SILOXANE BORONIC ACIDS AND SILOXANE BORONATES

SYNTHESIS AND APPLICATIONS OF SILOXANE BORONIC ACIDS AND SILOXANE BORONATES

By

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Abstract

Synthesis of new biocompatible siloxane surfactants, where hydrophobic siloxanes are modified by biocompatible hydrophilic functional groups (e.g., triethoxysilane (TES), polyethylene glycol (PEO), and carboxylic acid) is a research area of increasing interest. In this research project we have developed a new class of these biocompatible surfactants, based on siloxanes, as the hydrophobic part, and boronic acids as the hydrophilic part. The reasons for choosing boronic acid/boronates as a modifying agents include: their pH sensitivity, biocompatibility, possible interactions with sugars, and because of a broader general utility in synthesis. The promise of these properties combined with the hydrophobicity, flexibility and many other important features of siloxanes encouraged us to initiate these syntheses.

We have explored different synthetic strategies to prepare siloxane boronic acid surfactants, including Grignard reactions and metal-catalyzed hydroboration reactions. Nevertheless, the main approach that was investigated is metal-catalyzed hydrosilylation reactions of vinylphenylboronic acid. Two different approaches were developed to prepare the target compounds: (1) metal-catalyzed hydrosilylation using non-protected vinylphenylboronic acid and (2) metal-catalyzed hydrosilylation using protected vinylphenylboronic acid that can be removed under gentle conditions. The protected compounds underwent hydrosilylation smoothly, but led after separation using column chromatography to the unprotected compounds in moderate yield. The conversion of the hydrosilylation of unprotected boronic acids was quite good, but the compounds underwent decomposition during chromatography. Thus, the two approaches are

complementary, depending on whether pure molecules are required for further synthetic elaboration, or a mixture of materials is suitable for practical application as surfactants.

The amphiphilic nature of these siloxane boronic acid surfactants was studied and the compounds were found to be surface active. The limited solubility of our compounds in H_2O prevented us from studying their surface tension properties. However, their solubility in chloroform enabled us to study their interfacial properties.

Acknowledgements

It is my pleasure to express my appreciation and gratitude to my advisor, Professor Michael Brook, for his encouragement, support, and constructive discussions. I would also like to thank him for offering me the opportunity to work for him as a graduate student; I am very grateful for his help, guidance, and patience during writing my thesis. My experience in Dr. Brook's lab was very rich and it certainly made me a better chemist and will help me to pursue my dreams and goals in my life. I wish to extend my gratitude to my committee members, Dr. James McNulty and Dr. Fred Capretta for their valuable suggestions, discussions, and for reading my thesis in a very short time frame.

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Abbreviations

AIBN	azobis(isobutyronitrile)
BNCT	boron neutron capture therapy
CMC	critical micelle concentration
δ	chemical shift (NMR)
d	doublet (NMR)
DCM	dichloromethane
dd	doublet of doublets (NMR)
D_4	octamethycyclotetrasiloxane
ESI	electrospray ionization
IFT	interfacial tension
m	medium (IR)
m	multiplet (NMR)
mM	millimolar concentartion
M	molar concentration (mol/L)
Me	methyl
MeOH	methanol
MW	molecular weight
NMR	nuclear magnetic resonance
PEO	polyethylene glycol
PDMS	polydimethylsiloxane
s	singlet (NMR)

s	strong (IR)
t	triplet (NMR)
TES	triethoxysilane
THF	tetrahydrofuran
TLC	thin layer chromatography
VPBA	4-vinylphenylboronic acid
w	weak (IR)

CHAPTER ONE

INTRODUCTION

1 Introduction

A research area of increasing interest involves the synthesis of new biocompatible silicone surfactants, where hydrophobic silicones are modified by biocompatible hydrophilic functional groups including triethoxysilane (TES), polyethylene glycol (PEO), and carboxylic acid groups.[1] By introducing these functional groups it was possible to synthesize new surfactants with the general structure shown in (Figure 1).

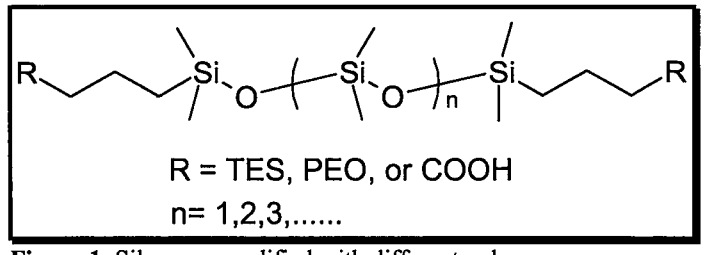


Figure 1. Siloxanes modified with different polar groups

1.1 Siloxane polymers

Siloxanes are compounds which contain silicon-oxygen bonds. Polydimethylsiloxanes, also called silicone polymers or silicones, are the most commonly used siloxanes; the general structure of silicones is shown below in (Figure 2).[2]

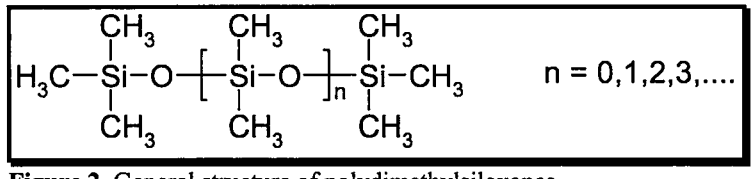
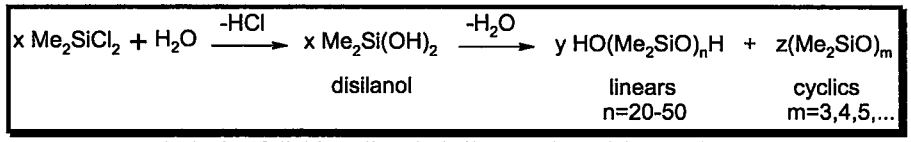


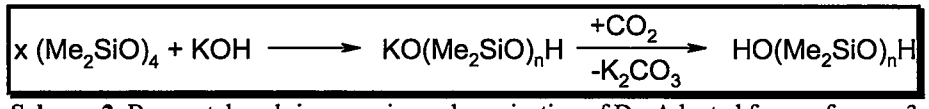
Figure 2. General structure of polydimethylsiloxanes

The most commonly used method for the synthesis of PDMS is the hydrolysis of dichlorodimethyl silane, (Scheme 1). The disilanol intermediate condenses intermolecularly to give linear oligomers and in an intramolecular way to give cyclic oligomers.[2,3]



Scheme 1. Hydrolysis of dichlorodimethyl silane. Adapted from reference 3.

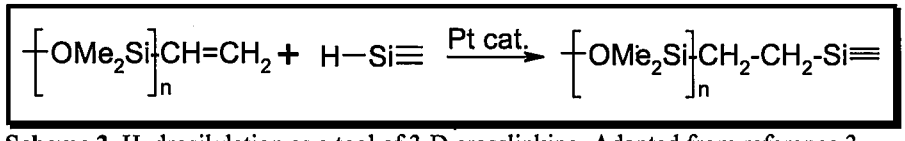
On the other hand, base catalyzed ring-opening polymerization of octamethyltetracyclosiloxane (D_4) (Scheme 2), is the preferable method for the synthesis of silicone polymers for pharmaceutical applications purposes, this is mainly because the resulting polymers are relatively more pure than those prepared using other methods.[3]



Scheme 2. Base catalyzed ring-opening polymerization of D_4. Adapted from reference 3.

1.2 Siloxane elastomers

Silicone elastomers can be prepared by the 3-dimentional crosslinking of polydimethylsiloxane chains. Hydrosilylation reaction (addition of Si-H bond to carbon-carbon double or triple bond) is the preferred method among other possible crosslinking reactions since it does not produce by-products (Scheme 3).[2,3]



Scheme 3. Hydrosilylation as a tool of 3-D crosslinking. Adapted from reference 3.

These addition reactions could be inhibited by nucleophiles when Pt is used as the catalyst. This is mainly because they form more stable complexes with platinum, which leads to poisoning of the catalyst.[2]

Polydimethylsiloxanes (PDMS) are generally stable towards thermal degradation because of their strong polar Si-O-Si bonds;[4] this property promoted the usage of PDMS

as sealants in kitchen and bathroom appliances.[2,3] Although PDMS contain these polar bonds, they are hydrophobic because the hydrophobic methyl groups shield the polar backbone effect. The energy required for rotation around the Me_2Si-O bond is low, which enhances the shielding effect of methyl groups. Consequently, PDMS can reduce surface tension by exposing more methyl groups. This property allowed PDMS utilization as antifoam agents in pharmaceutical formulations.[3] The hydrophobic nature of PDMS was also utilized in PDMS elastomers via using them as drug delivery systems, intraocular lenses, and contact lenses.[2]

1.3 Siloxane surfactants

Depending on the original siloxane that was used to prepare the surfactant, siloxane surfactants range in size from low to high molecular weight. These surfactants have been used in different types of applications because of their wide range of properties. They usually consist of a hydrophobic group, which can be a small siloxane or a polydimethylsiloxanes (PDMS), chemically linked to one or more polar groups.[5,6] The surface activity of siloxanes is mainly due to the presence of methyl groups which serve as the hydrophobic part, while Si-O-Si backbone gives the molecule it's flexible nature. Siloxane surfactants usually have surface energies of about 20 dyn/cm, while that of hydrocarbon surfactants is about 30 dyn/cm or more. This difference is mainly because hydrocarbon surfactants consist of alkyl groups as the hydrophobic part, which in turn are composed of CH_2 groups that behave differently compared to methyl groups of siloxanes because of their lower flexibility causing higher surface tension.[5]

Silicone surfactants have been used in many areas including the manufacture of polyurethane foams, where they serve as wetting and spreading agents in addition to foam stabilizers.[5,6] Also, because of their biocompatibility and their wide range of interesting properties, silicone surfactants have been used in many other applications related to pharmaceuticals[3] and personal care products.[5] For example, personal care applications include: skin care, e.g., hand and body lotions, facial treatment, aftershaves, and sun protection; hair care, e.g., shampoos, conditioner, fixative, and mousse; color cosmetics, e.g., foundations, mascaras and liners, and powders; e.g., antiperspirants and deodorants.[5]

1.4 Boronic acids

Boronic acids stem their importance from their wide range of applications, especially in medicine and because of their widely utilized chemical properties.[7] Structurally, boronic acids are composed of a boron atom linked to one alkyl substituent and two hydroxyl groups. The general formulas of boronic acids and other related boron compounds are shown in (Figure 3).

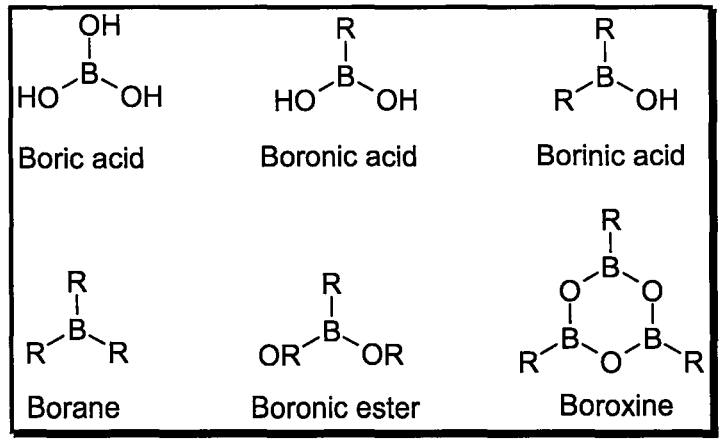


Figure 3. Boronic acid and related organoboron compounds. Adapted from reference 7

Generally, Boronic acids have low toxicity levels,[7] this fact is supported by their usage in medicine[8] as enzyme inhibitors,[9] boron neutron capture therapy (BNCT),[10] and drug delivery devices.[11]These applications indicate that boronic acids are biocompatible.

The most widely used definition of biocompatibility, is the well known William's definition, "the ability of a material to perform with an appropriate host response in a specific application".[12] Since these boronic acid compounds are very useful as enzyme inhibitors and in BNCT applications, one can say that they are biocompatible even though they have some level of toxicity.

Boronic acids have been also utilized in synthetic organic chemistry, especially in Suzuki-Miyaura cross coupling reactions,[13] sacharide sensors,[14,15] and protection of diols.[16,17] In addition, boronic acids have been recently utilized to prepare porous, crystalline, covalent organic materials.[18]

1.5 Goal of this research

In this work our goal was to synthesize different siloxane boronic acid compounds and to explore their surface active properties. A combination of siloxanes and boronic acids should generate surface-active materials that are also expected to be biocompatible and could lead to applications in pharmaceutical and personal care industries.

The desired product from the chemical linkage of siloxanes and boronic acids, should have interesting properties since the siloxane part is lipophilic and the boronic acid part is hydrophilic, (Figure 4). The combination of both parts will give a new kind of surfactant, hopefully with unique properties stemming from the introduction of the

boronic acid moiety to the siloxanes. The potential importance of this kind of compound is associated with the specific properties and chemistries of both siloxanes and boronic acids, which will be introduced in the following sections.

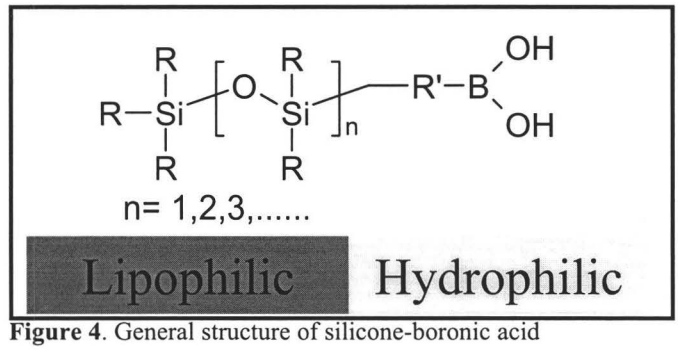


Figure 4. General structure of silicone-boronic acid

To achieve this synthetic goal we have tried different synthetic strategies including metal-catalyzed hydrosilylation, metal-catalyzed hydroboration, and Grignard chemistry. The former was explored extensively using protected and non-protected boronic acids. In the research conducted to date, we have established a general synthetic approach to different siloxane boronic acid compounds and we have examined their surface active properties.

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CHAPTER TWO

GRIGNARD AND HYDROBORATION

2 Siloxane boronic acids and boronates

The basic properties of both siloxanes and boronic acids have been described in the introduction. Our objective is to combine these two functionalities into a single molecule. Our thesis is that the combination of hydrophobicity of the siloxanes and hydrophilicity of the boronic acids will lead to a new class of surfactants, (Figure 1). If a generic synthetic method can be developed, a wide variety of structural morphologies could be prepared and their characteristics established. Siloxanes and boronic acids are each generally biocompatible and have been used in pharmaceutical formulations and personal care products, which suggests that a surfactant containing both moieties may be useful for *in-vivo* or *in-vitro* applications.

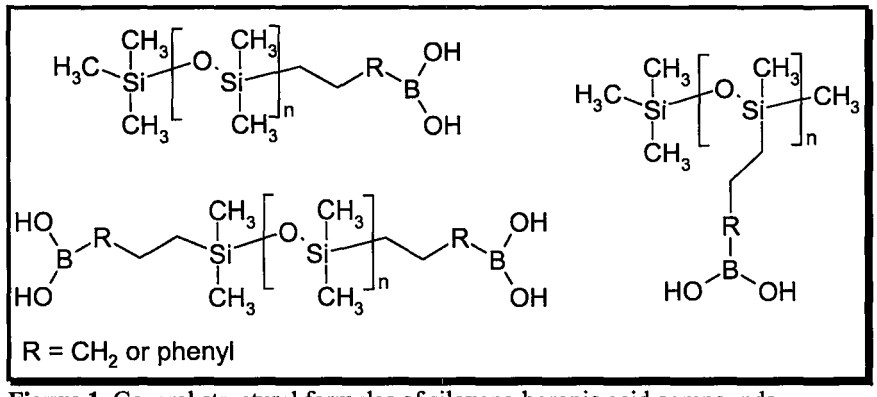


Figure 1. General structural formulas of siloxane-boronic acid compounds

A few polymeric compounds containing boronic acids and/or boronates have been prepared. Pelton and co-workers[1] have described polysaccharide structures that have potential application as tear film stabilizers. The polysaccharide binds borates through diol groups producing negatively charged macromolecules, which increases the local viscosity. The polysaccharide-borate structures, shown in (Figure 2), in turn complex with lysozyme, which is positively charged at the tear film pH (7.3-7.8). This suggests that

surfactant compounds based on such structures could have utility. However, we are not aware of siloxane/boronic acid compounds.

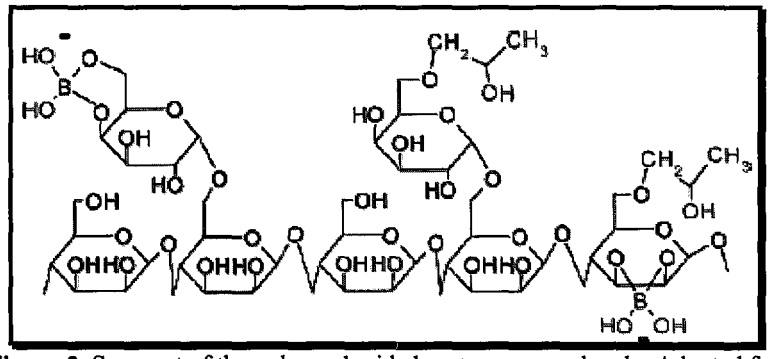


Figure 2. Segment of the polysaccharide borate macromolecule. Adapted from reference 1.

