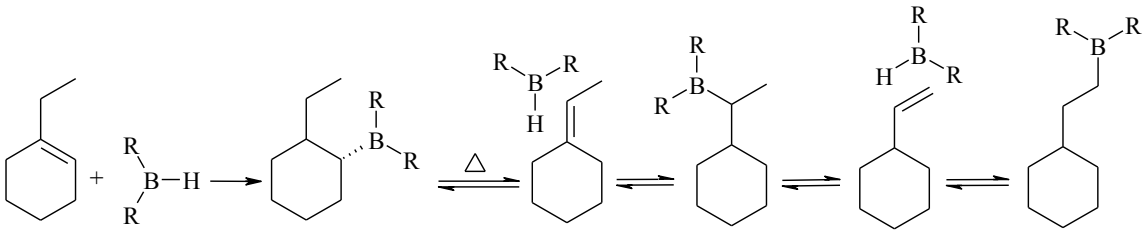


Scheme 2.29

It is reported, however, that these haloborane-etherate complexes are unstable on storage. The use of dimethyl sulfide as the coordinating solvent produces the haloborane-dimethyl sulfide adducts which have a prolonged shelf life and more importantly very similar behaviour to the corresponding etherates.[xix]

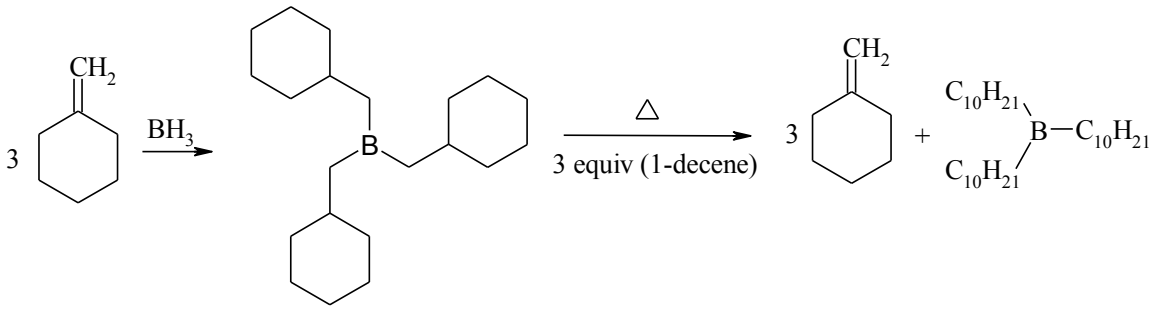
2.1.5 **ISOMERIZATION AND DISPLACEMENT**

In the mid 1960's Brown and Zweifel reported that organoboranes undergo isomerization at elevated temperatures (*ca*.160 ºC). The process involved the movement of the boron atom from the internal position to the least hindered position or the terminal position of the molecule.[lvi] A mechanism that involved partial dissociation and rehydroboration of organoborane into the alkene, until the boron ends up at the least hindered position of the molecule was proposed. Compounds with internal double bonds such as β-pinene have been successfully converted into the more stable *trans*-myrtanyl derivative upon heating (Scheme 2.30).[lvii]



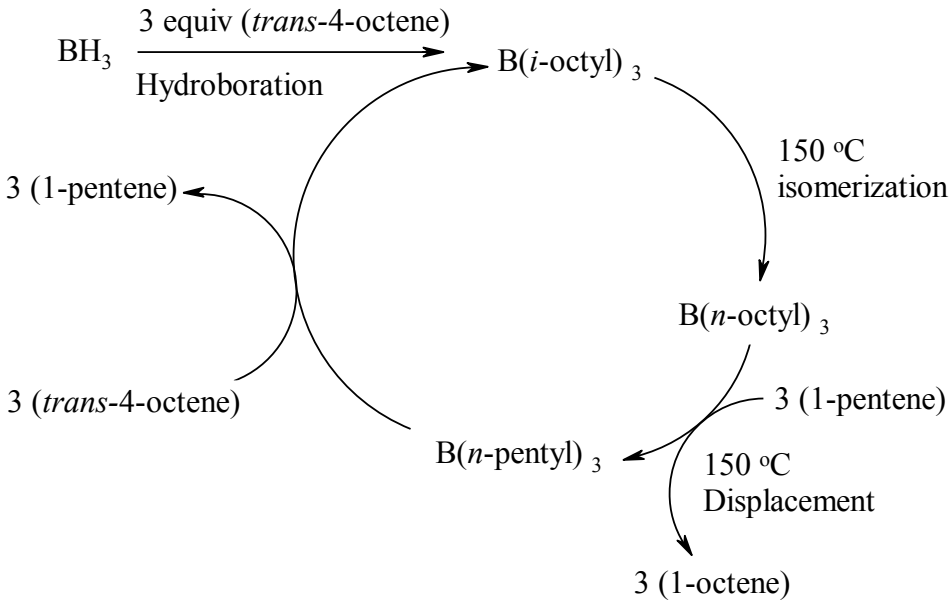
Scheme 2.30

Brown's group pioneered the hydroboration reactions including isomerization and displacement of the alkenes from organoboranes. Their studies showed that introduction of a second alkene at isomerization temperature lead to the capture of the boron-hydrogen moiety by the second alkene. If the alkene introduced has a higher boiling point, it permits distillation of the original alkene out of the reaction mixture (Scheme 2.31).[lviii]



Scheme 2.31

The combination of the three processes namely, hydroboration, isomerization and displacement birthed a practical synthetic route for the contrathermodynamic isomerization of olefins. This combination has opened a possible synthetic route for producing a large number of 1-alkenes from internal olefin feedstocks (Scheme 2.32).



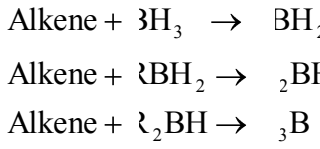
Scheme 2.32

The boron chemistry-based cycle involves hydroboration of three equivalents of the internal olefin producing internal trialkylborane, which at elevated temperature *ca*. 150 ºC would isomerise to form terminal trialkylborane, this is then followed by displacement of a linear alpha olefin triggered by the introduction of a sacrificial olefin. Our role in this

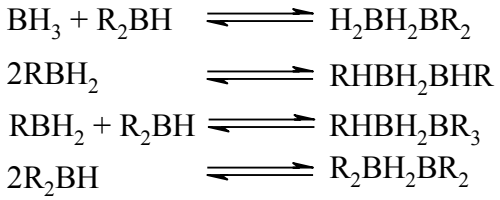
collaborative project was to synthesize hydroborating agents and to evaluate their reactivity in hydroboration.

2.2 **RESULTS AND DISCUSSION**

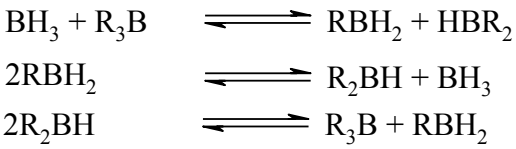
From the studies conducted within our group and from the literature it is evident that the kinetics of hydroboration is indeed complex, due to the potential number of possible reactions the boron group is able to undergo. Borane has three sites available for hydroboration, as a result the overall process involves three addition reactions (Scheme 2.33), five monomer dimer equilibria (Scheme 2.34), and three redistribution equilibria (Scheme 2.35).[lix]



Scheme 2.33



Scheme 2.34

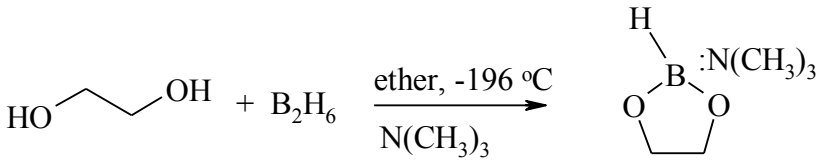


Scheme 2.35

Another problem associated with BH_3 hydroboration is that the reactions are too fast to be measured accurately using ^{11}B NMR spectroscopy. Consequently, it was decided to limit the focus of this study to single site boron compounds (which would avoid the difficulties illustrated in schemes 2.33, 2.34 and 2.35) with the aim of being able to study their potential for contrathermodynamic isomerisation of alkenes.

2.2.1 **OXYGEN BASED HYDROBORATING AGENTS**

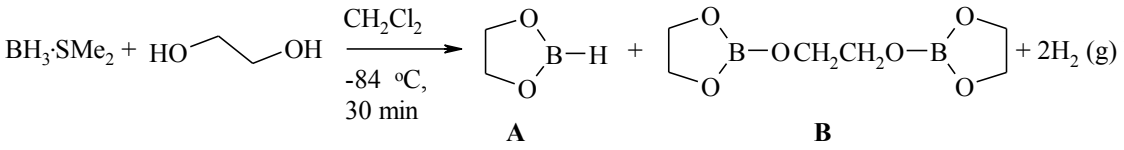
In the early 1960's Rose and Shore prepared 1,3,2-dioxaborolane from the reaction of B_2H_6 and ethylene gycol at -196 ºC.[lx] However, this compound was noted to be unstable and disproportionated at room temperature in an ethereal solvent. In addition they demonstrated that 1,3,2-dioxaborolane can be prepared as an amine adduct, in the presence of the coordinating solvent trimethylamine (Scheme 2.36).



trimethylamine-1,3,2-dioxaborolane

Scheme 2.36

We attempted to prepare 1,3,2-dioxaborolane from the reaction of $BH_3{\cdot}SMe_2$ with ethylene gycol at – 80 ºC in CH_2Cl_2 ^{11}B NMR spectroscopic analysis of the product mixture showed a doublet at 28.4 ppm (Figure 2.3) due to 1,3,2-dioxaborolane (**A**)**,** *ca*.15 % (Scheme 2.37). A singlet at 23.0 ppm was attributed to 2,2'-(ethylenedioxy)-bis-(1,3,2-dioxaborolane) (**B**) *ca.* 70 % (Scheme 2.37), the disproportionation product similar to that reported by Rose and Shore.



Scheme 2.37

Our study has shown that the use of BH_3 containing dimethyl sulfide as the coordinating solvent does yield 1,3,2-dioxaborolane. However, SMe_2 is not as strongly coordinating as trimethyl amine, and consequently the produced 1,3,2-dioxaborolane disproportionates to 2,2'-(ethylenedioxy)-bis-(1,3,2-dioxaborolane) (**B**) as proposed by Rose and Shore. As a result, 1,3,2-dioxaborolane was not accessible for hydroboration reactions. Several attempts to minimise the disproportionation product proved unsuccessful.

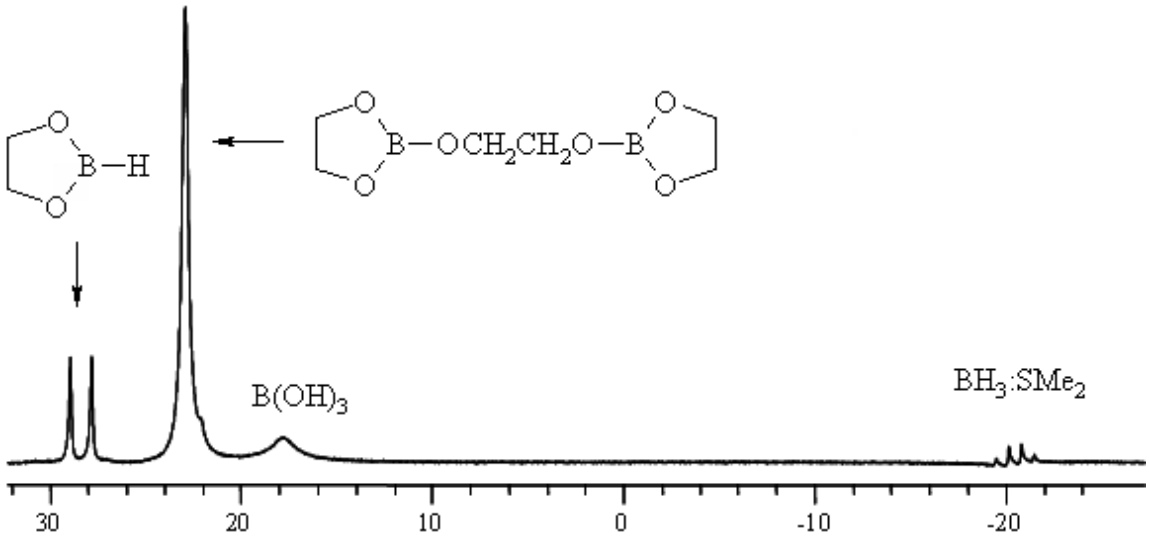
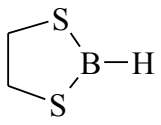


Figure 2.3 ^{11}B NMR spectrum obtained from the reaction of 1,2-ethanediol with borane-dimethyl sulfide at -84°C for 30 minutes

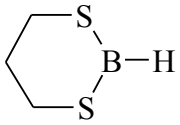
2.2.2 SULFUR BASED HYDROBORATING AGENTS

2.2.2.1 CYCLIC SULFUR-BASED BORANES

The sulfur substituted heterocyclic compounds 1,3,2-dithiaborolane and 1,3,2-dithiaborinane (Figure 2.4) were prepared successfully as dimethyl sulfide complexes from reactions of $BH_3{\cdot}SMe_2$ with 1,2-ethanedithiol or 1,3-propanedithiol respectively. These compounds were prepared following modified methods of Egan *et al*.[lxi] and Niedenzu *et al*.[xlvii]



1,3,2-dithiaborolane



1,3,2-dithiaborinane

Figure 2.4

The primary objective of this study was to synthesize sulfur-based heterocyclic compounds and to investigate their suitability in hydroboration reactions, with the intention to obtain the kinetic and thermodynamic data of the hydroboration process, and to study the role of sulfur heteroatom on reaction rates. Detailed investigation into the synthesis of 1,3,2-dithiaborolane and 1,3,2-dithiaborinane and subsequent utility in hydroboration reactions has been conducted. Results from this investigation have been accepted for publication in the South African Journal of Chemistry,[lxii] and a copy of the publication follows.* Hadebe, S. W. and Robinson, R. S. *S. Afr. J. Chem.* **2008**, Part 1, *Manuscript No. M683*, accepted for publication.

* Copy of the paper included in the body of text as per faculty guidelines. The raw data for concentration and temperature dependence studies is included in appendix A.

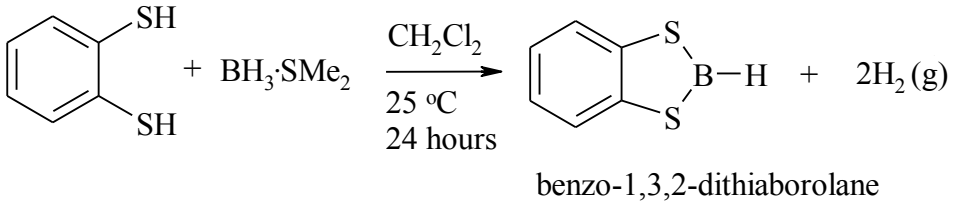
From the results of the above study, disproportionation of the sulfur based-hydroborating agents was noted, therefore in order to better understand and rationalize the observed disproportionation mechanism, a density functional theory (DFT) study was conducted. In this study, hydroboration and disproportionation mechanism were modelled and the transition state energies correspond for each mechanism were compared. Detailed discussion on findings of this study has been accepted for publication in the South African Journal of Chemistry[lxiii] and a copy of the paper follows.[*] Hadebe, S. W. and Robinson, R. S. *S. Afr. J. Chem.* **2008**, Part 2, *Manuscript No. M684*, accepted for publication.

[*] Copy of the paper included in the body of text as per faculty guidelines. Cartesian coordinates of geometry optimized structures of TS and products are included in appendix B.

From the investigations in the preceding publication (parts 1 and 2) it was discussed that the cyclic sulfur compounds hydroborate 1-octene at room temperature to yield the target organoborane. Kinetic and thermodynamic parameters for this process were determined. These boranes were also shown to undergo disproportionation during synthesis and upon storage at room temperature. A DFT study on these compounds has also shown that these boranes have enough thermal and kinetic energy to undergo disproportionation at room temperature. In order to increase the stability of these hydroborating agents, it was envisaged that the use of strongly coordinating heteroatoms or the presence of an aromatic ring on the borane would increase the stability, as reported in literature with catecholborane.[xl] Consequently, it was decided to investigate the role of the aromatic substituent on hydroboration rates and the effect of strongly coordinating heteroatoms such as nitrogen.

2.2.2.2 SYNTHESIS OF BENZO-1,3,2-DITHIABOROLANE

Benzo-1,3,2-dithiaborolane was easily prepared from the reaction of equimolar amounts of 1,2-benzenedithiol and borane-dimethyl sulfide complex in CH_2Cl_2 at room temperature under a dry nitrogen atmosphere (Scheme 2.38). The reaction was slow and mild with no observable effervescence at room temperature.



Scheme 2.38

^{11}B NMR analysis (Figure 2.5) of the product mixture stirred for 24 hours at 25 °C gave a clean spectrum with only a doublet at 53.4 ppm attributed to a B-H coupling signal correspond to benzo-1,3,2-dithiaborolane. The proton decoupled spectrum of the sample (Figure 2.6) showed a singlet at 53.4 ppm due to the boron atom in benzo-1,3,2-

dithiaborolane, this confirmed that the doublet was, in fact, due to B-H coupling of the target compound.

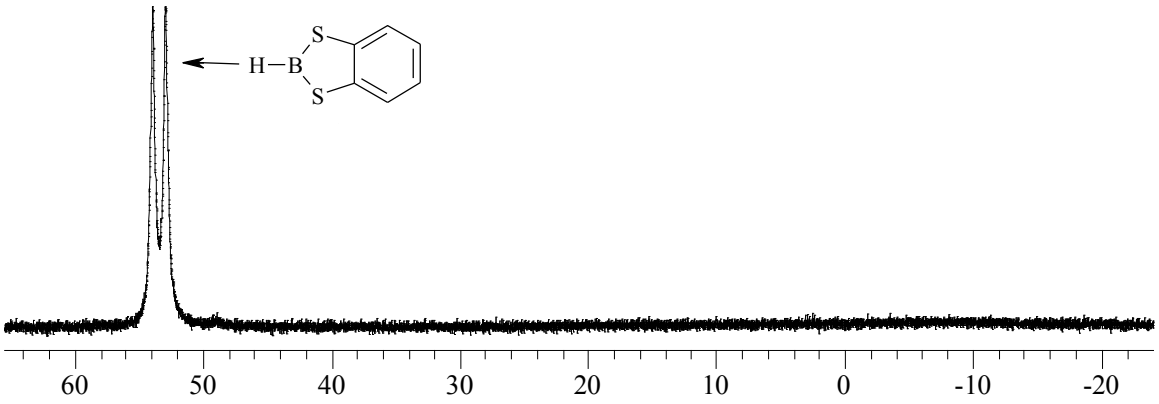


Figure 2.5 ^{11}B NMR spectrum showing a doublet of benzo-1,3,2-dithiaborolane

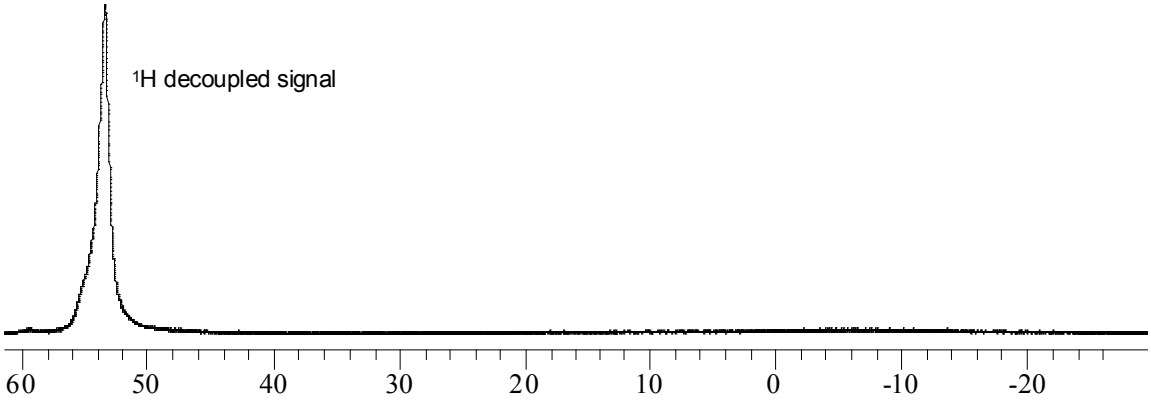


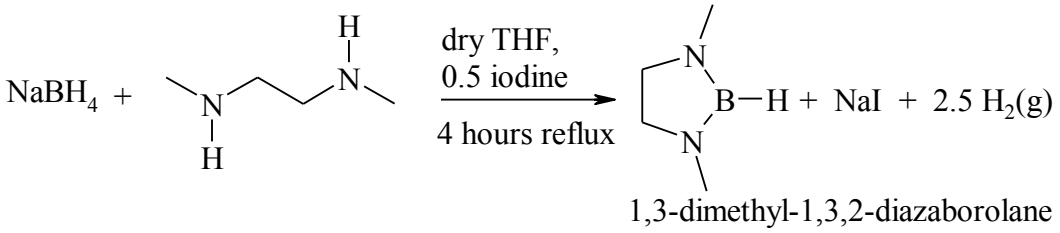
Figure 2.6 Showing a proton decoupled ^{11}B NMR spectrum of benzo-1,3,2-dithiaborolane

2.2.3 **NITROGEN BASED HYDROBORATING AGENTS**

2.2.3.1 **SYNTHESIS OF 1,3-DIMETHYL-1,3,2-DIAZABOROLANE**

1,3-Dimethyl-1,3,2-diazaborolane (Scheme 2.39) was synthesized using $NaBH_4$ as the source of borane instead of $BH_3{\cdot}SMe_2$ as proposed by Niedenzu *et al.*[li] *N,N'*-

dimethylethane-1,2-diamine (Scheme 2.39) reacted with $NaBH_4$ in a 1:1 stoichiometric ratio in refluxing THF in the presence of iodine solution, which was added slowly prior to refluxing. The role of iodine in the reaction is to capture the sodium ions from $NaBH_4$ to generate the NaI precipitate, this leads to a rapid evolution of hydrogen gas and the formation of BH_3·THF which reacts with *N,N'*-dimethylethane-1,2-diamine on heating. ^{11}B NMR spectroscopic analysis (Figure 2.7, taken after 4 hours of reflux) of the sample indicated a mixture of products and not only the target molecule as expected. Only *ca.* 58% of the target molecule was present as indicated by the doublet at 29.2 ppm for B-H coupling. 5% of a mono substituted borane, shown as a minor triplet at 0 ppm was also formed, a quartet at -15.3 ppm was attributed to BH_3·*N,N'*-dimethylethane-1,2-diamine complex *ca.* 32% yield, and lastly a quintet at -42.1 ppm for unreacted $NaBH_4$ *ca.* 2%. These structures are suppositions based on our readings and were assigned based on ^{11}B NMR spectroscopy, because no other experimental evidence was acquired to support these structures.



Scheme 2.39

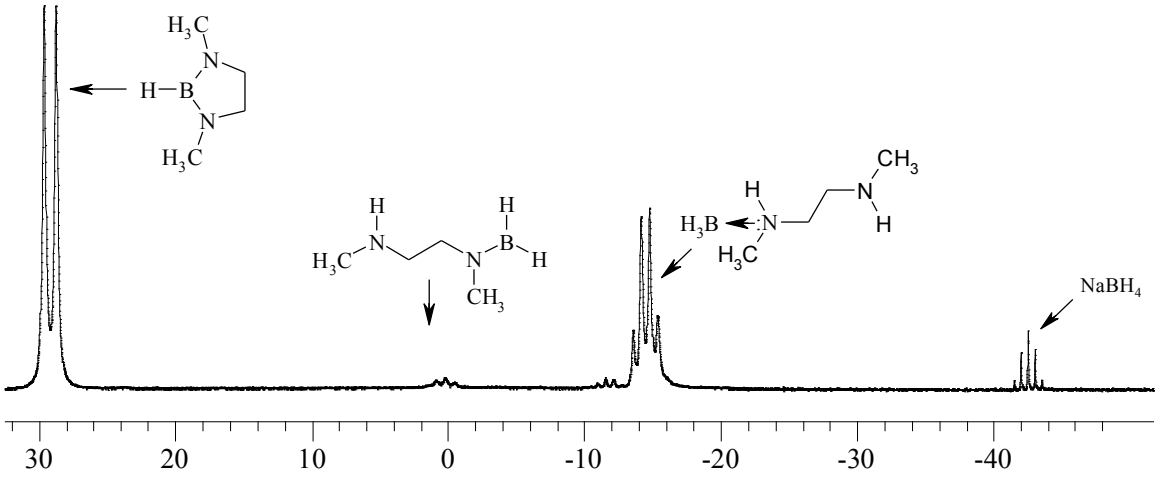


Figure 2.7 ^{11}B NMR spectrum obtained after 4 hours refluxing, showing the product distribution.

The reflux was allowed to proceed for a further 10 hours in order to drive the reaction to completion. After this period had elapsed, a clear liquid with a precipitate of NaI was obtained after cooling the reaction mixture. ^{11}B NMR analysis (Figure 2.8) of the liquid portion showed a doublet at 29.2 ppm attributed to the product 1,3-dimethyl-1,3,2-diazaborolane in 80% yield.

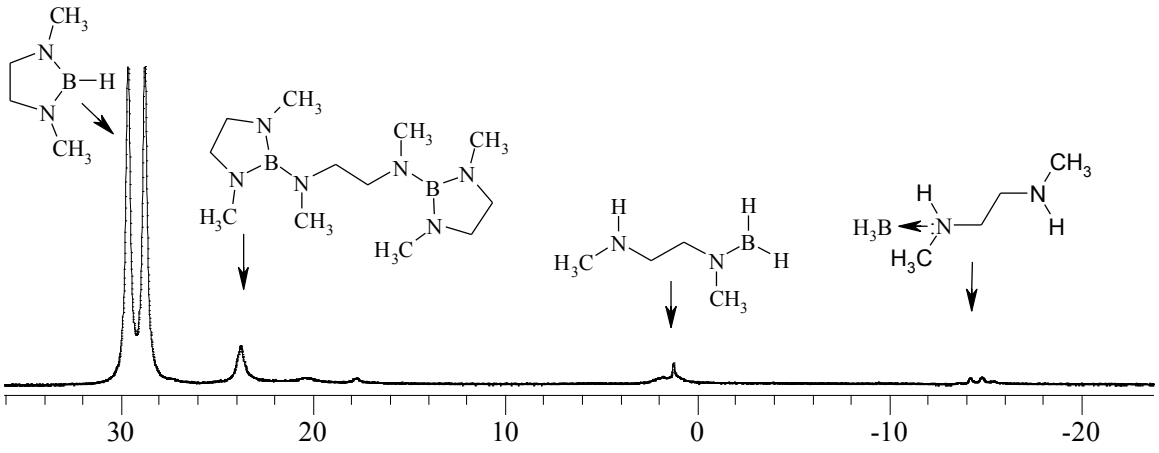
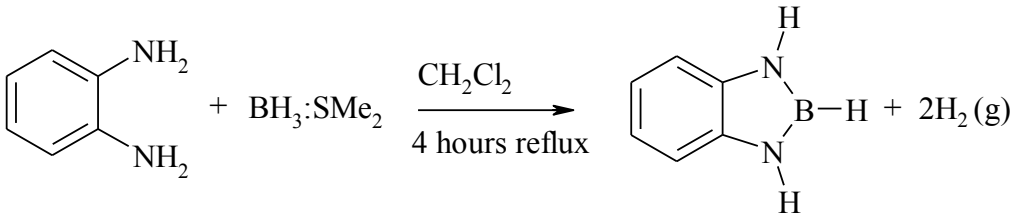


Figure 2.8 ^{11}B NMR spectrum showing about 80% of 1,3-dimethyl-1,3,2-diazaborolane achieved after boiling for 14 hours in THF

2.2.3.2 **SYNTHESIS OF BENZO-1,3,2-DIAZABOROLANE**

The reaction of 1,2 phenylenediamine with $BH_3{\cdot}SMe_2$ in a 1:1 mole ratio under reflux, afforded a light yellow liquid of benzo-1,3,2-diazaborolane (Scheme 2.40) in an excellent yield of 95%. The ^{11}B NMR analysis of this compound showed a clean spectrum with only one doublet at 23.9 ppm (Figure 2.9).



benzo-1,3,2-diazaborolane

Scheme 2.40

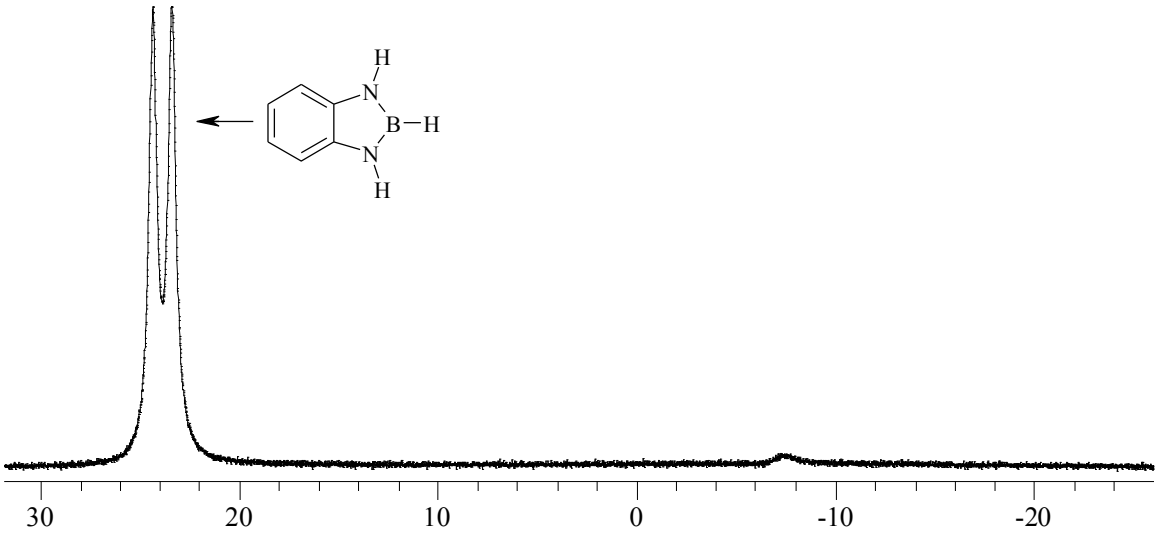


Figure 2.9 ^{11}B NMR spectrum of benzo-1,3,2-diazaborolane obtained after 4 hours of reflux in CH_2Cl_2

The formation of benzo-1,3,2-diazaborolane was corroborated by the MS analysis (Figure 2.10). The MS analysis showed an intense base peak with a molecular ion of 118.13 *m/z* ratio and a relative abundance of 100%. This was then assigned to benzo-1,3,2-dithiaborolane (MW = 117.9 g/mol).

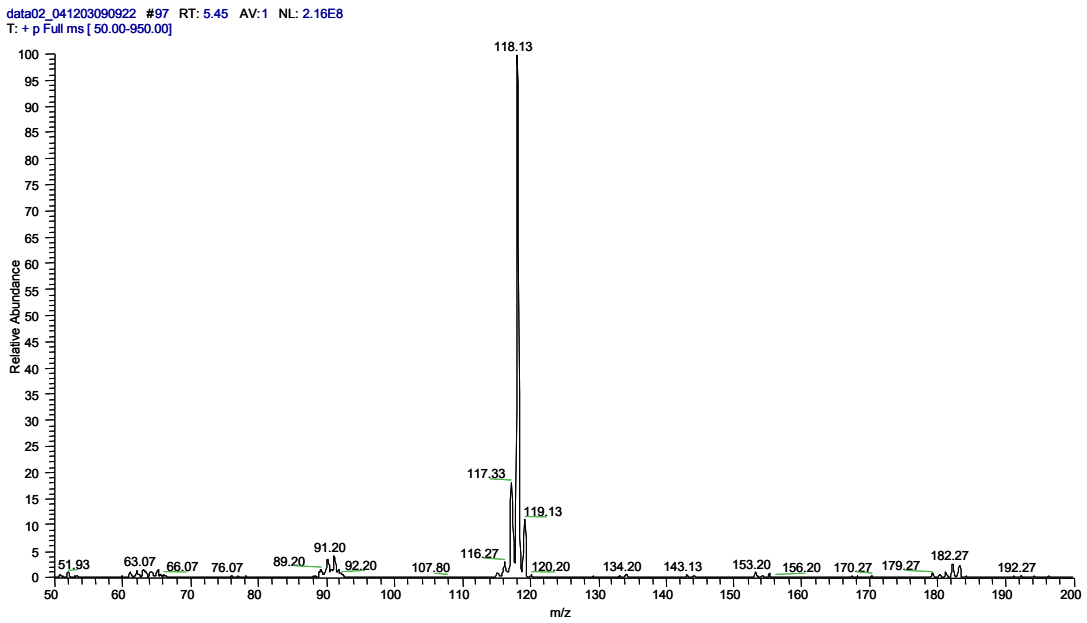


Figure 2.10 MS trace of benzo-1,3,2-diazaborolane

2.2.4 **HYDROBORATION REACTIONS**

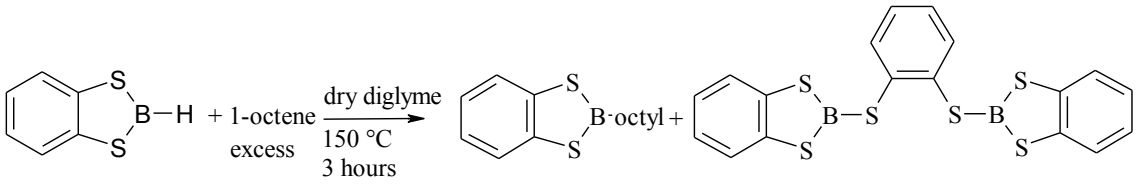
Hydroboration reactions conducted using 1,3-dimethyl-1,3,2-diazaborolane (prepared in section 2.2.3.1 above) did not proceed successfully. 1,3-Dimethyl-1,3,2-diazaborolane did not hydroborate internal or terminal olefins due to steric hindrance caused by methyl substituents on the nitrogen. The low reactivity was also attributed the overlap of the electron cloud from the nitrogen lone pair of electron into the vacant p_z-orbital. In order to evaluate the effect of an aromatic system on the reactivity of these compounds, aromatic hydroborating agents, benzo-1,3,2-diazaborolane, benzo-1,3,2-dithiaborolane, and commercially available benzo-1,3,2-dioxaborolane (Catecholborane) were utilized in a systematic study to investigate the reactivity trend towards 1-octene.

2.2.4.1 HYDROBORATION WITH BENZO-1,3,2-DITHIABOROLANE

Freshly prepared benzo-1,3,2-dithiaborinane was allowed to react with an excess of 1-octene in CH_2Cl_2 as the reaction solvent. No reaction was observed spectroscopically at 25 °C even after extended reaction times. The reaction was allowed to stir for 10 days, ^{11}B NMR analysis showed a neat spectrum with only a doublet at 53.4 ppm characteristic of the starting reagent, and no hydroboration reaction was observed even in refluxing CH_2Cl_2.

The reduced reactivity of benzo-1,3,2-dithiaborolane towards 1-octene compared to the cyclic derivative 1,3,2-dithiaborolane, was attributed to the fact that the electron cloud conjugated around the ring could be donated to the sulfur substituents which in turn donate electron density to the boron atom, thus making it less electropositive. The decrease in the electrophilic character of the boron atom results in the reduction of the interaction of the B-H bond with the carbon-carbon double bond of the alkene.

Interestingly, at higher temperatures (*ca*. 150 ºC), in refluxing diglyme hydroboration of 1-octene was noted (Scheme 2.41) (Figure 2.11). ^{11}B NMR spectroscopic analysis of the product mixture after 3 hours of reflux at 150 °C, showed about 65% of the target boronate ester octyl-benzo-1,3,2-dithiaborolane, 21% of the disproportionation product, and 4% of the starting hydroborating agent benzo-1,3,2-dithiaborolane.



Scheme 2.41

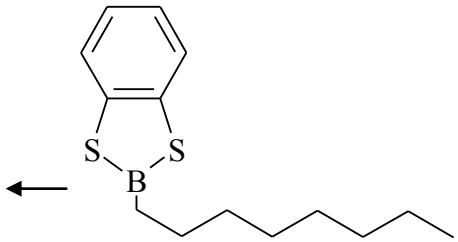


Figure 2.11 ^{11}B NMR spectrum of the product mixture after 3 hour

Kinetic studies of hydroboration of 1-octene with benzo-1,3,2-dithiaborolane could not be investigated using ^{11}B NMR spectroscopy due to the fact that 150 °C is far beyond the maximum probe temperature for the 500MHz NMR spectrometer used in this research.

2.2.4.2 **HYDROBORATION WITH BENZO-1,3,2-DIAZABOROLANE**

Synthesized benzo-1,3,2-diazaborlane was allowed to react with 1-octene under a dry nitrogen atmosphere. No reaction was observed after 2 days at 40 ºC. The reaction mixture was then heated at 100 °C for 10 days - subsequent ^{11}B NMR analysis of this mixture showed a doublet for the hydroborating reagent benzo-1,3,2-diazaborolane, but no octyl-boronate ester was formed . These observations were in agreement with those of Motry *et al*.[lxiv] who reported that the hydroboration reaction of 1-hexene with benzo-1,3,2-diazaborolane was not successful even after refluxing at 100 °C for 1 week, no hexyl-benzo-1,3,2-diazaborolane was formed.

When one compares benzo-1,3,2-diazaborolane to benzo-1,3,2-dithiaborolane , it can be seen that both reagents show reduced reactivity towards olefins. This is attributed to the fact that for both nitrogen and sulfur substituents a lone pair of electrons is donated to the vacant p-orbital on boron through back-donation and in both reagents the aromatic ring acts as a pool of electrons, thus allowing for more back-donation. However, for benzo-

1,3,2-dithiaborolane, the interaction between the Lewis acidic group B-H and the olefinic double bond can be established at elevated temperatures. Whilst benzo-1,3,2-diazaborolane showed no reaction even at elevated temperatures and extended reaction times. This discrepancy between the two reagents revealed that the magnitude of back-donation is greater for the nitrogen than for the sulfur substituents.

The results described above formed part of the paper published in the Industrial and Engineering Chemistry Research journal,[lxv] produced collectively with our research team in collaboration with Dr Arno de Klerk of Sasol Technology R &D. A copy of the paper is attached.[*] der Klark, A., Hadebe, S. W., Robinson, R. S., Govender, J., Jaganyi, D., Mzinyathi, A., Xaba, N. *Ind. Eng. Chem. Res.* **2007**, 400.

[*] Copy of the paper included in the body of text as per faculty guidelines.

2.3 **CONCLUDING REMARKS**

The overall objective of the collaborative project was to investigate the possibility of using boron containing molecules as a means of converting internal olefins to linear alpha olefins, and our main focus was on the synthesis of heteroatom containing hydroborating agent and to investigate their reactivity.

