

# Si-H-Si Stabilised OligosilanyIsilyl Cations and Dications with Multiple Si-H Functionalities

# Syntheses and Analyses by NMR Spectroscopy and Quantum Mechanical Methods

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#### Abstract

Silyl cations in general and silylium ions in particular are highly reactive silicon species. Due to the different size and electronegativity of carbon and silicon, the properties of silyl cations differ significantly compared to their lighter relatives, the carbocations. The trigonal-planar silylium ions [R<sub>3</sub>Si]<sup>+</sup> represent the archetype of silyl cations with silicon in the formal oxidation state +IV. Their synthesis and detection are only possible with sterically demanding substituents R that have additional electron-donating properties to attenuate the high Lewis acidity of the positive silicon centre. Additionally, stabilisation by Lewis-basic donor groups is possible. As examples, the coordination of solvents or anions as well as the formation of two-electron, three-centre (2e3c) Si-H-Si bonds can be used. Stabilisation by 2e3c Si-H-Si bonds can occur either intra- or intermolecularly and it allows to detect elusive and highly reactive cationic intermediates in rearrangement reactions of oligosilanes.

In the present thesis, the syntheses of Si-H-substituted oligosilanes, that contain up to four intramolecular Si-H functionalities, are described. The presence of Si-H groups allows the selective generation of cationic silicon centres by hydride transfer reactions following the Corey protocol. After hydride transfer reaction, the cationic charge is then stabilised by the formation of 2e3c Si-H-Si bridges. If multiple Si-H unit are present in the different oligosilanyl frameworks, it is examined how the additional Si-H units behave after formation of the oligosilanylsilyl cations. Depending on the molecular structure of the oligosilanylsilyl cation, intramolecular reactions under involvement of the 2e3c Si-H-Si bridge and the additional Si-H units are observed.

Furthermore, the presence of multiple Si-H units is used to synthesise, and NMR spectroscopically characterise the first example of an oligosilanylsilyl dication with two intramolecular 2e3c Si-H-Si bridges.

Additionally, the competition between stabilising effects due to the formation 2e3c Si-H-Si bridges and destabilising effects due to ring strain are investigated. It is shown that ring strain effects can lead to the formation of intermolecular instead of intramolecular Si-H-Si bridges even if their formation is entropically disadvantageous. This is observed if the formed rings after Si-H-Si bond formation are small and thus highly strained.

The structural properties of 2e3c Si-H-Si bridges in acyclic as well as (poly)cyclic oligosilanylsilyl cations are elucidated by quantum mechanical computations of the synthesised silyl cations and of various model compounds.

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#### Kurzzusammenfassung

Silylkationen im Allgemeinen und Silyliumionen im Besonderen sind hochreaktive Siliciumverbindungen, welche sich auf Grund der fundamentalen Unterschiede zwischen Silicium und Kohlenstoff signifikant von ihren leichteren Verwandten, den Carbokationen, unterscheiden. Die trigonal-planaren Silyliumionen [R<sub>3</sub>Si]<sup>+</sup> stellen hierbei die Prototypen der Silylkationen mit Silicium in der Oxidationsstufe +IV dar. Ihre Synthese und Detektion in kondensierten Medien gelingen nur mit sterisch anspruchsvollen Resten R, welche zugleich über elektronenschiebende Eigenschaften verfügen, um die hohe Lewisacidität des kationischen Siliciumzentrums abzuschwächen. Weiterhin ist die Stabilisierung über Lewis-basische Donorgruppen möglich. Beispiele hierfür liefern die Koordination von Lösungsmittelmolekülen oder Anionen sowie die Ausbildung von 2-Elektronen-3-Zentren-Bindung (2e3z) Si-H-Si Bindungen. Die Bildung der 2e3z Si-H-Si-Bindungen kann hierbei entweder intra- oder intermolekular erfolgen und es ist auf diese Weise möglich, hochreaktive, kationische Zwischenprodukte in Umlagerungsreaktionen von Oligosilanen zu detektiert.

In der vorliegenden Arbeit wird die Synthese von Si-H-substituierten Oligosilanen beschrieben, welche über bis zu vier intramolekulare Si-H-Einheiten verfügen. Das Vorhandensein von Si-H Gruppen ermöglicht die gezielte Erzeugung kationischer Ladungen im Oligosilangerüst durch eine Hydridtransferreaktion nach dem Corey Protokoll. Anschließend kommt es zur Stabilisierung der kationischen Ladung durch die Ausbildung von 2e3z Si-H-Si-Bindungen. Für den Fall, dass weitere Si-H-Funktionalitäten im Oligosilangerüst vorhanden sind, wird untersucht, wie sich diese zusätzlichen Einheiten verhalten. In Abhängigkeit von der molekularen Struktur der Si-H-Si-überbrückten Oligosilanylsilylkationen kommt es zu intramolekularen Reaktionen zwischen der gebildeten 2e3z Si-H-Si-Brücke und den verbleibenden Si-H-Einheiten.

Ebenso wird das Vorhandensein mehrerer Si-H-Einheiten genutzt, um das erste Beispiel eines Oligosilanylsilyldikations mit zwei intramolekularen 2e3z Si-H-Si-Brücken zu synthetisieren und mittels NMR-Spektroskopie zu untersuchen.

Weiterhin wird der Einfluss von Ringspannung aufgezeigt, indem die Konkurrenz zwischen stabilisierenden Effekten durch Ausbildung der 2e3z Si-H-Si-Bindungen und destabilisierenden Effekten durch die damit einhergehende Ausbildung kleiner, gespannter Ringe untersucht wird. Es wird gezeigt, dass die Ringspannung dazu führen kann, dass intermolekulare anstatt intramolekulare 2e3z Si-H-Si-Bindungen ausgebildet werden, obwohl deren Bildung entropisch benachteiligt ist.

Die strukturellen Eigenschaften von 2e3z Si-H-Si-Brücken in acyclischen, wie auch (poly)cyclischen Oligosilanylsilylkationen, werden mittels quantenmechanischer Berechnungen von Modelsystemen und von experimentell erhaltenen Oligosilanylsilylkationen beleuchtet.

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Für meinen Bruder

Fenno

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### 1. Introduction

#### 1.1. Oligosilanes

In general, the term *oligosilanes* is used for a class of compounds that contain multiple Si-Si bonds.<sup>[1]</sup> Oligosilanes are therefore the heavier congeners of alkanes. They can be further classified into non-functionalised and functionalised oligosilanes. In contrast to the C-H bond in alkanes, the Si-H bond is quite reactive. Therefore, *non-functionalised oligosilanes* is mostly used for polyalkylated and -arylated oligosilanes whereas (poly)hydrogenated oligosilanes are often counted as *functionalised oligosilanes*. Multiple reviews are published that enable an overview on oligosilanes and their characteristics.<sup>[2-7]</sup>

#### 1.2. Synthesis and Modification of Oligosilanes

A general access to oligosilanes is the use of Wurtz-type coupling reactions of silyl halides in the presence of alkali metals.<sup>[1, 8]</sup> This method often works quite well for smaller oligomeric silanes, for example disilanes,<sup>[9]</sup> and cyclic oligosilanes.<sup>[10-11]</sup> One notable example is the synthesis of the widely applied tetrakis(trimethylsilyl)silane, Si(SiMe<sub>3</sub>)<sub>4</sub> (**1**), which can be synthesised in a Wurtz-type coupling reaction starting from Me<sub>3</sub>SiCl and SiCl<sub>4</sub>. In this case, the Wurtz-type reaction enables the isolation of **1** in good yields (Scheme 1).<sup>[12]</sup>



Scheme 1: Wurtz-type coupling used to synthesise Si(SiMe<sub>3</sub>)<sub>4</sub> (1) from SiCl<sub>4</sub> and Me<sub>3</sub>SiCl.<sup>[12]</sup>

Unfortunately, Wurtz-type coupling reactions are often accompanied by side-reactions which result in the formation of mixtures instead of only one defined oligosilane.<sup>[13]</sup> As a result, further steps are necessary to isolate the target compounds. Such purification steps are often difficult to perform as the obtained oligosilanes have similar chemical and physical properties.<sup>[10]</sup> The need for quite harsh reaction conditions in combination with the inability to synthesise asymmetric products are other drawbacks of Wurtz-type coupling reactions to generate oligomeric silanes.<sup>[1]</sup> To circumvent the disadvantages, alternative synthetic protocols are needed. While electrochemical methods<sup>[8, 14-16]</sup> as well as dehydrocoupling reactions of hydrosilanes are possible,<sup>[8, 17-19]</sup> they are often not the methods of choice. Instead, multiple reaction procedures were developed which separate the two silyl moieties that are to be fused together in an electrophilic and a nucleophilic component (Scheme 2).

$$\begin{array}{rcl} & & & & & & & & \\ R_{3}Si^{+}LG & + & & & & M-SiR'_{3} & & \underline{Si-Si \ bond \ formation} \\ Silyl \ electrophile & & & Silyl \ nucleophile & & & \\ Silyl \ nucleophile & & & \\ LG = Leaving \ group \ (e.g. \ halide, \ triflate) \\ M = Electropositive \ metal \ (e.g. \ Li, \ Na, \ K) \end{array}$$

Scheme 2: Formation of Si-Si bonds by salt elimination reaction between a silyl electrophile and a silyl nucleophile.

Silyl compounds acting as electrophiles are widely available. Classical examples are silyl halides or silyl triflates. Exemplarily for silyl halides, access to different silyl chlorides (Scheme 3) is possible by chlorination reactions using acetyl chloride and AlCl<sub>3</sub>,<sup>[20]</sup> chlorination of hydrosilanes with trichloro*iso*cyanuric acid (TCCA),<sup>[21]</sup> or the chlorination of Si-H groups in CCl<sub>4</sub>.<sup>[22-24]</sup>



Scheme 3: Examples for different ways to obtained chlorosilanes.<sup>[20-23]</sup>

Extensive studies by Uhlig and co-workers also showed manyfold ways to synthesise silyl triflates from various starting materials and their subsequent functionalisation.<sup>[25-31]</sup> Thus, it is possible to obtain silyl triflates or even polytriflates from silyl compounds  $R_3SiX$  (X = NEt<sub>2</sub>, allyl, aryl, Cl, alkenyl, H, alkyl). The tendency to react with different groups X and to form the silyl

triflate decreases in the order NEt<sub>2</sub> > allyl, aryl > Cl > ethynyl > H  $\gg$  alkyl.<sup>[25, 27, 29-32]</sup> Often, phenyl substituents are chosen as reactive groups in the reaction with triflic acid to obtain silyl triflates. In course of the reaction (Scheme 4), the phenyl substituent of the phenyl-substituted silanes **2** gets protonated by the strong triflic acid.



Scheme 4: Mechanism for the protodesilylation of phenylsilanes using triflic acid.

Subsequently, the protonated aryl substituent is split off under formation of the silyl triflates **3** as well as benzene. If phenyl derivatives are used as leaving group, the reaction rate depends on the electronic properties of the aryl substituents. In general, electron-rich aryl substituents have a higher tendency to react than electron-poor aryl groups.<sup>[26]</sup> Apart from being electrophilic reagents in Si-Si bond forming reactions, the obtained silyl triflates **3** can also serve as starting materials for the introductions of various groups into the silyl framework. Hence, the reactions with inorganic halide salts enable to introduce of Si-Halogen functionalities, while reaction of the silyl triflate with hydride sources, e.g. Li[AIH<sub>4</sub>], allows the synthesis of hydrosilanes (Scheme 5).<sup>[28]</sup>



Scheme 5: Exemplary use of silyl triflates to introduce Si-H or Si-Halogen functionalities.<sup>[27-28, 33]</sup>

The situation is slightly more complicated for silvl compounds that can act as the nucleophilic component during the Si-Si bond forming reactions between silvl electrophiles and silvl nucleophiles (Scheme 2). The archetype of a silvl nucleophile, the silvl anion (*silanide*), differs from its carbon analogue, the carbanion. While carbanions are usually obtained in a convenient way by deprotonation of acidic C-H groups,<sup>[34]</sup> the situation cannot be directly transferred to silicon. Due to its decreased electronegativity compared to carbon (EN = 2.20 (H), 2.55 (C), 1.90 (Si) on the Pauling scale),<sup>[35]</sup> the Si-H hydrogen substituent is rather hydridic than protic.

As a result, other synthetic procedures are often needed.<sup>[1, 36]</sup> Early attempts where performed using the heterolytic Si-Si cleavage by organolithium compounds,<sup>[37-39]</sup> alkali metals,<sup>[40]</sup> or alkali ethanolates.<sup>[41-42]</sup> Thus, (Me<sub>3</sub>Si)<sub>3</sub>SiLi (**4**) can be obtained by Si-Si bond cleavage of pentasilane **1** using MeLi (Scheme 6). While lithium silanide **4** was successfully applied in various chemical reactions to introduce the so called *hypersilyl* group (Si(SiMe<sub>3</sub>)<sub>3</sub>),<sup>[43-49]</sup> the generation of silanides using MeLi is accompanied by some drawbacks.<sup>[50]</sup>

Lithium tris(trimethylsilyl)silanide

Scheme 6: Synthesis of lithium tris(trimethylsilyl)silanide (4) by Si-Si bond cleavage reaction between 1 and MeLi.<sup>[37]</sup>

One drawback can be exemplified if MeLi is reacted with larger oligosilanes than **1**. Hence, it was shown, that the reaction of MeLi with  $(Me_3Si)_3SiSi(SiMe_3)_3$  (**5**) resulted in the exclusive scission of the inner Si-Si bond resulting in the formation of one equivalent  $(Me_3Si)_3SiLi$  (**4**) and the tetrasilane MeSi(SiMe\_3)\_3 (Scheme 7, reaction a).



Scheme 7: Synthesis of lithium silanides by Si-Si bond cleavage reactions of oligosilane **5** by a) MeLi and b) bulkier cleavage reagents resulting in the formation of different silanides **4**, **6** and **7**.<sup>[51]</sup> The respective cleaved bonds are marked in red.

On the other hand, reaction of oligosilane **5** with more bulky cleavage reagents, e.g.  $Ph_3SiLi$  or **4**, resulted in the cleavage of the external Si-Si bonds (Scheme 7, reaction b).<sup>[51]</sup> As a result, mixtures of the monoanion **6** and dianion **7** were obtained.

Additional trials with the oligosilane **8** showed that preferentially the external Si-Si bonds were cleaved by MeLi (Scheme 8).<sup>[52]</sup> Depending on the stoichiometry, either the monoanion **9** or the dianion **10** were obtained.

Scheme 8: Synthesis of lithium silanides by Si-Si bond cleavage reactions of oligosilane 8 resulting in the bond cleavage of external Si-Si bonds. Depending on the stoichiometry, either monoanion 9 or dianion 10 are obtained.<sup>[52]</sup> The respective cleaved bonds are marked in red.

In contrast, the same study showed that the use of  $Me_2Si(Si(SiMe_3)_3)_2$  (11) resulted in the exclusive cleavage of one inner Si-Si bond (Scheme 9).<sup>[52]</sup> As a result, the lithium silanide 4 and the pentasilane 1 were formed.



Scheme 9: Synthesis of lithium silanides by Si-Si bond cleavage reactions of oligosilane **11** resulting in the bond cleavage of an internal Si-Si bond.<sup>[52]</sup> The respective cleaved bond is marked in red.

These observations illustrate that the outcome of the bond cleavage reactions is highly dependent on the used starting materials. While a large portion of the differences in reactivity can be explained by steric reasons, there is likely significant contribution from electronic effects.<sup>[52]</sup> Additionally, it was shown that for some reactions, the use of potassium silanides instead of respective lithium silanides can be favourable.<sup>[50]</sup> Therefore, an alternative access to potassium tris(trimethylsilyl)silanide, (Me<sub>3</sub>Si)<sub>3</sub>SiK (**12**), and ultimately silylsilanides in general was published by Marschner and co-workers.<sup>[50]</sup> For their synthesis of potassium silanide **12**, they used the Si-Si bond cleavage reaction of **1** with potassium *t*-butylate (Scheme 10).



Potassium tris(trimethylsilyl)silanide

Scheme 10: Synthesis of potassium tris(trimethylsilyl)silanide (**12**) by reaction of **1** with potassium *t*-butylate (K[O*t*-Bu]).<sup>[50]</sup>

The reaction proceeded in a clean manner with quantitative formation of the silanide. During the cleavage of the Si-Si bond, a trimethylsilyl group is abstracted and the ether Me<sub>3</sub>SiOt-Bu is formed. The reaction with potassium t-butylate was chosen as it is a very benign reagent that had already indicated its potential to cleave Si-Si bonds in the reaction with dodecamethylcyclohexasilane.<sup>[53]</sup> Additionally, potassium t-butylate is a solid and therefore easy to handle and simple to weigh accurately. In contrast, the concentration of MeLi-containing solutions can fluctuate. It is also less air- and moisture-sensitive than MeLi and non-flammable. Additionally, Marschner and co-workers were able to show that potassium t-butylate can cleave Si-Si bonds with a higher selectivity than MeLi. The group applied this knowledge in the synthesises of a wide variety of oligosilanes and oligosilanyl-substituted compounds.<sup>[50, 54-70]</sup> They also showed the possibility to obtain oligosilanylsilyl dianions,<sup>[57, 62-68,</sup> <sup>71-75]</sup> or even trianions,<sup>[74]</sup> using potassium *t*-butylate and the appropriate starting materials. Furthermore, it was shown that the method can be applied in the synthesis of (Me<sub>3</sub>Si)<sub>3</sub>GeK<sup>[76]</sup> and (Me<sub>3</sub>Si)<sub>3</sub>SnK.<sup>[77]</sup> Their synthetic potential was demonstrated as all three compounds (Me<sub>3</sub>Si)<sub>3</sub>EK (E = Si, Ge, Sn) were successfully used to obtain various transition metal and lanthanide complexes.[61, 78-80]

In a more recent example, it was shown that potassium tris(trimethylsilyl)silanide (**12**) can act as starting material in a multiple silyl exchange reaction with fluorosilanes which allows to synthesise acyclic, cyclic and even spirocyclic oligosilanes **13-15** (Scheme 11).<sup>[68]</sup>



Scheme 11: Synthesis of a) acyclic, b) cyclic and c) spirocyclic oligosilanes by multiple silyl exchange reactions between potassium silanide **12** and various fluorosilanes.<sup>[68]</sup>

The mechanism of the exchange reaction was postulated to be based on an equilibration process (Scheme 12). The silanide (nucleophile) attacks the fluorosilane (electrophile) whereby an anionic transition state with a pentacoordinated silicon atom is formed. The fluoride at the pentacoordinated silicon atom attacks a trimethylsilyl group in  $\beta$ -position and trimethylfluorosilane as well as a new silanide are formed. Due to the volatility of the formed fluorosilane, the equilibrium is driven to the right side.



Scheme 12: Postulated mechanism of the silyl exchange reaction between a silanide and a fluorosilane. [68]

If an excess fluorosilane is present, the exchange reaction can occur repeatedly under formation of trimethylfluorosilane and the respective substituted potassium silanides. In the last step of the exchange reaction, salt elimination occurs leading to the formation of potassium fluoride and the neutral silane. While salt elimination was described to be unfavoured

#### Introduction

compared to the attack of the fluoride at the silvl group in  $\beta$ -position, it can still occur prematurely. In this case, the reaction can be restarted by additional potassium *t*-butylate. A new silanide is formed which can further react with the remaining fluorosilane.

The phenylsilanide PhMe<sub>2</sub>SiLi (**16**) is another example for a suitable nucleophile in the synthesis of defined oligomeric silanes. It can be obtained by the reaction of PhMe<sub>2</sub>SiCl with lithium, or alternatively by the reaction of the disilane PhMe<sub>2</sub>SiSiMe<sub>2</sub>Ph with lithium (Scheme 13).<sup>[81-83]</sup> Its use for the build-up of oligosilanes has the advantage that the phenyl group that is introduced into the silane scaffold can be further derivatised. Among other things, derivatisation is possible by first forming the silyl triflate (Scheme 4) which can then react with all kinds of nucleophilic reagents.

PhSiCI 
$$\xrightarrow{2 \text{ Li}}$$
 PhSiLi  
- LiCl 16  
PhSi-SiPh  $\xrightarrow{2 \text{ Li}}$  PhSiLi  
16  
Si = SiMe<sub>2</sub>

Scheme 13: Synthesis of lithium silanide 16 by either reaction or PhMe<sub>2</sub>SiCl or PhMe<sub>2</sub>SiSiMe<sub>2</sub>Ph with lithium.<sup>[81-83]</sup>

#### 1.3. Synthesis, Stability and NMR Spectroscopic Data of Silylium Ions

#### 1.3.1. Definition and General Aspects

The term *silyl cation* summarises different types of cationic silyl species: The so called *silylium ions* [R<sub>3</sub>Si]<sup>+</sup>, four-valence electron *silyliumylidene* derivatives [RSi:]<sup>+</sup>, hypercoordinated (penta- and hexacoordinated) cationic silicon compounds (*siliconium ions*) and silicon-centred radical cations (Figure 1).<sup>[84-88]</sup> Examples for the different types of silyl cations are the tris(mesityl)silylium ion **17**,<sup>[89]</sup> the cationic silyliumylidene derivative **18**,<sup>[90]</sup> the siliconium ion **19**,<sup>[91]</sup> and the radical cation **20**.<sup>[92]</sup>



Figure 1: Examples for different types of silyl cations: Silylium ion **17**,<sup>[89]</sup> silyliumylidene-type silyl cation **18**,<sup>[93]</sup> hypercoordinated silyl cation **19**<sup>[91]</sup> (all detected in the condensed phase) and silicon-centred radical cation **20** (matrix detection).<sup>[92]</sup>

In this work, the spotlight is put on silvlium ions and silvlium-ion like cations. In this chapter, a general definition of silvlium ions as well as a summary of the synthetic approaches to such species and their special features compared to other cationic Group 14 compounds are presented. The heavier Group 14 homologues containing germanium, tin and lead are not discussed in detail.<sup>[94]</sup>

Silylium ions are tricoordinated and ideally triogonal-planar silyl cations with the general formula [R<sub>3</sub>Si]<sup>+</sup>. The six-valence electron species possess a vacant p-orbital that is oriented perpendicular to the R<sub>3</sub>Si plane. They are the heavier homologous of carbenium ions [R<sub>3</sub>C]<sup>+</sup> and are also isolobal to neutral borane compounds R<sub>3</sub>B.<sup>[87]</sup> While silylium ions are not thermodynamically disfavoured for most synthetically useful substituents R,<sup>[84, 95]</sup> their high electrophilicity and accompanied high reactivity make the choice of the right solvent and counter anion crucial for their synthesis and isolation in the condensed phase. Any kind of Lewis base is prone to reactions with silylium ions due to their high reactivity and Lewis acidity. Thus, the development of weakly coordinating anions (WCAs) is historically tightly bound to the research on silylium ions.<sup>[96]</sup> Additionally, the higher congeners of carbon, including silicon,

have an increased tendency to extend their coordination sphere. At the same time, their ability for  $\pi$ -conjugation and stabilising hyperconjugative effects is less distinct due to less effective orbital overlap with carbon substituents R (Scheme 14).

Aryl as substituent:  $\pi$ -conjugation Alkyl as substituent: hyperconjugative effects



Scheme 14: Representation of  $\pi$ -conjugation in case of aryl substituents and hyperconjugative effects to stabilise  $[R_3E]^+$ .

In combination with the smaller electronegativity of silicon versus carbon, this leads to an increased accumulation of positive charge at the silicon centre (Figure 2).<sup>[84-85]</sup>

### Carbenium ions $[R_3C]^+$ vs. Sil

## Silylium ions [R<sub>3</sub>Si]<sup>+</sup>





The larger size of the electron deficient centre in tricoordinated Group 14 (Si, Ge, Pb, Sn) cations compared to carbon makes steric protection of the positive centres more challenging. As a result of the high synthetic demands, silylium ion chemistry came out of its niche existence significantly later than the well-established carbenium chemistry that is wildly applied in different fields of organic chemistry. Although silylium ion chemistry arrived late to the party

given that the existence of carbenium ions was established more than 120 years ago,<sup>[97]</sup> and that the first solid evidence for the occurrence of silylium ions in the condensed phase is only about 20 years old,<sup>[89, 98]</sup> their potential for impact is just as great.<sup>[95]</sup> The high difficulties in the synthesis of silylium ions can be also illustrated if it is taken into account that silylium ions were already postulated to be involved in chemical reaction in the middle of the 20<sup>th</sup> century.<sup>[99]</sup>

The archetype of the silylium ion, the trigonal-planar [R<sub>3</sub>Si]<sup>+</sup>, requires specific substituents R which are sterically demanding enough to shield the cationic silicon centre (kinetic stabilisation) and at the same time electron-donating to attenuate the high Lewis acidity (thermodynamic stabilisation).<sup>[87]</sup> As a result of the high demand on the substituents, only a small number of known silylium ions fulfil the definition of a trigonal-planar coordinated [R<sub>3</sub>Si]<sup>+</sup>.<sup>[89, 100-103]</sup> Additional silylium ions are described in the literature that incorporate the positively charged silicon centre in a delocalised  $\pi$ -system (Figure 7, chapter 1.3.3).<sup>[104-108]</sup> Often, the coordination number is expanded from three (silylium ions) to four by coordination of external (**21**) or internal donor groups (**22**) to the cationic silicon centre. In this case, the term *stabilised silyl cations* can be used instead of silylium ion and a distorted tetrahedral coordination environment around the central silicon atom is observed (Figure 3).<sup>[85]</sup>



LB = Lewis-basic groups

Figure 3: Formation of stabilised silyl cations by coordination of internal or external Lewis basic groups to silylium ions.<sup>[85]</sup>

In some cases, the coordination number is further expanded to five which results in the formation of siliconium ions. These stabilisations were shown to occur either inter- (23) or intramolecularly (24). External donation can, for example, result from coordination of the solvent or counter anion, while internal coordination often occurs when additional Lewis basic groups are present in the molecule. The different forms of stabilisation are analysed in the following chapter.

#### 1.3.2. Synthesis and Stabilisation of Silylium lons and Silyl Cations

As a result of the high electrophilicity and high reactivity, conventional synthetic approaches that are successfully used in carbenium ion chemistry are not applicable. Other synthetic procedures (Scheme 15) are needed to overcome the inherently different chemical features of silylium versus carbenium ions.<sup>[85-86]</sup> The most frequently applied strategies are the cleavage of Si-H, Si-C and Si-Si bonds by strong electrophiles E<sup>+</sup> (Scheme 15, reactions a-c). The cleavage of Si-X (X = F, Cl, Br) is also possible (Scheme 15, reaction d), but only successful for strongly stabilised silyl cations. Furthermore, the addition of a cation species R<sup>+</sup> to silylenes (Scheme 15, reaction e) and the oxidation of silyl radicals are possible (Scheme 15, reaction f). Albeit possible, the last two synthetic accesses are rather limited due to the small number of stable substrates.



(d) Si-Halogen bond cleavage

Scheme 15: Synthetic procedures applied for the generation of silylium ions: (a) Cleavage of Si-H bonds, (b) cleavage of Si-C bonds, (c) cleavage of Si-Si bonds, (d) cleavage of Si-Halogen bonds, (e) addition of cationic R<sup>+</sup> to silylenes, (f) oxidation of silyl radicals. Decreasing synthetic importance in the order (a) to (f).<sup>[85]</sup>

Of the most used synthetic approaches for silylium ions and silylium ion-like species in the condensed phase, the cleavage of Si-H bonds by an electrophile, the so-called Corey reaction,<sup>[109]</sup> is the most applied (Scheme 16). The Corey reaction is a modification of the classical Barlett-Condon-Schneider (BCS) hydride transfer reaction.<sup>[110]</sup> In course of this

reaction, the hydrosilanes reacts with a strong Lewis acid whereby the cationic silyl species and the hydride adduct of the Lewis acid are formed. The hydride transfer reaction between hydrosilanes and carbenium ions was extensively investigated in the past,<sup>[111-114]</sup> and the triphenylcarbenium (*trityl*) cation, [Ph<sub>3</sub>C]<sup>+</sup>, is often used as relatively easy access to trityl salts with all kinds of WCAs are established.<sup>[115-119]</sup> In course of the hydride transfer reaction, Ph<sub>3</sub>CH (triphenylmethane) is formed.

$$R_3Si-H + [Ph_3C]^+$$
 Hydride transfer reaction  $[R_3Si]^+ + Ph_3C-H$ 

While it is generally assumed that one important reason for the successful hydride abstraction by  $[Ph_3C]^+$  is the relative strength of the Si-H bond compared to the C-H bond,<sup>[120]</sup> newer theoretical findings showed that this is not the case for alkyl- and/or aryl-substituted hydrosilanes.<sup>[95]</sup> Instead, inter- or intramolecular stabilisation of the initially formed silylium ions are considered to play an important role for the hydride transfer reaction of hydrosilanes and  $[Ph_3C]^+$ .<sup>[120]</sup>

Depending on the chosen silane and counter anion, the hydride abstraction happens within minutes.<sup>[121-123]</sup> However, the reaction can be significantly slowed down or even completely suppressed if very bulky substituents are used.<sup>[102]</sup> While the reaction can be performed in in polar solvents as sulfolanes, ethers and nitriles,<sup>[124]</sup> chlorinated alkanes or (chlorinated) aromatics as well as silanes are the solvents of choice (see below).<sup>[125]</sup>

The correct substituents at silicon, the correct counter anion and the choice of correct solvent are of paramount importance in the synthesis of silylium ions. Thus, the use of bulky aryl substituents allows for the isolation of truly tricoordinated silylium ions. This was first shown for the [Mes<sub>3</sub>Si]<sup>+</sup> (**17**) cation.<sup>[89, 98, 126]</sup> As a result of the steric demand of the trityl cation and the starting material, Mes<sub>3</sub>SiH, the silylium ion **14** is not accessibly by straightforward hydride transfer reaction (Scheme 16, R = Mes).<sup>[89, 100]</sup> A workaround, that enables the use of the trityl cation in the synthesis of various triaryl-substituted silylium ions [Ar<sub>3</sub>Si]<sup>+</sup>, makes use of a follow-up reaction between the starting material and the initially formed silylium ion (Scheme 17).<sup>[102-103]</sup> In course of the reaction, the primarily formed diarylmethylsilylium ion acts in a substituted silylium ion.

$$3 \xrightarrow{Ar}_{Ar} \xrightarrow{Me}_{H} + 2 \left[ Ph_{3}C \right]^{+} \xrightarrow{Benzene, r.t.} 2 \xrightarrow{Ar}_{Ar} \xrightarrow{+}_{Ar} Ar + Me_{3}SiH + 2 Ph_{3}C-H$$

Ar = 2,4,6-Trimethylphenyl (Mes), 2,6-Dimethylphenyl (Xylyl), 2,4,6-Tri*iso*propylphenyl (Tipp), 2,3,4,5,6-Pentamethylphenyl (Pemp)

Scheme 17: Synthesis of triaryl-substituted silylium ions by hydride transfer reaction of diarymethylsilanes with trityl cation and subsequent substituent exchange reaction. The  $[B(C_6F_5)_4]^-$  counter anion is omitted.<sup>[102-103]</sup>

As counter anions for the synthesis of silylium ions and silylium-ion like cations in the condensed phase, normally less coordinating anions like perchlorate or triflate are not suitable.<sup>[87-88]</sup> Instead, counter anions that are even less nucleophilic are needed (Figure 4).



Figure 4: Examples of weakly-coordinating anions (WCAs) suitable as counter anions in the synthesis of silylium ions and silylium ion-like species.

Often, the weakly-coordinating perfluorinated tetraphenylborate anion  $[(B(C_6F_5)_4]^{-1}]$  has shown to be a suitable counter anion in the synthesis of silylium ions and silylium ion-like species.<sup>[89, <sup>91, 103, 121-123, 125, 127-135]</sup> It is frequently applied in the synthesis of silyl cations in arene solvents resulting in the formation of silyl arenium borates,<sup>[136]</sup> or silylium borates if the steric and/or electronic stabilisation by the substituents is sufficiently enough.<sup>[89, 102-103]</sup> Other examples of WCAs used are halogenated *closo*-carborates of the constitution [RCB<sub>11</sub>H<sub>11-n</sub>X<sub>n</sub>]<sup>-</sup> and [RCB<sub>11</sub>Me<sub>11-n</sub>X<sub>n</sub>]<sup>-</sup> (R = H, alkyl; X = F, Cl, Br, I; n = 6, 11),<sup>[115, 118, 137-140]</sup>, perhalogenated *closo*-borates, [B<sub>12</sub>X<sub>12</sub>]<sup>2-</sup> (X = Cl, Br) and [Me<sub>3</sub>NB<sub>12</sub>Cl<sub>11</sub>],<sup>[116-117, 141]</sup> and the fluorinated alkoxyaluminate [Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]<sup>-</sup>.<sup>[142-144]</sup> Depending on the chosen counter anion, different aspects have to be considered. Although, fluorinated alkoxyaluminates can be applied in the synthesis of silyl cations,<sup>[145]</sup> their use is often accompanied by fluoride abstraction by the cationic silyl species.<sup>[146-147]</sup> If *closo*-borates or *closo*-caborates are employed with trialkylsilylium ions, the binding of the silylium ion to one of the halogen atoms of the counter anion is often observed. As a result, zwitterionic salts are obtained.<sup>[148-150]</sup> Due to the generally</sup> poor solubility of *closo*-(car)borates salts, the hydride transfer reactions usually need increased reaction times. At the same time, their use has the advantage that the salts formed after hydride abstraction have a higher tendency to crystallise compared to perfluorinated tetraarylborate (e.g.  $[B(C_6F_5)_4]^-$ ) salts.<sup>[101, 103, 116-117, 151-152]</sup>

Due to the tendency of silicon to form strong bonds with oxygen and halogens and the general reactivity of silyl cations with Lewis-basic groups, the choice of solvents is restricted. While sulfolanes, ethers and nitriles can be used, their high coordination ability significantly reduces their application. As a result, aromatic hydrocarbons as well as halogenated arenes are the preferred solvents for the synthesis of silylium ions or silylium ion-like species. Even in this solvents, truly non-coordinated silylium ions are only obtained if sufficient steric and/or electronic stabilisation of the cationic silicon centres is provided.<sup>[89, 102]</sup> Instead, side-reactions of the formed silylium ions with solvent molecules are usually observed (Figure 5). Thus, *silyl arenium ions* **25** or *silylated arylhalonium ions* **26** are detected if (halogenated) arenes are used.<sup>[152]</sup> If ethers, nitriles, or pyridines are used, *oxonium ions* **27**, *nitrilium ions* **28** and *pyridinium ions* **29** are obtained.<sup>[149, 153-154]</sup>





Aliphatic halogenated hydrocarbons, especially dichloromethane, can also be applied as solvents. Their use is often restricted due to possible reactions with the formed cationic silyl species which results in chlorinated silyl species or outright decomposition.<sup>[155-156]</sup> As a result, aliphatic halogenated hydrocarbons are in most cases only suitable for reactions at low temperature, generally below -50 °C. Hydrosilanes, R<sub>3</sub>SiH (R = Me (**31**), Et (**32**), *i*Pr (**33**)), were also shown to be suitable solvents. In this case, hydrogen-bridged cationic species of the type [R<sub>3</sub>Si-H-SiR<sub>3</sub>]<sup>+</sup> (**30**), so called *bissilylhydronium ions*, are obtained (Scheme 18).<sup>[152, 157-158]</sup>

xs. 
$$R_3Si-H$$
  $\xrightarrow{[Ph_3C][B(C_6F_5)_4]}$   $\xrightarrow{}$   $[R_3Si-H-SiR_3][B(C_6F_5)_4]$   
-  $Ph_3C-H$ 

R = Me (**31**), Et (**32**), *i*Pr (**33**)

Scheme 18: Synthesis of intermolecularly Si-H-Si-bridged silyl cations **31-33**. For the synthesis, the hydrosilanes are simultaneously used as reagent and as solvent. <sup>[152, 157-158]</sup>

While the cationic species obtained under these conditions were initially often characterised as the silylium salts [ $R_3Si$ ][ $B(C_6F_5)_4$ ], this identification was shown to be erroneously in later studies.<sup>[157]</sup> Instead, the Si-H group of a second molecule of the hydrosilane functions as donor group to stabilise the silylium ion's positive charge. The hydrosilane coordinates with its Si-H functionality to the silylium ion whereby an intermolecular two-electron, three-centre (2e3c) Si-H-Si bridge is established. While both silicon cations in the formed bissilylhydronium ions **30** (Figure 5) are tetracoordinated,<sup>[152, 158]</sup> the hydrosilane is only weakly bound to the silylium ion unit and can be easily replaced by other nucleophiles. Thus, even weak donors, as (halogenated) aromatic solvent molecules,<sup>[157-158]</sup> or halogenated (car)borate anions,<sup>[117-118, 141]</sup> can replace the hydrosilanes and form the respective cationic complex with the solvent or anion. As a result, the NMR spectroscopic analysis of intermolecularly bridged bissilylhydronium ions **30** is often hindered as not the hydrosilane-coordinated silylium ion is detected. Instead, the NMR spectroscopic data result from a rapid equilibrium between bissilylhydronium ions **30** as well as the solvent- and anion-coordinated silyl cations.<sup>[152, 158]</sup>

If the second Si-H unit is attached in the same molecule, the situation is different. In this case, the formation of intramolecularly Si-H-Si-bridged bissilylhydronium ions **34** is usually detected (Scheme 19). The intermolecular bridging is energetically favoured compared to intermolecular Si-H-Si bridges due to entropic reasons.<sup>[86]</sup> The equilibrium between anion or solvent complex and the bissilylhydronium ion is thus suppressed.