Branlard and co-workers have patented the synthesis and use of silanes and polyorganosilanes with boronate functionalities as composite materials.[2] They have synthesized different polyorganosilanes with a hydrolysable functionality, (e.g. trimethoxysilane, diethoxymethylsilane, etc.), (Figure 3), in order to prepare crosslinked composite materials. They claimed that the crosslinking takes place when the compounds are exposed to humidity and without the need of a catalyst.

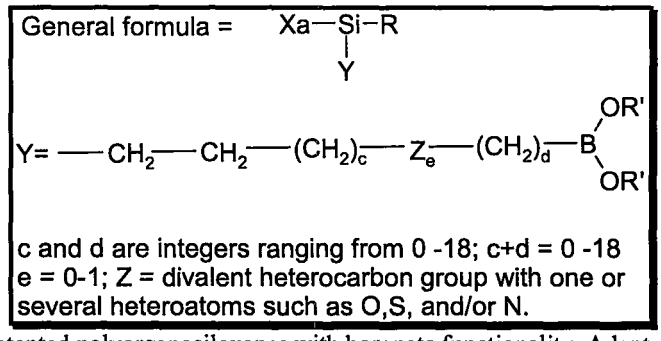
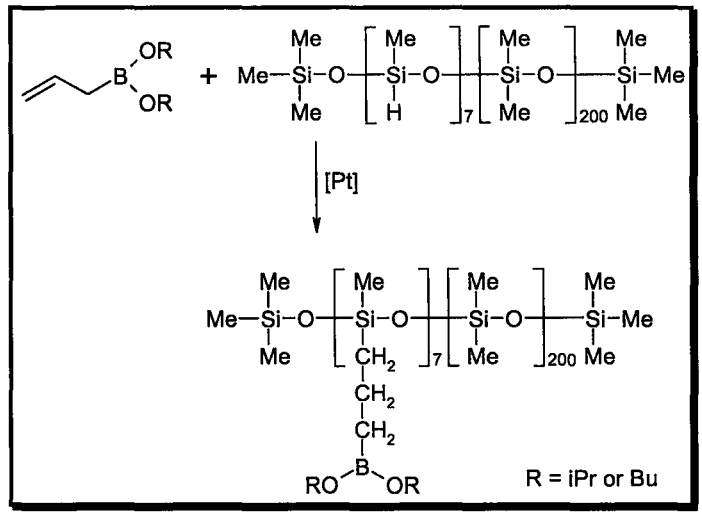


Figure 3. Patented polyorganosiloxanes with boronate functionality. Adapted from reference 2.

One of the approaches they used to prepare these polysiloxane boronates is the hydrosilylation reaction; where they have used pinacol-protected allylboronic acid,

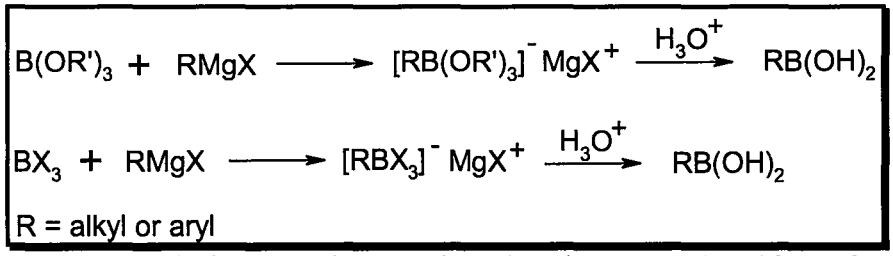
allyldiisopropyloxyborane and allydibutoxyborane as their source of boronates, (Scheme 1).



Scheme 1. Hydrosilylation of polyorganosiloxanes. Adapted from reference 2.

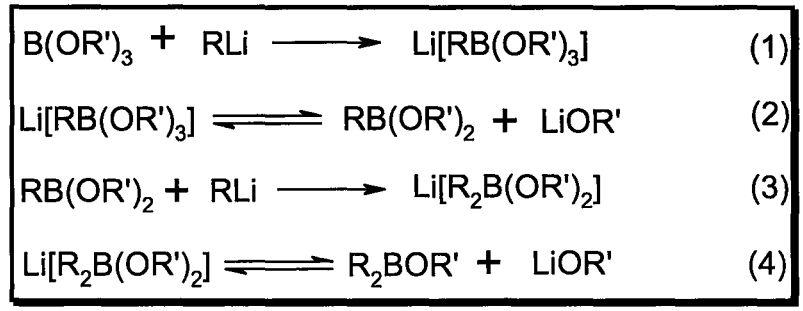
2.1 Preparation of organoboron compounds

Organoboron compounds can be synthesized using several methods.[3,4,5] The most widely used methods are based on Grignard and hydroboration reactions. Alkylboronic acids and arylboronic acids and their corresponding esters can be prepared via the reaction of a Grignard reagent with trialkoxyboranes or trihaloboranes,[6,7,8,9] (Scheme 2).



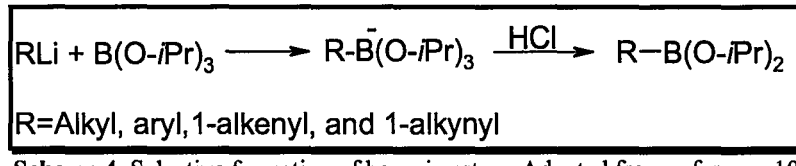
Scheme 2. Synthesis of organoboranes using Grignard reagents. Adapted from reference 4.

Also, alkyllithium reagents have been used to prepare organoboron compounds and they usually form the borinic esters as the major product.[10] The detailed steps leading to the formation of the borinic acid are shown in (Scheme 3). The nucleophilic attack of alky lithium on trialkoxyborane leads to the irreversible formation of monoalkyltrialkoxyborate Li[RB(OR`)$_3$] (eq.1). On the other hand, the resulting monoalkyltrialkoxyborate is in equilibrium with the corresponding boronic ester (eq.2). The boronic ester in turn, can be further attacked by alkyl lithium leading to the formation of dialkyldialkoxyborate (eq.3), which is in equilibrium with the corresponding borinic ester (eq.4). In addition, the reaction can proceed to the trialkylborane via the same mechanism.



Scheme 3. Alkylation of borane derivatives with alkyllithium. Adapted from reference 10.

The formation of the boronic ester can be controlled via controlling these equilibrium steps. If the equilibrium in (eq.2) is shifted to the left, the boronic ester can be formed selectively if the alkyltrialkoxyborate was protonated, (Scheme 4).



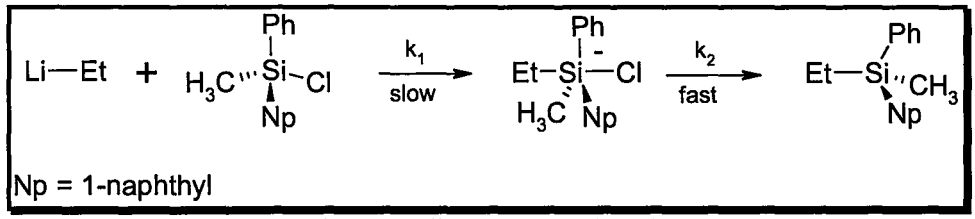
Scheme 4. Selective formation of boronic esters. Adapted from reference 10.

Brown and Cole reported the methylation of different boranes with methyllithium.[10] They found that trimethoxyborane yielded a mixture of boronic ester (8 %), borinic ester (3 %), and alkylboranes. The corresponding products with triethoxyborane were: boronic ester (65 %), borinic ester (10 %), and alkylboranes. On the other hand, triisopropoxyborane gave mainly the corresponding boronic esters. This is mainly because the solubility of lithium isopropoxide, in ether, is more than that of lithium ethoxide, which is in turn more than that of lithium methoxide. The precipitation of lithium alkoxide shifts the equilibrium in (eq. 2) towards the boronic ester which will lead to the formation of the dialkylborane (eq. 3) and may eventually lead to the formation of the trialkylborane.

Boron usually forms trigonal planar trivalent compounds with bond angles of 120°.[11] Since this type of boron compounds have only six valence electrons they are considered Lewis acids. The empty p orbital on boron is orthogonal to the other three substituents on boron. Boron-halogen and boron-oxygen bonds are shorter than expected bond lengths because of the pπ-pπ bond formation through the lone pairs of the p orbitals of the halogens and the vacant p orbital of boron. Also, because of the electronegativity differences between B and O (B = 2.04, and O = 3.44) B-O bond is actually shorter than expected.[11] In addition, B-O bond strengths (~500 kJ mol^{-1}) are greater than B-C bond strengths (350-400 kJ mol^{-1}), causing a stronger overlap between B empty p orbital and the electron pair on O.[11,12]

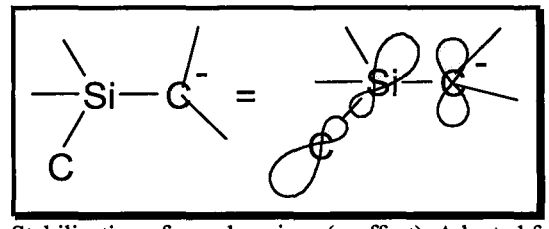
Silicon usually forms tetravalent compounds in a tetrahedral geometry. In general, silicon forms stronger bonds with electronegative atoms, than those formed by carbon and

electronegative atoms. The Si-Si bond (308 kJ mol^{-1}) is weaker than the C-C bond (356 kJ mol^{-1}) but the Si-O bond (477 kJ mol^{-1}) is stronger than C-O bond (340 kJ mol^{-1}). Although Si-C bond (369 kJ mol^{-1}) is stable towards some chemical reactions. On the other hand, nucleophiles can attack the Si-C bond, specifically attack the Si atom, since it's more electropositive than C atom (Si = 1.74 and C = 2.55).[13,14] The mechanism of this reaction is generally explained as S_N2 mechanism. Nevertheless, since Si can form pentacoordinate compounds and intermediates, due to the longer Si–C bond, themechanism is believed to involve a pentacoordinate Si intermediate (Scheme 5).[15]



Scheme 5. Nucleophilic substitution at silicon center. Adapted from reference 15, P48.

In their search for new methods to prepare polyfunctional carbosilanes and new organosilicon compounds using Grignard reagents, Corriu and co-workers prepared (triethoxysilyl)methylmagnesium chloride,[16] which was stable at low temperatures and polycondensed up on heating to room temperature. They attributed the relative stability of the Grignard reagent to the α-effect, where carboanions in α-position to a silicon can be be stabilized through the interaction between a low-lying σ* orbital on silicon and the electrons on the carboanion (Scheme 6). These observations encouraged us to attempt reactions using similar conditions.

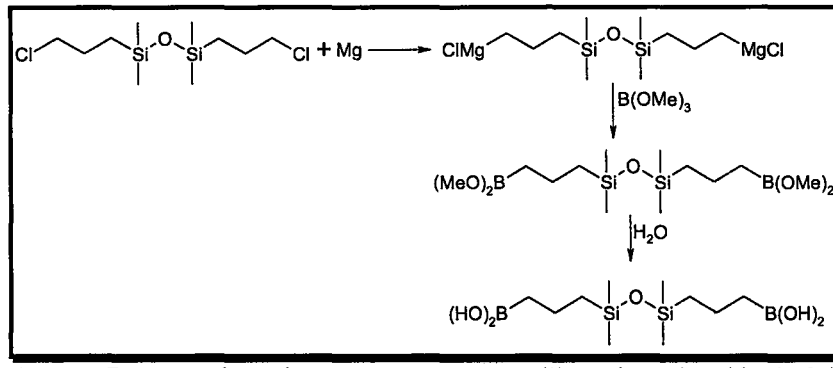


Scheme 6. Stabilization of α-carboanions (α-effect). Adapted from reference 13, P501.

2.2 Results and discussion of Grignard approach

Our initial studies utilized Grignard chemistry. In this approach, we examined the possibility of preparing siloxane-boronic acids by the *in situ* reaction of a Grignard reagent prepared from bischloropropyltetramethyldisiloxane with trimethyl borate. In this reaction there are two potential electrophilic sites, the boron and the silicon.

Our proposed reaction sequence to prepare silicone boronic acids via the Grignard route is shown in, (Scheme 7). We were cognizant that a mixture of products could result because of the presence of two different electrophilic sites, the boron and the silicon. The relative reactivity of these two positions depends on several factors associated with the two sites; silicon (Si = 1.74) is more electropositive than boron (B = 2.04) but boron is much better Lewis acid, which makes both sites susceptible to the attack of the carbonucleophile.



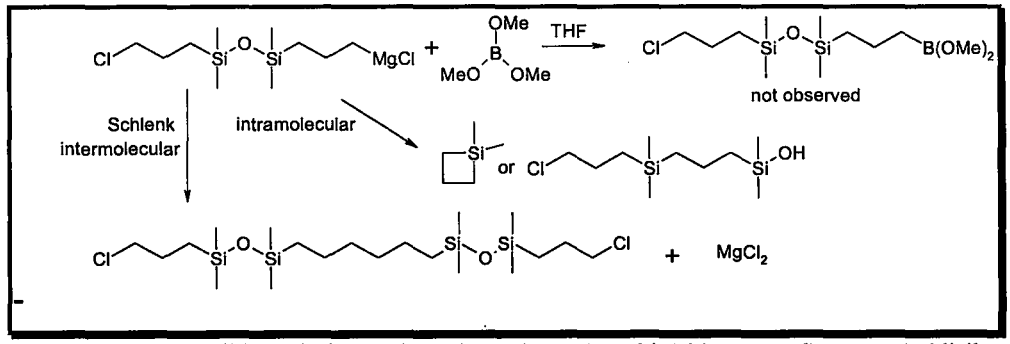
Scheme 7. Proposed reaction sequence to prepare silicone boronic acids via Grignard route

The boron atom in our starting material, trimethylborate, bears three methoxy groups and all back donate electron density to boron, which will decrease the electrophilicity of boron compared to one silicon-oxygen bond in the siloxane starting material. On the other hand, oxygen is the second most electronegative atom in the periodic table and this may neutralize the donation effect. In addition, the geometrical accessibility; the arrangement of methoxy groups around the boron center in trimethylborate takes a trigonal planar geometry, makes the boron much easier to be attacked than the silicon tetrahedral center.

The most important distinction between the two electrophilic sites is the possibility of intramolecular attack at silicon, while the reaction at boron is intermolecular. The reaction was run in such a manner that the chance for effective reaction was optimized. Thus, we prepared the Grignard reagent in the presence of excess trimethoxyborane to enhance the possibility of attacking the boron center. Also, in other attempts, the Grignard was prepared and then added dropwise to a solution containing the trimethylborate so as to keep the trimethylborate in large excess. Unfortunately, even using these precautions it was not possible to get the desired product. Instead, a mixture of unidentified compounds was produced.

It has not been possible to establish the specific reaction sequences that occurred. However, an analysis of the reaction conditions permits speculation. Once a Grignard reagent is formed from the chloropropylsilane, the nucleophile created can participate in the Schlenk equilibrium, involving halogen metal exchange, to give the dimeric structure. Alternatively, intramolecular attack of the carbanions at silicon could lead either to the

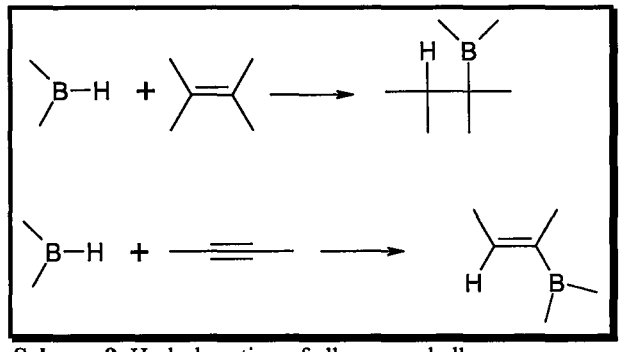
silacyclobutane, or the silanol (Scheme 8). Unfortunately, evidence for the intermolecular attack on boron was not observed. We therefore turned to hydroboration.



Scheme 8. Some possible undesired Grignard reactions of 1,3-bis(chloropropyl)tetramethyldisiloxane

2.3 Uncatalyzed hydroboration

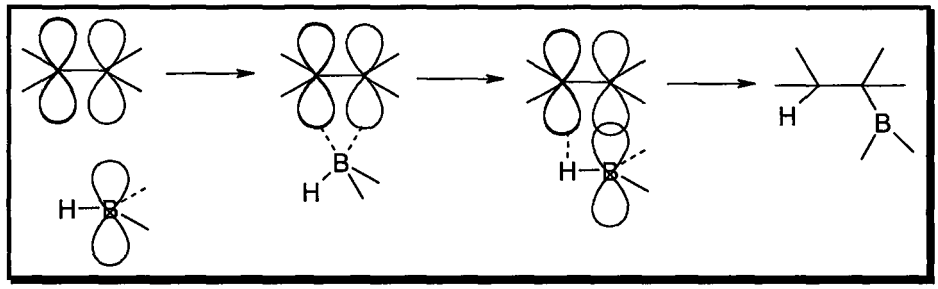
Hydroboration is one of the classical and most reliable transformations in synthetic organic chemistry.[17,18] The reaction is a simple addition of a hydrogen-boron bond to alkenes or alkynes (Scheme 9).