The outcome of our study has successfully demonstrated that the presence of the heteroatoms on the hydroborating reagent significantly slow their reactivity in the hydroboration reaction. However, significant amounts of disproportionation products were noted during synthesis of the oxygen and sulfur analogues. We have also accounted computationally for the observed disproportionation of the cyclic sulfur analogue. It has been shown that the activation energy barrier to disproportionation is lower than that of hydroboration, and cyclic sulfur hydroborating agent have enough energy at room temperature to undergo disproportionation.

A systematic study using aromatic oxygen-, sulfur- and nitrogen-based boranes has shown that their reactivity in hydroboration decreases in the order O > S > N, with increasing magnitude of electronic back-donation into the boron atom. This indicated that the Lewis acidity of the boron atom decrease with increasing magnitude of back-donation. Consequently, in order to gain the in-depth understanding of the hydroboration reaction and to explore and resolve the complexity of hydroboration reaction, the incorporation of computational molecular modelling was envisaged, and that forms the basis of following chapter (Chapter 3).

2.4 **REFERENCES**

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PREFACE

In the preceding chapter it has been elucidated how the presence of heteroatoms impede reactivity towards olefins, by donating the electron cloud into the boron vacant p_z orbital. The desire to fully understand the hydroboration mechanism and associated transition states prompted our investigation by the use of molecular modeling. Therefore, the primary objective in this chapter was to investigate computationally the existence of π-complexes and transition states occurring during the hydroboration reaction, with the intention to rationalize the experimentally determined reactivity trends. A selected range of aliphatic, cyclic and aromatic derivatives of oxygen, sulfur and nitrogen hydroborating agents was investigated.

3.1 **INTRODUCTION**

Quantum chemistry was born in the mid 1920's, two decades later, Hylleras[i] and others[ii] developed the solution of the Schrödinger equation for a single electron diatomic molecule. In 1970 interesting discoveries were achieved when the first quantum chemistry computer package Gaussian-70 was released by Pople's group.[iii] The impressive computer advancement and automatic optimization computer codes since that time have led to vast improvements in computational chemistry. Consequently, a vast number of chemistry problems are now being addressed using the computational approach.

Nowadays there are many computational chemistry software packages available commercially which utilize a number of different theoretical models. For example, Titan, Spartan, Hyperchem and Gaussian, to name but a few. The common theoretical models used are Molecular Mechanics (MM), Semi-Empirical (SE), Hartree-Fock (HF), Møller-Pleset (MP) and Density Functional Theory (DFT).[iv,v]

The principal aim of this introduction is to familiarize the reader with the basic understanding of the acronyms and terms used in this study. Whilst the scope of this dissertation does not include an in-depth and detailed mathematical description of computational chemistry, excellent text books by Hehre,[iv] Jensen,[v] and Cramer[vi] are recommended. For a general understanding of the major methods, concepts and acronyms sufficient to acquaint those unfamiliar with computational chemistry, a comprehensive text by Bachrach[vii] is recommended.

3.2 **THEORETICAL BACKGROUND**

In chemistry, the most interesting quantities that can be derived by the use of molecular modeling are equilibrium and transition state geometries and conformations, heats of reactions, activation energies and vibrational frequencies. These quantities are computed from the potential energy surface (PES) (Figure 3.1).

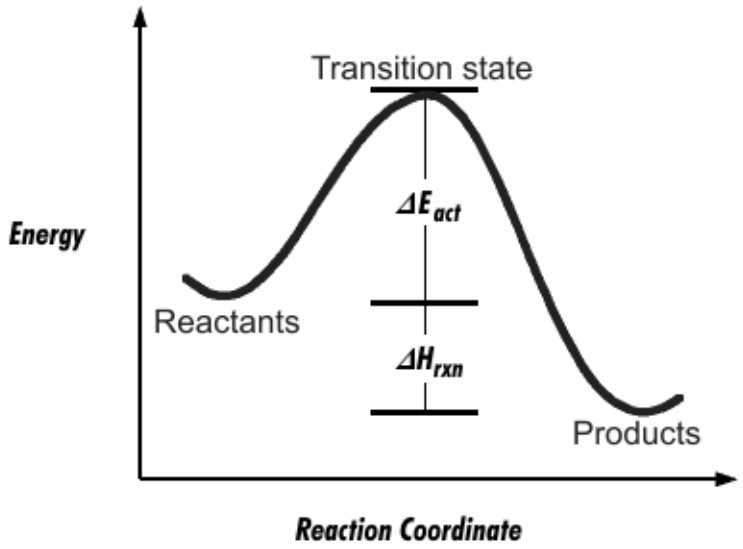

Figure 3.1 Potential energy surface (PES)

There are two stationary points on the PES, namely the energy minima and energy maxima. The energy minima are also known as the local minima, it indicates the stable molecules on the PES (that is, the reactants and products), and the lowest energy minimum is denoted as the global minimum. In other cases the PES is constructed for a single molecule upon change in its conformations or upon rotation of a dihedral angle, e.g. rotation of a dihedral angle of ethane (Figure 3.2). However, some energy minima are very reactive and too unstable to isolate for characterization, those species correspond to intermediates.

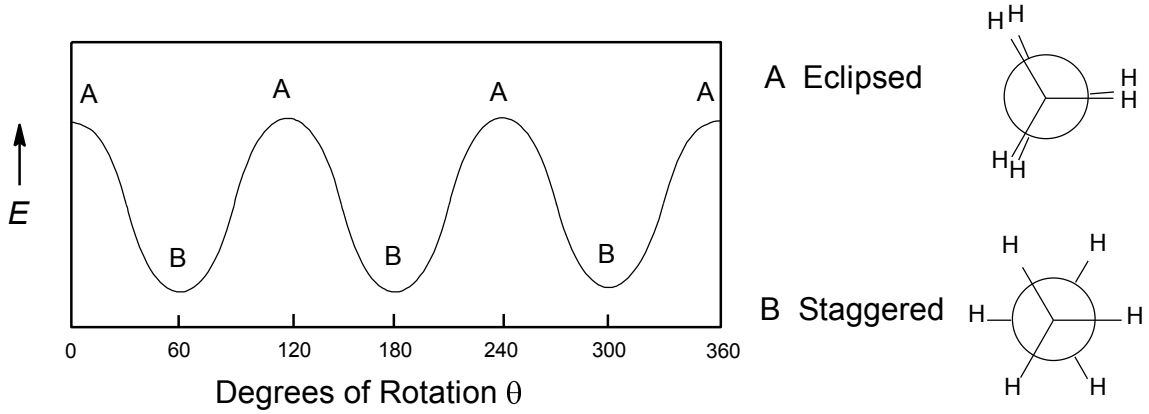

Figure 3.2 Potential energy surface for ethane dihedral angle rotation.[viii]

The top of the PES represents the transition state structure. These higher energy curves are termed energy maxima and their positions along the reaction coordinates correspond to the transition state geometries.[ix] The energy of the transition structure is required in order to determine the reaction activation energy and reaction rate. Its geometry is an important piece of information for elucidating the reaction mechanism. Mathematically, a transition structure is a geometry on the PES which has a zero derivative of energy with respect to moving all nuclear coordinates and has a positive second derivative of energy for all but one geometric movement, which has a negative curvature.[v] However, this describes many structures other than a reaction transition.

It is often challenging to predict what the transition structure would look like without assistance from computational simulation, due to a number of reasons. Usually a prediction is based on a proposed mechanism, which could be incorrect. The PES around the transition structure is much more flat than the surface around a stable geometry, and as a result, there may be significant discrepancies in the transition state geometries between two reactions that look similar and with very small energy difference.[v]

Recently, an experimental technique with the capability to directly examine reaction mechanisms was discovered, known as Femtosecond Pulsed Laser Spectroscopy. It will take some time before such techniques can be applicable to all compounds that are

accessible computationally. Moreover, vibrational analyses are acquired from this type of technique, and not the actual geometry for the transition structure, and for many years, computational molecular modeling has been successfully applied to determine transition state structures.

3.3 **COMPUTATIONAL METHOD**

3.3.1 **SOFTWARE**

3.3.1.1 **GAUSSIAN 03 REVISION B. 03 AND GAUSSVIEW 03**

All computational calculations in this study were computed using Gaussian 03, Revision B. 03 (G03) software package,[x] which is the latest in the Gaussian series of electronic structural programs. Gaussian software has been used for almost four decades by chemists, chemical engineers, biochemists, physicists and others for research in different areas of chemical interest.

G03 is capable of predicting reaction energies, molecular structures and vibrational frequencies of molecular systems and many other molecular properties that can be derived from the basic laws of quantum mechanics. It is used to study molecules and reactions under a wide range of conditions, that includes both unstable species and short-lived intermediates and transition states that are impossible to observe experimentally.[xi]

In addition, G03 has expanded the limits of computational chemistry, by introducing the newly improved ONIOM which was included for the first time in Gaussian 98. This facility enables researchers to model proteins and other large biological molecules that have been out of reach of electronic structure methods.[xi] It also gives performance gain for geometry optimization using a quadratic coupled algorithm and micro-iterations.

Moreover, G03 can be used to calculate spin-spin coupling constants, NMR shielding, and IR spectra, which are crucial in conformational analysis. In addition equilibrium geometries of transition states structures, reactivity and reaction energies of polymers can be computed.[xi]

However, Gaussian 03 does not have a facility for drawing and constructing molecular structures integrated into it. Structures are drawn separately from GaussView, which is a full-featured graphical user interface designed to build molecular systems.[xi] GaussView is used to set up and run Gaussian calculations and to visualize a variety of different Gaussian results, including molecular orbitals, optimization movies, electron densities, etc.[x] The facilities available on this software were used in this study in order to construct input files and also to visualize the results obtained.

3.3.2 **GAUSSIAN KEYWORDS**

In our study, a set of Gaussian keywords were implemented in order to locate the transition state (TS) and subsequent treatment of its structure to obtain the desired thermodynamic parameters. In all calculations the 'OPT' command was included before any special keyword, its purpose is to request that a geometry optimization be carried out. These keywords used are discussed briefly below.

3.3.2.1 **MODREDUNDANT (MODRED)**

This command requests that the current structure geometry be modified using redundant internal coordinates modification before the calculation is conducted.[xii] A geometry optimization can be performed in the presence of coordinates that are to be constrained, e.g. a dihedral angle could be frozen to a specified angle or a bond length to be scanned in specifies step sizes. The constraints are stated below the Cartesian coordinates in the input file.[xii]

3.3.2.2 **NOEIGENTEST**

In Gaussian, by default Berny optimizations are utilized for a TS search. In this type of optimization, the Eigen test method is implemented automatically to test for curvature during Berny optimization. If one Eigen value (imaginary frequency) is found, the calculation continues to find the transition state associated with that imaginary frequency. During the TS search it is possible to locate more than one Eigen value, nonetheless, this leads to the calculation being terminated. In order to avoid this from taking place, the Eigen test is turned off when the command 'NOEIGENTEST' is used.[x]

3.3.2.3 **TS**

This keyword is used for transition state search, and it requests optimization to a local maximum rather than a local minimum. In this calculation type, an initial starting structure is required as an input.[x]

3.3.2.4 **CALCFC**

This keyword requests that the force constant be calculated at the first point using the default method (this facility is available for HF, MP2, CASSCF, DFT and SE methods only).[xii] It is always better to use a transition state starting structure that was obtained previously using a lower level of theory and then use the 'calcfc' keyword on the new calculation.

3.3.2.5 **FREQ**

In order to obtain the analysis of vibrational frequencies, the 'freq' keyword is used. This leads to calculation of the infra red and Raman spectra. Thermochemical analysis is also carried out on this calculation type.[xiixii]

3.3.3 **HARDWARE**

All calculations were conducted on three personal computers and one laptop computer, system information is listed below:
Laptop: Acer TravelMate 2410, 512 MB RAM, 1600 MHz x86 Family 6 Model 13 Stepping 8 GenuineIntel processor, Microsoft Windows XP Professional, service pack 2. *Desktop* 1: 1024 MB RAM, Dual 3396 MHz x86 Family 15 Model 6 Stepping 4 GenuineIntel processors, Microsoft Windows XP Professional, service pack 2. *Desktop* 2: 1024 MB RAM, 2666 MHz x86 Family 15 Model 3 Stepping 4 GenuineIntel processor, Microsoft Windows XP Professional, service pack 1. *Desktop* 3: 512 MB RAM, 1817 MHz x86 Family 15 Model 1 Stepping 3 GenuineIntel processor, Microsoft Windows 2000 Professional, service pack 4.

3.4 **CALCULATION METHOD**

In this study, thermodynamic data of each of the species involved in the potential energy surface of the hydroboration reaction were computed using G03. The method used to treat reactants, transition states and products in order to yield the required parameters is discussed below.

3.4.1 **REACTANTS AND PRODUCTS**

GaussView 03 was used to build the molecular structures of reactants, that is, the hydroborating agents and the alkene as well as the product organoboranes. These were then saved individually as G03 input files. A full geometry optimization was carried out on each unconstrained molecule, using the ground state-density functional theory (DFT) B4LYP level of theory with 3-21+ G basis set. The OPT keyword was used in the input line in order to request a geometry optimization on the molecule until a stationary point on the energy minimum is reached. The FREQ keyword was also included on the same

calculation in order to verify that there are no imaginary frequencies (negative Eigen values) on all molecules of reagents and products.

3.4.2 **TRANSITION STATE SEARCH**

The approximate starting structure for a transition state was located by conducting a scan job. This job type scans the potential energy surface from two reactants to transition state and then product. This is done by drawing the hydroborating agent closer to the alkene, by reducing the bond length between the boron atom and the carbon atom (terminal carbon for anti-Markovnikov addition and internal carbon atom for the Markovnikov addition) in a stepwise manner in specified step sizes. The OPT, MODRED, and NOEIGENTEST keywords were used at DFT B3LYP/3-21+G level of theory. The bond length to be changed and the step sizes are specified at the bottom of the Z-matrix of the input file. The different stages of the scan yield different energies, which are plotted against reaction coordinates to produce the potential energy surface (PES) for the hydroboration reaction (Figure 3.3). The coordinates of the structure closest to the energy maximum were extracted and saved as a new input file, these Cartesian coordinates are close to the correct transition state, as proposed by Dewar *et al*.[xiii] to be a 4-center transition state for hydroboration (chapter 2).

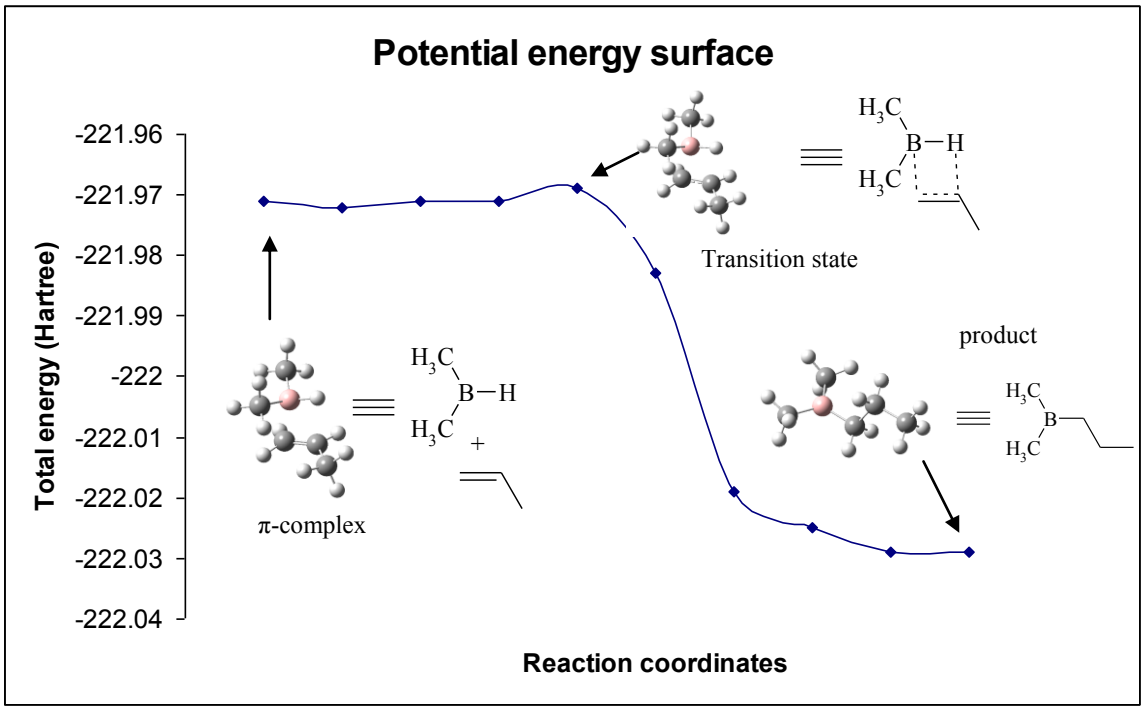

FIGURE 3.3 The PES scan for $(CH_3)_2BH$ with propene calculated at DFT/3-21 + G

The new coordinates obtained from the PES were then subjected to a second Gaussian job with the intention of further refining the approximate transition state structure. Three bond lengths, that is, B-C, B-H, and H-C on the 4-center transition state were frozen to their current values. The rest of the molecule was optimized to find the structure with the lowest possible energy. The OPT, TS, MODRED, and NOEIGENTEST keywords were used at DFT B3LYP/3-21G level of theory. The coordinates of the structure with the lowest possible energy were extracted from the output file, all constraints were removed and the coordinates saved as a new input file for final transition state structure verification.

Transition state corroboration was performed by the optimization and frequency calculations done on the newly extracted coordinates. The OPT, TS, NOEGENTEST, CALCFC and FREQ combination of keywords was used at DFT B3LYP/3-21G level of theory. This calculation type requests for a geometry optimization of the unconstrained molecule down hill, to the structure with the lowest possible energy at the transition state. Careful examination of the vibrational frequencies of the lowest energy structure, showed

the existence of a single negative Eigen value associated with movement of the correct atom in the transition state.

3.5 **RESULTS AND DISCUSSION**

The molecular modeling investigation conducted in this chapter, including computational methods and detailed discussion of results, has been written up for publication in the Journal of Molecular Structure (Theochem).[xiv] A copy of this paper follows.[*]

[*] Copy of the paper included in the body of text as per faculty guidelines. Cartesian coordinates of geometry optimized structures of TS and products are included in appendix C.

3.6 **CONCLUDING REMARKS**

The use of computational molecular modeling has revealed interesting and vital information concerning the hydroboration mechanism. Of particular interest is the dimerization of the cyclic sulfur-based borane which agrees with early studies by Egan *et al*.[xv] For nitrogen compounds it has been shown that a high activation energy barrier has to be overcome in order for hydroboration to take place. The study has also validated the experimental observation that aromatic derivatives are the least reactive towards olefins. The outcome of the study has clearly demonstrated that strongly coordinating heteroatoms such as sulfur and nitrogen have significantly lowered the reactivity of the borane and this effect is more pronounced in the presence of an aromatic ring on the hydroborating agent. In order to be able to utilize these reagents in hydroboration, an alternative or catalytic route to furnish hydroboration with these electron deficient boranes is desirable, and that forms the basis of the following investigation in chapter 4.

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PREFACE

Nowadays a vast amount of industrial processes utilize a number of different transition metal catalysts, which provide efficient, selective and economic synthetic routes to the target products. In order to evaluate the suitability of these electron deficient hydroborating agents as potential reagents in the final industrial process, the use of transition metal catalysts was explored. The primary aim of the investigation in this chapter was to study the use of transition metal catalysts with the intention to facilitate the hydroboration reaction with the synthesized electron deficient hydroborating agents.

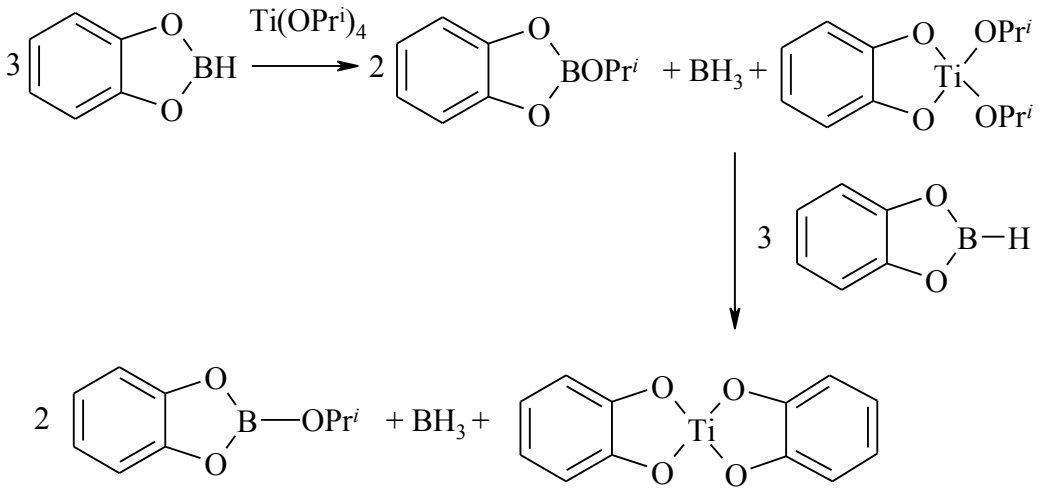
4.1 **INTRODUCTION**

In the preceding two chapters, the stability of the hydroborating reagents synthesized has clearly been demonstrated.[i,ii,iii] As a result, transition metal catalysts were investigated in hydroboration reactions. The aim of the following survey is to introduce the concepts of catalysis in hydroboration using different transition metal-based catalysts.

4.2 **TITANIUM-CATALYZED HYDROBORATION**

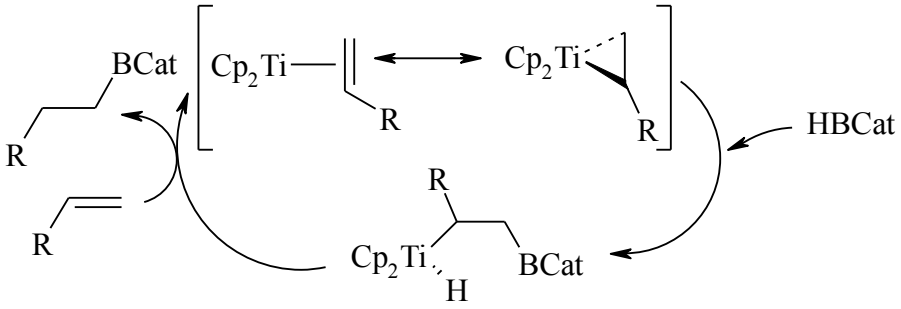
Many research groups have focused their investigations on catalytic hydroboration using early transition metal complexes, with the intention to discover new catalytic pathways and to reduce the cost of hydroboration.[iv,v] Accumulated literature precedent showed that the addition of the hydroborating agent such as catecholborane to olefins can be enhanced by these early transition metal catalysts.[iv,v,vi,vii,viii,ix,x,xi,xii]

Cyclopentadienyl titanium dichloride (Cp_2TiCl_2)[xiii] and $TiCl_3$[xiv] have been reported to promote hydroboration of alkenes with borohydrides, and the dicarbonyl derivative ($Cp_2Ti(CO)_2$) was known to catalyze hydroboration of alkynes. However, follow up investigations have subsequently shown that $TiCl_3$ led to rapid dismutation of $LiBH_4$ to borane which is in fact the active hydroborating agent.[xv] Titanium tetraisopropoxide ($Ti(O\text{-}Pr^i)_4$) likewise, has been shown to promote hydroboration of alkenes with catecholborane.[xv] It appears that this catalyst also causes borane formation (Scheme 4.1), like the previously reported $TiCl_3$. These results are in agreement with the investigation by Burgess and van der Donk that $(mesitylene)_2Nb$ also catalyzes decomposition of catecholborane to diborane and B_2Cat_3.[xvi] Harrison and Marks thus concluded that early transition metal complexes that cause production of diborane, which provides hydroboration, are not 'true' hydroboration catalysts.[xvii]



Scheme 4.1

Extensive studies by He *et al*.[iv] revealed that dimethyl titanocene led to hydroboration of alkenes without degradation of CatBH, since no trialkylborate esters were formed.[iv] this paper reported hydroboration of terminal alkenes at room temperature and internal alkenes at 55 ^oC in essentially quantitative yields.[iv] Anti-Markovnikov products were formed predominantly and entirely for aryl-substituted alkenes. This study demonstrated that Cp_2TiMe_2 is a 'true' hydroboration catalyst, since there was no evidence of catecholborane decomposition.[iv] From the results of the study, a mechanism was proposed, that is likely to proceed *via* a σ-bond metathesis between CatBH and one of the Ti-C bonds of the alkene or alkyne complex (Scheme 4.2)[iv] that adopts a significant metallacyclopropane character due to the strong back bonding ability of d^2 metals. This was followed by addition of CatBH leading to product formation.[xviii]

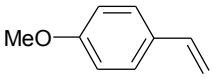
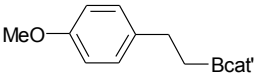
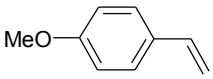
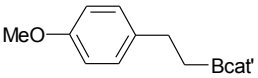
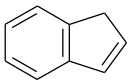
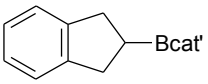
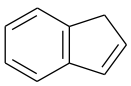
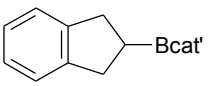


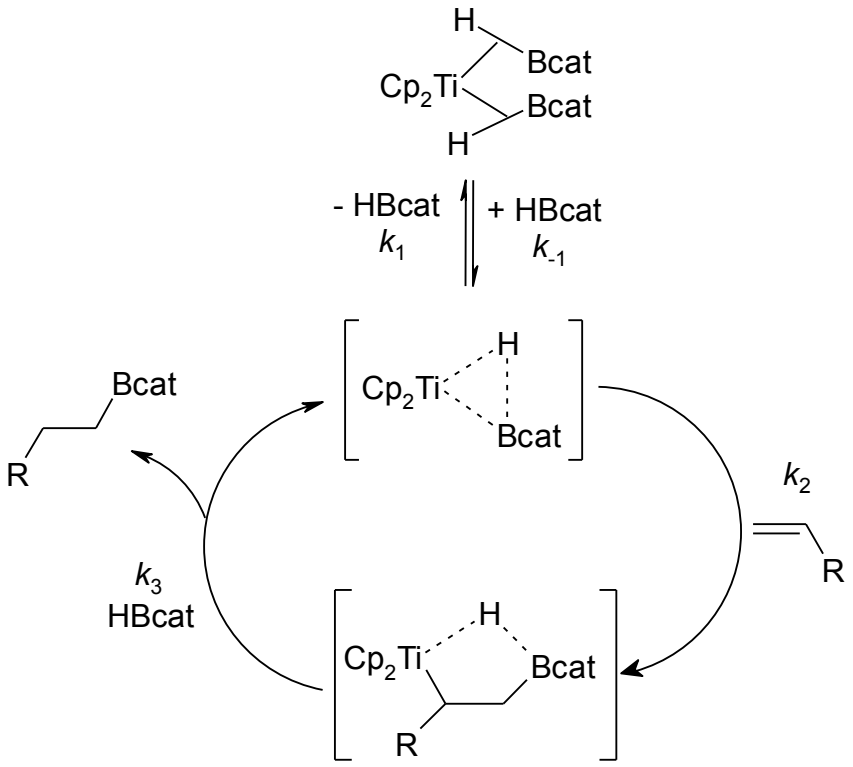
Scheme 4.2

Further mechanistic investigations on this system were conducted by Hartwig *et al*.[xix] and these led to a method for the discovery of titanocene bis(borane) σ-complex ($Cp_2Ti(HBCat)_2$), from the reaction of excess CatBH with Cp_2TiMe_2.[xix] Subsequent investigation by Hartwig *et al*.[xx] in early 2000, showed that no complexation of the alkene to Cp_2TiMe_2 was observed in the absence of catecholborane. This observation led to the speculation that $Cp_2Ti(HBCat)_2$ could be the active catalyst for hydroboration in this system instead of Cp_2TiMe_2.

A comparative study was conducted to evaluate the reactivities of both complexes, Cp_2TiMe_2 and $Cp_2Ti(HBCat)_2$ (Table 4.1). It was then evident from the results that $Cp_2Ti(HBCat)_2$ is indeed the more active catalyst, achieving 90-100% yields in 10 minutes compared to 10 hours with Cp_2TiMe_2.[xx] The mechanism that fitted experimental data was proposed (Scheme 4.3) in order to confirm that $Cp_2Ti(HBCat)_2$ complex has properties of a true hydroboration catalyst.[xx]

Table 4.1 Showing the reactivity comparison[xx]

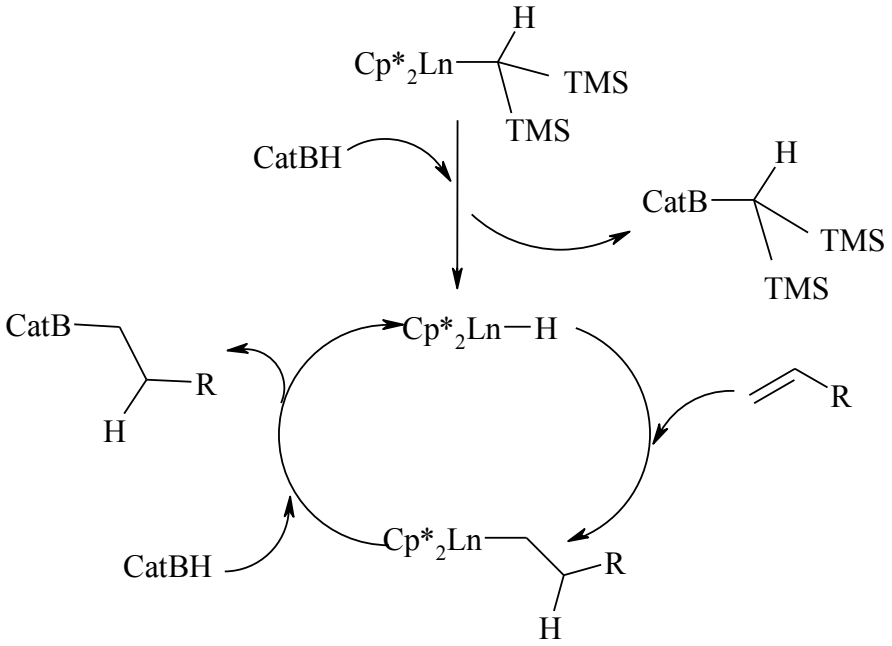
Substrate	Catalyst	Conditions	Product	Yield (%)
	$Cp_2Ti(HBcat\text{-}4\text{-}t\text{-}Bu)_2$	10 min 25 °C		90
	Cp_2TiMe_2	10 h 25 °C		96
	$Cp_2Ti(HBcat\text{-}4\text{-}t\text{-}Bu)_2$	10 min 25 °C		100
	Cp_2TiMe_2	10 h 25 °C		96



Scheme 4.3[xx]

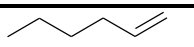
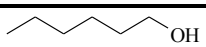
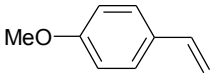
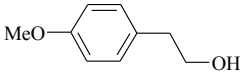
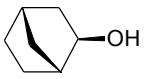
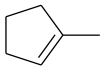
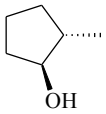
4.3 **LANTHANIDE-CATALYZED HYDROBORATION**

Marks research group pioneered the use of organolanthanide complexes as catalysts for hydroboration of alkenes.[xxi]A unique mechanism was proposed, which proceeds without the change in oxidation state of the metal centre (Scheme 4.4).[xxi] It is reported that organolanthanides such as Cp^*_2LnR (where Cp^*= η^5-Me_5C_5; Ln = La, Sm; R = H, $CH(SiMe_3)_2$) are effective homogenous catalysts for hydroboration of a wide variety of alkenes with CatBH at room temperature (Table 4.2).[xxi] Interestingly, even internal disubstituted and trisubstituted olefinic substrates are effectively hydroborated with remarkably high regioselectivity. The observed regioselectivities are exclusively anti-Markovnikov, even with electron rich substrates, such as vinyl anisole (Table 4.2).[xxi]



Scheme 4.4

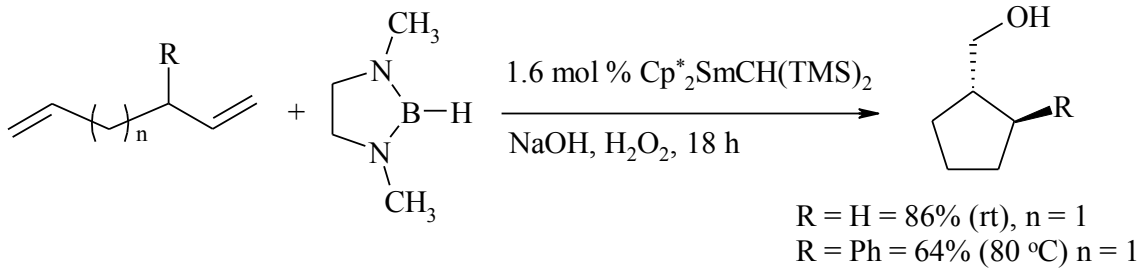
Table 4.2 Hydroboration of alkenes with CatBH catalyzed by organolanthanide[xxi]

Substrate	Product	Isolated Yield (%)
		98
		89
		71
		73

Evans *et al*., showed lanthanide hydroboration catalysis extended beyond the complexes reported by Marks and Harrison. This study demonstrated that the architecture of the ligand is important on the catalyst.[xxii] A range of trivalent samarium complexes were screened for catalytic activity in the hydroboration of 1-decene with catecholborane. SmI_3, (*t*-BuO)SmI_2, and (*i*-PrO)$_3$Sm were discovered as new catalysts. Upon the use of these new catalysts, 1-decanol was produced in 18 hours at 25 ^oC.[xxii] The observed

regioselectivity supported the mechanism proposed by Mark and Harrison. A range of olefinic substrates were investigated, including styrene, are hydroborated preferentially to primary alcohols. In addition, α-pinene and phenylcyclohexene are hydroborated to generate exclusively the *cis*- isomers.[xxii]

The application of organolanthanide-catalysis has been reported to broaden further than hydroboration, into cyclization reactions of 1,5- and 1,6-dienes, as reported by Molander and Pfeiffer in the early 2000s.[xxiii] This report showed that the widely utilized CatBH did not give appreciable yields due to partial decomposition. Pinacolborane also did not yield more than 50 % of the cyclized product. However, the use of the uncommon 1,3-diaza-2-boracycloalkane (Scheme 4.5) proved to be an efficient hydroboration reagent, producing an excellent 86 % yield.[xxiii]



Scheme 4.5

The transition metal-catalyzed hydroboration realm is still growing to date, with new catalyst systems being developed. $HZrCp_2Cl$ was reported by Srebnik and Pereira to be an excellent catalyst for hydroboration of alkynes at ambient temperature.[xxiv] The same group later reported that $HZrCp_2Cl$ was also capable of catalyzing the hydroboration of alkenes with pinacolborane.[xxv]

Murata *et al*.[xxvi] screened a wide range of ruthenium complexes, and reported that $[RuHCl(CO)(PPh_3)_3]$ yielded best results in the hydroboration of propargyl ethers with pinacolborane to furnish (*Z*)-allylboronates.[xxvi] Further additions by Yamamoto *et al*.[xxvii] were reported in 2004, on the use of iridium (I) phosphine complexes, such as

$[Ir(COD)Cl]_2$/2dppm and $[Ir(COD)Cl]_2$/2dppe as excellent catalysts for hydroboration of a range of alkenes, giving more than 99 % selectivity for 1-alkenes.[xxvii]

4.4 **RHODIUM-CATALYZED HYDROBORATION**

4.4.1 **RHODIUM (III)-CATALYSIS**

In the mid 1980's, rhodium(III) octaethylporphyrin (OEP) was utilized with sodium borohydride in an oxygen atmosphere, in order to achieve the reduction of carbonyl compounds.[xi] Application of the same methodology to hydroboration of alkenes and alkynes led to interesting results, that is, the alcohols were produced directly from either alkenes or alkynes.[xi]

The mechanism, by which this reaction proceeds has not been clarified.[xi] It is reported that regioselectivity is not very high during the hydroboration of styrene, where the primary to secondary ratio is 61:39. 1-Heptene produced 1- and 2-heptanols in the ratio 82:18 and with 1-octene, a 91:9 ratio is observed for 1- and 2-octanols respectively.[xi]

4.4.2 **RHODIUM (II)-CATALYSIS**

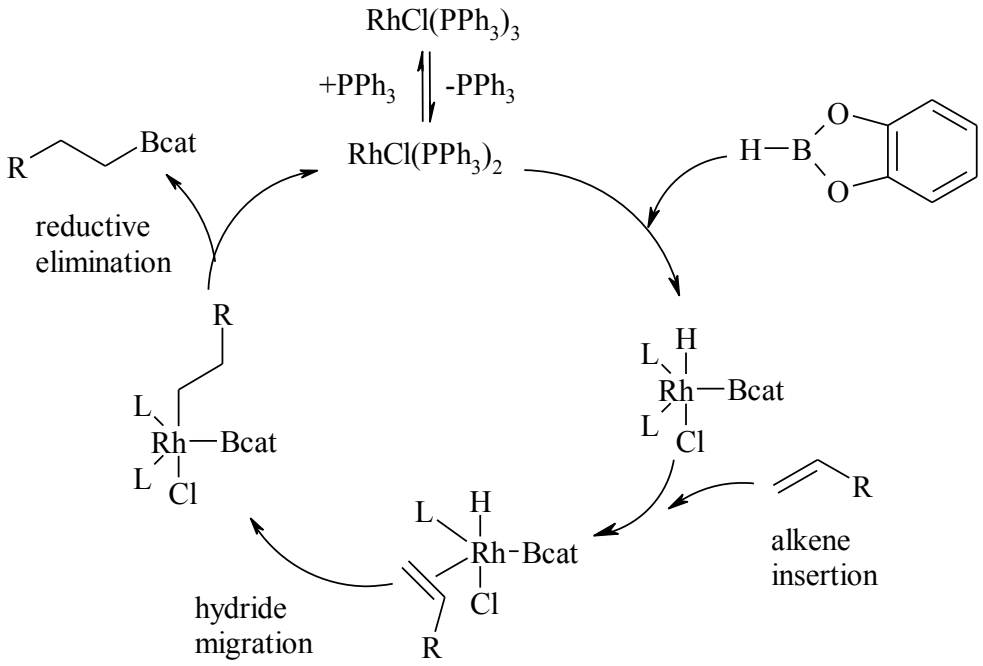
Rhodium (II) complexes have also been shown to be potential hydroboration catalysts, *viz*. rhodium(II) carboxamides and carboxylates.[xxviii] It has been reported that the solvent choice is very crucial in this type of reaction. Solvents such as THF are not used because they coordinate with dirhodium(II) compounds, thus inhibiting the hydroboration reaction.[xxviii] Typical reactions with these catalysts are normally conducted with CatBH and 0.5 mol % $Rh_2(OAc)_4$ in refluxing dichloromethane.[xxviii] This catalyst system has been shown to promote complete isomerization of allylbenzene to a mixture of (*E)*- and (*Z*)-1-phenylpropene, an 81:19 ratio was achieved with the use of $Rh_2(OAc)_4$ (1.0 mol %) and CatBH (3.0 mol %).[xxviii]