Scheme 19: Formation of intramolecularly Si-H-Si-bridged silyl cations **33** by hydride transfer reaction. The counter anion is omitted.<sup>[95]</sup>

Accordingly, the NMR spectroscopic as well as crystallographic examination of several of such silyl cations (Figure 6) show that no coordination by either solvent or counter anion occurs.<sup>[121-123, 135, 159-162]</sup>





Figure 6: Examples of silyl cations stabilised by intramolecular 2e3c Si-H-Si bridges.<sup>[121-123, 135, 159-162]</sup>. The counter anions are omitted.

Furthermore, the thermodynamic stability of the intramolecular Si-H-Si-stabilised silyl cations differs drastically depending on the general constitution of the cation. Whereas some cations are stable only at low temperatures (e.g. cation **35**),<sup>[122, 163]</sup> other can be synthesised at room temperatures (e.g. cations **36-39**),<sup>[121, 159, 162]</sup> or are even stable in boiling toluene (e.g. cation **39**).<sup>[135]</sup> Additionally, the cations **40** and **41** show an increased stability due to polyagostic Si-H··Si interactions which allows the use of chlorinated hydrocarbons (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl) even at elevated temperatures.<sup>[160-161]</sup>

Investigations of the bicyclic silyl cations **38** and **39** showed the high tendency of oligosilanylsilyl cations for skeletal rearrangement reactions and the ability to stabilise their cationic charge by establishing 2e3c Si-H-Si bridges. Thus, attempts to react oligosilane **43** with trityl salt to synthesise the secondary silyl cation **44** resulted in the exclusive formation of cation **39** (Scheme 20).<sup>[123]</sup> The mechanism of the rearrangement was also examined and detected to proceed via a succession of methyl- and hydrogen shifts. A very similar tendency to stabilise the cationic charge at silicon by the formation of a 2e3c Si-H-Si bridge was also observed experimentally for cation **38** and investigated by quantum mechanical methods.<sup>[162]</sup>



Scheme 20: Attempts to obtain the secondary silvlium ion **44** by reaction of the cyclic oligosilane **43** with trityl cation. The reaction results in the exclusive formation of the oligosilanylsilyl cation **39**.<sup>[123]</sup>

These insights were further used to investigate Lewis acid-induced rearrangement reactions of oligosilanes. By specific modification of the oligosilane backbone, it was possible to detected elusive rearrangement intermediates.<sup>[122-123, 133]</sup> Following this procedure, the reaction mechanisms of sila-Wagner-Meerwein-type rearrangement reactions was elucidated. While the rearrangement of the octasilane **45** to its isomers **46** and **5** was early on postulated to proceed via cationic intermediates,<sup>[164-165]</sup> the detection of the highly reactive intermediates was not possible (Scheme 21).



Scheme 21: AICl<sub>3</sub>-induced rearrangement of oligosilane 44 to its more branched isomers 45 and 46.

By introduction of Si-H functionalities in the structure of oligosilane **45**, Albers *et al.* inserted reactive groups into the molecule framework that enabled the generation of defined cationic centres by hydride transfer reaction. In this way, they were able to gain new insights into the sila-Wagner-Meerwein-type rearrangement reaction of oligosilanes.<sup>[122]</sup> Hence, the hydride transfer reactions of oligosilane **47** and digermaoligosilane **48** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] resulted in the formation of the Si-H-Si-bridged cationic species **35** and **49** (Scheme 22). The combination of the experimental results with quantum mechanical calculations allowed to clarify the reaction mechanism. The mechanism of the rearrangement was shown to consist of subsequent silyl shifts and a hydride shift. As it was demonstrated by the experiments with digermaoligosilane **48**, the trisilyl-substituted Si/Ge groups (marked blue) in the starting material increase their silyl substitution during the rearrangement.



 $Si = SiMe_x$ , x = 2 or 3

Scheme 22: Hydride transfer reaction between oligosilane **47** and digermaoligosilane **48** resulting the in formation of Si-H-Si-bridged silyl cations **35** and **49**.<sup>[122]</sup>

As a result, the groups are tetrasilyl-substituted in the silyl cations **35** and **49**. By density functional theory (DFT) calculations, it was further shown that attractive intramolecular London dispersion interactions<sup>[166]</sup> play a significant role as driving forces for the intramolecular rearrangement reactions in oligosilanylsilyl cations.<sup>[122]</sup>

Based on these results, it can be concluded that the modification of oligosilanes with Si-H functionalities opens a way to stabilise otherwise fleeting intermediates in the Lewis acid-induced rearrangement of the oligosilane framework. The reactive intermediates are stabilised by the formation of 2e3c Si-H-Si bridges which enables spectroscopic detection. Thus, the elucidation of reaction mechanisms is possible. The knowledge about the exact driving forces and mechanistic steps of the cationic rearrangement reactions can then be used in the synthesis of otherwise difficult to obtain oligosilanyl structures. One vivid example of such a rearrangement resulting in an oligosilanyl structure that is otherwise not easily accessible, is the AlCl<sub>3</sub>-induced rearrangement of the tricyclic oligosilane **50** to persilaadamantane (**51**) which was published by Marschner and co-workers (Scheme 23).<sup>[58]</sup>



Scheme 23: AICl<sub>3</sub>-induced rearrangement reaction of tricyclic oligosilane 50 to persilaadamantane (51).<sup>[58]</sup>

Yet another way to stabilise silvl cations was reported by Oestreich and co-workers who analysed ferrocenyl-substituted hydrosilanes and their behaviour in the hydride transfer reaction.<sup>[151, 167]</sup> The hydride abstraction of the ferrocene derivative **52** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] resulted in the formation of the silyl cation **53** (Scheme 24). The obtained cation was characterised by its downfield-shifted <sup>29</sup>Si NMR signal ( $\delta^{29}$ Si = 114.5 in dichloromethane-d<sub>2</sub>). Its <sup>29</sup>Si NMR shift was shown to be independent of the used solvent or counter anion ([B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> or [B<sub>12</sub>Cl<sub>12</sub>]<sup>2-</sup>). Moreover, the obtained crystal structure showed just small deviation from a trigonal-planar coordination around the silicon atom.<sup>[151]</sup>



Scheme 24: Synthesis of the ferrocenyl-stabilised silyl cation 53 and its <sup>29</sup>Si NMR chemical shift.<sup>[167-168]</sup>

At the same time, an extreme dip angle of 44.8° was detected in the crystal structure. Hence, the silicon atom is shifted towards the iron atom of the ferrocene unit. This observation was analysed by quantum chemical calculations which indicated the formation of two 2e3c bonds that involve the central iron atom, the carbon atoms  $C_{\alpha}/C'_{\alpha}$  of both Cp rings, and the cationic silicon atom. <sup>[151]</sup>

The same mode of stabilisation was later detected by Albers *et al.* for the 1,1'-bis(trimethylsilyl)silyl-substituted ferrocene derivative **54** (Scheme 25).<sup>[163]</sup> In her work, she was able to show by NMR spectroscopy that no 2e3c Si-H-Si bridge is formed after hydride transfer reaction between **54** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Instead, the ferrocenyl-stabilised silyl cation **55** was obtained.



Scheme 25: Synthesis of the ferrocenyl-stabilised silyl cation 55 and its <sup>29</sup>Si NMR chemical shift.<sup>[163]</sup>

#### 1.3.3. NMR Properties of Silylium Ions and Silylium Ion-like Cations

In general, the cationic silicon centres of silylium ions and silylium ion-like cations show characteristic downfield-shifted signals in their <sup>29</sup>Si NMR data.<sup>[84-85]</sup> The rare examples of truly tricoordinated silylium ions, the triarylsilylium ions **17** and **56-60** as well as the diarylalkylsilylium ion **61** all resonate far downfield around  $\delta^{29}$ Si = 215-245 and do not show a solvent-dependent chemical shift if arenes are used as solvents (Figure 7).<sup>[89, 98, 101-103, 126]</sup> Nonetheless, less sterically demanding and more electrophilic solvents, for example, nitriles still react with these sterically and electronically shielded silylium ions.<sup>[89, 103]</sup>

Compared to the triarylsilylium ions **17**,**56-60** and diarylalkylsilylium ion **61**, the silatropylium ion **63** in which the positively charged silicon is part of a conjugated  $\pi$ -system shows a more upfield-shifted <sup>29</sup>Si NMR resonance at  $\delta^{29}Si = 142.9$ ,<sup>[155-156]</sup> while the <sup>29</sup>Si NMR shifts of the silyl cations **64** and **65** are even further downfield-shifted. Sekiguchi and co-workers showed that the silyl cation **64** has  $2\pi$  electron homoaromatic character,<sup>[104]</sup> and that the silyl cation **65** is stabilised due to its persilaaromatic nature.<sup>[105]</sup> For both cations **64** and **65**, XRD structural analyses revealed no coordination with either solvent molecules or counter anions.

In contrast, solvent-stabilised silvl cations (e.g. silvlarenium ions **62a** and **62b** and silvlated chloronium ion **62c**) show <sup>29</sup>Si NMR chemical shifts around  $\delta^{29}Si = 80-100$  and a marked dependence on the type of coordinating solvent.<sup>[125, 128, 158, 169]</sup>

Tricoordinated silvlium ions: Et<sub>3</sub>Si H Ši+  $\delta^{29}$ Si = 225.3 (C<sub>6</sub>D<sub>6</sub>) R = R' = Mes (17): 62a  $\delta^{29}$ Si = 216.2 (C<sub>6</sub>D<sub>6</sub>) R = R'= Pemp (56):  $\delta^{29}$ Si = 92.3 (C<sub>6</sub>D<sub>6</sub>)  $\delta^{29}$ Si = 229.9 (C<sub>6</sub>D<sub>6</sub>) R = R' = Xylyl (57):  $\delta^{29}$ Si = 226.5 (C<sub>6</sub>D<sub>6</sub>) R = R' = Duryl (58): Et<sub>3</sub>Si H  $\delta^{29}$ Si = 229.8 (C<sub>6</sub>D<sub>6</sub>) R = R' = Tipp (**59**):  $\delta^{29}$ Si = 217.0 (C<sub>6</sub>D<sub>6</sub>) R = Mes, R' = Tipp (60):  $\delta^{29}$ Si = 244.7 (C<sub>6</sub>D<sub>6</sub>) R = Tipp, R' = Et(61): Mes = 2,4,6-Trimethylphenyl, 62b Pemp = 2,3,4,5,6-Pentamethylphenyl, Xy|y| = 2,6-Dimethylphenyl,  $\delta^{29}$ Si = 81.8 (C<sub>7</sub>D<sub>8</sub>) Duryl = 2,3,5,6-Tetramethylphenyl, Tipp = 2,4,6-Tri*iso*propylphenyl Et<sub>3</sub>Si~ 62c  $\delta^{29}$ Si = 99.9 (C<sub>6</sub>D<sub>5</sub>Cl) Silyl cations stabilised by  $\pi$ -conjugating systems: Mes ्र*t-*Bu SiMe(t-Bu)<sub>2</sub> (t-Bu)2MeS Si(*t*-Bu)<sub>3</sub> (t-Bu)<sub>3</sub>Si (t-Bu)<sub>2</sub>MeSi SiMe(t-Bu)2 63 64 65  $\delta^{29}$ Si = 142.9 (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta^{29}$ Si = 284.6 (C<sub>7</sub>D<sub>8</sub>)  $\delta^{29}$ Si = 77.3 (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta^{29}$ Si = 288.1 (C<sub>7</sub>D<sub>8</sub>)  $\delta^{29}$ Si = 315.7 (CD<sub>2</sub>Cl<sub>2</sub>)



A similar <sup>29</sup>Si NMR shift range is usually observed for silyl cations stabilised by either inter- or intramolecular 2e3c Si-H-Si bridges (Figure 8). The <sup>29</sup>Si NMR data for intermolecularly bridged silvl cations 31-33 were obtained as CPMAS NMR data of the respective

Solvent-stabilised silvl cations:

 $[R_3Si-H-SiR_3][B(C_6F_5)_4]$  salts,<sup>[125]</sup> while the <sup>29</sup>Si NMR data of the intramolecularly bridged silyl cations **35-42** were obtained in solution.<sup>[121-123, 135, 159-162]</sup>

Intermolecular 2e3c Si-H-Si bridge:

$$R_{3}Si^{H}SiR_{3} = Me (31): \delta^{29}Si = 84.8 \text{ (solid state)} \\R = Et (32): \delta^{29}Si = 94.3 \text{ (solid state)} \\R = iPr (33): \delta^{29}Si = 107.6 \text{ (solid state)}$$

Intramolecular 2e3c Si-H-Si bridge:



Figure 8: <sup>29</sup>Si NMR spectroscopic data of inter- and intramolecularly Si-H-Si-bridged silyl cations. <sup>[121-123, 135, 159-162]</sup> The counter anions are omitted.

With exception of the aryl-substituted silyl cations **40** ( $\delta^{29}$ Si = 54.4),<sup>[135]</sup> **41** ( $\delta^{29}$ Si = 24.9) and **42** ( $\delta^{29}$ Si = 34.3),<sup>[160]</sup> all silicon atoms involved in the 2e3c Si-H-Si bridges resonate at a narrow range around  $\delta^{29}$ Si = 77-110.<sup>[121-123, 159, 162]</sup> Additionally, the Si-H-Si-bridged cations all show <sup>1</sup>*J*<sub>Si,H</sub> coupling constants that are diagnostic for the occurrence of a 2e3c Si-H-Si bridge. The experimentally detected coupling constants are remarkably reduced compared to the respective couplings of free Si-H moieties (typically around <sup>1</sup>*J*<sub>Si,H</sub> = 170-220 Hz<sup>[170]</sup>). Their reported coupling constants range from <sup>1</sup>*J*<sub>Si,H</sub> = 16 Hz to 46 Hz.

Various studies investigated <sup>29</sup>Si NMR shifts of silylium ions and stabilised silyl cations by quantum mechanical calculations using different methods and basis sets. The results of the computations were used to distinguish between non-coordinated silylium ions and silyl cations that are stabilised by coordination of the solvent, the counter anion, or other Lewis-basic groups.<sup>[98, 126, 171-174]</sup>

For <sup>29</sup>Si NMR shift calculations of oligosilanylsilyl cations containing Si-H-Si bridges, calculations at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory were shown to deliver sufficiently accurate results.<sup>[122-123, 133, 163]</sup> The studies also verified that DFT calculations at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level can be used to estimate the <sup>1</sup> $J_{Si,H}$  coupling constants of the formed 2e3c Si-H-Si bridges.

#### 1.4. Dications of Group 14 Elements

Various examples for carbodications that contain two positively charged carbon centres in their organic framework are described in the literature.<sup>[175-178]</sup> Literature-known carbodications of this type were often synthesised in super acidic media (Figure 9).

Figure 9: Selected examples for a) acyclic and b) (poly)cyclic carbodications.<sup>[178-179]</sup>

Contrary to carbodications, dications of the heavier Group 14 elements (Si, Ge, Sn, Pb) are less represented. Thus, examples of heavier Group 14 dications often consist of the element in a low oxidation state, [E(II)]<sup>2+</sup>,<sup>[150]</sup> which are stabilised by NHCs,<sup>[180-181]</sup> coordination of arene ligands<sup>[182]</sup> or incorporated in a cryptand or crown ether framework.<sup>[183-184]</sup>

In this work, silyl cations and dications containing cationic silicon centres in the formal oxidation state of +IV are investigated. Examples of silyl dications containing the positively charged Si in the formal oxidation state +IV are scarce. One possible target for the successful synthesis is the incorporation of the cationic charge in a cyclobutadiene-like structure. This strategy is utilised as the corresponding carbodication is aromatic and various examples of cyclobutadiene dications are known.<sup>[185]</sup> Investigations by Roesky and co-workers revealed

aromatic character for the tetrasilacyclobutadiene dication **66** which contributes to its successful synthesis and isolation (Figure 10).<sup>[186]</sup>



Figure 10: All-carbon cyclobutadiene dication as a 2π aromatic compound, its heavier tetrasilacyclobutadiene relative and **66**[BPh<sub>4</sub>]<sub>2</sub> as examples of an isolable tetrasilacyclobutadiene dication.<sup>[186]</sup>

In contrast, dicationic silyl species that contain two positively charged silicon centres in the formal oxidation state of +IV and that that do not use charge delocalisation as a mean to stabilise the dication are even less reported in the literature. Very recently, a successful synthesis of dicationic silyl compounds was published by Oestreich and co-workers. In their work, they used the coordination of the two cationic Si centres with the WCA to stabilise the cationic charges of the dicationic compounds which enabled their isolation (Scheme 26).<sup>[150]</sup>



Linkage =  $CH_2CH_2$ , 1,5-naphthyl, 2,6-naphthyl [WCA]<sup>-</sup> = [ $CHB_{11}CI_{11}$ ]<sup>-</sup>, [ $CHB_{11}H_5Br_6$ ]<sup>-</sup>

#### Scheme 26: Synthesis of alkyl- or aryl-bridged, counter anion-stabilised silyl dications by Oestreich and coworkers.<sup>[150]</sup>

This stands in contrast to previous attempts to synthesise silvl dications by twofold hydride abstraction which were not effective and resulted in reactions with the WCA.<sup>[135]</sup> Nonetheless, it must be noted that the two cationic silvl centres of the formed dicationic molecules are connected by extended alkyl or aromatic moieties (Scheme 26). Attempts to transfer the chemistry to oligosilanylsilyl compounds are additionally hindered due to the tendency of oligosilanylsilyl cations to act in rearrangement reactions of the oligosilanyl framework.<sup>[122-123, [122-</sup>

<sup>133, 163]</sup> Therefore, no oligosilanylsilyl compounds that incorporate two cationic silicon centres in the formal oxidation state of +IV have been reported in the literature to date.

•
# 2. Motivation

The aim of this work is the synthesis of different hydrogen-substituted oligosilanes with varying numbers of intramolecular Si-H groups and their subsequent use as starting materials in the synthesis of oligosilanylsilyl cations (Scheme 27). The oligosilanyl structures shall be designed so that multiple Si-H functionalities are present in the molecular structure.

Hydride transfer reaction







Scheme 27: Schematic representation of the planned synthesis of different oligosilanylsilyl cations stabilised by 2e3c Si-H-Si bridges.

#### Motivation

Thus, if more than one additional Si-H functionality are present, the question arises how the additional groups will behave. They can either interact with the cationic silicon centres or behave as not-involved spectator groups. This shall be investigated by low-temperature NMR spectroscopy and by quantum mechanical calculations. For these investigations, the different oligosilanes are going to be equipped with either two, three or even four Si-H functionalities. The importance of ring strain for the formation of the Si-H-Si-bridged silyl cations will be also investigated by using specific oligosilanyl structures that result in either strained or more relaxed ring structures after formation of the stabilising 2e3c Si-H-Si bridges. For the hydride transfer reactions, the trityl salt [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is used. It is chosen, as the perfluorinated tetraphenylborate is less prone to coordinated to the cationic silicon centres than the also applicable *closo*-(car)borates (see chapter 1.3.2). Otherwise, coordination of the anion could compete against the formation of 2e3c Si-H-Si bridges.

The twofold hydride abstraction from oligosilanes bearing more than two Si-H functionalities is also planned (Scheme 28).



Stabilised silyl dication

# Twofold hydride abstraction possible? Do the two 2e3c Si-H-Si bridges interact?

Scheme 28: Schematic representation of the planned synthesis of an oligosilanylsilyl dication with two 2e3c Si-H-Si bridges.

As a result, it should be possible to see if a second hydride abstraction is feasible due to the presence of additional Si-H groups that can form a second intramolecular 2e3c Si-H-Si bridge. If the formation of the dicationic oligosilanyl structures is indeed possible, the behaviour and properties of the two formed 2e3c Si-H-Si bridges shall be investigated and compared to the Si-H-Si-bridged monocations.

As rearrangement reactions of the oligosilanyl framework are described in the literature for several oligosilanylsilyl cations,<sup>[58, 122-123, 133, 163-164, 187-190]</sup> it is also planned to investigate this behaviour for the silyl cations and dications described in the present work.

Furthermore, oligosilanyl-substituted ferrocene derivatives shall be synthesised and reacted in a hydride transfer reaction to obtain the respective ferrocene-substituted oligosilanylsilyl cations (Scheme 29). These cations can either stabilise their charge by formation of a 2e3c Si-H-Si bridge or by coordination to the ferrocene moiety (Chapter 1.3.2).<sup>[151, 163, 167-168]</sup>



**Rearrangement of the silyl units?** 

Scheme 29: Schematic representation of the planned synthesis of ferrocene-based oligosilanylsilyl cations.

Another focus of this work will be put on theoretical investigations of the stabilisation of silyl cations by the formation of 2e3c Si-H-Si bridges and of the properties of the 2e3c Si-H-Si bridges in general. The relation between bond properties of the Si-H-Si bridge and the oligosilanyl framework (acyclic vs. (poly)cyclic, ring strain effects) shall be investigated.



Properties of 2e3c Si-H-Si bridge

# Acyclic vs. (poly)cyclic oligosilanylsilyl cations Structural parameters (e.g. bond lengths and angles)

Scheme 30: Schematic representation of the different Si-H-Si-bridged silyl cations that shall be investigated by quantum mechanical calculations.

# 3. Results and Discussion

# 3.1. Theoretical Analysis Si-H-Si-Bridged Silyl Cations and 2e3c Si-H-Si Bonds

# 3.1.1. Computational Investigations of Polycyclic Oligosilanylsilyl Cations

Various DFT calculations were performed to estimate the stability of different cationic oligosilanyl polycycles (Figure 11).



Figure 11: Bicyclic silylium ions and tricyclic Si-H-Si-bridged silyl cations used to theoretically investigate polycyclic, cationic silyl species.

For the calculations, the sizes of the three bridges of the cyclic systems were varied to investigate the importance of ring strain for the stability of the cationic systems. For all systems, the bicyclic free silvlium ions A as well as the tricyclic Si-H-Si-bridged silvl cations B were structurally optimised, and their computed energies were compared. It was expected that the formation of the bridged silvl cations is energetically unfavourable for very small polycyclic oligosilanes as ring strain effects overcompensate the energy gain upon formation of the 2e3c Si-H-Si bridges. While the ring strain effects were expected to become less pronounced for larger cyclic systems, the distance of the respective Si-H functionality and the cationic bridgehead silicon atom also increases. Therefore, while ring strain effects decrease with larger ring sizes, the increased distance might result in adverse effects that are disadvantageous for the Si-H-Si bond formation. The calculated energies and Gibbs free energies can be used as a rough estimate for such effects. It must be noted that for most structures, hyperconjugative effects of one neighbouring Si-Me group are indicated in the optimised structures by an orientation of the respective groups towards the cationic silicon centres. The values used for comparison are therefore not the values of the completely free silylium ion, but also include energetic contributions due to hyperconjugative effects.

Furthermore, important structural parameters of the computed Si-H-Si-bridged species were compared. The nomenclature of the ring systems in this chapter was derived from the

respective bicyclic non-bridged silylium ions. Thus, if for example a = b = c = 2, the system (Figure 11) is named as [2.2.2]. The summarised data of the DFT calculations (Table 1) show a distinct influence of the size of the ring systems.

	Polycycle	$\Delta E(bridged-free)$ [kJ mol <sup>-1</sup> ]	$\Delta G^{298}$ (bridged-free) [kJ mol <sup>-1</sup> ]
67	[1.1.1]	_[a]	_[a]
68	[2.1.1]	128 <sup>[b]</sup>	123 <sup>[b]</sup>
69	[3.1.1]	53	57
70	[2.2.1]	_[c]	_[c]
71	[3.2.1]	-25	-21
72	[3.3.1]	-51	-56
73	[2.2.2]	58	55
74	[3.2.2]	-22	-18
75	[4.2.2]	-72	-65
76	[3.3.2]	-71	-71
77	[3.3.3]	-91	-91
78	[4.3.2]	-104	-100
79	[4.3.3]	-125	-122
80	[4.4.2]	-95	-106
81	[4.4.3]	-130	-126
82	[4.4.4]	-137	-140
83	[5.5.5]	-63	-50

Table 1: Computed energy and Gibbs free energy differences (at 298 K) of polycyclic, cationic silyl species with different ring sizes. The calculations were performed at the M06-2X/6-311+G(d,p) level of theory. Values for which the non-bridged compound is energetically favoured compared to the bridged compound are marked in red.

[a] Not possible due to connectivity change of non-bridged and bridged cationic structures. [b] Values for the all-H-substituted model system (Figure 13) are reported. [c] Not possible due to breakage of Si-Si bonds in the free silylium ion.

Thus, it was not possible to calculate the (Gibbs free) energy differences between non-bridged and Si-H-Si-bridged silyl cations for the [1.1.1] (67), [2.1.1] (68) and [2.2.1] (70) systems. In case of the smallest investigated polycycle, the [1.1.1] ring system, different attempts to optimise either the non-bridged silylium ion 67A or the bridged silyl cation 67B resulted in a change of the topology (Scheme 31). A very unusual structure 84 was computed that is characterised by two strongly pyramidalized silicon atoms at the bridgehead positions. Analysis of the computed molecular orbitals indicates a significant amount of delocalisation in the silicon framework.



Scheme 31: Change of topology detected during the DFT calculations of the [1.1.1] ring system **67B**. The structure was optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms except Si-H hydrogen atoms are omitted in the structure on the right side.

The structure optimisation of the slightly larger [2.1.1] and [2.2.1] structures **68** and **70** resulted in breakage of Si-Si bonds in the bridged silyl cation **68B** and the non-bridged silylium ion **70A**. Unusually elongated Si-Si bond lengths are detected in the computed structures (Figure 12).



Figure 12: Structures obtained after optimisation of the Si-H-Si-bridged cation **68B** of the [2.1.1] system (left) and the non-bridged silylium ion **70A** of the [2.2.1] system (right). The computed Si-Si bond lengths are noted. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms except Si-H hydrogen atoms are omitted.

Therefore, no comparison of the computed (Gibbs free) energies between the respective free silylium ion and Si-H-Si-bridged cation was performed. Nevertheless, it was possible to optimise both (bridged and non-bridged) cationic [2.1.1] structures if a model compound **85** is optimised in which the SiMe<sub>2</sub> groups of the ring system are exchanged by SiH<sub>2</sub> groups (Figure 13). Comparison of the (Gibbs free) energies of these simplified model compounds **85A** and **85B** shows that the bridged silyl cation **85B** is significantly destabilised compared to the

non-bridged silylium ion **85A** by  $\Delta E = 128 \text{ kJ mol}^{-1}$  ( $\Delta G^{298} = 123 \text{ kJ mol}^{-1}$ ). These results demonstrate that the energy gain usually associated with the formation of a 2e3c Si-H-Si bond is overcompensated by the energetically disfavoured ring strain in the bridged silyl cation **85B**.



Figure 13: Calculated relative energies and Gibbs free energies of the model compound **85** used for the calculation of the [2.1.1] system. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

The formation of the Si-H-Si-bridged silvl cation is also energetically disadvantageous for the [3.1.1] (**69**, Figure 14) and [2.2.2] (**73**, Figure 15) systems.



Figure 14: Calculated relative energies and Gibbs free energies of the [3.1.1] system **69**. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

In both cases, the calculated values for the non-bridged silylium ions **69A** and **73A** are computed approximately 50-60 kJ mol<sup>-1</sup> lower in energy than their bridged relatives **69B** and **73B**. Additionally, a silyl cation **86** with different molecular topology was found for the [2.2.2] system in which the 2e3c Si-H-Si bridge is not located between the bridgehead silicon atoms (Figure 15). This structure is characterised by two fused four-membered Si rings, and it is energetically favoured compared to the silyl cation **73B** bearing the 2e3c Si-H-Si bridge

between the bridgehead positions by more than 40 kJ mol<sup>-1</sup>. Nevertheless, it is still energetically disfavoured compared to the non-bridged silvlium ion **73A** by 15 kJ mol<sup>-1</sup>.



Figure 15: Calculated relative energies and Gibbs free energies of the [2.2.2] system **73** and its isomer **86**. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

The high ring strain in both Si-H-Si-bridged isomers can be elucidated if the structural parameters of the isomers **73B** and **86** are compared (Figure 16).





As can be seen, both polycyclic ring systems are highly strained which is evident by the strong deviation of the internal Si-Si-Si angles from a tetrahedral arrangement. In case of the isomer **73B**, the Si-H bond lengths of 154 pm is unusually short (Table 2 for further comparison). In the second isomer **86**, the location of the 2e3c Si-H-Si bridge between the flanking dimethylsilyl

groups instead of the bridgehead silicon atoms, allows higher structural flexibility of the 2e3c Si-H-Si bridge. Therefore, it can adopt a different bending angle and longer Si-H distance (165 pm). Thus, a higher energy gain is associated with the isomer **86** compared to the isomer **73B** that contains the Si-H-Si bridge between the bridgehead silicon atoms. Nonetheless, energetic disadvantageous ring strain effects due to the two fused four-membered silyl rings result in no total energy gain compared to the non-bridged silylium ion **73A**.

The results so far indicate that it is not feasible to try to obtain bridged silyl cations of a [X.1.1] (X = 1-3) system. For such systems, the bridged systems are either disfavoured or no energetic minima structure were found during optimisation. The same conclusions can be drawn for the [2.2.1] and [2.2.2] systems.

The energetic situation changes if the bigger systems are investigated. Thus, the bridged structures of the [3.2.1] (**71**) and [3.2.2] (**74**) system are favoured compared to the respective non-bridged silylium species (Figure 17). For both systems, the energetic preference of the bridged structures **71B** and **74B** is quite small (less than 30 kJ mol<sup>-1</sup>).



Figure 17: Calculated relative energies and Gibbs free energies of the [3.2.1] (**71**) and [3.2.2] (**74**) systems. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

In contrast, a higher energetical preference of the Si-H-Si-bridged cations is computed for the bigger polycyclic systems. Thus, for all the investigated bigger polycyclic compounds, the bridged cations **B** are favoured significantly compared to the non-bridged silylium ions **A** (Table 1). As a general trend, it can be noted that the energy difference increases with size of the polycyclic ring systems. The maximum was found for the [4.4.4] (**82**) system (Figure 18).



Figure 18: Calculated relative energies and Gibbs free energies of the [4.4.4] (82) and [5.5.5] (83) systems. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

In its case, an energetic preference of  $\Delta E = -137$  kJ mol<sup>-1</sup> ( $\Delta G^{298} = -140$  kJ mol<sup>-1</sup>) was found for the bridged cation **82B** compared to the non-bridged cation **82A**. Interestingly, a sharp reversal of that trend in energy is detected for the [5.5.5] (**83**) system. Instead of an even higher energetic preference of the bridged structure **83B**, the Si-H-Si-bridged silyl cation is computed as being only  $\Delta E = -63$  kJ mol<sup>-1</sup> ( $\Delta G^{298} = -55$  kJ mol<sup>-1</sup>) lower in energy than the respective non-bridged structure **83A** (Figure 18). This (Gibbs free) energy difference is less distinct than the respective values for the smaller polycyclic systems **72-77** and significantly smaller than computed for the systems **78-82** (Table 1). To elucidate this drop in energetic preference of the bridged cation **83B** compared to its non-bridged relative **83A**, it must be noted that the Si-H-Si-bridged cation **83B** shows high deviations of the Si-Si-Si angles from a tetrahedral angle (109.5°). This might contribute negatively to the stability of the Si-H-Si-bridged cation **83B** and thus result in a decreased (Gibbs free) energy difference between the bridged and non-bridged cations.

The calculated structural parameters of the Si-H-Si units of all bridged cations can help to obtain more information on the nature of the respective 2e3c Si-H-Si bonds (Table 2).

As can be seen from the summarised data, the Si-H bond lengths of the 2e3c Si-H-Si bridges show only minor deviations. The bond lengths are nearly always in the narrow range of 160-170 pm. The computed bond lengths thus fall in the range that was described in the literature for acyclic and cyclic Si-H-Si-bridged silyl cations.<sup>[121, 123, 131, 152, 160-162]</sup> The [1.1.1] system stands out as the detected bonding motif in structure **84** (Scheme 31) cannot be classified as a typical 2e3c Si-H-Si bridge. Also, the quite small Si-H distances (154 pm)

detected for the isomer **73B** of the [2.2.2] systems can be seen as an exception that results from the highly strained ring systems (Figure 16).

Even for the bigger polycycles, the Si-H distances of the respective Si-H-Si bridges are not elongated significantly. Instead, the Si-H-Si angle moves more towards linearity for the larger polycycles while the coordination of the bridgehead silicon atoms gets more pyramidal. Still, it must be noted that these trends are not universal, and the observation cannot be generalised for all investigated ring systems.

	Polycycle	d(Si-Si) [pm]	d(Si-H) [pm]	∠(Si-H-Si) [°]	Σ∠(around Si) [°]
67	[1.1.1] <sup>[a]</sup>	270	160/176	107	-
68	[2.1.1] <sup>[b]</sup>	274	168	109	310
69	[3.1.1]	264	166	105	335
70	[2.2.1] <sup>[c]</sup>	266	166	107	348
71	[3.2.1]	267	167	107	359
72	[3.3.1]	269	168	107	360
73	[2.2.2]	308	154	180	353
86	[2.2.2] <sup>[d]</sup>	304	166	133	351
74	[3.2.2]	297	161	136	360
75	[3.3.2]	305	163	138	358
76	[3.3.3]	324	162	174	355
77	[4.2.2]	298	165	129	358
78	[4.3.2]	307	165	137	352
79	[4.3.3]	323	163	162	352
80	[4.4.2]	304	165	134	349
81	[4.4.3]	324	165	158	340
82	[4.4.4]	321	164	156	338
83	[5.5.5]	327	163	175	332

Table 2: Calculated structural parameters of the 2e3c Si-H-Si bridges of the bridged structures. Structures for which the non-bridged cation is energetically favoured are marked in red.

[a] Values for the structure obtained during structure optimisation (Scheme 31). [b] Values for the all-*H*-substituted model system **85** (Figure 15). [c] Si-Si bond breakage during optimisation of the non-bridged compound. [d] Values for the product after change of topology.

As examples, the [4.4.2] (**80**), [4.4.3] (**81**) and [4.4.4] (**82**) system can be used (Figure 19). An increase in the ring size results in an increased pyramidalization of the bridgehead silicon atoms. The increased pyramidalization is visible by a decrease of the sum of bond angles

around this silicon atoms. At the same time, the trend for linearisation of the Si-H-Si bridge is not visible. While the Si-H-Si bridge at first gets significant more linear going from **80B** to **81B** (134° vs. 158°), the next bigger cation **82B** shows no further significant linearisation (156°). Instead, even a small, but notable, increased bending of the Si-H-Si angle is detected for the computed structure.



Figure 19: Computed structures of three different, cationic Si-H-Si-bridged silyl polycycles **80B-82B**. Si-H-Si angles marked in black, sum of bond angles around bridgehead Si atoms marked in red. The structures were optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms except Si-H-Si hydrogen atoms are omitted.