Scheme 9. Hydroboration of alkenes and alkynes

The reaction of borane (BH_3) with alkenes to form monoalkylborane as the initial product continues to form the dialkylborane, and finally the trialkylborane.[17,19] The formation of the monoalkylborane and dialkylborane is faster than the formation of the

trialkylborane, because the steric hindrance increases around B upon replacing more hydrogens with alkyl groups.[15,17] The hydroboration reaction is a regiochemical reaction because borom in B-H bond adds to the least hindered carbon of the double bond to minimize steric repulsion. In addiotn, the reaction is also stereochemical since the addition of the B-H bond to the C=C bond is a *cis* addition.[12,15,17] The addition occurs via the four-center transition state shown in (Scheme 10). Where, the electrons of the alkene π orbitals interact with the empty p orbitals of the boron.[15,20]

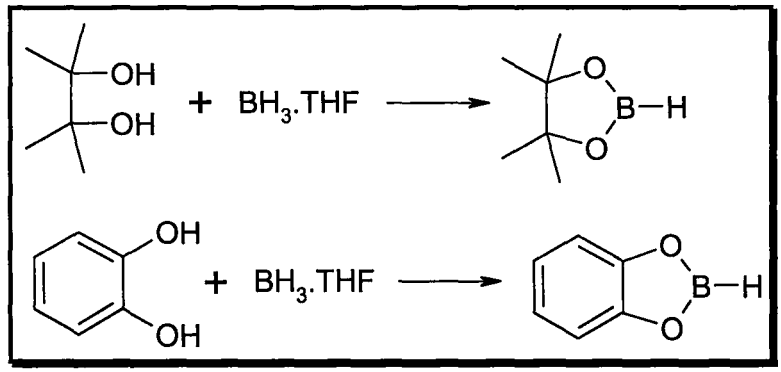


Scheme 10. Interaction of filled π orbitals of an alkene with the empty p orbitals of boron. Adapted from reference 20.

Hydroboration reaction is usually done by using borane (BH_3) as the hydroborating agent or one of its derivatives. However, (BH_3) does not have steric demand and contains 3 active (B-H) bonds that could lead to multiple hydroboration, for these reasons borane derivatives have been more frequently used as hydroborating agents since they are more sterically demanding and they can be designed to contain only one B-H bond.[15,17,21]

2.3.1 Hydroboration reagents

Pinacolborane and catecholborane are common hydroborating agents and they can be prepared via the reaction of BH_3.THF with the corresponding diol at room temperature, (Scheme 11).[15]



Scheme 11. Preparation of Pinacolborane and catecholborane

Generally oxygenated boranes such as pinacolborane and catecholborane react very slowly with olefins because the overlap of oxygen lone pairs with boron empty p orbitals decreases the Lewis acidity of boron and subsequently its ability to complex with olefins.[12,15] In order for this type of hydroborating agents to be useful and reliable a suitable metal catalyst has to be used.

In our initial experimental attempts, vinylpentamethyldisiloxane was exposed to BH_3.THF solution at different temperatures and with different mole ratios (equimolar and excess BH_3.THF). In all cases ^{1}H-NMR data showed the disappearance of the vinyl peaks at around 6.0 ppm, which mean the hydroboration reaction took place very efficiently, but very complex mixtures were obtained. Similar observations were noted earlier by Brown and Soderquist,[22] where they examined the hydroboration of vinyltrimethylsilane using BH_3.THF. Based on their ^{11}B-NMR studies, they found that 1:1 stoichiometric ratio of

borane and vinyltrimethylsilane would give a relatively simple mixture of products. On the other hand, when they increased the stoichiometric ratio and/or the temperature, the product mixture was very complex and it was not possible to characterize it.

In order to avoid these complexities associated with the hydroboration via BH_3 and to achieve a better regioselectivity, other borane derivatives have been used such as dialkylboranes and boronates. The drawback associated with the latter approach is their lower reactivity especially when boronates are used as the hydroborating agents. For example, catecholborane hydroborates alkynes at around 100 °C to give mainly the linear product, while diborane reacts smoothly around 0°C.[23,24] To overcome the reactivity problem associated with boronates, e.g., catecholborane and pinacolborane, different types of metal catalysts have been used. [25]

2.4 Metal-catalyzed hydroboration

Metal-catalyzed hydroborations of alkenes and alkynes using pinacolborane and catecholborane as the hydroborating agent have been extensively studied. The importance of the hydroboration reaction in organic synthesis stems from its reliability in chemoselectivety[26], regioselectivety,[26,26] and stereoselectivety.[27,28] organic chemists have usually used the hydroboration reaction as an intermediate for further chemical modification, where the produced boronates have been oxidized to furnish desired alcohols[15,23] or an amines after treating with RMgBr and H_2NOSO_3H.[29]

Rhodium complexes have been the most widely used metal catalysts in hydroboration reactions when catecholborane or pinacolborane are chosen as the

hydroborating agents. However, because catecholborane is air sensitive and decomposes in the presence of rhodium complexes and nucleophiles[30] pinacolborane proved to be a better hydroborating agent in many cases since it is more stable in air and can tolerate a variety of nucleophiles.[31]

There have been only few reports on metal-catalyzed hydroborations where the substrate included a silane moiety.[31,32,33] The key work was done by Pereira and Srebnik; they used pinacolboronate as their hydroborating agent along with $Rh(PPh_3)_3Cl$, $HZrCp_2Cl$, $Rh(CO)(PPh_3)_2Cl$, or $NiCp(PPh_3)Cl$ as their catalysts. The results obtained from these different catalysts with different silane-containing substrates in addition to our model compound, vinylpentamethyldisiloxane, are summarized in (Table 1).

The results show that the yields are generally better when Wilkinson's catalyst was used instead of $HZrCp_2Cl$. In addition, the major product was the internal isomer (boron attached to the terminal carbon) when pinacolborane was used. The mechanism for alkene hydroboration, which was proposed by Mannig,[26] involves oxidative addition of the B-H bond to Rh(I), followed by alkene insertion into the Rh-H bond and subsequent reductive elimination of the B-C bond (Scheme 12). The mechanism shown is associated with catecholborane, which gives both internal and terminal products. Pereira and Srebnik attributed the formation of the terminal products associated with pinacolborane to its large steric requirements.[31]

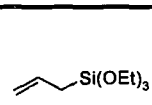
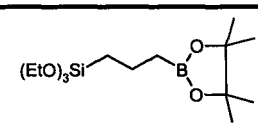
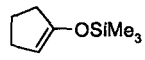
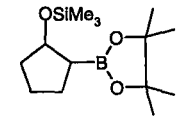
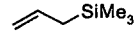
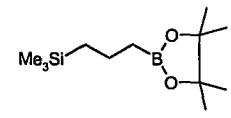
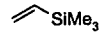
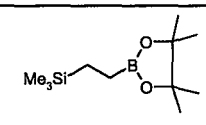
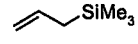
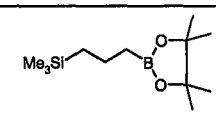
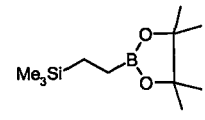
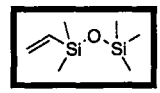
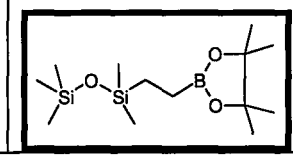
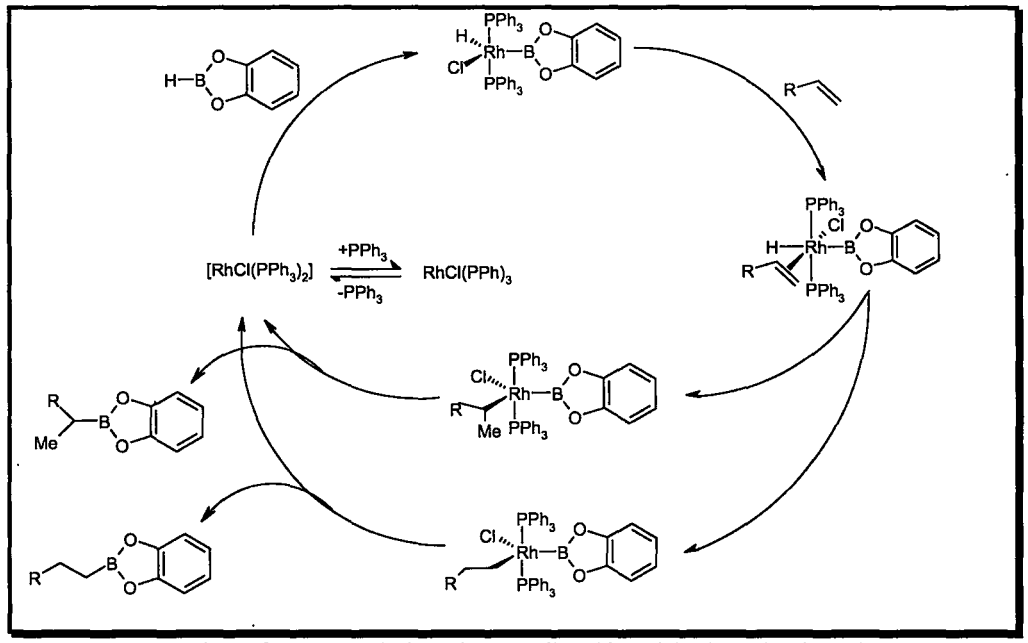
Silane-containing substrate	Catalyst	Hydroboration product	Yield, %
	$Rh(PPh_3)_3Cl$		90
	$Rh(PPh_3)_3Cl$		63
	$Rh(PPh_3)_3Cl$		99
	$Rh(PPh_3)_3Cl$		93
	$HZrCp_2Cl$		72
	$HZrCp_2Cl$		66
	$Rh(PPh_3)_3Cl$		68

Table 1. Hydroboration of different silane-containing substrates including our compound. Adapted from references 31-33

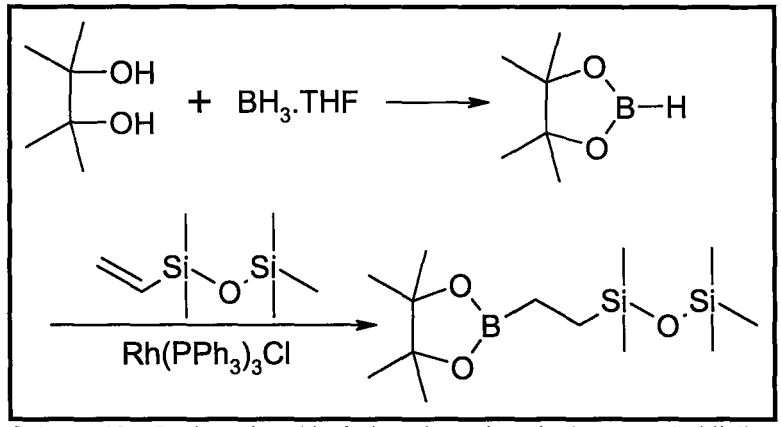


Scheme 12. Mechanism of alkene hydroborations mediated by $Rh(PPh_3)_3Cl$.Adapted from reference 26.

2.5 Results and discussion of metal-catalyzed hydroboration

Based on these reports, an attempt was made by us to convert the borane to a protected boronic acid. On the one hand, this will reduce the reactivity of the borane, such that catalysts will be needed. On the other hand, it was anticipated that the protected silicone borane could be directly formed. Thus, in this approach, borane (BH_3.THF) was protected with pinacol and the resulting dialkoxyborane was used as the hydroborating agent. The first attempt, a non-metal-catalyzed reaction of the protected borane with vinylpentamethyldisiloxane, led to 80 % recovery of the starting materials. Therefore, a catalyst had to be used. Based on the successful $Rh(PPh_3)_3Cl$ catalyzed hydroborations performed by Pereira and Srebnik,[31,32] we performed our reaction under the same conditions they have used. We started by protecting BH_3.THF with pinacol based on the

published procedure,[34] then after isolating the protected borane, it was redissolved in dry DCM, then added to the siloxane-alkene and catalyst mixture, (Scheme 13).



Scheme 13. Metal-catalyzed hydroboration using vinylpentamethyldisiloxane

The crude product was purified on a silica gel column, and ^{1}H-NMR, (Figure 4) of the pure compound, was recorded in $CDCl_3$ and proved to be exclusively the terminal regioisomer (yield =68%) which agrees with the findings of Pereira and Srebnik.[31] Based on the ^{1}H NMR spectra of crude and isolated product, there was no degradation occurred on the column. It is perhaps, therefore, not surprising that it is necessary to use somewhat harsh conditions to deprotect the pinacol.[35] Conditions that have to be used include both high and low pH, which are not tolerated by silicone linkages.[36]

The products of this kind of metal-catalyzed hydroboration are usually further reacted in a way that would cleave out the boron portion of the compound to eventually modify the organic part to give an alcohol or amine. In our particular case, however, we did not need to cleave the boron, and it was also necessary to keep the silicone backbone intact. Consequently, any protecting group should be designed to be eventually cleaved without affecting the siloxane backbone (Si-O-Si) or/and the boron-carbon bond.

However, initial experiments suggest that conditions required for the decomposition of the boron alkoxide aslso degraded the silicone.

As a consequence of the observations described above, a different strategy was employed: the hydrosilylation of boranes bearing alkenyl groups, as will be discussed in the following chapter.

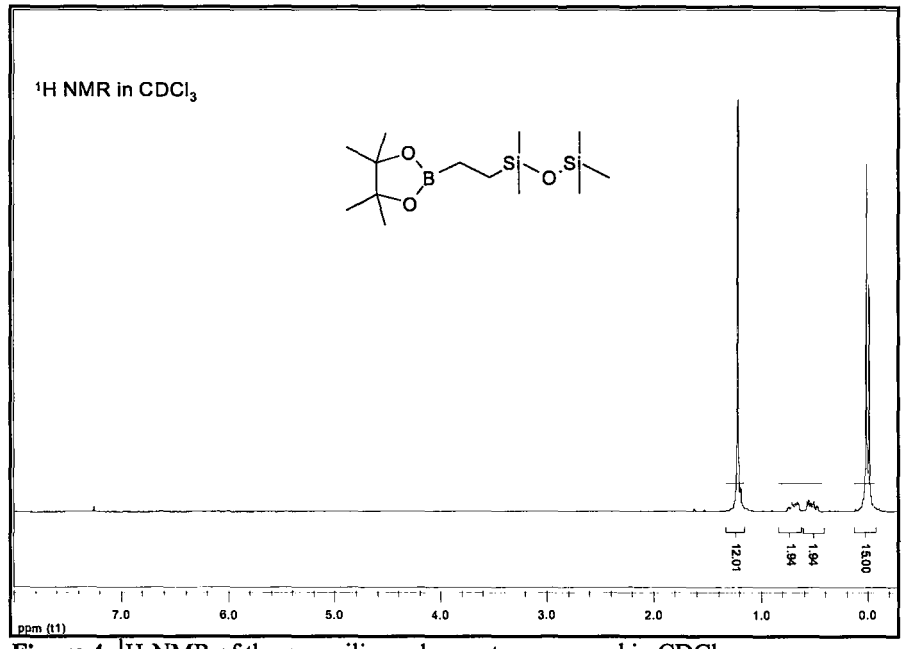


Figure 4. ^{1}H-NMR of the pure silicone boronate compound in $CDCl_3$

2.6 Experimental*

Materials

Trimethyl borate (98%), magnesium turnings (98%), pinacol (98%), BH_3.THF (1M solution) and chlorotris(triphenylphosphine)rhodium(I) were purchased from Aldrich. Vinylpentamethyldisiloxane and 1,3-bis(chloropropyl)tetramethyldisiloxane were purchased from Gelest. Purification using column chromatography was performed using silica gel 60 (230-400 Mesh ASTM) purchased from EMD; EMD also supplied anhydrous sodium sulfate. Reagent grade toluene, THF, diethyl ether, pentane, hexanes, and dichloromethane (DCM) were purchased from CALEDON. All reactions were carried out in dry solvents under an atmosphere of nitrogen. Solvents were dried using a SOLV-TEK drying system.

Equipment and measurements

^{1}H-NMR spectra were recorded at room temperature on a Bruker AV-200 (at 200.13 MHz) Fourier transform spectrometer. ^{1}H chemical shifts are reported with respect to $CDCl_3$ as an internal standard, set at 7.26 ppm. Coupling constants (*J*) are recorded in Hertz (Hz). The abbreviations, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, are used to report NMR spectra.

* Note: The experimental section of this chapter is very short as the notebook that contained the exact experimental details was lost during a fire in the lab. In addition, because the work associated with this chapter was not very promising, the committee

advised that only the work related to chapter III (hydrosilylation), which was more promising, should be repeated.

Preparation of Pinacolborane

A solution of pinacol (20 mmol, 2.36 g) in dry THF (10 mL) was stirred and cooled to 0 °C. A solution of BH_3.THF (20 mmol, 20 mL of 1.0 M in THF) was added dropwise, leading to effervescence. The reaction mixture was stirred for 1 h at 0 °C and was then warmed to 25 °C and stirred until no further evolution of hydrogen was observed (about 1 h). The solvent was evaporated and the crude oily product was used without further purification,

^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.23 (s, 12H).

Typical Procedure for the Hydroboration of Siloxane Alkenes by Pinacolborane Catalyzed by $Rh(PPh_3)_3Cl$.