4.4.3 **RHODIUM (I)-CATALYSIS**

In the mid 1970's Kono *et al*.[xxix] discovered that the B-H bond of catecholborane can be added oxidatively to the metal centre of Wilkinson's catalyst $RhCl(PPh_3)_3$. This catalyst was previously utilized to achieve hydrosilylation[xxx] and hydrogenation[xxxi] of alkenes. Following Kono's report Männig and Nöth demonstrated the first reaction that showed that $RhCl(PPh_3)_3$ catalyzed hydroboration of alkenes with CatBH.[viii]

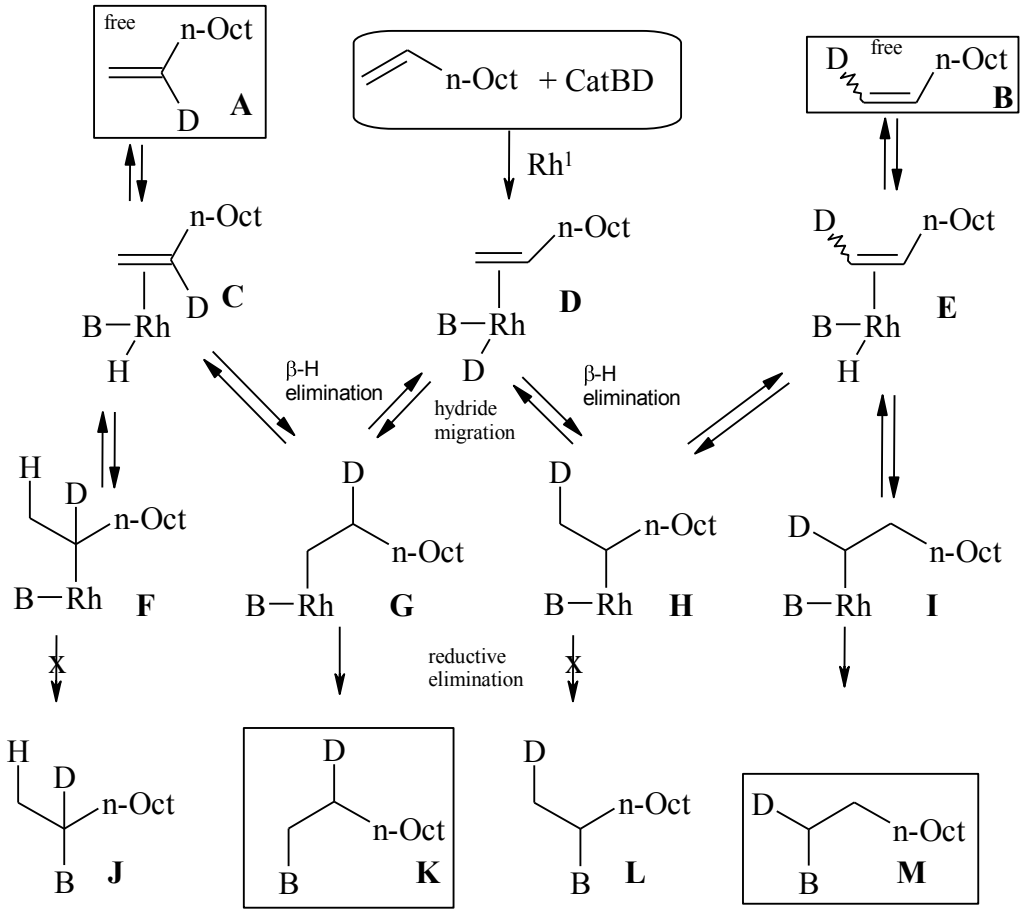
4.4.3.1 **MECHANISM OF RHODIUM (I)-CATALYSIS**

A mechanism different from that proposed for titanium[iv] or lanthanide[xvii] was initially proposed in 1985 by Männig and Nöth (Scheme 4.6), based on the hydrogenation model.[xxxii] The reaction involves the oxidative addition of the B-H bond to the coordinatively unsaturated metal centre, followed by alkene insertion and then the hydride migration to the coordinated alkene leading to reductive elimination of the product B-C bond.[viii]



Scheme 4.6

Subsequent mechanistic investigations by Evans *et al*.,[vii,ix] performed with the use of deuteriocatecholborane and 1-decene as a substrate, showed that significant amount of deuterium was present at C1 of the recovered olefin and as expected, on the α- and β-carbons of the product alcohols.[xxxiii] It was apparent that the mechanism of hydroboration is rather more complicated than that initially presented by Männig and Nöth. Evans *et al*.[xxxiii] proposed a mechanism that shows six deuterium containing compounds (Scheme 4.7) that are expected to form if the olefin complexation to rhodium and hydride migration are in fact reversible.[xxxiii]



Scheme 4.7[xxxiii]

The products enclosed in boxes, were characterized in their study. Compound **L** is not formed due to the fact that reductive elimination of alkylboronate from secondary

alkylrhodium complex is slower than other processes occurring during catalysis.[xxxiii] This observation led to the discovery that the passiveness of reductive elimination of compound **H** is the driving force for the high level of regioselectivity found in rhodium catalyzed hydroboration of terminal alkenes, about 99 (primary alcohol): 1 (secondary alcohol).[xxxiii] This study revealed that the route followed by Rh(I) catalyzed hydroboration is substrate dependent. For 1-decene, the reductive elimination was found to be the regioselectivity -determining step, while the hydride migration determines the regioselectivity for styrene.[xxxiii]

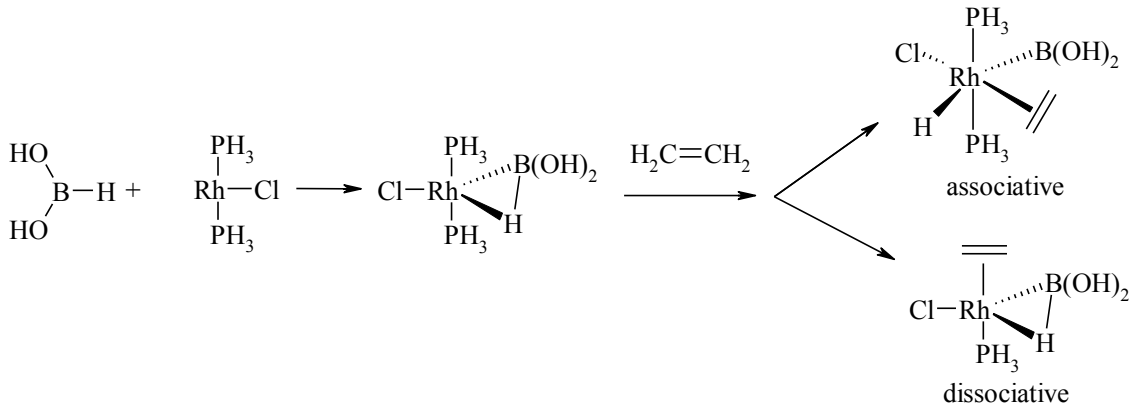
4.4.3.2 **MOLECULAR MODELING OF RHODIUM (I)-CATALYSIS**

A number of questions have been raised concerning the mechanism of catalyzed hydroboration. Hence, a detailed *Ab Initio* molecular modeling study of possible reaction pathways was first conducted by Musaev *et al*. in 1994.[xxxiv] The stability and structures of intermediates involved and transition states were studied, using the reaction of ethylene and $HB(OH)_2$ or $HBO_2(CH_2)_3$ as models, in the presence of $RhCl(PH_3)_2$ as the model Wilkinson's catalyst.[xxxiv] It was concluded that the most favourable catalytic pathway proceed *via* the oxidative addition of the B-H bond to the model catalyst, followed by coordination of the alkene between the boron and the hydride ligand.[xxxiv] The following step involves the insertion of the C=C double bond into the Rh-B bond. The reaction is completed by the dehydrogenative reductive elimination of the product $C_2H_5B(OH)_2$.

It is reported therein, that for reductive elimination or dissociation to occur, activation energy of about 20 kcal/mol is required. The authors report that the reductive elimination step is very slow, during catalysis and this step was calculated to be the rate determining step of the reaction.[xxxiv] Musaev *et al*.'s supported the literature precedent.[vi,ix,xxxiii] Subsequent *ab initio* studies by Dorigo and Schleyer[xxxv] also supported the original catalytic cycle by Männig and Nöth.

Recently, a more detailed DFT/BP86 study was conducted by Widauer *et al*. with the objective to compare the calculated energy profiles for the two proposed pathways for

catalyzed hydroboration reaction.[xxxvi] The two pathways are, the associative mechanism, where the alkene addition occurs without phosphine dissociation, and the dissociative mechanism, where alkene addition and simultaneous loss of the phosphine ligand take place (Scheme 4.8).[xxxvi]



Scheme 4.8

This study demonstrated that both mechanisms are in fact allowed. The proposed two mechanisms, dissociative and associative, can each undergo two further pathways to initiate product formation, namely, the boron migration or hydride migration pathways.[xxxvi] It is reported that for the associative mechanism, the boryl and hydride migrations require similar energies. The activation energy barrier (9 kcal/mol) has to be overcome in order to produce the complex [RhCl(H_3CCH_2-$B(OH)_2(PH_3)_2$] by reductive elimination. The authors proposed that the hydride migration may be favourable for an associative mechanism.[xxxvi]

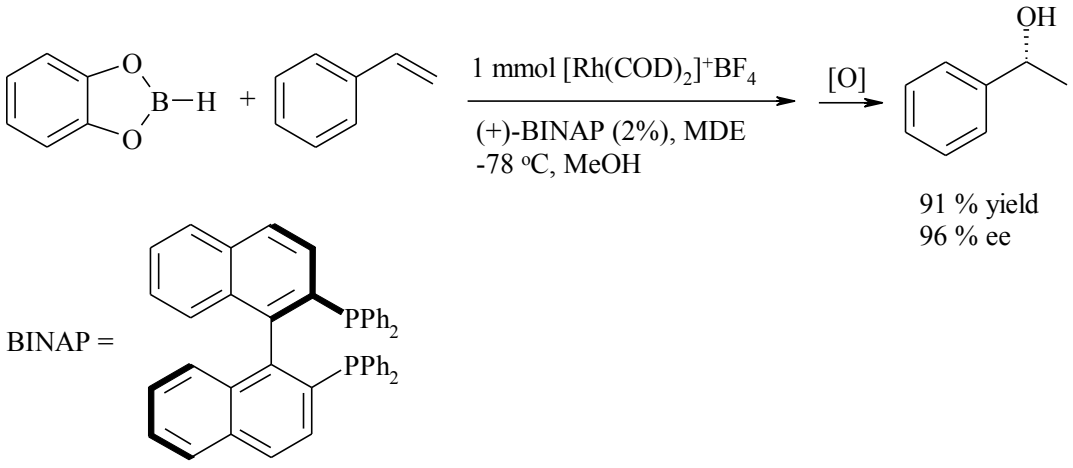
Conversely, in the dissociative mechanism, the boryl and hydride migration energy profiles differ significantly. For boryl migration pathway, the C-B bond formation required overcoming a high activation barrier (19.5 kcal/mol) whereas reductive C-H coupling required a low barrier (6.5 kcal/mol). For the hydride migration pathway, C-H formation required 8.5 kcal/mol while the reductive formation of the C-B bond required a higher barrier (15.8 kcal/mol). The authors concluded that, though boryl migration is more preferable that hydride migration, side products are formed through boryl migration

pathway in both associative and dissociative mechanisms.[xxxvi,xxxvii] Thus, it is suggested that the catalyzed hydroboration could be driven into a dissociative mechanism involving the hydride migration pathway by utilizing bulky electron-withdrawing phosphine ligands.[xxxvi,xxxvii7,xxxviii] This investigation shed light into the choice and number of phosphine ligands used in asymmetric hydroboration catalyzed by the Wilkinson's type catalysts.[xxxviii]

4.4.3.3 **ENANTIOSELECTIVITY IN RHODIUM (I)-CATALYSIS**

4.4.3.3.1 **CHIRAL LIGANDS**

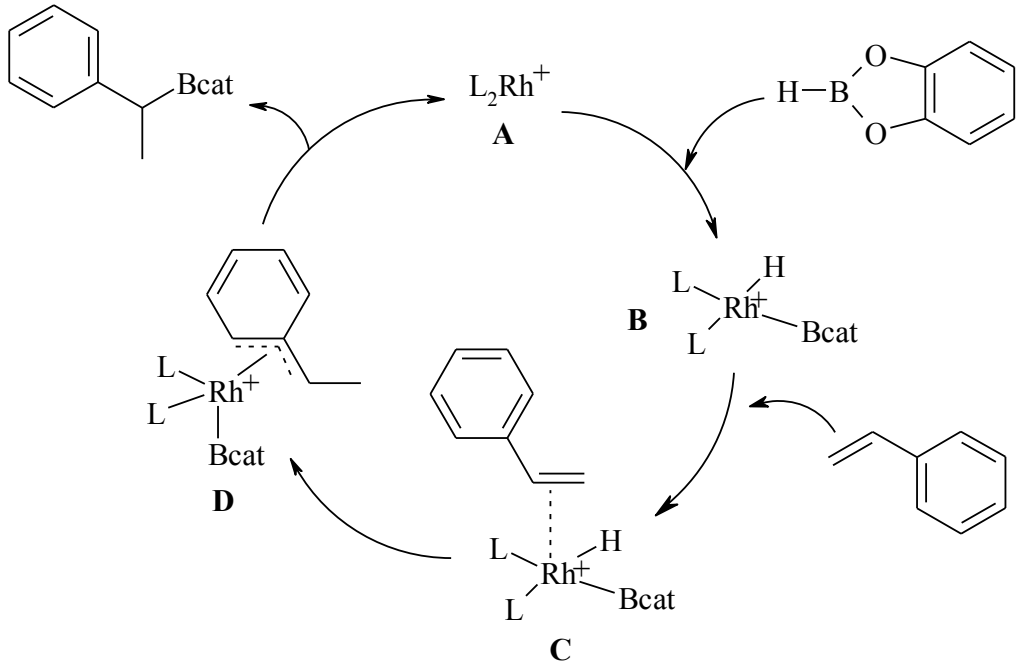
Hayashi *et al*. reported that the use of cationic chiral phosphine-rhodium(I) complexes to promote asymmetric hydroboration of styrenes gave rise to optically active (*R*)-1-arylethanols (Scheme 4.9).[xxxix] In this study, a range of substituted styrenes including vinylanisole were studied, the obtained enantiomeric purities of alcohols were in the range of 82 – 96 % ee.



Scheme 4.9[xxxix]

Hayashi supported the preferential formation of the branched isomer by a proposed catalytic mechanism similar to that by Männig and Nöth. However, in this mechanism, after alkene insertion into the rhodium-boryl complex, the next step generates a π-

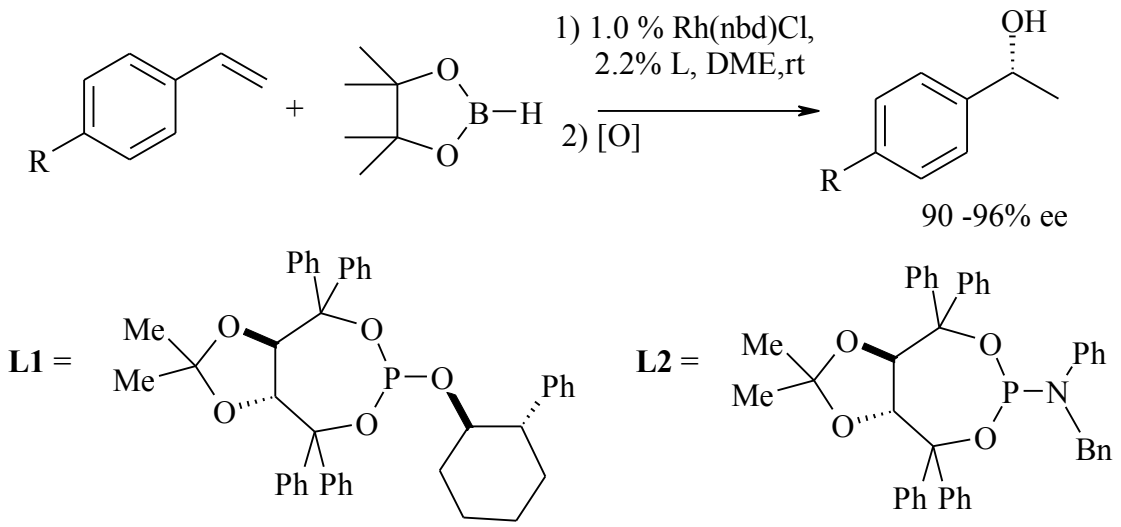
complex (**D**) (Scheme 4.10).[xxxix] The potential interaction of the catalyst with the arene through the π-benzyl complex formation prevents addition of the Rh-H bond to the internal carbon of the coordinated olefin.[xxxviii,xxxix]



Scheme 4.10

Further investigations by Burgess *et al*.[xl] broadened the scope using readily available chiral biphosphine ligands and structurally diverse prochiral substrates. This study showed that chiral induction is dependant upon the ligand type, the alkene structure and not much to the charge contained on the rhodium complex.[xl]

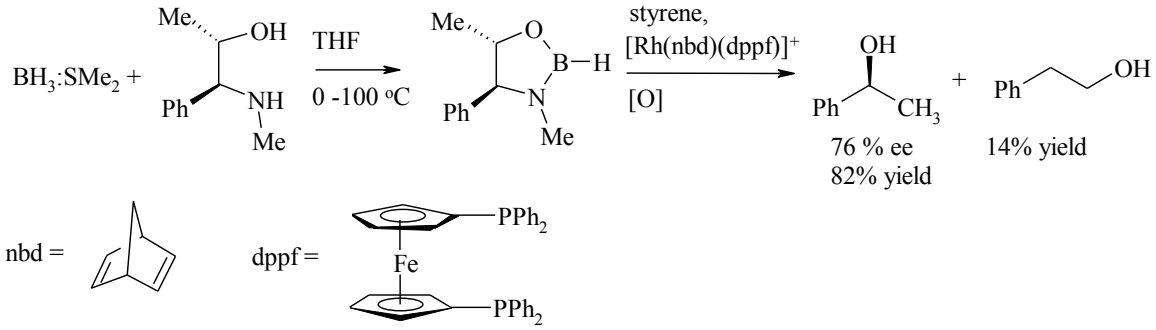
The realm of catalyzed asymmetric hydroboration has advanced over the last decade. In 2006, Moteki *et al*.[xli] reported that the use of monodentate ligands such as (1*R*,2*S*)-2-phenylcyclohexanol-derived phosphite **L1** and *N*,*N*-(phenylbenzyl)-phosphoramidite **L2** (Scheme 4.11) led to high level of enantioselectivity (up to 96 % ee) with Rh(I) type catalysts, during hydroboration of styrenes.[xli]



Scheme 4.11[xli]

4.4.3.3.2 **CHIRAL HYDROBORATING AGENTS**

Homochiral hydroborating agents have been shown by Brown and LIoyd-Jones to induce enantioselective hydroboration (Scheme 4.12).[xlii] The hydroborating agent employed {(4S, 5R)-ephedrineborane[xliii] and the (4S, 5S) diastereomer} were easily produced from inexpensive chiral auxilaries ephedrine and pseudophedrine respectively.[xlii]



Scheme 4.12[xlii,xxxviii]

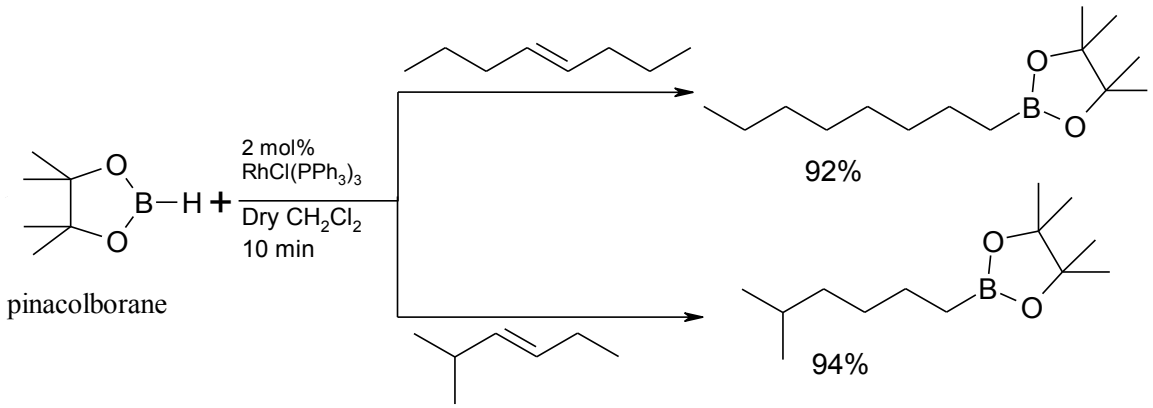
Further mechanistic studies by Brown and LIoyd-Jones on the effect of steric hindrance at the nitrogen atom of the oxazaborolidine, showed that asymmetric hydroboration can

be hampered significantly by the size of the substituent on the nitrogen atom. This was evident upon replacement of the methyl group with an isopropyl group, which led to dehydrogenative borylation rather than the anticipated rhodium-catalyzed asymmetric hydroboration.[xlii]

4.5 **RESULTS AND DISCUSSION**

4.5.1 **CATALYZED HYDROBORATION WITH PINACOLBORANE**

In 1996 Pereira and Srebnik[xxv] reported the use of Rh(I) to catalyze the hydroboration of alkenes with pinacolborane which was previously reported by Tucker *et al.*[xliv] to be unsuccessful. Pereira and Srebnik reported that 92 % terminal octylpinacolboronate was obtained during the $RhCl(PPH_3)_3$-catalyzed hydroboration of *trans*-4-octene in 10 minutes (Scheme 4.13).



Scheme 4.13

Upon the use of *cis*-2-methyl-3-hexene, it was reported that the boron atom isomerized to the non branched carbon, while on the other hand catecholborane gave the expected internal boronate.[xxv] Pereira and Srebnik attributed the difference between the pinacolborane and catecholborane to the higher steric requirement of pinacolborane, which causes a fast β-hydride elimination/ recomplexation sequence. This leads to the

placement of the rhodium on the least hindered carbon, followed by a slow boron insertion.

From our perspective, the possibility to hydroborate internal olefins and isomerize simultaneously was envisaged as an interesting route to achieve α-olefins, because the resulting terminal pinacol alkylborane can be displaced to generate the desired α-olefin.

We employed $RhCl(PPh_3)_3$ to catalyze the hydroboration of *trans*-4-octene with pinacolborane at 25 °C. This reaction was conducted in a flame dried quartz NMR tube in order to monitor the progress of the catalyzed hydroboration reaction *in situ*. Surprisingly no reaction was observed after 10 minutes which contradicted findings by Pereira and Srebnik. After 24 hours, ^{11}B NMR analysis showed a doublet at 28.5 ppm attributed to B-H coupling of pinacolborane (Figure 4.1), a singlet 22 ppm which was attributed to the disproportionation product, although this signal was originally present in small amount in the stock solution of pinacolborane before addition of the catalyst and the olefin. The catalyst increased the amount of the disproportionation product, and disappointingly no hydroboration was achieved.

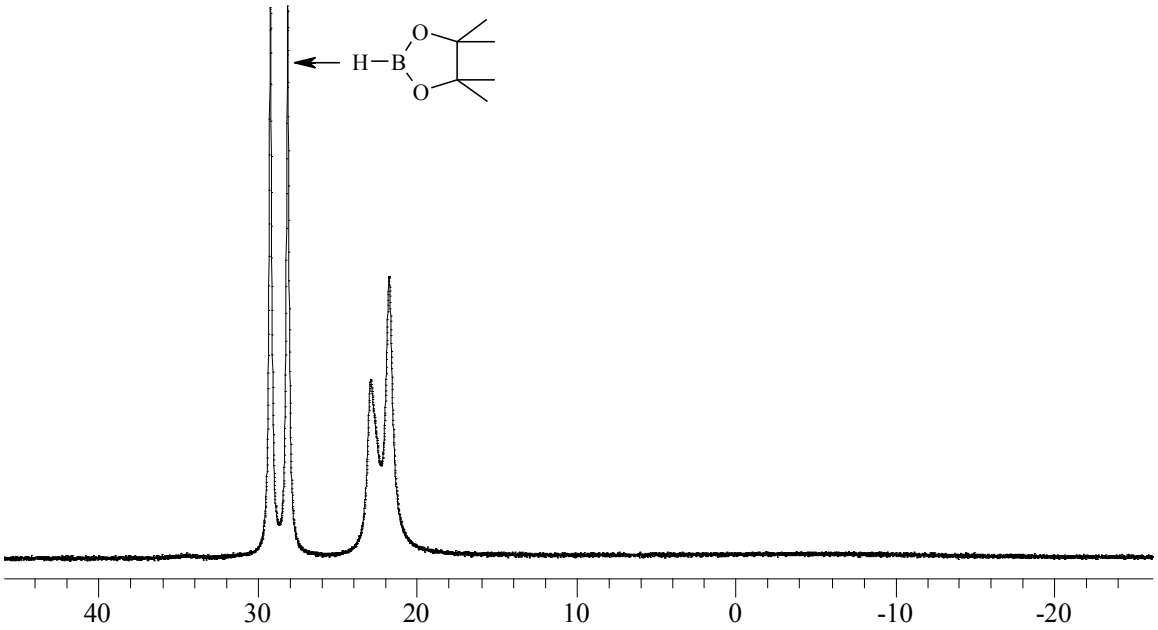


Figure 4.1 ^{11}B NMR spectrum obtained from the reaction pinacolborane and 4-octene after 24 hours at 25 °C in the presence of rhodium catalyst.

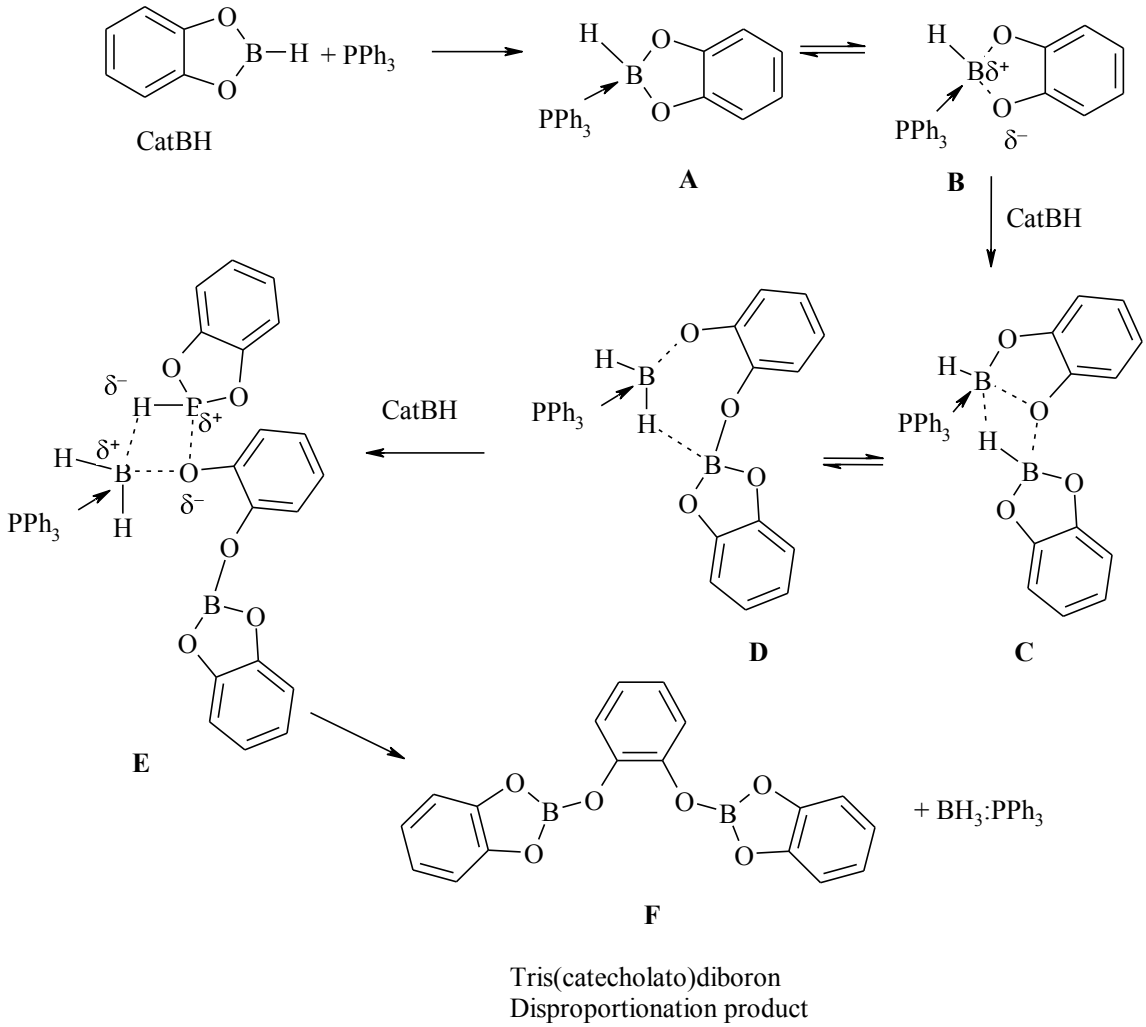
However, in our project we have found a much more convenient and effective route to hydroborate internal alkenes and isomerize simultaneously *via* the use of microwave irradiation in conjunction with $RhCl(PPh_3)_3$. The results from this study were accepted by Tetrahedron Letters for publication,[xlv] and a copy of the paper follows.[*] Hadebe, S. W.; Robinson, R. S. *Tetrahedron Lett.* **2006**, *47*, 1299.

[*] Copy of the paper included in the body of text as per faculty guidelines.

4.5.2 CATALYZED HYDROBORATION WITH S- AND N-BORANES

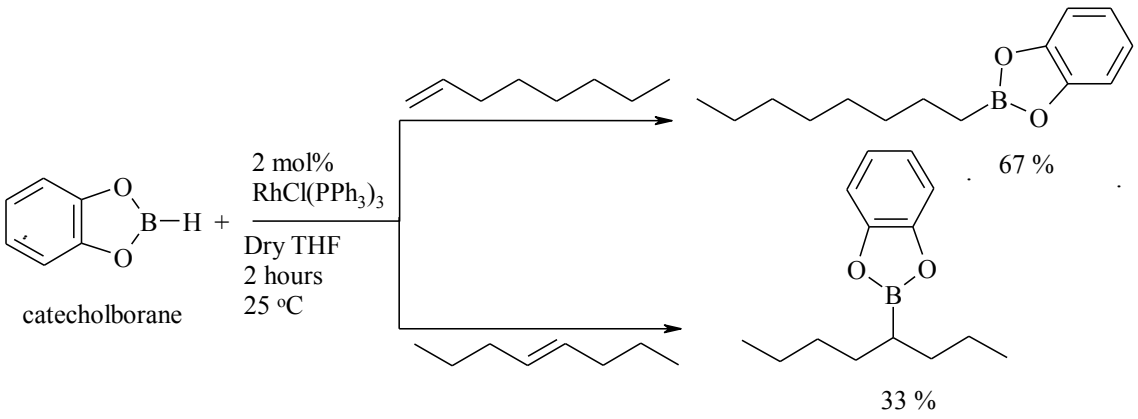
Our success with the use of the Wilkinson's catalyst in conjunction with microwave irradiation or oxygen treated Wilkinson's catalyst to effectively hydroborate and isomerize *trans*-4-octene, prompted our investigation into the use of the Wilkinson's catalyst in hydroboration with electron deficient sulfur and nitrogen analogues of catecholborane.

In our preceding investigation on catalyzed hydroboration with pinacolborane, a significant amount of disproportionation (pinacolborane degradation) was noted. Our observations support the early report by Burgess *et al*. who noted disproportionation in catalyzed hydroboration with catecholborane.[xlvi] Shortly after the report by Burgess *et al.*, Westcott and co-workers reported a disproportionation mechanism which accounted for degradation of catecholborane and pinacolborane.[xlvii] It is reported therein that triphenylphosphine reductively eliminated from $RhCl(PPh_3)_3$ coordinates to catecholborane, thus increasing the electron density at the boron atom *via* σ-donation (Scheme 4.14).[xlvii] This then leads to the weakening of the B-O bond and then addition of a second molecule of catecholborane to form the borenium-type cation **D** which in turn incorporates a third catecholborane molecule to yield the disproportionation product $B_2(Cat)_3$ **F** (Scheme 4.14).



Scheme 4.14

In order to verify the instability of catecholborane during the rhodium catalyzed hydroboration reaction, catecholborane was allowed to react with 1-octene or *trans*-4-octene in the presence of catalytic amounts of $RhCl(PPh_3)_3$ yielding *ca*. 67 % of 2-octyl-benezo-1,3,2-dioxaborolane for 1-octene (Scheme 4.15) and as expected, significant disproportionation of CatBH was noted from the ^{11}B NMR spectroscopic analysis of the product mixture (Figure 4.2). Disproportionation was even more pronounced in hydroboration of *trans*-4-octene (Scheme 4.15), indicating that disproportionation reaction does compete with the catalyzed hydroboration reaction.



Scheme 4.15

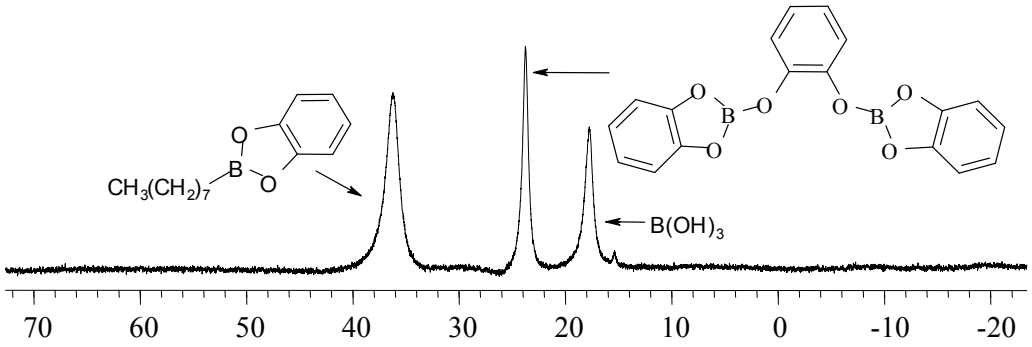


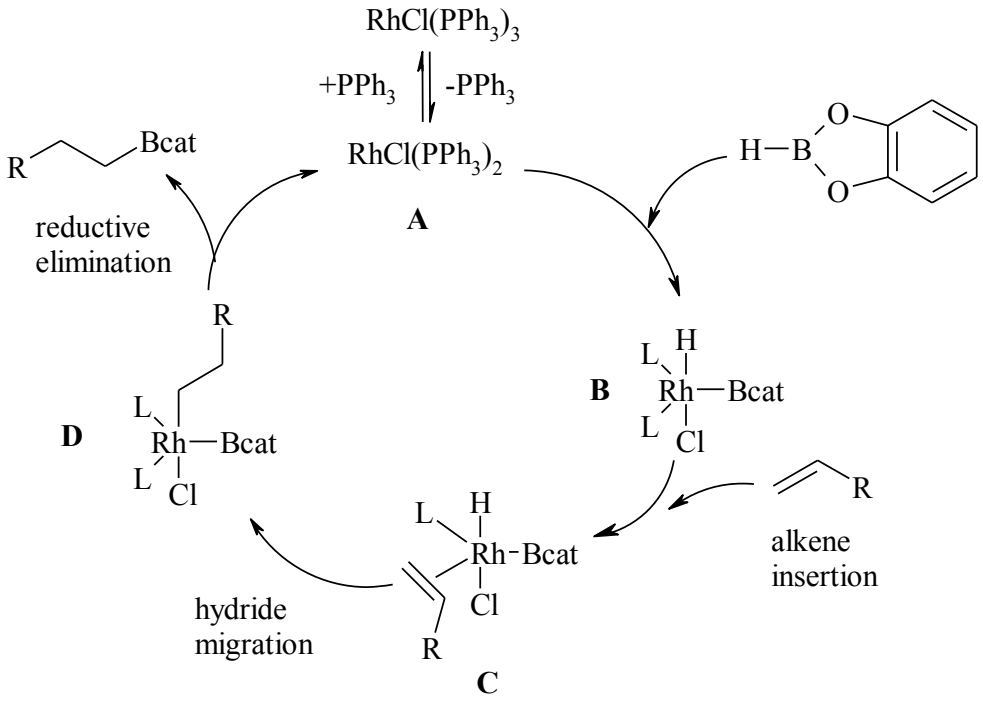
Figure 4.2 ^{11}B NMR spectrum of the product mixture of catalyzed hydroboration of 1-octene with CatBH

Nevertheless, our synthesized sulfur and nitrogen analogues of catecholborane have been shown in the preceding chapters to be less reactive and more robust, which indicated that the sulfur and nitrogen derivatives would be less susceptible to PPh_3 coordination during the catalyzed hydroboration. The Wilkinson's catalyst was then employed in a study of catalyzed hydroboration of 1- and *trans*-4-octenes with benzo-1,3,2-dithiaborolane and benzo-1,3,2-diazaborolane. The outcomes achieved in this study were accepted for publication in the European Journal of Organic Chemistry,[xlviii] and a copy of the paper follows.* Hadebe, S. W.; Robinson, R. S. *Eur. J. Org. Chem*. **2006**, *21*, 4898.

* Copy of the paper included in the body of text as per faculty guidelines.

4.5.3 **INSERTION OF THE B–H BOND INTO $RhCl(PPh_3)_3$**

The discovery by Kono *et al*.[xxix] in the 1970's that the boron-hydrogen bond could be added into the rhodium metal centre was followed by a report by Männig and Nöth on the mechanism of rhodium catalyzed hydroboration.[viii] A number of research groups have focused on the effort to further elucidate and rationalize the mechanism of rhodium catalyzed hydroboration, as discussed in the introductory survey of this chapter. Labelling studies with deuteriocatecholborane have also been conducted to elucidate the mechanism.[vii,ix] To the best of our knowledge, no research group has managed to isolate the Rhodium-boryl complex ($RhCl(PPh_3)_2HBCat$) **B** (Scheme 4.6), the product of the oxidative addition in the catalytic cycle, in order to validate the mechanism.



Scheme 4.6

Baker *et al*. isolated and characterized $RhCl(BCat)_2(PPh_3)_2$ and also demonstrated the alkene insertion into the Rh-B bond of this complex.[xlix] Despite the ability of $RhCl(BCat)_2(PPh_3)_2$ to insert olefins, it is not exactly the Rh-B species proposed in the catalytic cycle. Consequently, our objective was to study the oxidative addition products

of the catalytic cycle, using the sulfur analogue of HBCat due to its enhanced stability relative to catecholborane and also better reactivity than the nitrogen analogue as shown in the previous discussions. We intended to isolate the rhodium-boryl complex which is the key intermediate in the catalytic cycle (Scheme 4.6) initially proposed by Männig and Nöth.[viii] However, attempted investigation into the isolation of the rhodium-boryl species did not yield the anticipated complex, and a new Rh^{III} complex containing a Rh_2S_2 dinuclear core was discovered. The results of this study were accepted for publication in the Acta Crystallographica Section E,[1] and a copy of the paper follows.[*] Hadebe, S. W.; Robinson, R. S.; Munro, O. *Acta. Cryst*, **2007**, *E 63*, m175.