In summary, the results of the calculations suggest that ring strain effects are important for the possible existence of polycyclic oligosilanylsilyl cations bearing 2e3c Si-H-Si bridges. The results demonstrate that it is not possible to synthesise the respective Si-H-Si-bridged cations **B** out of a [X.1.1] bicyclic system (**67-69**, X = 1-3). Furthermore, it seems that the applicable size of the system is also limited as shown by the sharp drop in (Gibbs free) energy differences between the bridged and free cations that is detected for the largest investigated [5.5.5] (**83**) system. Additionally, it must be considered that larger molecule size (longer silicon chains) also enables the possibilities for rearrangement reactions of the respective oligosilanyl framework.<sup>[58, 122-123, 133, 163, 187]</sup> Except for the [2.2.2] (**73**) system (Figure 15), such possible rearrangement reactions were not considered in the calculations, but might be highly important if attempts are made to synthesise polycyclic oligosilanylsilyl cations stabilised by 2e3c Si-H-Si bridges. It is also indicated by the results of the DFT calculations, that the structure of the 2e3c Si-H-Si bridges is quite flexible in terms of linearity (Si-H-Si angle) and Si-Si distance, while the Si-H bonds are nearly invariant.

# 3.1.2. Energetic Contributions of the Pyramidalization Around Si\*

To investigate the effects of pyramidalization around the cationic silicon atom, the model compound  $[(H_3Si)_3Si]^+$  (87) was studied by DFT calculations. Therefore, the model cation 87 was optimised in C<sub>3v</sub> symmetry as a Z-matrix. The angle X-Si<sup>+</sup>-SiH<sub>3</sub> between the dummy atom X and one SiH<sub>3</sub> group was varied in steps of 2.5° which results in increasing pyramidalization around the central silicon atom (Scheme 32). In previous investigations, it was already shown by quantum mechanical calculations of the model systems [SiH<sub>3</sub>]<sup>+</sup> and [SiMe<sub>3</sub>]<sup>+</sup> that the trigonal-planar coordination of the respective silylium ions is preferred and that deviations from planarity lead to energetic destabilisation.<sup>[172]</sup>



Scheme 32: Model system **87** used to estimate the influence of the coordination around the cation silicon centre on the energy of tricoordinated silylium ions.

The sum of the angles was varied between 360° to 327° and the energies for each value were calculated (Table 3). As expected, <sup>[171, 191-192]</sup> the planar silylium ion (sum of angles 360°) has the lowest computed energy. This value was therefore set to  $\Delta E = 0$  KJ mol<sup>-1</sup> and all other energies  $\Delta E$  are related relative to this value.

Table 3: Energies calculated for the model compound [(H<sub>3</sub>Si)<sub>3</sub>Si]<sup>+</sup> (**87**) depending on the sum of angles around the central Si<sup>+</sup> unit as an indicator for the pyramidalization.

X-Si⁺-SiH₃ angle [°]	Sum of angles around Si <sup>+</sup> [°]	ΔE [kJ mol <sup>-1</sup> ] <sup>[a]</sup>
90.0	360	0
92.5	359	1
95.0	358	4
97.5	355	10
100.0	351	17
102.5	346	27
105.0	341	39
107.5	334	53
110.0	327	69

The energies were computed at the M06-2X/6-311+G(d,p) level of theory.

[a] Relative energy to the value computed for a trigonal-planar coordination around Si<sup>+</sup>.

The computed energy values can be plotted versus the sum of Si-H-Si angles to visualise the strong dependency between computed energies and pyramidalization around the central silicon atom (Figure 20).



Figure 20: Plot of the computed relative energies of model compound  $[(H_3Si)_3Si]^+$  (87) depending on the sum of angles around the central silicon atom as an indicator for the pyramidalization. The energies were computed at the M06-2X/6-311+G(d,p) level of theory.

These results show that the energy of trisilyl-substituted silvlium ions is also highly related to the coordination around the cationic silicon centre. In the model calculations, deviations from a perfectly planar coordination destabilise the respective structurally rigid cationic structure.

Nonetheless, it can be noted that for the initially investigated polycyclic systems (Chapter 3.1.1), the pyramidalization around the bridging Si atoms is not the most dominant factor if the bridged and non-bridged oligosilanyl cations are compared. While the pyramidalization increases starting from the bridged cation **74B** of the [3.2.2] system to the bridged cation **82B** of the [4.4.4] system (Table 2), the stability of the respective bridged cations compared to non-bridged silylium ions also increases (Table 1).

## 3.1.3. Influence of London Dispersion Interaction on the 2e3c Si-H-Si Bridge

To investigate the possible importance of London dispersion interactions and of the used computational methods, quantum mechanical calculations on two model systems were performed (Figure 21). The Si-H-Si-bridged silyl cations  $[H_3Si-H-SiH_3]^+$  (88) and  $[Me_3Si-H-SiMe_3]^+$  (31) were chosen as model compounds. The cations were optimised in C<sub>2</sub> symmetry with molecular coordinates given in form of a Z-matrix. The Si-H-Si angle was varied in steps between 180° to 120° for 88 or 180° to 134° for 31. While the Si-H-Si angle was held constant during optimisation, other structural parameters were variable under the restrictions of C<sub>2</sub> symmetry.

For comparison, the DFT methods B3LYP, B3LYP-D3, B3LYP-D3(BJ), M06-2X as well as the *ab initio* method MP2 were chosen.



Figure 21: Model cations **31** and **88** used to estimate the influence of London dispersion interactions in Si-H-Si-bridged silyl cations. Different methods that account or do not account for dispersion interaction were used during the optimisations.

To exclude that the observed effects result from a too small basis set instead of the applied methods, the correlation-consistent polarised triple-zeta cc-pVTZ<sup>[193]</sup> basis set was used instead of the 6-311+G(d,p) basis set that is usually applied in this work. For all five computational methods that were investigated, the computed energies  $\Delta E$  relative to the energy obtained for an angle of 180° were plotted against the varying Si-H-Si angles. For model compound **88**, the graphs (Figure 22) obtained for the different methods allow the

following interpretation: If B3LYP is used as a method, the graph shows only a very minor drop in energy if the Si-H-Si angle is decreased. Nonetheless, it must be noted that the linear structure with an Si-H-Si angle of 180° is not the structure which is lowest in energy if B3LYP is applied. Instead, the energetic minimum is located near 150°. Independent structure optimisation at the B3LYP/cc-pVTZ level of theory without any structural constraints computed an energetic minimum structure with an Si-H-Si angle of 149° for silyl cation **88**. Furthermore, it can be seen in the graph that the energetic differences at various angles are quite small for B3LYP. The maximum energetic difference between the energy calculated at an Si-H-Si angle of 180° and the energetically preferred angle is  $\Delta E = -0.5$  kJ mol<sup>-1</sup>. The slight drop in energy if the angle moves from linearity towards 150° is not based on London dispersion interactions as such interactions are not considered in the B3LYP method. For more acute angles, the relative energy ascends steeply. Thus, the most acute Si-H-Si angle (120°) that was examined during the model calculations is energetically disfavoured by  $\Delta E = 5.3$  kJ mol<sup>-1</sup> compared to a perfectly linear Si-H-Si bridge.



Figure 22: Computed relative energies of model compound **88** vs. Si-H-Si bond angles depending on the method used for computation.

For the other tested computational methods, it can be seen in the graphs (Figure 22) that the energetic minima move to more acute angles. Also, the relative energy differences between the energy obtained for an angle of 180° compared to the energetically most preferred angles increase.

Thus, the energetically preferred Si-H-Si angle is found at 145° when B3LYP-D3 is applied ( $\Delta E = -1.0$ ) and at 140° if B3LYP-D3(BJ) is used ( $\Delta E = -1.5$ ). For both dispersion-corrected methods, a steep rise in energy is detected if the Si-H-Si angle gets more acute. Whereas the relative energy at an Si-H-Si angle of 120° is  $\Delta E = 4.3$  kJ mol<sup>-1</sup> if B3LYP-D3 is used, it is  $\Delta E = 2.8 \text{ kJ mol}^{-1}$  for B3LYP-D3(BJ). Both methods, B3LYP-D3 and B3LYP-D3(BJ), differ from plain B3LYP as Grimme's D3 dispersion correction<sup>[194]</sup> is included. Grimme's D3 dispersion correction adds dispersion coefficients to the DFT method which allow to compute dispersion energies. The B3LYP-D3(BJ) method additionally includes Becke and Johnson (BJ) dampening.<sup>[195-197]</sup> Application of BJ dampening to the DFT-D3 method has the advantage that it scales repulsive interatomic forces at shorter distance more realistic. Extensive theoretical studies have shown that DFT-D3(BJ) gives slightly more accurate results than DFT-D3 for most tested DFT methods.<sup>[198]</sup> These differences between DFT-D3 and DFT-D3(BJ) can explain why the calculations at the B3LYP-D3(BJ) level of theory compute a more acute Si-H-Si angle for the model compound 88 than computed at the B3LYP-D3 level of theory. It also explains why the energy ascends faster for B3LYP-D3 than B3LYP-D3(BJ) if the Si-H-Si angles become smaller. Hence, the more acute Si-H-Si bond angles result in smaller interatomic distances of the non-bridging hydrogen atoms as well as both Si atoms which results in repulsive forces which are weighted more heavily if B3LYP-D3 is applied instead of B3LYP-D3(BJ).

The energetic minimum is shifted to even smaller Si-H-Si angles if either MP2 or M06-2X are utilised as methods for the calculations of the model compound **88**. Therefore, the energetically most preferred Si-H-Si angles using MP2 or M06-2X are at 135°. Compared to B3LYP, B3LYP-D3 and B3LYP-D3(BJ), it can be further seen that both methods estimate a much higher energetic preference between the structures with energetically most favourable Si-H-Si angle and the respective structures with a perfectly linear Si-H-Si bridge. The relative energy differences are  $\Delta E = -4.6$  kJ mol<sup>-1</sup> for M06-2X and  $\Delta E = -3.1$  kJ mol<sup>-1</sup> for the MP2 method. Interestingly, while the energy increases again for Si-H-Si angles smaller than 135°, even at an angle of 120° the calculated energies are still lower than the values for structures with perfectly linear Si-H-Si bridges (180°).

Independent structure optimisation of **88** gave Si-H-Si angles of 133° (M06-2x/cc-pVZT) and 135° (MP2/cc-pVTZ) if all structural parameters were allowed to be optimised during computation. A bent structure of  $[H_3Si-H-SiH_3]^+$  (**88**) in the gas-phase was already verified by IR spectroscopy in previous studies by Dopfer and co-workers.<sup>[199]</sup>

Proceeding from the results obtained for model cation **88**, a similar behaviour was expected for the second model compound **31**. While the plotted data for the different methods show

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some similarities, it also shows some significant differences between the results of the calculations performed for model compound **31** (Figure 23) compared to **88** (Figure 22).

Figure 23: Computed relative energies of model compound **31** vs. Si-H-Si bond angles depending on the method used for computation.

In contrast to **88**, no energetic preferred structure with a deviation of the Si-H-Si angle from 180° is computed for **31** if plain B3LYP is chosen as computation method. Instead, the energy increases constantly with decreasing Si-H-Si angle. To elucidate this difference between **88** and **31** if B3LYP is used as method, the electrostatic potentials were computed for the independently optimised structures at the B3LYP/6-311+G(d,p) level of theory (Figure 24).



Figure 24: Electrostatic potential projected on the electron density isosurface (0.02 au) of **88** (left) and **31** (right). Structure optimisation performed at the B3LYP/6-311+G(d,p) level of theory.

At this level of theory, a Si-H-Si angle of 180° is computed for  $[Me_3Si-H-SiMe_3]^+$  (88) while a bent angle of 156° is obtained for  $[H_3Si-H-SiH_3]^+$  (88). For both  $R_3Si-H-SiR_3$  (R = H or  $CH_3$ ) structures, R-Si-Si-R torsion angles of 180° are measured in the calculated structures. For compound 88, an increased positive charge between the R groups is visible while a decreased charge is visible at the position of the hydrogen substituents. Thus, the bending might be influenced by electrostatic effects that are overcompensated for 31 due to steric reasons by the more shielding  $CH_3$  groups. The same results are obtained if the basis set cc-pVTZ is used instead of 6-311+G(d,p). In this case, the Si-H-Si angle of 88 decreases slightly (149°) while the Si-H-Si angle of 31 stays linear (180°). Thus, significant effects due to the used basis set are excluded.

For all other methods than B3LYP, energetically preferred structures with angles smaller than 180° are obtained for model compound **31** (Figure 23). If B3LYP-D3 is used, the lowest energy is computed for an Si-H-Si angle of 160°. Compared to the linear case, the energy of the structure with this angle shows just a minor energetic preference of  $\Delta E = -0.4$  kJ mol<sup>-1</sup>. For smaller angles, a steady increase in energy is visible.

A very similar behaviour is observed for B3LYP-D3(BJ). The energetically preferred Si-H-Si angles is moved to even smaller values around 155° while the energetic preference compared to the linear Si-H-Si structure is slightly increased ( $\Delta E = -0.8 \text{ kJ mol}^{-1}$ ). Furthermore, a flattened increase in energy with decreasing Si-H-Si angles is detected if B3LYP-D3(BJ) instead of B3LYP-D3 is utilised. Similar to compound **88**, this can be reasoned based on the inclusion of BJ dampening. Independent optimisation of both structures at the B3LYP-D3/cc-pVTZ and B3LYP-D3(BJ)/cc-pVTZ level of theory resulted in Si-H-Si angles of 159° and 156°, respectively.

In contrast, use of M06-2X during screening of different Si-H-Si angles results in a preferred arrangement with an even more acute angle around 146°. A distinctly higher energy difference between the structure with linear Si-H-Si bridge and the structure with the energetically preferred angle ( $\Delta E = -3.0 \text{ kJ mol}^{-1}$ ) are computed when M06-2X is chosen as computational method. Additionally, no smooth curve is obtained for M06-2X (Figure 23). This phenomenon is known in the literature for various M06 functionals if they are used in quantum mechanical investigations of the relative energies versus interatomic distances.<sup>[200]</sup> As a result, multiple energetic minima at different Si-H-Si angles are found for M06-2X. This shows the limits of the method in conjunction with the used model calculation.

If MP2 is applied instead, the value of the energetically preferred Si-H-Si angle increases again to 150° while the relative energy difference decreases ( $\Delta E = -1.4 \text{ kJ mol}^{-1}$ ).

Based on the computational findings (Figure 22 and Figure 23), the following conclusions concerning 2e3c Si-H-Si bridges in (acyclic) Si-H-Si-bridged silyl cations can be drawn:

The parameter Si-H-Si bond angle shows the high dependency on the computational method that is used. In general, the angle decreases if London dispersion interactions are considered (B3LYP vs. B3LYP-D3 or B3LYP-D3(BJ)). This dependency is found for both basis sets, 6-311+G(d,p) or cc-pVTZ, that were used during optimisation. Albeit the calculations performed on the model compounds **88** (Figure 22) and **31** (Figure 23) suggest just a small energetic preference of the bent geometries compared to structures with linear Si-H-Si bridges, the values are still consistent for all performed computations. Also, it can be summarised that the method at the highest level of theory (MP2) gives Si-H-Si bond angles that are more reminiscent to the values obtained using B3LYP-D3 or B3LYP-D3(BJ) compared to the respective values obtained using M06-2X. For both model systems, the M06-2X method always results in the most acute energetically preferred angles. This might result from the parameterisation of London dispersion interaction might result.<sup>[200]</sup> The results show that the size of the Si-H-Si angle is influenced by London dispersion interactions while additional contribution of electrostatic interactions is also suggested (Figure 24).

It must be noted that the experimental XRD structure of the bridged silyl cation **31** (counter anion: [CHB<sub>11</sub>Cl<sub>11</sub>]<sup>-</sup>) shows a bonding angle of 160° and therefore also a significant deviation from linearity. The original paper justified the deviation on basis of crystal packing effects and on the absence of the counter anion in the calculated structure.<sup>[152]</sup> While both reasons are plausible and have to be taken into account, the findings of the present study show that the effects of London dispersion interaction should also be considered.

# 3.2. Syntheses of H-Substituted Oligosilanes

To investigate the influence of additional Si-H units in oligosilanylsilyl cations stabilised by intramolecular 2e3c Si-H-Si bridges, three different hydrogen-substituted oligosilanes **89**, **90** and **91** were synthesised (Figure 25).



## Branching increases

Figure 25: Hydrogen-substituted oligosilanes **89-91**. The pentasilane unit appearing in each structure is marked in red. The numbering of the Si groups used throughout this work is as follows: Starting from the most central Si unit of the branched oligosilane with ascending numbering.

All three oligosilanes can be seen as a series of similar silyl compounds with a varying degree of branching. Thus, the hydrogen-substituted pentasilane unit (Figure 25, marked in red) represented by **89** is included in all three structures. The more branched oligosilanes **90** and **91** are characterised by one or two additional hydrogen-substituted disilyl substituents at the central silicon unit of this pentasilane moiety. The possible interactions of these additional silyl substituents with the formed 2e3c Si-H-Si bridges will be investigated.

In this chapter the syntheses of the three oligosilanes is described as well as a more detailed characterisation of the branched oligosilanes **90** and **91**. For the ease of communication, the magnetically inequivalent Si groups in the branched oligosilanes are numbered as noted in the figure above.

# 3.2.1. Synthesis and Characterisation of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>4</sub>

For the synthesise of the most branched oligosilane **91**, the phenyl-substituted silane  $Si(SiMe_2SiMe_2Ph)_4$  (**92**) was chosen as precursor as its phenyl groups can easily be functionalised via triflate intermediates.<sup>[25-28]</sup>

First trials to synthesise  $Si(SiMe_2SiMe_2Ph)_4$  (**92**) by reaction of  $Si(SiMe_2Cl)_4$  (**93**) with four equivalents of PhMe<sub>2</sub>SiLi (**16**) were not successful (Scheme 33).



Scheme 33: Synthesis of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>4</sub> (**92**) by reaction of Si(SiMe<sub>2</sub>Cl)<sub>4</sub> (**93**) with PhMe<sub>2</sub>SiLi (**16**) and further functionalisation to the hydrogen-substituted oligosilane **91**.

Following this reaction scheme, the phenyl-substituted silane **92** could not be isolated. The reactions of the chlorosilane **93** with the phenylsilanide **16** gave product mixtures from which the phenyl-substituted silane **92** was not isolable in its pure form. The product was accompanied by different side-products that could not be separated from the target compound. Due to the high impurity, the isolated silane **92** was not suitable for further reactions.

Another synthesis strategy was needed which was found in the elegant synthesis described by Marschner and co-workers who reported the reaction of easily accessible (Me<sub>3</sub>Si)<sub>3</sub>SiK (**12**)<sup>[50]</sup> with an excess of fluorosilanes in which all four substituents of the silanide can be exchanged in a clean manner.<sup>[68]</sup> By using FMe<sub>2</sub>SiSiMe<sub>2</sub>Ph (**94**) as substrate in this reaction, the expected product is the targeted oligosilane **92** (Scheme 34).



Scheme 34: Alternative synthesis of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>4</sub> (**91**) by reacting (Me<sub>3</sub>Si)<sub>3</sub>SiK (**12**) with an excess of fluorosilane **94**.

The needed silanide **12** was generated as its solution in THF. Subsequently, an excess of fluorosilane **94** was added to the silanide-containing solution. After 7 days reaction time, the NMR spectra, which were taken to monitor the reaction process, showed the clean formation of one product whose <sup>29</sup>Si NMR signals were in the range expected for the oligosilane **92** (Figure 26).



Spectrum recorded after 7 days reaction time (THF/no lock, 99.31 MHz, 32 °C, # = excess fluorosilane **94**, ° = Me<sub>3</sub>SiO*t*-Bu, \* = unidentified side-products).

As additional NMR samples did not show any further change and the NMR signals of oligosilane **92** were, next to the excess fluorosilane **94**, the main signals visible in the NMR spectra, the reaction mixture was worked-up to give **92** in high yield (86%) and high purity.



The <sup>1</sup>H NMR spectrum (Figure 27) of the isolated product shows the expected set of signals.

Figure 27: <sup>1</sup>H NMR spectrum of **92** (CDCI<sub>3</sub>, 499.87 MHz, 32 °C).

In the spectrum, two upfield-shifted singlets at  $\delta^{1}H = 0.21$  and 0.51 with relative integrals of 24H each can be detected. By 2D NMR spectroscopy (see experimental section), both signals are assigned to the internal dimethylsilyl groups (Si<sup>2</sup>) and the phenyl-substituted dimethylsilyl groups at the end of the disilyl units (Si<sup>3</sup>), respectively. Additionally, two multiplets between  $\delta^{1}H = 7.31-7.42$  and  $\delta^{1}H = 7.49-7.51$  with a total relative integral of 20H are visible in the aromatic region of the <sup>1</sup>H NMR spectrum. These multiplets result from the four phenyl groups of the oligosilane **92**. The assignment to the hydrogen atoms at *ortho*-, *meta*- and *para*-position of the phenyl substituents was also possible by 2D NMR spectroscopy (see experimental section).

The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum shows three signals (Figure 28). One signal is upfield-shifted at  $\delta^{29}$ Si = -105.1 and appears in the typical NMR shift range of a tetrasilyl-substituted silicon atoms.<sup>[203-204]</sup> Therefore, it is assigned to the central silicon atom Si<sup>1</sup>.



Figure 28: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of 92 (CDCl<sub>3</sub>, 99.31 MHz, 32 °C).

The signal shows <sup>29</sup>Si satellites with a coupling of <sup>1</sup>*J*<sub>Si,Si</sub> = 38 Hz. The second NMR signal at  $\delta^{29}$ Si = -38.3 appears in the typical range for dimethylsilyl groups in a silicon chain.<sup>[55, 205]</sup> Thus, the signal is assigned to silicon atom Si<sup>2</sup>. It possesses <sup>29</sup>Si satellites with a splitting of <sup>1</sup>*J*<sub>Si,Si</sub> = 74 Hz. The expected <sup>29</sup>Si satellites with a splitting of <sup>1</sup>*J*<sub>Si,Si</sub> = 38 Hz are also visible albeit the upfield-shifted flank of this satellites is not very well resolved (Figure 28). The third signal at  $\delta^{29}$ Si = -16.8 appears in the shift range of phenyl-substituted dimethylsilyl groups.<sup>[75, 206-207]</sup> It also shows <sup>29</sup>Si satellites with a splitting of <sup>1</sup>*J*<sub>Si,Si</sub> = 74 Hz. Therefore, it is assigned to the phenyl-substituted silyl groups Si<sup>3</sup>. The described assignment can be verified by the analysis of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 172, experimental section).

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 29), a total of six different NMR signals is detectable. Two upfield-shifted signals that appear at  $\delta^{13}C = -1.7$  and  $\delta^{13}C = 0.6$  and which can be assigned via analyses of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum (Figure 168, experimental section) to the methyl groups at Si<sup>3</sup> ( $\delta^{13}C = -1.7$ ) and at Si<sup>2</sup> ( $\delta^{13}C = 0.6$ ). Additionally, four signals appear in the aryl region of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at  $\delta^{13}C = 127.8$  (C<sub>para</sub>), 128.5 (C<sub>meta</sub>), 134.3 ( $C_{ortho}$ ) and 139.7 ( $C_{ipso}$ ) which result from the four magnetically inequivalent carbon atoms of the phenyl groups at Si<sup>3</sup>.





It was also possible to crystallise **92** from acetone at -20 °C. The obtained colourless crystals were suitable for analysis via X-ray diffraction (XRD). The compound crystallised in the monoclinic P2<sub>1</sub> space group with one phenyl substituent disordered. The solid-state structure (Figure 30) shows a tetrahedral arrangement around the central silicon atom Si<sup>1</sup> with angles ranging from 106.1° to 114.8°. The bond lengths fall in the range expected for the respective bonding (Si-Si, Si-C, C-C, C-H).<sup>[208-209]</sup> If the conformations of the SiMe<sub>2</sub>SiMe<sub>2</sub>Ph units of the molecule are analysed, it can be seen (Figure 30, right side) that in the crystal structure an anti-periplanar conformation is adopted, in which the phenyl group at Si<sup>3</sup> and the central silicon atom Si<sup>1</sup> at the other end occupy different sides of a Si<sup>1</sup>-Si<sup>2</sup>Me<sub>2</sub>-Si<sup>3</sup>Me<sub>2</sub>Ph unit. The torsion angles of these silyl fragments range from 160.9° to 173.7°. It must be noted that one torsion angle (173.7°) differs distinctly from the three remaining Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup>-C<sub>ipso</sub> torsion angles (160.9°, 162.3° and 165.2°). A special reason for this deviation was not obvious from the XRD structure and thus likely results from crystal packaging effects.



Figure 30: Left: XRD structure of **92**. Hydrogen atoms are omitted for clarity. Right: Newman project along the Si<sup>2</sup>-Si<sup>3</sup> unit of one disilyl group. The methyl groups at the remaining three silyl substituents are omitted for clarity. Thermal ellipsoids at 50% probability level. Selected bond length [pm] and angles [°]: Si<sup>1</sup>-Si<sup>2</sup> 236.37(4)-238.14(4), Si<sup>2</sup>-Si<sup>3</sup> 235.46(4)-236.51(5), Si<sup>2</sup>-Si<sup>1</sup>-Si<sup>2</sup> 106.06(2)-114.80(2), Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup> 117.87(2)-122.85(2), Si<sup>2</sup>-Si<sup>3</sup>-C<sub>ipso</sub> 101.08(4)-104.96(4), Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup>-C<sub>ipso</sub> 160.92(4)-173.75(4).

# 3.2.2. Synthesis and Characterisation of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub>

Further derivatisation of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>4</sub> (**92**) was performed to obtain Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (**91**) in a two-step procedure (Scheme 35). In the first step of the reaction scheme, the phenyl-substituted oligosilane **92** was reacted with triflic acid to generate the corresponding silyl tetratriflate, Si(SiMe<sub>2</sub>SiMe<sub>2</sub>OTf)<sub>4</sub> (**95**).



Scheme 35: Two-step reaction scheme for the synthesis of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (91).

The formation of the silvl triflate **95** proceeded in a clean manner. Its completion was easily detectable by the appearance of a new <sup>29</sup>Si NMR signal at  $\delta^{29}$ Si = 44.5 (Si<sup>3</sup>), a typical chemical shift range for dimethylsilyl triflates.<sup>[25-27, 75]</sup>



(*n*-pentane/D<sub>2</sub>O lock, 99.31 MHz, 32 °C, # = unidentified side-product).

After completed formation, the triflate **95** was added directly to a suspension of lithium aluminium hydride (Li[AlH<sub>4</sub>]) in diethyl ether to yield the hydrogen-substituted silane **91** in a clean reaction. After work-up, the silane was obtained as a colourless oil in a high yield (94% relative to starting material **92**).

In the <sup>1</sup>H NMR spectrum of hydrogen-substituted oligosilane **91**, three NMR signals are visible (Figure 32). A doublet with a coupling of  ${}^{3}J_{H,H} = 4.5$  Hz and a relative integral of 24H corresponding to the hydrogen atoms of the dimethylsilyl groups bearing the Si-H functionality (Si<sup>3</sup> position) is detected at a chemical shift of  $\delta^{1}H = 0.25$ .



Figure 32: <sup>1</sup>H NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).

The signal of the Si<sup>3</sup>-H hydrogen atom is found at  $\delta^{1}$ H = 4.11 with a relative integral of 4H and <sup>29</sup>Si satellites with <sup>1</sup>*J*<sub>H,Si</sub> = 177.9 Hz, the typical size of a direct <sup>1</sup>H,<sup>29</sup>Si coupling.<sup>[170]</sup> As expected, it shows the same <sup>1</sup>H,<sup>1</sup>H coupling constant (<sup>3</sup>*J*<sub>H,H</sub> = 4.5 Hz) as the more upfield-shifted doublet at  $\delta^{1}$ H = 0.25. The third signal, a singlet at  $\delta^{1}$ H = 0.43 with a relative integral of 24H, belongs to the hydrogen atoms of the methyl groups at Si<sup>2</sup>.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 33) shows two signals at  $\delta^{13}C = -0.5$  and -5.4. Both signals are assigned via <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectroscopy (Figure 179 and Figure 180, experimental section) to the carbon atoms of the methyl groups at Si<sup>2</sup> ( $\delta^{13}C = -0.5$ ) and to the carbon atoms of the methyl groups at Si<sup>3</sup> ( $\delta^{13}C = -5.4$ ).



Figure 33: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 32 °C, \* = C<sub>6</sub>D<sub>6</sub>).

In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 34), three different signals are visible. One signal at  $\delta^{29}$ Si = -119.2 that corresponds to the tetrasilyl-substituted silicon atom Si<sup>1</sup>. The other two signals appear more downfield-shifted at  $\delta^{29}$ Si = -38.3 and at  $\delta^{29}$ Si = -34.1. By <sup>1</sup>H,<sup>29</sup>Si HMQC and HMBC NMR spectroscopy (Figure 183 and Figure 184, experimental section) the signal at  $\delta^{29}$ Si = -34.1 is assigned to the silicon atom Si<sup>3</sup> while the signal at  $\delta^{29}$ Si = -38.3 is assigned to the silicon atom Si<sup>3</sup> while the signal at  $\delta^{29}$ Si = -38.3 is assigned to the silicon atom Si<sup>2</sup>. As already described for the phenyl-substituted oligosilane **92**, the connectivity of the three magnetically inequivalent silicon nuclei in oligosilane **91** can also be verified by analysis of the <sup>29</sup>Si satellite signals of each signal in the recorded <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 182, experimental section).



Figure 34: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 32 °C).

The formation of the hydrogen-substituted oligosilane **91** is also detectable in the recorded ATR IR spectrum (Figure 35, right spectrum). Compared to the ATR IR spectrum of phenyl-substituted oligosilane **92** (Figure 35, left spectrum), the absorption resulting from IR active frequencies of the phenyl substituents ( $\nu > 3000 \text{ cm}^{-1}$ ) disappear while a new band for the Si-H stretching frequency becomes visible ( $\nu = 2108 \text{ cm}^{-1}$ ). The band appears at the characteristic range for IR-active Si-H stretching frequencies.<sup>[210]</sup>



Figure 35: Comparison of the ATR-IR spectra of phenyl-substituted oligosilane **92** (left side) and hydrogen-substituted oligosilane **91** (right side).

#### 3.2.3. Synthesis and Characterisation of MeSi(SiMe<sub>2</sub>HSiMe<sub>2</sub>H)<sub>3</sub>

MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (**90**) was synthesised in multiple steps starting from MeSiCl<sub>3</sub> (Scheme 36). In the first step of the reaction scheme, MeSiCl<sub>3</sub> was reacted with lithium silanide **16** to give Si(SiMe<sub>2</sub>Ph)<sub>3</sub> (**96**) in moderate yields (41%). In the second step, the dearylation of the phenyl-substituted silane **96** was performed by reacting it with triflic acid.<sup>[25-27]</sup> The formed triflate was then directly used for further reaction with **16** to extend its oligosilanyl framework by three terminal phenyl-substituted dimethylsilyl groups. After removal of the solvents and salts, a yellow oil was obtained from which MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>3</sub> (**97**) was isolated (21% yield). In the next step of the reaction scheme, **97** was first transformed to its corresponding triflate by reaction with triflic acid. The triflate was then transformed to its chloro-substituted equivalent by reaction with [HNEt<sub>3</sub>]Cl in diethyl ether. Further reaction of the obtained chlorosilane with Li[AlH<sub>4</sub>] gave the hydrogen-substituted silane MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (**90**) as a colourless oil. Analytical data of the colourless oil showed the silane **90** in the presence of small amounts of side-products (64% total yield).



Scheme 36: Synthesis of MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (90) in a multi-step reaction scheme starting from MeSiCl<sub>3</sub>.

Four different signals are visible in the recorded <sup>1</sup>H NMR spectrum (Figure 36) that are assigned to the hydrogen-substituted oligosilane **90**.



Figure 36: <sup>1</sup>H NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).

The Si<sup>3</sup>-H hydrogen atoms appear as a septet with a chemical shift of  $\delta^{1}H = 4.08$  and a relative integral of 3H in the spectrum. The septet shows a coupling of  ${}^{3}J_{H,H} = 4.4$  Hz, which is also detected for the doublet at  $\delta^{1}H = 0.22$ . The doublet has a relative integral of 18H and results from the six magnetically equivalent methyl groups at Si<sup>3</sup>. The remaining two signals are found slightly further downfield. A singlet at  $\delta^{1}H = 0.31$  with a relative integral of 3H and a singlet at  $\delta^{1}H = 0.33$  with a relative integral of 18H. The signals result from the methyl groups at Si<sup>1</sup> ( $\delta^{1}H = 0.31$ ) and from the six methyl groups at Si<sup>2</sup> ( $\delta^{1}H = 0.33$ ). It must be noted that it is not possible to accurately measure the  ${}^{1}J_{H,Si}$  coupling from the signal at  $\delta^{1}H = 4.08$  as the  ${}^{29}Si$  satellites overlap with signals due to impurities. Instead, the value for the  ${}^{1}J_{H,Si}$  coupling constant can be extracted from the  ${}^{1}H,{}^{29}Si$  HMBC NMR spectrum (Figure 204, experimental section) as  ${}^{1}J_{H,Si} = 175$  Hz. This value is in the expected range for direct  ${}^{1}H,{}^{29}Si$  couplings.[170]

The <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 37) shows three signals that are assigned to oligosilane **90**. Two signals with similar NMR chemical shifts at  $\delta^{29}Si = -35.3$  and -40.3 and one further upfield-shifted signal at  $\delta^{29}Si = -76.9$ . Due to its marked and characteristic upfield shift,<sup>[203-204]</sup> the signal at  $\delta^{29}Si = -76.9$  is assigned to the trisilyl-substituted silicon atom Si<sup>1</sup>.



Figure 37: <sup>29</sup>Si{<sup>1</sup>H} NMR INEPT NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 23 °C).

Additionally, <sup>29</sup>Si satellites with a coupling of <sup>1</sup>*J*<sub>Si,Si</sub> = 52 Hz are visible for the signal at  $\delta^{29}$ Si = -76.9. As <sup>29</sup>Si satellites with the same coupling are detected for the signal at  $\delta^{29}$ Si = -40.3, it is concluded that this signal corresponds to the Si<sup>2</sup> silicon atoms that are directly bound to Si<sup>1</sup>. Although <sup>29</sup>Si satellites are not visible for the signal at  $\delta^{29}$ Si = -35.3, it can be assigned to the Si<sup>3</sup> silicon atoms via 2D <sup>29</sup>Si NMR spectroscopy. In the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 203, experimental section) the signal at  $\delta^{29}$ Si = -35.3 correlates to the doublet at  $\delta^{1}$ H = 0.22 as well as to the septet at  $\delta^{1}$ H = 4.08. The upfield-shifted signal at  $\delta^{29}$ Si = -76.9 shows in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum a correlation to the singlet at  $\delta^{1}$ H = 0.31 which was assigned to the methyl group at the central silicon atom. This observation verifies the assignment of this <sup>29</sup>Si NMR signal to silicon atom Si<sup>1</sup>. Additionally, the correlation between the singlet at  $\delta^{1}$ H = 0.33 and the singlet at  $\delta^{29}$ Si = -40.3 (Si<sup>2</sup>) is visible in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR Spectrum.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 38) shows three signals assigned to oligosilane **90**. All signals appear at a similar shift range in the upfield-shifted region of the spectrum. Thus, the three NMR signals show resonances at  $\delta^{13}C = -10.0$  (MeSi<sup>1</sup>), -5.6 (Me<sub>2</sub>Si<sup>3</sup>) and -3.3 (Me<sub>2</sub>Si<sup>2</sup>). Assignment of all three signals to the three magnetically inequivalent methyl groups of oligosilane **90** is possible by 2D <sup>13</sup>C NMR spectroscopy (Figure 200 and Figure 201, experimental section).



Figure 38: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 32 °C, \* = C<sub>6</sub>D<sub>6</sub>, # = *n*-hexane).

An additional ATR IR spectrum was measured (Figure 205, experimental section) in which the Si-H stretching frequency is detected as a distinct band at  $\nu = 2097$  cm<sup>-1</sup>. The frequency is comparable to the band detected for Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> ( $\nu = 2108$  cm<sup>-1</sup>).