To a 100 mL one neck round bottomed flask, $Rh(PPh_3)_3Cl$ (0.1 mmol, 92 mg) was introduced and dissolved in 10 mL dry CH_2Cl_2 at room temperature under an atmosphere of N_2. Then vinylpentamethyldisiloxane (10.0 mmol, 1.74 g) was added, followed by the dropwise addition of pinacolborane (10.0 mmol, 1.28 g dissolved in 20 mL dry CH_2Cl_2). The reaction mixture was stirred under an atmosphere of N_2 for 3 h at room temperature. CH_2Cl_2 was removed in *vacuo* to afford a dark residue, which was subjected to chromatography (silica gel, 95: 5 hexanes:ether) to yield a clear oil (2.05 g, 68% yield).

^{1}H-NMR (200 MHz, $CDCl_3$) δ -0.71-0.42 (m, 15H), 0.43-0.55 (m, 2H), 0.61-0.76 (m, 2H), 1.23 (s, 12H).

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CHAPTER THREE

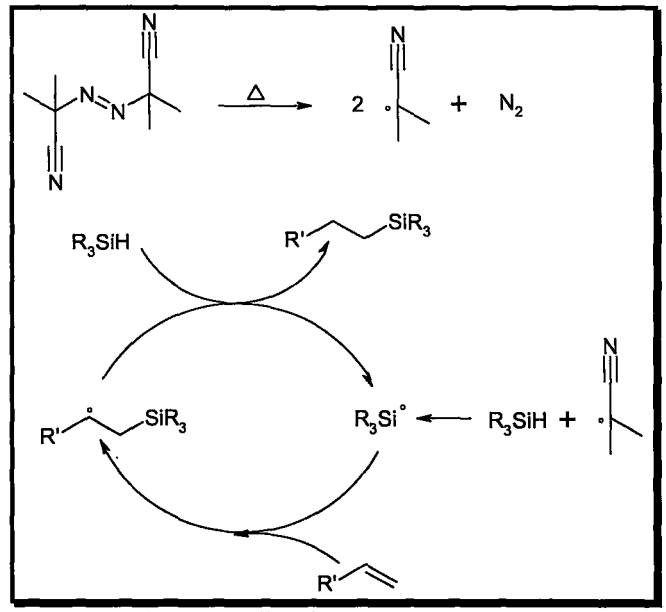
HYDROSILYLATION

3 Hydrosilylation

As we saw in Chapter 2, silicone-modified boronic acids are not readily accessible using Grignard chemistry, nor hydroboration. Therefore, we turned our attention to other approaches using hydrosilylation chemistry. Hydrosilylation is an addition reaction of a silicon-hydrogen bond across a π bond, mostly alkenes and alkynes. Hydrosilylation is a widely used synthetic tool in organic chemistry. The hydrosilylation reaction can be performed in the presence of a transition metal catalyst or initiated via a radical initiator source.[1]

3.1 Radical hydrosilylation

Radical hydrosilylation reactions, (Scheme 1), are very similar to carbon radical reactions. Both are performed under thermal or photochemical conditions and they involve the following sequence of steps: 1-initiation, 2-propagation, and 3-termination. In radical hydrosilylation, initiation step is usually started by heating a radical source to form the active radicals, e.g., azobis(isobutyronitrile) (AIBN). Once the active radicals have been formed, they can abstract hydrogen radicals from the silane (Si-H), which leads to the formation of a silyl radical ($R_3Si^{\bullet}$). In the propagation step, the newly formed silyl radical adds to the C=C bond, forming a new radical on one of the carbon atoms. In the termination step, the carbon radical abstracts a hydrogen radical from the silane to form the hydrosilylated compound and a new silyl radical, that can start another propagation step.[1]



Scheme 1. Radical hydrosilylation process. Adapted from reference 1, P401.

3.2 Metal-catalyzed hydrosilylation

Transition metal catalyzed hydrosilylation has been thoroughly studied.[2,3,4] A wide range of transition metal complexes have been used to catalyze the hydrosilylation reaction including catalysts based on: Pt [Karstedt's catalyst $[Pt_2(H_2C{=}CHSiMe_2)_2O)_3]$,[5,6] Speier's catalyst $[H_2PtCl_6]$,[7,8]); Rh $[(PPh_3)_2RhCl(CO)]$;[9] Ni $[CpNi(PPh_3)Ph$ and $\{CpNi(\mu\text{-}CO)\}_2$,[10] in addition to many other transition metal complexes.[1,2,3,4] Among all these hydrosilylation catalysts, platinum-based complexes have been the most important ones.

3.2.1 Platinum catalysts

Platinum catalysts are the most widely used in the hydrosilylation reaction. Usually, the hydrosilylation reaction requires low concentrations (ppm) of Pt catalysts to successfully catalyze the reaction. Hydrosilylation reaction can be homogenously catalyzed in both nonpolar solvents and polar solvents.[1] In addition to the homogenous

catalyzed reactions, heterogeneous supported Pt catalysts have been widely investigated by the Brook group and others.[11,12,13,14]

Interest in platinum based catalysts has been growing since Speier's reported that hexachloroplatinic acid (H_2PtCl_6)[7] was a very efficient and superior catalyst. The second generation of platinum catalysts was Karstedt's catalyst, (Figure 1), which was patented in 1974.[5]

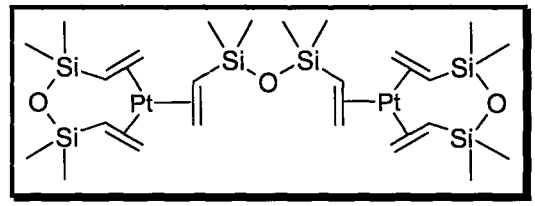
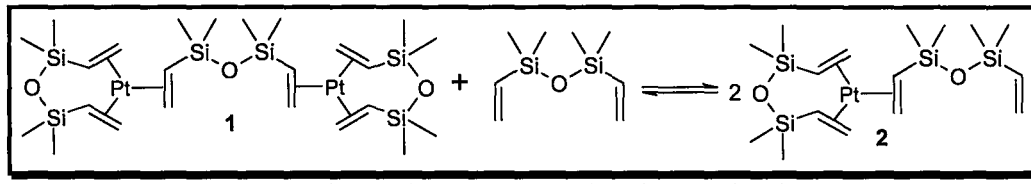


Figure 1. Karstedt's catalyst

Karstedt's catalyst can be prepared by the reaction of chloroplatinic acid with divinyltetramethyldisiloxane.[5] The active catalyst precursor is believed to be the Pt^0 complex[6,15] $[Pt_2((H_2C{=}CHSiMe_2)_2O)_3]$ **(1),** (Scheme 2), which was characterized in 1991 by Hitchcock, Lappert and Warhurst mainly by $^{195}Pt\{^1H\}$ NMR spectroscopy, and X-ray. In 1995, Lappert and Scott studied the reaction of Speier's catalyst $[H_2PtCl_6]$ with divinyltetramethyldisiloxane to give Karstedt's catalyst.[16] They found that adding an excess of the disiloxane to Karstedt's catalyst (**1**) will establish equilibrium between **1** and **2**, (Scheme 2); and by increasing the concentration of the disiloxane the equilibrium was shifted towards **2**. Also, they studied the liability of the bridging ligand of **1** in the presence of styrene and they found that **1** will favourably bind to the alkene, which will still have one vacant site for the oxidative addition step of $R_3Si\text{-}H$.[16]

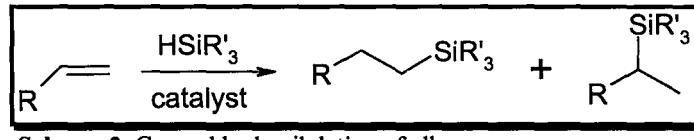


Scheme 2. Reaction of Karstedt's catalyst with excess divinyltetramethyldisiloxane. Adapted from reference 16.

3.3 Hydrosilylation of alkenes

Hydrosilylation of alkenes can yield different types of products. The variables that enable us to better control the reaction rate and type of product are the metal catalyst, hydrosilane, and the solvent used.[1]

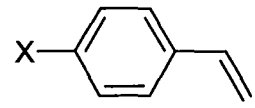
Hydrosilylation of alkenes usually produces two regioisomers via both terminal and internal additions, (Scheme 3). Platinum and rhodium catalysts generally yield the terminal products while palladium sometimes prefers the internal product.[4] Also, Fu of Dow Corning has shown that some organolanthanide catalysts favor the formation of the internal product.[17] Furthermore, Tanaka and co-workers[18] examined the hydrosilylation of styrene with different hydrosilanes using a neodymium catalyst and they were able to achieve high terminal product selectivity (up to 91%). The product distribution also depends on the ratio of the alkene and hydrosilane used; if large excess of alkene is used, hydrogenative hydrosilylation product becomes the major product.[19,20]



Scheme 3. General hydrosilylation of alkenes

It has been shown that electron withdrawing substituents on the hydrosilane increase the rate of Si-H addition to olefins, while electron donating groups decrease the

rate of addition.[21] Lewis has studied the effect of electronic factors on the rate of the hydrosilylation reaction of para-substituted styrenes,[21] he found that the relative activity for the addition of $(EtO)_3SiH$ to substituted styrenes depend on the type of the substituents, (Table 1). The rate of addition decreased in the following order: Me > H > OMe > Cl.



X	% Conversion
H	79.6
Me	99.7
OMe	68.6
Cl	58

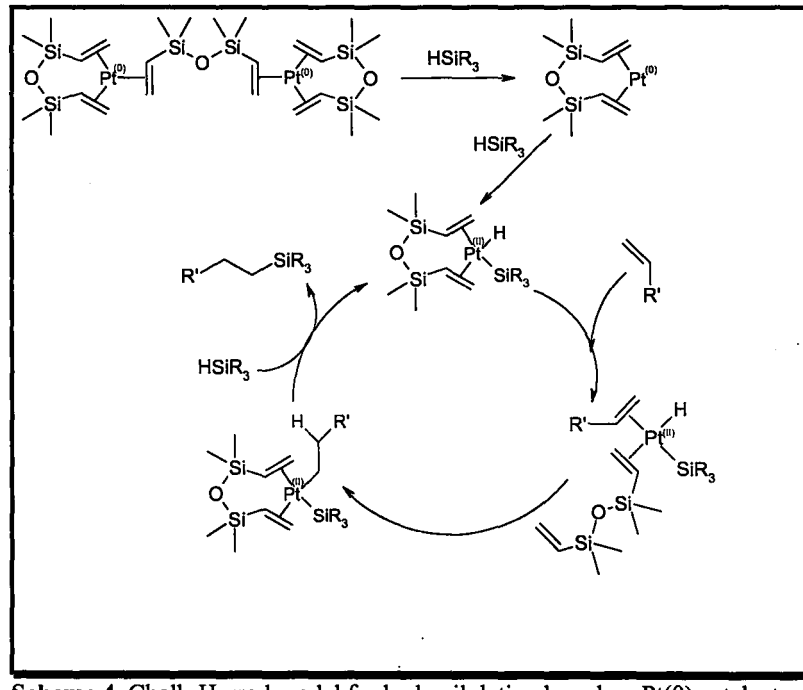
Table 1. Percent conversion for the reaction of $(EtO)_3SiH$ with various styrenes. Adapted from reference 21.

3.4 Mechanism of metal-catalyzed hydrosilylation

The mechanism of metal-catalyzed hydrosilylation is usually explained in terms of the Chalk-Harrod mechanism, which successfully explained most of the experimental observations. Chalk and Harrod proposed their mechanism based on isolated iridium complexes.[22,2] The general mechanism steps involve coordination of the metal center with the substrate alkene, oxidative addition of the hydrosilane to give a hydrido-silyl complex, and then the new complex undergoes migratory insertion of the alkene into the

M-H bond to give an alkyl-silyl intermediate. Finally, reductive elimination of the alkyl and silyl ligands forms the desired hydrosilylation product.

Lewis and co-workers[23] studied the mechanism of hydrosilylation using both Karstedt's and Speier's catalysts. They found that the labile vinylsiloxane ligands in Karstedt's catalyst are hydrosilylated away, providing a vacant coordination site on platinum, (Scheme 4), which accounts for the induction period associated with hydrosilylation reaction using Karstedt's and Speier's catalysts. Based on the presence of Pt-C and Pt-Si species during the reaction they concluded that the species responsible for hydrosilylation catalysis is mononuclear and homogenous. This was also supported by observations based on work done by Osborn and co-workers,[15] who used a quinone-modified Karstedt's catalyst and compared it to Karstedt's catalyst itself. They found that the naphthoquinone-modified catalysts are more active than Karstedt's catalyst.

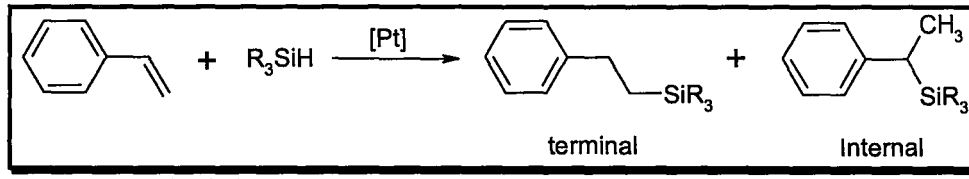


Scheme 4. Chalk-Harrod model for hydrosilylation based on Pt(0) catalysts.

3.5 Regiochemistry of the hydrosilylation of alkenes

The regioselectivity of Si-H bond addition to the C=C bond is an important issue associated with the hydrosilylation reaction. As mentioned earlier, the anti-Markovnikov addition of a hydrosilane to a terminal alkene yields the internal or branched (α) silyl product, while the Markovnikov addition of a hydrosilane yields the terminal or linear (β) silyl product.

Hydrosilylation of styrene using platinum catalysts have been studied extensively.[21,24] Typically, the products of hydrosilylation of styrene are composed of a mixture of terminal and internal isomers (60:40),[21] (Scheme 5).



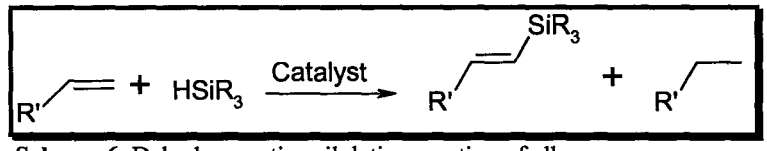
Scheme 5. Hydrosilylation of styrene using platinum catalyst.

Speier and Musolf studied the metal-catalyzed hydrosilylation of styrene derivatives, using Speier's catalyst and they found that a mixture of internal and terminal products is formed.[25] Also, they have studied the effect of changing the substituents on the benzene ring, on the terminal:internal products ratio. Unsubstituted styrenes gave a ratio of terminal: internal of 57:43 when Cl_3SiH was used as the silane and 69:31 when the silane used was $MeCl_2SiH$, which may be attributed to the larger steric demand of the latter. Both silanes were further investigated with the substituted styrenes and gave very close regiochemical results. Upon the introduction of Cl- group on the *ortho* position the ratio became 96:4 (terminal: internal), whereas the ratio was 68:32 when the Cl- group was in the *para* position. In addition, when the substituents were pentafluoro, the product

was exclusively the terminal isomer. Similarly, -2,4,5-trichloro, -2,6-dimethyl substituents gave the terminal product exclusively, which clearly shows the steric effect of the substituents.[25]

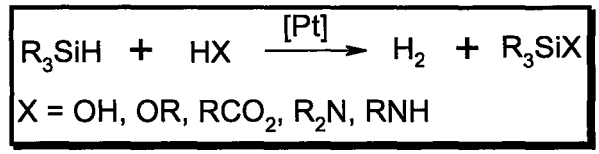
3.6 Side reactions

Metal-catalyzed hydrosilylation of alkenes can yield some side products such as those shown in (Scheme 6). Side reactions like isomerization and dehydrogenative silylation can be a problem in hydrosilylation reactions.



Scheme 6. Dehydrogenative silylation reaction of alkenes

One important side reaction that could accompany hydrosilylation reactions is catalyst poisoning, which usually takes place when a good nucleophile attackes the platinum center and replace the alkene. Also, alkene substrates that contain substituents with reactive hydrogens such as OH and NH react with hydrosilanes and give alkoxysilanes and hydrogen gas,[1,21,26] (Scheme 7). Caseri and Pregosin[26] have examined the alcoholysis of $PhMe_2SiH$ with different alcohols using *cis*-$PtCl_2(PhCH{=}CH_2)_2$ at room temperature and they found that the reaction is exothermic and leads to the formation of H_2 gas and the corresponding alkoxysilane ($PhMe_2SiOR$). On the other hand, the behavior of the –OH groups of a boronic acid compound is expected to be similar to that of alcohols, since they have similar pKa values. For example, the pKa[27] of phenylboronic acid is (8.8) which is comparable to that of phenol (9.9).



Scheme 7. Metal-catalyzed reaction of hydrosilanes and active hydrogens. Adapted from reference 1.

This reaction is much slower than the hydrosilylation reaction and can be minimized by using proper stoichiometry and controlling the reaction conditions, including lowering the temperature to -78 °C before adding the catalyst.[1] Simionescu and co-workers[28] have reported the hydrosilylation of a vinylpropyl alcohol and vinylethoxypropyl alcohol with pentamethyldisiloxane, tetramethyldisiloxane, and other polydimethylsiloxanes using Karstedt's catalyst and toluene as a solvent at room temperature. Based on ^{1}H-NMR, they found that the main product was the terminal addition isomer and that there were no side products of the possible condensation between the Si-H and hydroxyl groups. Nevertheless, they have noticed that the reactions were highly exothermic and the lower molecular weight hydrosiloxanes gave more exothermic reactions.