[*] Copy of the paper included in the body of text as per faculty guidelines. Crystal data and tables of geometric parameters are included in appendix D as supportive informtion.

4.6 **CONCLUDING REMARKS**

The application of the Wilkinson's catalyst in our studies to enhance hydroboration reactions has unveiled a number of remarkable findings; namely, we have demonstrated that internal olefins undergo hydroboration and isomerization using rhodium and microwave irradiations. We have also attempted to isolate the rhodium-boryl complex which is the proposed key intermediate in elucidation of the mechanistic aspects of the catalyzed hydroboration. However, owing to its air sensitivity and high reactivity, this intermediate decomposes into a new centrosymmetric dinuclear Rh^{III} complex that belongs to a class of cluster compounds with a Rh_2S_2 core.

In addition, our research has clearly demonstrated for the first time, that the sulfur and nitrogen analogues of catecholborane are potentially superior in the rhodium catalyzed hydroboration reaction, forming the desired compounds in excellent yields. Our success on the use of $RhCl(PPh_3)_3$ in hydroboration reactions with sulfur- and nitrogen-based boranes to synthesize anticipated boronate esters prompted our research into the investigation of the suitability of these boronate esters within metal-catalyzed cross coupling reactions, that is, the realm of Suzuki-coupling type chemistry, and that constitutes the basis of the succeeding investigation in chapter 5.

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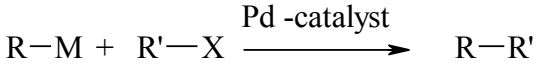
PREFACE

Transition metal-catalyzed cross-coupling reactions have become powerful tools for the construction of new organic compounds. They provide a fundamental synthetic methodology for the formation of carbon-carbon bonds. The stability of 2-octyl-benzo-1,3,2-diazaborolane in flash column chromatography and the ability to be handled in air without degradation motivated the investigation of the suitability of the *N*-based boronate esters in metal catalyzed coupling transformation. In order to gain a better understanding on the reactivity of *N*-based boronate esters in Suzuki type reactions, the primary aim of the study was to synthesize aliphatic, aromatic, and substituted aromatic boronate esters and subsequently explore their coupling reactions with aryl halides.

5.1 **INTRODUCTION**

The formation of carbon-carbon bonds is the key step in the synthesis of simple and more complex organic molecules. The cross-coupling reactions have been developed during the last three decades for the formation of carbon-carbon bonds (Scheme 5.1).[i] Much emphasis has been on the development of aromatic-aromatic, aromatic-heteroaromatic and heteroaromatic-heteroaromatic coupling reactions, in order to synthesize biaryls and their homologues.[ii]

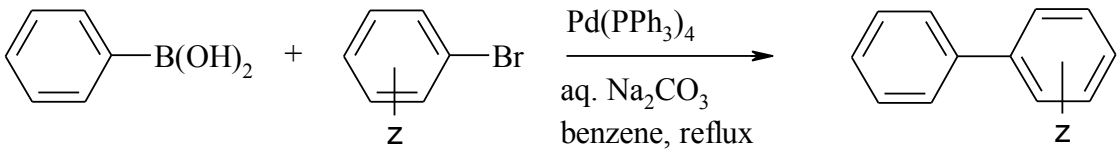


Scheme 5.1

There are four methods that are commonly used to synthesize biaryls, that is, the Kharasch coupling reaction which was invented in the mid 1970's.[iii] In this reaction, biaryls are synthesized *via* the reaction of an aryl Grignard reagent (Ar'MgX, X= halogen) and an aryl halide (ArX) in the presence of a catalyst.[iii] Other functionalized aryls such as triflates, phenolics, mesylates, ethers and sulfides have been used as partners in the Grignard reaction. However, the nucleophilic nature of the Grignard reagent does not allow the use of aldehydes, ketones, esters and nitro groups as coupling partners.[iii]

The Negishi coupling reaction also became important in the mid 1970's for the synthesis of biaryls.[iii] In this reaction, arylzinc reagents (Ar'ZnX) are coupled with aryl halides. The arylzinc reagent was found to be tolerant of functional groups such as esters and ketones unlike the Kharasch reaction. In 1979, Stille *et al*. reported the synthesis of biaryls using arylstannanes ($Ar'SnR_3$, R= Me, Bu) and aryl halides or triflates as coupling partners.[iv] This reaction proceeded under neutral conditions and was reported to tolerate a wide range of substituents on both coupling partners. Consequently, it has become an extremely versatile tool for biaryl synthesis.[iii]

During the same year, Miyaura and Suzuki reported the most important discovery in the history of boronic acid type chemistry. This paper reported a convenient route to the synthesis of arylated alkenes *via* the Pd(0)-catalyzed coupling reaction between alkenylborane or the catecholate derivative and aryl halides.[v] Two years later, Miyaura, Yanagi and Suzuki reported that biaryls could be synthesized in excellent yields (> 90%) from the coupling reaction of phenylboronic acid with haloarenes.[vi] The reaction was reported to proceed smoothly in the presence of a base and the palladium catalyst ($Pd(PPh_3)_4$) (Scheme 5.2).[vi,vii]



Scheme 5.2

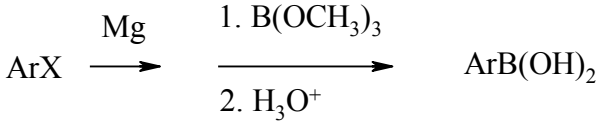
Like the Stille coupling reaction, the Suzuki-Miyaura coupling reaction has been shown to be extremely versatile due to its tolerance of a wide range of substituents on both coupling partners.[vi,vii] Subsequently it has found extensive use in natural product synthesis and has played a significant role in the synthesis of many interesting molecules, because of high selectivity obtained from this reaction. In addition, organoboronic acids and esters used are stable, less toxic and easy to handle in comparison with other organometallic reagents.[vii]

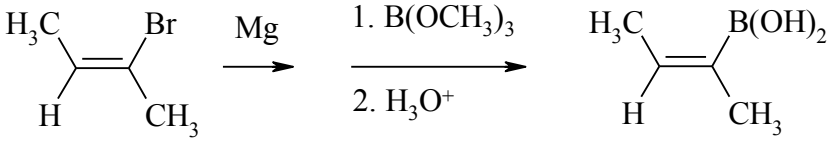
5.2 **SYNTHESIS OF BORONIC ACIDS AND ESTERS**

5.2.1 **PREPARATION FROM GRIGNARD REAGENTS**

Boronic acid was prepared and isolated for the first time by Frankland *et al*. in the 1860's,[viii] from the reaction of diethylzinc and triethylborate. This reaction led to the production of an air sensitive triethylborane (Et_3B), which was oxidised in air producing borinic acid (Et_2BOH). Further oxidation produced ethylboronic acid ($EtB(OH)_2$), which is robust to air and heat.[ii]

A century later, boronic acids and their esters were reported to be produced from the reaction of trialkylborate with Grignard reagents (Scheme 5.3).[ix] A report by Matteson and Liedtke demonstrated the first example of stereocontrolled synthesis of alkenylboronic acids and esters from the reaction of (*Z*)- or (*E*)-2-buten-2-ylmagnesium bromide with trialkylborate $B(OR)_3$ (Scheme 5.3).[x]

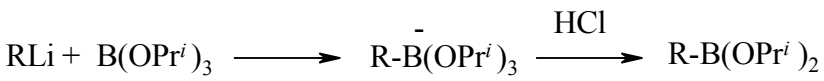




Scheme 5.3

5.2.2 **PREPARATION FROM ORGANOLITHIUM REAGENTS**

The investigation by Brown and Cole showed that the use of Grignard reagents in stereocontrolled synthesis led to contamination by bis-alkylation and the formation of trialkylboranes and borinic acid.[xi] An alternative variation was reported utilizing organolithium and triisopropylborate as the source of boron. The reaction was then acidified with HCl to produce alkyl-, aryl-, 1-alkynyl-, and 1-alkenylboronic esters in high 90% yield (Scheme 5.4).[xi]



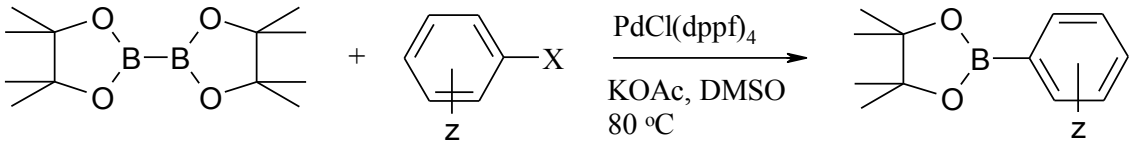
R= allyl, aryl, alkenyl, alkynyl

Scheme 5.4

Despite the fact the reaction of organolithium with boronic esters is an excellent method for preparation of poyfunctional boronic esters, its scope is limited by the high reactivity of the intermediate organolithium. Low temperatures are required during synthesis with organolithium and the reactions were found to be intolerant of a number of functional groups.[xii]

5.2.3 **PREPARATION BY CROSS-COUPLING REACTION**

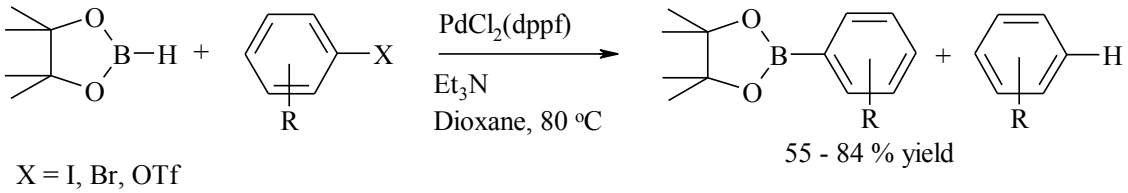
A few years after the discovery of pinacolborane as the new hydroborating agent by Turker *et al*. in the 1990's,[xiii] much attention was shifted to the use of pinacolborane as the source of boron in hydroboration and borylation type chemistry. Ishiyama *et al*. reported the use of bis(pinacolato)diboron (Scheme 5.5) in preparation of arylboronic esters.[xiv] The esters are produced directly from palladium-catalyzed cross coupling of bis(pinacolato)diboron and aryl halides.[i] This convenient method led to the production of a variety of substituted arylboronic ester derivatives due to tolerance exhibited by the diboron to many functional groups such as nitro, nitrile and acyl.[xiv]



X= I, Br, OTf

Scheme 5.5

In 1997, Masuda and co-workers showed that arylboronic esters could be prepared from the coupling reaction of pinacolborane with aryl halides or triflates catalyzed by PdCl(dppf) with the aid of triethylamine as the base. This reaction opened up a new synthetic route to a wide range of functionalized arylboronic acids with functional groups such as cyano, nitro and acylamino (Scheme 5.6).[xii,xv] In their study, the effect of different ligands, solvents and bases were investigated. The results showed that the product distribution between the target boronic ester and the reduction product was base dependant.[vii]

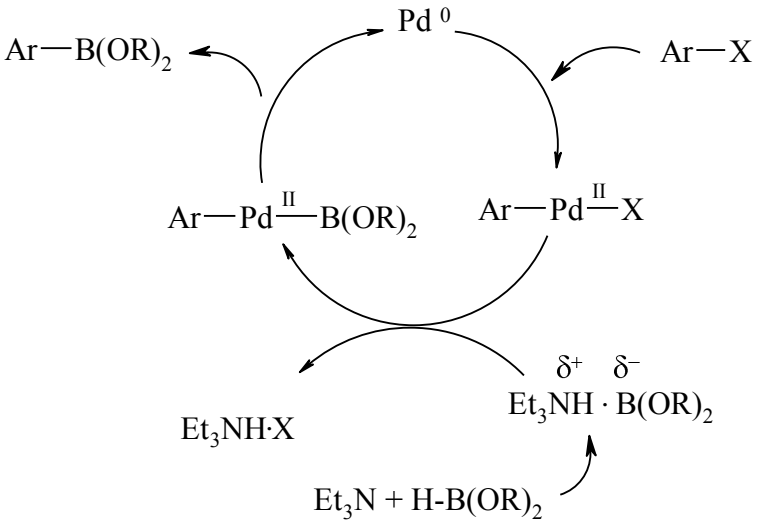


X = I, Br, OTf
R = 4-Cl, 4-CN,4-NMe_2, 4-NHAc, 4-CH_2CN, 4-COMe, 4-CO_2Me, 3-COMe

Scheme 5.6

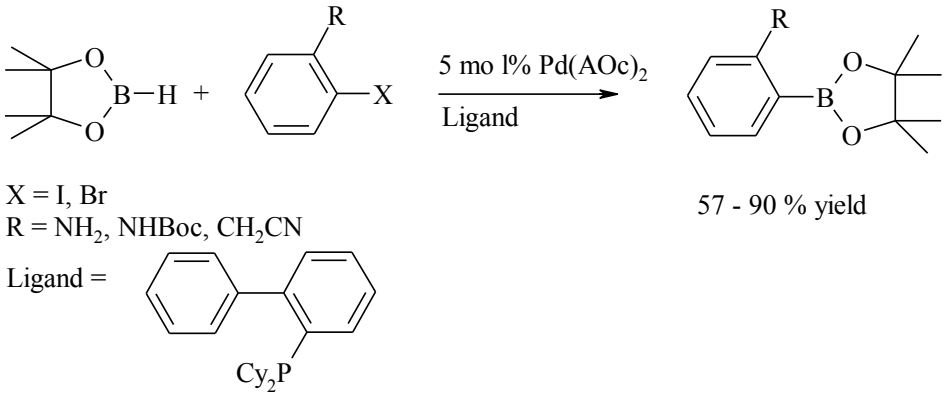
Further mechanistic investigations conducted by Masuda's group showed that electrophiles are oxidatively added to the palladium (0) to afford R-Pd^{II}-X, which in turn transmetalates with the hydride to produce R-Pd^{II}-H complex.[xvi] The produced complex is eliminated reductively to give rise to R-H, the reduced product. An interesting observation was noted, that the use of triethylamine as the base played a significant role in the prevention of reduction product formation, and also facilitated B-C bond formation (Scheme 5.7).[xvi]

The proposed mechanism (Scheme 5.7) demonstrated that the first step would involve oxidative addition of the aryl halide to palladium (0) to produce the Ar-Pd^{II}-X complex. This is then followed by ligand exchange between X of the Ar-Pd^{II}-X and the boryl anion (generated *in situ* from the reaction between triethylamine and borane) yielding the intermediate species Ar-Pd^{II}-$B(OR)_2$, which reductively eliminates the desired arylboronic ester.[xvi] The authors also suggested that the initial addition of the boryl anion to Pd(0) followed by metathesis with aryl halide may take place.



Scheme 5.7[xvi]

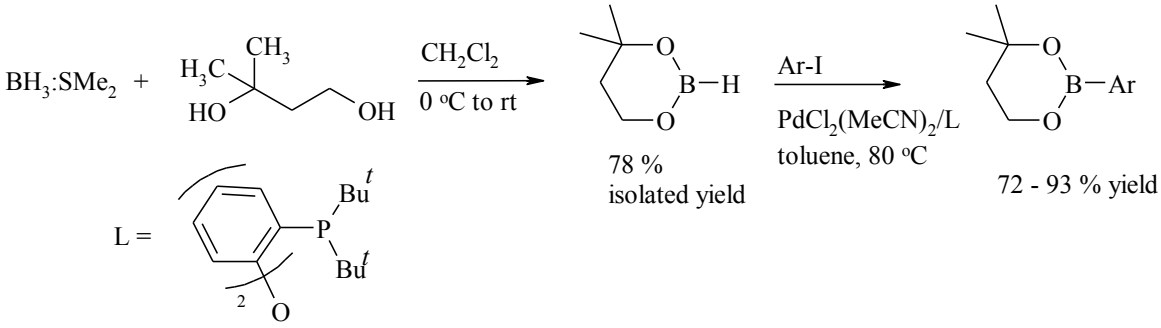
The scope of the use of pinacolborane to produce functionalized arylboronic esters was further expanded by Baudoin *et al*.[xvii] whose report showed that $Pd(OAc)_2$ in conjunction with sterically hindered phosphine ligands catalyzed the coupling of pinacolborane with *ortho*-substituted phenyl halides, to furnish a range of sterically crowded *ortho*-substituted arylboronic esters (Scheme 5.8).[xvii,xii]



Scheme 5.8

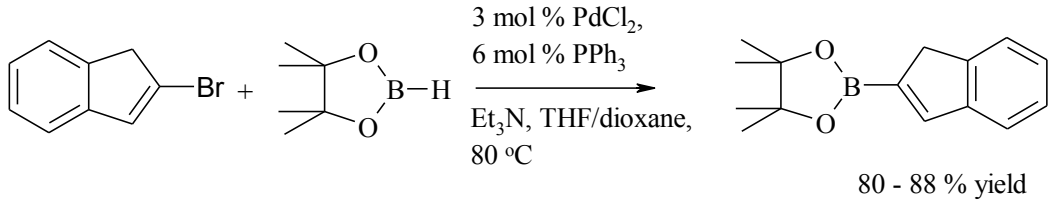
Masuda's group pursued the borylation type chemistry in the quest for alternative borylation reagents. In 2007, the authors reported that 4,4,6-trimethyl-1,3,2-dioxaborinane could be used as an alternative reagent.[xviii] This compound was prepared easily from inexpensive hexylene glycol, which afforded much better yields when

compared with pinacolborane (Scheme 5.9). From an economic point of view, the authors support the use of 4,4,6-trimethyl-1,3,2-dioxaborinane instead of pinacolborane to furnish functionalized arylboronic esters (Scheme 5.9).[xviii]



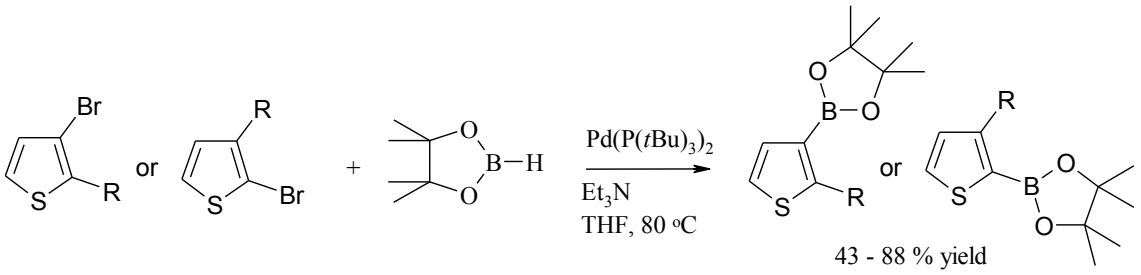
Scheme 5.9

Lee and Yun reported that Masuda's borylation methodology with pinacolborane could be modified and employed in the preparation of indenylboronic esters.[xix] The desired indenylboronates were synthesized in high (80 – 88 %) yield when $PdCl_2$, PPh_3 and Et_3N were employed in refluxing THF or dioxane (Scheme 5.10).[xix]



Scheme 5.10

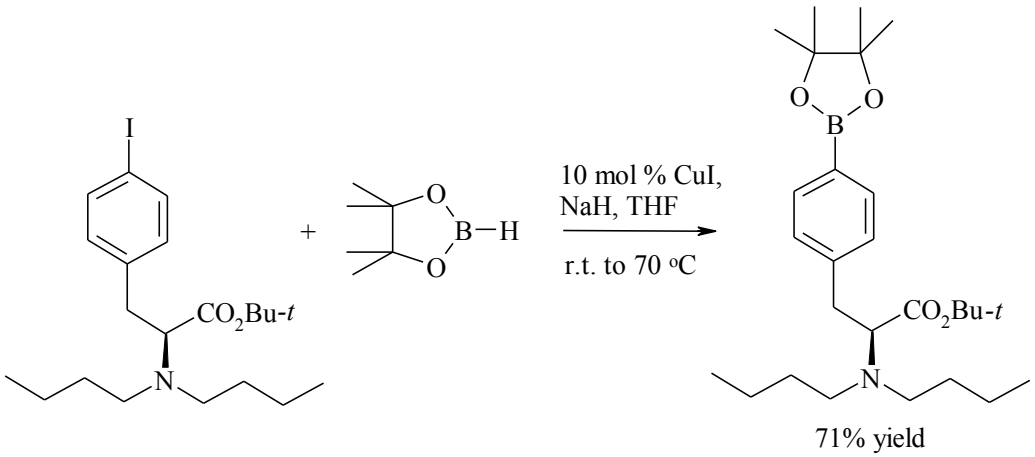
The cross-coupling reaction methodology with pinacolborane has flourished beyond coupling with aryl halides, to electrophiles such as 2-bromo-3-substituted or 3-bromo-2-substituted thiophenes to produce 2,3-substituted thienylboronic esters (Scheme 5.11).[xx] It was reported that the use of $Pd(P(tBu)_3)_2$ provided the desired thienylboronic esters in good to excellent yields. Despite the tolerance to a wide range of functional groups, strong electron withdrawing substituents are reported to reduce the stability of the product thienylboronic acid or ester product.[xx]



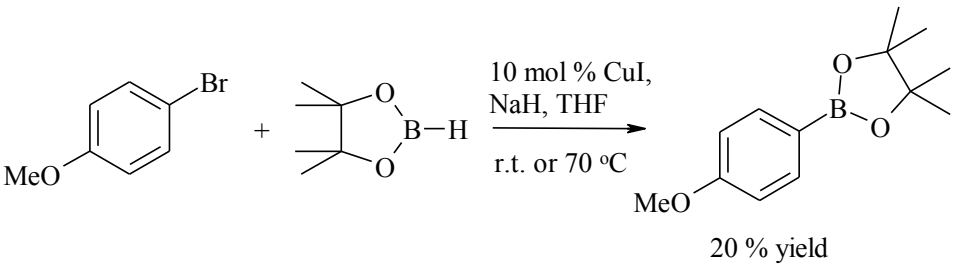
R = CO_2Et, CONH*t*Bu, CHO, CN, COMe, NO_2, $SiMe_3$

Scheme 5.11[xii, xx]

In 2006, Zhu and Ma reported the use of CuI as the new catalyst for the coupling reaction of aryliodides with pinacolborane at room temperature.[xxi] It was found that CuI together with NaH provided an inexpensive route to furnish the coupling reaction (Scheme 5.12). However the new methodology gave poor conversions with the aryl bromide derivatives (Scheme 5.13).[xxi]

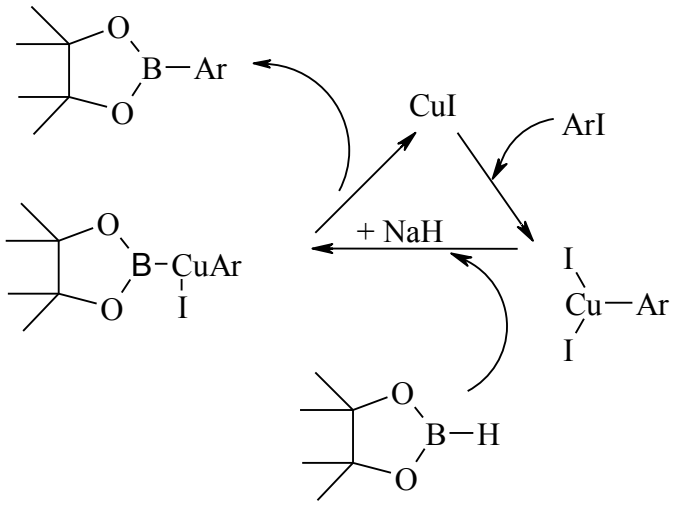


Scheme 5.12



Scheme 5.13

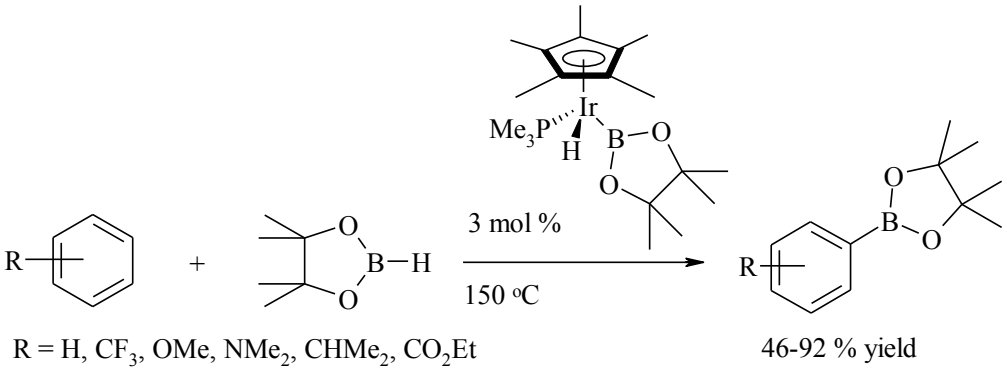
The authors tentatively proposed a mechanism for the CuI catalyzed coupling reaction based on a modification of the catalytic cycle proposed for Ullmann and Miyaura-Masuda type coupling reactions.[xxi] The mechanism involved the oxidative addition of the electrophile to the metal centre producing the Ar-Cu^{II}-I_2 intermediate (Scheme 5.14). The boryl anion formed from the *in situ* reaction of pinacolborane with NaH, reacts with the aryl-copper intermediate to yield the boryl-copper complex. The target arylboronic ester or acid is then reductively eliminated and the catalyst regenerated (Scheme 5.14).[xxi]



Scheme 5.14

Aromatic borylation has also been achieved with pinacolborane using iridium catalysts such as $Ir(OMe)(COD)_2$,[xxii] $[IrCl(COD)]_2$dtbpy,[xxiii] A different approach was reported by Cho and co-workers in early 2000,[xxiv] using $Cp^*Ir(PMe_3)(H)(Bpin)$. In this type of

reaction, arylhalides are not necessary because the C-H bond is activated by the transition metal preferentially (Scheme 5.15).[xxiv]



Scheme 5.15

A wide range of range of boronic esters were also synthesis *via* hydroboration of alkenes and alkynes with different hydroborating agents as discussed in detail in the preceding chapters 2, and 4.

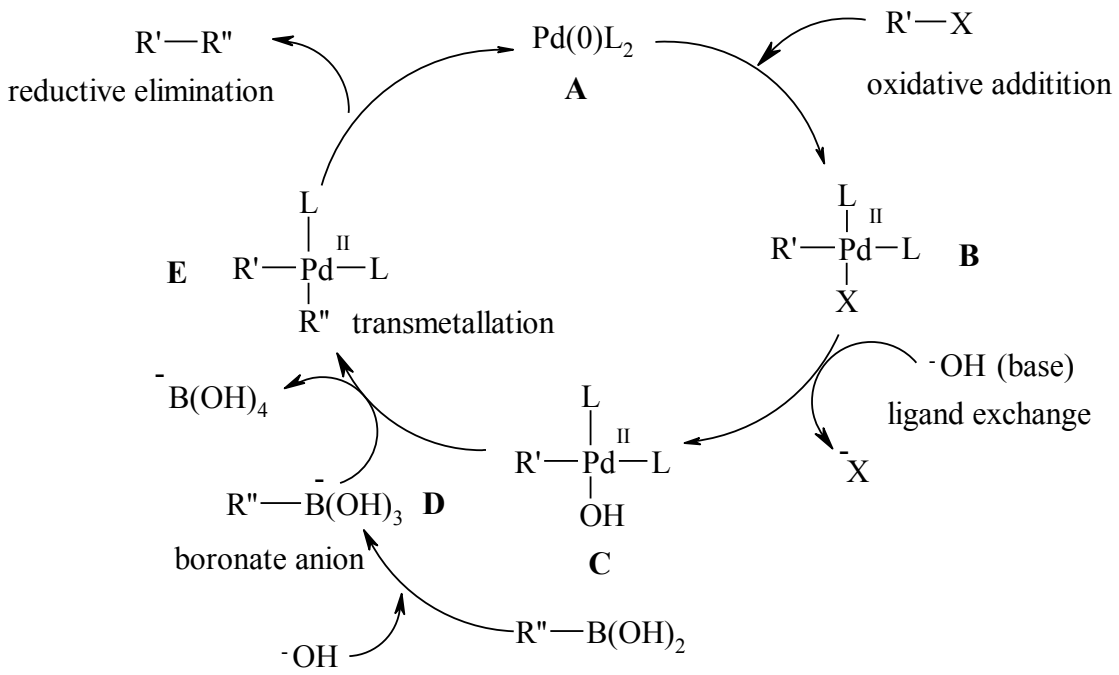
5.3 **MECHANISM OF THE SUZUKI-COUPLING REACTION**

About half a decade after their discovery, Suzuki and Miyaura proposed a mechanism that accounted for the palladium catalyzed cross coupling reactions.[xxv] The initial step involved the oxidative addition of the 1-alkenyl, 1-alkynyl, 1-allyl, benzyl and aryl halide to the metal centre to give the stable *trans*-σ-Pd^{II} complex [R'-$Pd^{II}L_2$-X] (Scheme 5.16).[ii]

The initial step is very crucial for the configuration of the product formed. It has been reported that alkenyl halides are added with complete retention of configuration, whereas for allylic and benylic halides, it proceeds with inversion of configuration.[i] Alkyl halides possessing β-hydrogens are not favourable because of the competing β-hydride elimination process. However, Netherton *et al*., in 2001 have reported the first method for achieving Suzuki-cross coupling of alkyl bromides that contained β-hydrogens.[xxvi]

The oxidative addition step has been reported to be the rate determining step of the process, the relative reactivity of alkyl and aryl halides towards the palladium complex have been studied and it was found to decrease in the order I > OTf > Br >> Cl.[i] It has also been shown that electron withdrawing groups that are in close proximity to the alkenyl and aryl halide increased the reactivity towards oxidative addition compared to electron donating substituents.[i] The investigation by Farina and Krishnan showed that the choice of ligand on the palladium catalyst played an important role to alleviate the oxidative addition. Formation of the coordinatively unsaturated palladium complex proceeded with ease on catalysts that contained less than four phosphine ligands.[xxvii]

The *trans*-σ-Pd^{II} complex **B** (Scheme 5.16) formed, then undergoes ligand exchange with the base producing the R'-Pd^{II}-OH **C**, which has a higher activity than the R'-Pd-X complex.[ii] This is then followed by the transmetallation step, where the boryl-alkyl bond is transferred to the palladium-hydroxy complex. However, it has been reported that the boronic acids or esters are less nucleophilic, consequently, it is difficulty to coordinate the boron species into the metal centre during the transmetallation step.[ii] The nucleophilicity of the boron atom is increased by the reaction of the boronic acid with the second equivalent of the base, producing the tetravalent boron atom R"-$(OH)_3B^-$ **D** (Scheme 5.16),[xxviii] which in turn, transmetalate to give R'-Pd-R'' complex **E**. Reductive elimination then yields the desired carbon-carbon bond, with concomitant regeneration of the catalyst (Scheme 5.16).[i,ii,xxv]



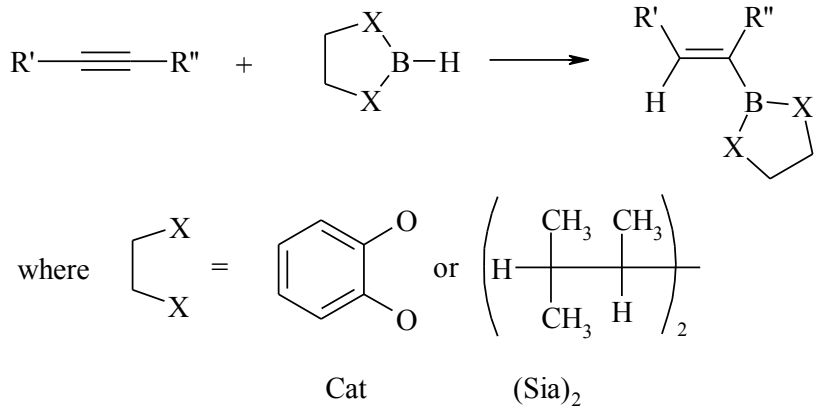
Scheme 5.16

5.4 **SUZUKI-MIYAURA COUPLING IN ORGANIC SYNTHESIS**

5.4.1 **PREPARATION OF ALKADIENES AND ALKENYNES**

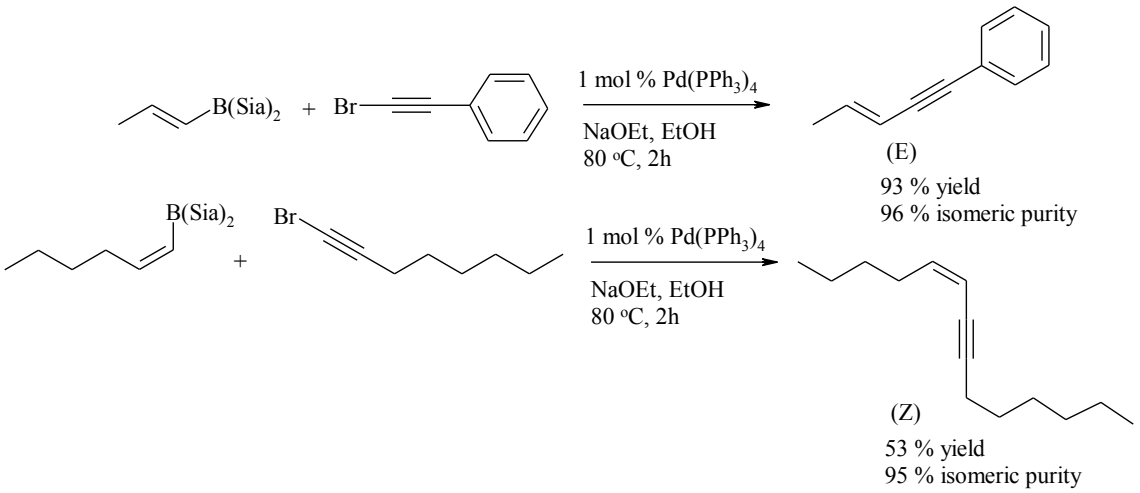
The importance of alkadienes in organic chemistry as building blocks for more interesting and complex organic molecules has led to the development of a number of methods for their preparation.[xxix,xxx,iv] However, the scope of some of these methods is limited by the nature of the organometallic compound involved.[xxv]

From the early report by Brown, who showed that stereodefined 1-alkenyldiorganoboranes such as (*E*)-1-alkenyldiorganoboranes are readily prepared from monohydroboration of alkynes with catecholborane or disiamylborane (Scheme 5.17).[xxxi] Consequently, Miyaura *et al*. employed these alkenylboranes in the cross-coupling reaction with the intention to conveniently synthesize stereodefined conjugated alkadienes.[xxv]

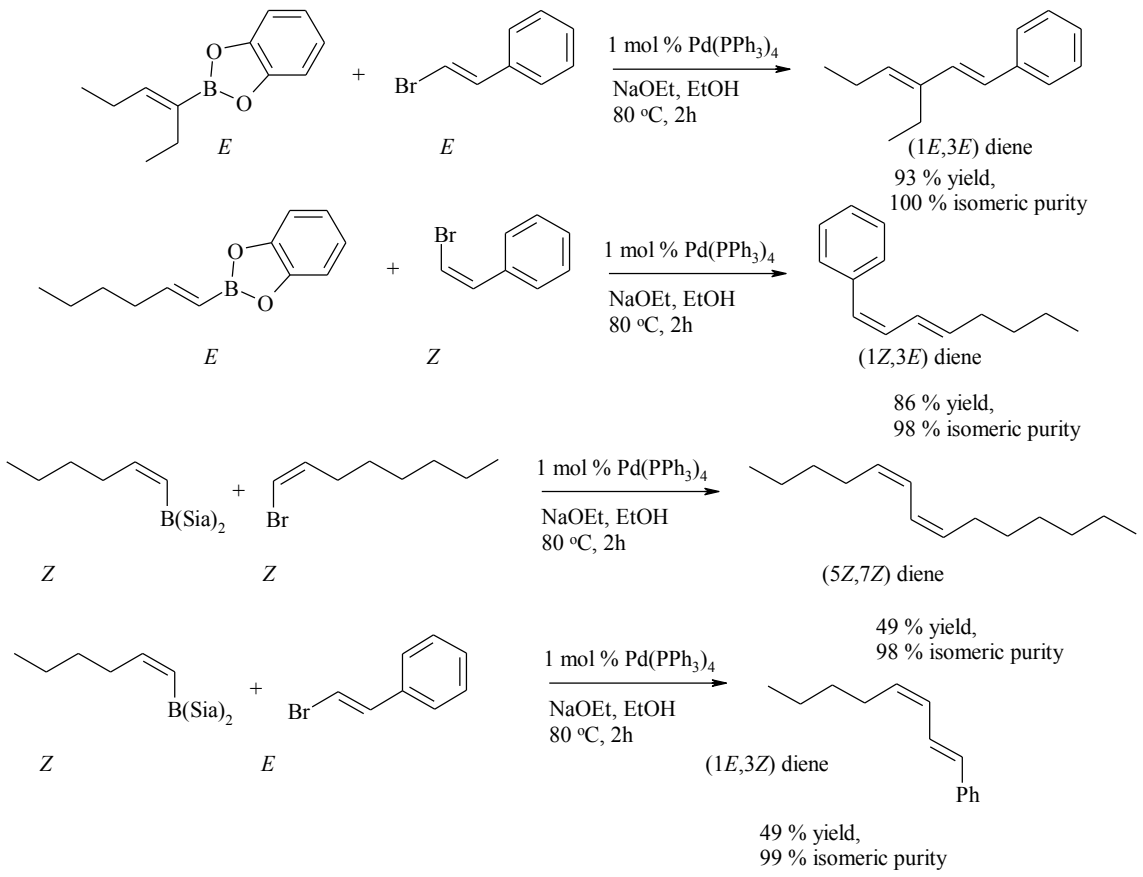


Scheme 5.17

Miyaura's report showed that the use of (*E*)- or (*Z*)- disiamylborane or 2-((*E*)-1-alkenyl)-1,3,2,-benzodioxaborolane with (*E*)- or (*Z*)-1-alkenylbromides in the $Pd(PPh_3)_4$-catalyzed reaction, in the presence of a base such as sodium ethoxide proceeded with complete retention of configuration for both coupling partners.[xxv] This method provided a convenient route to the synthesis of stereodefined (*E*)- or (*Z*)- conjugated enynes (Scheme 5.18) and conjugated (*E*,*E*)-, (*E*,*Z*)-, (*Z*,*E*)- and (*Z*,*Z*)-alkadienes (Scheme 5.19).[xxv]