### 3.2.4. Synthesis of HMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H

HMe<sub>2</sub>(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H (**89**) was synthesised in a multi-step reaction scheme starting from Me<sub>2</sub>SiCl<sub>2</sub> (Scheme 37). In general, the synthesis strategy is comparable to the one applied for MeSi(SiMe<sub>2</sub>HSiMe<sub>2</sub>H)<sub>3</sub> (**90**) with only minor deviations. Therefore, only a short overview on the different steps is given. In the first step, Me<sub>2</sub>SiCl<sub>2</sub> was reacted with freshly prepared PhMe<sub>2</sub>SiLi (**16**), to yield the trisilane PhMe<sub>2</sub>SiSiMe<sub>2</sub>SiMe<sub>2</sub>Ph (**98**) as a colourless oil in 65% yield. In the next step of the reaction scheme, the silane **98** was transformed to its corresponding ditriflate by reacting it with triflic acid. After conversion to the ditriflate, reaction of the formed silyl triflate with silanide **16** afforded PhMe<sub>2</sub>(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>Ph (**99**) as a colourless solid in 28% yield. The phenyl-substituted pentasilane **99** was then again reacted with triflic acid to convert it to its respective ditriflate and subsequently added to a suspension of Li[AlH<sub>4</sub>] in diethyl ether. After work-up and purification by distillation, a colourless oil was obtained which contained the

hydrogen-substituted pentasilane **89** in the presence of small amounts of impurities (33% total yield). Further purification was not achieved. Trials to purify the compound **89** via chromatography resulted in decomposition of the oligosilane. The NMR data were in accordance with literature values.<sup>[211]</sup>



Scheme 37: Synthesis of linear HMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H (89) in a multi-step reaction starting from Me<sub>2</sub>SiCl<sub>2</sub>

### 3.2.5. Comparison of the NMR data of the H-Substituted Oligosilanes

If the important NMR data of the hydrogen-substituted oligosilanes **89-91** are summarised and compared, a lot of similarities as well as some deviations are visible (Table 4). Additionally,  $Si(SiMe_2H_{)4}$  (**100**) is listed as it was also used for the synthesis of silyl cations stabilised by 2e3c Si-H-Si bonds (Chapter 3.4.6).

The  ${}^{1}J_{H,Si}$  as well as the  ${}^{3}J_{H,Si}$  coupling constants of all oligosilanes are in a very narrow range. The same can be said about the NMR shifts of the silicon atoms Si<sup>2</sup> of the internal dimethylsilyl groups and silicon atoms Si<sup>3</sup> at terminal positions (Si<sup>2</sup> in case of **100**). The combined NMR data show a small upfield shift for the disilyl-substituted silicon atom Si<sup>2</sup> compared to the monosilyl-substituted Si<sup>3</sup> in the <sup>29</sup>Si NMR spectra. More notably, the <sup>13</sup>C NMR signal of the methyl group at the central Si<sup>1</sup> silicon atom of oligosilane **90** experiences a marked upfield shift compared to the other methyl <sup>13</sup>C NMR signals. Such upfield-shifted <sup>13</sup>C resonances of methyl groups at trisilyl-substituted silicon atoms are known from other oligosilanyl compounds.<sup>[75]</sup> Additionally, it can be detected that the tetrasilyl-substituted silicon atom Si<sup>1</sup> of oligosilane **91** ( $\delta^{29}$ Si = -119.2) shifts significantly further downfield compared to the tetrasilyl-substituted silicon atom Si<sup>1</sup> of the pentasilane **100** ( $\delta^{29}$ Si = -140.0).
The NMR data (<sup>29</sup>Si NMR chemical shifts, <sup>1</sup>J<sub>H,Si</sub> couplings) of the synthesised hydrogen-substituted oligosilanes **89-91** and **100** were compared to the computed NMR data of the respective compounds. The <sup>29</sup>Si NMR shifts were calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory while the coupling constants were calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory. The results of the DFT calculations (Table 4, values in italic) agree well with the experimentally observed NMR data even without taking solvent effects into account.

Table 4: Summary of NMR spectroscopic data of hydrogen-substituted oligosilanes **89-91** and **100** used in the synthesis of silyl cations containing stabilising 2e3c Si-H-Si bridges. Calculated values in *italic*. NMR shift calculations performed at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constants calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p).



δ¹Η	δ <sup>13</sup> C	δ <sup>29</sup> Si		<sup>1</sup> <i>J</i> <sub>H,Si</sub> [Hz]		<sup>3</sup> Ј <sub>Н,Н</sub> [Hz]
		exp.	calc.	exp.	calc.	
0.19 (d, 12H)	_[d]	-43.6	-45 (Si²)			
0.23 (s, 12H)	_[d]	-41.2	-41 (Si¹)			
0.25 (s, 6H)	_[d]	-36.6	-38 (Si <sup>3</sup> )			
4.05 (sept, 2H)				174.3	182	4.5
0.22 (d, 18H)	-10.0 ( <u>Me</u> Si <sup>1</sup> )	-76.9	<i>-81</i> (Si <sup>1</sup> )			
0.31 (s, 3H)	-5.6 ( <u>Me</u> ₂Si³)	-40.3	-40 (Si <sup>2</sup> )			
0.33 (s, 18H)	-3.3 ( <u>Me</u> ₂Si²)	-35.3	-35 (Si <sup>3</sup> )			
4.08 (sept, 3H)				175 <sup>[c]</sup>	185	4.4
0.25 (d, 24H)	-0.5 ( <u>Me</u> ₂Si²)	-119.2	<i>-128</i> (Si <sup>1</sup> )			
0.43 (s, 24H)	-5.4 ( <u>Me</u> ₂Si³)	-38.3	-38 (Si <sup>2</sup> )			
4.11 (sept, 4H)		-34.1	-34 (Si <sup>3</sup> )	177.9	183	4.5
0.31 (d, 24H)	_[d]	-140.0	-147 (Si <sup>1</sup> )			
4.34 (sept, 2H)		-33.6	-32 (Si <sup>2</sup> )	181.0	188	4.4
	$δ^{1}$ H 0.19 (d, 12H) 0.23 (s, 12H) 0.25 (s, 6H) 4.05 (sept, 2H) 0.22 (d, 18H) 0.31 (s, 3H) 0.33 (s, 18H) 4.08 (sept, 3H) 0.25 (d, 24H) 0.43 (s, 24H) 4.11 (sept, 4H) 0.31 (d, 24H) 4.34 (sept, 2H)	δ <sup>1</sup> Hδ <sup>13</sup> C0.19 (d, 12H) $-[d]$ 0.23 (s, 12H) $-[d]$ 0.23 (s, 12H) $-[d]$ 0.25 (s, 6H) $-[d]$ 4.05 (sept, 2H) $-10.0$ (MeSi <sup>1</sup> )0.22 (d, 18H) $-10.0$ (MeSi <sup>1</sup> )0.31 (s, 3H) $-5.6$ (Me <sub>2</sub> Si <sup>3</sup> )0.33 (s, 18H) $-3.3$ (Me <sub>2</sub> Si <sup>2</sup> )4.08 (sept, 3H) $-0.5$ (Me <sub>2</sub> Si <sup>2</sup> )0.43 (s, 24H) $-0.5$ (Me <sub>2</sub> Si <sup>3</sup> )4.11 (sept, 4H) $-[d]$ 0.31 (d, 24H) $-[d]$	$\delta^1 H$ $\delta^{13} C$ $\delta^{2}$ 0.19 (d, 12H) $-[d]$ -43.60.23 (s, 12H) $-[d]$ -41.20.25 (s, 6H) $-[d]$ -36.64.05 (sept, 2H) $-10.0 (MeSi^1)$ -76.90.32 (d, 18H) $-10.0 (MeSi^1)$ -76.90.31 (s, 3H) $-5.6 (Me_2Si^3)$ -40.30.33 (s, 18H) $-3.3 (Me_2Si^2)$ -35.34.08 (sept, 3H) $-0.5 (Me_2Si^2)$ -119.20.43 (s, 24H) $-0.5 (Me_2Si^3)$ -38.34.11 (sept, 4H) $-34.1$ $-34.1$ 0.31 (d, 24H) $-[d]$ $-140.0$ 4.34 (sept, 2H) $-33.6$	$\delta^{1}$ H $\delta^{13}$ C $\delta^{29}$ Siexp.calc.0.19 (d, 12H)-[d]-43.6-45 (Si <sup>2</sup> )0.23 (s, 12H)-[d]-41.2-41 (Si <sup>1</sup> )0.25 (s, 6H)-[d]-36.6-38 (Si <sup>3</sup> )4.05 (sept, 2H)-10.0 (MeSi <sup>1</sup> )0.22 (d, 18H)-10.0 (MeSi <sup>1</sup> )0.31 (s, 3H)-5.6 (Me <sub>2</sub> Si <sup>3</sup> )-40.3 (s, 18H)-3.3 (Me <sub>2</sub> Si <sup>2</sup> )0.33 (s, 18H)-3.3 (Me <sub>2</sub> Si <sup>2</sup> )-35.3-35 (Si <sup>3</sup> )4.08 (sept, 3H)-0.5 (Me <sub>2</sub> Si <sup>2</sup> )0.25 (d, 24H)-0.5 (Me <sub>2</sub> Si <sup>3</sup> )-34.1-34 (Si <sup>1</sup> )0.43 (s, 24H)-5.4 (Me <sub>2</sub> Si <sup>3</sup> )-34.1-34 (Si <sup>3</sup> )0.31 (d, 24H)-[d]-[d]-140.0-147 (Si <sup>1</sup> )4.34 (sept, 2H)-33.6	$\delta^{1}$ H $\delta^{13}$ C $\delta^{29}$ Si $^{1}J_{H,Si}$ exp.exp.exp.exp.0.19 (d, 12H) $^{[d]}$ -43.6 $^{-45}$ (Si <sup>2</sup> )0.23 (s, 12H) $^{[d]}$ -41.2 $^{-41}$ (Si <sup>1</sup> )0.25 (s, 6H) $^{[d]}$ -36.6 $^{-38}$ (Si <sup>3</sup> )4.05 (sept, 2H) $^{[d]}$ $^{-76.9}$ $^{-81}$ (Si <sup>1</sup> )0.22 (d, 18H) $^{-10.0}$ (MeSi <sup>1</sup> ) $^{-76.9}$ $^{-81}$ (Si <sup>1</sup> )0.31 (s, 3H) $^{-5.6}$ (Me <sub>2</sub> Si <sup>3</sup> ) $^{-40.3}$ $^{-40}$ (Si <sup>2</sup> )0.33 (s, 18H) $^{-3.3}$ (Me <sub>2</sub> Si <sup>2</sup> ) $^{-35.3}$ $^{-35}$ (Si <sup>3</sup> )4.08 (sept, 3H) $^{-0.5}$ (Me <sub>2</sub> Si <sup>2</sup> ) $^{-119.2}$ $^{-128}$ (Si <sup>1</sup> )0.43 (s, 24H) $^{-5.4}$ (Me <sub>2</sub> Si <sup>3</sup> ) $^{-38.3}$ $^{-38}$ (Si <sup>2</sup> )4.11 (sept, 4H) $^{-[d]}$ $^{-140.0$ $^{-147}$ (Si <sup>1</sup> )0.31 (d, 24H) $^{-[d]}$ $^{-140.0$ $^{-147}$ (Si <sup>1</sup> )4.34 (sept, 2H) $^{-[d]}$ $^{-33.6}$ $^{-32}$ (Si <sup>2</sup> )	$\delta^{1}$ H $\delta^{13}$ C $\delta^{29}$ Si $^{1}J_{H,Si}$ [Hz]exp.calc.exp.calc.exp.calc.0.19 (d, 12H) $^{[d]}$ -43.6-45 (Si <sup>2</sup> )0.23 (s, 12H) $^{[d]}$ -41.2-41 (Si <sup>1</sup> )0.25 (s, 6H) $^{[d]}$ -36.6-38 (Si <sup>3</sup> )4.05 (sept, 2H).174.31820.22 (d, 18H)-10.0 (MeSi <sup>1</sup> )-76.9-81 (Si <sup>1</sup> )0.31 (s, 3H)-5.6 (Me <sub>2</sub> Si <sup>3</sup> )-40.3-40 (Si <sup>2</sup> )0.33 (s, 18H)-3.3 (Me <sub>2</sub> Si <sup>2</sup> )-35.3-35 (Si <sup>3</sup> )4.08 (sept, 3H)-0.5 (Me <sub>2</sub> Si <sup>2</sup> )-119.2-128 (Si <sup>1</sup> )0.43 (s, 24H)-5.4 (Me <sub>2</sub> Si <sup>3</sup> )-38.3-38 (Si <sup>2</sup> )4.11 (sept, 4H)4.34 (sept, 2H)

 $Si = SiMe_x$ , x = 1 or 2

[a] Recorded in C<sub>6</sub>D<sub>6</sub> at 32 °C. [b] <sup>29</sup>Si NMR data at 23 °C. [c] Detected via <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectroscopy. [d] Not measured.

While comprehensive benchmark studies on <sup>29</sup>Si NMR data are published,<sup>[212-215]</sup> the results enable an estimate of expected deviations between computed and experimental NMR data in neutral and Si-H-Si-bridged oligosilanes presented in this work.

Thus, the calculations can distinguish the internal dimethylsilyl groups and terminal hydrogen-substituted dimethylsilyl groups with high accuracy. The deviation between *calc.* and exp. <sup>29</sup>Si shifts of both groups is less than  $\Delta(\delta^{29}Si) < 2$ . The deviations of the trisilyl-substituted silicon atom of **90** of the tetrasilyl-substituted silicon atoms of **91** and **100** are a little higher with a maximum deviation of  $\Delta(\delta^{29}Si) = 9$  for **91**. The value of the tetrasilyl-substituted silicon atom

is generally calculated a little too far upfield-shifted. With a mean deviation of  $\Delta(\delta^{29}Si) = 7$ , the calculations are still accurate for this silicon moiety. A similar observation is made for the calculated  ${}^{1}J_{H,Si}$  coupling constants. While the results of the DFT calculations predict slightly higher coupling than observed in the experiment, the deviations are less than  $\Delta({}^{1}J_{H,Si}) = 10$  Hz. All in all, it can be shown that the used method/basis set are able to reproduce the experimental  ${}^{29}Si$  NMR shifts and  ${}^{1}J_{H,Si}$  coupling constants with good accuracy.

# 3.3. Synthesis of Silyl-Substituted Ferrocene Derivatives

Next to the hydrogen-substituted oligosilanes described in the previous chapter, the silyl-substituted ferrocene derivative **101** was another target of this work (Figure 39). The silyl substitution pattern at the ferrocene scaffold was chosen as the behaviour of a similar ferrocene derivative **102** in the hydride transfer reaction with  $[Ph_3C][B(C_6F_5)_4]$  was already investigated in our working group.<sup>[163]</sup>



 $Si = SiMe_x$ , x = 2 or 3

Figure 39: Silyl-substituted ferrocene derivative **101** synthesised in this work and its isomer **102** that was already synthesised and investigated in previous works.<sup>[163]</sup>

The ferrocene derivative **101** was synthesised in multiple steps. Inspired by the procedure described by Marschner and co-works for their synthesis of silyl-substituted ferrocene compounds,<sup>[65]</sup> the silyl-substituted ferrocene derivative **103** was first synthesised starting from the cyclopentadienyl-substituted oligosilane **104** and FeBr<sub>2</sub> (Figure 74). In earlier works, Kumada *et al.* already showed that the lithiation of silyl-substituted cyclopentadienyl derivatives followed by salt metathesis reaction with FeCl<sub>2</sub> can be used in the synthesis of various silyl-substituted ferrocene derivatives.<sup>[216-217]</sup>



Scheme 38: Synthesis of ferrocene derivative 103.

Following the described protocol, the ferrocene derivative **103** was obtained after aqueous work-up in good yield. The <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR signals were successfully assigned by oneand two-dimensional NMR spectroscopy (Table 5, see experimental section for the respective 1D/2D NMR spectra).

Table 5: NMR data of the silyl-substituted ferrocene derivative 103.



1	0	3
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$\delta^{1}H^{[a]}$	$\delta^{13} C^{[a]}$	$\delta^{29} Si^{[a]}$
0.26 (s, 54H, Si <u>Me</u> <sub>3</sub> )	1.8 (s, Si <u>Me</u> ₂)	-133.0 (s, <u>Si</u> Si₄)
0.59 (s, 12H, Si <u>Me</u> ₂)	3.1 (s, Si <u>Me</u> ₃)	-13.7 (s, <u>Si</u> Me <sub>2</sub> )
4.11 (s, 4H, β- <u>H</u> <sub>Cp</sub> )	71.4 (s, γ- <u>C</u> <sub>Cp</sub> )	-10.0 (s, <u>Si</u> Me₃)
4.29 (s, 4H, γ- <u>H</u> <sub>Cp</sub> )	73.6 (s, β- <u>C</u> <sub>Cp</sub> )	
	74.6 (s, α- <u>C</u> <sub>Cp</sub> )	

[a] Recorded in C<sub>6</sub>D<sub>6</sub> at 32 °C.

Additionally, it was possible to obtain a XRD structure by recrystallisation of **103** from *n*-hexane. The molecule crystallises in the triclinic P1 space group with a half *n*-hexane molecule per unit cell. Both Cp rings are oriented in a nearly parallel arrangement with a mean deviation of both rings around 0.7°. The two Cp rings of the ferrocene moiety have an equal Fe-Cp<sub>centroid</sub> distance to the iron centre of 165.1-165.2 pm. This distance is in the range described for other 1,1'-silyl-substituted ferrocene derivatives.<sup>[65, 218]</sup> The Cp rings adopt an eclipsed arrangement where the two silyl substituents are turned away from each other. In

case of **103**, both rings show a deviation of around 10° from a perfectly eclipsed arrangement. Additionally, the Si<sup>1</sup>-Cp<sub>centroid</sub>-Cp'<sub>centroid</sub>-Si<sup>1</sup> torsion angle measures as 153.8°. The alignment of both 1,1'-silyl substituents is therefore comparable to the 1,1'bis(bis(trimethylsilyl)silyl)ferrocenylpotassium compound described by Marschner and coworkers,<sup>[65]</sup> which also showed a nearly eclipsed arrangement of both Cp rings and a detected angle between the silicon atoms attached to the Cp rings of 151°. In contrast, the Cp rings in 1,1'-bis(trimethylsilyl)ferrocene were shown to adopt a staggered arrangement in the solid state with both silvl substituents pointing in opposite directions.<sup>[218]</sup> In case of the ferrocene derivative 103, the displacement of the cyclopentadienyl-substituted silvl units from 180° is likely explained by crystal packaging effects. All Si-Si-Si, Si-Si-C and Si-C-C angles show only small deviation from a perfectly tetrahedral coordination environment. The angles range from 106.9° to 112.4°. The Si-S, Si-C, C-C, C-H and C-C bond lengths show no significant deviation from the expected values.[208-209]



Figure 40: XRD structure of **103**. Hydrogen atoms are omitted for clarity. Left: Side view. Right: Top view. Selected bond length [pm] and angles [°]: Fe-Cp<sub>centroid</sub> 165.10(3), Fe-Cp'<sub>centroid</sub> 165.22(3), C<sub>α</sub>-Si<sup>1</sup> 186.25(18), C'<sub>α</sub>-Si'<sup>1</sup> 186.35(17), Si<sup>1</sup>-C<sub>Me</sub> 187.35(17)-187.60(18), Si<sup>1</sup>-Si<sup>2</sup> 235.13(5), Si'<sup>1</sup>-Si'<sup>2</sup> 235.03(5), Si<sup>2</sup>-Si<sup>3</sup> 234.31(7)-234.80(7), Si'<sup>2</sup>-Si'<sup>3</sup> 234.72(7)-235.25(7), Si<sup>3</sup>-C<sub>Me</sub> 187.14(22)-188.20(18), Si'<sup>3</sup>-C'<sub>Me</sub> 187.18(25)-188.07(19), C<sub>α</sub>-Si<sup>1</sup>-Si<sup>2</sup> 109.34(5), C'<sub>α</sub>-Si'<sup>1</sup>-Si'<sup>2</sup> 108.89(5), C<sub>Me</sub>-Si<sup>1</sup>-C<sub>Me</sub> 110.19(8), C'<sub>Me</sub>-Si'<sup>1</sup>-C'<sub>Me</sub> 110.35(8), Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup> 108.10(2)-110.97(2), Si'<sup>1</sup>-Si'<sup>2</sup>-Si'<sup>3</sup> 108.69(2)-111.05(2), Si<sup>2</sup>-Si<sup>3</sup>-C<sub>Me</sub> 108.91(7)-112.29(7), Si'<sup>2</sup>-Si'<sup>3</sup>-C'<sub>Me</sub> 109.67(7)-112.43(7), Si<sup>1</sup>-Cp<sub>centroid</sub>-Cp'<sub>centroid</sub>-Si'<sup>1</sup> 153.78(1).

Subsequently, the ferrocene compound **103** was reacted with potassium *t*-butylate in the presence of 18-crown-6 ether using benzene as a solvent to generate the dianion **105** (Figure 41).



 $Si = SiMe_x$ , x = 2 or 3

18-crown-6 ether (18cr6) = 1,4,7,10,13,16-hexaoxacyclooctadecane

Figure 41: Reaction of **103** with potassium *t*-butylate to generate the dianion **105**.

The formation of the dianion was monitored by NMR spectroscopy. In the <sup>29</sup>Si[<sup>1</sup>H} INEPT NMR spectrum (Figure 42) that was measured after 16 h reaction time, the formation of Me<sub>3</sub>SiO*t*-Bu can be detected. The signals of the neutral ferrocene compound **103** have disappeared. Instead, the formation of a new compound with chemical shifts of  $\delta^{29}Si = -5.6$  and -4.7 and -185.4 can be detected. The <sup>29</sup>Si NMR shift of the anionic, trisilyl-substituted silicon atom ( $\delta^{29}Si = -185.4$ ) is therefore similar to other oligosilanylsilyl dianions.<sup>[55, 73]</sup>



Figure 42: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of the dianion **105** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 32 °C,  $\# = Me_3SiOt-Bu$ ).

After formation of the dianion **105**, the dianion-containing solution was slowly added to the ethereal phase of a cooled mixture of  $H_2SO_4$  and  $Et_2O$  to obtain the ferrocene derivative **101** (Figure 43).



Figure 43: Protonation of dianion 105 to obtain the oligosilanyl-substituted ferrocene derivative 101.

After work-up (see experimental section), the ferrocene derivative was obtained as a red solid. The <sup>1</sup>H NMR spectrum (Figure 44) shows a total of five signals which are assigned to the 1,1'-oligosilanyl-substituted ferrocene compound **101**.



Figure 44: <sup>1</sup>H NMR spectrum of ferrocene compound **101** ( $C_6D_6$ , 499.87 MHz, 32 °C, \* =  $C_6D_5H$ )

In the upfield area of the spectrum, two singlets are visible at  $\delta^{29}Si = 0.22$  and 0.55. Due to their chemical shift range and relative integrals of 36H and 12H, they are assigned to the

trimethylsilyl ( $\delta^{1}$ H = 0.22) and dimethylsilyl ( $\delta^{1}$ H = 0.22) groups of the ferrocene compound. The two Si-H hydrogen atoms are detected at a chemical shift of  $\delta^{1}$ H = 2.60. The signal shows a set of <sup>29</sup>Si satellites with a coupling of <sup>1</sup>*J*<sub>H,Si</sub> = 154.4 Hz which is again in the expected range.<sup>[170]</sup> The chemical shift and coupling constant are very similar to the values reported for (Me<sub>3</sub>Si)<sub>3</sub>SiH ( $\delta^{1}$ H = 2.52, <sup>1</sup>*J*<sub>H,Si</sub> = 154.4 Hz in C<sub>6</sub>D<sub>6</sub>).<sup>[219]</sup> Further downfield in the <sup>1</sup>H NMR spectrum, two pseudo-triplets are visible at  $\delta^{1}$ H = 4.07 and 4.29 that show relative integrals of 4H each. Both signals result from the two cyclopentadienyl units of the ferrocene moiety. Due to their correlations in the two-dimensional <sup>1</sup>H, <sup>13</sup>C and <sup>1</sup>H,<sup>29</sup>Si NMR spectra (experimental section), the signals are assigned to the hydrogen atoms in β-position ( $\delta^{1}$ H = 4.07) and γ-position ( $\delta^{1}$ H = 4.29) of the Cp rings.

Five signals are visible the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 45). The two singlets in the upfield area of the spectrum are assigned to the dimethylsilyl ( $\delta^{13}C = 1.1$ ) and trimethylsilyl groups ( $\delta^{13}C = 2.1$ ) by two-dimensional <sup>13</sup>C NMR spectroscopy (Figure 218 and Figure 219, experimental section).



Figure 45: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of ferrocene compound **101** (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 32 °C, \* = C<sub>6</sub>D<sub>6</sub>).

Three additional singlets appear further downfield at  $\delta^{13}C = 71.5$  ( $\gamma$ -position), 73.4 ( $\beta$ -position), 73.6 ( $\alpha$ -position) which are assigned to the three magnetically inequivalent carbon atoms of the cyclopentadienyl units. Interestingly, the order of the <sup>13</sup>C signals assigned to the

cyclopentadienyl rings is different compared to the 1,1'-oligosilanyl-substituted ferrocene **102**. In compound **102**, the cyclopentadienyl carbon atoms shift at  $\delta^{13}C = 67.0$  ( $\alpha$ -position), 72.4 ( $\beta$ -position) and 75.4 ( $\gamma$ -position).<sup>[163]</sup> Hence, the carbon atom bearing the silyl substituents shifts more upfield than the other two signals. This order is inversed in the <sup>13</sup>C{<sup>1</sup>H} spectrum of **101**. In comparison, the ferrocene derivative **103** shows the same order of signals compared to its relative **101** (Table 5).

The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 46) shows three singlets which are assigned by their chemical shift and by 2D NMR spectroscopy (Figure 221, experimental section) to the three magnetically inequivalent silicon atoms of **101**. The trisilyl-substituted silicon atom resonates at  $\delta^{29}$ Si = -114.2 while the trimethylsilyl groups appear at  $\delta^{29}$ Si = -11.9. Both values are again very similar to the ones reported for (Me<sub>3</sub>Si)<sub>3</sub>SiH ( $\delta^{29}$ Si = -115.6, -11.6 in C<sub>6</sub>D<sub>6</sub>).<sup>[219]</sup> A slight upfield shift is visible for the dimethylsilyl groups directly bound to the cyclopentadienyl unit of the ferrocene ( $\delta^{29}$ Si = -15.3).





In the recorded IR spectrum (Figure 222, experimental section), the Si-H unit can be detected by a vibration at  $\nu = 2056$  cm<sup>-1</sup> which is in the expected range and nearly identical to the frequency reported by Marschner and co-workers for the 1,1'-H(Me<sub>3</sub>Si)<sub>3</sub>Si-substituted ferrocene compound ( $\nu = 2066$  cm<sup>-1</sup>).<sup>[65]</sup> Recrystallisation of **101** from *i*-propanol at -20 °C gave crystals that were suitable for XRD analysis (Figure 47). The ferrocene derivative crystallises in the monoclinic P2<sub>1</sub>/c space group. The cyclopentadienyl rings are planar and both rings, Cp and Cp', are in parallel arrangement. The distance of the centroids of the rings and the iron atom of the ferrocene (166.3 pm) are slightly longer than found in the XRD structure of ferrocene derivative **103** (165.1-165.2 pm). Both oligosilanyl substituents at the Cp rings of **101** show equivalent bond parameters. This stands in contrast to **103** as its XRD structure reveals some small differences in bond lengths and angles between both oligosilanyl moieties (Figure 47). A marked planarization is visible of the hydrogen-bearing silicon atoms. Thus, the sum of Si-Si-Si bond angle around the hydrogen-substituted silicon atoms Si<sup>1</sup> add up to 337.8° compared to 328.5° in a perfectly tetrahedral surrounding. Such planarization is known in the literature for sterically crowded silanes.<sup>[219-220]</sup>



Figure 47: XRD structure of **101**. Hydrogen atoms expect Si-H hydrogen atoms are omitted for clarity. Left: Side view. Right: Top view. Fe-Cp<sub>centroid</sub> 166.32(1), C<sub>α</sub>-Si<sup>1</sup> 186.49(12), Si<sup>1</sup>-C<sub>Me</sub> 187.31(13)-187.38(14), Si<sup>1</sup>-Si<sup>2</sup> 235.19(8), Si<sup>2</sup>-Si<sup>3</sup> 234.15(17)-234.62(5), Si<sup>3</sup>-C<sub>Me</sub> 187.12(14)-187.46(15), C<sub>α</sub>-Si<sup>1</sup>-Si<sup>2</sup> 110.04(4), C<sub>Me</sub>-Si<sup>1</sup>-C<sub>Me</sub> 109.83(6), Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup> 110.83(2)-113.83(2), Si<sup>3</sup>-Si<sup>2</sup>-Si<sup>3</sup> 113,92(2), Si<sup>2</sup>-Si<sup>3</sup>-C<sub>Me</sub> 108.48(5)-111.51(6), C<sub>Me</sub>-Si<sup>3</sup>-C<sub>Me</sub> 107.75(8)-109.86(8), Si<sup>1</sup>-Cp<sub>centroid</sub>-Cp<sup>'</sup><sub>centroid</sub>-Si<sup>'1</sup> 180.00(7).

The remaining Si-Si-Si, Si-Si-C, C-Si-C bond angles show only minor deviations from the tetrahedral coordination.<sup>[208-209]</sup> In comparison with the XRD structure of **103** (Figure 40), a change in the arrangement of the cyclopentadienyl substituents can be detected. For compound **101**, the cyclopentadienyl rings are arranged staggered, while the silyl substituents are exactly opposite to each other. Thus, the torsion angle Si<sup>1</sup>-Cp<sub>centroid</sub>-Cp'<sub>centroid</sub>-Si'<sup>1</sup> in the structure of **101** measures as 180.0° in contrast to 153.8° in the structure of **103**. The alignment

of the Cp rings is therefore very similar to 1,1'-bis(trimethylsilyl)ferrocene.<sup>[218]</sup> Additionally, the oligosilanyl substituents at both Cp moieties adopt a structure in the solid state in which the Si-H units point at different sides. Hence, a torsion angle of 180.0° is measured for H-Si<sup>2</sup>-Si'<sup>2</sup>-H'. It must be noted that the position of the hydrogen atoms is not necessarily perfectly refined in the XRD measurements. Alternatively, the Si<sup>1</sup>-Cp<sub>centroid</sub>-Cp'<sub>centroid</sub>-Si<sup>1</sup> torsion angle can be used which also measures as 180.0°.

# 3.4. Synthesis and Characterisation of Silyl Mono- and Dications

All silvl cations described in this chapter were synthesised according to the Corey protocol,<sup>[109, 221]</sup> a variation of the Barlett-Condon-Schneider (BCS) hydride transfer reaction.<sup>[110]</sup> In this reaction (Scheme 39)., the silvl cation is obtained by the hydride transfer reaction of the respective hydrosilanes with trityl cation ([Ph<sub>3</sub>C]<sup>+</sup>).

Hydride  $R_3Si-H$  +  $[Ph_3C]^+$  abstraction  $[R_3Si]^+$  +  $Ph_3C-H$ 

a) Intermolecular Si-H-Si bond formation

 $[R_{3}Si-H]$ Intermolecular  $[R_{3}Si]^{+} \xrightarrow{\text{stabilisation}} [R_{3}Si-H-SiR_{3}]^{+}$ by
2e3c SiHSi

b) Intramolecular Si-H-Si bond formation



R = alkyl, silyl

Scheme 39: General representation of the formation of silyl cations by reaction of the respective hydrosilanes with trityl cation (Corey reaction) and a) inter- or b) intramolecular stabilisation of the formed silyl cations by 2e3c Si-H-Si bridges. The counter anions are omitted.

If dichloromethane or halogenated aromatic solvents are used, a single-phase reaction mixture is obtained after hydride abstraction. This has the advantage that small amounts of starting material can be used while it is disadvantageous as no purification step can be performed prior to investigation via NMR spectroscopy. Polar and non-polar components of the reaction are present in the reaction mixture. In contrast, if non-halogenated aromatics are used as solvent, a biphasic mixture is obtained. The top phase contains non-polar components, while the bottom phase contains polar components including the target silyl cations. This allows for a purification of the polar phase by separating the upper phase and washing of the bottom phase with the respective solvent. Importantly, the amount of polar phase is defined by the amount of silyl cation formed and hence by the amount of hydrosilanes used in the abstraction reaction. Thus, if NMR spectroscopy is used for characterisation, higher amounts of silane are needed if non-halogenated aromatic solvents are used. See the respective part in the experimental section (Chapter 5.3) for the general protocol to synthesise the silyl cations.

## 3.4.1. H-Bridged Monocation of HMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H

The linear oligosilane **89** was reacted in a hydride transfer reaction with  $[Ph_3C][B(C_6F_5)_4]$  to synthesise the Si-H-Si-bridged cation **106** (Scheme 40). The reaction was carried out as an NMR experiment in deuterated chlorobenzene at -40 °C.

$$\begin{array}{c} H_{Si} Si_{Si} Si_{Si} H_{C_{6}D_{5}CI, -40 \ C} \\ 89 \\ Si = SiMe_{2} \end{array}$$

Scheme 40: Hydride transfer reaction of  $HSiMe_2Si(SiMe_2)_3SiMe_2H$  (89) and  $[Ph_3C][B(C_6F_5)_4]$  to generate Si-H-Si-bridged silyl cation 106.

The recorded NMR spectra are in accordance with the spectroscopic data expected for the six-membered, hydrogen-bridged silyl cation **106**. The <sup>1</sup>H NMR spectrum (Figure 48) shows three signals associated with silyl cation **106**. One singlet at a chemical shift of  $\delta^{1}H = 0.10$  (Si<sup>1</sup> position) and a relative integral of 6H, a singlet at  $\delta^{1}H = 0.13$  (Si<sup>2</sup> position) with a relative integral of 12H and a doublet at  $\delta^{1}H = 0.39$  (Si<sup>3</sup> position) with a small coupling of  ${}^{3}J_{H,H} = 1.9$  Hz barely resolved in the recorded <sup>1</sup>H NMR spectrum. The doublet has a relative integral of 12H.



Figure 48: <sup>1</sup>H NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C, \* = C<sub>6</sub>HD<sub>4</sub>Cl, # = Ph<sub>3</sub>CH).

The corresponding <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 49) shows three signals with chemical shifts and integrals fitting to the postulated silyl cation **106**. A signal at  $\delta^{29}$ Si = 87.1 (Si<sup>3</sup>) which is distinguished by its strong downfield shift and which appears in the typical shift range expected for the silicon atoms of a 2e3c Me<sub>2</sub>Si-H-SiMe<sub>2</sub> bridge. The NMR signal possesses <sup>29</sup>Si satellites with coupling of <sup>1</sup>*J*<sub>Si,Si</sub> = 58 Hz. Next to it, two other signals at  $\delta^{29}$ Si = -38.1 and -43.3 are visible in the spectrum. Both signals are in the typical shift range of dimethylsilyl groups in a silicon chain.<sup>[203-204]</sup> For the signal at  $\delta^{29}$ Si = -38.1 (Si<sup>1</sup>), <sup>29</sup>Si satellites with a coupling of <sup>1</sup>*J*<sub>Si,Si</sub> = 64 Hz are visible. The third signal at  $\delta^{29}$ Si = -43.3 (Si<sup>2</sup>) shows two <sup>29</sup>Si satellites with <sup>1</sup>*J*<sub>Si,Si</sub> = 64 Hz and <sup>1</sup>*J*<sub>Si,Si</sub> = 58 Hz. The visible <sup>29</sup>Si satellites already hint to the connectivity of the different silicon atoms (Scheme 41).

$$J_{Si,Si} = 64 Hz + J_{Si,Si} = 58 Hz \begin{pmatrix} Si^{-}Si^{1} \\ Si^{-}Si^{-}Si^{2} \\ Si^{-}H^{-}Si^{3} \end{pmatrix} Si = SiMe_{2}$$
106
$$[B(C_{6}F_{5})_{4}]^{-}$$

Scheme 41: Connectivity assigned via detectable <sup>29</sup>Si,<sup>29</sup>Si coupling.

The assignment is further supported by the detected integrals of each signal: The signal with a chemical shift of  $\delta^{29}$ Si = -38.1 ( ${}^{1}J_{Si,Si}$  = 64 Hz) and a relative integral of 1Si belongs to the central Si<sup>1</sup> unit of the silvl cation. The signal with a chemical shift of  $\delta^{29}$ Si = -43.3 ( ${}^{1}J_{Si,Si}$  = 64 Hz and  ${}^{1}J_{Si,Si}$  = 58 Hz) and a relative integral of 2Si belongs to the dimethylsilyl groups at Si<sup>2</sup>.