3.7 Our strategy

Our strategy is to synthesis siloxane boronic acids and boronates utilizing the hydrosilylation reaction. Combining these two functionalities into single molecules basically involves combining hydrophobic siloxane on one hand with a hydrophilic boronic acid on the other hand, which will lead to a new class of surfactants. We were aiming to develop a generic synthetic method that can be used for a wide variety of siloxanes. Silicones and boronic acids are each generally biocompatible and have been

used in pharmaceutical formulations and personal care products, which may promote these surfactant to be used in *in-vivo* or *in-vitro* applications.

In this work we performed metal-catalyzed hydrosilylation on boronic acid compounds which contain C=C bonds with mono- and di-functional hydrosiloxanes using Karstedt's catalyst. Our choice of catalyst was based on its commercial availability and its better reactivity as a hydrosilylation catalyst than Speier's catalyst.[29]

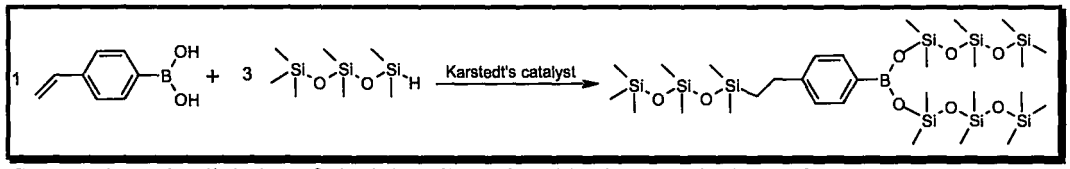
In this approach, both allylboronic acid and 4-vinylphenylboronic acid were investigated. We explored the hydrosilylation reaction under two main conditions: (1) hydrosilylation using protected boronic acids and (2) hydrosilylation using unprotected boronic acids. To our knowledge, there have been no reports about using the hydrosilylation reaction to prepare silicone-boronic acid compounds.

3.8 Results

3.8.1 Potential problems

As discussed earlier, active hydrogens including boronic acid hydrogens, BO-H, may react with hydrosilanes in the presence of a metal catalyst to produce the corresponding alkoxysilanes. We have confirmed that this side reaction can take place with in our system. The hydrosilylation of vinylphenylboronic acid with heptamethyltrisiloxane at room temperature using Karstedt's catalyst was very vigorous and produced a gas, presumably, hydrogen gas. To further confirm the side reaction, 1 equivalent of vinylphenylboronic acid was hydrosilylated using 3 equivalents of heptamethyltrisiloxane, (Scheme 8). After the solvent was evaporated using the rotovap, high vacuum was applied to make sure that any unreacted hydrosilane was evaporated

too. ^{1}H-NMR of the crude product showed that there was no vinyl hydrogens remaining and that the amount of CH_3 protons on silicon was triple the usual amount. This means that the hydrosilylation not only took place at the double bond but also at the two boronic acid O-H's.



Scheme 8. Hydrosilylation of vinylphenylboronic acid using 3 equivalents of hydrosilane

Although we attempted to purify the compound over silica gel using (80:20) hexanes: Et_2O, the trisilylated product was not retrieved. On the other hand, the monosilylated product was obtained in 53% yield, which we attributed to the hydrolysis of the BO-Si bond over silica gel.

In order to avoid the reaction of boronic acid hydrogens we applied two different techniques: (1) we started the reaction at low temperature (-78°C) and then let it heat up gradually or (2) we protected the boronic acid first and then do the hydrosilylation reaction.

3.8.2 Hydrosilylation of allylboronic acid

While some phenylboronic acids can be purchased as crystalline powders that can be handled in air, allylboronic acid is reported to be unstable and even the concentrated allylboronic acid is not stable under N_2.[30] The relative stability of phenylboronic acids, specifically the B-C bond is attributed to the fact that p-orbitals in the benzene ring

interact with empty p-orbitals of boron and strengthen the bond through a pπ-pπ interaction, (Figure 2).

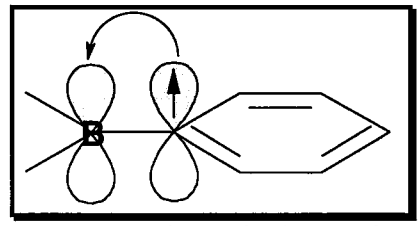
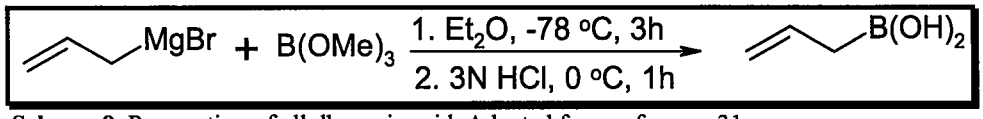


Figure 2. pπ-pπ interaction between boron and benzene ring

Allylboronic acid was prepared according to (Scheme 9), below, using a published procedure,[31] where allylmagnesium bromide in ether was added slowly to trimethoxyborane at -78 °C, under an atmosphere of N_2 and then quenched with aqueous hydrochloric acid. Evaporating the combined ether extracts after drying over Na_2SO_4, furnished a white solid with a low mass recovery (25 %).

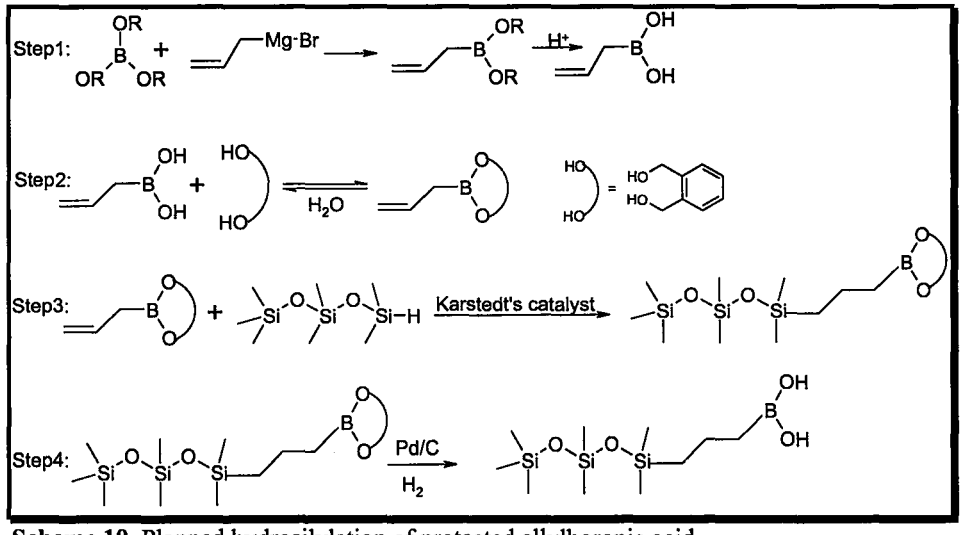


Scheme 9. Preparation of allylboronic acid. Adapted from reference 31.

^{1}H-NMR of the solid did not show any allyl protons peaks. This reaction was particularly challenging until we learned that concentrated allylboronic acid is not a stable compound even under an inert atmosphere, which is most probably due to an inter-nucleophilic attack between allylboronic acid molecules, where a lone pair on oxygen would attack a vacant p-orbital on boron of another molecule.

To overcome the stability problem of concentrated allyboronic acid, we attempted the hydrosilylation of allylboronic acid by first protecting the prepared allylboronic acid *in situ* and then employ the hydrosilylation reaction, (Scheme 10). We were able to confirm that the hydrosilylation reaction is taking place on the allyl group by following

the reaction using ^{1}H-NMR; both allyl multiplet around 6 ppm and Si-H multiplet around 4.7 ppm disappeared. On the other hand, purification on silica gel was not possible and the pure silicone-boronic acid or silicone-boronate could not be recovered, which was attributed to the hydrolysis of the protecting group on silica gel and then a subsequent interaction of the naked silicone-allylboronic acid with silica gel. Because of these stability issues of allylboronic acid we decided to use the significantly more stable 4-vinylphenylboronic acid, which is a commercially available air-stable crystalline powder.



Scheme 10. Planned hydrosilylation of protected allylboronic acid

Usually, if we need to protect boronic acids during synthesis we use a diol as a protecting group. The boronate formed is some times too stable and it's very difficult to deprotect it and get the free boronic acid afterwards. For example, boronates formed using pinacol require harsh conditions, including strong acids and bases, to cleave it.[32] Therefore, protection should be performed using a diol which can be cleaved in a way that would not affect the silicone backbone eventually e.g., deprotection has to be performed using relatively mild conditions. Morin *et al.*[33] have reported two reducible

protecting groups for boronic acids which can be readily prepared, namely, 1,2-benzenedimethanol[34] and 1,3-diphenylpropane-1,3-diol,[35] (Figure 3).

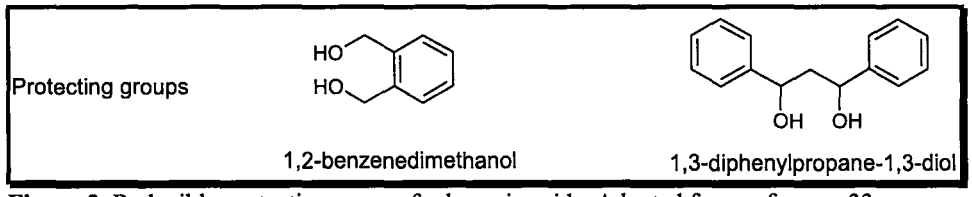
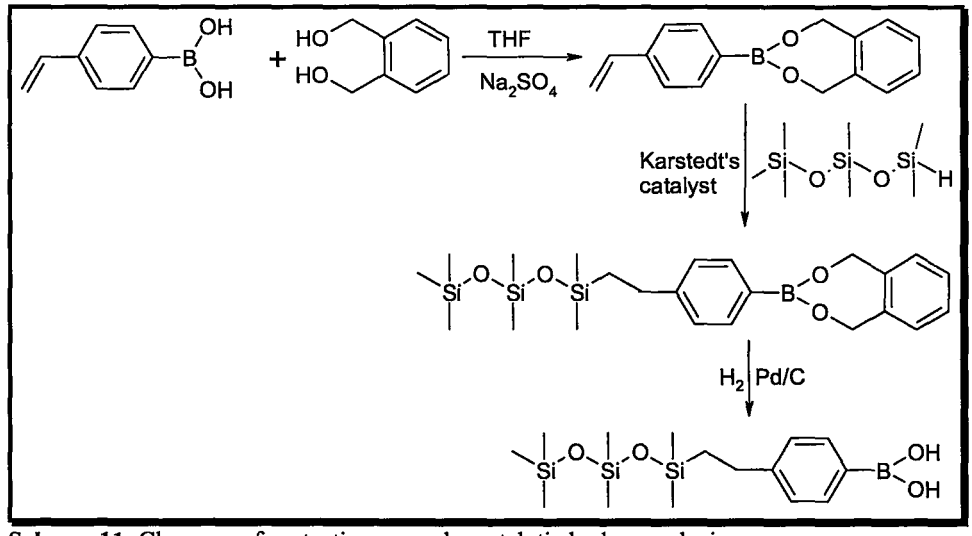


Figure 3. Reducible protecting groups for boronic acids. Adapted from reference 33.

These diols can easily form the corresponding esters with boronic acids in the presence of a dehydrating agent at room temperature and using THF as solvent. Regeneration of the boronic acid can be achieved efficiently by catalytic hydrogenolysis. We chose to work with 1,2-benzenedimethanol because the boronic acid can be regenerated by filtering the reaction mixture and evaporating the volatile byproduct, *o*-xylene, b.p.=143-145 °C; whereas, in the case of 1,3-diphenylpropane-1,3-diol, the separation of the non-volatile byproduct, 1,3-diphenylpropane, had to be done by extractive work up with an organic solvent such as CH_2Cl_2, which is not suitable with our products as they can be dissolved in CH_2Cl_2 too.

A model reaction, (Scheme 11), was performed to ensure the effectiveness of the catalytic hydrogenation under our reaction conditions and to make sure that hydrogenation in the presence of Pd/C is compatible with siloxanes. The product was prepared by first protecting 4-vinylphenylboronic acid, and then hydrosilylation was performed. Hydrogen gas, in the presence of Pd/C, was bubbled overnight through a solution of the crude product. A ^{1}H-NMR was taken after filtration and evaporation of the

volatiles, which positively proved that catalytic hydrogenolysis was working with out affecting our siloxanes.



Scheme 11. Cleavage of protecting group by catalytic hydrogenolysis

3.8.3 Hydrosilylation of 4-vinylphenylboronic acid

3.8.3.1 Protected 4-vinylphenylboronic acid

Platinum-catalyzed hydrosilylation of 1,2-benzenedimethanol-protected vinylphenylboronic acid (VPBA) was investigated using different hydrosiloxanes, (Figure 4), including mono- and difunctional hydrosiloxanes in addition to high molecular weight hydrosiloxanes.

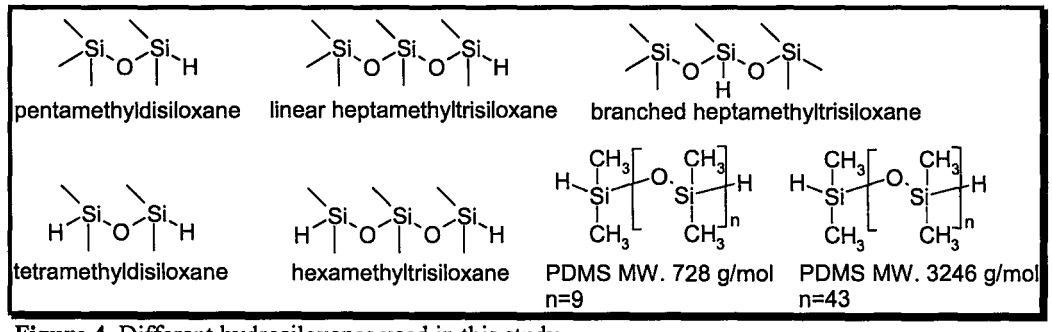


Figure 4. Different hydrosiloxanes used in this study

The hydrosilylation of all protected hydrosiloxanes was performed in toluene. The progress of the reaction was monitored with ^{1}H-NMR spectroscopy, which revealed gradual disappearance of peaks associated with Si-H (δ ~ 4.6 ppm) and vinyl (δ 5.2-6.8 ppm) groups and the appearance of new peaks in the methylene region (δ 0.5-2.7 ppm). The total disappearance of peaks associated with starting materials was only observed after refluxing in toluene for 24 hours. After the completion of the reaction, activated carbon was added to get rid of Pt nanoparticles. The products, silicone-boronates, were isolated by evaporating the solvent in *vacuo.*

Vinylphenylboronic acid and protected 4-vinylphenylboronic acid are analogous to *para*-substituted styrenes with an electron withdrawing group. The latter have been shown to be less reactive than the electron donating substituted analogs.[21] The inductive effect of the protecting group, 1,2-benzenedimethanol, renders the protected boronic acids even more electron withdrawing, and therefore even less reactive. This may explain why we needed higher temperatures, 115 °C (refluxing toluene), to bring the reactions to completion in the case of protected boronic acids, while refluxing THF (70 °C) was sufficient in the case of non-protected boronic acids. In some cases, hydrosilylation could not be driven to completion even after refluxing in toluene for 24 hours, for example with tetraisopropyldisiloxane, which is attributed to steric hindrance of the isopropyl groups. Based on ^{1}H-NMR, the reaction was only about 20 % complete, which is in agreement with the results Denmark and Wang[36] reported for the hydrosilylation of terminal alkynes. They reported that there no reaction taking place when either Karstedt's or Speier's catalyst were used to hydrosilylated terminal alkynes at 50 °C.

The regiochemistry of the hydrosilylation of protected boronic acids was expected to be similar of that of styrene, where the typical regioisomers ratio is 60:40 (terminal:internal).[21] Indeed, this was the case for most of the hydrosiloxanes used as shown in (Table 2). Although there was no obvious trend regarding regiochemistry of hydrosilylation, the highest terminal: internal ratios were obtained when branched heptamethyltrisiloxane was used, which can be attributed to steric factors.

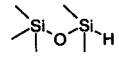
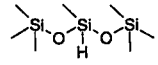
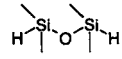
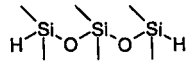
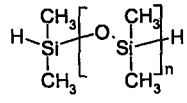
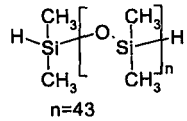
Hydrosiloxane	Terminal:internal	Yield (%)
	64:36	84
	75:25	89
	57:43	91
	51:49	93
	69:31	68
	63:37	91

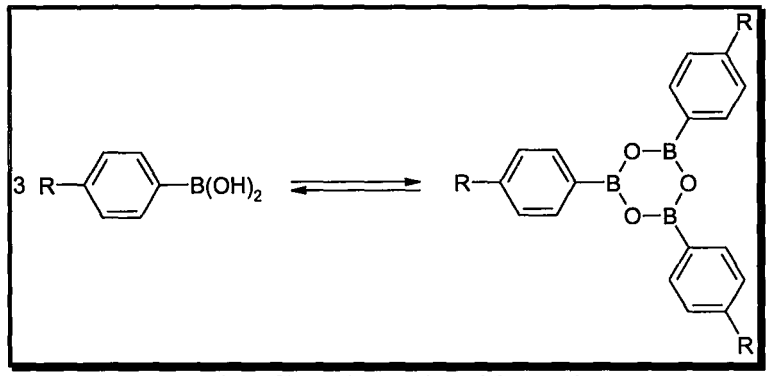
Table 2. Hydrosilylation of protected 4-vinylphenylboronic acid with different hydrosiloxanes using Karstedt's catalyst at 150 °C in toluene.