Scheme 5.18



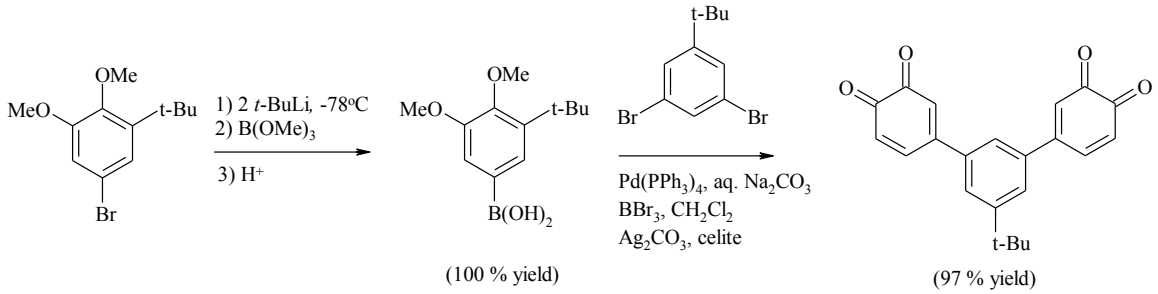
Scheme 5.19

5.4.2 **PREPARATION OF BIARYLS**

Biaryls are an important class of organic compounds because many kinds of interesting compounds, such as herbicides, pharmaceuticals, liquid crystals, natural products, polymers, engineering material such as molecular wires and conducting polymers, include the biaryl unit.[iii] Subsequently, tremendous interest from the chemical community has been focused on the development of new synthetic methods for biaryls.[vii]

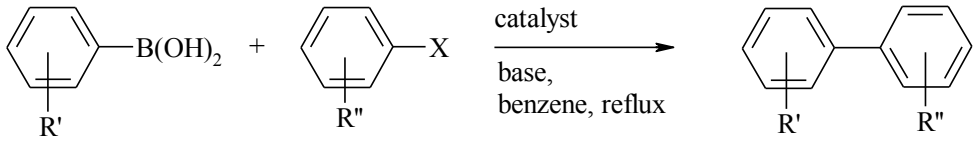
From the initial reports by Miyaura and Suzuki,[v,vi,xxv] a number of research groups have utilized and improved the methodology of carbon-carbon bond formation over the last two decades. In 1995, Shultz *et al.* employed the Suzuki-Miyaura coupling reaction

methodology for the synthesis of a magnetic chelating ligand in an excellent 97 % yield (Scheme 5.20) used in the manufacture of magnetic materials.[xxxii]



Scheme 5.20

The Suzuki-Miyaura coupling reaction has been shown to be extremely powerful and versatile for the formation of biaryls in high yields, with aryl halides and triflates even when coupling partners contained a wide range of functional groups (Scheme 5.21), (Table 5.1).[vii]

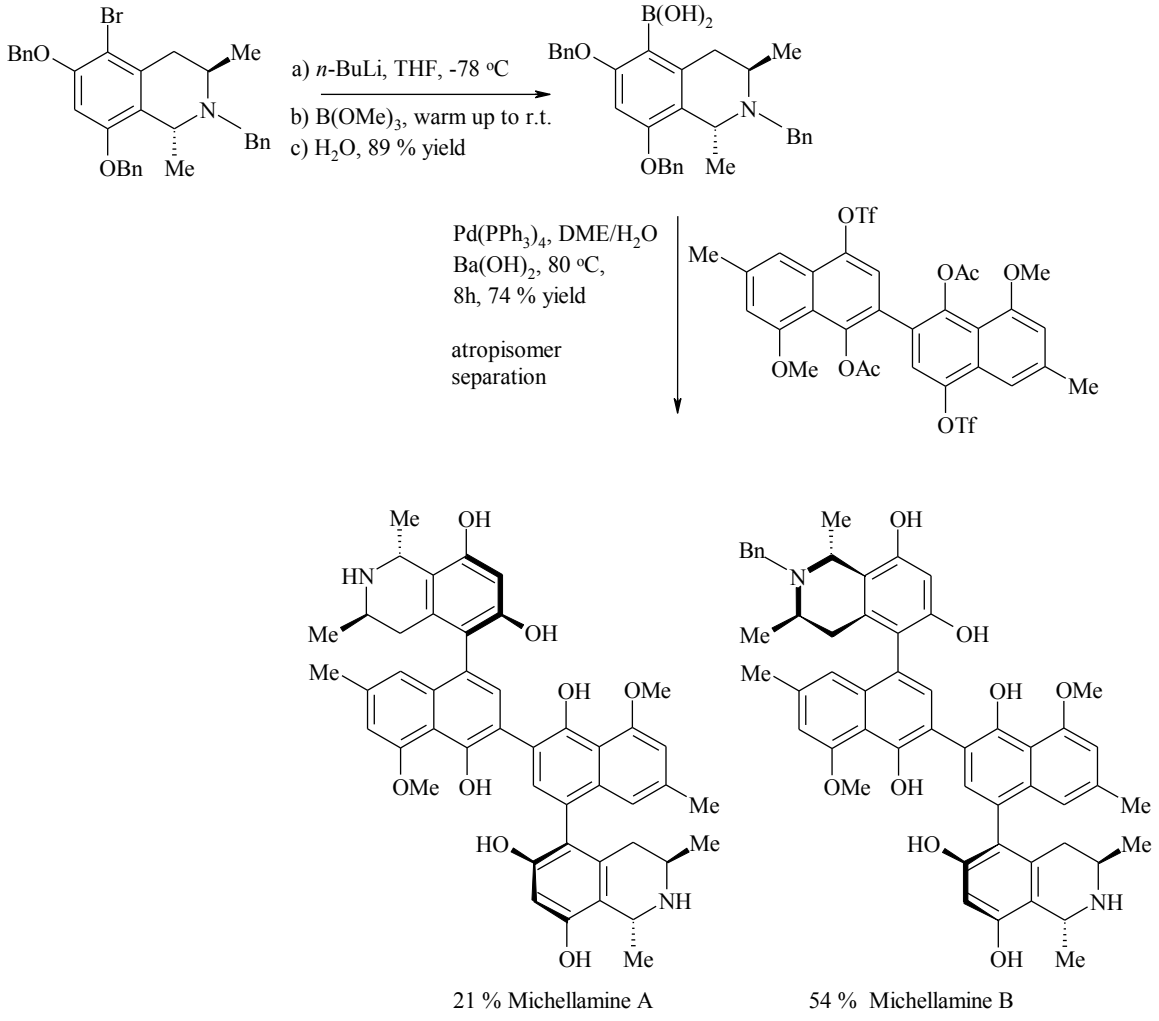


Scheme 5.21

Table 5.1

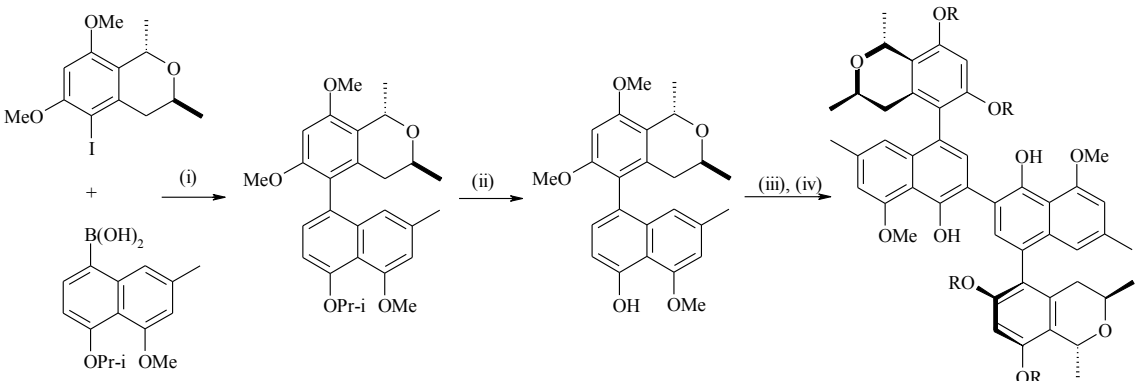
R'	***R''***	***X***	***Catalyst***	***Base***	Yield (%)
H	2-Me	Br	$Pd(PPh_3)_4$	Na_2CO_3	94
H	4-OH	I	$Pd(OAc)_2$	Na_2CO_3	80
H	4-COOH	I	$Pd(OAc)_2$	Na_2CO_3	95
4-F	4-CHO	Br	Pd/C + PPh_3	Na_2CO_3	84
2-CHO	2-NO_2	Br	$Pd(PPh_3)_4$	Et_3N	82
3-NO_2	H	Br	$Pd(PPh_3)_4$	Na_2CO_3	95

The methodology has found use in the synthesis of analogues of biologically active compounds such as the anti-HIV alkaloid Michellamine.[vii] Bringmann *et al*.[xxxiii] reported the synthesis of Michellamine A, B and C from the Suzuki-Miyaura coupling reaction of the ditriflate with the isoquinoline boronic acid (Scheme 5.22), to afford 5',5"-*O*-diacetyl-*N,N*-dibenzyl-6,6",8,8"'-tetra-*O*-benzylmichellamine as a mixture of atropisomers in 74 % yield (Scheme 5.22).[xxxiii]



Scheme 5.22

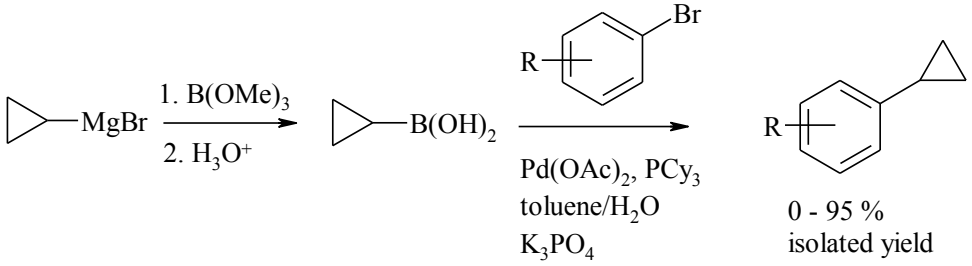
Shortly after this report, de Koning *et al*. reported the synthesis of a racemic isochroman analogue of Michellamines. The Suzuki-coupling reaction was shown to play a major role in the formation of the biaryl units in excellent 85% yield (Scheme 5.23).[xxxiv]



(i) 20 % $Pd(PPh_3)_4$, K_3PO_4, DMF, 95 °C, 85 %; (ii) BCl_3, CH_2Cl_2, -78 °C, 58 %, (iii) Ag_2O, 0.2% Et_2NH, $CHCl_3$, (iv) H_2 (1 atm), Pd/C, MeOH-CH_2Cl_2, 75 %.

Scheme 5.23

Cyclopropyl groups have become a common structural motif in biologically active molecules. Recently, Wallace and Chen reported the efficient synthesis of cyclopropylboronic acid, subsequent coupling of this acid with arylbromides provided a convenient method of introducing the cyclopropyl substituent into the aryl groups (Scheme 5.24).[xxxv]

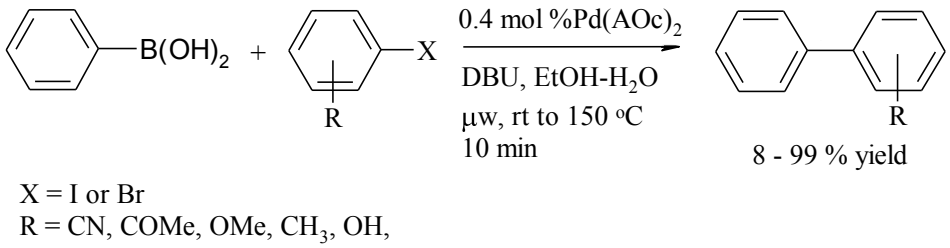


R = OMe, NH_2, CHO, CN, H, Ac

Scheme 5.24

Many researchers in the same field have focused on the development of new palladium catalyst systems,[xxxvi,xxxvii,xxxviii] more effective ligands,[xxxix] bases[xl] and more recently, Chanthavong and Leadbeater[xli] reported the use of organic bases such as DBU and DABCO. This report demonstrated the formation of biaryls from the reaction of phenylboronic acid and arylhalide promoted by microwave irradiation in the presence of

$Pd(OAc)_2$ as the catalyst. The biaryls were formed in high yield in the absence of mineral bases (Scheme 5.25).[xli]

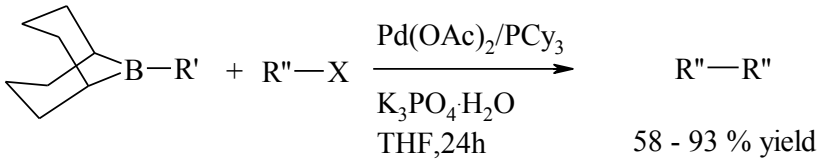


X = I or Br
R = CN, COMe, OMe, CH_3, OH,

Scheme 5.25

5.4.3 **THE SCOPE OF ORGANOBORANES**

The scope of organoboranes used in the Suzuki-Miyaura coupling reactions has not received much investigation, only a few publications are available to date. In 2001 Netherton *et al*.,[xxvi] reported the $Pd(AOc)_2/PCy_3$ catalyzed cross coupling of the unprecedented coupling partners, *B*-n-octyl-9-BBN with alkylbromides in the presence of $K_3PO_4{\cdot}H_2O$. In this investigation, coupling of a range of β-hydrogen bearing alkyl bromides with alkyl- and alkenylboranes (prepared *in situ* from hydroboration of the corresponding alkene or alkyne with 9-BBN) was achieved at room temperature (Scheme 5.26).[xxvi]

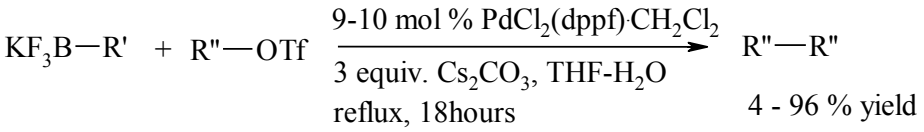


R' = *n*-Hexyl, $(CH_2)_2$-Ph-CH_2NMe, 4-$(CH_2)_2$-cyclohexene, $(CH_2)_5$TESO, $(CH_2)_3$-*p*-OMe(C_6H_5)
R" = *n*-decyl, $(CH_2)_5CO_2Et$, *n*-hexyl, $(CH_2)_6CN$, $(CH_2)_6Cl$, $(CH_2)_2(Me)_2$

Scheme 5.26

Molander and Ito reported the first example of palladium catalyzed cross coupling of potassium alkyltrifluoroborates with aryl and alkyl triflates.[xlii] It is reported that the

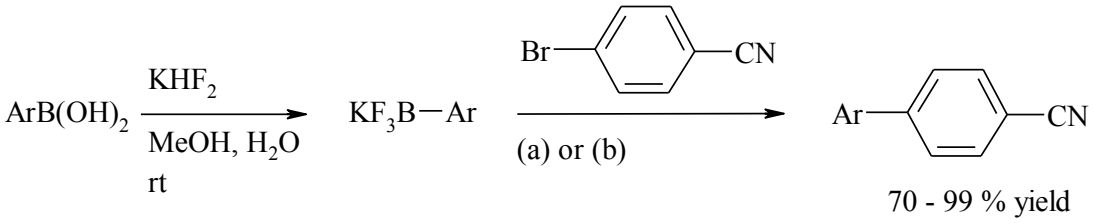
efficiency of the catalyst $PdCl_2$(dppf) was enhanced in the presence of Cs_2CO_3 as a base in refluxing THF/H_2O solvent. The reaction tolerated a wide range of functional groups either on the borate or on the triflate (Scheme 5.27).[xlii]



R' = alkyl
R" = alkenyl, aryl

Scheme 5.27

Further detailed studies by Molander and Biolatto[xliii] on the use of aryl and hetero aryl trifluoroborates, showed that these borates are robust and easy to handle. Cross-coupling of these borates with aryl bromides was achieved with ease when low catalyst loading, low temperature and reaction times were employed. In addition, inert atmosphere was not necessary during synthesis of the biaryls (Scheme 5.28).[xliii]



Ar = 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-FC_6H_4, 4-$MeCOC_6H_4$, 3-$NO_2C_6H_4$

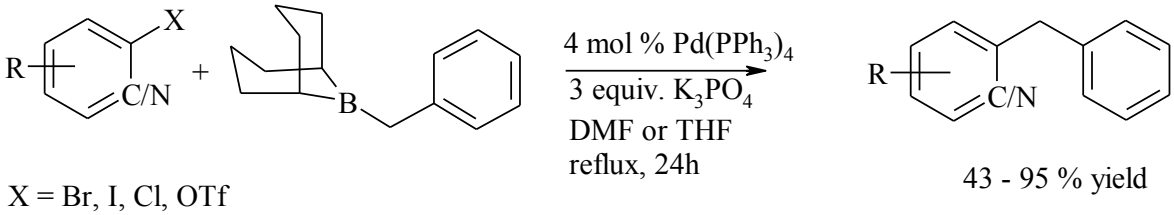
(a) = $Pd(OAc)_2$ (0.5 mol %)
K_2CO_3 (3 equiv.)
MeOH, reflux

(b) = $PdCl_2$(dppf)·CH_2Cl_2 (0.5 mol %)
PPh_3 (0.5 mol %) or without ligand
Et_3N (3 equiv.), EtOH, reflux

Scheme 5.28

The scope of organoboranes in biaryl synthesis was further expanded in 2005 by Flaherty *et al*.[xliv] Their report entailed the use of uncommon coupling partners in the Suzuki-Miyaura coupling reaction, that is, the coupling of *B*-benzyl-9-BBN with a range of aryl-, heteroaryl halides and triflates (Scheme 5.29). The reaction furnished methylene linked

biaryls which are building blocks of pharmacologically important molecules. The authors found that the use of $Pd(PPh_3)_4$ with K_3PO_4 was best for this type of coupling reaction.[xliv]

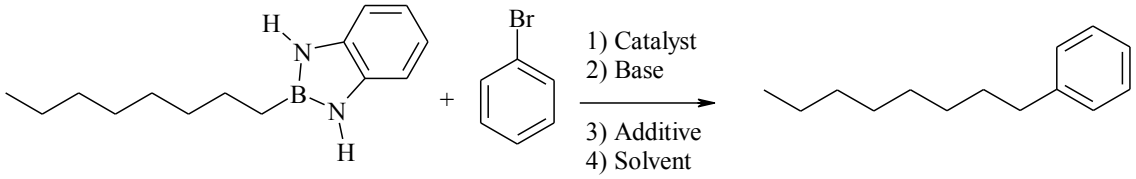


X = Br, I, Cl, OTf
R' = CO_2R', CN, COH, SO_2NH_2, OH, OMe, Me, *i*-Pr

Scheme 5.29

5.5 **RESULTS AND DISCUSSION**

The focus of the investigation was to explore the suitability of nitrogen based boronate esters within Suzuki type chemistry. Studies towards exploring the reactivity of 2-octyl-benzo-1,3,2-diazaborolane were conducted. Reaction conditions, catalysts, bases, and additives were varied in order to establish optimum reaction conditions for coupling nitrogen based boronate esters with aryl halides (Scheme 5.30).



2-octyl-benzo-1,3,2-diazaborolane

Catalysts : $Pd(PPh_3)_3$, $Pd(AOc)_2$
Bases : Na_2CO_3, K_2CO_3, K_3PO_4
Additives : PPh_3, PCy_3
Solvents : Benzene, DMF, EtOH-H_2O
Reaction conditions: r.t. to reflux, microwave irradiation

Scheme 5.30

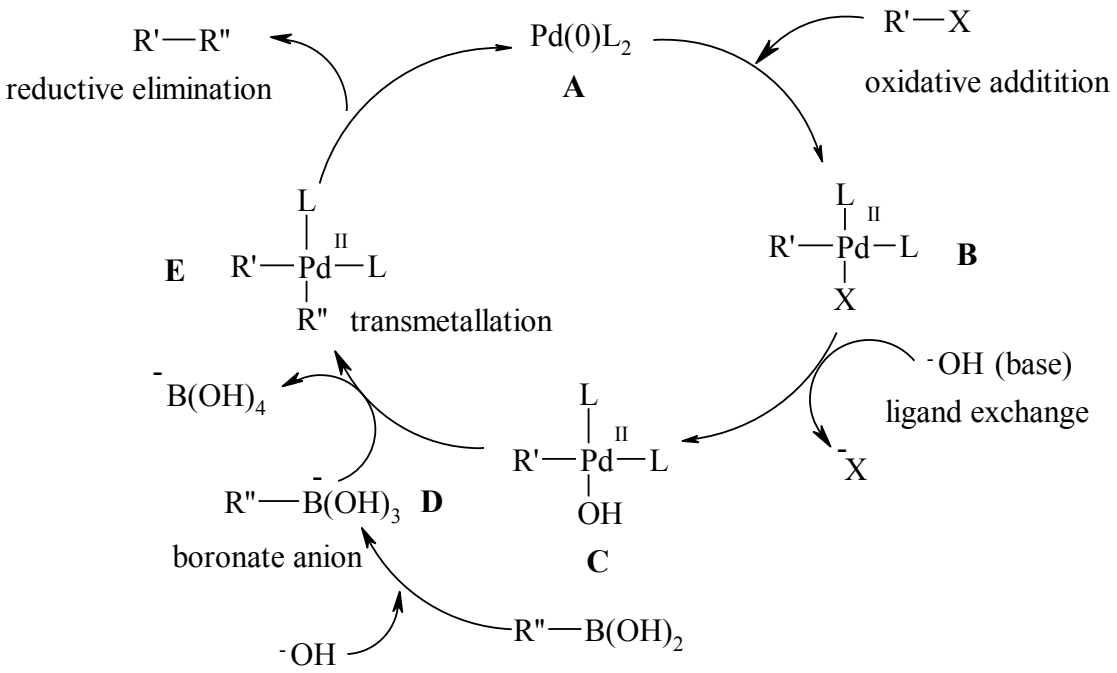
Of all reactions attempted, none gave the coupling product in more than 5%. It was noted that the starting boronate ester degraded in reactions utilizing aqueous containing bases or solvents, (Table 5.2, entries 1, 2, 9 and 10). This study showed that the nitrogen-based boronate esters are very robust and less reactive in coupling reaction.

Table 5.2 Catalyzed coupling reactions with 2-octyl-benzo-1,3,2-diazaborolane.*

Entry	Catalyst	Base	Additive	Solvent	Condition	Starting material %	Product %
1	$Pd(PPh_3)_4$	aq. Na_2CO_3	none	benzene	90 ºC	20	0
2	$Pd(PPh_3)_4$	Aq. K_2CO_3	none	benzene	90 ºC	50	0
3	$Pd(PPh_3)_4$	K_2CO_3	none	DMF	150 ºC	80	< 2
4	$Pd(PPh_3)_4$	K_2CO_3	none	DMF	µ-wave, 100W, 1h	40	< 2
5	$Pd(OAc)_2$	K_2CO_3	PPh_3	DMF	µ-wave, 100W, 1h	80	< 2
6	$Pd(OAc)_2$	K_2CO_3	PPh_3	DMF	150 ºC	40	< 5
7	$Pd(OAc)_2$	$K_3PO_4 \cdot H_2O$	PCy_3	DMF	25 ºC	35	0
8	$Pd(OAc)_2$	$K_3PO_4 \cdot H_2O$	PCy_3	DMF	µ-wave, 100W, 1h	40	0
9	$Pd(OAc)_2$	$K_3PO_4 \cdot H_2O$	PPH_3	DMF-H_2O	150 ºC	0	0
10	$Pd(OAc)_2$	$K_3PO_4 \cdot H_2O$	PCy_3	EtOH-H_2O	90 ºC	0	0

* Percentages of starting material and product are based on isolated yields.

According to the mechanism of Suzuki-coupling reactions proposed by Miyaura *et al.*,[xxv] boronate esters or acids are less nucleophilic, therefore require activation by a second equivalent of the base forming the tetravalent boron atom **D**, which is expected to subsequently transmetalate to give the R'-Pd-R" complex **E** (Scheme 5.16). However, in our case, it was proposed that the reduced reactivity of the nitrogen based boronate ester may be due to the strong overlap of the electron cloud from the nitrogen atom into the vacant p_z-orbital on the boron atom. This overlap prevents the formation of the tetravalent boron species, consequently, no coupling product would form.



Scheme 5.16

It was envisaged that the use of electron withdrawing substituents such as silicon α to the nitrogen heteroatom, would allow the nitrogen lone pair of electrons to overlap into the vacant p-orbital of the silicon, thus significantly reducing the overlap into the boron atom making it more susceptible to nucleophilic attack by the base. This attack would produce the tetravalent boron species, which in turn could couple to yield the anticipated product.

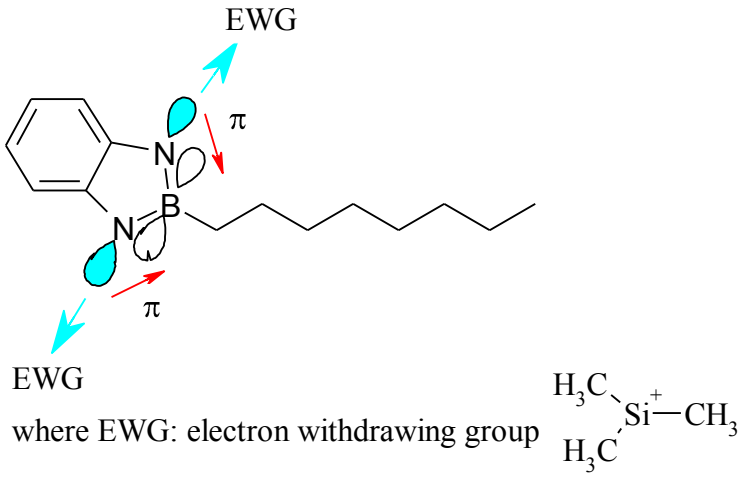


Figure 5.1

Studies into the use of an electron withdrawing group to disrupt electron cloud overlap into the boron atom in order to effect coupling reaction were conducted. Microwave irradiation was also employed with the intention to aid the coupling reaction of the nitrogen based boronate esters. In both studies it was demonstrated that the use of an electron withdrawing group or microwave irradiation provides an effective method to furnish coupling reactions with nitrogen based boronate esters. The results of these studies have been written for publication in the Organic Letters journal,[xlv] and a copy of this paper follows.*

* Copy of paper included in the body of text as per faculty guidelines. Prepartion methods are included in the experimental section, chapter 6. Selected ^{1}H and ^{13}C NMR spectra, and cartesian coordinates for geometry optimized structures of **2**, **3** and **4** are included in appendix E.

5.6 **CONCLUDING REMARKS**

The suitability of the nitrogen-based boronate esters in metal catalyzed cross coupling reactions has been explored, and this investigation has demonstrated the enhanced stability of these boronate esters, which in turn extensively hampered their reactivity in coupling transformations. However, interestingly, these studies have demonstrated that the use of electron withdrawing substituents bonded directly to the nitrogen hetero atom, redirect the electron cloud into the electron withdrawing group, thus unlocking the boronate ester for coupling reactions. Most importantly, this research has shown that these boronate esters are desirable coupling partners in solvent-free, microwave accelerated Suzuki-coupling reactions to furnish desired octylaryls or ethylene bridged biaryls in excellent yields.

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PREFACE

Synthetic methodologies for the preparation of hydroborating agents, boronate esters, catalyzed and uncatalyzed hydroboration reactions discussed in this chapter have also been mentioned within publications written for each of the preceding chapters. Unsuccessful reactions are not given in this section, because they have already been accounted for in the discussion section for each chapter.

6.1 **GENERAL**

All glassware was thoroughly dried overnight in an oven at *ca*. 150˚C. The glassware was further flame-dried by heating with a hot air gun under reduced pressure and allowed to cool under a stream of dry nitrogen, which was passed through a mixture of silica gel and 0.4 nm molecular sieves prior to use. Glass syringes, cannulae, and needles were oven dried and stored in a desiccator (charged with a mixture of silica gel and 0.4 nm molecular sieves) prior to use. Disposable syringes and needles were stored in the desiccator before use, and they were discarded after single use. On assembling the glassware, all joints were wrapped with Teflon® tape, and were subsequently sealed with a Parafilm "M"® to ensure a closed system.

^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian Unity-Inova 500 MHz and/or Bruker 400 MHz UltraShield spectrometers. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and were referenced using the residual chloroform signal at 7.25 ppm and 77.0 ppm respectively. ^{29}Si NMR spectra were referenced to TMS as an external standard (0.0 ppm). All ^{11}B NMR spectra were referenced to $BF_3{\cdot}OEt_2$ as an external standard (0.0 ppm) contained within a sealed capillary insert. ^{11}B spectroscopy was utilised in order to identify the compounds as well as to monitor the progress of the reactions. ^{13}C, ^{1}H NMR spectroscopy and GC-MS were used to identify the hydroboration and coupling products. Quartz NMR tubes (5 cm) were used for the ^{11}B NMR spectroscopic experiments and were all oven dried and flushed with dry nitrogen and sealed with a rubber septum prior to injection of the sample or reagents.

GC-MS analyses were performed on a Thermofinnigan® (GC) coupled with a PolarisQ® (MS) system. Thin layer chromatography was performed on silica gel (60 F_{254}) plates from Merck. Flash column chromatography was performed on SP Silica Gel 60 (230-400-mesh ASTM) from Merck.

All solvents were purified by distillation and dried prior to use.[i] CH_2Cl_2 was distilled over P_2O_5 under dry nitrogen; THF, benzene, diglyme, 1-octene, and *trans*-4-octene were all

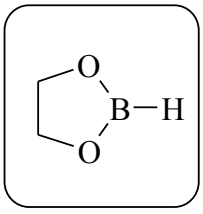
distilled over sodium wire in the presence of an indicator benzophenone. The solvents were distilled and transferred *via* cannula to a flame-dried, nitrogen flushed flask containing 0.4 nm molecular sieves (activated in the furnace at 600 ^{o}C and cooled under dry nitrogen) prior use.

1,2-Ethanedithiol, 1,3-propanedithiol, and 1,2-phenylenediamine were obtained from Merck-Schuchardt. Catecholborane**,** 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane), $BH_3{\cdot}SMe_2$ in CH_2Cl_2, 1,2-benzenedithiol, *N,N'*-diemethylethane-1,2-diamine and Tris-(triphenylphosphine)-rhodium(I)-chloride, were obtained from Sigma-Aldrich Co, and all these reagents were used without further purification. 1,2-Ethanediol was obtained from Sigma-Aldrich Co., this compound was purified by distillation under dry nitrogen and stored over 0.4 nm molecular sieves.

The yields for all prepared hydroborating agents and sulfur-based boronate esters were based on ^{11}B NMR spectroscopy, and the yields of nitrogen-based boronate esters and coupling products were determined from isolated amounts after flash column chromatography.

6.2 **SYNTHESIS OF HYDROBORATING AGENTS IN CHAPTER 2**

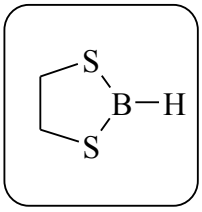
6.2.1 **1,3,2-DIOXABOROLANE**



Borane-dimethyl sulfide complex in CH_2Cl_2 (1.0 M, 5.0 ml, 5.0 mmol) was placed in a two necked, round-bottomed flask (25 ml) and cooled to -84 °C in a liquid nitrogen/ethyl acetate slurry. 1,2-Ethanediol (0.28 ml, 5.0 mmol) in CH_2Cl_2 (5 ml) was added drop- wise

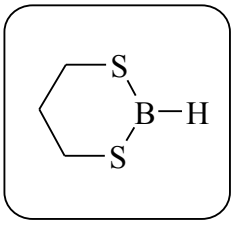
over a period of 15 minutes through a nitrogen purged syringe. The resulting solution was allowed to warm to room temperature and maintained at this temperature for a further 30 minutes to afford a mixture of 1,3,2-dioxaborolane (15%) and 2,2'- (ethylenedioxy)bis-(1,3,2-dioxaborolane), the disproportionation product in *ca*. 70% yield. 1,3,2-dioxaborolane, ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 28.4 (d, J = 177.4 Hz, 1H, B*H*); 2,2'- (ethylenedioxy)bis-(1,3,2-dioxaborolane) ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 22.9 (s).

6.2.2 **1,3,2-DITHIABOROLANE**



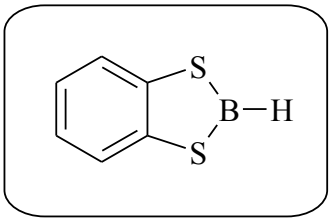
Following a modification to the procedure described by Egan *et al*.,[ii] borane-dimethyl sulfide complex in CH_2Cl_2 (5.0 ml, 5.0 mmol) was transferred into a flame-dried, nitrogen purged 25 ml two necked round-bottomed flask. The contents of the flask were subsequently cooled to -84 °C in a liquid nitrogen/ethyl acetate slurry, following which a solution of 1,2-ethanedithiol (471 mg, 5.0 mmol) in CH_2Cl_2 (3 ml) was added dropwise to the stirred flask. The reaction mixture was subsequently stirred for 30 min at -84 ^{o}C and allowed to warm up to -60 °C. The flask was then transferred to the cryostat (chiller), and allowed to stir for 14 days at -55 ^{o}C under dry atmosphere of nitrogen to afford a clear liquid comprising a mixture of 1,3,2-dithiaborolane (58%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 60.5 (d, J = 156.4 Hz, 1H, B*H*); and 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (40%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 64.0 (s); and unreacted $BH_3{\cdot}SMe_2$ (2%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = –20.5 (q, J = 105.5 Hz, 3H, BH_3)

6.2.3 **1,3,2-DITHIABORINANE**



Borane-dimethyl sulfide complex in CH_2Cl_2 (1.0 M, 5.0 ml, 5.0 mmol) was stirred at 0 ^oC under a nitrogen atmosphere. 1,3-Propanedithiol (0.50 ml, 5.0 mmol) was added drop wise over a period of 10 min. The resulting mixture was allowed to stir at room temperature for 7 days to afford a cloudy liquid of 1,3,2-dithiaborinane[iii] (35%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 52.2 (d, J = 145.8 Hz, 1H, B*H*); and 2,2'-(propylenedithio)bis-(1,3,2-dithiaborinane) (55%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 56.6 (s); $BH_3{\cdot}SMe_2$ (3%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = –20.5 (q, J = 105.5 Hz, 3H, BH_3); and $HSCH_2CH_2SBH_2$ (7%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = –16.9 (t, J = 122.3 Hz, 2H, BH_2).

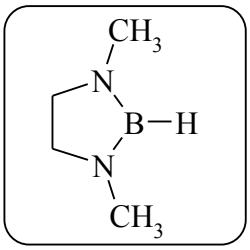
6.2.4 **BENZO-1,3,2-DITHIABOROLANE**



1,2-Benzenedithiol (497 mg, 3.50 mmol) in dichloromethane (5 ml) was added to a stirred solution of borane-dimethyl sulfide complex (1.0 M solution in dichloromethane, 3.50 ml, 3.50 mmol) at 25 °C. The reaction was mild with no observable liberation of hydrogen gas. The reaction mixture was allowed to stir for 24 hours at room temperature to afford the desired product benzo-1,3,2-dithiaborolane, as a light yellow liquid (>99 %),

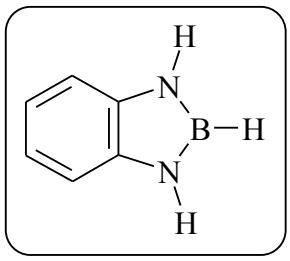
^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 53.4 (d, J = 162.6 Hz, 1H, B*H*). Proton noise decoupling was carried out with subsequent collapse of the doublet to the expected singlet. ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): P.N.D δ (ppm) = 53.4 (s).

6.2.5 **1,3-DIMETHYL-1,3,2-DIAZABOROLANE**



N,N'-Dimethylethane-1,2-diamine (1.21 ml, 11.3 mmol) and sodium borohydride (429 mg, 11.3 mmol) were mixed in dry THF (8 ml) in a dry, nitrogen purged two necked round-bottomed flask. A solution of iodine (1.44g, 5.67 mmol) in THF (8 ml) was slowly added while stirring the contents of the flask. Rapid evolution of H_2 gas was noted upon addition of the iodine solution. On completion of iodine addition, the resulting solution was refluxed for 14 hours. The reaction mixture was subsequently cooled to room temperature, following which sodium iodide precipitated out from the solution. The clear liquid was then drawn from this flask by a nitrogen-flushed syringe and was filtered through a 0.45 Nylon Cameo filter fitted between the needle and the syringe. 1,3-dimethyl-1,3,2-diazaborolane was obtained as a clear liquid (80%), ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 22.9 (d, J = 140.6 Hz, 1H, B*H*). ^{11}B NMR analysis of this compound was consistent with that reported by Rothgery *et al*.[iv]

6.2.6 **BENZO-1,3,2-DIAZABOROLANE**



1,2-Diaminobenzene (541 mg, 5.0 mmol) was dissolved in dichloromethane (5 ml) in a flame-dried round-bottomed flask. After complete dissolution of the solid 1,2-diaminobenzene, borane-dimethyl sulfide complex (1 M solution in dichloromethane, 5.0 ml, 5.0 mmol) was introduced drop wise through the septum. The resulting mixture was stirred under reflux for 4 hours under a dry atmosphere of nitrogen, benzo-1,3,2-diazaborolane was obtained as a clear liquid (95%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 23.9 (d, J = 153.2 Hz, 1H, B*H*).

6.3 **HYDROBORATION REACTIONS CONDUCTED IN CHAPTER 2**

6.3.1 **KINETIC STUDIES**

In order to determine the rate constant for hydroboration of 1-octene with 1,3,2-dithiaborolane or with 1,3,2-dithiaborinane, the following standard procedure for conducting a concentration dependence study was employed.

To an oven dried, nitrogen purged quartz NMR tube 1,3,2-dithiaborolane (0.40 ml, 0.16 M), was added *via* syringe. The sample was analyzed to verify that no degradation of the compound had taken place prior to addition of the other reagents. 1-Octene in CH_2Cl_2 (0.40 ml, 10× [1,3,2-dithiaborolane] = 1.6 M) was then added to the to the NMR tube. The tube was then agitated prior to analysis. The time delay taken from injection of the 1-octene to the first scan in the spectrometer was measured by a stopwatch (time delay

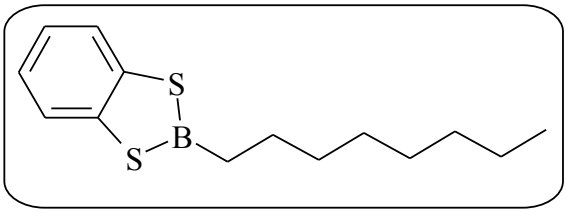
ranged between 35 to 40 seconds), the time delay was used to accurately measure the time interval between each data set in the NMR spectrometer. The spectrometer program was set to scan the contents of the tube initially very regularly and with time at slower intervals. Initially scans were recorded after every 5 min for the first 50 min, then after every 10 min for a subsequent 100 min, then after every 15 min for 75 min, then every 30 min for 150 min and finally every 1 hour for a further 5 hours, 120 transients were used for each acquisition set which in turn represented a single data point.

The concentrations of 1-octene were increased from 10 fold to 25 fold that of the hydroborating agent and the above method was repeated for each concentration. The data obtained was fitted using Microcal™ Origin™ 5.0 software. The raw data for each concentration dependence experiment is included in appendix **A** as supportive information.

In order to determine the thermodynamic parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for the hydroboration of 1-octene with 1,3,2-dithiaborolane or with 1,3,2-dithiaborinane, the following typical procedure for temperature dependence study was employed.