Figure 49: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, -40 °C, # = unidentified side-product, \* = hydrolysis product **107**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

The signal of the silicon atoms which are involved in the cationic 2e3c Si-H-Si bond at Si<sup>3</sup> position ( $\delta^{29}$ Si = 87.1, <sup>1</sup>*J*<sub>Si,Si</sub> = 58 Hz) also shows a relative integral of 2Si as expected for the cationic structure **106**.

The experimentally observed <sup>29</sup>Si chemical shifts are in good agreement with the calculated values of the cyclic silyl cation **106** (Table 6) with a maximum deviation of  $\Delta(\delta^{29}Si) = 8$  between both values for the silicon atoms of the Si-H-Si bond. The calculated values are further downfield-shifted than the experimental observed <sup>29</sup>Si NMR shifts.

Table 6: Comparison of calculated and experimentally detected <sup>29</sup>Si NMR chemical shifts of cyclic silyl cation **106**. NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory.



Silicon atom	$\delta^{_{29}}Si$		<sup>1</sup> <i>J</i> <sub>Si,Н</sub> [Hz]	
	exp. <sup>[a]</sup>	calc.	exp. <sup>[a]</sup>	calc.
Si <sup>1</sup>	-38.1	-35		
Si <sup>2</sup>	-43.3	-42		
Si <sup>3</sup>	87.1	95	53	48

[a] NMR spectra recorded in C<sub>6</sub>D<sub>5</sub>Cl at -40 °C, counter anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

Furthermore, some signals due to impurities are visible in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 49). Calculations on some conceivable side-products indicate that three signals likely result from the protonated siloxane **107**, a conceivable hydrolysis product during the synthesis of silyl cation **106** (Scheme 42). Its <sup>29</sup>Si NMR shifts are calculated at  $\delta^{29}$ Si(*calc.*) = 77 ([Si-O(H)-Si]<sup>+</sup>), -44 (2x SiMe<sub>2</sub>), -46 (1x SiMe<sub>2</sub>) which fits quite well to the signals detected at  $\delta^{29}$ Si = 66, -47 and -48. Integration in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum also allows a quantification of the side-product. Thus, around 8% of the hydrolysis product **107** are calculated based on the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum. Another minor signal due to impurities is detected at  $\delta^{29}$ Si = -8 which could not be assigned to a specific side-product.



Scheme 42: Formation of the possible hydrolysis product 107 by reaction of cation 106 with traces of moisture.

A hydrogen-coupled <sup>29</sup>Si INEPT NMR spectrum (Figure 50) was also recorded to see if the typical splitting of the downfield-shifted signal at  $\delta^{29}$ Si = 87.1 can be detected. While no distinctive splitting of both <sup>29</sup>Si signals at  $\delta^{29}$ Si = -43.3 and -38.1 is visible in the NMR data, the signal at  $\delta^{29}$ Si = 87.1 splits up with a measured coupling constant of <sup>1</sup>*J*<sub>Si,H</sub> = 53 Hz. The value is in accordance with values reported for the direct Si-H coupling of 2e3c Si-H-Si bonds in other silyl cations.<sup>[84-85, 121-123, 131, 135, 159-160]</sup> The observed value also agrees well with the



calculated value at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory of  ${}^{1}J_{Si,H}(calc.) = 48$  Hz.

Figure 50: <sup>29</sup>Si INEPT NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Expansion showing the splitting of the downfield-shifted <sup>29</sup>Si NMR signal of the 2e3c Si-H-Si bridge of the silyl cation (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, -40 °C). Resolution enhancement of the expansion by using em = -1.00 and gm = 3.30.

While an assignment of the <sup>29</sup>Si NMR signals is already possible by analysis of the <sup>29</sup>Si,<sup>29</sup>Si couplings, by comparison of the integrals of the <sup>29</sup>Si signals as well as by a referencing to common <sup>29</sup>Si chemical shift ranges and the calculated <sup>29</sup>Si chemical shift values, further elucidation is achieved by 2D <sup>29</sup>Si NMR spectroscopy (visible correlations summarised in Scheme 43).



Scheme 43: Visible <sup>1</sup>H,<sup>29</sup>Si couplings in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR and in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of silyl cation **106.** The  $[B(C_6F_5)_4]^-$  counter anion is omitted.

In the <sup>1</sup>H,<sup>29</sup>Si HMBC spectrum (Figure 51), correlations of the <sup>1</sup>H NMR signal at  $\delta^{1}H = 0.13$  and 0.39 with the cationic <sup>29</sup>Si signal at  $\delta^{29}Si = 87.1$  (Si<sup>3</sup> position) are visible. In contrast, no correlation of the <sup>1</sup>H NMR signal at  $\delta^{1}H = 0.10$  with this <sup>29</sup>Si NMR signal can be detected. Therefore, it is verified that the <sup>1</sup>H NMR signals at  $\delta^{1}H = 0.10$  corresponds to the central dimethylsilyl group at Si<sup>1</sup>. Although, the expected correlation between this <sup>1</sup>H NMR signal with the respective Si<sup>1</sup> atom at  $\delta^{29}Si = -38.1$  can be seen, its detection is hindered due to the overlap with the cross peak at  $\delta^{1}H = 0.13/\delta^{29}Si = -43.3$ .



Figure 51: Excerpt of the  ${}^{1}$ H, ${}^{29}$ Si HMBC NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C).

The assignment is in accordance with its relative integral in the <sup>1</sup>H NMR spectrum of 6H ( $\delta^{1}$ H = 0.10). In the <sup>1</sup>H,<sup>29</sup>Si HMBC spectrum (Figure 51), the signal at  $\delta^{1}$ H = 0.13 shows a

correlation with the <sup>29</sup>Si signal at  $\delta^{29}Si = -43.3$  (Si<sup>2</sup> position) which has a relative integral of 2Si in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 49). As it also shows a correlation to the cationic signal at  $\delta^{29}Si = 87.1$ , the assignment of the signal at  $\delta^{1}H = 0.13$  to methyl groups at Si<sup>2</sup> position is confirmed. Hence, the doublet at  $\delta^{1}H = 0.39$  results from the silicon atoms Si<sup>3</sup> involved in the 2e3c Si-H-Si bridge which is seen in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum by the correlation of the doublet to the downfield-shifted signal at  $\delta^{29}Si = 87.1$  (Si<sup>3</sup>). Other correlations for the signal at  $\delta^{1}H = 0.39$  are not observable.

The <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum with parameters optimised for a coupling of  $J_{H,Si} = 45$  Hz (Figure 52) shows the same correlations and therefore verifies the assignments made on basis of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 51). Additionally, another cross peak between the cationic silicon atom Si<sup>3</sup> at  $\delta^{29}$ Si = 87.1 and a small signal in the <sup>1</sup>H NMR spectrum at  $\delta^{1}H = 0.44$  can be seen. This cross peak indicates the correlation of the directly bound hydrogen atom of the 2e3c Si<sup>3</sup>-H-Si<sup>3</sup> bridge.



 $(C_6D_5CI, 499.87 \text{ MHz}, -40 \text{ °C}, \text{ optimised for } J_{H,Si} = 45 \text{ Hz}).$ 

Additional evidence for the resonance of the bridging Si<sup>3</sup>-H-Si<sup>3</sup> hydrogen atom at  $\delta^{1}H = 0.44$  results from the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum (Figure 53) in which a cross peak is visible between the doublet at  $\delta^{1}H = 0.39$  (Me<sub>2</sub>Si<sup>3</sup>) with a signal at  $\delta^{1}H = 0.44$  (Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub>). Accordingly, the appearance of the signal at  $\delta^{1}H = 0.39$  as a doublet with a coupling of

 ${}^{3}J_{H,H} = 1.9$  Hz results from the coupling between the Si<sup>3</sup>-H-Si<sup>3</sup> hydrogen atom with the methyl groups at Si<sup>3</sup>. Unfortunately, integration of the signal at  $\delta^{1}H = 0.44$  is not possible in the <sup>1</sup>H NMR spectrum as there is an overlap of the <sup>1</sup>H NMR signal at this chemical shift.



Figure 53: Excerpt of the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C).

The <sup>13</sup>C NMR spectrum (Figure 54) shows three different <sup>13</sup>C NMR signals for the silvl cation **106**. All signals appear in the upfield region of the spectrum at  $\delta^{13}C = -7.7$ , -7.1 and -2.5. An exact assignment of the <sup>13</sup>C NMR signals was possible using the also recorded <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum (Figure 55). In the 2D NMR spectrum, the correlation of the <sup>1</sup>H signal at  $\delta^{1}H = 0.10$  (Si<sup>1</sup> position) and the <sup>13</sup>C signal at  $\delta^{13}C = -7.1$  is detectable. Therefore, it is concluded that the <sup>13</sup>C NMR signal at  $\delta^{13}C = -7.1$  belongs to the methyl groups at Si<sup>1</sup> position. The <sup>1</sup>H NMR signal at  $\delta^{1}H = 0.13$ , previously assigned to the hydrogen atoms at the Si<sup>2</sup> position, shows a correlation to the <sup>13</sup>C atoms with a chemical shift of  $\delta^{13}C = -7.7$ , and the signal is therefore assigned to the carbon atoms of the respective dimethylsilyl group (Si<sup>2</sup> position). The last correlation visible in the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum results from the correlation of the doublet at  $\delta^{1}H = 0.39$  (Si<sup>3</sup> position) with the most downfield-shifted <sup>13</sup>C NMR signal at a chemical shift of  $\delta^{13}C = -2.7$ . Hence, it is concluded that the signal at  $\delta^{13}C = -2.5$  belongs to the methyl groups at Si<sup>3</sup> position. The detected correlations in the also recorded <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum (Figure 226, experimental section) also verify this assignment of the signals.



Figure 55: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C).

The formation of the cyclic silyl cation **106** was also examined by quantum mechanical calculations. The computed data give an energetic preference of the bridged cation **106** compared to the linear, open silyl cation **108** of  $\Delta E = -81$  kJ mol<sup>-1</sup> and  $\Delta G^{*233} = -78$  kJ mol<sup>-1</sup> (Scheme 44). It must be noted that a stationary point on the potential energy surface was only found for the *anti,anti*-conformer of the non-bridged cation **108a**. No stationary point was found for the *syn,syn*-conformer **108b**. Trials to optimise the structure resulted in the formation of the bridged silyl cation **106**.



no minimum found

Scheme 44: Results of the calculations showing the energetic preferences of the cyclic silyl cation **106** containing a 2e3c Si-H-Si bond compared to the non-bridged silyl cations **108a** and **108b**. The molecular structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

In halogenated arene solvents, such as the used chlorobenzene- $d_5$ , an alternative way to stabilise the silyl cation **108a** under formation of the silylated chloronium ion **109** is possible (Scheme 45).



Scheme 45: Results of the calculations showing the energetic gain  $\Delta E$  and  $\Delta G^{*233}$  upon formation of the chloronium ion **109**. The molecular structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

The computations show that the formation of the chloronium ion **109** from the non-bridged silvl cation **108a** and chlorobenzene is accompanied by an energy gain of  $\Delta E = -91$  kJ mol<sup>-1</sup>. Thus, the formation of the chloronium ion 109 is slightly more exothermic than the formation of the Si-H-Si-bridged silvl cation **106** (Scheme 44,  $\Delta E = -81$  kJ mol<sup>-1</sup>). Nonetheless, it must be considered that the formation of 109 is a bimolecular reaction between the non-bridged cation 108a and a chlorobenzene molecule (Scheme 45) whereas the formation of the bridged cation 106 is a unimolecular reaction (Scheme 44). In reactions with change of the molecularity, physical parameters as temperature and pressure can have a significant influence on the Gibbs free energy of the respective reactions. Thus, a proposed correction by Martin et al. was applied to simulate the pressure conditions in the respective solvents and temperatures (Chapter 7.1).<sup>[222]</sup> The Gibbs free energies for which the specific pressure correction is applied are marked with an asterisk (e.g.  $\Delta G^{*233}$ ). For consistency, the correction was generally applied if DFT calculations were performed for reactions that were experimentally performed during this work. In this case, the results of the DFT calculations show that the Gibbs free energy of the bimolecular reaction is less exergonic (Scheme 45,  $\Delta G^{*233}$ = -61 kJ mol<sup>-1</sup>) than the formation of the intramolecularly bridged cation **106** (Scheme 44,  $\Delta G^{*233}$ = -78 kJ mol<sup>-1</sup>). The results of the DFT calculations therefore support the detection of the intramolecularly Si-H-Si-bridged silvl cation **106** instead of the formation of the silvlated chloronium ion **109**.

In another representation of this DFT results, the formation of **109** by the reaction between the Si-H-Si-bridged cation **105** and chlorobenzene can be considered (Figure 56). The reaction is computed as being endergonic ( $\Delta G^{*233} = 18 \text{ kJ mol}^{-1}$ ).



Figure 56: Results of the calculations showing the energetic properties  $\Delta E$  and  $\Delta G^{*233}$  upon formation of the chloronium ion **109** by the reaction of **106** with chlorobenzene. The molecular structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

#### 3.4.2. CI-bridged Monocation of HMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H

The synthesis of the cyclic silyl cation **106** was also performed using dichloromethane-d<sub>2</sub> at -80 °C (Scheme 46).



Scheme 46: Hydride abstraction in dichloromethane-d<sub>2</sub> and subsequent reaction with the solvent to form the Si-Cl-Si-bridged silyl cation **110**.

The <sup>1</sup>H NMR spectrum of the reaction mixture (Figure 57) shows six signals in the range where the NMR resonances of the hydrogen atoms of the dimethylsilyl groups are expected.



Figure 57: <sup>1</sup>H NMR spectrum after hydride transfer reaction of HSiMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H (**89**) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] prior to renewed mixing. A mixture of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]] and **110**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is detected. (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -80 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH, \$ = unidentified side-product).

The signals appear at  $\delta^{1}$ H = 0.30, 0.32, 0.36 (2x), 0.80, 0.89. As the starting silane **89** has only five dimethylsilyl groups, the spectrum suggests a mixture of at least two different silanes.

Additionally, left-over trityl cation can be detected in the <sup>1</sup>H NMR spectrum as well as a sharp signal at  $\delta^{1}$ H = 7.34.

The notion that more than one silvl species are present is verified in the <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 58, top spectrum). Six intense <sup>29</sup>Si signals at  $\delta^{29}$ Si = -44.2, -43.4, -40.2, -37.7, 87.6, 94.8 are detected. Comparison of this <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum with the <sup>29</sup>Si{<sup>1</sup>H} INEPT spectrum measured for the cyclic silvl cation **106** in chlorobenzene-d<sub>5</sub> (Figure 58, bottom spectrum), shows that three additional signals are visible. The signals at  $\delta^{29}$ Si = -43.4 (Si<sup>2</sup> position), -37.7 (Si<sup>1</sup> position), 87.6 (Si<sup>3</sup> position) fit very well to the signals which were assigned to the cyclic silvl cation **106** in chlorobenzene-d<sub>5</sub> (Table 6). A slight variance is justified using a different solvent and the measurement at a different temperature.



Figure 58: Comparison of <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectra obtained after hydride transfer reaction of HSiMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H (**89**) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in different solvents and at different temperatures (Top spectrum: CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, bottom spectrum: C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, -40 °C, \* = signals assigned to **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

The sample was removed from the NMR spectrometer, mixed again in the NMR tube, and returned to the spectrometer. The newly measured <sup>1</sup>H NMR (Figure 59) shows only three signals in the upfield region of the spectrum. The signals appear at  $\delta^{1}H = 0.32$ , 0.36 and 0.89. All three signals appear as singlets in the <sup>1</sup>H NMR spectrum and show relative integrals of 6H, 12H and 12H respectively. It can also be seen that the amount of Ph<sub>3</sub>CH decreased while the

amount of the component associated with the signal at  $\delta^{1}H = 7.34$  increased compared to the <sup>1</sup>H spectrum prior to renewed mixing of the sample (Figure 57).



Figure 59: <sup>1</sup>H NMR spectrum of **110**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Spectrum recorded after renewed mixing/warm-up of the NMR sample (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -80 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH, \$ = unidentified side-product).

The signals visible in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 236, experimental section) correspond to only one cationic silvl species. The methyl groups of silvl cation **110** resonate at  $\delta^{13}C = -7.7$ (Si<sup>2</sup> position), -7.5 (Si<sup>1</sup> position) and 3.1 (Si<sup>3</sup> position). The assignment was possible by analysis of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum (Figure 237, experimental section)

The newly measured <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 60) also fits to the observation made in the <sup>1</sup>H NMR spectrum, as only three signals are visible at  $\delta^{29}$ Si = -44.2 (Si<sup>1</sup>), -40.2 (Si<sup>2</sup>) and 94.8 (Si<sup>3</sup>). The visible signals correspond to all the six signals visible before mixing minus the signals associated with the cyclic silyl cation **106** containing the 2e3c Si-H-Si bond (Figure 58). By <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectroscopy (Figure 240, experimental section), the signal can be assigned to the different dimethylsilyl groups of silyl cation **110**. If the <sup>29</sup>Si chemical shifts of the Si-H-Si-bridged silyl cation **106** and the Si-Cl-Si-bridged silyl cation **110** are compared, it is noticeable that the order of the signal associated with the central dimethylsilyl group in Si<sup>1</sup> position, and the signal assigned to the internal dimethylsilyl groups at Si<sup>2</sup> position are inverted. While for silyl cation **106** the central silicon atom at Si<sup>1</sup> position ( $\delta^{29}$ Si = -38.1) appears further downfield-shifted than the internal dimethylsilyl groups at Si<sup>2</sup> position ( $\delta^{29}$ Si = -43.3), the order is reversed for the Si-Cl-Si-bridged silyl cation **110** (Figure 60).



Figure 60: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **110**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Spectrum recorded after renewed mixing/warm-up of the NMR sample (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, # = unidentified side-products).

An additional hydrogen-coupled <sup>29</sup>Si INEPT NMR spectrum was measured (Figure 61) in which no splitting typical for a 2e3c Si-H-Si unit is visible for the signal at  $\delta^{29}$ Si = 94.8 (Si<sup>3</sup> position). The observations in the NMR spectra are explained by the reaction of the formed cyclic silyl cation 106 with the solvent dichloromethane. In course of this reaction, the bridging hydrogen atom gets substituted by a chlorine atom. This behaviour has been described in the literature if Si-H-Si-bridged silvl cations are formed in dichloromethane.<sup>[163]</sup> The reaction between the silyl cation and the solvent happens if the cation-containing solution gets too warm. In this case, this happened for the first time while the starting silane 89 was initially reacted with  $[Ph_{3}C][B(C_{6}F_{5})_{4}]$  to form the Si-H-Si-bridged cation **106** (Scheme 46), generating a mixture of the cyclic silyl cation 106 containing a 2e3c Si-H-Si bridge on the one hand and the Si-Cl-Si-bridged silyl cation 110 on the other hand (Figure 57 and upper part in Figure 58). When the NMR sample was taken out of the spectrometer and mixed again, the sample warmed up for the second time. This time the warm-up resulted in the complete consumption of the Si-H-Si-bridged cation 106 and the transformation to its chlorine-containing equivalent **110** (Figure 59-Figure 61). The formation of the chlorine-bridged silvl cation **110** is accompanied by the decomposition of the formed Ph<sub>3</sub>CH.



Figure 61: <sup>29</sup>Si INEPT NMR spectrum of **110**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Spectrum recorded after renewed mixing/warm-up of the NMR sample (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, # = unidentified side-products). Resolution enhancement of the expansion using em = -3.70 and gm = 2.60.

This can be seen by the decrease of the signals of Ph<sub>3</sub>CH in the <sup>1</sup>H NMR spectra before (Figure 57) and after renewed mixing (Figure 59). The decomposition of Ph<sub>3</sub>CH is also visible by the detection of a sharp signal at  $\delta^{1}$ H = 7.34 which likely results from benzene that is formed during the decomposition.<sup>[223]</sup>

In contrast, no decomposition of the counter anion  $[B(C_6F_5)_4]^-$  was detected in either the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (Figure 241, experimental section), nor in the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum (Figure 243, experimental section).

Additional quantum mechanical calculations at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory were performed. The results support the formation of the chlorine-bridged silyl cation **110**. The calculated NMR chemicals shifts fit well to the experimentally observed values (Table 7). The largest deviation of experimentally observed and calculated values can be found between the silicon atoms Si<sup>3</sup> of the Si-Cl-Si bridge. Interestingly, the quantum chemical calculations at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory also predict the experimentally observed change in the order of the <sup>29</sup>Si NMR chemical shifts between cation **106** and **110**.

Table 7: Calculated and experimentally detected <sup>29</sup>Si NMR chemical shifts of the cyclic silyl cation **110** containing a 4e3c Si-Cl-Si bond. NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory.

$$Si^{Si_{Si^{2}}^{+}}$$
  
 $Si^{Si_{Si^{2}}^{+}}$   
 $Si_{CI}^{-}Si^{3}$  Si = SiMe<sub>2</sub>  
**110**

Silicon atom	$\delta^{_{29}}Si$	
	exp. <sup>[a]</sup>	calc.
Si <sup>1</sup>	-44.2	-43
Si <sup>2</sup>	-40.2	-38
Si <sup>3</sup>	103	87.6

[a] NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> at -80 °C, counter anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

The facile formation of the chlorine-bridged silyl cation **110** indicates the high reactivity of the hydrogen-bridged cation **106** towards dichloromethane and confirms the high reactivity of the hydrogen-bridged silyl cation **106** in general.

### 3.4.3. Monocation of MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub>

After the hydride transfer reaction of  $HMe_2Si(SiMe_2)_3SiMe_2H$  (89) resulted in the formation of the Si-H-Si-bridged silyl cation 106, the hydride transfer reaction using  $Me(SiMe_2SiMe_2H)_3$  (90) was also attempted (Scheme 47).



Scheme 47: Hydride transfer reaction of MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (90) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to generate 111[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

Compared to linear silane **89**, which resulted in a silyl cation with a static structure and one 2e3c Si-H-Si bridge after hydride abstraction (Chapter 3.4.1), the oligosilanylsilyl cation **111** 

possess an additional SiMe<sub>2</sub>SiMe<sub>2</sub>H substituent. This additional oligosilanyl group could be involved in a dynamic behaviour with the formed 2e3c Si-H-Si bridge. If the hydrogen-substituted disilyl unit would interact with the 2e3c Si-H-Si bridge, it was expected that in this intramolecular reaction, the 2e3c Si-H-Si bridge changes between all three oligosilanyl moieties while passing through a transition state **112** (Scheme 48). Depending on the rate constant of this possible dynamic reaction, it could result in an averaging of all three disilyl units.



 $Si = SiMe_x$ , x = 1 or 2

Scheme 48: Possible degenerated equilibrium for the silyl cation **111**. The  $[B(C_6F_5)_4]^-$  counter anion is omitted.

In a second possibility, the newly introduced disilyl unit would not interact with the formed 2e3c Si-H-Si bridge. In this case, spectroscopic data comparable to silyl cation **106** were expected for the formed six-membered ring with some important differences resulting from the newly introduced disilyl unit (Figure 63).



 $Si = SiMe_x$ , x = 1 or 2

Figure 62: Comparison of the expected differences in the <sup>1</sup>H and <sup>29</sup>Si NMR signals of cations **106** and **111** if the newly introduced dislyl unit is not involved in any dynamic behaviour. The  $[B(C_6F_5)_4]$  counter anion is omitted.

While an upfield shift of the central silicon atom in Si<sup>1</sup> position due to change from disilyl (cation **106**) to trisilyl substitution (cation **111**) was expected in both possible cases, the uninvolved disilyl unit in the second case would be identifiable by two additional <sup>29</sup>Si NMR signals of the SiMe<sub>2</sub>SiMe<sub>2</sub>H unit whereby one of those signals would show a diagnostic Si-H coupling constant (usually  ${}^{1}J_{H,Si} = 170-220 \text{ Hz}^{[170]}$ ). Moreover, an uninvolved SiMe<sub>2</sub>SiMe<sub>2</sub>H unit would add three additional NMR signals to the <sup>1</sup>H NMR spectrum resulting from the methyl groups and the directly silicon-bound hydrogen atom.

For the hydride transfer reaction dichloromethane-d<sub>2</sub> was chosen as a solvent. The hydride abstraction was performed at -90 °C and NMR spectroscopic data were recorded at the same temperature.

Interestingly, an intramolecular reaction (Scheme 48), which should result in a broadening the NMR signals, is not indicated in the recorded NMR spectra. The spectra rather suggest the formation of a silyl cation with a static behaviour on the NMR time scale. In this structure, the asymmetric substitution at Si<sup>1</sup> results in magnetic inequivalence of the methyl groups of the dimethylsilyl units of the six-membered ring (Figure 63).



Expected <sup>1</sup>H integrals (ring): 1H (1x Me<sub>2</sub>Si-<u>H</u>-SiMe<sub>2</sub>) 3H (1x MeSi) 24H (4x SiMe<sub>2</sub>)  $\longrightarrow$ 

Different signals for Me *syn/anti* relative to disilyl group at Si<sup>1</sup>

Figure 63: Schematic representation of the silyl cation **111** with methyl groups in *syn-* and *anti*-position. The  $[B(C_6F_5)_4]^-$  counter anion is omitted.

In the <sup>1</sup>H NMR spectrum (Figure 64), a total of seven different signals in the area around  $\delta^{1}H = 0.00-1.00$  are assigned to the formed silvl cation **111** (Table 8). Five signals appear crowded together between  $\delta^{1}H = 0.15-0.43$  while one signal appears as a sharp peak further downfield at  $\delta^{1}H = 0.80$ , next to a broad signal at  $\delta^{1}H = 0.74$ . Additionally, a signal at  $\delta^{1}H = 3.71$  is visible, which is in the typical shift range for the hydrogen atoms of dimethylsilyl groups.



Figure 64: <sup>1</sup>H NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).

If a relative integral of 1H is assigned for the signal at  $\delta^1$ H = 3.71 (Si<sup>5</sup> position), the relative integrals of the other six signals add up to 39H. These integrals fit to the 13 methyl groups present in silyl cation **111** in position Si<sup>1</sup>-Si<sup>5</sup>. Due to its relative integral of 3H, the signal at  $\delta^1$ H = 0.21 is assigned to the methyl group at the central silicon atom (Si<sup>1</sup> position). That the other signals in this area show all the same relative integrals of 6H each suggest that each signal results from two methyl groups (Si<sup>2</sup>, Si<sup>4</sup> and Si<sup>5</sup> position). In contrast, the signal slightly further downfield at  $\delta^1$ H = 0.80 has a relative integral of 12H which fits to four methyl groups (Si<sup>3</sup> position). Moreover, the signal at  $\delta^1$ H = 0.74 is assigned to the hydrogen atom of the bridging Si<sup>3</sup>-H-Si<sup>3</sup> moiety (see 2D spectra below). The relative integral of this signal is higher than the expected 1H. This is explained by an overlap with the bottom of the signal at  $\delta^1$ H = 0.80 (Figure 64, expansion).

Table 8: Assignment of the <sup>1</sup>H NMR spectrum of  $111[B(C_6F_5)_4]$  and relative <sup>1</sup>H integrals (CD<sub>2</sub>Cl<sub>2</sub>, -90 °C).



δ <sup>1</sup> H	Relative Integral	Assignment
0.15	6H	Si⁵ <u>Me</u> ₂H
0.21	3H	Si¹ <u>Me</u>
0.27	6H	Si⁴ <u>Me</u> ₂
0.37	6H	Si² <u>Me</u> ₂ (s <i>yn/anti</i> )
0.43	6H	Si² <u>Me</u> ₂ (s <i>yn/anti</i> )
0.74	2H <sup>[a]</sup>	[Me <sub>2</sub> Si <sup>3</sup> - <u>H</u> -Si <sup>3</sup> Me <sub>2</sub> ] <sup>+</sup>
0.80	12H	[ <u>Me</u> ₂Si <sup>3</sup> -H-Si <sup>3</sup> <u>Me</u> ₂] <sup>+</sup>
3.71	1H	SiMe <sub>2</sub> H

[a] Due to overlap with the signal at  $\delta^{1}$ H = 0.80, the integral measures as more than the expected 1H.

If the structural properties of the postulated silyl cation **111** (Figure 63) are analysed, the following conclusions can be drawn:

Due to the asymmetric substitution pattern at Si<sup>1</sup>, the six-membered ring adopts a preferred conformation. This preference for one conformation is observed in the low temperature <sup>1</sup>H NMR spectrum. As a result, methyl groups in *syn-* or *anti-*position relative to the SiMe<sub>2</sub>SiMe<sub>2</sub>H moiety are magnetically inequivalent which explains the multitude of signals visible in the <sup>1</sup>H NMR spectrum. Additional analysis by 1D/2D NMR spectroscopy allows to further clarify the structure and assignment of the different signals to the various groups in silyl cation **111**.

In the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum (Figure 245, experimental section), only the correlation between the signal at  $\delta^{1}$ H = 0.15 with the downfield-shifted signal at  $\delta^{1}$ H = 3.71 are detected. As the signal at  $\delta^{1}$ H = 3.71 was assigned due to its characteristic shift to the directly bound

Si<sup>5</sup>-H hydrogen atom, the signal at  $\delta^{1}$ H = 0.15 is assigned to the respective two methyl groups at Si<sup>5</sup> position (<sup>3</sup>*J*<sub>H,H</sub> coupling visible in the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum).

The <sup>29</sup>Si{<sup>1</sup>H} and <sup>29</sup>Si NMR spectra also show signals that are in line with a static structure for silyl cation **111** on the NMR time scale. In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 65), five <sup>29</sup>Si NMR signals ( $\delta^{29}$ Si = -76.6, -37.8, -37.2, -34.8, 90.3) are assigned to the formed silyl cation.



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -90 °C, # = unidentified side-products).

The origin of two of these signals can be already established due to their specific <sup>29</sup>Si NMR shifts. The signal at  $\delta^{29}Si = -76.6$  appears at the expected shift area of trisilyl-substituted methylsilyl groups.<sup>[170, 204]</sup> It is therefore assigned to silicon atom Si<sup>1</sup>. The chemical shift is also very similar to the chemical shift of the respective group in the starting material ( $\delta^{29}Si = -76.9$ ), oligosilane **90** (Table 4). The downfield-shifted signal at  $\delta^{29}Si = 90.3$  is also at the shift range expected for silicon atoms involved in a cationic 2e3c Si-H-Si bridge.<sup>[84-86]</sup> It is therefore assigned to the two Si<sup>3</sup> atoms. The three remaining signals at  $\delta^{29}Si = -37.8$ , -37.2 and -34.8 appear all in the area expected for either dimethylsilyl groups in a silicon chain (Si<sup>2</sup> and Si<sup>4</sup>) or hydrogen-substituted dimethylsilyl groups at terminal position (Si<sup>5</sup>). The relative integrals of this signals (2 : 1 : 1) indicate that the signal with a chemical shift of  $\delta^{29}Si = -37.8$  and a relative integral of 2Si results from the two Si<sup>2</sup> dimethylsilyl groups of the formed hexacycle. It follows,

that both remaining signals at  $\delta^{29}$ Si = -37.2 and -34.8 with each having a relative integral of 1Si belong to the free SiMe<sub>2</sub>SiMe<sub>2</sub>H unit.

Further assignment of the <sup>29</sup>Si NMR signals is achieved by analysis of the hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 66). In the spectrum, the downfield-shifted signal at  $\delta^{29}$ Si = 90.3 and the signal at  $\delta^{29}$ Si = -34.8 each show signal splitting due to <sup>1</sup>*J*<sub>Si,H</sub> coupling.



The detected splitting of approximately  ${}^{1}J_{Si,H} = 176$  Hz verifies the assignment of the signal at  $\delta^{29}Si = -34.8$  to hydrogen-substituted dimethylsilyl group (Si<sup>5</sup>).<sup>[170]</sup> The splitting of the downfield-shifted signal measures as  ${}^{1}J_{Si,H} = 42$  Hz. This is in the typical size of the expected  ${}^{1}J_{Si,H}$  splitting detected for 2e3c Si-H-Si bridges.<sup>[84-86]</sup> The detection of a splitting with this size also verifies the assignment of the resonance at  $\delta^{29}Si = 90.3$  to the two Si<sup>3</sup> silicon atoms. Table 9 summarises all assignments made on basis of  ${}^{29}Si$  chemical shifts and the detected splittings in the hydrogen-coupled  ${}^{29}Si$  NMR spectrum.

Table 9: Assignment of the <sup>29</sup>Si{<sup>1</sup>H} and <sup>29</sup>Si NMR spectra of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, -90 °C).



**111** [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>

δ <sup>29</sup> Si	Detected ${}^{1}J_{Si,H}$ coupling [Hz]	Assignment	
-76.6	-	Si <sup>1</sup>	
-37.8	-	Si <sup>2</sup>	
-37.2	-	Si <sup>4</sup>	
-34.8	176	Si <sup>5</sup>	
90.3	42	Si <sup>3</sup>	

Two-dimensional <sup>29</sup>Si NMR spectra can be used to affirm the assignments in the <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopic data. Various correlations are detectable in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 67). As shown in the expansion, the <sup>1</sup>H NMR signal at  $\delta^{1}$ H = 3.71 correlates to the <sup>29</sup>Si NMR signals at  $\delta^{29}$ Si = -37.2 (Si<sup>4</sup>) and -34.8 (Si<sup>5</sup>). Additionally, the signal at  $\delta^{1}$ H = 0.80 correlates only to the downfield-shifted <sup>29</sup>Si NMR signal at  $\delta^{29}$ Si = 90.3 which was assigned to the cationic 2e3c Si<sup>3</sup>-H-Si<sup>3</sup> bridge. Therefore, the signal at  $\delta^{1}$ H = 0.80 (relative integral 12H) unambiguously belongs to the four methyl groups of the [Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub>]<sup>+</sup> unit. In this case, no shift difference of the methyl groups in syn- and anti-position relative to the free oligosilaryl substituent is measurable in the <sup>1</sup>H NMR spectrum. The two <sup>1</sup>H NMR signals at  $\delta^{1}$ H = 0.37 and 0.43 also correlate with the downfield signal at  $\delta^{29}$ Si = 90.3. Therefore, they are assigned to the methyl groups at the Si<sup>2</sup> silicon atoms of the six-membered ring. In this case, two signals with relative integrals of each 6H result from the magnetically inequivalent methyl groups in syn- and anti-position (Figure 63). The expected correlations to the <sup>29</sup>Si NMR signal at  $\delta^{29}$ Si = -37.8 (Si<sup>2</sup>) are difficult to specify exactly, as the resolution in the <sup>29</sup>Si domain of the 2D spectrum does not allow an exact assignment in this area. The remaining three signals at  $\delta^{1}$ H = 0.15, 0.21 and 0.27 show no correlation to the downfield signal at  $\delta^{29}$ Si = 90.3. Instead, correlations to the signal at  $\delta^{29}Si = -76.6$  (Si<sup>1</sup>) are detected for the signals at
$\delta^{1}$ H = 0.21 and 0.27 while no such correlation is detected for the signal at  $\delta^{1}$ H = 0.15. All three signals ( $\delta^{1}$ H = 0.15, 0.21 and 0.27) show correlations into the area around  $\delta^{29}$ Si = -38.0 to -34.5. Again, an exact specification of this correlations in the <sup>29</sup>Si domain of the HMBC spectrum is no possible due to the insufficient spectral resolution.



Figure 67: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of silyl cation **111** (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C). Expansion showing the correlations of the Si-H signal at  $\delta$ <sup>1</sup>H = 3.71.

The <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 68) which was recorded with modifications for  $J_{H,Si} = 45$  Hz also verifies the assignments of the <sup>1</sup>H NMR signals. Additionally, it allows for an assignment of the two remaining signals at  $\delta^{1}H = 0.15$  and 0.27 due to a higher resolution in the spectroscopic data (Figure 69). The signal at  $\delta^{1}H = 0.27$  correlates to the <sup>29</sup>Si signals at  $\delta^{29}Si = -76.6$  (Si<sup>1</sup>) and to the signal at  $\delta^{29}Si = -37.2$  (Si<sup>4</sup>), whereas the signal at  $\delta^{1}H = 0.15$  correlates only to the signal at  $\delta^{29}Si = -34.8$  (Si<sup>5</sup>).

In summary, it can be said that the assignments made based on the <sup>29</sup>Si NMR chemical shifts and detected coupling constants (Table 9) are verified by analysis of the visible couplings in the <sup>1</sup>H,<sup>29</sup>Si HMBC and HMQC NMR spectra. Furthermore, it can be noted that in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 67) as well as in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 68), correlations between the downfield-shifted signal at  $\delta^{29}$ Si = 90.3 and a signal around  $\delta^{1}$ H = 0.74 are noticeable. The visible correlations result from the bridging hydrogen atom of the cationic 2e3c Si-H-Si unit in silyl cation **111**.