^{1}H-NMR data of the protected boronic acids shows that a mixture of two regioisomers (α and β) was formed in the case of monofunctional hydrosiloxanes, which

were assigned by the presence of two multiplets around 0.8 and 2.6 ppm. In addition, the singlet at around 5.2 ppm was assigned to the benzylic hydrogens. On the other hand, difunctional siloxanes showed more complex ^{1}H-NMR spectra because of the possibility of the formation of (αβ, αα, and ββ) regioisomers.

Infrared spectra of the protected VPBA, **8**, reveals the disappearance of the O-H bands, which were characteristic for both VPBA and 1,2-benzenedimethanol, confirming that the protection reaction was complete. On the other hand, the IR spectra of the hydrosilylated VPBA revealed two characteristic peaks; a very strong band attributed to the B-O stretch[27,37,38,39] (1350-1290 cm^{-1}) and another strong band attributed to the Si-O-Si stretch[37] (1030-1090 cm^{-1}). In addition, the disappearance of the Si-H band at around 2100 cm^{-1} indicates that the reaction was complete.

Mass spectroscopy provides very useful diagnostic information about boronic acid compounds and their boronate derivatives, which is marked by the presence of boron isotopic pattern, [(^{11}B:^{10}B) 80:20]. Nevertheless, due to the low volatility of these compounds, low intensity signals are usually obtained unless the presence of other functional groups is used to help increase the intensity. The low volatility of these compounds is attributed to the formation of the corresponding boroxines, (Scheme 12), which is facilitated by the gas phase dehydration.[27]



Scheme 12. Formation of boroxines. Adapted from reference 27

Mass spectra, ESI and MALDI-TOF, of the protected monofunctional hydrosilylation products show that deprotection is taking place during the ionization process. The main peaks were produced by the ammonium acetate, or formate, adducts with the deprotected siloxanes. However, molecular ion adducts were only associated with the protected pentamethyldisiloxane derivative. On the other hand, difunctional siloxanes did not show any possible adducts neither for the protected nor the non-protected boronic acid siloxane derivatives. Other low molecular fragment ions were present in various spectra such as: (MeSiO) 59 and (Me_3Si) 73.

^{13}C-NMR spin sort data for the protected compounds show two aliphatic CH_2 carbons(+), corresponding to the β hydrosilylation product, one CH_3 and one CH carbons, corresponding to the α hydrosilylation product, in addition to the benzylic carbons peak produced by the protecting group at around δ =67 ppm. Also, peaks corresponding to the two aromatic benzene rings appeared in the region between δ =127-134 ppm. Quaternary benzene ring carbons (+) appeared as low intensity peaks around δ =147 and 148 ppm. The ^{13}C signal corresponding to the quaternary carbon attached to the boron atom was usually not detected because of the line broadening associated with the short relaxation

time and the quadrupole moment of boron-11 (I=3/2).[27] This observation is in correspondence with the results of the study conducted by Voss and coworkers.[40] They studied ^{1}H and ^{13}C NMR chemical shift increments in different areneboronic acids. When they used $CDCl_3$ as a solvent, they were not able to detect the ^{13}C signal of the *ipso* position, while DMSO, a better solvent, allowed them to detect a broad signal at around 138 ppm corresponding to the carbon at the ipso position.

All ^{29}Si-NMR spectra show signals around δ=7 ppm, which correspond to terminal Me_3SiO- silicon and signals around δ=-20 ppm which correspond to internal O-$SiMe_2$-O silicon. The exception was compound **8**, which is consistent with reported values of ^{29}Si-NMR.[1,41,42] ^{29}Si-NMR chemical shifts (ppm) are summarized in (Table 3). Multiple values of ^{29}Si-NMR chemical shifts may be attributed to the presence of regioisomers and/or impurities.

Compound	^{29}Si-NMR chemical shifts (ppm)
8	7.461, 7.260, 5.509
10	7.738, 7.392, -22.223
11	7.801, 7.436, 6.299, 5.724, -21.380, -21.525
12	7.228, 7.055, 5.533, 5.427, -20.701
13	7.248, 5.632, -21.289, -21.849
14	7.176, 5.580, -21.374, -21.947

Table 3. ^{29}Si-NMR chemical shifts of siloxane boronates in $CDCl_3$

All ^{11}B-NMR spectra show a signal at about 27.3 ppm, which is consistent with the reported values of ^{11}B chemical shift for boronates.[33,43,44] ^{11}B-NMR chemical shifts (ppm) are summarized in (Table 4).

Compound	^{11}B-NMR chemical shifts (ppm)
8	27.259
10	27.284
11	27.269
12	27.254
13	27.154
14	27.081

Table 4. ^{11}B-NMR chemical shifts of siloxane boronates in $CDCl_3$

3.8.3.2 Deprotection of siloxane boronates on silica gel column

In the previous section, we discussed the need for protection chemistry in order to overcome the possible interactions of boronic acids with silica gel during purification. Also, we have rationalized our choice of the protecting group, 1,2-benzenedimethanol, which was associated with the sensitivity of siloxanes towards common deprotection methods of boronates.

Nonetheless, during our attempts to purify silicone boronates on silica we found that deprotection of 1,2-benezendimethanol took place on silica, affording the deprotected silicone boronates. The produced monofunctional siloxane boronic acids were pure but had lower yields than those prepared using the direct hydrosilylation without protection (see below). The yield of the purified pentamethyldisiloxane derivative was 42% and the

yield of heptamethyltrisiloxane derivative was 68%. On the other hand, protected difunctional siloxane boronates were deprotected on silica gel column with very low yields. The yield of the tetramethyldisiloxane derivative was 34%, while the hexamethyltrisiloxane derivative was isolated in 40%. Also, the fractions collected contained more impurities than the products obtained by the direct method.

3.8.3.3 Unprotected 4-vinylphenylboronic acid

Platinum-catalyzed hydrosilylation of unprotected vinylphenylboronic acid was also investigated using the same hydrosiloxanes used with protected VPBA. It had initially been expected that the free B-OH groups would interfere with C=C hydrosilylation. This turned out not to be the case if we initially run the reaction at low temperature (below 0 °C). Hydrosilylation of monofunctional hydrosiloxanes was performed in THF while a mixture of diethyl ether and toluene (1:5) was used for difunctional hydrosiloxanes for reasons of solubility. The progress of the reaction was followed using ^{1}H-NMR spectroscopy. The disappearance of peaks associated with Si-H ($\delta \sim 4.6$ppm) and vinyl (δ 5.2-6.8 ppm) groups and the appearance of new peaks in the methylene region (δ 0.5-2.7 ppm) indicated the completion of the reaction. Total disappearance of peaks associated with starting materials was observed after overnight reflux in THF for monofunctional hydrosiloxanes and only after 24 hours reflux in toluene for difunctional hydrosiloxanes. Karstedt's catalyst should be added at low temperature (less than 0 °C) since starting the reaction at higher temperature led to a very fast and exothermic reaction and unidentified products. After adding the catalyst at low

temperature, the reaction was allowed to reach room temperature and then refluxed. Activated carbon had to be added to the reaction mixture to adsorb colloidal platinum particles which can not be removed by filtration over Celite alone.

The amphiphilic nature of siloxane-boronic acid compounds makes their purification a very difficult task.[27] Although boronic acids can be generally crystallized, siloxane-boronic acids crystallization was not possible, mainly because of the presence of the siloxane backbone, which gives the products their oily nature. Also, all attempts to purify siloxane-boronic acids using silica gel columns failed because of the strong interaction with the stationary phase in addition to the possibility of siloxane hydrolysis over silica; elution was not successful even with polar eluting solvents such as methanol or (methanol-3% acetic acid). High vacuum distillation was also attempted to purify siloxane-boronic acids, where temperatures up to 160 °C and vacuum of (~ 0.1 mmHg) were reached,but with out any successful purification.

The only successful purification method was achieved by dissolving siloxane-boronic acids in a minimum amount of a slightly polar organic solvent, for example, dichloromethane, and then precipitating the impurities by adding excess nonpolar organic solvent such as pentane and cooling in the freezer. ^{1}H-NMR (200 MHz, CD_3OD) of the white precipitate showed only two major peaks at δ 2.16 and 2.39 (3:1), which indicates that it is not vinylphenylboronic acid.

The regiochemistry of siloxane boronic acid compounds was similar to that of siloxane boronates, with regioisomers ratios ranging from 60:40 (terminal:internal)[21] to about 80:20 as shown in (Table 5).

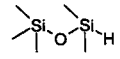
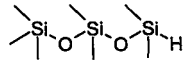
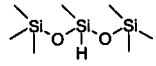
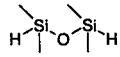
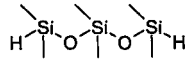
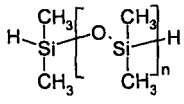
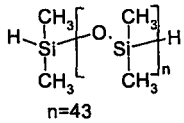
Hydrosiloxane	Terminal:internal	Yield (%)
	68:32	79
	64:36	93
	69:31	82
	78:22	86
	52:48	82
 n=9	66:34	73
 n=43	60:40	81

Table 5. Hydrosilylation of VPBA with different hydrosiloxanes using Karstedt's catalyst at 70 °C in THF

The ^{1}H-NMR data of siloxane boronic acids shows that a mixture of two regioisomers (α and β) was formed in the case of monofunctional hydrosiloxanes, which were assigned by the presence of two multiplets around 0.8 and 2.6 ppm. On the other hand, difunctional siloxanes showed more complex ^{1}H-NMR spectra because of the possibility of the formation of (αβ, αα, and ββ) regioisomers.

^{13}C-NMR spin sort data shows two aliphatic CH_2 carbons (+) corresponding to the β hydrosilylation isomer, in addition to one CH_3 and one CH carbons corresponding to

the α hydrosilylation isomer. Further more, two low intensity peaks appeared at around 147.00, 148.00 ppm, which correspond to quaternary phenyl ring carbons.

Infrared spectra of the starting material, 4-vinylphenylboronic acid, shows a peak at 3351 cm^{-1}, which corresponds to BO-H stretching frequency. However, the IR spectra of siloxane boronic acids did not show this peak; the disappearance of BO-H peak maybe attributed to the formation of the trimeric anhydride of boronic acids (boroxines), which are easily formed in anhydrous solvents because of their quasiaromatic nature.[27] In addition, the two strong bands corresponding to B-O stretching frequency (1350-1290 cm-^{1}), and Si-O-Si stretching frequency (1030-1090 cm^{-1}) were observed, while Si-H band at around 2100 cm^{-1} disappeared.

Mass spectra, ESI and MALDI-TOF, of monofunctional siloxane boronic acids shows the [M+ acetate]$^{-}$ signal in the negative mode and [M+ ammonium]$^{+}$ signal in the positive mode. On the other hand, difunctional siloxane boronic acids did not show any possible adducts with the molecular ion except for compound **5,** which shows the M^{+} ammonium peak at only 20% abundance.

All ^{29}Si-NMR spectra show signals between δ=7-11 ppm which correspond to terminal Me_3SiO- silicon and signals around δ=-20 ppm which correspond to internal O-$SiMe_2$-O silicon, except compound **1**, which is consistent with reported values of ^{29}Si-NMR.[1,41,42] ^{29}Si-NMR chemical shifts (ppm) are summarized in (Table 6). Multiple values of ^{29}Si-NMR chemical shifts may be attributed to the presence of regioisomers and/or impurities.

Compound	^{29}Si-NMR chemical shifts (ppm)
1	8.169, 7.689, 7.122, 5.372
2	7.297, 7.176, 7.074, 5.387, -20.647
3	8.016, 7.866, 7.505, 7.301, -20.651, -22.514
4[a]	8.065, 7.405, -10.174, -12.679, -21.062
5	7.159, 7.009, 5.473, -20.640
6	7.193, 5.580, -21.220, -21.897
7	11.115, -17.924

Table 6. ^{29}Si-NMR chemical shifts of siloxane boronic acids in $CDCl_3$. (a) Done in CD_3OD

All ^{11}B-NMR spectra of siloxane boronic acids, (Table 7), show a signal at about 28 ppm which is consistent with the reported values of ^{11}B chemical shift for boronic acids.[27,33,43]

Compound	^{11}B-NMR chemical shifts (ppm)
1	27.547
2	28.779
3	28.041
4[a]	28.959
5	28.457
6	28.394
7	28.657

Table 7. ^{11}B-NMR chemical shifts of silicone boronates in $CDCl_3$. (a) CD_3OD

3.9 Properties

3.9.1 Interfacial tension of siloxane boronic acids

Many types of polar groups in surfactant systems have been described but boronic acids have never been reported as a polar group with siloxanes. On the other hand, there have been few reports where boronic acids were used as the polar head in a surfactant system; Matondo and co-workers[45] have reported the synthesis of pyridinylboronic acids as novel amphiphilic compounds, while Baboulene and Toumelin[46] have reported the synthesis of aminoalkylboronic acid salts and studied their surfactant properties.

The amphiphilic nature of siloxane boronic acid compounds encouraged us to study their surface active properties. The limited solubility of our compounds in H_2O prevented us from studying their surface tension properties (H_2O/air interface). However, their solubility in chloroform enabled us to study their interfacial properties (liquid/liquid interface, usually H_2O and less polar liquid).

In order to measure the interfacial tension we used the pendant drop method, which uses a camera to follow the behaviour of a drop of a certain liquid upon interaction with the surface of another liquid. We have prepared different concentrations of each of our siloxane boronic acid compounds, ranging from 0.5-300 mM. The interfacial tension (IFT) (mN/m) of each compound individually was studied as a function of concentration (M).

All the compounds, except compound **1** (MW= 3246) were able to reduce the IFT between $CHCl_3$ and H_2O from 31.2 mN/m (control value) down to 5.7 mN/m in the case

of compound **2** (linear trisiloxane derivative). In addition, critical micelle concentrations (CMC) of these compounds were measured from the plotted graphs of IFT vs. concentration, via extrapolating the appropriate plateaus at which the IFT remained constant while increasing the concentration of the compound.[47] The difference (Δ) of interfacial tension values at CMC (IFT at CMC - IFT of control) and CMC values of these compounds are presented in (Table 8).

Compound	ΔIFT mN/m	CMC (M)
1	6.7	0.025
2	5.7	0.080
3	11.2	0.040
4[a]	8.5	0.016
5	13.7	0.017
6	8.7	0.010

Table 8. ΔIFT at CMC and CMC values of siloxane boronic acids in $CHCl_3$ tested in H_2O at RT

Among the monofunctional siloxane boronic acid compounds, compound 3 (branched heptamethyltrisiloxane derivative) was the most effective surfactant and lowered the interfacial tension by 11.2 mN/m at a CMC of 0.04 M, while compound 1 (disiloxane derivative) and 2 (linear trisiloxane derivative) lowered the IFT by only 6.7 and 5.7 mN/m, respectively. This maybe due to the more efficient spreading of the branched siloxane chain in chloroform as these three compounds have the same polar head. On the other hand, compound 5 (difunctional trisiloxane derivative) was the most effective compound among

the difunctional siloxane boronic acids and lowered the IFT by 13.7 mN/m at a CMC of 0.017 M. Generally, the difunctional siloxane boronic acids were more effective as surfactants than the monofunctional ones, which is maybe attributed to the presence of two boronic acid polar heads in these compounds. The difunctional siloxane derivative with higher MW=3246 did not behave as a surfactant. The IFT value increased by 2.25 mN/m instead of decreasing, which maybe attributed to the very large non-polar fragment (PDMS chain of n=43) compared to two polar boronic acid heads which maybe even buried inside the huge silicone chain.

3.10 Discussion

The protection of boronic acids leading to boronates was an effective tool to deactivate the B-OH groups, which are, as we have experienced, very reactive towards hydrosilylation reaction except if the reaction medium temperature is lowered (0 °C or below). After protecting the B-OH groups of the boronic acid, we were able to selectively hydrosilylate only the vinyl group on the phenyl ring. The conversion of B-OH groups to B-OR groups also made them less polar and less nucleophilic towards the platinum center, which in turn allowed the vinyl group to complex with platinum without competition from B-OH and therefore the desired reaction took place.

Thermodynamically, the stability of B-O bonds in boronic acids is comparable to that of their corresponding boronic esters.[27] Consequently, boronic esters are susceptible to hydrolysis when exposed to water or atmospheric moisture. Yamamoto and co-workers[48] have demonstrated that acyclic boronic esters hydrolyze very rapidly. Also, Roush and coworkers[49] have shown that small unhindered cyclic boronic esters, such as

those derived from ethylene and propylene glycols, are also hydrolyzed rapidly. Conversely, hydrolysis can be slowed down or even prevented, towards aqueous workup and silica gel chromatography, when hindered diols are used as the protecting groups, e.g., pinacol.[32] The protecting group of our choice, 1,2-benzenedimethanol, was hydrolyzed on silica affording the non-protected siloxane boronic acids but with relatively lower yields: upon extensive elution, the protecting group itself was retrieved.

Most boronic acids interact very strongly with silica gel which makes chromatography and TLC very difficult or impossible.[27] We have noticed that unprotected siloxane boronic acids spread all over the TLC plate and can not be eluted using silica gel chromatography, even when very polar solvents such as MeOH and (MeOH +3% CH_3COOH) were used. This property of boronic acids is likely, much like carboxylic acids, due to the strong interaction of the B-OH groups with the Si-OH groups on silica surface, which leads to their high degree of retention. This relatively high retention, due to surface interactions, may subsequently lead to the hydrolysis of the siloxane bonds, -Si-O-Si, leading to even more complicated interactions.