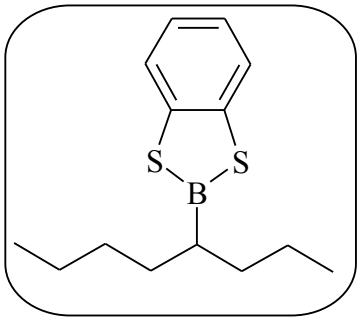
1,3,2-Dithiaborolane (0.40 ml, 0.16 M) in CH_2Cl_2 was injected into an oven dried, nitrogen purged quartz NMR tube, 1-octene (0.40 ml, 15× [1,3,2-dithiaborolane] = 2.4 M) was then added to this solution. The resulting mixture was shaken vigorously, vented and placed in the NMR probe for analysis. Time delay measurements and acquisition time intervals were done in the same manner as discussed in the preceding section. Hydroboration experiments were conducted at 20 to 35 °C increasing in steps of 5 °C. For each experiment, the concentrations of the hydroborating agent and the olefin were kept constant. The data acquired was fitted with Microcal™ Origin™ 5.0 software to yield the activation parameters for each compound towards 1-octene. The raw data for each temperature dependence experiment is included in appendix **A** as supportive information.

6.3.2 **SYNTHESIS OF 2-OCTYL-BENZO-1,3,2-DITHIABOROLANE**



Benzo-1,3,2-dithiaborolane (25.3 mg, 0.165 mmol) in diglyme (0.4 ml) was mixed with 1-octene (0.26 ml, 1.65 mmol) in a dry nitrogen purged NMR tube, capped with a rubber septum and sealed with parafilm®. The tube was then inserted in an aluminium heating block, which was immersed in a silicon oil bath set to 150 °C. The contents of the tube were heated under reflux; the pressure build up in the tube was vented with a nitrogen purged syringe every 20 min for 3 hours. This afforded a clear liquid of 2-octyl-benzo-1,3,2-dithiaborolane (65%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 59.6 (s).

6.3.3 **SYNTHESIS OF 2-(PENTYL-1-PROPYL)-BENZO-1,3,2-DITHIABOROLANE**



The above method in 6.3.1 was also employed and *trans*-4-octene was used instead of 1-octene, to afford 2-(pentyl-1-propyl)-benzo-1,3,2-dithiaborolane (15 %). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 59.6 (s).

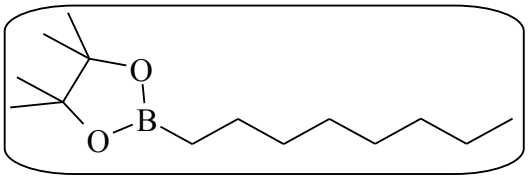
6.3.4 **SYNTHESIS OF 2-OCTYL-BENZO-1,3,2-DIAZABOROLANE**

Benzo-1,3,2-diazaborolane (23.6 mg, 0.20 mmol) in diglyme (0.4 ml) and 1-octene (0.31 ml, 2.0 mmol) were allowed to mix in an NMR tube with a rubber septum. The resulting mixture was heated under reflux at 100 °C in a aluminium heating block for 10 days. Over this period there was no observable formation of 2-octyl-benzo-1,3,2-diazaborolane and the starting material benzo-1,3,2-diazaborolane was recovered

6.4 **RHODIUM-CATALYZED HYDROBORATION REACTIONS**

The hydroborating agent under investigation was injected into an oven dried, nitrogen purged and septum capped quartz NMR tube and then analyzed by high field ^{11}B NMR spectroscopy prior to the addition of the other reagents in order to confirm its purity. To this solution was added simultaneously the olefin and Tris-(triphenylphosphine)-rhodium(I)-chloride (2 mol%) which had been dissolved in dichloromethane or THF (0.5ml) in a separate flame dried, nitrogen flushed flask The contents of the tube were shaken vigorously and the tube was inserted into the NMR spectrometer. The contents of the tube were subsequently analyzed every 2 hours for 24 hours at 25 ºC to monitor the progress of formation of the target alkylboronate ester. Oxygen based boronate esters were quenched with water and extracted with ether, whereas sulfur- and nitrogen-based boronate esters were not quenched. Quenching sulfur and nitrogen boronate ester would produce the alcohols which can not be utilized in subsequent coupling reactions. This representative procedure was employed in rhodium catalyzed hydroboration reactions discussed in the following sections. The amounts for each reactant used and yields of alkylboronate esters produced for each experiment are given in the following sections.

6.4.1 **SYNTHESIS OF 2-OCTYL-4,4,5,5-TETRAMETHYL-[1,3,2]-DIOXABOROLANE.**



Pinacolborane (1M solution in THF, 0.4 ml, 0.4 mmol), 1-octene (63µl, 0.4 mmol), and $RhCl(PPh_3)_3$ (7.4mg, 0.008mmol). Orange-yellow solution (79 %, based on ^{11}B NMR spectroscopy). ^{11}B NMR (160MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 34.4 (s), 21.7 (s, $B_2(O_2C_6H_{12})_3$). The contents of the tube were subsequently quenched by addition of water (1 ml). The product was extracted with 3 × 2 ml ether and dried over $MgSO_4$. Flash column chromatography on silica gel with ethyl acetate: hexane mixture (2:98) and removal of solvent in *vacuo* afforded 2-octyl-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane. ^{11}B NMR (160 MHz; $BF_3{\cdot}OEt_2$) δ (ppm) = 34.3 (s). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 0.71 (t, J = 7.9 Hz, 2H), 0.82 (t, J = 5.6 Hz, 3H), 1.19 (s, 12H), 1.20-1.24 (m, 10H), 1.32 - 1.39 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 14.7, 22.7, 23.1, 24.0, 24.8, 29.7, 30.1, 32.1, 82.7. IR (neat): $\tilde{\nu}$ = 2960 (s), 1744 (s), 1376 (s), 1234 (s), 1146 (s), 1073 (s) cm^{-1}. MS (EI): m/z (%) = 241 [M^+] (40), 225 (100), 224 (24), 183 (10), 127 (22), 97 (30), 69 (54).

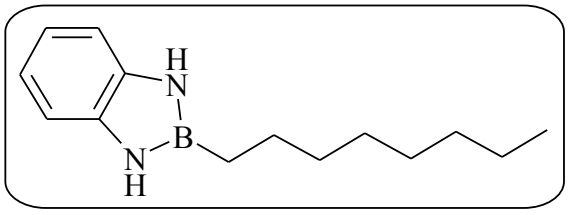
6.4.2 **SYNTHESIS OF 2-OCTYL-BENZO-1,3,2-DITHIABOROLANE**

Benzo-1,3,2-dithiaborolane (0.40 ml, 0.248 mmol), 1-octene (0.39 ml, 2.48 mmol), $RhCl(PPh_3)_3$ (46.3 mg, 0.050 mmol) CH_2Cl_2 (0.50 ml), and using the above representative method, afforded 2-octyl-benzo-1,3,2-dithiaborolane (85 %). ^{11}B NMR (160MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 59.6 (s).

6.4.3 **SYNTHESIS OF 2-(PENTYL-1-PROPYL)-BENZO-1,3,2-DITHIABOROLANE**

Benzo-1,3,2-dithiaborolane (0.40 ml, 0.248 mmol), *trans*-4-octene (0.39 ml, 2.48 mmol), $RhCl(PPh_3)_3$ (46.3 mg, 0.050 mmol) CH_2Cl_2 (0.50 ml), afforded 2-(pentyl-1-propyl)-benzo-1,3,2-dithiaborolane (80%) as a clear liquid, ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 59.6 (s). This product was subsequently oxidized by addition of NaOH (0.83 ml, 3 M) and H_2O_2 (0.02 ml of 50% v/v) solution to afford 4-octanol ^1H NMR (500 MHz; $CDCl_3$) δ (ppm) = 0.95 (t, J = 7.1 Hz, 3H, 2 ×CH_3, 1.41 (m, 2H, 2 × $CH_3CH_2CH_2$), 1.32 (m, 2H, $CH_3CH_2CH_2CHOHCH_2$), 4.71 (s, 1H, $CH_2CHOHCH_2$), 3.61 (m, 1H, $CH_2CHOHCH_2$), 1.49 (m, 2H, $CH_3CH_2CH_2CHOHCH_2$) 1.39 (m, 2H, $CH_3CH_2CH_2CHOHCH_2CH_2$). MS (EI): m/z (%) = 130 [M^+] (20), 87 (100) 73 (52), 69 (36), 55 (66).

6.4.4 **SYNTHESIS OF 2-OCTYL-BENZO-1,3,2-DIAZABOROLANE**



Benzo-1,3,2-diazaborolane (0.40 ml, 0.20 mmol), 1-octene (0.31 ml, 2.0 mmol), $RhCl(PPh_3)_3$ (37.0 mg, 0.040 mmol) CH_2Cl_2 (0.50 ml), Orange-yellow solution (70 %). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 31.6 (s). MS (EI): m/z (%) = 231 [M^+] (18), 230 (100), 229 (15), 145 (15), 132 (16), 119 (17), 118 (31).

6.4.5 MICROWAVE SYNTHESIS OF 2-OCTYL-4,4,5,5-TETRAMETHYL-[13,2]-DIOXABOROLANE.

A solution of pinacolborane in THF (0.4 ml, 0.4mmol) was injected into an oven dried, nitrogen purged and septum capped quartz NMR tube. The solution was then analyzed using ^{11}B NMR spectroscopy for purity. To this solution was added simultaneously, *trans*-4-octene (63 µl, 0.4 mmol) and $RhCl(PPh_3)_3$ (8 µmol, 7.4 mg) which had been dissolved in THF (0.5 ml) in a separate flame dried, nitrogen purged flask.

The contents of the tube were shaken vigorously, vented under nitrogen atmosphere and inserted into the microwave cavity. The sample was then irradiated with microwave energy (100 W) using a CEM discovery® microwave reactor, for 20 minutes with concomitant cooling. The sample temperature was monitored by a non-contact, infrared sensor (located under the microwave cavity floor)[v] and remained at 25°C. The resulting orange-yellow solution was analyzed by high-field ^{11}B NMR spectroscopy which indicated a singlet at 34.3 ppm characteristic of octyl-boronate ester (73%).
^{11}B, ^{1}H, ^{13}C NMR and MS spectroscopic analysis of the product was identical to that in 6.4.1 above.

6.4.6 SYNTHESIS OF 2-OCTYL-4,4,5,5-TETRAMETHYL-[13,2]-DIOXABOROLANE FROM $[RhCl(PPh_3)_2(O)_2]_2$.

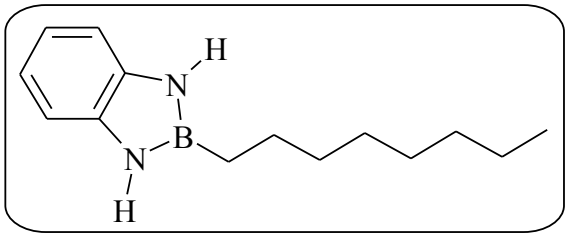
$RhCl(PPh_3)_3$ (0.2g) was dissolved in CH_2Cl_2 (5 ml), oxygen gas was passed through this solution for 5 minutes, followed by solvent evaporation *in vacuo*[vi] to yield $[RhCl(PPh_3)_2(O)_2]_2$ as a dark brown powder. The oxidized catalyst was used in a procedure analogous to that in 6.4.5 above in hydroboration of *trans*-4-octene with pinacolborane. After mixing of all reagents the reaction mixture was not irradiated with microwave energy, but allowed to react at 25°C for 48 hours to afford 72% octyl-pinacolboronate ester, that is identical to that prepared in 6.4.5 above.

6.4.7 **SYNTHESIS OF BIS(*μ*-BENZENE-1,2-DITHIOLATO)BIS[(2-MERCAPTOBENZENETHIOLATO)TRIPHENYLPHOSPHINE)-RHODIUM(III)]**

A solution of benzo-1,3,2-dithiaborolane in CH_2Cl_2 (0.4 ml, 0.16 mmol) was injected into a flame dried, nitrogen purged and septum capped test tube. To this solution was added $RhCl(PPh_3)_3$ (4.72 mg, 5.1umol) which had been dissolved in dichloromethane (3.5 ml) in a separate flame dried and nitrogen flushed test tube. The resulting mixture was shaken vigorously and allowed to stand for *ca.* 2 weeks, the solvent slowly evaporated through the septum to afford a dark green powder containing brick red crystals as a minor component. These were manually hand picked under a microscope, analyzed and assigned as crystals of bis(*μ*-benzene-1,2-dithiolato)bis[(2-mercaptobenzenethiolato)triphenylphosphine)rhodium(III)] dichloromethane tetrasolvate. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.67 (s, 2x 1H) 7.02 − 7.21 (m, 12H), 7.26 (m, 6H), 7.43 − 7.56 (m, 16H), 7.65 − 7.69 (m, 12H).^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 59.5, 76.7, 77.0, 77.2, 126.7, 129.9, 130.1, 130.7, 130.8, 131.9, 131.96, 132.0, 132.1, 132.8, 133.1, 133.2, 134.8 136.7. The melting point of 145.5–149.6°C was determined with the Electrothermal 9100 apparatus.[vii]

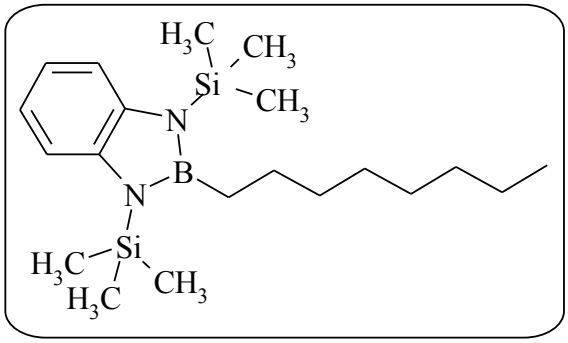
6.5 **BULK SYNTHESIS OF N-BASED BORONATE ESTERS**

6.5.1 **SYNTHESIS OF 2-OCTYL-BENZO-1,3,2-DIAZABOROLANE**



Freshly prepared benzo-1,3,2-diazaborolane (20.0 ml, 46.2 mmol) in dichloromethane, was injected into an oven dried, nitrogen purged two necked round bottom flask, followed by 1-octene (7.26 ml, 46.2 mmol), with continuous stirring. To this solution was added $RhCl(PPh_3)_3$ (2 mol%, 855 mg) which had been dissolved in dichloromethane (5 ml) in a separate flame dried, nitrogen flushed flask. The reaction mixture was allowed to stir at 25 ºC for 24 hours. The solvent was then removed *in vacuo*, and the remaining orange-yellow paste was purified through flash column chromatography on silica gel with hexane as an eluent, removal of solvent in *vacuo* afforded 2-octyl-benzo-1,3,2-diazaborolane, as low melting orange yellow wax (92 %). mp = 26 – 28 ºC, ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 31.6 (s). MS (EI): m/z (%) = 231 [M^+] (18), 230 (100), 229 (15), 145 (15), 132 (16), 119 (17), 118 (31).

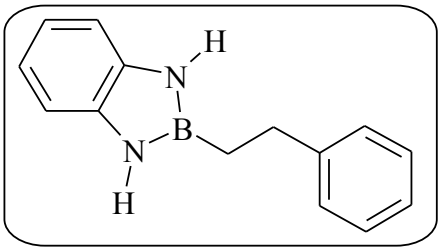
6.5.2 SYNTHESIS OF 2-OCTYL-1,3-BIS-TRIMETHYLSILANYL-BENZO-1,3,2-DIAZABOROLANE



2-Octyl-benzo-1,3,2-diazaborolane (3.0 g, 13.04 mmol) prepared above was placed in a flame dried, nitrogen purged two necked round bottom flask and then dissolved in THF (15 ml), to this solution was injected gradually tetramethyl ethylenediamine (TMEDA) (3.88 ml, 26.1 mmol) *via* a syringe. The mixture was stirred for 5 minutes and a slight excess of BuLi (17.4 ml, 1.6 M) was added drop wise for 30 minutes, followed by continuous stirring for 24 hours at ambient temperature. ^{11} B NMR spectroscopic analysis of the reaction mixture showed complete conversion of the starting boronate. The solvent was removed *in vacuo*, and the light brown solid was purified without quenching, using

flash column chromatography on silica gel with hexane. Subsequent removal of hexane *in vacuo* afforded 2-octyl-1,3-bis-tetramethylsilanyl-benzo-1,3,2-diazaborolane (83 %). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 37.6 (s). ^{29}Si NMR (99 MHz, TMS): δ (ppm) = 6.31 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.74 (s, 18H), 1.13 – 1.20 (m, 13H), 1.57 (m, 4H), 7.18 (dd, 2H), 7.48 (dd, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 2.0, 14.2, 22.9, 29.3, 30.4, 32.2, 113.4, 118.4, 142.2. This compound was sensitive to air and moisture, thus decomposed gradually after flash column chromatography.

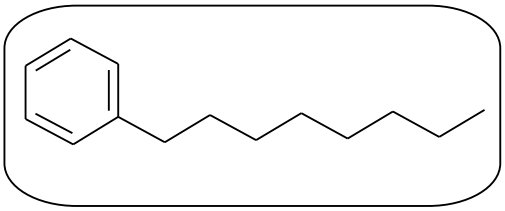
6.5.3 SYNTHESIS OF 2-PHENETHYL-BENZO-1,3,2-DIAZABORO-LANE



The synthetic procedure in 6.5.1 was followed, benzo-1,3,2-diazaborolane (20.0 ml, 46.2 mmol) in CH_2Cl_2, styrene (5.30 ml, 46.2 mmol), $RhCl(PPh_3)_3$ (2 mol%, 855 mg). However, in this case the reaction mixture was heated to *ca.* 60 ºC, and kept at that temperature for 48 hours. ^{11}B NMR analysis of the product mixture showed that the starting material had disappeared completely. The boronate prepared emitted intense blue colour under UV light, consequently, migration of this boronate ester during radial chromatography was followed using a standard hand held UV lamp (350 nm). Cream powder (81%). ^{11}B NMR (128 MHz, $BF_3{\cdot}OEt_2$): δ (ppm) = 31.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.49 (t, J = 7.9 Hz, 2H), 2.8 (t, J = 8.14 Hz, 2H), 6.18 (s, NH), 6.80 (dd, 2H), 6.88 (dd, 2H), 7.09 – 7.25 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 31.9, 110.6, 118.9, 125.77, 128.0, 128.4, 136.1, 144.3. MS (EI): m/z (%) = 223 [M^+] (16), 222 (100), 221 (27), 132 (17), 131 (44), 118 (29).

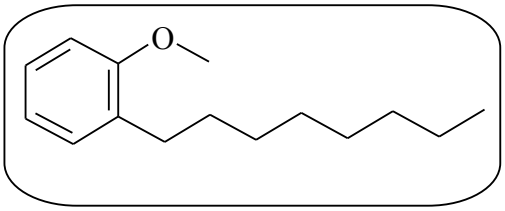
6.6 **SOLVENT FREE SUZUKI COUPLING REACTIONS**

6.6.1 **PREPARATION OF OCTYLBENZENE**



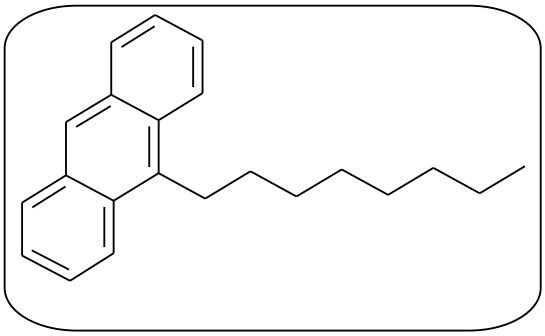
To a flame dried, nitrogen purged microwave pressure vial (10 ml) containing a magnetic stirring bar, was placed bromobenzene (0.23 ml, 2.17 mmol), $K_3PO_4 \cdot H_2O$ (1.0 g, 4.34 mmol), PCy_3 (48.7 mg, 0.173 mmol), $Pd(OAc)_2$ (19.5 mg, 86.8 μmol). The vial was agitated in order to mix the reagents, then purged with nitrogen. To this heterogeneous mixture was added 2-octyl-benzo-1,3,2-diazaborolane (0.5 g, 2.17 mmol), with subsequent nitrogen purging for 5 minutes. The vial was sealed with a snap on cap and inserted into the CEM discovery® microwave reactor cavity. The microwave cavity was then close with an Intellivent pressure control system.[v] The sample was then irradiated with microwave energy (50 W) for 5 minutes, and the sample temperature was monitored by a non-contact, infrared sensor. After 5 minutes, TLC analysis showed no evidence of unreacted boronate ester or arylbromide. The remaining material solidified at the bottom of the vial, and the target octylbenzene was decanted as clear oil. The remaining solid was washed with ethyl acetate (2.0 ml), the ethyl acetate wash was concentrated in *vacuo*, combined with the decanted oil and chromatographed eluting with hexane to afford octylbenzene (88%). ^{1}H NMR, ^{13}C NMR spectroscopic analysis and GC-MS traces of this sample were identical to the commercial samples. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.85 (t, *J* = 6.71 Hz, 3H), 1.21 – 1.40 (m, 10H), 1.60 (m, 2H), 3.65 (t, *J* = 7.81, 2H), 7.18 – 7.31 (m, 2H), 7.42 – 7.56 (m, 2H), 7.66 – 7.72 (dd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2, 22.7, 29.3, 29.5, 29.6, 29.7, 31.5, 31.9, 125.6, 128.3, 128.4, 143.0. MS (EI): m/z (%) = 191 [M^+] (3), 190 (5), 133 (10), 92 (100), 91 (72), 65 (7), 41 (12).

6.6.2 **PREPARATION OF 1-METHOXY-2-OCTYL-BENZENE**



The above method was adopted as a general procedure for microwave mediated coupling reactions, and was employed in this reaction. 1-Bromo-2-methoxy-benzene (0.27 ml, 2.17 mmol), $K_3PO_4 \cdot H_2O$ (1.0 g, 4.34 mmol), PCy_3 (48.7 mg, 0.173 mmol), $Pd(OAc)_2$ (19.5 mg, 86.8 μmol), and 2-octyl-benzo-1,3,2-diazaborolane (0.5 g, 2.17 mmol), reaction mixture irradiated with microwave energy (50 W) for 40 minutes to afford 1-methoxy-2-octyl-benzene as clear oil (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.78 (t, J = 7.05 Hz, 3H), 1.10 – 1.47 (m, 10H), 1.47 (m, 2H), 2.50 (t, J = 7.66Hz, 2H), 3.71 (s, 3H), 6.71 – 7.23 (m, 4H).

6.6.3 **PREPARATION OF 9-OCTYL-ANTHRACENE**



Representative procedure in 6.6.1 was employed. 9-Bromo-anthracene (0.598 g, 2.17 mmol), $K_3PO_4 \cdot H_2O$ (1.0 g, 4.34 mmol), PCy_3 (48.7 mg, 0.173 mmol), $Pd(OAc)_2$ (19.5 mg, 86.8 μmol), and 2-octyl-benzo-1,3,2-diazaborolane (0.5 g, 2.17 mmol). Solid product

was dissolved in hexane, chromatographed, and afforded 9-octyl-anthracene as glassy crystals (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.79 (t, *J* = 7.30 Hz, 3H), 1.11 – 1.34 (m, 8H), 1.46 (m, 2H), 1.69 (m, 2H), 3.46 (t, *J* = 7.30 Hz, 2H), 7.28 – 7.40 (m, 4H), 7.82 – 7.89 (m, 2H), 8.12 – 8.20 (m, 2H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2, 22.8, 28.2, 29.4, 29.7, 30.5, 31.5, 32.0, 124.6, 124.8, 125.4, 128.2, 129.3, 131.8, 135.5.

6.7 **REFERENCES**

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[v] Discover LabMate, Web: www.cem.com/synthesis/discoverLM.asp, [data of access: 26 November 2008]

[vi] Evans, D. A.; Fu, G. C.; Anderson, A. B. *J. Am. Chem. Soc.*, **1992**, *114*, 6679.

[vii] Crystal data including a table of geometric parameters is included as supportive information in appendix D.

Project Overview

Kinetic and thermodynamic studies on the hydroboration of 1-octene with 1,3,2-dithiaborolane and 1,3,2-dithiaborinane has shown that the presence of sulfur hetero atoms on the hydroborating agent slows the rate of hydroboration when compared with $BH_3{\cdot}SMe_2$ of dialkylboranes. The entropy values obtained from this study suggested that hydroboration proceeded *via* an associative mechanism. The hydroboration and disproportionation mechanisms have been verified using DFT at B3LYP/3-21+G and 6-31+G(d) levels. DFT investigation has shed light into these two mechanisms. It has been demonstrated computationally that disproportionation required lower activation energy than hydroboration, which allowed the heterocyclic boranes to disproportionate upon storage at room temperature. This investigation has also shown the existence of a four-membered transition state for the hydroboration reactions, and this confirmed the fact that hydroboration proceeded *via* an associative mechanism.

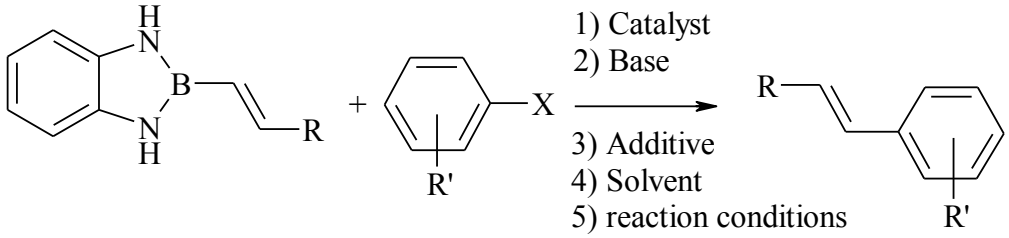
The use of a transition metal catalyst, that is, $RhCl(PPh_3)_3$ in our studies to enhance hydroboration reactions with sulfur- and nitrogen-based analogues of catecholborane has proven extremely versatile in the synthesis of desired sulfur- or nitrogen-based boronate esters. Our study has also shown that the sulfur- and nitrogen analogues are highly stable due to the overlap of electrons from the hetero atom, and are less prone to disproportionation than catecholborane during rhodium-catalyzed transformations, consequently resulted in enhanced yields of the desired boronate esters. Subsequent investigations into the suitability of the produced boronate esters in cross-coupling reactions with arylbromides have revealed outstanding outcomes; namely, the silicon hetero atom as an electron withdrawing substituent bonded directly to the nitrogen hetero atom, strongly disrupted the overlap of electrons from the nitrogen atom into the boron atom, which resulted in enhanced nucleophilicity of the boron atom. The reduced overlap ultimately led to an increased reactivity of the boronate ester during the coupling reactions. The use of microwave irradiation has been shown to accelerate the coupling of nitrogen-based boronate ester with arylbromides, in solvent-free Suzuki-coupling reactions to furnish desired coupling products in excellent yields.

Future Work

Our success in the use of molecular modeling to rationalize experimental findings, the use of $RhCl(PPh_3)_3$ in hydroboration reactions with sulfur- and nitrogen-based boranes to synthesize desired boronate esters, and the application of nitrogen-based boronates has identified various areas for future investigation, including the following:

- A molecular modeling study focused towards understanding the effect of coordinating solvents such as THF, dimethyl sulfide, and a range of trialkyl amines. This study may shed light into the understanding of the mechanism of hydroboration reactions with solvent stabilized hydroborating agents.

- To further expand the scope of nitrogen-based boronate esters by synthesizing a range of *N*-based boronate, including stereo-defined alkenyl-boronate esters (Scheme A) and to explore their coupling reactions with aryl halides or triflates to furnish building blocks of pharmaceutical importance. To investigate the tolerance of other functional groups on the aryl halide or triflate may be of particular interest in synthetic chemistry.



Catalysts : $Pd(PPh_3)_3$, $Pd(AOc)_2$
Bases : Na_2CO_3, K_2CO_3, K_3PO_4
Additives : PPh_3, PCy_3
Solvents : Benzene, DMF, EtOH-H_2O
Reaction conditions: r.t. to reflux, microwave irradiation

X = I, Br, OTf
R = *n*-Hexyl, Aryl,
R' = 4-NO_2, 4-CN,4-NMe_2, 4-OH, 4-CH_2CN, 4-COMe, 4-CO_2Me, 3-COMe

Scheme A

APPENDIX A

1 Hydroboration of 1-octene with 1,3,2-dithiaborolane (4)(concentration dependence study at 25 °C)

Table 1.1 Original data for hydroboration of 10× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	73	0.158	0.000
60	92	1	72	0.156	0.002
480	512	6	62	0.134	0.013
900	932	11	57	0.123	0.024
1320	1352	14	52	0.112	0.030
1740	1772	16	47	0.102	0.035
2160	2192	18	43	0.093	0.039
2580	2612	20	41	0.089	0.043
3000	3032	21	38	0.082	0.045
3420	3452	23	36	0.078	0.050
3840	3872	24	34	0.073	0.052
4260	4292	25	32	0.069	0.054
4980	5012	26	29	0.063	0.056
5700	5732	27	27	0.058	0.058
6420	6452	28	25	0.054	0.061
7140	7172	29	24	0.052	0.063
7860	7892	30	22	0.048	0.065
8580	8612	31	21	0.045	0.067
9300	9332	31	20	0.043	0.067
10020	10052	32	19	0.041	0.069
10740	10772	32	18	0.039	0.069
11460	11492	33	17	0.037	0.071
12480	12512	33	16	0.035	0.071
13500	13532	34	15	0.032	0.073
14520	14552	34	15	0.032	0.073
15540	15572	35	14	0.030	0.076
16560	16592	35	13	0.028	0.076
18480	18512	35	12	0.026	0.076
20400	20432	36	12	0.026	0.078
22320	22352	36	11	0.024	0.078
24240	24272	37	10	0.022	0.080
27960	27992	37	9	0.019	0.080
31680	31712	38	8	0.017	0.082

Table 1.2 Original data for hydroboration of 15× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	67	0.161	0.000
60	107	2	67	0.161	0.005
480	527	7	56	0.134	0.017
900	947	10	47	0.113	0.024
1320	1367	13	41	0.098	0.031
1740	1787	15	37	0.089	0.036
2160	2207	16	33	0.079	0.038
2580	2627	18	31	0.074	0.043
3000	3047	19	28	0.067	0.046
3420	3467	20	26	0.062	0.048
3840	3887	20	24	0.058	0.048
4260	4307	21	23	0.055	0.050
4980	5027	22	21	0.050	0.053
5700	5747	23	19	0.046	0.055
6420	6467	23	18	0.043	0.055
7140	7187	24	16	0.038	0.058
7860	7907	24	15	0.036	0.058
8580	8627	25	14	0.034	0.060
9300	9347	25	13	0.031	0.060
10020	10067	26	13	0.031	0.062
10740	10787	26	12	0.029	0.062
11460	11507	26	12	0.029	0.062
12480	12527	26	11	0.026	0.062
13500	13547	27	10	0.024	0.065
14520	14567	27	10	0.024	0.065
15540	15587	27	9	0.022	0.065
16560	16607	27	9	0.022	0.065
18480	18527	28	8	0.019	0.067
20400	20447	28	7	0.017	0.067
22320	22367	28	7	0.017	0.067
24240	24287	28	6	0.014	0.067
27960	28007	29	5	0.012	0.070
31680	31727	29	5	0.012	0.070
35400	35447	29	5	0.012	0.070
39120	39167	29	4	0.010	0.070
42840	42887	29	4	0.010	0.070

Table 1.3 Original data for hydroboration of 20×[1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	67	0.131	0.000
60	104	2	65	0.127	0.004
480	524	8	52	0.101	0.016
900	944	12	44	0.086	0.023
1320	1364	14	38	0.074	0.027
1740	1784	16	34	0.066	0.031
2160	2204	18	30	0.059	0.035
2580	2624	19	28	0.055	0.037
3000	3044	20	26	0.051	0.039
3420	3464	21	24	0.047	0.041
3840	3884	22	22	0.043	0.043
4260	4304	22	21	0.041	0.043
4980	5024	23	19	0.037	0.045
5700	5744	24	17	0.033	0.047
6420	6464	25	16	0.031	0.049
7140	7184	25	15	0.029	0.049
7860	7904	26	14	0.027	0.051
8580	8624	26	13	0.025	0.051
9300	9344	26	12	0.023	0.051
10020	10064	27	12	0.023	0.053
10740	10784	27	11	0.021	0.053
11460	11504	27	10	0.020	0.053
12480	12524	28	10	0.020	0.055
13500	13544	28	9	0.018	0.055
14520	14564	28	9	0.018	0.055
15540	15584	28	8	0.016	0.055
16560	16604	28	8	0.016	0.055
18480	18524	29	7	0.014	0.057
20400	20444	29	7	0.014	0.057
22320	22364	29	6	0.012	0.057
24240	24284	29	6	0.012	0.057
26160	26204	30	3	0.006	0.059
29880	29924	30	3	0.006	0.059
33600	33644	30	3	0.006	0.059
37320	37364	30	3	0.006	0.059
41040	41084	31	3	0.006	0.060

Table 1.4 Original data for hydroboration of 25× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	57	0.123	0.000
60	103	1	56	0.120	0.002
480	523	6	44	0.095	0.013
900	943	7	37	0.080	0.015
1320	1363	11	32	0.069	0.024
1740	1783	12	28	0.060	0.026
2160	2203	13	25	0.054	0.028
2580	2623	14	23	0.049	0.030
3000	3043	15	21	0.045	0.032
3420	3463	15	19	0.041	0.032
3840	3883	16	18	0.039	0.034
4260	4303	16	17	0.037	0.034
4980	5023	17	15	0.032	0.037
5700	5743	17	14	0.030	0.037
6420	6463	18	13	0.028	0.039
7140	7183	18	12	0.026	0.039
7860	7903	19	11	0.024	0.041
8580	8623	19	10	0.022	0.041
9300	9343	19	10	0.022	0.041
10020	10063	19	9	0.019	0.041
10740	10783	20	9	0.019	0.043
11460	11503	20	8	0.017	0.043
12480	12523	20	8	0.017	0.043
13500	13543	20	7	0.015	0.043
14520	14563	20	7	0.015	0.043
15540	15583	20	7	0.015	0.043
16560	16603	20	6	0.013	0.043
18480	18523	21	6	0.013	0.045
20400	20443	21	5	0.011	0.045
22320	22363	21	5	0.011	0.045
24240	24283	21	5	0.011	0.045
27960	28003	21	4	0.009	0.045
31680	31723	21	4	0.009	0.045
35400	35443	21	3	0.006	0.045
39120	39163	22	3	0.006	0.047
42840	42883	22	3	0.006	0.047

2 Hydroboration of 1-octene with 1,3,2-dithiaborinane (6)(concentration dependence study at 25 °C)

Table 2.1 Original data for hydroboration of 10× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	38	0.156	0.000
60	113	1	38	0.156	0.004
480	533	2	37	0.151	0.008
900	953	3	33	0.135	0.012
1320	1373	4	30	0.123	0.016
1740	1793	5	28	0.115	0.020
2160	2213	5	26	0.106	0.020
2580	2633	6	24	0.098	0.025
3000	3053	6	23	0.094	0.025
3420	3473	6	21	0.086	0.025
3840	3893	7	20	0.082	0.029
4260	4313	7	19	0.078	0.029
4980	5033	7	18	0.074	0.029
5700	5753	8	17	0.070	0.033
6420	6473	8	15	0.061	0.033
7140	7193	8	15	0.061	0.033
7860	7913	9	14	0.057	0.037
8580	8633	9	13	0.053	0.037
9300	9353	9	13	0.053	0.037
10020	10073	9	12	0.049	0.037
10740	10793	9	12	0.049	0.037
11460	11513	9	12	0.049	0.037
12480	12533	10	11	0.045	0.041
13500	13553	10	12	0.049	0.041
14520	14573	10	11	0.045	0.041
15540	15593	11	11	0.045	0.045
16560	16613	11	10	0.041	0.045
18480	18533	11	10	0.041	0.045
20400	20453	11	10	0.041	0.045
22320	22373	12	10	0.041	0.049
24240	24293	12	10	0.041	0.049
26160	26213	12	10	0.041	0.049
28080	28133	13	10	0.041	0.053
31800	31853	14	10	0.041	0.057
35520	35573	14	10	0.041	0.057

Table 2.2 Original data for hydroboration of 15× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	46	0.130	0.000
60	100	1	43	0.121	0.003
480	520	2	38	0.107	0.006
900	940	3	34	0.096	0.008
1320	1360	3	31	0.087	0.008
1740	1780	4	29	0.082	0.011
2160	2200	4	27	0.076	0.011
2580	2620	5	23	0.065	0.014
3000	3040	5	23	0.065	0.014
3420	3460	6	22	0.062	0.017
3840	3880	6	21	0.059	0.017
4260	4300	6	19	0.054	0.017
4980	5020	7	18	0.051	0.020
5700	5740	7	17	0.048	0.020
6420	6460	7	17	0.048	0.020
7140	7180	8	16	0.045	0.023
7860	7900	8	15	0.042	0.023
8580	8620	8	14	0.039	0.023
9300	9340	8	14	0.039	0.023
10020	10060	8	13	0.037	0.023
10740	10780	9	13	0.037	0.025
11460	11500	9	12	0.034	0.025
12480	12520	9	12	0.034	0.025
13500	13540	9	12	0.034	0.025
14520	14560	9	12	0.034	0.025
15540	15580	9	11	0.031	0.025
16560	16600	10	11	0.031	0.028
18480	18520	11	11	0.031	0.031
20400	20440	11	11	0.031	0.031
22320	22360	11	11	0.031	0.031
24240	24280	12	10	0.028	0.034
26160	26200	12	10	0.028	0.034
28080	28120	13	10	0.028	0.037
31800	31840	13	10	0.028	0.037
35520	35560	14	10	0.028	0.039
39240	39280	15	10	0.028	0.042
42960	43000	15	10	0.028	0.042
46680	46720	16	10	0.028	0.045
50400	50440	17	10	0.028	0.048

Table 2.3 Original data for hydroboration of 20× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	41	0.137	0.000
60	100	1	41	0.137	0.003
480	520	2	34	0.114	0.007
900	940	3	31	0.104	0.010
1320	1360	4	28	0.094	0.013
1740	1780	4	25	0.084	0.013
2160	2200	5	23	0.077	0.017
2580	2620	5	22	0.074	0.017
3000	3040	5	21	0.070	0.017
3420	3460	6	19	0.064	0.020
3840	3880	6	18	0.060	0.020
4260	4300	6	18	0.060	0.020
4980	5020	7	16	0.054	0.023
5700	5740	7	15	0.050	0.023
6420	6460	8	14	0.047	0.027
7140	7180	8	13	0.044	0.027
7860	7900	8	13	0.044	0.027
8580	8620	8	12	0.040	0.027
9300	9340	9	12	0.040	0.030
10020	10060	9	11	0.037	0.030
10740	10780	9	11	0.037	0.030
11460	11500	10	11	0.037	0.033
12480	12520	10	10	0.033	0.033
13500	13540	10	10	0.033	0.033
14520	14560	11	10	0.033	0.037

Table 2.4 Original data for hydroboration of 25× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	31	0.108	0.000
60	100	1	36	0.108	0.003
480	520	2	31	0.093	0.006
900	940	3	27	0.081	0.009
1320	1360	4	24	0.072	0.012
1740	1780	4	22	0.066	0.012
2160	2200	5	20	0.060	0.015
2580	2620	5	19	0.057	0.015
3000	3040	5	18	0.054	0.015
3420	3460	6	17	0.051	0.018
3840	3880	6	16	0.048	0.018
4260	4300	6	15	0.045	0.018
4980	5020	7	14	0.042	0.021
5700	5740	7	13	0.039	0.021
6420	6460	7	12	0.036	0.021
7140	7180	8	11	0.033	0.024
7860	7900	8	11	0.033	0.024
8580	8620	8	10	0.030	0.024
9300	9340	9	10	0.030	0.027
10020	10060	9	9	0.027	0.027
10740	10780	9	9	0.027	0.027
11460	11500	9	9	0.027	0.027
12480	12520	9	8	0.024	0.027
13500	13540	10	8	0.024	0.030
14520	14560	10	8	0.024	0.030
15540	15580	11	8	0.024	0.033
16560	16600	11	7	0.021	0.033
18480	18520	11	7	0.021	0.033
20400	20440	12	7	0.021	0.036

3 Hydroboration of 15× [1-octene] with 1,3,2-dithiaborolane (4) (temperature dependence study)

Table 3.1 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 20°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	53	0.124	0.000
60	398	3	51	0.119	0.007
480	818	5	51	0.119	0.012
900	1238	7	47	0.110	0.016
1320	1658	8	43	0.100	0.019
1740	2078	10	40	0.093	0.023
2160	2498	11	38	0.089	0.026
2580	2918	11	35	0.082	0.026
3000	3338	12	33	0.077	0.028
3420	3758	13	32	0.075	0.030
3840	4178	14	30	0.070	0.033
4260	4598	14	28	0.065	0.033
4980	5318	15	27	0.063	0.035
5700	6038	16	25	0.058	0.037
6420	6758	16	23	0.054	0.037
7140	7478	17	22	0.051	0.040
7860	8198	17	21	0.049	0.040
8580	8918	18	19	0.044	0.042
9300	9638	18	19	0.044	0.042
10020	10358	18	18	0.042	0.042
10740	11078	19	17	0.040	0.044
11460	11798	19	16	0.037	0.044
12480	12818	19	15	0.035	0.044
13500	13838	20	15	0.035	0.047
14520	14858	20	14	0.033	0.047
15540	15878	20	13	0.030	0.047
16560	16898	21	13	0.030	0.049
18480	18818	21	12	0.028	0.049
20400	20738	21	11	0.026	0.049
22320	22658	21	10	0.023	0.049
24240	24578	22	10	0.023	0.051
26160	26498	22	9	0.021	0.051
28080	28418	22	8	0.019	0.051
31800	32138	22	8	0.019	0.051

Table 3.2 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 25°C.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	67	0.161	0.000
60	107	2	67	0.161	0.005
480	527	7	56	0.134	0.017
900	947	10	47	0.113	0.024
1320	1367	13	41	0.098	0.031
1740	1787	15	37	0.089	0.036
2160	2207	16	33	0.079	0.038
2580	2627	18	31	0.074	0.043
3000	3047	19	28	0.067	0.046
3420	3467	20	26	0.062	0.048
3840	3887	20	24	0.058	0.048
4260	4307	21	23	0.055	0.050
4980	5027	22	21	0.050	0.053
5700	5747	23	19	0.046	0.055
6420	6467	23	18	0.043	0.055
7140	7187	24	16	0.038	0.058
7860	7907	24	15	0.036	0.058
8580	8627	25	14	0.034	0.060
9300	9347	25	13	0.031	0.060
10020	10067	26	13	0.031	0.062
10740	10787	26	12	0.029	0.062
11460	11507	26	12	0.029	0.062
12480	12527	26	11	0.026	0.062
13500	13547	27	10	0.024	0.065
14520	14567	27	10	0.024	0.065
15540	15587	27	9	0.022	0.065
16560	16607	27	9	0.022	0.065
18480	18527	28	8	0.019	0.067
20400	20447	28	7	0.017	0.067
22320	22367	28	7	0.017	0.067
24240	24287	28	6	0.014	0.067
27960	28007	29	5	0.012	0.070
31680	31727	29	5	0.012	0.070
35400	35447	29	5	0.012	0.070
39120	39167	29	4	0.010	0.070
42840	42887	29	4	0.010	0.070

Table 3.3 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 30°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	62	0.142	0.000
60	102	4	59	0.135	0.009
480	522	11	51	0.117	0.025
900	942	15	43	0.099	0.034
1320	1362	18	38	0.087	0.041
1740	1782	19	34	0.078	0.044
2160	2202	21	31	0.071	0.048
2580	2622	22	29	0.066	0.050
3000	3042	23	27	0.062	0.053
3420	3462	24	25	0.057	0.055
3840	3882	25	24	0.055	0.057
4260	4302	25	23	0.053	0.057
4980	5022	27	20	0.046	0.062
5700	5742	27	19	0.044	0.062
6420	6462	28	18	0.041	0.064
7140	7182	28	17	0.039	0.064
7860	7902	29	15	0.034	0.066
8580	8622	29	15	0.034	0.066
9300	9342	30	14	0.032	0.069
10020	10062	30	13	0.030	0.069
10740	10782	30	13	0.030	0.069
11460	11502	31	12	0.027	0.071
12480	12522	31	12	0.027	0.071
13500	13542	32	11	0.025	0.073
14520	14562	31	11	0.025	0.071
15540	15582	32	10	0.023	0.073
16560	16602	32	9	0.021	0.073
18480	18522	33	9	0.021	0.076
20400	20442	33	8	0.018	0.076
22320	22362	33	8	0.018	0.076
24240	24282	33	7	0.016	0.076
26160	26202	33	7	0.016	0.076
28080	28122	34	7	0.016	0.078
31800	31842	34	6	0.014	0.078
35520	35562	34	6	0.014	0.078
39240	39282	35	5	0.011	0.080
42960	43002	35	5	0.011	0.080
46680	46722	35	5	0.011	0.080
50400	50442	34	4	0.009	0.078

Table 3.4 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 35°C.