Figure 68: Extract of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of silyl cation **111** showing the area  $\delta^{1}$ H 0.10-1.00. (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, optimised for  $J_{H,Si}$  = 45 Hz).



Figure 69: Extract of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of silyl cation **111** showing the area  $\delta^1$ H = 0.12-0.36. (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, optimised for J = 45 Hz).

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 70), a total of seven <sup>13</sup>C signals assigned to silvl cation **111** are detected. All signals appear as sharp singlets at  $\delta^{13}C = -11.8$ , -7.0, -6.8, -5.3, -4.9, -1.9 and -1.4. The most upfield-shifted signal at  $\delta^{13}C = -11.8$  shows a similar resonance as the methyl group at the central silicon atom of the starting material, oligosilane **90** (Table 4,  $\delta^{13}C = -10.0$ ).



 $= [B(C_6F_5)_4]^{-}).$ 

The assignments of the <sup>13</sup>C NMR signals (Table 10) to the different groups present in the molecular structure of silyl cation **111** can be derived from 2D <sup>13</sup>C NMR spectroscopic data.

Table 10: Assignment of the  ${}^{29}Si{}^{1}H$  and  ${}^{29}Si$  NMR spectra of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, -90 °C).



$$[B(C_6F_5)_4]^-$$

δ <sup>13</sup>	C ${}^{1}J_{\rm H,C}$ with	$\delta^1$ H $^3J_{ m H,C}$ with $\delta$	<sup>5</sup> <sup>1</sup> H Assignment
-11	.8 0.21	not detecte	ed Si¹ <u>Me</u>
-7.	0 0.43	0.37	Si² <u>Me</u> ₂ ( <i>syn/anti</i> )
-6.	8 0.15	not detecte	ed Si⁵ <u>Me</u> ₂H
-5.	3 0.37	0.43	Si² <u>Me</u> ₂ ( <i>syn/anti</i> )
-4.	9 0.27	not detecte	ed Si <sup>4</sup> <u>Me</u> <sub>2</sub>
-1.5	9 0.80	0.80	[ <u>Me</u> ₂Si³-H-Si³ <u>Me</u> ₂]+ (s <i>yn/anti</i> )
-1	4 0.80	0.80	[ <u>Me</u> ₂Si³-H-Si³ <u>Me</u> ₂]+ ( <i>syn/anti</i> )

While correlations can be detected in the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum (Figure 247, experimental section), the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum (Figure 71) shows a higher spectral resolution. Assignment is therefore primary done by analysis of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum. The upfield-shifted signal at  $\delta^{13}C = -11.8$  correlates only to the <sup>1</sup>H NMR signal with a relative integral of 3H at  $\delta^{1}H = 0.21$ . Thus, the assignment of the signal at  $\delta^{13}C = -11.8$  to the methyl group at Si<sup>1</sup> is verified. Moreover, the signal at  $\delta^{1}H = 0.8$  ([Me<sub>2</sub>Si<sup>3</sup>-Si<sup>3</sup>Me<sub>2</sub>]<sup>+</sup>) correlates to two most downfield-shifted <sup>13</sup>C signals at  $\delta^{13}C = -1.9$  and -1.4. Both signals are therefore assigned to the methyl groups in *anti-/syn*-position at Si<sup>3</sup>. The signals of the free SiMe<sub>2</sub>SiMe<sub>2</sub>H unit at  $\delta^{1}H = 0.15$  (Si<sup>5</sup>Me<sub>2</sub>H) and 0.27 (Si<sup>4</sup>Me<sub>2</sub>) correlate to signals at  $\delta^{13}C = -6.8$  and -4.9, respectively. The signals of the methyl groups (*syn/anti*) attached to Si<sup>2</sup> at  $\delta^{1}H = 0.37$  and 0.43 can also be assigned due to their correlations. The signal at  $\delta^{13}C = -7.0$ . While the <sup>1</sup>H,<sup>13</sup>C HMBC spectrum is quite crowded, some <sup>3</sup>J<sub>H,C</sub> correlations between the methyl





Figure 71: <sup>1</sup>H, <sup>13</sup>C HMBC NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C).

While all NMR spectroscopic data concur with a static structure of silyl cation **111** at -90 °C (Table 11), it is not possible to conclude which methyl groups are in *syn-/anti*-position relative to the free disilyl unit at Si<sup>1</sup> position. Furthermore, an exact conformation of **111**, e.g. chair-like or boat-like, cannot be derived from the experimental NMR data. Therefore, DFT calculations were performed to further analyse the formed silyl cation (Chapter 3.5).

Table 11: Summarised NMR spectroscopic data of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, -90 °C).



**111** [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>

$\delta^1 H$	δ <sup>13</sup> C (Me)	δ <sup>29</sup> Si	<sup>1</sup> <i>J</i> <sub>Si,Н</sub> [Hz]
0.21	-11.8	-76.6	
0.37/0.43 (syn/anti)	-7.0/-5.3 (syn/anti)	-37.8	
0.80 ( <i>syn/anti</i> )	-1.9/-1.4 ( <i>syn/anti</i> )	90.3	42
0.74 (Si- <u>H</u> -Si)	-		
0.27	-4.9	-37.2	
0.15 (Si <u>Me</u> 2H)/3.72 (SiMe2 <u>H</u> )	-6.8	-34.8	176
	δ <sup>1</sup> H           0.21           0.37/0.43 (syn/anti)           0.80 (syn/anti)           0.74 (Si- <u>H</u> -Si)           0.27           0.15 (Si <u>Me</u> <sub>2</sub> H)/3.72 (SiMe <sub>2</sub> <u>H</u> )	δ¹Η         δ¹³C (Me)           0.21         -11.8           0.37/0.43 (syn/anti)         -7.0/-5.3 (syn/anti)           0.80 (syn/anti)         -1.9/-1.4 (syn/anti)           0.74 (Si-H-Si)         -           0.27         -4.9           0.15 (SiMe <sub>2</sub> H)/3.72 (SiMe <sub>2</sub> H)         -6.8	δ¹H         δ¹³C (Me)         δ²ºSi           0.21         -11.8         -76.6           0.37/0.43 (syn/anti)         -7.0/-5.3 (syn/anti)         -37.8           0.80 (syn/anti)         -1.9/-1.4 (syn/anti)         90.3           0.74 (Si-H-Si)         -         -           0.27         -4.9         -37.2           0.15 (SiMe <sub>2</sub> H)/3.72 (SiMe <sub>2</sub> H)         -6.8         -34.8

## 3.4.4. Monocation of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub>

In contrast to the silyl cation **111**, the respective silyl cation **113** of the branched oligosilane  $Si(SiMe_2SiMe_2H)_4$  (**91**) has two hydrogen-substituted disilyl units attached to the central silicon atom at Si<sup>1</sup> position (Figure 72).



Figure 72: Comparison of Si-H-Si-bridged silyl cations **111** and **113**. The  $[B(C_6F_5)_4]^-$  counter anions are omitted.

Thus, the position is not asymmetrically substituted anymore. As a result, a different behaviour of the silyl cation **113** in the NMR spectra was likely to occur. Based on the substitution pattern, an involvement of the hydrogen-substituted disilyl units with the formed 2e3c Si-H-Si bridge was expected.

## 3.4.4.1. Synthesis and Characterisation of the Silyl Cation

The oligosilane Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (**91**) was reacted with one equivalent of  $[Ph_3C][B(C_6F_5)_4]$  to obtain the bridged oligosilanylsilyl cation **113** (Scheme 49). The reaction was performed as an NMR experiment in dichlormethane-d<sub>2</sub> at -90 °C.



Scheme 49: Generation of  $113[B(C_6F_5)_4]$  by hydride transfer reaction of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (91) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)].

The <sup>1</sup>H NMR spectrum shows an accumulation of broad signals in the upfield area of the spectrum (around  $\delta^{1}H = 0.1$ ) from which no structure can be elucidated (Figure 73). Nonetheless, the formation of Ph<sub>3</sub>CH is clearly detectable in the spectrum which verifies a successful hydride transfer reaction between oligosilane **91** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Additionally, the appearance of broadened signals already indicated a dynamic process.



Figure 73: <sup>1</sup>H NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).

In contrast, the measured <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 74) shows five different <sup>29</sup>Si NMR signals. Analysis of the spectrum enables a further characterisation of the formed silyl cation. In the spectrum, a sharp signal at  $\delta^{29}$ Si = -124.8 can be detected. By its marked upfield shift, the signal is assigned to a tetrasilyl-substituted silicon atom like the central silicon atom Si<sup>1</sup>.<sup>[203-204]</sup> Further downfield, three broadened signals at  $\delta^{29}$ Si = -37.1, -35.0 and -34.3 are visible in the spectrum. The chemical shifts are in the area expected for dimethylsilyl groups in a silicon change or hydrogen-substituted dimethylsilyl groups (Table 4). Even further downfield, there is an additional broad singlet at  $\delta^{29}$ Si = 89.1. The signal at  $\delta^{29}$ Si = 89.1 is characterised by its downfield shift and appears in the <sup>29</sup>Si chemical shift range of similar oligosilanylsilyl cations bearing 2e3c Si-H-Si bridges. <sup>[84-85, 121-123, 159]</sup> It is thus assigned to Si<sup>3</sup>. Interestingly, the relative integrals in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum show an approximate 2 : 6 ratio between the downfield-shifted signal and the three signals at  $\delta^{29}$ Si = -37.1, -35.0 and -34.3 which fits to the integrals expected for oligosilanylsilyl cation **113**. The broadening of the <sup>29</sup>Si NMR signals of **113** compared to the signals of silyl cation **111** also suggests different behaviours of both cations on the NMR time scale.



Figure 74: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -90 °C, # = hydrolysis products **114**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]). Resolution enhancement of the expansion performed by em = -7.50 and gm = 9.70.

Additionally, signals associated with side-products are detected at  $\delta^{29}Si = 62.8$  and 55.3. While the side-products could not be isolated, the detected chemical shifts indicate their assignment to the two possible hydrolysis products **114**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. For both structures, downfield-shifted <sup>29</sup>Si NMR shifts at  $\delta^{29}Si(calc.) = 72$  (**114**, [Si-O(H)-Si]<sup>+</sup>) and  $\delta^{29}Si(calc.) = 56$ (**115**, [Si<sub>3</sub>O]<sup>+</sup>) were computed.



Figure 75: Possible hydrolysis products of silyl cation **113**. The  $[B(C_6F_5)_4]^-$  counter anions are omitted.

Integration of both <sup>29</sup>Si NMR signals and comparison to the downfield-shifted <sup>29</sup>Si NMR signal of cation **113** show that the side-products occur just in minor quantities of less than 10% combined. The other <sup>29</sup>Si NMR signals of both compounds are likely obscured by the NMR signals of the main compound **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

In the hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 76), it is observable that the signal at  $\delta^{29}$ Si = -34.3 splits up with a coupling of approximately  ${}^{1}J_{Si,H}$  = 170-180 Hz which is similar to the respective coupling detected for the starting material, oligosilane **91** (Table 4,  ${}^{1}J_{H,Si}$  = 177.9 Hz). The coupling constant is in the range of a typical coupling constant between directly bound hydrogen and silicon atoms.<sup>[55, 72, 170]</sup> Therefore, it is concluded that this signal belongs to hydrogen-substituted silicon Si<sup>5</sup>. The other two signals at  $\delta^{29}$ Si = -37.1 and -35.0 do not show any splitting so that they are assigned to internal dimethylsilyl groups Si<sup>2</sup> and Si<sup>4</sup> of the formed silyl cation. It is not possible to distinguish both dimethylsilyl groups based on the <sup>29</sup>Si NMR data.



Figure 76: Comparison of the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (top) and in the <sup>29</sup>Si NMR spectrum (bottom) of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Expansion showing the area around  $\delta^{29}$ Si = -46 to -28 in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum and in the <sup>29</sup>Si NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -90 °C, # = hydrolysis products **114**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]and **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

For the signal at  $\delta^{29}Si = 89.1$  (Si<sup>1</sup>) no splitting resulting from coupling of the Si-H-Si moiety (calculated at  ${}^{1}J_{H,Si}(calc.) = 47$  Hz, see below) can be observed. It must be considered that the signal at  $\delta^{29}Si = 89.1$  is already quite broadened at -90 °C (FWHM = 54 Hz) in the

hydrogen-decoupled <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 74). Thus, the splitting might be obscured in the hydrogen-coupled <sup>29</sup>Si NMR spectrum. If the temperature is further lowered to -93 °C, a sharpening of the downfield-shifted signal is observed in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 77, top spectrum, FWHM = 36 Hz). In the coupled <sup>29</sup>Si NMR spectrum at -93 °C (Figure 77, bottom spectrum), a splitting of the signal at  $\delta^{29}$ Si = 89.1 becomes visible. The signal splits up with a coupling of <sup>1</sup>*J*<sub>Si,H</sub> = 31 Hz which is in the range of <sup>1</sup>*J*<sub>Si,H</sub> coupling constants detected for other silylium ions that are intramolecularly stabilised by 2e3c Si-H-Si bond.<sup>[84-86]</sup> In contrast to other Si-H-Si-bridged silyl cations it was not possible to detect the bridging hydrogen atom in either the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum (Figure 257, see experimental section) or in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 265. experimental section).



Figure 77: Expansions of the <sup>29</sup>Si{<sup>1</sup>H} and <sup>29</sup>Si NMR spectra of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Top spectrum: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -93 °C), bottom spectrum: <sup>29</sup>Si NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -93 °C). Resolution enhancement of the bottom spectrum by em = -65.00 and gm = 33.00.

The observed sharpening of the <sup>29</sup>Si signals with decreasing temperature suggested a temperature-dependent dynamic process. To investigate the dynamic behaviour of **113** in solution, the temperature of the NMR sample was varied and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were measured at the different temperatures.

The temperature was therefore raised from -90 °C to -75 °C and then gradually cooled down again. In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectra at different temperatures (Figure 78) a reversible change

of the signals is detectable. The temperature was first directly raised from -90 °C to -75 °C. In the recorded spectrum at that temperature, the downfield-shifted signal at  $\delta^{29}Si = 89.1$  is significantly broadened but still visible. A broadening of the signals in the shift area around  $\delta^{29}Si = -30$  to -40 is also visible next to the appearance of a new signal around  $\delta^{29}Si = -36.6$ . The temperature was then lowered again in steps of 5 °C.



Figure 78: Variable temperature (VT) <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] showing a reversible temperature dependency of the NMR signals. The temperature first raised from -90 °C (1. Spectrum) to -75 °C (2. Spectrum) and then gradually lowered again until the former temperature of -90 °C (5. Spectrum) was reached again (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, variable temperatures, # = hydrolysis product **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

Hence, <sup>29</sup>Si{<sup>1</sup>H} spectra were recorded at -80 °C, -85 °C and again at -90 °C. The signal at  $\delta^{29}$ Si = 89.1 sharpens again with decreasing temperature. The signal at  $\delta^{29}$ Si = -36.6 which was detectable at -75 °C broadens and finally disappears again while the three formerly visible signals at  $\delta^{29}$ Si = -34.1, -35.0 and -37.1 reappear. The spectrum recorded after renewed cooling of the NMR sample to -90 °C resembles the spectrum recorded before warm-up and renewed decrease of temperature.

As already mentioned, the observations are indicative for a reversible intramolecular process in silyl cation **113**. To further investigate the dynamic behaviour, the temperature of the reaction mixture was increased even further in an additional NMR experiment and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded at the different temperatures (Figure 79). While the downfield-shifted signal at

 $\delta^{29}$ Si = 89.1 is barely detectable at -75 °C, it disappears completely at higher temperatures. Additionally, the newly appearing signal at  $\delta^{29}$ Si = -36.6 sharpens further with increasing temperature. No significant change is detectable for the upfield-shifted <sup>29</sup>Si NMR signal around  $\delta^{29}$ Si = -124.8 (Si<sup>1</sup>).



Figure 79: VT <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of silyl cation **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] showing change in the <sup>29</sup>Si signals with increasing temperature (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, variable temperatures, # = hydrolysis products **114**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

These observations are explained by the two additional hydrogen-substituted oligosilanyl substituents in the silyl cation **113** which are involved in the intramolecular dynamic process (Scheme 50). Even at low temperatures, the intramolecular reaction occurs which results in the alternating position of the formed 2e3c Si-H-Si bridge. The reaction happens with a rate so that the <sup>29</sup>Si spectra show a total of five signals at temperatures of -85 °C or lower: The downfield-shifted signal constitutes of the two silicon atoms involved in the 2e3c Si-H-Si bridge (Si<sup>3</sup>), while the three signals in the <sup>29</sup>Si NMR shift range of  $\delta^{29}Si = -40$  to -30 result from the two dimethylsilyl (Si<sup>2</sup>) groups of the hexacycle formed after bridging and from the two internal dimethylsilyl (Si<sup>4</sup>) and two terminal hydrogen-substituted dimethylsilyl (Si<sup>5</sup>) groups of the free oligosilanyl substituents. The rate gets slowed down upon further cooling which can be seen

by a sharpening of the <sup>29</sup>Si NMR signals. At -93 °C, the rate is sufficiently slowed down to make observation of the <sup>1</sup> $J_{Si,H}$  Si-H-Si splitting of the downfield-shifted signal possible.



Scheme 50: Representation of the intramolecular reaction postulated to occur for the silyl cation **113**. During the intramolecular reaction, the 2e3c Si-H-Si bridge is alternating between the different oligosilanyl substituents of the molecule rather than being located at one Si-H-Si unit.

The existence of free hydrogen-substituted oligosilanyl moieties is detectable by the splitting of the signal at  $\delta^{29}$ Si = -34.3 (Si<sup>5</sup>) in the hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 76) with a coupling in the typical range of <sup>1</sup>*J*<sub>H,Si</sub> couplings. The fifth signal results from the central tetrasilyl-substituted silicon atom which resonates at higher field around  $\delta^{29}$ Si = -124.8 (Si<sup>1</sup>). With increasing temperatures, broadening of all signals except for the central silicon atoms are visible due to an increased rate of the intramolecular reaction. Hence, at a temperature of around -70 °C and higher, the cationic Si-H-Si bridge alternates between all four oligosilanyl units with a rate constant that results in a loss of the downfield-shifted <sup>29</sup>Si NMR signals. Accordingly, the same effect is observed for the <sup>29</sup>Si NMR signal at  $\delta^{29}$ Si = -34.3 (Si<sup>5</sup>Me<sub>2</sub>H). In its case, the increase in temperature also results in a similar broadening, and finally a loss of signal. The expected appearance of a new <sup>29</sup>Si NMR signal that results from the averaged signals of the Si<sup>3</sup> and Si<sup>5</sup> silicon atoms cannot be observed. As noted below, decomposition of the formed silyl cation occurs before any new signals in the <sup>29</sup>Si NMR spectra resulting from an averaging of the Si<sup>3</sup>-H-Si<sup>3</sup> unit and the free Si<sup>5</sup>-H functionalities involved in the intramolecular reaction become visible.

Instead, the sharp signal at  $\delta^{29}$ Si = -36.6, which appears when the temperature is gradually increased, results from the averaged NMR chemical shifts of the central dimethylsilyl groups (Si<sup>2</sup>/Si<sup>4</sup>) which appeared at low temperature at  $\delta^{29}$ Si = -37.1 and -35.0. Interestingly, the <sup>29</sup>Si{<sup>1</sup>H} NMR spectra at temperatures as high as -45 °C do not indicate a reactivity of the formed silyl cation with the solvent dichloromethane (Figure 79). This stands in contrast to the

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cyclic silyl cation **106** (Chapter 3.4.1) and observations made for other silyl cations containing 2e3c Si-H-Si bridges which show reactivity with the solvent already at lower temperatures.<sup>[163]</sup>

Furthermore, a pronounced sharpening of the NMR signals can be observed, Thus, at -35 °C two signals at  $\delta^{1}$ H = 0.47 and 0.56 with the same integral can be detected in the <sup>1</sup>H NMR spectrum (Figure 273, experimental section). Also, a very broad signal can be detected further downfield at  $\delta^{1}$ H = 2.87.

If the temperature is raised even higher, decomposition occurs which can be monitored via <sup>1</sup>H NMR spectroscopy (Figure 80).



Figure 80: VT  $^{1}$ H NMR spectra showing decomposition of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, variable temperatures).

In course of the decomposition, the signals associated with Ph<sub>3</sub>CH disappear while two sharp peaks at  $\delta^{1}$ H = 7.37 and  $\delta^{1}$ H = 0.46 appear. Interestingly, the signal at  $\delta^{1}$ H = 7.37 resonates similarly to the hydrogen atoms of benzene in dichloromethane-d<sub>2</sub>.<sup>[223]</sup> Therefore, it seems likely that during the decomposition of silyl cation **113**, the Ph<sub>3</sub>CH also decomposes which results in the formation of benzene or a benzene derivative. The second intense signal at  $\delta^{1}$ H = 0.47 shows a correlation in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 278,experimental section) with a <sup>29</sup>Si signal at  $\delta^{29}$ Si = 31.7 (Figure 277, experimental section). This is in the typical <sup>29</sup>Si NMR shift range for chloro-substituted dimethylsilyl groups.<sup>[224]</sup> The detections of such groups at higher temperatures is expected as decomposition reactions of silvl cations in dichloromethane are often associated with the formation of chlorinated silvl species.<sup>[155-156]</sup> While the main decomposition product was not analysed any further, it must be noted that a broad featureless signal in the area  $\delta^{1}H = 0$  to  $\delta^{1}H = 1$  is also visible in the <sup>1</sup>H NMR spectrum next to multitude of sharper peaks (Figure 276, experimental section).

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at -93 °C (Figure 81, top spectrum) shows broad signals in the upfield region of the spectrum.



Figure 81: Excerpt of the upfield region of the VT  ${}^{13}C{}^{1}H$  NMR spectra of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, variable temperatures).

The signals appear in the shift range expected for methyl groups attached to a silicon atom. The visible signals are a broad singlet at  $\delta^{13}C = -6.9$ , a cluster of three peaks that overlap at  $\delta^{13}C = -3.1$ , -2.4 and -1.7. Also visible is a broad featureless signal between  $\delta^{13}C = -1.3$  to 2.5. In addition to the broad signals, a multitude of some small and sharper signals is visible which partial overlap with the broad signals. If the temperature is raised to -90 °C (Figure 81, middle spectrum), a slight broadening of the signals become visible. If the temperature is raised further to -75 °C, more pronounced changes in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 81, bottom spectrum) become visible. The most notable change can be seen for the three signals at  $\delta^{13}C = -3.1$ , -2.4 and -1.7 which are not visible at -75 °C. Instead, a new signal at  $\delta^{13}C = -2.6$ 

appears in the <sup>13</sup>C{<sup>1</sup>H} spectrum. While a change of the signal with a change of temperature also indicates a dynamic behaviour for the silyl cation **113**, analysis of the two-dimensional <sup>1</sup>H,<sup>13</sup>C NMR data was not possible due to overlap of the broad signals. Thus, while some correlations are visible in the <sup>1</sup>H,<sup>13</sup>C HQMC NMR spectrum at -75°C (Figure 271, experimental section), the visible correlations do not allow a further clarification of the molecular structure of silyl cation **113** due to the broadness of the respective signals in the <sup>1</sup>H as well as the <sup>13</sup>C domain.

As already mentioned above for the <sup>1</sup>H NMR spectrum, the corresponding <sup>13</sup>C{<sup>1</sup>H} NMR (Figure 274, experimental section) shows also only two sharp signals at  $\delta^{13}C = -3.8$  and -1.8 if the temperature is raised further to -35 °C. While this can be explained by the averaging of the <sup>1</sup>H and <sup>13</sup>C signals of the methyl groups in Si<sup>3</sup> and Si<sup>5</sup> position as well as the methyl groups in Si<sup>2</sup> and Si<sup>4</sup> position, an exact assignment of the <sup>1</sup>H and <sup>13</sup>C signals at this temperature was not performed.

It is possible for silvl cation **113** to estimate the Gibbs free energy of the postulated intramolecular reaction (Scheme 51) which results in the coalescence of the downfield-shifted signal via variable temperature NMR spectroscopy (Figure 79).<sup>[225]</sup>





**116** with pentacoordinated silicon atom is passed through. The transition state is shown only once.

The coalescence was determined to appear near -70 °C. With this value and a frequency difference of the signal of the Si-H-Si bridge (Figure 76,  $\delta^{29}$ Si = 89.1) and the signal of the free oligosilanyl units (Figure 76,  $\delta^{29}$ Si = -34.3) of  $\Delta v = 12253$  Hz, a rate constant was calculated as  $k_{coal} = 27202$  s<sup>-1</sup>.

This value was then used to calculate the energy barrier of the reaction as:[225]

$$\Delta G \ddagger (exp.) = 19.13 \cdot 203 \text{ K} \cdot (9.97 + \log 9.97 + 203 \text{ K}27202 \text{ s} - 1 = 31 \text{ kJ mol} - 1$$

It must be noted that the energy barrier calculated on basis of this method gives only a rough estimate. For better results, line broadening experiments at different temperatures would be needed. Unfortunately, this was not possible due to the insufficient quality of the NMR data. Thus, further investigations were performed by DFT calculations, which will be discussed in more detail in chapter 3.5.

Additionally, NMR shifts and coupling constants were computed (Table 12). The NMR shift calculations were performed at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory.

Table 12: Comparison of experimental and calculated <sup>29</sup>Si NMR chemical shifts (averaged values) and direct Si-H coupling of silyl cation **113**. NMR shifts were calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. The coupling constants were calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



Silicon atom	$\delta^{ m 29}{ m Si}$		<sup>1</sup> <i>J</i> <sub>Si,H</sub> [Hz]	
	exp. <sup>[a]</sup>	calc.	exp. <sup>[a]</sup>	calc.
Si <sup>1</sup>	-124.8	-120		
Si <sup>2</sup>	-35.0/-37.1 <sup>[b]</sup>	-35		
Si <sup>3</sup>	89.1	97	31 <sup>[c]</sup>	49
Si <sup>4</sup>	-37.1/-35.0 <sup>[b]</sup>	-34		
Si <sup>5</sup>	-34.3	-33	170-180 <sup>[d]</sup>	176

[a] NMR spectra recorded in  $CD_2Cl_2$  at -90 °C, counter anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. [b] No distinction possible on basis of the NMR data. [c] Detected at -93 °C.[d] Due to overlap with neighbouring signals not measurable more accurately.

The computations estimate a chemical shift of  $\delta^{29}Si(calc.) = 97$  and Si-H coupling of  ${}^{1}J_{Si,H}(calc.) = 49$  Hz for the cationic Si-H-Si bridge (Si<sup>3</sup>). For the central silicon atom Si<sup>1</sup>, a chemical shift of  $\delta^{29}Si(calc.) = -120$  is obtained. Chemical shifts of  $\delta^{29}Si(calc.) = -35$  (Si<sup>2</sup>), -34 (Si<sup>4</sup>) and -33 (Si<sup>5</sup>) are calculated for the SiMe<sub>2</sub>SiMe<sub>2</sub>H substituents and for the central dimethyl silyl groups of the six-membered ring (Table 12). The coupling constants for the two Si-H units

not involved in the 2e3c Si-H-Si bridge are calculated as  ${}^{1}J_{Si,H}(calc.) = 169$  Hz and 182 Hz (average 176 Hz). Therefore, the calculated values are in good agreement with the  ${}^{29}$ Si chemical shifts observed in the experiment. In contrast to silyl cations **106** (Table 6) and **111** (Table 22), the difference between experimentally measured and calculated value for the Si-H-Si coupling are more pronounced. The experimentally detected  ${}^{1}J_{Si,H}$  coupling of the 2e3c Si-H-Si bridge is around 18 Hz smaller than the calculated value for silyl cation **113**.

#### 3.4.4.2. Trapping Reaction of the Monocation with (*n*-Bu)<sub>3</sub>SnD

To verify that the postulated silyl cation **113** was formed after hydride abstraction with  $[Ph_3C][B(C_6F_5)_4]$  and that no rearrangement of the molecule occurred, a trapping reaction was performed (Scheme 52). Tributyltin deuteride was used as trapping agent and the reaction was performed in toluene at -40 °C. As trapping product, the monodeuterated oligosilane **117** was expected. Toluene was chosen as its use results in a biphasic mixture with an upper layer containing the non-polar components and a bottom layer containing polar components which makes separation and purification very convenient. Trials to trap the cation in other solvents did not work well, most likely because of side reactions with the formed cationic tin species.





The GCMS of the non-polar phase after reaction with the tin deuteride shows a main component whose mass spectrum (Figure 82, bottom part) is very similar to the mass spectrum of the starting silane **91** (Figure 82, upper part).



Figure 82: Upper part: Mass spectrum of the non-deuterated silane **91**. Bottom part: Mass spectrum of the deuterated oligosilane **117** obtained from the GCMS data of the non-polar phase after trapping with tributyltin deuteride.

Other components found in the GCMS of the non-polar phase are Ph<sub>3</sub>CH and the pyridine derivative which was additionally used as a proton sponge (2,4-di-*t*-butyl-4-Me-pyridine) during the trapping reaction (Figure 357, experimental section). While the relative intensities of the fragments differ a little, both mass spectra are identical with the exception that the highest m/z that is detected for the trapping product **117** is one unit higher than detected for the hydrogen-substituted silane **91** (m/z = 438.2 vs. m/z = 437.2). This implies an equal molecular structure with one hydrogen atom substituted by a deuterium atom. It must be noted that not the [M<sup>+</sup>] signal of the molecules is detected in both cases. Instead, the highest m/z corresponds to the [M<sup>+</sup> -SiMe<sub>2</sub>H] fragment after elimination of one dimethylsilyl group.

The obtained NMR spectra confirm the formation of the deuterated oligosilane **117**. In the <sup>1</sup>H NMR spectrum (Figure 83), a singlet at  $\delta^{1}H = 0.54$  and a relative integral of 24H is visible. It belongs to the three dimethylsilyl groups at Si<sup>2</sup> position and the one dimethylsilyl group at Si<sup>4</sup> position. While both positions are not equivalent, as Si<sup>2</sup> is attached to a hydrogen-substituted silyl unit, while Si<sup>4</sup> is attached to a deuterium-substituted silyl unit, the difference does not result in a detectable magnetic inequivalence.



Figure 83: <sup>1</sup>H NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C, # = Ph<sub>3</sub>CH, \* = 2,4-di-*t*-butyl-4-Me-pyridine).

Further downfield, a septet with a coupling constant of  ${}^{3}J_{H,H} = 4.4$  Hz and a relative integral of 3H is visible at  $\delta^{1}$ H = 4.22. Additionally, <sup>29</sup>Si satellites with <sup>1</sup>J<sub>H,Si</sub> = 177.6 Hz are observable for the septet. By its shift range and by the detectable  ${}^{1}J_{H,Si}$  coupling constant, the signal is assigned to the three Si<sup>3</sup>-H moieties. Additionally, there is a doublet at  $\delta^{1}$ H = 0.35 and the same coupling constant of  ${}^{3}J_{H,H} = 4.4$  Hz which results from the methyl groups at Si<sup>3</sup>. Interestingly, the doublet at  $\delta^1 H = 0.35$  does not show a relative integral of 18H as it is expected for the three Si<sup>3</sup>Me<sub>2</sub>H groups. Instead, the doublet is highly asymmetrical with left and right flank of the doublet showing different relative integrals. While its left flank has a relative integral of 9H, the right flank has an increased relative integral of 15H. The total measured relative integral of the doublet is therefore 24H. This observation is explained by an overlap of the right flank of the doublet with the <sup>1</sup>H NMR signal arising from the deuterated dimethylsilyl group (Si<sup>5</sup>Me<sub>2</sub>D). Therefore, a total relative integral of 24H (18H (3x Si<u>Me<sub>2</sub>H) + 6H (1x SiMe<sub>2</sub>D))</u> results for the doublet. The  ${}^{3}J_{H,D}$  coupling constant cannot be extracted from the shown NMR spectrum as the overlapping doublet obscures the splitting. Other than that, the <sup>1</sup>H NMR spectrum looks identical to the one obtained for the starting silane 91 which again confirms the observation made in the GCMS that both silanes, the non-deuterated 91 as well as the monodeuterated silane 117, have an identical molecular structure.



The <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 84) shows five signals which are assigned to the deuterated product **117**.

Figure 84: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of deuterated silane **117** and expansions showing the triplets resulting from Si-D coupling ( $C_6D_6$ , 99.31 MHz, 32 °C, # = unidentified side-product).

The signals appear as a singlet at  $\delta^{29}$ Si = -34.0 (Si<sup>3</sup>), a triplet at  $\delta^{29}$ Si = -34.6 (Si<sup>5</sup>), a singlet at  $\delta^{29}$ Si = -38.3 (Si<sup>2</sup>), a second triplet at  $\delta^{29}$ Si = -38.4 (Si<sup>4</sup>) and another signal at  $\delta^{29}$ Si = -119.2 (Si<sup>1</sup>). The <sup>29</sup>Si signal at  $\delta^{29}$ Si = -34.0 shows negative phase in the <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum and can be assigned via <sup>1</sup>H, <sup>29</sup>Si HMQC NMR (Figure 85) to the Si<sup>3</sup> silicon atom of the hydrogen-substituted dimethylsilyl groups. The triplet directly next to it at  $\delta^{29}$ Si = -34.6 shows a coupling constant of <sup>1</sup>*J*<sub>Si,D</sub> = 27 Hz which is in the expected magnitude of the coupling to a directly bonded deuterium atom (<sup>1</sup>*J*<sub>D,Si</sub> =  $\gamma_D/\gamma_H \cdot {}^1J_{H,Si}$  = 0.154<sup>[225]</sup> · 177.6 Hz = 27.4 Hz). Therefore, the triplet visible at  $\delta^{29}$ Si = -34.6 belongs to Si<sup>5</sup>. The second singlet at  $\delta^{29}$ Si = -38.3 results from the resonance of the three central dimethylsilyl groups Si<sup>2</sup> of the non-deuterated oligosilanyl substituents. This assignment is supported in the <sup>1</sup>H, <sup>29</sup>Si HMQC NMR spectrum (Figure 85). An intense correlation of this <sup>29</sup>Si = -38.3 shows a splitting of <sup>2</sup>*J*<sub>D,Si</sub> = 2 Hz. By its NMR shift and the visible coupling, the signal is assigned to the Si<sup>4</sup> silicon atoms of the internal dimethylsilyl group of the deuterated disilyl unit. The upfield-shifted signal at  $\delta^{29}$ Si = -119.2 can



be assigned by its typical shift range<sup>[204]</sup> and by its coupling in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 86) to the tetrasilyl-substituted silicon atom Si<sup>1</sup> at the centre of the oligosilane **117**.

Figure 85: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).



Figure 86: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).

Interestingly, the signal also splits up into a triplet with a coupling constant of about  ${}^{3}J_{D,Si} = 2$  Hz in the  ${}^{29}Si{}^{1}H$  INEPT NMR spectrum (Figure 84). The  ${}^{3}J_{D,Si}$  splitting has therefore the same size as the experimentally measured  ${}^{2}J_{D,Si}$  coupling constant.

Both 2D <sup>29</sup>Si NMR spectra (Figure 85 and Figure 86) are not able to accurately detect the correlation resulting from the deuterated oligosilanyl moiety. The NMR shift differences between the deuterated and the non-deuterated substituents are too small to be distinguishable in the 2D NMR data.

Additionally, a <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 354, experimental section) was measured. The detected relative integrals fit to the assignments made on basis of the <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 84) as well as the two 2D <sup>29</sup>Si NMR spectra (Figure 85 and Figure 86). While the triplet splitting (<sup>3</sup>*J*<sub>D,Si</sub> = 2 Hz) of the upfield-shifted <sup>29</sup>Si signal at  $\delta^{29}$ Si = -119.2 is also visible in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum, the splitting of the signal at  $\delta^{29}$ Si = -38.3 is not resolved in this NMR spectrum.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 87) shows three signals in the area in which the methyl carbon of **117** are expected.



Figure 87:  ${}^{13}C{}^{1}H$  NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 32 °C, # = Ph<sub>3</sub>CH, \* = 2,4-di-*t*-butyl-4-Me-pyridine).