Boronic esters are less reactive than boronic acids towards silica gel, but the presence of H_2O on silica in addition to it's relatively acidic nature, pH= ~ 4.0, leads to the gradual hydrolysis of boronic esters. We believe that the initially hydrolyzed boronic esters did not escape from the column at all because the boronic acid produced had sufficient time to further react and hydrolyze on silica gel. On the other hand, the portions of boronic esters that were hydrolyzed only near the end of the silica gel column eluted, since there was not enough time for further surface reactions. We believe this is the

reason behind the low yields of the siloxane boronic acids retrieved after silica gel chromatography. Also, the difunctional siloxane boronates had even lower yields than the monofunctional ones because of their dual action on silica gel which means higher retention times and stronger interaction with silica.

3.11 Summary

In this work we have shown that siloxane boronic acids can be prepared via the hydrosilylation reaction using unprotected boronic acids in reasonable yields, but the purification of these siloxane boronic acids using silica gel is not possible. On the other hand, protected siloxane boronic acids can be purified on silica gel to furnish the corresponding pure siloxane boronic acids, after their spontaneous deprotection on silica, but with much lower yields.

The regiochemistry of hydrosilylation of vinylphenylboronic acid using both protected and unprotected boronic acids was in most cases similar to that of substituted styrene. There were no general trends among the different hydrosiloxanes for the regioselectivities observed.

Finally, we believe that we have developed a generic synthetic method that can be used to synthesize different siloxane boronic acid compounds irrespective of siloxane molecular weight, and branched or linear structure. These compounds have interesting surface activities as judged by their interfacial tension.

3.12 Conclusion

The goal of this work was to synthesize boronic acids-modified silicones. This goal was achieved using metal-catalyzed hydrosilylation reactions. We have used this methodology to successfully prepare a wide range of siloxane boronic acids, we have prepared: monofunctional- and difunctional- siloxane boronic acids, as well as branched, linear, and high molecular weight siloxane boronic acids.

Moreover, we have also shown that these compounds can be prepared using protected boronic acids, where deprotection takes place spontaneously on silica gel to furnish the pure boronic acid. Also, unprotected boronic acids were used to prepare the desired compounds with higher yields but lower purity as silica gel columns were not suitable to purify unprotected siloxane boronic acids.

The regiochemistry of the hydrosilylation reactions was studied based on ^{1}H-NMR spectroscopy. In addition, the prepared compounds were characterized using all the conventional techniques (^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, and ^{11}B-NMR, in addition to ESI-MS, and IR spectroscopy. There were no special regiochemical characteristics that could be attributed to the presence of the boronic acid.

We have also studied the interfacial tension properties of these siloxane boronic acids and found that they could be good compounds for surfactant applications since they have good surfactancy. The amphiphilic character of these compounds, in addition to the ability of boronic acids to bind sugars, makes them very good candidates as sugar-based surfactants. Moreover, the biocompatible nature of both parts (siloxane and boronic acid)

makes these compounds applicable as special emulsifiers in pharmaceutical and personal care formulations.

3.13 Experimental

3.13.1 Materials

1,1,1,3,5,5,5-Heptamethyltrisiloxane (97%), 1,1,3,3,5,5-hexamethyltrisiloxane (95%), Celite 521 (filtering agent), and 4-vinylphenylboronic acid were purchased from Aldrich. 1,1,1,3,3,5,5-Heptamethyltrisiloxane (90%), pentamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, hydride terminated polydimethylsiloxanes (MW= 728 and MW= 3246), and Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex in xylene, 2.1-2.4 % Pt) were purchased from Gelest. Purification using column chromatography was performed using silica gel 60 (230-400 Mesh ASTM) purchased from EMD; EMD also supplied anhydrous sodium sulfate. Reagent grade toluene, THF, diethyl ether, pentane, hexanes, and dichloromethane (DCM) were purchased from Caledon. All siloxane-boronic acid derivatives were prepared in dry solvents under an atmosphere of nitrogen. Solvents were dried using a SOLV-TEK drying system. The protecting group, 1,2-benzenedimethanol, was either purchased from Aldrich (97%) or prepared according to a literature procedure.[50]

3.13.2 Equipment and measurements

^{1}H and ^{13}C-NMR spectra were recorded at room temperature on a Bruker AV-200 (at 200.13 MHz for protons, 50.32 MHz for ^{13}C) Fourier transform spectrometer. ^{29}Si-NMR and ^{11}B-NMR were performed on a Bruker DRX-500 at 99.36 MHz and 160.46 MHz respectively. ^{1}H and ^{13}C-NMR spectra were also performed on a Bruker AV-600 (at 600.13 MHz for protons, 150.90 MHz for ^{13}C). ^{1}H chemical shifts are reported with

respect to $CDCl_3$ as an internal standard, set at 7.26 ppm. ^{13}C chemical shifts are reported with respect to $CDCl_3$ as an internal standard, set at 77.26. Coupling constants (*J*) are recorded in Hertz (Hz). The abbreviations, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, are used to report NMR spectra.

Infrared spectra were recorded on a Bruker Tensor 37 Fourier transform IR spectrometer. The abbreviations, s = strong, m = medium, w = weak, are used to report IR spectra. Electrospray ionization mass spectroscopy was performed using a Micromass Quattro LC system using both positive and negative modes.

3.13.3 Procedures and preparations

***General procedure 1 for the preparation of silicone boronic acids, shown for pentamethyldisiloxane derivative* 1.**

To a 100 mL one neck round bottomed flask, 4-vinylphenylboronic acid (1.48 g, 10.0 mmol), pentamethyldisiloxane (1.48 g, 10.0 mmol), and THF (50 mL) were added and stirred under an atmosphere of N_2. The mixture was cooled to -78 °C, then 5 drops of Karstedt's catalyst were added and the mixture was allowed to reach room temperature, and then refluxed over night at 70 °C. After that, carbon black (2 g) was added and the reaction was stirred for 1 h at 60 °C, followed by vacuum filtration over Celite 521. Finally, THF was removed in *vacuo* and the compound was purified by dissolving it in a DCM/pentane (or hexanes) (1:12) mixture and keeping it in the freezer over night, a

white-grayish precipitate was formed that was filtered off and solvents were removed in *vacuo* to afford a clear bright-yellow viscous liquid, (2.34 g, 79%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 68:32.

Isomer 1: terminal (major) **1t**.

^{1}H-NMR (CD_3OD) δ 0.04-0.06 (m, 15H), 0.79-0.94 (m, 2H), 2.57-2.65 (m, 2H), 7.02-7.16 (m, 2H), 7.43-7.63 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) (CD_3OD) δ -0.49(-), 1.55(-), 3.21(-), 21.09(+), 30.06(+), 127.48(-), 127.95(-), 134.69(-), 135.43(-), 148.00(+).

Isomer 2: Internal (minor) **1i**.

^{1}H-NMR (CD_3OD) δ 0.04-0.06 (m, 15H), 1.31 (d, J = 7.4 Hz, 3H), 2.14 (q, J = 7.4 Hz, 1H), 7.02-7.16 (m, 2H), 7.43-7.63 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) (CD_3OD) δ -0.49(-), 1.55(-), 3.21(-), 15.37(-), 31.96(-), 127.48(-), 127.95(-), 134.69(-), 135.43(-), 148.00(+).

^{29}Si-NMR ($CDCl_3$) δ: 8.169, 7.689, 7.122, 5.372; ^{11}B-NMR ($CDCl_3$) δ: 27.547

Mass spectrum: ESI- m/z, [M+ acetate]$^-$: 355; [M+ formate]$^-$: 341

FT-IR ν (cm^{-1}): (C-H) 2957 (w), (aromatic C=C) 1607 (w), (B-O) 1340 (s), (Si-O-Si) 1047 (s).

Preparation of 1,1,1,3,3,5,5-Heptamethyltrisiloxane derivative 2.

Procedure 1: 4-vinylphenylboronic acid (1.48 g, 10.0 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.47 g, 10.0 mmol); clear bright yellow viscous liquid, (3.47 g, 93%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 64:36.

Isomer 1: terminal (major) **2t.**

^{1}H-NMR ($CDCl_3$) δ 0.01-0.24 (m, 21H), 0.93-1.01 (m, 2H), 2.71-2.75 (m, 2H), 7.21-7.2 (m, 2H), 7.43-7.63 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$) δ -1.21(-), -0.71(-), 0.93(-), 1.93(-), 2.58(-), 20.80(+), 30.49(+), 127.76(-), 128.24(-), 136.19(-), 136.53(-), 150.86(+), 151.22(+).

Isomer 2: internal (minor) **2i.**

^{1}H-NMR ($CDCl_3$) δ 0.01-0.24 (m, 21H), 1.31 (d, J = 7.3 Hz, 3H), 2.14 (q, J =7.4 Hz, 1H), 7.21-7.2 (m, 2H), 7.43-7.63 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$) δ -1.21(-), -0.71(-), 0.93(-), 1.93(-), 2.58(-), 14.89(-), 32.90(-), 127.76(-), 128.24(-), 136.19(-), 136.53(-), 150.86(+), 151.22(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.297, 7.176, 7.074, 5.387, -20.647; ^{11}B-NMR ($CDCl_3$) δ: 28.779

Mass spectrum: ESI- m/z, [M+ acetate]$^{-}$: 429; ESI+ m/z, [M+ ammonium]$^{+}$: 388

FT-IR ν (cm^{-1}): (C-H) 2958 (w), (aromatic C=C) 1607 (m), (B-O) 1344 (s), (Si-O-Si) 1041 (s).

***Preparation of 1,1,1,3,5,5,5-Heptamethyltrisiloxane derivative* 3.**

Procedure 1: 4-Vinylphenylboronic acid (1.48 g, 10.0 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.29 g, 10.0 mmol); clear bright yellow viscous liquid, (3.04 g, 82%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 69:31.

Isomer 1: terminal (major) **3t.**

^{1}H-NMR ($CDCl_3$) δ -0.17-0.42 (m, 21H), 0.79-0.92 (m, 2H), 2.62-2.76 (m, 2H), 7.09-7.36 (m, 2H), 8.08-8.17 (m, 2H) ; ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ 0.45(-), 2.51(-), 2.62(-), 20.32(+), 30.41(+), 128.03(-), 128.25(-), 136.15(-), 136.54(-), 150.89(+).

Isomer 2: internal (minor) **3i**.

^{1}H-NMR ($CDCl_3$) δ -0.17-0.42 (m, 21H), 1.40 (d, *J* = 7.4 Hz, 3H), 2.22 (q, *J* = 7.3 Hz, 1H), 7.09-7.36 (m, 2H), 8.08-8.17 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ 0.45(-), 2.51(-), 2.62(-), 15.08(-), 32.42(-), 128.03(-), 128.25(-), 136.15(-), 136.54(-), 150.89(+).

^{29}Si-NMR ($CDCl_3$) δ: 8.016, 7.866, 7.505, 7.301, -20.651, -22.514; ^{11}B-NMR ($CDCl_3$) δ: 28.041.

Mass spectrum: ESI- m/z, [M+ acetate]$^-$: 429; ESI+ m/z, [M+ ammonium]$^+$: 388

FT-IR ν (cm^{-1}): (C-H) 2957 (w), (aromatic C=C) 1608 (w), (B-O) 1343 (s), (Si-O-Si) 1043 (s).

***General procedure 2 for the preparation of difunctional siloxanes, shown for 1,1,3,3-tetramethyldisiloxane derivative,* 4.**

In a 100 mL round bottomed flask, 4-vinylphenylboronic acid (0.74 g, 5.0 mmol) was dissolved in 10 mL diethyl ether, then 1,1,3,3 tetramethyldisiloxane (0.34 g, 2.5 mmol) and toluene (50 mL) were added and stirred under an atmosphere of N_2. The mixture was cooled to -78 °C, then 5 drops of Karstedt's catalyst were added and the mixture was allowed to reach room temperature, and then refluxed for 24 h at 115 °C.

After that, 2 g of carbon black was added and the reaction was mixed for 1 h at 60 °C, followed by vacuum filtration over Celite 521. Finally, toluene was removed in *vacuo* and the compound was purified by dissolving it in DCM/pentane (or hexanes) (1:12) mixture and keeping it in the freezer over night, a white-grayish precipitate was formed which was filtered off and solvents were removed in *vacuo* to afford a colorless viscous liquid, (0.93 g, 86%).

We report the NMR of two separate isomers (terminal: internal) formed in a ratio of 78:22. However, it was not possible to separate or determine by NMR the ratio of diterminal and diinternal compounds compared to the compound with one terminal and one internal silicone;

Isomer 1: terminal (major) **4t**.

^{1}H-NMR (CD_3OD) δ -0.02-0.35 (m, 12H), 0.86-0.94 (m, 2H), 2.61-2.69 (m, 2H), 7.07-7.18 (m, 2H), 7.43-7.64 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -0.75(-), 0.82(-), 1.81(-), 20.66(+), 30.11(+), 127.79(-), 128.04(-), 134.28(-), 135.51(-).

Isomer 2: internal (minor) **4i**.

^{1}H-NMR (CD_3OD) δ -0.02-0.35 (m, 12H), 1.339 (d, J = 7.4 Hz, 3H), 2.18 (q, J = 7.4 Hz, 1H),7.07-7.18 (m, 2H), 7.43-7.64 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -0.75(-), 0.82(-), 1.81(-), 14.81(-), 32.25(-), 127.79(-), 128.04(-), 134.28(-), 135.51(-).

^{29}Si-NMR (CD_3OD) δ: 8.065, 7.405, -10.174, -12.679, -21.062; ^{11}B-NMR (CD_3OD) δ: 28.959.

Mass spectrum: ESI- and ESI+ did not show any possible m/z adduct for the molecular ion. The highest MW peak was observed at m/z = 272 in the ESI+ mode and m/z =225 in the ESI- mode.

FT-IR ν (cm^{-1}): (C-H) 2961 (w), (aromatic C=C) 1607 (w), (B-O) 1329 (s), (Si-O-Si) 1046 (s).

***Preparation of 1,1,3,3,5,5-hexamethyltrisiloxane derivative* 5.**

Procedure 2: 4-vinylphenylboronic acid (1.48 g, 10.0 mmol), 1,1,3,3,5,5,-hexamethyltrisiloxane (1.1 g, 5.0 mmol), yellow transparent rubbery material, (2.08 g, 82%).

We report the NMR of two separate isomers (terminal: internal) formed in a ratio of 52:48. (Note: it was not possible to discriminate between mixture of the diterminal and diinternal compounds and the compound with one terminal and one internal silicone).

Isomer 1: terminal (major) **5t**.

^{1}H-NMR ($CDCl_3$+ 2 drops CD_3OD) δ -0.10-0.29 (m, 18H), 0.83-0.91 (m, 4H), 2.58-2.65 (m, 4H), 7.04-7.23 (m, 4H), 7.37-7.64 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$+ 2 drops CD_3OD) δ -1.29(-), -0.77(-), 0.85(-), 1.70(-), 20.72(+), 30.12(+), 127.57(-), 128.00(-), 133.95(-), 134.11(-).

Isomer 2: internal (minor) **5i**.

^{1}H-NMR ($CDCl_3$ + 2 drops CD_3OD) δ -0.10-0.29 (m, 18H), 1.35 (d, J = 7.3 Hz, 6H), 2.16-2.33 (m, 2H), 7.04-7.23 (m, 4H), 7.37-7.64 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and

*C*H$_3$ -, *C*H$_2$ and *C* +) ($CDCl_3$ + 2 drops CD_3OD) δ -1.29(-), -0.77(-), 0.85(-), 1.70(-), 14.87(-), 32.32(-), 127.57(-), 128.00(-), 133.95(-), 134.11(-).

^{29}Si-NMR ($CDCl_3$) δ: 7.159, 7.009, 5.473, -20.640; ^{11}B-NMR ($CDCl_3$) δ: 28.457.

Mass spectrum: ESI+ m/z, $[M+\text{ammonium}]^+$: 522

FT-IR ν (cm^{-1}): (C-H) 2959 (w), (aromatic C=C) 1607 (w), (B-O) 1340 (s), (Si-O-Si) 1039 (s).

***Preparation of hydride terminated polydimethylsiloxane derivative (MW = 728)* 6.**

Procedure 2: 4-vinylphenylboronic acid (1.48 g, 10.0 mmol), hydride terminated polydimethylsiloxanes MW 728 (3.6 g, 5.0 mmol); yellow highly transparent thin layer rubbery material, (3.75 g, 73%).

We report the NMR of two separate isomers (terminal: internal) formed in a ratio of 66:34. (Note: it was not possible to discriminate between mixture of the diterminal and diinternal compounds and the compound with one terminal and one internal silicone).

Isomer 1: terminal (major) **6t**.

^{1}H-NMR ($CDCl_3$+ 2 drops CD_3OD) δ -0.26-0.33 (m, 62H), 0.83-0.91 (m, 4H), 2.58-2.67 (m, 4H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.54-7.57 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H$_3$ -, *C*H$_2$ and *C* +) ($CDCl_3$+ 2 drops CD_3OD) δ -1.33(-), -0.69(-), 0.91(-), 1.80(-), 20.76(+), 30.47(+), 127.75(-), 128.24(-), 136.19(-), 136.52(-), 150.81(+).