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	56	0.118	0.000
60	95	4	56	0.118	0.008
480	515	13	37	0.078	0.027
900	935	17	28	0.059	0.036
1320	1355	20	23	0.048	0.042
1740	1775	22	20	0.042	0.046
2160	2195	23	18	0.038	0.048
2580	2615	23	16	0.034	0.048
3000	3035	24	15	0.031	0.050
3420	3455	25	13	0.027	0.052
3840	3875	25	12	0.025	0.052
4260	4295	25	12	0.025	0.052
4980	5015	26	11	0.023	0.055
5700	5735	27	10	0.021	0.057
6420	6455	27	9	0.019	0.057
7140	7175	27	8	0.017	0.057
7860	7895	27	8	0.017	0.057
8580	8615	28	7	0.015	0.059
9300	9335	28	7	0.015	0.059
10020	10055	28	7	0.015	0.059
10740	10775	28	7	0.015	0.059
11460	11495	28	6	0.013	0.059
12480	12515	28	6	0.013	0.059
13500	13535	29	6	0.013	0.061
14520	14555	29	6	0.013	0.061
15540	15575	29	5	0.010	0.061
16560	16595	29	5	0.010	0.061
18480	18515	29	5	0.010	0.061
20400	20435	29	4	0.008	0.061
22320	22355	29	4	0.008	0.061
24240	24275	29	4	0.008	0.061
26160	26195	29	4	0.008	0.061
28080	28115	29	4	0.008	0.061

4 Hydroboration of 15× [1-octene] with 1,3,2-dithiaborinane (6)(temperature dependence study)

Table 4.1 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane at 20°C

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	45	0.162	0.000
60	101	1	44	0.158	0.004
480	521	2	40	0.144	0.007
900	941	2	36	0.130	0.007
1320	1361	3	34	0.122	0.011
1740	1781	3	32	0.115	0.011
2160	2201	4	30	0.108	0.014
2580	2621	4	29	0.104	0.014
3000	3041	4	27	0.097	0.014
3420	3461	5	26	0.094	0.018
3840	3881	5	25	0.090	0.018
4260	4301	5	24	0.086	0.018
4980	5021	5	23	0.083	0.018
5700	5741	6	22	0.079	0.022
6420	6461	6	20	0.072	0.022
7140	7181	6	19	0.068	0.022
7860	7901	7	18	0.065	0.025
8580	8621	7	17	0.061	0.025
9300	9341	7	16	0.058	0.025
10020	10061	7	16	0.058	0.025
10740	10781	8	15	0.054	0.029
11460	11501	8	14	0.050	0.029
12480	12521	8	14	0.050	0.029
13500	13541	8	13	0.047	0.029
14520	14561	8	12	0.043	0.029
15540	15581	9	12	0.043	0.032
16560	16601	9	12	0.043	0.032
18480	18521	9	11	0.040	0.032
20400	20441	10	10	0.036	0.036
22320	22361	10	10	0.036	0.036
24240	24281	10	10	0.036	0.036
26160	26201	11	9	0.032	0.040
28080	28121	11	9	0.032	0.040
31800	31841	12	9	0.032	0.043
35520	35561	12	8	0.029	0.043

Table 4.2 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 25°C

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	46	0.130	0.000
60	100	1	43	0.121	0.003
480	520	2	38	0.107	0.006
900	940	3	34	0.096	0.008
1320	1360	3	31	0.087	0.008
1740	1780	4	29	0.082	0.011
2160	2200	4	27	0.076	0.011
2580	2620	5	23	0.065	0.014
3000	3040	5	23	0.065	0.014
3420	3460	6	22	0.062	0.017
3840	3880	6	21	0.059	0.017
4260	4300	6	19	0.054	0.017
4980	5020	7	18	0.051	0.020
5700	5740	7	17	0.048	0.020
6420	6460	7	17	0.048	0.020
7140	7180	8	16	0.045	0.023
7860	7900	8	15	0.042	0.023
8580	8620	8	14	0.039	0.023
9300	9340	8	14	0.039	0.023
10020	10060	8	13	0.037	0.023
10740	10780	9	13	0.037	0.025
11460	11500	9	12	0.034	0.025
12480	12520	9	12	0.034	0.025
13500	13540	9	12	0.034	0.025
14520	14560	9	12	0.034	0.025
15540	15580	9	11	0.031	0.025
16560	16600	10	11	0.031	0.028
18480	18520	11	11	0.031	0.031
20400	20440	11	11	0.031	0.031
22320	22360	11	11	0.031	0.031
24240	24280	12	10	0.028	0.034
26160	26200	12	10	0.028	0.034
28080	28120	13	10	0.028	0.037
31800	31840	13	10	0.028	0.037
35520	35560	14	10	0.028	0.039
39240	39280	15	10	0.028	0.042
42960	43000	15	10	0.028	0.042
46680	46720	16	10	0.028	0.045
50400	50440	17	10	0.028	0.048

Table 4.3 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 30°C

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	41	0.142	0.000
60	102	1	44	0.142	0.003
480	522	2	38	0.123	0.006
900	942	3	32	0.103	0.010
1320	1362	4	30	0.097	0.013
1740	1782	4	27	0.087	0.013
2160	2202	5	25	0.081	0.016
2580	2622	5	24	0.078	0.016
3000	3042	6	22	0.071	0.019
3420	3462	6	21	0.068	0.019
3840	3882	6	20	0.065	0.019
4260	4302	7	19	0.061	0.023
4980	5022	7	18	0.058	0.023
5700	5742	8	17	0.055	0.026
6420	6462	8	16	0.052	0.026
7140	7182	8	15	0.048	0.026
7860	7902	9	14	0.045	0.029
8580	8622	9	14	0.045	0.029
9300	9342	9	13	0.042	0.029
10020	10062	10	13	0.042	0.032
10740	10782	10	13	0.042	0.032
11460	11502	10	12	0.039	0.032
12480	12522	11	12	0.039	0.036
13500	13542	11	12	0.039	0.036
14520	14562	11	11	0.036	0.036
15540	15582	12	11	0.036	0.039
16560	16602	12	11	0.036	0.039
18480	18522	13	11	0.036	0.042
20400	20442	14	11	0.036	0.045
22320	22362	14	10	0.032	0.045
24240	24282	15	10	0.032	0.048
26160	26202	16	10	0.032	0.052
28080	28122	16	10	0.032	0.052
31800	31842	18	10	0.032	0.058
35520	35562	19	10	0.032	0.061
39240	39282	21	10	0.032	0.068
42960	43002	22	10	0.032	0.071

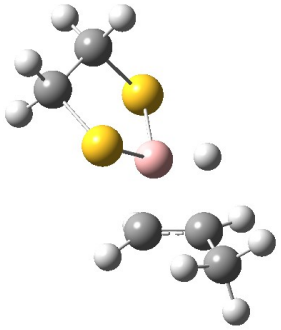
Table 4.4 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 35°C

Time (sec)	Corrected time (sec)	Product (% integral)	Reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	37	0.123	0.000
60	100	0	44	0.123	0.000
480	520	2	36	0.101	0.006
900	940	3	31	0.087	0.008
1320	1360	4	28	0.078	0.011
1740	1780	5	25	0.070	0.014
2160	2200	5	23	0.064	0.014
2580	2620	6	22	0.061	0.017
3000	3040	6	20	0.056	0.017
3420	3460	7	19	0.053	0.020
3840	3880	7	18	0.050	0.020
4260	4300	8	17	0.048	0.022
4980	5020	8	16	0.045	0.022
5700	5740	9	15	0.042	0.025
6420	6460	9	14	0.039	0.025
7140	7180	10	13	0.036	0.028
7860	7900	10	13	0.036	0.028
8580	8620	11	13	0.036	0.031
9300	9340	11	12	0.034	0.031
10020	10060	12	12	0.034	0.034
10740	10780	13	12	0.034	0.036
11460	11500	13	12	0.034	0.036
12480	12520	14	11	0.031	0.039
13500	13540	14	11	0.031	0.039
14520	14560	15	11	0.031	0.042
15540	15580	16	11	0.031	0.045
16560	16600	16	11	0.031	0.045
18480	18520	19	11	0.031	0.053
20400	20440	20	11	0.031	0.056

APPENDIX B

5. Cartesian coordinates of geometry optimized TS and products of hydroboration

Co-ordinates for the transition state structure TS 1 (1,3,2-dithiaborolane + propene)

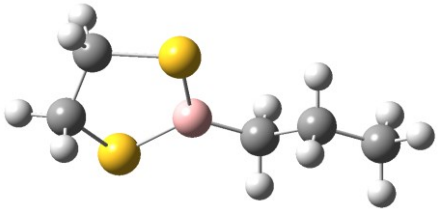


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1018.3876905 a.u.)

0,1
C,-0.6738328189,-2.0673878651,0.7950439506
H,-0.5929467711,-2.1470192095,1.8781589557
C,0.5123734895,-1.8937890624,0.0564220938
H,1.4682126073,-1.9863190097,0.5629208766
H,0.5075030897,-2.1331519031,-1.0031061239
C,-1.9639710123,-2.5603217908,0.1958554749
H,-1.960451611,-3.6567948355,0.2659616925
H,-2.8400243272,-2.1862110713,0.7337921997
H,-2.0455472553,-2.2885067475,-0.8601526679
B,-0.1433906354,-0.298061347,0.3073097611
H,-1.1648164037,-0.4050421386,0.9963016296
S,-0.7128013118,0.569391613,-1.3078457779
S,1.1221460792,0.7900792896,1.2646978759
C,0.9157445286,2.2461307126,0.1499388732
H,0.0711678985,2.8547881643,0.4874900271
H,1.8324971457,2.8423960944,0.2247078601
C,0.6900538332,1.7669180674,-1.2833061714
H,0.414297547,2.6012241748,-1.9380171961
H,1.59533686,1.2941084041,-1.6779649525

Co-ordinates for the product compound 9 (2-propyl-1,3,2-dithiaborolane)

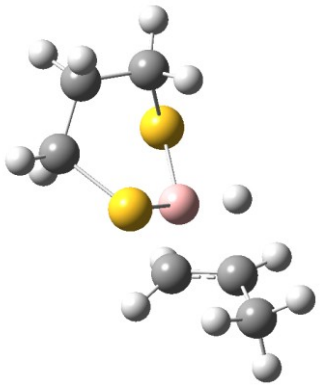


B3LYP/6-31+G(D) OPT FREQ

(HF=-1018.4748188 a.u.)

0,1
B,0.0375364961,-0.0972358947,-0.2760314339
S,0.0692088851,-0.1101706408,1.541164132
S,1.686360356,-0.0869889052,-1.0394096334
C,2.6266678221,0.1980411763,0.5287798851
H,3.626929164,-0.2313944175,0.4154077414
H,2.7238938101,1.2794795342,0.6688272545
C,1.8837295481,-0.4403803624,1.6969173085
H,2.2266905094,-0.0336905442,2.6534220001
H,2.0268480442,-1.5257510596,1.7069413951
C,-1.2915330944,-0.134620414,-1.125220963
H,-1.1287883622,0.3475016347,-2.1003324118
H,-1.4855806014,-1.195947905,-1.359965796
C,-2.5499097121,0.4611303839,-0.4610109365
H,-2.7320241028,-0.0422595665,0.4983631127
H,-2.3703231493,1.5181332544,-0.2214100529
C,-3.8010577275,0.3457961824,-1.3398127312
H,-4.0304354877,-0.7037095312,-1.5659419324
H,-4.6784059245,0.7808011489,-0.8455184196
H,-3.6629752556,0.8677678641,-2.2956230756

Co-ordinates for the transition state structure TS 2 (1,3,2-dithiaborinane + propene)

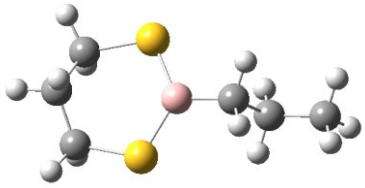


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1057.7008416 a.u.)

0,1
C,-2.4757143445,0.5942531895,-0.0279990699
H,-2.6393721779,1.5782638471,-0.4646889786
C,-1.738252145,0.5226469323,1.1666725311
H,-1.500272037,1.4417461126,1.6951771014
H,-1.8174206299,-0.3714915671,1.7783371102
C,-3.3655086285,-0.5112472715,-0.526413242
H,-4.3606525477,-0.3576912264,-0.0861691325
H,-3.468786238,-0.4991100135,-1.6154952982
H,-3.0017368166,-1.4918866481,-0.207548427
B,-0.5788523893,0.2512788548,-0.1204457265
H,-1.1647110162,0.3695738,-1.2026516454
S,0.0932254398,-1.5447758239,-0.1509149614
S,0.7230587921,1.6516616199,-0.0005039289
C,2.095849834,0.7548093784,-0.8495615177
H,1.7201996956,0.3824687556,-1.806565405
H,2.8675927686,1.5006574244,-1.0639085971
C,1.6516233963,-1.2221315128,0.7847495926
H,1.3964858,-0.7165696842,1.7201918826
H,2.0665430802,-2.2019301198,1.0405506541
C,2.6810074475,-0.3964410069,-0.0104020645
H,3.4091813986,0.0072386866,0.7071606719
H,3.2326295991,-1.0591746309,-0.6917364378

Co-ordinates for the product compound 10 (2-propyl-1,3,2-dithiaborinane)



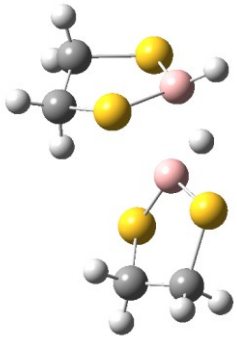
B3LYP/6-31+G(D) OPT FREQ

(HF=-1057.7870344 a.u)

0,1
C,0.0001887045,2.7214808059,-0.0218634455
C,-1.282528645,2.2150115036,0.6363163882
C,1.2827805588,2.214823051,0.6364158098
H,-1.2825583398,2.4470515252,1.7070420159
H,-2.1532894043,2.7065795304,0.1925428852
H,0.0002121484,2.4733847019,-1.0903381876
H,0.0002662731,3.8190487097,0.0520754502
H,1.2827580266,2.4468562691,1.7071428964
H,2.1536474779,2.7062683497,0.1927148421
B,-0.0000520724,-0.4090619285,0.3389536674
S,-1.6102555048,0.4049898852,0.4418446339
S,1.6102633007,0.4047559201,0.4419580362
C,-0.0001616617,-1.9746606518,0.0760796762
H,-0.8796414234,-2.4363684182,0.5494846369
H,0.8791559039,-2.4365175259,0.5496411038
C,-0.0000588429,-2.3406779948,-1.4293351436
H,0.8788930869,-1.8926963248,-1.9122210186
H,-0.8788330452,-1.8925214926,-1.9123833751
C,-0.0001882792,-3.8547063116,-1.6745401849
H,-0.0001079925,-4.0841758004,-2.7475159308
H,0.8855119196,-4.3276674813,-1.2310319739
H,-0.8860700112,-4.3274876993,-1.2312030038

6. Cartesian coordinates of geometry optimized TS and products of disproportionation

Co-ordinates for the transition state structure TS 3 (2× (1,3,2-dithiaborolane))

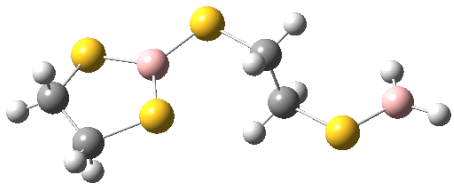


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1801.0048887 a.u.)

0,1
C,3.1442986099,0.6483659513,0.4109210023
C,1.8500308614,0.9473406207,1.1629885242
H,3.8600512658,0.123545685,1.0504167288
H,3.6055718803,1.5806025603,0.0698990753
H,2.0490312042,1.2649778352,2.1916710955
H,1.2568390905,1.7206856282,0.6645391335
B,1.2998853656,-1.2276326014,-0.4311501613
H,1.0453584069,-2.3589947691,-0.6904168044
C,-3.3802740882,-0.0479470682,-0.1210172693
C,-2.7372654316,1.2660485177,0.3117671938
H,-4.1770830897,-0.3402814825,0.5707539093
H,-3.8012843892,0.039643966,-1.1271315824
H,-2.5192216201,1.2623966796,1.3846509851
H,-3.3876123166,2.1180977976,0.0879633385
B,-0.6740030767,-0.2684810459,-0.4157539346
H,0.1404458246,-0.6331065996,-1.2777670546
S,-2.1156843312,-1.4045218989,-0.1380953821
S,-1.1598893071,1.5021797474,-0.6252113313
S,2.8198573234,-0.4110139802,-1.0758396042
S,0.8018258518,-0.5728843179,1.259270377

Co-ordinates for the product compound 4C (name)

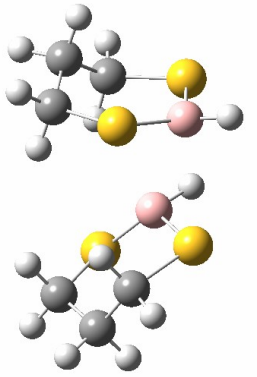


B3LYP/6-31+G(D) OPT FREQ

(HF=-1801.0287237)

0,1
C,-2.8228006532,-1.7266859125,-0.186781876
C,-3.7751692403,-0.5539240796,0.0128543804
H,-3.1829941963,-2.6234771663,0.3269751268
H,-2.6950140135,-1.9554527036,-1.2492841515
H,-4.0916732763,-0.4774666182,1.0577043871
H,-4.6638560327,-0.6557057387,-0.617896918
B,-1.2822824082,0.4768877995,0.1260031032
S,-1.1628513505,-1.2991123892,0.512786032
S,-2.9211262226,1.0202752256,-0.4534465518
S,0.0498152685,1.6890665982,0.3015065357
C,1.5631129917,0.6801374471,0.6535061208
H,2.2572236064,1.3745000048,1.1355538549
H,1.3203900983,-0.1028689853,1.3769328486
C,2.1832572598,0.09858176,-0.6146605786
H,2.4545627606,0.8896300408,-1.3174107454
H,1.4854946635,-0.5821068067,-1.108864718
S,3.6963767161,-0.9030604393,-0.2358449508
B,5.0221506748,0.2740770489,-0.2064370301
H,4.823887667,1.4299995134,-0.4288499079
H,6.1068046585,-0.1552349948,0.0377845361

Co-ordinates for the transition state structure TS 4 (2× (1,3,2-dithiaborinane))

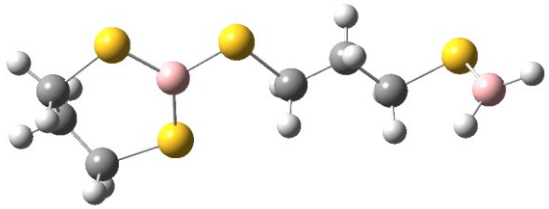


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1879.6344576 a.u.)

0,1
B,-1.5612408072,0.1417394908,1.1370290244
H,-1.5479979701,-0.0593844959,2.309191305
B,0.5733155428,0.3091268676,0.652596196
H,-0.2880830576,1.0657762916,1.1343073781
S,1.6502512697,-0.3299504744,2.0222071613
S,1.2740625426,1.1365513011,-0.8534826117
S,-2.9193590996,1.2098158367,0.546661251
S,-0.8378239929,-1.2884977418,0.1469498383
C,-1.3801313513,-1.019138252,-1.6027011652
H,-1.3428556934,-2.019287137,-2.0447766777
H,-0.6116181731,-0.3986562711,-2.0773756557
C,-2.8876851959,1.0380460858,-1.2918991452
H,-3.8375098694,1.469815742,-1.6206912459
H,-2.0823346286,1.6588960853,-1.698992505
C,-2.7675012798,-0.402609333,-1.7903493244
H,-3.5370797601,-1.0276473901,-1.3213614969
H,-2.9679055689,-0.4071011825,-2.8718876753
C,2.9957605011,-1.1361643199,1.0481952979
H,3.7441163567,-1.4237651416,1.7928235912
H,2.60508376,-2.0598098271,0.6028251617
C,2.7298377168,0.0525815394,-1.2207276735
H,3.2886157306,0.5955280549,-1.9890339849
H,2.3703862306,-0.8798888888,-1.673268828
C,3.6364875799,-0.2519830134,-0.0255469248
H,3.992110064,0.6830985706,0.4229930915
H,4.5199995605,-0.7830051894,-0.4120751714

Co-ordinates for the product compound 6C (name)



B3LYP/6-31+G(D) OPT FREQ

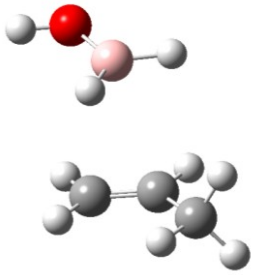
(HF=-1879.6540132)

0,1
C,4.333504948,-0.4026665239,-1.4994377847
C,3.8496028622,0.8760492469,0.6619849446
C,4.4207235661,0.9263901883,-0.7529465391
H,4.7883241681,-1.2054643118,-0.9088757955
H,4.8757717069,-0.3410123399,-2.4473204721
H,4.04459202,1.8172138643,1.1842036683
H,4.3205763473,0.0724069185,1.2381383159
H,3.93564045,1.7210630426,-1.3324489073
H,5.4848018358,1.1922516876,-0.6690860135
B,1.5347399521,-0.3278962533,-0.6656518986
S,2.0154162987,0.6606917786,0.7776590566
S,2.6289850411,-0.9323797098,-1.9844476018
C,-1.112859128,-0.0052473552,0.5101953305
H,-0.6981899053,-0.4042375816,1.4414809356
H,-0.94784115,1.0768178614,0.4977269108
C,-2.6079578867,-0.326809347,0.4023893373
H,-2.7541833187,-1.4138024602,0.3822454851
H,-3.0070335339,0.0661594569,-0.5404371316
C,-3.3845379628,0.2765600922,1.5779718429
H,-3.3041605328,1.3674583717,1.5903888746
H,-2.9995619868,-0.1021697609,2.5308318965
B,-5.9690301096,1.1626389801,0.6796823821
H,-7.1476937723,1.0701427395,0.5276358618
H,-5.3411110713,2.0974106035,0.2832513707
S,-0.2177033601,-0.7655017983,-0.9181990834
S,-5.1810316586,-0.1661608663,1.5469357408

APPENDIX C

7. Cartesian coordinates of geometry optimized structures of oxygen-based boranes

Co-ordinates for the precomplex structure O1-precomplex

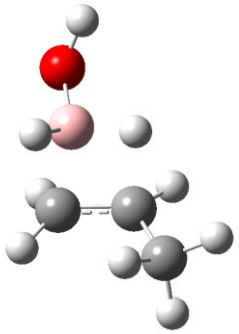


B3LYP/6-31+G(D) OPT FREQ

(HF=-219.8288764 a.u.)

0,1
C,-0.8890011496,1.4132383894,0.311501819
H,-0.2373208405,2.179001257,-0.1021499218
H,-1.1588219958,1.5147250168,1.3617289273
B,1.8115953997,-0.9217183228,0.3097458978
H,1.23164654,-1.7310803115,-0.3505839687
H,1.6493585454,-0.8103119309,1.4937014694
C,-1.344265221,0.4015417966,-0.436007807
H,-1.0444709508,0.3478775081,-1.4839025239
C,-2.2530831897,-0.6934295963,0.0463573218
H,-3.1853474921,-0.7151235653,-0.5343372304
H,-1.7814316513,-1.67787364,-0.0758995644
H,-2.5115274172,-0.5664625076,1.1036126508
O,2.7166536285,-0.1440708497,-0.3409637327
H,3.164806598,0.4923030467,0.2357025317

Co-ordinates for the transition state structure O1-TS

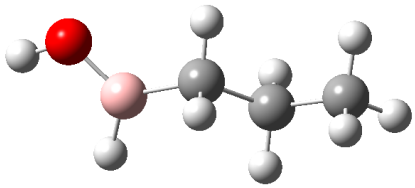


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-219.8033789 a.u.)

0,1
C,-0.726561223,0.051139508,-0.4617694059
H,-0.4621575885,-0.2445825369,-1.4746938823
C,-0.0433094829,1.144078801,0.1020732603
H,0.6283971632,1.7312734668,-0.5172899733
H,-0.4797239518,1.6532644453,0.956535902
C,-2.0588697028,-0.4280121691,0.0574729235
H,-2.8494671973,0.1882145307,-0.3917060433
H,-2.251955006,-1.4746819498,-0.1977428089
H,-2.1226386078,-0.311579725,1.1442571383
B,0.870649584,-0.2766823785,0.5190904119
H,0.1490349729,-1.2725799999,0.2605050997
H,0.8499756834,-0.2830349422,1.7280449713
O,2.0791972129,-0.2609811672,-0.2552501057
H,2.5241513608,-1.1182688982,-0.2480222852

Co-ordinates for the product structure O1-prod



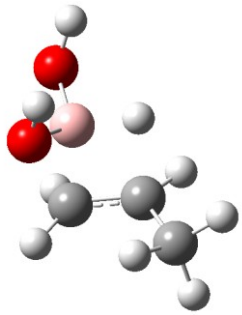
B3LYP/6-31+G(D) OPT FREQ

(HF=-219.8751499 a.u.)

0,1
C,0.6526804733,2.4218588625,0.0836273098

H,0.5657264339,2.5223222345,1.1731838047
H,1.7211628952,2.3428335967,-0.1562633947
H,0.2754336279,3.3475476872,-0.3688199218
C,-0.11653019,1.1950605906,-0.4212533694
H,-1.185963059,1.3267056899,-0.2015860716
H,-0.0378094607,1.1401997592,-1.5162376894
C,0.3758591847,-0.1312316779,0.1949891479
H,1.4540697774,-0.2360544494,-0.0273234927
H,0.3017686047,-0.0961965856,1.2918473581
B,-0.3255408325,-1.4207459538,-0.3652438512
H,-0.5604131842,-1.5654951957,-1.539761453
O,-0.6639410859,-2.4253760492,0.4961033749
H,-1.0667995933,-3.1892512256,0.0581745876

Co-ordinates for the transition state structure O2-TS

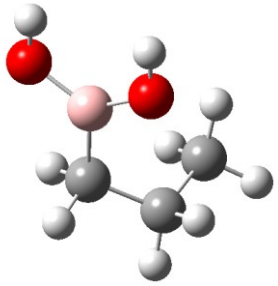


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-295.0621141 a.u.)

0,1
C,0.8302994965,-0.9087571535,-0.1057561386
H,0.5420553104,-1.8338586139,-0.6018998153
C,0.1887010754,-0.5802796554,1.0994115591
H,-0.4844889395,-1.2990309785,1.5559728344
H,0.64863998,0.1564312701,1.752330409
C,2.1391532093,-0.3017388263,-0.52996455
H,2.9449648288,-0.8867451511,-0.0654205662
H,2.2763846976,-0.3289842376,-1.6152178924
H,2.2202552151,0.7307214863,-0.179042545
B,-0.71983105,0.2730762711,-0.1335992887
H,-0.1521473771,-0.0373633162,-1.2383057854
O,-2.0301614404,-0.3223048012,-0.1272092334
H,-2.5164825268,-0.1465388779,-0.9436964456
O,-0.4852888679,1.6731252138,0.1117804455
H,-0.7053461594,2.218077574,-0.6554386698

Co-ordinates for the product structure O2-prod

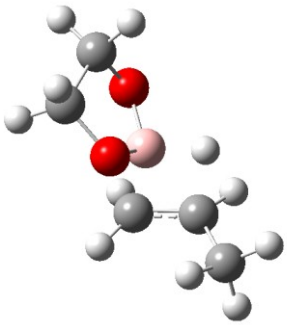


B3LYP/6-31+G(D) OPT FREQ

(HF=-295.1618757 a.u.)

0,1
C,0.8118219055,-0.4620504958,0.4895080115
H,0.7025661216,-0.5230867195,1.5818426471
H,1.9000234436,-0.5010215316,0.3114775098
C,0.1477583641,-1.6797129069,-0.1824821329
H,0.257495979,-1.6008627032,-1.2717020962
H,0.6778149812,-2.5945102896,0.1178618287
C,-1.3385735103,-1.8289315904,0.1666412331
H,-1.7722790666,-2.7181878306,-0.3075217334
H,-1.4820838815,-1.9263133043,1.2510357799
H,-1.9163204945,-0.9594981595,-0.1713362175
B,0.3324687799,0.9606765703,-0.0009667684
O,-0.143620931,1.0987816951,-1.2874111877
H,-0.3992275452,1.9925723908,-1.5585502979
O,0.4493860048,2.021308846,0.8725920311
H,0.1975054168,2.8909709263,0.5282770053

Co-ordinates for the transition state structure O3-TS

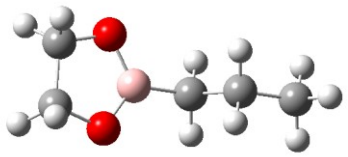


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-372.4603604 a.u.)

0,1
C,0.8355586011,-0.4125951812,-1.7043752477
H,1.9005590485,-0.1925074412,-1.7604740272
C,-0.0497724857,0.6721395628,-1.5859269724
H,0.3392358128,1.68432393,-1.630656754
H,-1.0974854541,0.5259189133,-1.833134286
C,0.4176269142,-1.7657899164,-2.2186873611
H,0.467603274,-1.7287850943,-3.3152681774
H,1.0788854352,-2.5625245419,-1.865728637
H,-0.6106078025,-1.9980508772,-1.9289300074
B,0.2226893535,0.0356123041,0.0494773853
H,1.0678277069,-0.9080028156,-0.1101597112
O,0.7638680721,1.0692228045,0.8954151201
O,-0.9648925761,-0.5393514841,0.634983778
C,-1.2545990541,0.2780175386,1.7693973685
H,-1.9758164061,1.0649030536,1.4955536924
H,-1.6895712751,-0.3414498026,2.5618955943
C,0.1037052917,0.8909438203,2.1486121235
H,0.6793932168,0.2030499275,2.7888756979
H,0.0196101043,1.8597977198,2.6533290397

Co-ordinates for the product structure O3-prod



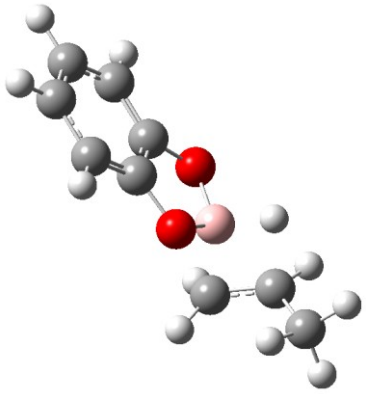
B3LYP/6-31+G(D) OPT FREQ

(HF=-372.5701735 a.u.)

0,1
C,0.8914004568,-3.4254060416,0.6286568394
H,0.906723437,-3.4663219935,1.7254529954
H,1.9317166236,-3.4649584371,0.2807465045
H,0.3827817912,-4.3278989648,0.2669499836
C,0.1932147207,-2.1526552234,0.1345563296
H,0.1653688665,-2.1576212549,-0.9639302268
H,-0.8529824351,-2.1593437421,0.4705414986
C,0.8828418744,-0.8559639496,0.6257307724
H,1.9274322482,-0.858481109,0.2840930298
H,0.9046395074,-0.8603367061,1.7245574677
C,-0.4163029483,2.1932239956,-1.2446840555

C,-1.3171806848,2.1896546043,0.0192686632
H,-0.9843135571,2.0570018917,-2.1708594479
H,0.1870336183,3.1025968913,-1.3338023894
H,-2.3776614609,2.0517908813,-0.2160249955
H,-1.2067709129,3.0969504136,0.6222164564
B,0.1627876693,0.4447239236,0.116150066
O,0.465265599,1.0696214804,-1.0739987575
O,-0.8654839223,1.0641137945,0.7925159448

Co-ordinates for the transition state structure O4-TS



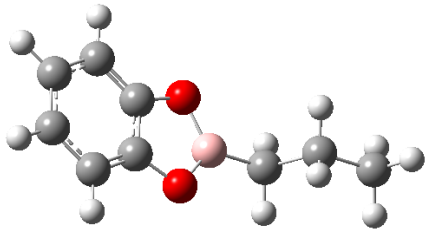
B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-524.9053957 a.u.)

0,1
C,-0.9569788054,-2.5378692477,1.5056072551
H,-0.8522326741,-2.4288043104,2.5841870247
C,0.2169609905,-2.5473026317,0.728330619
H,1.1819230871,-2.5507282657,1.2261878206
H,0.1758692322,-2.9569104848,-0.2774194797
C,-2.2705669593,-3.0958788319,1.0267339242
H,-2.2643347405,-4.170976348,1.2516597194
H,-3.1236221217,-2.6390470427,1.5362273698
H,-2.3859226486,-2.9732216582,-0.0534973976
B,-0.388815413,-0.9051462699,0.6970934147
H,-1.4267219246,-0.9113320199,1.42761068
O,0.5737711386,0.0397644381,1.2530858487
O,-0.7639740785,-0.4917696635,-0.6520442567
C,-0.0677290839,0.6739493729,-0.8504451848
C,0.7189450003,0.9870354542,0.2711072786
C,1.5152322422,2.1199359431,0.3013469598
H,2.1193557672,2.3515835274,1.1736266602
C,1.5085498069,2.9506221155,-0.8362799246

H,2.1225979833,3.8473155804,-0.8413469471
C,0.7271450355,2.6392670799,-1.9510888195
H,0.7373107003,3.2955013149,-2.8173369733
C,-0.0794308914,1.4845331834,-1.9734758922
H,-0.6912860895,1.2326382339,-2.8347155794

Co-ordinates for the product structure O4-prod



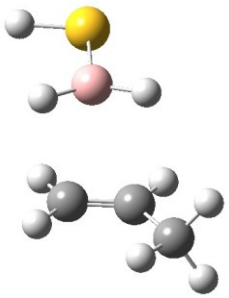
B3LYP/6-31+G(D) OPT FREQ

(HF=-525.0110538 a.u.)