The signals appear as singlets at  $\delta^{13}C = -5.5$ , -5.4 and -0.5. The signal at  $\delta^{13}C = -0.5$  is assigned via <sup>1</sup>H,<sup>13</sup>C NMR spectroscopy (Figure 88 and Figure 89) to the internal dimethylsilyl groups at Si<sup>4</sup> and Si<sup>2</sup> positions. The signal at  $\delta^{13}C = -5.4$  is assigned to the methyl groups at the non-deuterated silicon atoms in Si<sup>3</sup> position. The signal appears at the same <sup>13</sup>C NMR shifts as for the analogous non-deuterated silane **91** (Figure 33). Although the resolution in the 2D <sup>13</sup>C NMR spectra misses the resolution to do an exact assignment of the signal at  $\delta^{13}C = -5.5$ , it is assigned to the methyl groups at the deuterated Si<sup>5</sup> position due to its small, but measurable, shift difference (intrinsic isotope effect<sup>[226]</sup>) compared to the <sup>13</sup>C NMR signal of the respective hydrogen-substituted groups.



Figure 88: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).



Figure 89: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of deuterated silane **117** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C).

Additionally, the polar phase was dried *in vacuo* and analysed by NMR spectroscopy (chlorobenzene with D<sub>2</sub>O lock). The obtained spectra reveal a quite clean reaction. The recorded <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 90) shows no significant amount of silyl species. In the recorded <sup>129</sup>Sn{<sup>1</sup>H} NMR spectrum (Figure 91), one main component with a chemical shift of  $\delta^{119}$ Si = 213.8 is visible. In accordance with the reaction scheme (Scheme 52), the signal likely results from the formed tributyltin cation. While no experimental data for the formation of [(*n*-Bu<sub>3</sub>)Sn][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene are described in the literature, Lambert and co-workers described the formation of [(*n*-Bu<sub>3</sub>)Sn][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in benzene.<sup>[100]</sup> The chemical shift was detected as  $\delta^{119}$ Sn = 262.8 and reasoned by the formation of [(*n*-Bu<sub>3</sub>)Sn(benzene)]<sup>+</sup>, in which the stannylium cation is solvated by benzene. While the purely tricoordinated stannylium cation is expected to shift even further downfield ( $\delta^{119}$ Sn > 1000),<sup>[100, 227]</sup> a significant dependence of the <sup>119</sup>Sn shift and the used solvent and counter anion are described in the literature which indicates significant interactions with the formed cationic tin species.<sup>[100, 227-229]</sup> Therefore, the signal at  $\delta^{119}$ Si = 213.8 likely results from the chlorobenzene adduct of the formed tin cation, [(*n*-Bu<sub>3</sub>)Sn(chlorobenzene)]<sup>+</sup>.

The also recorded and <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (Figure 360, experimental section) and <sup>19</sup>F{1H} NMR spectrum (Figure 361, experimental section) do not show a reaction with the counter anion  $[B(C_6F_5)_4]^{-}$ .





### 3.4.5. Dication of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub>

# 3.4.5.1. Synthesis and Characterisation of the Silyl Dication

It was also tried to react  $Si(SiMe_2SiMe_2H)_4$  (91) with two equivalents of trityl cation to generate the corresponding silyl dication 118 (Scheme 53).



Scheme 53: Hydride transfer reaction of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (91) with two equivalents of  $[Ph_3C][B(C_6F_5)_4]$  to 118 $[B(C_6F_5)_4]_2$ .

The postulated dication **118** could behave like the monocation **113** of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> and show a dynamic behaviour or it could behave like the cation **106** of the linear  $Me_2Si(SiMe_2SiMe_2H)_2$  (**89**) with its static 2e3c Si-H-Si bond. In the first case, a dynamic molecular process in which the 2e3c Si-H-Si bonds alternate between all four oligosilanyl groups happens (Scheme 54).



Scheme 54: Degenerated equilibrium of the silyl dication **118** with alternation of the 2e3c Si-H-Si bond between the four oligosilanyl groups. The  $[B(C_6F_5)_4]$ <sup>-</sup> counter anions are omitted.

In the second case, this intramolecular reaction does not occur. Thus, a static *spiro* compound with two separated, 2e3c Si-H-Si bridges is observed in the NMR spectroscopic data. In this case, NMR spectra very similar to the ones obtained for the cation **106** are expected. In contrast to cation **106**, the central SiMe<sub>2</sub> unit is substituted by a tetrasilyl-substituted silicon atom. Therefore, a significant upfield shift of that silicon atom in the <sup>29</sup>Si NMR data is expected.<sup>[203-204]</sup> It must be noted, that depending on the rate constant of the possible

intramolecular reaction (Scheme 54), both cases could be indistinguishable by NMR spectroscopy.

To investigate both possibilities in advance, DFT calculations were performed. During the quantum mechanical calculations on the dication **118**, additional stationary points were found for the dicationic structures with one (**119**) or even two (**120**) non-bridged, cationic oligosilanyl substituents instead of 2e3c Si-H-Si bridges (Figure 92). A comparison of the relative computed Gibbs free energies  $\Delta G^{*193}$  shows that the twofold Si-H-Si-bridged structure **118** is energetically preferred by  $\Delta G^{*193} = -97$  kJ mol<sup>-1</sup> compared to dication **119** and by  $\Delta G^{*193} = -205$  kJ mol<sup>-1</sup> compared to dication **120**.





Figure 92: Comparison of the energies E and Gibbs free energies at 247 atm ΔG<sup>\*193</sup> for the calculated structures of the twofold Si-H-Si-bridged cation **118** and the two cations **119** and **120**. The non-bridged cationic silicon centres of **119** and **120** are marked in red.

Therefore, a static structure for silvl dication **118** is more likely. Otherwise, the 2e3c Si-H-Si bonds must be broken which is unlikely considering the high energetic preference of the bridged species **118** compared to its non-bridged relatives **119** and **120**.

A third conceivable structure of the silyl dication, the  $\mu^3$ -hydrido-bridged silyl cation **121** (Figure 93), was ruled out as a possible structure based on quantum mechanical calculations. Different trials to optimise the molecular structure with a  $\mu^3$ -hydrido-bridge resulted in the breakage of a Si-H bond and the formation of a free silyl cationic centre. Thus, an energetic minimum structure for **121** could not be found.



Figure 93: Alternative silyl dication **121** containing a  $\mu^3$ -hydrido-bridge instead of two cationic 2e3c Si-H-Si bridges. The  $[B(C_6F_5)_4]^-$  counter anions are omitted.

The hydride transfer reaction was performed at -80 °C as an NMR experiment using dichloromethane-d<sub>2</sub> as solvent.

The recorded <sup>1</sup>H NMR spectrum (Figure 94) shows two comparatively sharp signal at  $\delta^{1}$ H = 0.55 and 0.89 (Si<sup>2</sup> and Si<sup>3</sup> position). Additionally, no significant signal in the range of  $\delta^{1}$ H = 3-5 is visible which suggests the lack of a free silyl arm containing a terminal hydrogen-substituted dimethylsilyl group as the Si-H hydrogen atom is usually detected at this shift range.





Although, an exact integration of both signals at  $\delta^{1}$ H = 0.55 and 0.89 is not possible as there is an overlap with some NMR signals of impurities, the quite sharp lineshapes of both singlets already suggests the formation of the dication **118** with a static behaviour on the NMR time scale. Albeit not completely accurate due to the described overlap of NMR signals, a rough integration results in equal relative integrals for both signals. The expected molecular structure of dication **118** is characterised by its two 2e3c Si-H-Si bonds. Resulting from the highly symmetrical molecular structure, two signals with the same relative integrals in the <sup>1</sup>H NMR spectrum are expected (Figure 95). This results from the four dimethylsilyl groups (relative integral of 24H) at Si<sup>2</sup> position and from the two magnetically equivalent [Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub>]<sup>+</sup> fragments (relative integral of 24H). The signal of the bridging hydrogen atom of the 2e3c Si<sup>3</sup>-H-Si<sup>3</sup> unit cannot be directly detected in the shown <sup>1</sup>H NMR spectrum.



Figure 95: Expected <sup>1</sup>H NMR signal for dication **118** with a static structure.

An <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum (Figure 282, experimental section) was measured to see the  ${}^{3}J_{H,H}$  correlation of the methyl groups of the [Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub>]<sup>+</sup> fragments with the bridging hydrogen atom. Unfortunately, the spectrum does not enable a definite assignment of the Si-H-Si hydrogen atom.

Analysis of the also recorded <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 96) supports the assumptions made on basis of the <sup>1</sup>H NMR spectrum (Figure 94). In the spectrum, sharp and defined <sup>29</sup>Si NMR signals are detected which stands in strong contrast to the broad NMR signals observed for the monocation **113** (Figure 74). A total of three <sup>29</sup>Si NMR signals with specific chemical shifts are visible which are assigned to the oligosilanylsilyl dication **118**. There is one upfield-shifted signal appearing at  $\delta^{29}$ Si = -121.4 which resonates in the characteristic chemical shift range of tetrasilyl-substituted silicon atoms.<sup>[203-204]</sup> Therefore, it is assigned to the silicon atom at Si<sup>1</sup> position. The second signal appears further downfield at  $\delta^{29}$ Si = -34.4 (FWHM = 15 Hz). Its resonance frequency is in the expected chemical shift range of dimethylsilyl groups in a silicon chain as expect for the Si<sup>2</sup> silicon atoms of dication **118** (Figure 95),<sup>[203-204]</sup> or alternatively hydrogen-substituted dimethylsilyl group at a terminal position

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(Table 4). The second possibility can be ruled out as no characteristic Si-H signal was visible in the <sup>1</sup>H NMR spectrum (Figure 94). The third and last <sup>29</sup>Si NMR signal that is assigned to silyl dication **118** appears significantly further downfield.



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, # = hydrolysis product **122**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>).

By its NMR resonance at  $\delta^{29}$ Si = 88.1 (FWHM = 18 Hz), which is in the typical shift range of cationic Me<sub>2</sub>Si-H-SiMe<sub>2</sub> bridges,<sup>[122-123]</sup> it is assigned to the silicon atoms in Si<sup>3</sup> position. The observed <sup>29</sup>Si chemical shift is very similar to the broad signal detected for the monocation **113** ( $\delta^{29}$ Si = 89.1 at -90 °C in dichlormethane-d<sub>2</sub>) of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (**91**) and the downfield-shifted signal of the monocation **106** ( $\delta^{29}$ Si = 87.1 at -40 °C in chlorobenzene-d<sub>5</sub>) of the linear oligosilane Me<sub>2</sub>Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>2</sub> (**89**). A set of signals due to impurities is also visible in the spectrum. The signals show <sup>29</sup>Si NMR resonances at  $\delta^{29}$ Si = 88.7, 62.6, -34.5, -40.8 and -131.4. The results of DFT calculations estimate comparable <sup>29</sup>Si NMR shifts for the dicationic species **122** (Figure 97), a possible hydrolysis product during the synthesis of dication **118**. Its shifts are calculated at  $\delta^{29}$ Si(*calc.*) = *96*, *74*, -*35*, -*38* and -*126*. Integration of the signals of the hydrolysis product **122** and comparison to the integrals of dication **118** estimate a contamination of less than 10%.





The recorded hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 98) clarifies the structure of the formed dication **118** even further.



 $(CD_2Cl_2, 99.31 \text{ MHz}, -80 \text{ °C}, \# = hydrolysis product$ **122** $[B(C_6F_5)4]_2).$ 

In the hydrogen-coupled <sup>29</sup>Si NMR spectrum, no splitting for the signal at  $\delta^{29}Si = -34.4$  (Si<sup>2</sup>) is detectable which definitely rules out the possibility of a terminal hydrogen-substituted dimethylsilyl group as a splitting with the typical coupling of directly bound Si-H at a dimethylsilyl group (typically around <sup>1</sup>*J*<sub>Si,H</sub> = 170-220 Hz<sup>[170]</sup>) would occur. Therefore, the signal must result from internal dimethyl silyl groups in a silicon chain. Additionally, a splitting of the

downfield-shifted signal at  $\delta^{29}$ Si = 88.1 (Si<sup>3</sup>) is visible in the spectrum. The signal splits up with a coupling of  ${}^{1}J_{Si,H}$  = 41 Hz which is in the typical range expected for the direct Si,H coupling in a 2e3c Si-H-Si bridge.<sup>[121-123]</sup> As expected, no splitting of the upfield-shifted signal at  $\delta^{29}$ Si = -121.4 (Si<sup>1</sup>) is detected which fits the assignment to the tetrasilyl-substituted Si<sup>1</sup> atom.

Therefore, it can be summarised that all <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopic data fit to the silyl dication **118**. A comparison with the calculated values for the <sup>29</sup>Si chemical shifts and with the calculated Si,H coupling constant of the 2e3c Si-H-Si bridge supports the detection of dication **118** in the NMR spectra (Table 13). All calculated and experimentally detected values show a high agreement with a maximum variance between the calculated <sup>29</sup>Si chemical shift of the silicon atoms involved in the 2e3c Si-H-Si bridge of about 8 ppm.

Table 13: Comparison of calculated and experimentally detected <sup>29</sup>Si chemical shifts and direct <sup>1</sup>H,<sup>29</sup>Si coupling constant of silyl dication **118**. NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constant calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



[a] NMR data recorded in  $CD_2CI_2$  at -80 °C, counter anions  $[B(C_6F_5)_4]$ .

Knowing which <sup>29</sup>Si signal belongs to which silicon atom of dication **118**, it is possible to assign both signals in the <sup>1</sup>H NMR to the corresponding dimethylsilyl groups by 2D <sup>29</sup>Si NMR spectroscopy. In the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 99), the <sup>1</sup>H signal with a chemical shift of  $\delta^{1}$ H = 0.89 correlates intensely with the <sup>29</sup>Si signal at  $\delta^{29}$ Si = 88.1 (Si<sup>3</sup>) and weakly with the signal at  $\delta^{29}$ Si = -34.4 (Si<sup>2</sup>). No correlation of the <sup>1</sup>H signal at  $\delta^{1}$ H = 0.89 to the <sup>29</sup>Si signal at  $\delta^{29}$ Si = -121.4 (Si<sup>1</sup>) is detectable. It follows that the signal at  $\delta^{1}$ H = 0.89 belongs to the methyl groups at Si<sup>3</sup> position. The visible correlations are the <sup>2</sup>*J*<sub>H,Si</sub> coupling between this methyl hydrogen atoms and the cationic silicon atoms at  $\delta^{29}$ Si = 88.1, which appears intensely in <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum. The second, much weaker correlation results from the <sup>3</sup>*J*<sub>H,Si</sub> coupling of the same groups with the internal Si<sup>2</sup> silicon atoms of the silyl arms at  $\delta^{29}$ Si = -34.4. Accordingly, the second singlet at  $\delta^{1}$ H = 0.55 is assigned to the methyl groups at the Si<sup>2</sup> position. In the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 99), this <sup>1</sup>H NMR signal correlates with all three magnetically inequivalent silyl groups of the dication **118**. Thus, the <sup>2</sup>J<sub>H,Si</sub> coupling to the silicon atoms Si<sup>2</sup> ( $\delta^{29}$ Si = -34.4), the <sup>3</sup>J<sub>H,Si</sub> coupling to the silicon atoms Si<sup>3</sup> of the 2e3c Si-HSi bond ( $\delta^{29}$ Si = 88.1) and the <sup>3</sup>J<sub>H,Si</sub> coupling to the central silicon atom Si<sup>1</sup> ( $\delta^{29}$ Si = -121.4) are detected in the spectrum.



Figure 99: Excerpt of the  ${}^{1}H,{}^{29}Si$  HMBC spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, # = hydrolysis product **122**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>).

Identical correlations are visible in the also recorded <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 100). The HMQC experiment was optimised for a coupling of  $J_{H,Si} = 45$  Hz. Interestingly, there are three cross peaks detectable for the downfield-shifted signal at  $\delta^{29}Si = 88.1$ . On the one hand, the correlations with the signals at  $\delta^{1}H = 0.55$  and 0.89 that were already detected in the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 99), are visible. On the other hand, a new correlation to the area around  $\delta^{1}H = 0.81$  can be seen in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum. This correlation indicates the appearance of the bridging hydrogen atom of the 2e3c Si<sup>3</sup>-H-Si<sup>3</sup> unit at a chemical shift around  $\delta^{1}H = 0.81$ . Due to the overlap with the other signals, it is not possible to detect the bridging hydrogen atom accurately in the 1D <sup>1</sup>H NMR spectrum (Figure 94). An integration of this signal is also not possible resulting from the signal overlap.



Figure 100: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, optimised for  $J_{H,Si} = 45$  Hz, spectrum processed using sine square 0.00° and sine square II with -30% and 50% in F1 and sine square 4.00° and sine square II with -5% and 50% in F2).

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 101) shows two signals associated with the dication **118**. A singlet appearing at  $\delta^{13}$ C = -3.1 and one other singlet at  $\delta^{13}$ C = -2.2 both can be assigned to the methyl groups at Si<sup>2</sup> and Si<sup>3</sup> position by 2D <sup>13</sup>C NMR spectroscopy. Hence, in the <sup>1</sup>H, <sup>13</sup>C HMQC spectrum (Figure 102), a correlation of the <sup>1</sup>H signal at  $\delta^{1}$ H = 0.55, which was prior assigned to the methyl groups at Si<sup>2</sup>, to the signal at  $\delta^{13}$ C = -3.1 is detected. Therefore, the signal is assigned to the methyl carbon atoms at the Si<sup>2</sup> position. As expected, the second signal at  $\delta^{1}$ H = 0.88 (Si<sup>3</sup> position) shows a correlation to the second signal in the <sup>13</sup>C NMR with a chemical shift of  $\delta^{13}$ C = -2.1. As a result, the <sup>13</sup>C NMR signal at  $\delta^{13}$ C = -2.2 is assigned to the methyl carbon atoms at Si<sup>3</sup> position that are involved in the 2e3c Si-H-Si bridge.


Figure 101: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, \* = Ph<sub>3</sub>CH, # = *n*-hexane,  $\label{eq:constraint} \$ = [B(C_6F_5)_4]^2.$ 



Figure 102: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C).

In an alternative approach, the monocation **113** was obtained by first reacting **91** with one equivalent of  $[Ph_3C][B(C_6F_5)_4]$ . Subsequently, a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$  was added to generate the dication **118** in a two-step procedure (Scheme 55).



Scheme 55: Alternative synthesis of dication **118** by reaction of silyl monocation **113** with one additional equivalent of  $[Ph_3C][B(C_6F_5)_4]$ .

The product mixture after addition of the first equivalent of  $[Ph_3C][B(C_6F_5)_4]$  was analysed via NMR spectroscopy. All spectroscopic data showed the signals which were assigned to the monocation **113** (Chapter 3.4.4). All its described features, like the change of the NMR signals with temperature, were observed in this NMR experiment.

Afterwards, a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$  was added to the NMR sample at -80 °C, the resulting product mixture was mixed and directly examined by NMR spectroscopy.

The recorded <sup>29</sup>Si{<sup>1</sup>H} and <sup>29</sup>Si NMR spectra (Figure 103) clearly show the formation of dication **118** after reaction with the second equivalent of  $[Ph_3C][B(C_6F_5)_4]$ . While the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 103, top spectrum) after addition of one equivalent of trityl salt shows the signals assigned to the monocation **113** which are characterised by their broadness (Chapter 3.4.4), a significant change is visible after addition of the second equivalent trityl salt. In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 103, middle spectrum) after addition of the second equivalent trityl salt, the signals which were detected in the independent synthesis of dication **118** appear. In the hydrogen-coupled spectrum <sup>29</sup>Si NMR spectrum (Figure 103, bottom spectrum), the splitting of the downfield-shifted signal at  $\delta^{29}$ Si = 89.1 of <sup>1</sup>*J*<sub>Si,H</sub> = 41 Hz is also detectable. The <sup>1</sup>H NMR spectrum (Figure 295, experimental section) and the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 296, experimental section) also show the same signals as already detected in the respective spectra of the independently synthesised silyl dication **118**.

The observations made in this experiment show that the formation of the dication **118** is also possible in a two-step procedure. Furthermore, the results of the experiment support the assumption of a dynamic behaviour in the monocation **113** which result in the broad signals



and a temperature dependency of the NMR spectra, and that no rearrangement of its molecular framework occurs.

Figure 103: <sup>29</sup>Si spectra showing the formation of dication **118** from monocation **113** after addition of a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$ . Top spectrum: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum before addition of the second equivalent  $[Ph_3C][B(C_6F_5)_4]$  showing the signals assigned to of **113** $[B(C_6F_5)_4]$  (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -85 °C). Middle spectrum: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum after addition of second equivalent  $[Ph_3C][B(C_6F_5)_4]$  (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C). Bottom spectrum: <sup>29</sup>Si NMR spectrum after addition of second equivalent  $[Ph_3C][B(C_6F_5)_4]$  (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C). The  $[B(C_6F_5)_4]$  counter anion is omitted in the inserted reaction schemes.

Interestingly, the second hydride abstraction to form the dication **118** from the monocation **113** was not measurably slowed down compared to the first hydride abstraction. This contrasts with the formation of other silyl dications which either took a longer time for the second abstraction to happen, or where the second abstraction could not be observed at all (Chapter 3.5.1).<sup>[150]</sup> Additionally in previous attempts, the formed dicationic silyl species showed a high tendency to follow-up reactions with the counter anion.<sup>[135]</sup> In the case of oligosilane **91** both abstractions seem to be nearly independent from each other and no reaction of the dication with the counter anion was observed. This can be rationalised by the quite far distance of both positive charges from each other in the molecule on the one hand and by the strong stabilising effect upon formation of the 2e3c Si-H-Si bridge on the other hand.





Scheme 56: Twofold hydride abstraction of oligosilane **91** and subsequent trapping of the silyl dication **118** via reaction with tributyltin deuteride.

Analogous to the monocation **113**, a trapping reaction was performed (Scheme 56). The first trial was done in toluene following the protocol described for the trapping reaction of the monocation **113** (Chapter 3.4.4.2). In contrast to the monocation, the trapping reaction of dication **118** in toluene was more difficult as the polar phase became highly viscous. As a result, stirring at low temperatures was impossible. The trapping reaction was therefore performed in a different solvent. As a suitable solvent, 3-Fluorotoluene was chosen as it allows for reactions at temperatures below -80 °C. At the same time, it does not suffer from the drawbacks of other solvents like dichloromethane (reactivity with silyl cations). In contrast to the trapping of monocation **113** in toluene, no pyridine derivative was used for the trapping reaction with tributyltin deuteride were performed in a single-phase reaction mixture. Subsequently, *n*-hexane was added until a biphasic mixture was formed. The non-polar phase was then examined by NMR spectroscopy and GCMS.

The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 104) reveals a complex product mixture. The spectrum indicates at least three silyl species as three signals in the upfield section of the spectrum at  $\delta^{29}$ Si = -134.1, -126.9, -119.2 are visible. The signals appear in the typical shift range of tetrasilyl-substituted silicon atoms.<sup>[203-204]</sup> At least two triplets resulting from Si-D units are visible around  $\delta^{29}$ Si = -34.5. Additionally, two more downfield-shifted signals are visible at  $\delta^{29}$ Si = 8.2 and 8.6. The shift region of both signals is near the expected shift range of cyclic siloxanes.<sup>[230]</sup> Hence, a partial hydrolysis of the silyl cation seems plausible.



Figure 104: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of the trapping products of dication **118** and tributyltin deuteride in 3-fluorotoluene ( $C_6D_6$ , 99.31 MHz, 32 °C)

In the GCMS data of the non-polar phase after trapping reaction with tributyltin hydride (Figure 105) a band associated with a mass spectrum very similar to the ones obtained for the all hydrogen-substituted oligosilane **91** (Figure 82, upper part) and for the monodeuterated oligosilane **117** (Figure 82, bottom part) can be detected. After trapping of the dication **118**, the highest detectable mass peak (m/z = 439.1) shows a m/z which is two units higher than for the all hydrogen-substituted silane **91**. Also, the fragmentation pattern (Figure 82). These observations indicate the formation of the dideuterated oligosilane **123** by trapping of the dication **118** with tributyltin hydride. The detected mass peak does not correspond to the [M<sup>+</sup>] signal of dideuterated silane **123** (ex. mass = 498.2 Da). Instead, it corresponds to the [M<sup>+</sup> - SiMe<sub>2</sub>H] fragment of **123**. The same was already observed and described for the educt silane **91** as well as the monodeuterated silane **117**. Additionally, it must be noted that different signals were detected during analysis of the sample by GCMS (Figure 364-Figure 365, experimental section) which were assigned to the *spiro*-siloxane **124** and monodeuterated siloxane **125** (Figure 106).



Figure 105: Mass spectrum of the dideuterated silane **123** extracted from the GCMS data after trapping with tributyltin deuteride.

The formation of both compounds can be rationalised by partial or full hydrolysis of the dication **118** by moisture present during the trapping reaction. The side-products **124** and **125** that are identified in the GCMS data also explain the appearance of more than one silyl species in the NMR spectra. An exact assignment of the NMR data of each different oligosilanes **123-125** was not performed.



Figure 106: Products **123-125** detected in the GCMS after trapping reaction of dication **118** with tributyltin deuteride in 3-fluorotoluene.

## 3.4.6. Reactions of Si(SiMe<sub>2</sub>H)<sub>4</sub> with Trityl Cation

## 3.4.6.1. Synthesis and Characterisation of the Silyl Cation

Complementary to the silyl cations presented so far, the reaction of Si(SiMe<sub>2</sub>H)<sub>4</sub> (**100**) with trityl salt was also tried (Scheme 57). The silyl cation **126** that can be formulated after hydride abstraction and subsequent formation of a stabilising 2e3c Si-H-Si bond possess some interesting structural features that make its formation and analysis worthwhile. Compared to the oligosilanylsilyl cations **106**, **111** and **113** as well as oligosilanylsilyl dication **118**, a four-membered ring is formed after establishing of the Si-H-Si bridge. Therefore, it is to be expected that for silyl cation **126** the stabilising effects of the 2e3c Si-H-Si bridge compete with the ring strain of the four-membered cycle.



Scheme 57: Hydride transfer reaction of oligosilane 100 with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

If the cationic ring structure **126** is indeed formed, the influence of the ring size on the dynamic behaviour that was previously observed for silyl cation **113** (Chapter 3.4.4) can be investigated. Thus, if the structure of the postulated silyl cation **126** is compared to the silyl cation **113**, the lack of longer and more flexible disilyl moieties might inhibit the intramolecular reaction.

Before the experimental studies, DFT calculations were performed to estimate the NMR properties of silyl cation **126** and the likelihood of its formation. An energetic minimum structure for cation **126** was found which revealed quite interesting chemical shifts (Table 14). The calculations predict a <sup>29</sup>Si NMR shift of  $\delta^{29}Si(calc.) = -183$  for the tetrasilyl-substituted silicon atom. The predicted value is remarkably further upfield-shifted than the corresponding <sup>29</sup>Si signal of the educt **100** ( $\delta^{29}Si = -140.0$  in benzene-d<sub>6</sub>). The signal is also calculated significantly further upfield as the experimental <sup>29</sup>Si NMR shifts of the tetrasilyl-substituted silicon atoms in either cation **113** ( $\delta^{29}Si = -124.8$  in dichloromethane-d<sub>2</sub>) or dication **118** ( $\delta^{29}Si = -121.4$  in dichloromethane-d<sub>2</sub>). At the same time, the Si<sup>3</sup> silicon atoms of **126** that are involved in the 2e3c Si-H-Si bridge are calculated a lot more upfield-shifted ( $\delta^{29}Si(calc.) = 12$ ) than the values calculated or measured for any other Si-H-Si-bridged silyl cation mentioned in this work (all around  $\delta^{29}Si = 90$ ).

Table 14: Calculated NMR data for silyl cation 126.

NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constant calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



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Silicon atom	δ <sup>29</sup> Si( <i>calc</i> .)	<sup>1</sup> <i>J</i> <sub>H,Si</sub> ( <i>calc.</i> ) [Hz]
Si <sup>1</sup>	-183	
Si <sup>2</sup>	-29	206
Si <sup>3</sup>	12	32

Therefore, the calculated values already suggest a special case for silyl cation **126**, likely resulting from the strained four membered ring.

Additionally, an isodesmic reaction was calculated for a similar model system (Scheme 58). The computed energies  $\Delta E$  of the reaction were then correlated with the ring size of the formed cyclic silyl cation containing a 2e3c Si-H-Si bridge.

$$Si - H - Si$$
 +  $H (Si)_n H$   $\Delta E$   $Si (Si)_n + 2 Si H$   
 $Si = SiMe_x, x = 2 \text{ or } 3$   
 $n = 0-5$ 

Scheme 58: Isodesmic reaction used to estimate the energetic contribution of ring strain on the formation of 2e3c Si-H-Si-bridged cyclic silyl cations (n = 0.5).

The results (Table 15) of the calculations reveal destabilising effects for systems with n = 0-2 which corresponds to three-, four- and five-membered ring systems upon formation of the 2e3c Si-H-Si bridge. The results allow an estimate of the destabilising effect resulting from the strained four-membered ring in the silyl cation **126**. Thus, the four-membered Si<sub>3</sub>H cycle of cation **126** corresponds to the values calculated for n = 1 (Ring size: 4). For this ring system, a significant destabilising effect is computed ( $\Delta E = 51 \text{ kJ mol}^{-1}$ ). Due to this high instability of the four-membered ring system, it can be expected that the formation of an intramolecular 2e3c Si-H-Si bridge is strongly hindered in case of the potential formation of the intramolecularly bridged silyl cation **126**.

using the isodesmic reaction in which the respective Si-H-Si-brid	dged ring system is formed (Scheme 58).
Calculations were performed at the M06-2X/6-3	11G+(d,p) level of theory.

Number of SiMe <sub>2</sub> groups (n)	Ring size	ΔE [kJ mol <sup>-1</sup> ]
0	3	133
1	4	51
2	5	10
3	6	-12
4	7	-25
5	8	-38

First trials to react **100** in a hydride transfer reaction was performed using dichloromethane- $d_2$  as solvent. The reaction was executed at -90 °C as an NMR experiment (Scheme 59).



Scheme 59: Attempted synthesis of  $126[B(C_6F_5)_4]$  using dichlormethane-d<sub>2</sub> as solvent.

The <sup>1</sup>H NMR spectrum (Figure 107) measured after usual cation preparation (Chapter 5.3) reveals a complex mixture and does not indicate a clean reaction. An accumulation of broadened signals is visible in the upfield area of the spectrum around  $\delta^1$ H = 0-1. Additional signals in the area around  $\delta^1$ H = 4-5 are visible which is in the shift range expected for directly bound Si-H hydrogen atoms of terminal hydrogen-substituted dimethylsilyl groups (Table 4). While a successful hydride abstraction by [Ph<sub>3</sub>C]<sup>+</sup> is indicated in the <sup>1</sup>H NMR spectrum by the formation of Ph<sub>3</sub>CH, it must be noted that unexpectedly high amounts of left-over trityl cation are also visible.



Figure 107: <sup>1</sup>H NMR spectrum obtained after hydride transfer reaction of oligosilane **100** with  $[Ph_3C][B(C_6F_5)_4]$ . Spectrum measured before renewed mixing of the sample (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).

The corresponding <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum also shows a rather complex mixture with a bad S/N ratio in the NMR spectrum. Furthermore, no signals fitting to the calculated values of silyl cation **126** (Table 14) are detectable in the spectrum.

As the spectroscopic data showed no clean formation of a silyl cation, the mixture was taken out of the NMR spectrometer, mixed and again returned to the NMR spectrometer.





Mixing was performed as fast as possible to minimise the risk of warming of the sample which facilitates side reactions with the solvent.<sup>[84-85, 156]</sup> The <sup>1</sup>H NMR spectrum (Figure 109, bottom spectrum) after renewed mixing of the sample differs completely from the spectrum before renewed mixing (Figure 109, top spectrum). Instead of various broad signals, one very intense singlet is visible in the upfield area of the spectrum. The signal appears at a chemical shift of  $\delta^{1}H = 0.69$ . Compared to the <sup>1</sup>H spectrum prior to mixing (Figure 109, top spectrum), all signals in the area around  $\delta^{1}H = 4-5$  have disappeared. Interestingly, while signals resulting from left-over trityl salt can be still detected in the <sup>1</sup>H NMR spectrum, the signals of the formed Ph<sub>3</sub>CH have also disappeared. Instead, a broad featureless resonance at  $\delta^{1}H = 7.19$  as well as a sharp signal at  $\delta^{1}H = 7.30$  are detected after renewed mixing.



Figure 109: <sup>1</sup>H NMR spectrum obtained after hydride transfer reaction of oligosilane **100** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Top spectrum measured before renewed mixing of the sample (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, \* = CDHCl<sub>2</sub>). Bottom spectrum measured after renewed mixing of the sample (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -90 °C, \* = CDHCl<sub>2</sub>).

After renewed mixing, the recorded <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 110) shows a very clean spectrum with only two dominant NMR signals. This observation suggests the preferred formation of only one compound after renewed mixing. One of the two NMR signals resonates at a chemical shifts of  $\delta^{29}$ Si = -117.2 (Si<sup>1</sup>), the typical <sup>29</sup>Si NMR shift range of tetrasilyl-substituted silicon atoms.<sup>[203-204]</sup>. The second NMR signal is detected at  $\delta^{29}$ Si = 28.7 (Si<sup>2</sup>), which is in the typical range of halogen-substituted dimethylsilyl groups.<sup>[224]</sup> In this case, only substitution by chlorine, resulting from the reaction of the silyl cation with CD<sub>2</sub>Cl<sub>2</sub>,<sup>[156, 163]</sup> or fluorine, resulting from the reaction of the silyl cation with [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>,<sup>[135]</sup> seems feasible. The occurrence of a Si-F functionality can be ruled out as no <sup>1</sup>J<sub>Si,F</sub> splitting<sup>[170]</sup> of the signals is visible in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum. Both NMR signals show <sup>29</sup>Si satellites of the same magnitude (<sup>1</sup>J<sub>Si,Si</sub> = 60 Hz) in the also recorded <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum (Figure 328, experimental section) which verifies their connectivity. It must be also noted, that the <sup>29</sup>Si{<sup>1</sup>H} spectrum after mixing (Figure 110) shows a vastly superior S/N ratio than the spectrum recorded before renewed mixing of the sample (Figure 108).





Furthermore, no splitting in the size expected for a 2e3c Si-H-Si bridge is detected in the hydrogen-coupled <sup>29</sup>Si INEPT NMR spectrum (Figure 111). In the hydrogen-coupled spectrum, the signal at  $\delta^{29}$ Si = 28.7 (Si<sup>2</sup>) splits up into a multiplet with rather small detected couplings in the magnitude of  $J_{Si,H}$  = 7-9 Hz. By the size of the couplings, it is evident that they do not result from <sup>1</sup> $J_{Si,H}$  coupling but rather from <sup>2</sup> $J_{Si,H}$  or <sup>3</sup> $J_{Si,H}$  couplings.<sup>[170]</sup> By 2D <sup>1</sup>H,<sup>29</sup>Si NMR spectroscopy (Figure 330, experimental section), the connectivity of the intense singlet in the <sup>1</sup>H NMR spectrum at  $\delta^{1}$ H = 0.69 with both signals at  $\delta^{29}$ Si = 28.7 (Si<sup>2</sup>) as well as  $\delta^{29}$ Si = -117.2 (Si<sup>1</sup>) is confirmed.



Figure 111: <sup>29</sup>Si INEPT NMR spectrum obtained after hydride transfer reaction of oligosilane **100** with  $[Ph_3C][B(C_6F_5)_4]$ . Spectrum measured after renewed mixing of the sample (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -90 °C). Resolution enhancement of the expansion using em = 0.50 and gm = 0.90.

After the NMR measurements at low temperature, the sample was warmed up to room temperature. The <sup>1</sup>H NMR spectrum measured at room temperature (Figure 112) shows no further change compared to the spectrum at low temperature. This observation indicates pronounced temperature stability for the formed product. At room temperature, its <sup>1</sup>H NMR signal appears at  $\delta^{1}H = 0.78$ . Additionally, a sharp signal a  $\delta^{1}H = 7.36$  is visible while no signals for Ph<sub>3</sub>CH can be found in the spectrum. The signals assigned to left-over [Ph<sub>3</sub>C]<sup>+</sup>, that were already identified in the <sup>1</sup>H NMR spectrum at -90 °C (Figure 109, bottom spectrum), are still visible in the <sup>1</sup>H NMR spectrum at room temperature (Figure 112).