Isomer 2: internal (minor) **6i**.

^{1}H-NMR ($CDCl_3$+ 2 drops CD_3OD) δ -0.26-0.33 (m, 62H), 1.34 (d, *J* = 7.5, 6H), 2.21 (q, *J* = 7.4, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.54-7.57 (m, 4H); ^{13}C-

NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$+ 2 drops CD_3OD) δ -1.33(-), -0.69(-), 0.91(-), 1.80(-), 14.87(-), 32.87(-), 127.75(-), 128.24(-), 136.19(-), 136.52(-), 150.81(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.193, 5.580, -21.220, -21.897; ^{11}B-NMR ($CDCl_3$) δ: 28.394.

Mass spectrum: ESI- and ESI+ and MALDI- TOF did not show any possible m/z adduct for the molecular ion. The highest MW peak was observed at m/z = 145 in the ESI+ mode and m/z = 103 in the ESI- mode.

FT-IR ν (cm^{-1}): (C-H) 2961 (w), (aromatic C=C) 1608 (w), (B-O) 1344 (s), (Si-O-Si) 1017 (s).

***Preparation of hydride terminated polydimethylsiloxane derivative (MW= 3246)* 7.**

Procedure 2: 4-vinylphenylboronic acid (0.30 g, 2.0 mmol), hydride terminated polydimethylsiloxanes MW 3246 (3.3 g, 1.0 mmol); yellow transparent very viscous liquid (2.87 g, 81%).

We report the NMR of two separate isomers (terminal: internal) formed in a ratio of 60:40. (Note: it was not possible to discriminate between mixture of the diterminal and diinternal compounds and the compound with one terminal and one internal silicone).

Isomer 1: terminal (major) **7t**.

^{1}H-NMR ($CDCl_3$) δ -0.22-0.57 (m, 268H), 0.92-0.96 (m, 4H), 2.61-2.70 (m, 4H), 6.98-7.36 (m, 4H), 8.13-8.17 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$) δ 1.02(-), 1.76(-), 2.49(-), 20.79(+), 30.48(+), 128.05(-), 128.24(-), 136.20(-), 136.53(-).

Isomer 2: internal silicone (minor) **7i.**

^{1}H-NMR ($CDCl_3$) δ -0.22-0.57 (m, 268H), 0.92-0.96 (m, 6H), 2.61-2.70 (m, 2H), 6.98-7.36 (m, 4H), 8.13-8.17 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ 1.02(-), 1.76(-), 2.49(-), 14.87(-), 31.04(-), 128.05(-), 128.24(-), 136.20(-), 136.53(-).

^{29}Si-NMR ($CDCl_3$) δ: 11.115, -17.924; ^{11}B-NMR ($CDCl_3$) δ: 28.657.

Mass spectrum: ESI- and ESI+ and MALDI-TOF did not show any possible m/z adduct for the molecular ion. The highest MW peak was observed at m/z = 2118 in the ESI+ mode and m/z = 1465 in the ESI- mode.

FT-IR ν (cm^{-1}): (C-H) 2962 (w), (aromatic C=C) 1720 (w), (Si-O-Si) 1011 (s).

Reactions with 1,2-benezenedimethanol-protected boronic acids

***Preparation of protected 4-vinylphenylboronic acid* 8.**

To a 100 mL one neck round bottomed flask, 4-vinylphenylboronic acid (2.96 g, 20.0 mmol), 1,2-benzenedimethanol (2.84 g, 20.0 mmol), 4 g molecular sieves and dry THF (60 mL) were added and stirred under atmosphere of N_2 for 1 h at room temperature then dried with anhydrous sodium sulfate and filtered. Finally, THF was removed in *vacuo* to afford light-yellow solid, (4.72 g, 95%).

^{1}H-NMR ($CDCl_3$) δ 5.28-5.33 (m, 1H), 5.28 (s, 4H), 5.83 (d, J = 17.6 Hz, 1H), 6.76 (dd, J = 10.8 Hz, *and* J = 17.6 Hz), 7.32-7.35 (m, 6H), 7.70 (d, J = 7.9 Hz, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ 67.29(+), 115.05(+), 126.10(-), 129.34(-), 129.56(-), 134.95(-), 137.87(-), 140.07(+).

Mass spectrum: ESI- m/z, $[M+ \text{formate}]^-$: 295; ESI+ m/z, $[M+H]^+$: 251

FT-IR ν (cm^{-1}): (C-H) 2892 (w), (aromatic C=C) 1605 (w), (B-O) 1290 (s).

***General procedure 3 for the preparation of protected siloxanes, shown for 1,1,1,3,3-Pentamethyldisiloxane derivative* 9**

In a 100 mL round bottomed flask, 1,2-benzenedimethanol-protected vinylphenylboronic acid **8** (1.25 g, 5.0 mmol), pentamethyldisiloxane (0.74 g, 5.0 mmol), toluene (50 mL), and 5 drops of Karstedt's catalyst were added and stirred under an atmosphere of N_2 at room tempeature. Then refluxed for 24 h at 115 °C. After that, 2 g of carbon black were added and the reaction was mixed for 1 h at 60 °C, followed by vacuum filtration over Celite 521. Finally, toluene was removed in *vacuo* to afford a yellowish soft paste (1.67 g, 84%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 64:36.

Isomer 1: terminal (major) **9t.**

^{1}H-NMR ($CDCl_3$) δ -0.12-0.08 (m, 15H), 0.86-0.91 (m, 2H), 2.51-2.66 (m, 2H), 5.24 (s, 4H), 7.01-7.16 (m, 2H), 7.29-7.34 (s, 4H), 7.61-7.68 (m, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.12(-), -0.60(-), 1.09(-), 2.76(-), 20.96(+), 30.29(+), 67.20(+), 127.33(-), 127.76(-), 129.25(-), 129.45(-), 134.39(-), 134.74(-), 140.13(+), 148.42(+).

Isomer 2: Internal (minor) **9i.**

^{1}H-NMR ($CDCl_3$) δ -0.12-0.08 (m, 15H), 1.34 (d, J = 7.4 Hz, 3H), 2.14 (q, J = 7.2 Hz, 1H), 5.24 (s, 4H), 7.01-7.16 (m, 2H), 7.34 (s, 4H), 7.61-7.68 (m, 2H); ^{13}C-NMR Spin Sort

(*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.12(-), -0.60(-), 1.09(-), 2.76(-), 14.93(-), 32.43(-), 67.20(+), 127.33(-), 127.76(-), 129.25(-), 129.45(-), 134.39(-), 134.74(-), 140.13(+), 148.42(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.461, 7.260, 5.509; ^{11}B-NMR ($CDCl_3$) δ: 27.259.

Mass spectrum: ESI- m/z, [M+ formate]$^-$: 443

FT-IR ν (cm^{-1}): (C-H) 2957 (w), (aromatic C=C) 1607 (w), (B-O) 1294 (s), (Si-O-Si) 1055 (s).

***Preparation of 1,1,1,3,5,5,5-Heptamethyltrisiloxane derivative* 10.**

Procedure 3: **8** (1.25 g, 5.0 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.15 g, 5.0 mmol); light-brown viscous liquid, (2.10 g, 89%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 75:25.

Isomer 1: terminal (major) **10t**.

^{1}H-NMR ($CDCl_3$) δ -0.10-0.11 (m, 21H), 0.76-0.84 (m, 2H), 2.57-2.66 (m, 2H), 5.25 (s, 4H), 7.14 (d, J = 7.8 Hz, 2H), 7.34 (s, 4H), 7.67 (d, J = 7.9 Hz, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.65(-), 0.51(-), 2.58(-), 2.69(-), 20.43(+), 30.18(+), 67.22(+), 127.64(-), 127.77(-), 129.27(-), 129.48(-), 134.42(-), 134.82(-), 140.17(+), 148.43(+)

Isomer 2: internal (minor) **10i**.

^{1}H-NMR ($CDCl_3$) δ -0.10-0.11 (m, 21H), 1.31 (d, J = 7.5 Hz, 3H), 2.09 (q, J = 7.4 Hz, 1H), 5.25 (s, 4H), 7.14 (d, J = 7.8 Hz, 2H), 7.34 (s, 4H), 7.67 (d, J = 7.9 Hz, 2H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.65(-), 0.51(-), 2.58(-), 2.69(-),

15.18(-), 31.93(-), 67.22(+), 127.64(-), 127.77(-), 129.27(-), 129.48(-), 134.42(-), 134.82(-), 140.17(+), 148.43(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.738, 7.392, -22.223; ^{11}B-NMR ($CDCl_3$) δ: 27.284.

Mass spectrum: ESI- m/z, [boronic acid + formate]$^-$: 415; ESI+ m/z, [boronic acid + ammonium]$^+$: 388. ESI- and ESI+ did not show any possible m/z adduct for the molecular ion.

FT-IR ν (cm^{-1}): (C-H) 2957 (w), (aromatic C=C) 1608 (w), (B-O) 1295 (s), (Si-O-Si) 1042 (s).

***Preparation of 1,1,3,3-tetramethyldisiloxane derivative,* 11.**

Procedure 3: **8** (1.25 g, 5.0 mmol), 1,1,3,3-tetramethyldisiloxane (0.34 g, 2.5 mmol); white gummy solid, (1.3 g, 91%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 57:43.

Isomer 1: terminal (major) **11t**.

^{1}H-NMR ($CDCl_3$) δ -0.12-0.19 (m, 12H), 0.76-0.91 (m, 4H), 2.47-2.67 (m, 4H), 5.24 (s, 8H), 7.01-7.30 (m, 4H), 7.34 (s, 8H), 7.60-7.68 (m, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.01(-), -0.56(-), 1.00(-), 1.15(-), 1.89(-), 20.93(+), 30.21(+), 67.20(+), 127.33(-), 127.76(-), 129.25(-), 129.45(-), 134.41(-), 134.74(-), 140.13(+), 148.53(+).

Isomer 2: internal (minor) **11i**.

^{1}H-NMR ($CDCl_3$) δ -0.12-0.19 (m, 12H), 1.34 (d, J = 7.4 Hz, 6H), 2.13 (q, J = 7.5 Hz, 2H), 5.24 (s, 8H), 7.01-7.30 (m, 4H), 7.34 (s, 8H), 7.60-7.68 (m, 4H); ^{13}C-NMR Spin Sort

(*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.01(-), -0.56(-), 1.00(-), 1.15(-), 1.89(-), 14.96(-), 32.43(-), 67.20(+), 127.33(-), 127.76(-), 129.25(-), 129.45(-), 134.41(-), 134.74(-), 140.13(+), 148.53(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.801, 7.436, 6.299, 5.724, -21.380, -21.525; ^{11}B-NMR ($CDCl_3$) δ: 27.269.

Mass spectrum: Mass spectrum: ESI- m/z, [boronic acid + acetate]$^-$: 489. ESI- and ESI+ did not show any possible m/z adduct for the molecular ion.

FT-IR ν (cm^{-1}): (C-H) 2957 (w), (aromatic C=C) 1606 (m), (B-O) 1293 (s), (Si-O-Si) 1053 (s).

***Preparation of 1,1,3,3,5,5-hexamethyltrisiloxane derivative* 12.**

Procedure 3: **8** (1.25 g, 5.0 mmol), 1,1,3,3,5,5-hexamethyldisiloxane (0.55 g, 2.5 mmol); white gummy material, (1.65 g, 93%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 51:49.

Isomer 1: terminal (major) **12t**.

^{1}H-NMR ($CDCl_3$) δ -0.07-0.08 (m, 18H), 0.84-0.87 (m, 4H), 2.59-2.63 (m, 4H), 5.24 (s, 8H), 7.03 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.34 (s, 8H), 7.63 (d, J = 7.5 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.39(-), -0.63(-), 0.95(-), 1.99(-), 20.78(+), 30.21(+), 67.19(+), 127.32(-), 127.74(-), 129.24(-), 129.44(-), 134.40(-), 134.72(-), 140.12(+), 148.48(+).

Isomer 2: internal (minor) **12i**.

^{1}H-NMR ($CDCl_3$) δ -0.07-0.08 (m, 18H), 1.33-1.37 (m, 6H), 2.05-2.25 (m, 2H), 5.24 (s, 8H), 7.03 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.34 (s, 8H), 7.63 (d, J = 7.5 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$) δ -1.39(-), -0.63(-), 0.95(-), 1.99(-), 14.93(-), 32.36(-), 67.19(+), 127.32(-), 127.74(-), 129.24(-), 129.44(-), 134.40(-), 134.72(-), 140.12(+), 148.48(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.228, 7.055, 5.533, 5.427, -20.701; ^{11}B-NMR ($CDCl_3$) δ: 27.254.

Mass spectrum: ESI- and ESI+ did not show any possible m/z adduct for the molecular ion. The highest MW peak was observed at m/z = 277 in the ESI+ mode and m/z = 553 in the ESI- mode.

FT-IR ν (cm^{-1}): (C-H) 2958 (w), (aromatic C=C) 1606 (m), (B-O) 1294 (s), (Si-O-Si) 1042 (s).

Preparation of hydride terminated polydimethylsiloxane derivative (MW = 728) **13.**

Procedure 3: **8** (0.50 g, 2.0 mmol), hydride terminated polydimethylsiloxanes MW 728 (0.72 g, 1.0 mmol); light-yellow viscous oil, (0.83 g, 68%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 69:31.

Isomer 1: terminal (major) **13t**.

^{1}H-NMR ($CDCl_3$) δ -0.02-0.17 (m, 62H), 0.86-0.95 (m, 4H), 2.61-2.69 (m, 4H), 5.25 (s, 8H), 7.05 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.38 (s, 8H), 7.65 (d, J = 7.8 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and CH_3 -, CH_2 and *C* +) ($CDCl_3$) δ -1.49(-), -0.64(-), 0.93(-), 1.84(-), 20.80(+), 30.21(+), 67.19(+), 127.33(-), 127.74(-), 129.24(-), 129.45(-), 134.40(-), 134.73(-), 140.14(+), 148.36(+).

Isomer 2: internal (minor) **13i**.

^{1}H-NMR ($CDCl_3$) δ -0.02-0.17 (m, 62H), 1.38 (d, J = 7.5 Hz, 6H), 2.21 (q, J = 7.5 Hz, 2H), 5.25 (s, 8H), 7.05 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.38 (s, 8H), 7.65 (d, J = 7.8 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.49(-), -0.64(-), 0.93(-), 1.84(-), 14.92(-), 32.37(-), 67.19(+), 127.33(-), 127.74(-), 129.24(-), 129.45(-), 134.40(-), 134.73(-), 140.14(+), 148.36.

^{29}Si-NMR ($CDCl_3$) δ: 7.248, 5.632, -21.289, -21.849; ^{11}B-NMR ($CDCl_3$) δ: 27.154.

Mass spectrum: ESI- and ESI+ did not show any possible m/z adduct for the molecular ion. The highest MW peak was observed at m/z = 180 in the ESI+ mode and m/z = 193 in the ESI- mode.

FT-IR ν (cm^{-1}): (C-H) 2961 (w), (aromatic C=C) 1610 (w), (B-O) 1296 (s), (Si-O-Si) 1017 (s).

Preparation of hydride terminated polydimethylsiloxane derivative (MW= 3246) **14.**

Procedure 3: **8** (0.25 g, 1.0 mmol), hydride terminated polydimethylsiloxanes MW 3246 (1.62 g, 0.5 mmol); yellow viscous oil, (1.72 g, 91%).

A mixture of two regioisomers (terminal: internal) was formed in a ratio of 63:37.

Isomer 1: terminal (major) **14t**.

^{1}H-NMR ($CDCl_3$) δ -0.01-0.37 (m, 267H), 0.83-0.92 (m, 4H), 2.58-2.67 (m, 4H), 5.24 (s, 8H), 7.02 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.34 (s, 8H), 7.65 (d, J = 7.9 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.54(-), -0.68(-),

1.02(-), 1.76(-), 2.50(-) 20.78(+), 30.18(+), 67.17(+), 127.30(-), 127.71(-), 129.21(-), 129.42(-), 134.37(-), 134.69(-), 140.10(+), 148.30(+).

Isomer 2: internal (minor) **14i**.

^{1}H-NMR ($CDCl_3$) δ -0.01-0.37 (m, 267H), 1.35 (d, J = 7.5 Hz, 6H), 2.18 (q, J = 7.5 Hz, 2H), 5.24 (s, 8H), 7.02 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0Hz, 2H), 7.34 (s, 8H), 7.65 (d, J = 7.9 Hz, 4H); ^{13}C-NMR Spin Sort (*C*H and *C*H_3 -, *C*H_2 and *C* +) ($CDCl_3$) δ -1.54(-), -0.68(-), 1.02(-), 1.76(-), 2.50(-) 14.88(-), 32.35(-), 67.17(+), 127.30(-), 127.71(-), 129.21(-), 129.42(-), 134.37(-), 134.69(-), 140.10(+), 148.30(+).

^{29}Si-NMR ($CDCl_3$) δ: 7.176, 5.580, -21.374, -21.947; ^{11}B-NMR ($CDCl_3$) δ: 27.081.

Mass spectrum: The highest MW peak was observed at m/z = 592 in the ESI+ mode and m/z = 1465 in the ESI- mode. ESI- and ESI+ did not show any possible m/z adduct for the molecular ion.

FT-IR ν (cm^{-1}): (C-H) 2962 (w), (B-O) 1258 (s), (Si-O-Si) 1010 (s).

3.14 References

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