0,1
O,0.1307110929,-1.1523424021,-0.3190670301
O,0.1366276719,1.1399293866,-0.3337617525
C,-1.1519985242,0.6963162385,-0.1116327325
C,-1.1556053254,-0.699260609,-0.1026249623
C,-2.3148003698,-1.430240978,0.0966479781
H,-2.3061257074,-2.515631649,0.1011375603
C,-3.4947269063,-0.6937249886,0.2911815945
H,-4.4291352286,-1.2241826139,0.4517347147
C,-3.4911369756,0.7078883254,0.2819931061
H,-4.4228249068,1.2451754103,0.4354896138
C,-2.3074558715,1.4357532854,0.0779461923
H,-2.2932453846,2.5210508646,0.0682361647
B,0.9194988523,-0.0091046407,-0.4582146387
C,2.4672786542,-0.0143043921,-0.6821594706
H,2.7535198192,0.8569486051,-1.2880247981
H,2.7524668935,-0.9078254296,-1.2550355859
C,3.2727207779,0.0105113973,0.642107864
H,2.994293657,0.901016649,1.2221042281
H,2.9939075108,-0.8572797103,1.2554467692
C,4.7890046287,0.0057451748,0.4157737252
H,5.3335231523,0.0227199593,1.3678918298
H,5.1034687122,-0.890400248,-0.1343263615
H,5.1042665744,0.8811347675,-0.1663504502

8. Cartesian coordinates of geometry optimized structures of sulphur-based boranes

Co-ordinates for the precomplex structure S1-precomplex

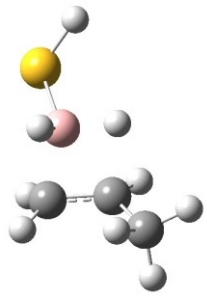


B3LYP/6-31+G(D) OPT FREQ

(HF=-542.7735826 a.u.)

0,1
C,0.7598792728,-1.9735379405,-0.1950774636
H,0.6292271965,-2.0788472864,0.8789871842
H,1.7846114415,-1.9418345234,-0.5625262004
B,-0.0085347143,1.6713542752,0.1002261863
H,-1.0147709291,1.5089899727,-0.5153058644
H,1.0653581907,1.6871077386,-0.4115578035
C,-0.2857549217,-1.8912961004,-1.0250431837
H,-1.2925715665,-1.9299282934,-0.6053659463
C,-0.1998138459,-1.7486087724,-2.5184738002
H,-0.7061393763,-2.5823094784,-3.0239047229
H,-0.6948361026,-0.827662366,-2.8555663655
H,0.8405674447,-1.7222529431,-2.8613809685
S,-0.2064736055,1.9446476175,1.854835445
H,1.0889419291,2.0962608034,2.2096893199

Co-ordinates for the transition state structure S1-TS



B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-542.7601349 a.u.)

0,1
C,-1.2137617441,0.0417007709,-0.4987376604
H,-0.886689643,-0.2814330082,-1.4846978714
C,-0.6013310556,1.1759668508,0.0540053119
H,0.0504535001,1.7842004072,-0.5664653223
H,-1.0927896071,1.6955442595,0.8715536663
C,-2.5265012975,-0.5042429901,-0.0034644554
H,-3.3381202049,0.0268143037,-0.5193376027
H,-2.634130284,-1.5734842755,-0.2094713968
H,-2.6450278234,-0.3348941727,1.0713838109
B,0.3024729174,-0.2073149666,0.6398051567
H,-0.2140230678,-1.2601829892,0.2746672857
H,0.1168507787,-0.1829416767,1.8262686925
S,2.0517013898,-0.1059822779,-0.1063603783
H,2.3534541108,-1.4218793589,-0.0719801686

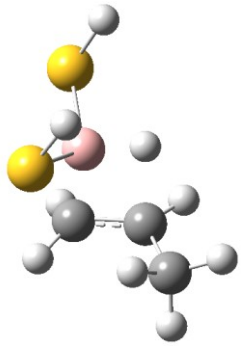
Co-ordinates for the product structure S1-prod

B3LYP/6-31+G(D) OPT FREQ

(HF=-542.8180617 a.u.)

0,1
C,-2.0092873697,2.2019620189,-0.6131438625
H,-1.7781121855,2.7354320651,0.3177371055
H,-1.5210423086,2.7421594369,-1.4346267889
H,-3.0933046946,2.2603018658,-0.7712256145
C,-1.5316448953,0.7461444559,-0.5499206888
H,-2.068512653,0.2249062201,0.2550602006
H,-1.8026474693,0.2296573906,-1.4809361607
C,-0.0081923682,0.6166867273,-0.3188260874
H,0.5088176182,1.1418505718,-1.1429419795
H,0.2758843914,1.1521592823,0.5988518176
B,0.5163079641,-0.8638553644,-0.3461264212
H,0.2008455905,-1.6240314312,-1.2135568311
S,1.634859022,-1.4511640986,0.9371924699
H,1.8335353372,-2.7132922157,0.4985346706

Co-ordinates for the transition state structure S2-TS

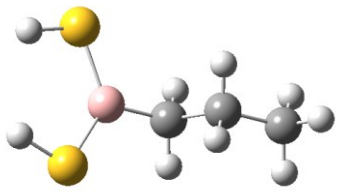


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-940.9726021 a.u.)

0,1
C,1.3861920438,-1.1224123206,-0.030691182
H,1.0887039231,-2.0339975403,-0.5460979949
C,0.7028974673,-0.7725647377,1.1085674637
H,0.0189145606,-1.4750379633,1.574038859
H,1.065401353,0.0376812572,1.7337853374
C,2.6110257421,-0.4201527189,-0.5295324957
H,3.4934637139,-0.9603102149,-0.1577402202
H,2.6615216168,-0.4151383457,-1.622663408
H,2.6599123451,0.6076281534,-0.1573710381
B,-0.345290928,0.0558099078,-0.3037105469
H,0.0711409189,-0.1332127463,-1.4151012735
S,-1.9832160186,-0.8946080725,-0.0407499125
H,-2.5003392149,-0.6349147723,-1.2608888283
S,-0.2139834024,1.9120752853,0.1157601472
H,0.1222346409,2.3395558909,-1.1196351706

Co-ordinates for the product structure S2-prod

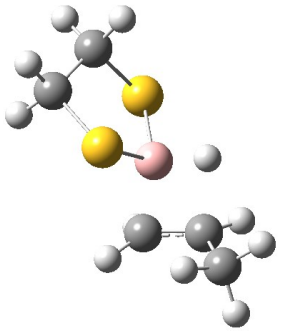


B3LYP/6-31+G(D) OPT FREQ

(HF=-941.0452735 a.u.)

0,1
C,0.7793177514,3.212606167,0.5466891244
H,0.7975294974,3.2470026744,1.6435022405
H,1.818706855,3.245607365,0.195838163
H,0.2768926322,4.1206885161,0.19140571
C,0.0664516765,1.9510564097,0.0450505087
H,-0.9781145626,1.9617591039,0.3835302223
H,0.0348409575,1.9604003026,-1.0525425294
C,0.7520299018,0.6462279052,0.5298539985
H,1.7984383013,0.655333305,0.1917356357
H,0.7846238313,0.6566816105,1.629036134
B,0.0200993686,-0.6589223596,0.0147857581
S,-1.3111480276,-1.333256418,1.0534106817
H,-1.7295628598,-2.3589577347,0.2800047958
S,0.5504401839,-1.335055067,-1.5874909976
H,-0.3193219746,-2.3602624771,-1.7207158973

Co-ordinates for the transition state structure S3-TS



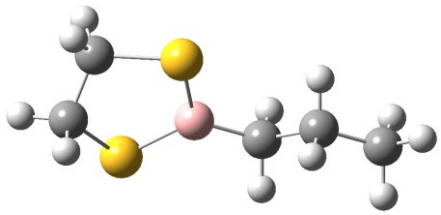
B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1018.3876905 a.u.)

0,1
C,-0.6738328189,-2.0673878651,0.7950439506
H,-0.5929467711,-2.1470192095,1.8781589557
C,0.5123734895,-1.8937890624,0.0564220938
H,1.4682126073,-1.9863190097,0.5629208766
H,0.5075030897,-2.1331519031,-1.0031061239
C,-1.9639710123,-2.5603217908,0.1958554749
H,-1.960451611,-3.6567948355,0.2659616925
H,-2.8400243272,-2.1862110713,0.7337921997
H,-2.0455472553,-2.2885067475,-0.8601526679
B,-0.1433906354,-0.298061347,0.3073097611

H,-1.1648164037,-0.4050421386,0.9963016296
S,-0.7128013118,0.569391613,-1.3078457779
S,1.1221460792,0.7900792896,1.2646978759
C,0.9157445286,2.2461307126,0.1499388732
H,0.0711678985,2.8547881643,0.4874900271
H,1.8324971457,2.8423960944,0.2247078601
C,0.6900538332,1.7669180674,-1.2833061714
H,0.414297547,2.6012241748,-1.9380171961
H,1.59533686,1.2941084041,-1.6779649525

Co-ordinates for the product structure S3-prod

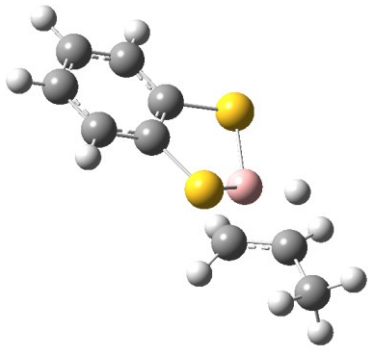


B3LYP/6-31+G(D) OPT FREQ

(HF=-1018.4748188 a.u.)

0,1
B,0.0375364961,-0.0972358947,-0.2760314339
S,0.0692088851,-0.1101706408,1.541164132
S,1.686360356,-0.0869889052,-1.0394096334
C,2.6266678221,0.1980411763,0.5287798851
H,3.626929164,-0.2313944175,0.4154077414
H,2.7238938101,1.2794795342,0.6688272545
C,1.8837295481,-0.4403803624,1.6969173085
H,2.2266905094,-0.0336905442,2.6534220001
H,2.0268480442,-1.5257510596,1.7069413951
C,-1.2915330944,-0.134620414,-1.125220963
H,-1.1287883622,0.3475016347,-2.1003324118
H,-1.4855806014,-1.195947905,-1.359965796
C,-2.5499097121,0.4611303839,-0.4610109365
H,-2.7320241028,-0.0422595665,0.4983631127
H,-2.3703231493,1.5181332544,-0.2214100529
C,-3.8010577275,0.3457961824,-1.3398127312
H,-4.0304354877,-0.7037095312,-1.5659419324
H,-4.6784059245,0.7808011489,-0.8455184196
H,-3.6629752556,0.8677678641,-2.2956230756

Co-ordinates for the transition state structure S4-TS

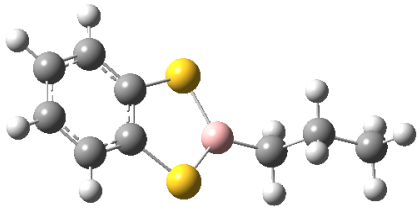


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-1170.8241594 a.u.)

0,1
C,-3.182774132,0.429723038,0.3096760492
H,-3.5371980567,1.4226864528,0.0352626174
C,-2.1599807454,0.344030763,1.3001046237
H,-1.887628612,1.247633849,1.8371733635
H,-2.0771963581,-0.5833343329,1.8609491785
C,-4.1281758441,-0.7060715056,0.0066865564
H,-4.9603702556,-0.6361780943,0.7194469312
H,-4.5375784527,-0.649354861,-1.0064711088
H,-3.6437691314,-1.6762537852,0.1474283401
B,-1.3872898486,0.252926201,-0.2066962615
H,-2.3121649198,0.3474078747,-1.0480063582
S,-0.504249502,-1.4063446947,-0.5428372378
S,-0.1836179057,1.6908347101,-0.5608315606
C,1.0895001059,-0.7135734523,-0.1310659084
C,1.235541722,0.6913421456,-0.1411702223
C,2.1953588318,-1.5238155588,0.151286289
H,2.0789588277,-2.6043064382,0.166481391
C,3.4418227906,-0.9474767542,0.4097078018
H,4.2949074987,-1.5859131457,0.6241826567
C,3.586503274,0.4431145043,0.3997560889
H,4.5531259414,0.8951345089,0.6063527413
C,2.4851308454,1.2601358463,0.1313545321
H,2.593680195,2.3415525622,0.1313674674

Co-ordinates for the product structure S4-prod



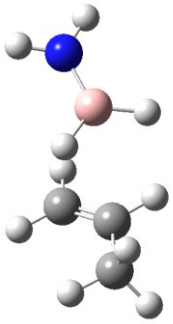
B3LYP/6-31+G(D) OPT FREQ

(HF=-1170.9147577 a.u.)

0,1
S,0.1702904423,1.5096870104,-0.2883225492
S,0.1726401467,-1.5064278166,-0.2944269769
C,-1.391579958,0.7040928501,-0.0433971355
C,-1.3904774327,-0.7042348677,-0.0462898857
C,-2.5887248178,-1.4068041195,0.1365595723
H,-2.5860159474,-2.4933953474,0.1335085348
C,-3.7781175545,-0.7035660552,0.3219327691
H,-4.7072771209,-1.2486077873,0.4643636998
C,-3.7792060564,0.6981972123,0.3248589816
H,-4.7092054745,1.2411986305,0.4695824792
C,-2.590907484,1.4040413232,0.1423919337
H,-2.5898781709,2.4906395321,0.14386632
B,1.1676442167,0.0027454775,-0.4409163978
C,2.7325690329,0.0043745488,-0.6267934409
H,3.0434536495,-0.8704960175,-1.216371519
H,3.0430396925,0.8865249516,-1.205604501
C,3.5069845139,-0.0036887822,0.716800515
H,3.2119247628,0.8704890109,1.3126967714
H,3.2130915391,-0.8857654551,1.3015127005
C,5.0281553757,-0.0014150227,0.5245388345
H,5.3561281198,0.8882121552,-0.0282827644
H,5.5500953449,-0.007236469,1.4893346913
H,5.3573593824,-0.8834202136,-0.0396448695

9. <u>Cartesian coordinates of geometry optimized structures of nitrogen-based boranes</u>

Co-ordinates for the precomplex structure N1-precomplex

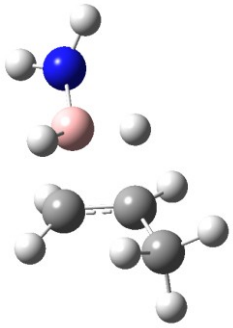


B3LYP/6-31+G(D) OPT FREQ

(HF=-198.8617801 a.u.)

0,1
C,1.2439013766,-1.0640755265,0.9977207843
H,1.0472125308,-0.9206678819,2.0552985462
H,2.2483460754,-0.8312569188,0.6545472962
B,-1.0866655451,1.631267689,-0.4018704497
H,-1.9917634332,0.8485058489,-0.4012352935
H,-0.2759914215,1.6487309782,-1.2806957133
C,0.3054728379,-1.5043091828,0.160284359
H,-0.6906210218,-1.7264235457,0.5395169992
C,0.5060842722,-1.7216599965,-1.3204884442
H,0.2759985596,-2.7584195299,-1.5986773336
H,-0.1635928509,-1.0688521309,-1.894721359
H,1.5378054135,-1.5026630351,-1.6135756869
N,-0.9967565745,2.5732896795,0.6324517026
H,-0.2534654488,3.2660992063,0.6900391054
H,-1.6560555765,2.6158490428,1.4065935752

Co-ordinates for the transition state structure N1-TS

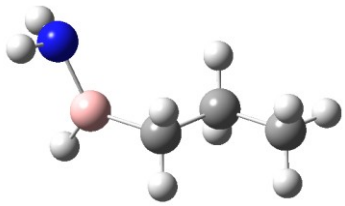


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-199.9228504 a.u.)

0,1
C,-0.7503454625,0.0716577845,-0.4692916553
H,-0.4944207456,-0.1956124001,-1.491781174
C,-0.059106954,1.1483741874,0.1158505101
H,0.5918919738,1.7548920459,-0.5066059979
H,-0.4919657606,1.6428196404,0.9809782895
C,-2.0813117548,-0.4117015224,0.0503925357
H,-2.8737796604,0.2219073709,-0.3695532542
H,-2.2848905867,-1.4492664157,-0.2333365317
H,-2.1298058767,-0.3284512701,1.1411377306
B,0.8323107438,-0.3058157804,0.5213685129
H,0.11611227,-1.2707467716,0.1801884003
H,0.7193302604,-0.3600497332,1.7269612723
N,2.0971894721,-0.3491605459,-0.2728543536
H,2.7835012904,0.3569814491,-0.0229561398
H,2.5667318395,-1.2492538894,-0.2836030279

Co-ordinates for the product structure N1-prod



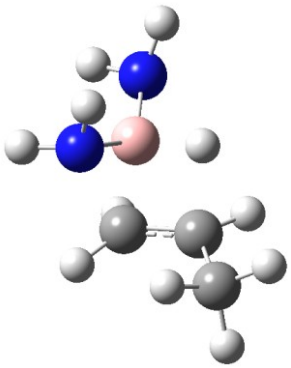
B3LYP/6-31+G(D) OPT FREQ

(HF=-200.0039537 a.u.)

0,1
C,-1.532178971,1.9774401578,-0.2763725821
H,-1.2520888974,2.453978589,0.6722387176
H,-1.0351793065,2.5316740146,-1.083416239
H,-2.6152950554,2.0991784697,-0.4043009845
C,-1.1251218195,0.4986998997,-0.2932552353
H,-1.6699434312,-0.0333621202,0.5002430637
H,-1.4481083864,0.0419417382,-1.2392452066
C,0.3925493564,0.2770475096,-0.1139594017
H,0.9146048139,0.8254715562,-0.91768388
H,0.720968046,0.746329817,0.8280555425
B,0.8348355264,-1.2393625116,-0.1991221688
H,0.5036797325,-1.9303899233,-1.1260607877
N,1.6287456985,-1.8421999814,0.7872775106

H,1.9323278477,-2.806404736,0.7453046516
H,1.9621457202,-1.35533038,1.611056706

Co-ordinates for the transition state structure N2-TS

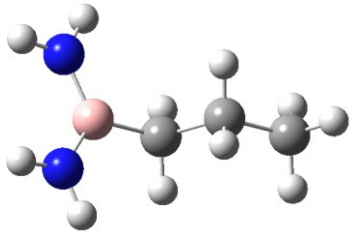


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-255.2999199 a.u.)

0,1
C,-0.4698947372,-0.999418969,0.5680393725
H,-0.4528560036,-1.0243946851,1.6554680206
C,0.7639296677,-1.0104507042,-0.0990416154
H,1.6694223172,-1.1769040328,0.4756230052
H,0.7817373832,-1.2962515955,-1.1473611188
C,-1.7636888751,-1.368403816,-0.1063691842
H,-1.8508603242,-2.4633061093,-0.1115580564
H,-2.6325730012,-0.9572288852,0.4172776197
H,-1.7659793389,-1.0126358829,-1.1407548597
B,0.3077336224,0.7061174272,0.0531099522
H,-0.7999642703,0.6970386377,0.64975114
N,-0.0146554853,1.1644909642,-1.3473863121
H,-0.4809093316,2.0663387413,-1.3936088584
H,0.779287655,1.1956457769,-1.9823116942
N,1.2702413375,1.2869616992,1.0600680041
H,2.2355844535,1.3438123506,0.7433750592
H,1.0072650516,2.2067708398,1.4040067002

Co-ordinates for the product structure N2-prod

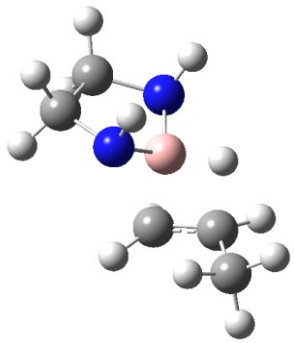


B3LYP/6-31+G(D) OPT FREQ

(HF=-255.4075448 a.u.)

0,1
C,0.6845048647,2.6964149059,0.4746870573
H,0.6966723162,2.7152000166,1.5725260579
H,1.7284289136,2.7075601241,0.1342700223
H,0.2101115139,3.6240497427,0.1295148296
C,-0.0520996687,1.4560051194,-0.0471189209
H,-0.078634794,1.4856857781,-1.1457664389
H,-1.1013328125,1.4935948741,0.2791373185
C,0.5836790643,0.1249098178,0.4167517691
H,1.6362538616,0.1095140895,0.0919462028
H,0.6152018829,0.118819799,1.5178672724
B,-0.1804970671,-1.1681595324,-0.1224064433
N,0.1706724324,-1.7251456084,-1.388216081
H,0.9179773171,-1.3505890351,-1.9547922657
H,-0.287522247,-2.5189157916,-1.8160372725
N,-1.2338223832,-1.7440731928,0.6484283383
H,-1.7884436087,-2.5402884985,0.3629202678
H,-1.5006829134,-1.3832808878,1.5530409886

Co-ordinates for the transition state structure N3-TS

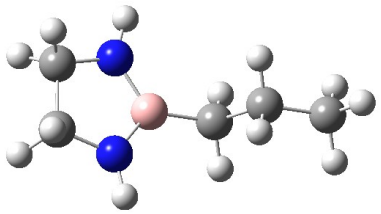


B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-332.6898983 a.u.)

0,1
C,-0.7721601801,-1.513043832,0.8823473827
H,-0.6471808521,-1.600793094,1.9606023389
C,0.4072815536,-1.4594361749,0.0906077983
H,1.3626323664,-1.6131609324,0.5822759251
H,0.3306533457,-1.7678893461,-0.9485865209
C,-2.0910992541,-1.9982027373,0.3287663378
H,-2.0858262984,-3.0953700461,0.3609371556
H,-2.9450630935,-1.6401336685,0.9133369154
H,-2.2105491582,-1.684755669,-0.7120212529
B,-0.1413896009,0.1596829745,0.3063113595
H,-1.1734465299,0.0127764705,1.0317103459
N,-0.5134021783,0.7791899431,-1.0264245217
H,-1.2083268862,1.5133968918,-0.9048697737
C,0.7744468531,1.4010741178,-1.4116243704
H,1.3017566987,0.7339199045,-2.1058710156
H,0.6049492248,2.3478459684,-1.9381093398
N,0.8957050514,0.9928242121,1.0325751553
H,0.4619352892,1.737554084,1.5729812354
C,1.6433449474,1.5908345295,-0.100938717
H,1.8607147834,2.6473188079,0.0983715618
H,2.6076954831,1.0794212511,-0.2203193961

Co-ordinates for the product structure N3-prod



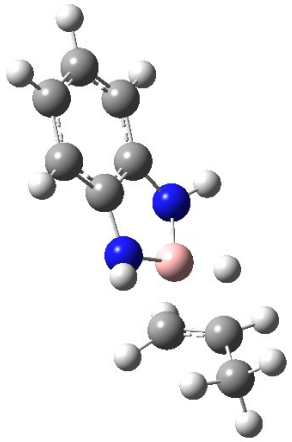
B3LYP/6-31+G(D) OPT FREQ

(HF=-332.8086228 a.u.)

0,1
C,1.4630259236,-2.5376733518,2.1875947673
H,1.469503009,-2.5527048101,3.2850822686
H,2.5061671802,-2.5720777977,1.8465003829
H,0.973640887,-3.4583834617,1.8434049734
C,0.7456934141,-1.2954283621,1.6444836675
H,-0.2822473084,-1.2715711658,2.0334005438
H,1.2364954301,-0.3932353618,2.0364647714

C,0.7125728961,-1.2327649239,0.0992311492
H,0.2279847673,-2.1468385707,-0.2778941059
H,1.7476608926,-1.2679847113,-0.274838491
B,-0.028665479,0.0509795957,-0.4632934902
C,-0.4260370825,2.3014709731,-1.20548615
H,-0.1842429736,2.6755093733,-2.2103155433
H,-0.4749096323,3.1712010467,-0.5352143646
C,-1.7784401675,1.5197310365,-1.2079386079
H,-2.509562339,1.9951442047,-0.5389812251
H,-2.2204360334,1.4983124196,-2.2140275545
N,-1.4202892586,0.1755281426,-0.7480700012
H,-2.1422481163,-0.5245559919,-0.6708898258
N,0.55872819,1.319464773,-0.7446656142
H,1.5255592084,1.5953242071,-0.6643840277

Co-ordinates for the transition state structure N4-TS



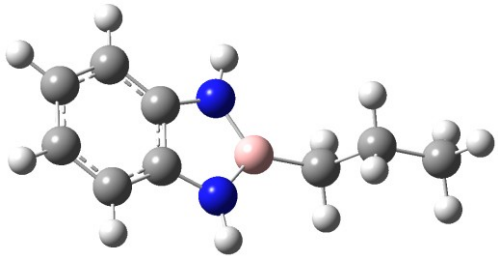
B3LYP/6-31+G(D) OPT=(CALCFC,TS,NOEIGENTEST)

(HF=-485.1412058 a.u.)

0,1
C,3.1414043029,-0.4166105377,-0.1460946566
H,3.3711441523,-1.3394945351,-0.6774789877
C,2.5577972723,-0.5180487019,1.1268800278
H,2.4125569712,-1.4937175771,1.578821566
H,2.5975506273,0.3330466974,1.8001784222
C,3.9150368466,0.7928963524,-0.6066489442
H,4.9539336685,0.6629697895,-0.2752065593
H,3.9080793388,0.9007614253,-1.6954682926
H,3.5330474809,1.7109442359,-0.1504461262
B,1.2295375518,-0.2488248592,-0.0405538225
H,1.8295652825,-0.1810096363,-1.1672553258

N,0.4323127982,1.0051759967,0.2314707583
H,0.7038503062,1.9315583702,-0.0689700297
N,0.1966112944,-1.3491054644,-0.0328109074
H,0.2920831652,-2.2324609174,-0.5152152679
C,-0.9239108334,0.668448859,0.0910120924
C,-1.0641216176,-0.7339508517,-0.0666640893
C,-2.3250699134,-1.3046053099,-0.2053429529
H,-2.4337713927,-2.3805585906,-0.3266870174
C,-3.4579188793,-0.4682109258,-0.1939010219
H,-4.4459653618,-0.9072252575,-0.3073492617
C,-3.3201047918,0.9110182949,-0.0388312442
H,-4.2004445351,1.5487738529,-0.0312246615
C,-2.0453436322,1.4908861367,0.1093120985
H,-1.9383986352,2.567102817,0.2301238402

Co-ordinates for the product structure N4-prod



B3LYP/6-31+G(D) OPT FREQ

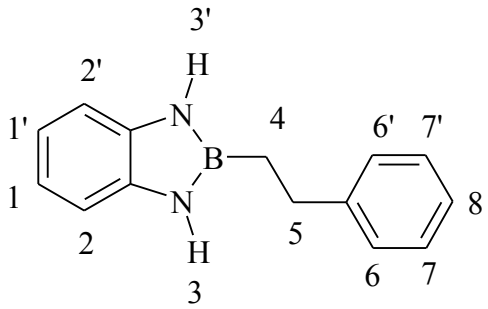
(HF=-485.2679595 a.u.)

0,1
N,-0.1086209224,1.1422791032,-0.3074731916
H,-0.3318488,2.1265256279,-0.3433660363
N,-0.1127607616,-1.1325505685,-0.3253821482
H,-0.3393500503,-2.1153271804,-0.3769922989
C,1.2027172006,0.7086566029,-0.0962778123
C,1.2001305711,-0.7070349353,-0.1074806816
C,2.3805835577,-1.4237565106,0.0769660026
H,2.3814125974,-2.5113067182,0.0682939038
C,3.56860615,-0.7072708288,0.2743744425
H,4.4995432698,-1.2485426745,0.4205254372
C,3.5711419366,0.6942754493,0.2855581477
H,4.5040151923,1.2297830633,0.4403393529
C,2.3857187174,1.4180934928,0.0995852179
H,2.3904566744,2.5056337556,0.1082343893
B,-0.985072652,0.0076126261,-0.4575985479

C,-2.5491563762,0.0123589031,-0.6761525228
H,-2.8463523316,-0.8540517975,-1.2871658607
H,-2.8449118257,0.8989561879,-1.2581861112
C,-3.3661959972,-0.0087431667,0.63846962
H,-3.091292727,-0.896211567,1.2258967272
H,-3.0886949128,0.8574988901,1.2555916209
C,-4.8824146123,-0.0026161629,0.4090469669
H,-5.1976115314,-0.877483705,-0.1744919309
H,-5.4320561477,-0.0182918172,1.3585356366
H,-5.1950612456,0.8928779992,-0.1437709976

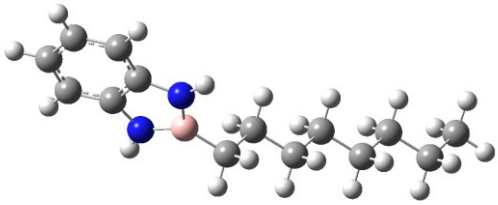
APPENDIX D

APPENDIX E


3'
H
2'
N
4
6'
7'
1'
B
1
N
8
5
2
H
6
7
3

Cartesian coordinates of geometry optimized structures of boronate esters

Co-ordinates of 2-octyl-benzo-1,3,2-diazaborolane (2)



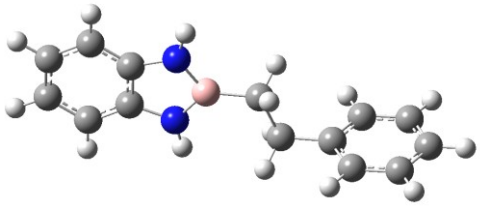
B3LYP/6-31 OPT FREQ

(HF=-681.6555764 a.u.)

0,1
N,-2.4741540912,-1.5899731809,0.6222459522
H,-2.4654559511,-1.5882667225,1.6294621906
N,-1.9516937066,-1.5985109307,-1.5974523443
H,-1.4948085358,-1.6039796272,-2.4951033528
C,-3.6778861489,-1.6106552325,-0.1031392819
C,-3.3526654241,-1.6160552799,-1.4849025261
C,-4.3548858565,-1.6384052385,-2.4538678263
H,-4.1098978762,-1.6430370084,-3.5115955239
C,-5.6913858323,-1.6545436347,-2.0270103054
H,-6.4861811447,-1.671519672,-2.765740969
C,-6.0129347256,-1.6489326018,-0.6609057749
H,-7.0538147153,-1.6613220546,-0.3541071717
C,-5.0071155401,-1.627142607,0.3171747231
H,-5.2597301686,-1.6228228507,1.3731111134
B,-1.3474063185,-1.5820041706,-0.2838950405
C,0.1834551387,-1.5143421735,0.0756590737
H,0.7729387302,-2.0631848918,-0.6751842932
H,0.3701700047,-2.0238397375,1.0337131796
C,0.7308090492,-0.0627586488,0.1711936964
H,0.5598335581,0.4558653781,-0.7839623162
H,0.1564497567,0.4948626875,0.925931497
C,2.2282587401,0.0035305895,0.5228929808
H,2.8021101476,-0.5523979183,-0.2347474605
H,2.3980830031,-0.5166747265,1.4783995332
C,2.7717560799,1.4404240328,0.6211837226
H,2.197179504,1.9944056963,1.3795211558
H,2.5991854065,1.9599377422,-0.3340688082
C,4.2696352715,1.5074854151,0.9712524358
H,4.844796105,0.9557314778,0.2117117519
H,4.4427942913,0.9864742177,1.9255982803

C,4.811178687,2.9448636134,1.0725863259
H,4.2370222832,3.4967932984,1.8328681938
H,4.6379034312,3.4669452202,0.1187704452
C,6.3093530936,3.0135418961,1.421809327
H,6.8828368765,2.4638071767,0.6608095561
H,6.4822497676,2.4896110448,2.3735994982
C,6.8396818199,4.452655561,1.5240399331
H,6.3064199468,5.0145405351,2.3012652034
H,7.9074499809,4.4699698794,1.7716552572
H,6.7069056613,4.9895163431,0.5762139646

Co-ordinates of 2-phenethyl-benzo-1,3,2-diazaborolane (3)



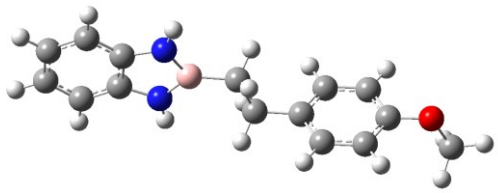
B3LYP/6-31 OPT FREQ

(HF= HF=-676.8296905 a.u.)

0,1
N,1.8856723517,1.416800614,-0.0000492153
H,1.8009480826,2.4204768945,-0.0000386915
N,1.5334242632,-0.8374464031,-0.0000582901
H,1.1472571487,-1.767584474,-0.0000637868
C,3.14123751,0.7844354697,-0.0000073325
C,2.9225154478,-0.6177165095,-0.000029744
C,3.9949997773,-1.5081734775,-0.0000069951
H,3.8309653193,-2.5814289226,-0.0000224962
C,5.2953904496,-0.9810939856,0.0000430763
H,6.1441128315,-1.6573299024,0.0000630214
C,5.5120121266,0.405501287,0.0000741312
H,6.5266801949,0.7903648364,0.0001162396
C,4.4348377285,1.3046423264,0.000049241
H,4.6064653789,2.3766821346,0.0000726803
B,0.8323817749,0.425944,-0.0000659918
C,-0.7240170882,0.672290324,-0.0000388635
H,-1.0037058331,1.2821033099,-0.8738191767
H,-1.0036799847,1.2820076953,0.873820741
C,-1.5820237112,-0.6233241346,-0.000078247

H,-1.3199937565,-1.2246576011,-0.8816758097
H,-1.3199675693,-1.2247112079,0.8814770211
C,-3.0754685184,-0.3579468053,-0.0000294733
C,-3.7814703701,-0.213741874,-1.2070326254
C,-3.7813577032,-0.2136521586,1.2070284357
C,-5.1518281047,0.0687149025,-1.2094343162
H,-3.2528885776,-0.3282242533,-2.1500667235
C,-5.1517148851,0.0687991983,1.2095387773
H,-3.2526856549,-0.3280641654,2.1500205609
C,-5.8420050411,0.2116363144,0.000079151
H,-5.6800655634,0.1725811975,-2.1524947143
H,-5.6798649255,0.1727308204,2.1526409402
H,-6.9058079773,0.4276288994,0.0001213992

Co-ordinates of 2-phenethyl-benzo-1,3,2-diazaborolane (4)



B3LYP/6-31 OPT FREQ

(HF=-791.3076361 a.u.)

0,1
N,0.,0.,0.
H,0.0001279395,1.0072613618,0.0000110679
N,-0.5394058806,-2.216568511,-0.0407766051
H,-1.0009679207,-3.1109933072,-0.0756671836
C,1.194421516,-0.7359438653,0.090284948
C,0.8593261919,-2.1146426464,0.0649532795
C,1.8500088858,-3.0924202528,0.1398373348
H,1.5967369314,-4.1480192329,0.1206911187
C,3.1863836586,-2.6768947537,0.2408540845
H,3.9728398724,-3.4222605286,0.300301043
C,3.5181502443,-1.3134765446,0.2659341135
H,4.5586814322,-1.0155342209,0.3445879711
C,2.5235042956,-0.3266821155,0.1907504894
H,2.7842019378,0.7270442706,0.2104580084
B,-1.1297420788,-0.8984987063,-0.0853981154
C,-2.6556805272,-0.522331227,-0.2007428291
H,-2.8168693315,0.1090070624,-1.0889699308

H,-2.9487101005,0.1084550562,0.6535174989
C,-3.6159367956,-1.7418135448,-0.2737813183
H,-3.3383184625,-2.3628075738,-1.1368244363
H,-3.4712492117,-2.3634087869,0.6207778414
C,-5.0784868465,-1.3554841401,-0.3842487442
C,-5.6777245366,-1.1497456212,-1.6394387231
C,-5.8597657258,-1.1509021718,0.7666837211
C,-7.0151314566,-0.7564738246,-1.7469512971
H,-5.0903828143,-1.2995470883,-2.541552036
C,-7.1981821601,-0.757712431,0.6721279096
H,-5.4148393089,-1.3016405771,1.7467531809
C,-7.7723222389,-0.5611072269,-0.587672099
H,-7.4735387375,-0.5871518979,-2.7153584486
H,-7.7971845444,-0.5893998071,1.5606518824
O,-9.1067734898,-0.120366052,-0.6882358137
C,-10.1145774429,-1.1762107351,-0.7687976071
H,-10.0951162826,-1.8086544371,0.127228045
H,-11.0742363175,-0.6640212171,-0.8402642748
H,-9.9591058123,-1.8025264081,-1.6558063105

APPENDIX F

PRESENTATIONS AND ACHIEVEMENTS

The results of this research have been presented in national conferences, student colloquiums and yearly progress meeting with Sasol representatives. Conferences at which this work was presented are listed below.[1]

1. The South African Chemical Institute (SACI) Colloquium, April 2005, University of KwaZulu-Natal, Westville campus. Oral presentation.
2. 9th Frank Warren Organic Chemistry Conference, January 2006, University of Cape Town, South Africa. Poster presentation.
3. The South African Chemical Institute (SACI) Conference, December 2006, University of KwaZulu-Natal, Howard Collage. Poster presentation.
4. The South African Chemical Institute (SACI) Postgraduate Colloquium, 23 October 2008, University of KwaZulu-Natal, Westville campus. Plenary speaker.

This work has been accepted by a number of internationally renowned journals as listed on the publications declaration section. Our research articles have received recognition from a number of internationally distinguished researchers, who have cited our contribution in prestigious journals.[2] Poster presentation of this work at the SACI conference in 2006 was recognized as the best poster and was awarded the poster prize by the International Union of Pure and Applied Chemistry (IUPAC).[3] In 2008, our work was awarded the Sasol Post-Graduate Silver Medal by the South African Chemical Institute Council, for innovation, independence, and enterprise.[4]

[1] Copies of abstracts attached.
[2] (a) Stevens, B. D.; Bungard, C. J.; Nelson, S. G. *J. Org. Chem.* **2006**, *71*, 6397. (b) Kanas, D. A.; Geier, S. J.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Inorg. Chem.* **2008**, *47*, 8727. (c) Fritschi, C. B.; Wernitz, S. M.; Vogels, C. M.; Shaver, M. P.; Decken, A.; Bell, A.; Westcott, S. A. *Eur. J. Inorg. Chem*. **2008**, *5*, 779. (d) Smith, S. M.; Thacker, N. C.; Takacs, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 3734. (e) Jayakumar, S. V.; Srinivas, K. A.; Hiriyanna, S. G.; Pati, H. N. *Rasayan. J. Chem*. **2008**, *1*, 326. (f) Ide, D. M.; Eastlund, M. P.; Jupe, C. L.; Stockland, R. A., Jr. *Curr. Org. Chem.* **2008**, *12*, 1258.
[3] Copy of certificate attached.
[4] Copy of award letter attached.