Further analysis of the sample via GCMS marked the formed product as the chlorinated oligosilane **93** (Figure 113). The NMR data of **93** ( $\delta^{1}H = 0.76$ ;  $\delta^{29}Si = -113.5$  for Si<sup>1</sup> and 28.0 for Si<sup>2</sup>, recorded in dichloromethane-d2 at 32 °C) fit well to the observed NMR chemical shifts ( $\delta^{1}H = 0.69$ ,  $\delta^{29}Si = -117.2$  and 28.7, recorded in dichloromethane-d2 at -90 °C).



Figure 113: Comparison of the mass spectrum of the main product detected after hydride transfer reaction of oligosilane **100** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in dichloromethane-d<sub>2</sub> (upper part) and the mass spectrum of the chlorinated oligosilane **93** (bottom part)..

The formation of the chlorinated silane **93** is explained by the reaction of the formed cationic silyl species with the solvent dichloromethane- $d_2$ .<sup>[156, 163]</sup> In course of the reaction, side reactions occur which result in the decomposition of the formed [Ph<sub>3</sub>CH] whereby benzene (Figure 112,  $\delta^1$ H = 7.36) is formed as one decomposition product.<sup>[223]</sup>

The reaction was repeated once more with two equivalents trityl salt. The NMR experiment resulted in the same spectroscopic data except for more left-over trityl salt visible in the spectra (Figure 333-Figure 335, experimental section).

The NMR experiments in dichloromethane- $d_2$  therefore suggest that the hydride transfer reaction works at -90 °C which is visible by the formation of Ph<sub>3</sub>CH in the <sup>1</sup>H NMR spectra. While a cationic silyl species is formed, the detection of high amounts of left-over [Ph<sub>3</sub>C]<sup>+</sup> indicates that the hydride transfer reaction does not occur in a 1 : 1 stoichiometry of [Ph<sub>3</sub>C]<sup>+</sup> relative to the neutral hydrosilane **100**. The formed cationic silyl species is very reactive and an increase in temperature (renewed mixing of the sample) results in rapid reaction with the solvent dichloromethane. Interestingly, the reaction with the solvent results in the exchange of all hydride atoms of the silane/silyl cation as well as the formation of a neutral product **93** in the end. The process also seems to be somehow autocatalytic left-over [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is still detected in the NMR spectra after decomposition reaction and formation of the chlorinated product **93**. Additionally, it must be noted that no change in the NMR spectra was observable if the reaction was monitored for a longer time at -90 °C before renewed mixing. At this temperature, no visible change in the NMR spectra was detected even after 1 h which shows that the initially formed unidentified, cationic silyl species is stable at that temperature.

After the NMR experiment in dichloromethane- $d_2$  did not show the formation of the desired product, the same reaction was repeated using different solvents which are less prone to reaction with the silyl cation. At first, chlorobenzene- $d_5$  was tried as its use gave good results with other silyl cations in the past (Scheme 60).<sup>[163]</sup>



Scheme 60: Attempted synthesis of  $126[B(C_6F_5)_4]$  using chlorobenzene-d<sub>5</sub> as solvent.

As already seen in dichloromethane- $d_2$  (Figure 107), the <sup>1</sup>H NMR spectrum (Figure 114) shows the formation of Ph<sub>3</sub>CH which indicates that the hydride transfer reaction between oligosilane

**100** and  $[Ph_3C]^+$  occurred. Nonetheless, an unexpectedly complex spectrum is obtained (Figure 114) which does not correspond to the silyl cation **126** (Table 14). While no further elucidation of the structure is possible due to the broad and overlapping signals in the upfield region of the spectrum, remarkably less left-over trityl salt, as compared to the reaction in dichlormethane-d<sub>2</sub>, is visible in the <sup>1</sup>H NMR spectrum.

0.40

0.240.232



Figure 114: <sup>1</sup>H NMR spectrum obtained after hydride transfer reaction of oligosilane **100** with  $[Ph_3C][B(C_6F_5)_4]$ (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C, # = Ph<sub>3</sub>CH).

The corresponding <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 115) is characterised by its low S/N ratio and not structure of the formed silyl cation can be elucidated from the detected <sup>29</sup>Si NMR signals. As no NMR signals of the silyl cation **126** are visible in either the <sup>1</sup>H or <sup>29</sup>Si{<sup>1</sup>H} NMR, it is concluded that rapid decomposition of the formed silyl cation obtained after hydride abstraction occurs in chlorobenzene-d<sub>5</sub> at -40 °C.





As chlorobenzene-d<sub>5</sub> is not suitable to monitor the reaction at lower temperatures than -40 °C, the same reaction was repeated using 3-fluorotoluene as a solvent (Scheme 61). Due to the much lower melting point of 3-fluorotoluene compared to chlorobenzene, the reaction can be performed at lower temperatures. This allows to monitor the reaction at decreased temperatures and thus helps to suppress decomposition reactions of the formed cationic silvl species. At the same time, the reactivity of the solvent towards silvl cations is expected to be lowered compared to halogenated alkanes (e.g. dichloromethane). Unfortunately, perdeuterated 3-fluorotouene is not commercially available. Therefore, an external capillary filled with acetone-d<sub>6</sub> was used for the NMR experiments in 3-fluorotoluene. The NMR reactions using 3-fluorotoluene were performed at -80 °C.

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Scheme 61: Attempted synthesis of  $126[B(C_6F_5)_4]$  using 3-fluorotoluene as solvent and identified product  $127[B(C_6F_5)_4]$ .

If the reaction is performed under these conditions, the NMR spectra suggest the clean formation of one single product. Its NMR spectroscopic data are not in accordance with the intramolecularly bridged silyl cation **126** (Table 14). It is evident by the NMR spectra that some other type of silyl cation is formed after the hydride transfer reaction of **100** in 3-fluorotoluene. Instead, all spectroscopic data fit to the formation of the intermolecularly via 2e3c Si-H-Si bridge stabilised silyl cation **127** (Figure 116).



Figure 116: Comparison of the <sup>1</sup>H NMR data expected for the intramolecularly stabilised silyl cation **126** and the intermolecularly stabilised silyl cation **127** which was obtained after hydride transfer reaction of oligosilane **100** with  $[Ph_3C][B(C_6F_5)_4]$  in 3-fluorotoluene. The  $[B(C_6F_5)_4]^-$  counter anion is omitted.

For such a structure, three signals in the <sup>1</sup>H NMR spectrum are expected. One signal due to the methyl groups at the two dimethylsilyl groups in Si<sup>3</sup> position and one signal for the methyl groups of the six hydrogen-substituted dimethylsilyl groups in Si<sup>2</sup> position are anticipated. Both groups are expected to appear in the upfield area of the <sup>1</sup>H NMR spectrum. The third signal results from the six Si-H hydrogen atoms of the dimethylsilyl groups in Si<sup>2</sup> position. This directly silicon-bound hydrogen atoms are expected to appear significantly further downfield (around  $\delta^{1}$ H = 3-5) compared to the hydrogen atoms of silicon-substituted methyl groups (Table 4).

Additional DFT calculations were performed. The computed <sup>29</sup>Si NMR chemical shifts and  ${}^{1}J_{H,Si}$ for the intramolecular bridged cation 126 and the intermolecularly bridged cation 127 show significant discrepancies (Table 16). Thus, marked differences are calculated for the tetrasilyl-substituted silicon atoms in Si<sup>1</sup> position. ( $\delta^{29}$ Si(*calc.*) = -183 (**126**) vs. -130 (**127**)) and the Si-H-Si silicon atoms in Si<sup>3</sup> position. ( $\delta^{29}$ Si(*calc.*) = 12 (**126**) vs. 98 (**127**)). The computed  ${}^{1}J_{\text{H.Si}}$  couplings of the 2e3c Si-H-Si bridges also show strong variations ( ${}^{1}J_{\text{H.Si}}(calc.) = 32$  Hz (126) vs. 50 Hz (127)). In contrast, the <sup>29</sup>Si NMR chemical shifts of the free dimethylsilyl groups  $(\delta^{29}Si(calc.) = -29 (126)$  vs. -33 (127)) as well as well as their respective  ${}^{1}J_{H,Si}$  couplings  $({}^{1}J_{H,Si}(calc.) = 206 \text{ Hz}$  (126) vs. 200 Hz (127)) are computed at very similar values.

Table 16: Comparison of the calculated <sup>29</sup>Si chemical shifts and  ${}^{1}J_{H,Si}$  coupling constants for the intramolecularly stabilised silvl cation 126 and the intermolecularly stabilised silvl cation 127.

NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constants calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



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 $Si = SiMe_2$ 

Silicon atom	δ <sup>29</sup> Si( <i>calc.</i> ) of		<sup>1</sup> <i>J</i> <sub>H,Si</sub> ( <i>cal</i> e	c.) [Hz] of
	126	127	126	127
Si <sup>1</sup>	-183	-130		
Si <sup>2</sup>	-29	-33	206	200
Si <sup>3</sup>	12	98	32	50





(3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, -80 °C, \* = 3-fluorotoluene).

The signals appear at  $\delta^{1}H = 0.32$  (Si<sup>2</sup> position) and  $\delta^{1}H = 0.79$  (Si<sup>3</sup> position), respectively. Both signals have relative integrals of 1 : 3 which does not fit to the intramolecularly stabilised silyl cation **126**. For a static structure of **126** an integral ratio of 1 (SiMe<sub>2</sub>H) : 1 ([Me<sub>2</sub>Si-H-SiMe<sub>2</sub>]<sup>+</sup>) is expected (Figure 116). Alternatively, if the 2e3c Si-H-Si bridge changes place between all silyl group, one broadened signal would be expected. The <sup>1</sup>H NMR spectrum also shows a signal at  $\delta^{1}H = 4.22$  which appears in the expected range for hydrogen-substituted dimethylsilyl groups (Si<sup>1</sup> position). If the signal at  $\delta^{1}H = 4.22$  is set to a relative integral of 6H, the two other signals show relative integrals of 12H and 36H which corresponds to an intermolecularly bridged silyl cation **127**.

Furthermore, two <sup>1</sup>H NMR signals that are slightly more downfield-shifted ( $\delta^{1}H = 7.36$  and 7.75) than the intense <sup>1</sup>H NMR of the aromatic ring of the non-deuterated 3-fluorotoluene are detected. Due to their downfield shift, the <sup>1</sup>H NMR signals likely belong to left-over [Ph<sub>3</sub>C]<sup>+</sup>. To verify the assignment to the trityl cation, an <sup>1</sup>H NMR spectrum of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in 3-fluorotoluene at 32 °C was measured. The <sup>1</sup>H resonances of the phenyl groups were

detected at  $\delta^{1}$ H = 7.27, 7.48 and 7.83 which is very similar to the two <sup>1</sup>H NMR signals detected the spectrum at -80 °C (Figure 117).

A <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum (Figure 118) was also recorded in which the correlation due to  ${}^{3}J_{H,H}$  coupling of the signal at  $\delta^{1}H = 4.22$  and the signal at  $\delta^{1}H = 0.32$  is visible. Thus, the shown <sup>1</sup>H,<sup>1</sup>H COSY spectrum verifies the assignment of the signals that resonate at  $\delta^{1}H = 0.32$  and 4.22 to the methyl groups and to the Si-H hydrogen atoms of the six SiMe<sub>2</sub>H groups in Si<sup>3</sup> position. The bridging hydrogen atom of the 2e3c Si-H-Si bond is not detected in the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum.





The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 119) supports the clean formation of one product in 3-fluorotoluene. Only three <sup>29</sup>Si NMR signals are visible in the spectrum. The signals appear as sharp singlets at  $\delta^{29}$ Si = -133.2, -34.0 and 93.1. It must be emphasised that none of the three signals is significantly broadened which stands in stark contrast to the spectroscopic data of silyl cation **113** (Chapter 3.4.4). As the broadening of the NMR signals was reasoned on basis of an intramolecular reaction, the spectroscopic data of **127** suggest a lack of any dynamic process in the formed cation. By its chemical shift, the signal at  $\delta^{29}$ Si = -133.2 can be assigned to the tetrasilyl-substituted silicon atoms at Si<sup>1</sup> position.<sup>[203-204]</sup> Additionally, the downfield-shifted signal at  $\delta^{29}$ Si = 93.1 appears in <sup>29</sup>Si shift range associated with silicon atoms

of cationic 2e3c Si-H-Si bridges.<sup>[84-86]</sup> Therefore, it can be assigned to the silicon atoms at Si<sup>3</sup> position. The signal at  $\delta^{29}$ Si = -34.0 (Si<sup>2</sup> position) appears at a shift expected for terminal hydrogen-substituted dimethylsilyl groups (Table 4).



Figure 119: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, -80 °C).

While the detected <sup>29</sup>Si NMR shifts are again vastly different to the calculated values for silyl cation **126**, they are comparable to the computed <sup>29</sup>Si shifts of the intermolecularly bridged silyl cation **127** (Table 16).

The hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 120) shows a splitting of both signals at  $\delta^{29}$ Si = 93.1 (Si<sup>3</sup> position) and -34.0 (Si<sup>2</sup> position). The downfield-shifted signal splits up with a coupling of <sup>1</sup>*J*<sub>Si,H</sub> = 53 Hz which is diagnostic for the formation of a 2e3c Si-H-Si bridge.<sup>[84-86, 95]</sup> The signal at  $\delta^{29}$ Si = -34.0 splits up with a coupling of <sup>1</sup>*J*<sub>Si,H</sub> = 185 Hz which supports its assignment to the hydrogen-substituted dimethylsilyl groups in Si<sup>2</sup> position.<sup>[170]</sup>



Figure 120: <sup>29</sup>Si NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, -80 °C).

Further clarification of the molecular structure of the formed silyl cation was achieved by analysis of the 2D <sup>29</sup>Si NMR data. In the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 121) optimised for  $J_{H,Si} = 50$  Hz, the correlations of the signal at  $\delta^{1}H = 0.32$  with the signals at  $\delta^{29}Si = -133.2$  (Si<sup>1</sup> position) and -34.0 (Si<sup>2</sup> position) are visible. No correlation between the <sup>1</sup>H NMR signal and the downfield-shifted signal at  $\delta^{29}Si = 93.1$  (Si<sup>3</sup> position) is detectable. The visible correlations verify that the <sup>1</sup>H signal at  $\delta^{1}H = 0.32$  belongs to the Si<sup>2</sup>Me<sub>2</sub>H groups that are so far away from the 2e3c Si-H-Si bridge that no correlation is visible. In contrast, a correlation of the downfield-shifted <sup>29</sup>Si NMR signal with the second singlet in the <sup>1</sup>H NMR spectrum at  $\delta^{1}H = 0.79$  is detected. It follows that the signal at  $\delta^{1}H = 0.79$  belongs to the methyl groups of the Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub> unit. Additionally, correlations between the signals at  $\delta^{29}Si = -133.2$  (Si<sup>1</sup> position) as well as  $\delta^{29}Si = -34.0$  (Si<sup>2</sup> position) with the signal at  $\delta^{1}H = 4.22$  are visible. Based on this observation, the <sup>1</sup>H NMR signal is unambiguously assigned to the Si<sup>2</sup>-H hydrogen atoms. Like mentioned for the <sup>1</sup>H, <sup>1</sup>H COSY NMR spectrum (Figure 118), the bridging hydrogen atom of the 2e3c Si-H-Si bond is not detected in the <sup>1</sup>H, <sup>29</sup>Si HMQC NMR spectrum (Figure 121).

In a second <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum (Figure 310, experimental section) optimised for  $J_{H,Si} = 180$  Hz, only the correlation between the <sup>1</sup>H NMR signal at  $\delta^{1}H = 4.22$  (Si<sup>2</sup><u>H</u>) and the <sup>29</sup>Si NMR signal at  $\delta^{29}Si = -34.0$  (<u>Si</u><sup>2</sup>H) is visible.



Figure 121: Excerpt of the  ${}^{1}$ H, ${}^{29}$ Si HMQC NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.31 MHz, -80 °C, optimised for  $J_{H,Si} = 50$  Hz).

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 122) shows two signals that are assigned to the cationic silvl species. Via analysis of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum (Figure 306, experimental section) as well as the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum (Figure 307, experimental section), the <sup>13</sup>C NMR signals are assigned to the hydrogen-substituted dimethylsilyl groups ( $\delta^{13}C = -2.9$ ) and the dimethylsilyl groups involved in the 2e3c Si-H-Si bridge ( $\delta^{13}C = 1.4$ ).

Furthermore, the formation of Ph<sub>3</sub>CH is clearly detected by the appearance of the Ph<sub>3</sub>CH <sup>13</sup>C atom at a chemical shift of  $\delta^{13}$ C = 56.9 in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 122). At the same time, the expected signals of left-over [Ph<sub>3</sub>C]<sup>+</sup> are not unambiguously identifiable in the spectrum.





Additional attempts to react oligosilane **100** with two equivalents of  $[Ph_3C][B(C_6F_5)_4]$  were also performed in 3-fluorotoluene at -80 °C (Figure 123).



Figure 123: Synthesis of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] by the reaction of oligosilane **100** with two equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. In the <sup>1</sup>H NMR spectrum after reaction of oligosilane **100** with two equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Figure 124, bottom spectrum), the same signals as after reaction with one equivalent of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Figure 124, top spectrum) are visible. Additionally, higher amounts of left-over [Ph<sub>3</sub>C]<sup>+</sup> can be identified in the spectrum obtained after reaction with two equivalents [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].



Figure 124: <sup>1</sup>H NMR spectra obtained after reaction of **100** with one equivalent of  $[Ph_3C][B(C_6F_5)_4]$  (top spectrum) and with two equivalents of  $[Ph_3C][B(C_6F_5)_4]$  (bottom spectrum) showing the formation of **127** $[B(C_6F_5)_4]$  (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, -80 °C).

The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 125, bottom spectrum) also shows the same signals as visible after the reaction with one equivalent of  $[Ph_3C][B(C_6F_5)_4]$  (Figure 125, top spectrum). These observations show that a second hydride transfer reaction between  $[Ph_3C]^+$  and the intermolecular stabilised silyl cation **127** is not possible under the reaction conditions.



Figure 125: <sup>29</sup>Si{<sup>1</sup>H} NMR spectra obtained after reaction of **100** with one equivalent of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (top spectrum) and with two equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (bottom spectrum) showing the formation of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, -80 °C).

To verify that the intermolecularly stabilised cationic silvl species **127** is formed, the hydride transfer reaction of oligosilane **100** with 0.5 equivalents of  $[Ph_3C][B(C_6F_5)_4]$  was also performed. The first trial was done in 3-fluorotoluene at -80 °C (Scheme 61).





The recorded <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 126) shows again the clean formation of the intermolecular stabilised silyl cation **127** characterised by its three <sup>29</sup>Si NMR peaks at  $\delta^{29}$ Si = -133.3 (SiSi<sub>4</sub>), -34.0 (SiMe<sub>2</sub>H) and 93.1 ([Me<sub>2</sub>Si-H-SiMe<sub>2</sub>]<sup>+</sup>).



Figure 126: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum obtained after reaction of **100** with 0.5 equivalents of  $[Ph_3C][B(C_6F_5)_4]$ (3-Fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, -80 °C).

Subsequently, the identical reaction using 0.5 equivalents of  $[Ph_3C][B(C_6F_5)_4]$  in the hydride transfer reaction was repeated in dichloromethane-d<sub>2</sub> (Scheme 63).





While the <sup>1</sup>H NMR spectrum (Figure 319, experimental section) was not suitable for an analysis due bad quality of the NMR spectrum (broad lines, overlap of signals), the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 127) suggests a quite clean reaction. Three main <sup>29</sup>Si NMR signals are visible in the shown spectrum. The three signals appear at  $\delta^{29}Si = -133.0$  (SiSi<sub>4</sub>), -32.6 (SiMe<sub>2</sub>H) and 93.9 ([Me<sub>2</sub>Si-H-SiMe<sub>2</sub>]<sup>+</sup>). All three signals show nearly the same shifts that were detected after hydride abstraction with either 0.5 equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Figure 125, upper spectrum) or two equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Figure

125, bottom spectrum) and use of 3-fluorotoluene as a solvent. The appearance of the same set of <sup>29</sup>Si NMR signals in the spectra obtained under these different conditions, show that the same product, the intermolecularly stabilised silyl cation **127**, is formed in all four cases. Albeit one main product can be identified in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 127) obtained after reaction with 0.5 equivalents of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in dichloromethane-d<sub>2</sub>, there are already some side-products that are not visible in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectra (Figure 125 and Figure 126) obtained after reaction in 3-fluorotoluene. These findings show again that 3-fluorotoluene is more suitable for the synthesis of silyl cation **125** as side-reactions with dichloromethane are avoided.



Figure 127: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum obtained after reaction of **100** with 0.5 equivalents of  $[Ph_3C][B(C_6F_5)_4]$ (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -90 °C, \* = unidentified side-products).

It can be concluded from all experiments, that the formation of the intramolecularly bridged silyl cation **126** is not possible. If the synthesis is attempted, either the formation of the intermolecularly stabilised silyl cation **127** or decomposition reactions can be observed. If decomposition occurs in dichloromethane, the decomposition is accompanied by the degradation of Ph<sub>3</sub>CH. As a result of the decomposition, the chlorinated silane Si(SiMe<sub>2</sub>)<sub>4</sub>Cl (**100**) is obtained (Scheme 59). It is also evident from the experiments, that 3-fluorotoluene is the most appropriate solvent to obtain the cationic species **127**. The computed <sup>29</sup>Si NMR values fit well to the experimentally detected values of cation **127** (Table 17).

Table 17: Comparison of experimental and calculated values for the <sup>29</sup>Si chemical shift and Si,H coupling constant of the intramolecularly 2e3c Si-H-Si bridge in silyl cation **127**.

NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constant calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



	δ <sup>29</sup> Si		¹ <i>J</i> ⊦	I,Si
Silicon atom	exp. <sup>[a]</sup>	calc.	exp. <sup>[a]</sup>	calc.
Si <sup>1</sup>	-133.2	-130		
Si <sup>2</sup>	-34.0	-33		
Si <sup>3</sup>	93.1	98	49	50

[a] NMR spectra recorded at -80 °C using 3-fluorotoluene as solvent, counter anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

## 3.4.6.2. Trapping Reaction of the Monocation with (*n*-Bu)<sub>3</sub>SnD

To verify the formation of the intramolecularly Si-H-Si-bridged silyl cation **127** and to definitely exclude any rearrangement of the molecular framework after cation formation, a trapping reaction was performed (Scheme 64).

HSi∖, <i>,</i> SiH	1) [Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] 2) ( <i>n</i> -Bu) <sub>3</sub> Sn <mark>D</mark>	H <i>Si</i> ∖_,Si <mark>D</mark>
Ši H <i>Si</i> S <i>i</i> H	3-Fluorotoluene, -80 °C	Si H <i>Si ́</i> S <i>i</i> H
100	2) - [( <i>n</i> -Bu) <sub>3</sub> Sn][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	128

$$Si = SiMe_2$$

Scheme 64: Trapping reaction of the product after hydride transfer reaction of oligosilane **100** with  $[Ph_3C][B(C_6F_5)_4]$ .

For the trapping reaction, the oligosilane **100** was reacted with  $[Ph_3C][B(C_6F_5)_4]$  in 3-fluorotoluene at -80 °C. The reaction mixture was stirred for five minutes to guarantee the finalisation of the hydride transfer reaction. Subsequently, tributyltin deuteride was added at low temperature. After addition of the tin deuteride, *n*-hexane was added until separation of two layers became visible. The upper layer, containing non-polar components of the reaction

mixture was separated via syringe. Volatile components were removed under reduced pressure and the obtained residue was analysed via NMR spectroscopy and GCMS. The analytical data suggest the exclusive formation of the monodeuterated oligosilane **128**.

The <sup>1</sup>H NMR spectrum shows a septet at  $\delta^{1}$ H = 4.29 with a relative integral of 3H and a coupling of <sup>3</sup>J<sub>H,H</sub> = 4.4 Hz. The expected <sup>1</sup>J<sub>Si,H</sub> coupling resulting from <sup>29</sup>Si satellites cannot be accurately extract from the <sup>1</sup>H NMR spectrum due to an overlap of the satellite signals by impurities. The signal is assigned to the three Si-H hydrogen atoms of the Si<sup>2</sup>Me<sub>2</sub>H units. The corresponding <sup>3</sup>J<sub>H,H</sub> coupling with the methyl groups at Si<sup>2</sup> can be detected for a doublet at  $\delta^{1}$ H = 0.27. The doublet has a total relative integral of 24H with both flanks having different integrals. The same observation was already made for the monodeuterated oligosilane **117** that was obtained after trapping of silyl cation **113** with tributyltin deuteride (Chapter 3.4.4.2). The asymmetry of the doublet results from the overlap of its right flank with the <sup>1</sup>H NMR signals of the Si<sup>3</sup>Me<sub>2</sub>D group. The triplet resulting from the <sup>3</sup>J<sub>H,D</sub> coupling is obscured by the overlapping doublet.



Figure 128: <sup>1</sup>H NMR spectrum of the deuterated oligosilane **128** obtained after trapping with tributyltin deuteride ( $C_6D_6$ , 499.87 MHz, 32 °C, # = 3-fluorotoluene and *n*-hexane).

The corresponding <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum also shows the clean formation of one deuterium-containing silane (Figure 129). The non-deuterated dimethylsilyl groups resonate at  $\delta^{29}$ Si = -33.5 (Si<sup>2</sup> position) while the deuterated dimethylsilyl group appears slightly further upfield at  $\delta^{29}$ Si = -33.9 (Si<sup>3</sup> position). The expected deuterium triplet is well resolved and its

coupling constant is measured as  ${}^{1}J_{Si,D} = 28$  Hz. The Si-D coupling is therefore very similar to the value detected for the monodeuterated trapping product **113** (Figure 84,  ${}^{1}J_{Si,D} = 27$  Hz). The tetrasilyl-substituted silicon atom ( $\delta^{29}Si = -140.3$ ) is barely visible in the  ${}^{29}Si\{^{1}H\}$  INEPT NMR spectrum. Another side-product is visible at a chemical shift of  $\delta^{29}Si = 10.9$  which was not characterised further.



Figure 129: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of the deuterated oligosilane **128** obtained after trapping with tributyltin deuteride ( $C_6D_6$ , 99.31 MHz, 32 °C, # = unidentified side-product).

While its resonance is not unambiguously detected in the <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum, the tetrasilyl-substituted silicon atom can be detected via <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectroscopy (Figure 130). Next to the correlations between the doublet at  $\delta^{1}$ H = 0.27 (methyl groups in Si<sup>2</sup> position) and the signals at  $\delta^{29}$ Si = -33.9 (Si<sup>3</sup> position) and -33.5 (Si<sup>2</sup> position), the correlation to a small signal at  $\delta^{29}$ Si = -140.3 is visible in the 2D <sup>29</sup>Si NMR spectrum. Hence, the signal at  $\delta^{29}$ Si = -140.3 is assigned to the tetrasilyl-substituted silicon atom at Si<sup>1</sup> position. The <sup>1</sup>H,<sup>29</sup>Si HMBC NMR also shows that the signal at  $\delta^{29}$ Si = 10.9 does not correlate to any <sup>1</sup>H signal assigned to the deuterated silane **128**, and therefore does not belong to the molecule.



Figure 130: <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of the deuterated oligosilane **128** obtained after trapping with tributyltin deuteride (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 32 °C, # = unidentified side-product).

The GCMS data (Figure 131) also indicate a very clean trapping reaction. Only two main signals are visible in the GC. Next to  $Ph_3CH$  ( $R_t = 9.3$  min) and some bands due to minor side-products, the deuterated oligosilane **128** ( $R_t = 6.6$  min) is the only product of the trapping reaction. The detected fragment with highest m/z value (m/z = 250.1) corresponds to the [M<sup>+</sup> -Me] fragment.

It must be noted, that the non-deuterated oligosilane **100** as well as deuterated triphenylmethane ( $Ph_3CD$ ) are not detected in either the NMR spectra or in the GCMS data.



Figure 131: GCMS data of the deuterated oligosilane **128**. Upper part: GC trace showing the very clean trapping reaction. Bottom part: Mass spectrum of the band at Rt = 6.6 min.

## 3.4.7. Silyl Cations of a 1,1'-Silyl-Substituted Ferrocene Derivative

The ferrocene derivative **101** was used as a starting material in the hydride transfer reaction with the  $[Ph_3C][B(C_6F_5)_4]$  (Scheme 65).



Scheme 65: Hydride transfer reaction between ferrocene derivative **101** and trityl salt and subsequent stabilisation by a) 2e3c Si-H-Si bond formation or b) coordination to the ferrocene moiety.

After the abstraction reaction, a silylium ion **129** is obtained which is not expected to be stable. Instead, it can stabilise its cationic charge by different mechanisms. Stabilisation is possible by formation of an intramolecularly 2e3c Si-H-Si-bridged cation **130** (Scheme 65, reaction a). Alternatively, stabilisation can occur by coordination of the cationic silicon centre with the ferrocene moiety (Scheme 65, reaction b) whereby the stabilised silyl cation **131** is formed.
Such stabilisation was previously detected for the silyl cations **53** (Scheme 24) and **55** (Scheme 25).<sup>[151, 163, 167-168]</sup>

Furthermore, the formation of the respective silyl cation and subsequent stabilisation of the cationic charge can be accompanied by rearrangement reaction of the oligosilanyl groups that are attached to the ferrocene unit.<sup>[58, 122-123, 133, 163]</sup>

## 3.4.7.1. Theoretical Investigation on Ferrocene-Based Silyl Cations

The ferrocene compound **101** is an isomer of the silyl-substituted ferrocene derivative **102** whose behaviour in the hydride transfer reaction with trityl salt was already investigated in previous studies (Scheme 66).<sup>[163]</sup> It was shown by NMR spectroscopy that the cationic charge is stabilised by formation of silyl cation **132** that is stabilised by a 2e3c Si-H-Si bridge between both oligosilanyl units. No coordination of the cationic silyl centre towards the ferrocene moiety was detected.



Scheme 66: Formation of **132**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)] by hydride transfer reaction of **102** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)]. Experimental <sup>29</sup>Si NMR shifts and <sup>1</sup> $J_{Si,H}$  coupling constant of the cation are given (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C).

The energetic properties of the two different ferrocene-based silyl cation isomers were investigated by DFT calculation. Hence, calculations were performed for the Si-H-Si-bridged silyl cationic species **130** and **132** as well as on the corresponding non-bridged, ferrocenyl-stabilised cations **131** and **133**. For both non-bridged silyl cations, a distinct coordination of the cationic silicon atom with the Cp ring on the opposite side of the ferrocene moiety was visible. The structures of the cations were first optimised at the M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) level of theory. Additionally, single point (SP) calculations of the obtained structures were performed using the *ab initio* MP2<sup>[231-232]</sup> method (MP2/6-31G(d,p)//M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) level of theory). In the following discussion of the quantum mechanical results, the respective SP energies are used for the comparison of computed energies of the different cationic compounds **130-133**. The DFT calculations suggest that the stabilisation of the generated silylium ions by formation of a

2e3c Si-H-Si bridge (cation **130**) is energetically more favourable than stabilisation by the ferrocene moiety (cation **131**) by 49 kJ mol<sup>-1</sup> (Scheme 67).



Scheme 67: Comparison of the calculated relative energies E of different ferrocene-based silyl cations **130-133**. The energies were calculated at the M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) and MP2/6-31G(d,p)//M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) (*italic*) level of theory.

A similar preference is detected if the computed relative energies of the Si-H-Si-bridged cation **132** and the respective ferrocene-coordinated silyl cation **133** are compared. The results of the calculations indicate an energetical preference for the Si-H-Si-bridged structure **132** by 44 kJ mol<sup>-1</sup>. Furthermore, the DFT calculations reveal an energetic preference of the bridged cation **132** compared to its isomer **130** by 12 kJ mol<sup>-1</sup>. Thus, after formation of **130**, a rearrangement of the oligosilanyl units seems plausible from an energetical point of view.

As attractive London dispersion interactions were shown to have an important influence on the stability of oligosilanylsilyl cations an thus influence the cationic skeletal rearrangement reactions,<sup>[122]</sup> additional SP energies of silyl cations **123** and **132** were computed using the methods B3LYP and B3LYP with Grimme's D3 correction (B3LYP-D3) on the structures computed at the M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) level of theory. The results show that if the B3LYP method is used, which does not account for London dispersion interactions,

the energy difference between both Si-H-Si-bridged silyl cations **130** and **132** increases significantly (Scheme 68,  $\Delta E = 39$  kJ mol<sup>-1</sup>). If Grimme's D3 correction is applied, the energy difference (Scheme 68,  $\Delta E = 15$  kJ mol<sup>-1</sup>) again approaches the values that were obtained using either the M06-2X (Scheme 67,  $\Delta E = 16$  kJ mol<sup>-1</sup>) or MP2 method (Scheme 67,  $\Delta E = 12$  kJ mol<sup>-1</sup>). As a result of these calculations, it can be concluded that the silyl cation **130** experiences stronger attractive London dispersion interaction than silyl cation **132**. However, the attractive London dispersion interaction do not result in an energetic preference of the cationic species **130**.



Scheme 68: Comparison of the calculated relative energies E of different ferrocene-based silyl cations **130** and **132**. The energies were calculated at the B3LYP/6-31G(d,p)//M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) and B3LYP-D3/6-31G(d,p)//M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) (*italic*) level of theory.

#### 3.4.7.2. Attempts to Synthesise a Ferrocene-Based Silyl Cation

First trials to react ferrocene derivative **101** in a hydride transfer reaction with  $[Ph_3C][B(C_6F_5)_4)]$  were performed at -40 °C using chlorobenzene-d<sub>5</sub> as solvent (Scheme 69).



Scheme 69: Hydride transfer reaction between ferrocene compound **101** and  $[Ph_3C][B(C_6F_5)_4)]$  in chlorobenzene-d<sub>5</sub>.

The <sup>1</sup>H NMR spectrum (Figure 132) shows the formation of Ph<sub>3</sub>CH which indicates the successful hydride transfer reaction between the 1,1'-silyl-substituted ferrocene derivative **101** and [Ph<sub>3</sub>C]<sup>+</sup>. Additionally, a conglomeration of at least six signals is visible in the area around  $\delta^{1}H = 0.11-0.31$ . Due to the overlap of the signals, no integration and elucidation of the structure is possible on basis of the <sup>1</sup>H NMR spectrum.



Figure 132: <sup>1</sup>H NMR spectrum after hydride transfer reaction between ferrocene compound **101** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, -40 °C)

A <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum was also measured (Figure 133). The spectrum is characterised by its low S/N ratio and the appearance of a multitude of signal. The signals fit neither to the experimental <sup>29</sup>Si NMR signals that were reported for the silyl cation **132** (Scheme 66)<sup>[163]</sup> nor to the values calculated for silyl cation **130** (Table 18). The spectra rather suggest that decomposition occurred after hydride abstraction in chlorobenzene-d<sub>5</sub> at -40 °C. The experiment was repeated once more under identical conditions with essentially the same results. The NMR spectroscopic data also showed decomposition and no identifiable products.



Figure 133:  $^{29}Si\{^{1}H]$  NMR spectrum after hydride transfer reaction between ferrocene compound 101 and  $\label{eq:29} [Ph_{3}C][B(C_{6}F_{5})_{4}] \ (C_{6}D_{5}CI,\ 99.31\ \text{MHz},\ -40\ ^{\circ}C)$ 

Table 18: Calculated <sup>29</sup>Si NMR shifts of cation **130**. NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p)(Si,C,H),def2tzvpd(Fe) level of theory.



130

$$Si = SiMe_x$$
, x = 2 or 3

Silicon atom	δ <sup>29</sup> Si ( <i>calc.</i> )
Si <sup>1</sup>	-5
Si <sup>2</sup>	78
Si <sup>3</sup>	-6/-2

The reaction was therefore repeated using dichloromethane- $d_2$  as it allows to perform the reaction at lower temperatures (Scheme 70).



Scheme 70: Hydride transfer reaction between ferrocene compound **101** and  $[Ph_3C][B(C_6F_5)_4)]$  in dichloromethane-d<sub>2</sub>.

In the recorded <sup>1</sup>H NMR spectrum (Figure 134), the formation of  $Ph_3CH$  is again visible, indicating a successful hydride abstraction by  $[Ph_3C]^+$ .



Figure 134: <sup>1</sup>H NMR spectrum after hydride transfer reaction between ferrocene compound **101** and  $[Ph_3C][B(C_6F_5)_4]$  (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).

An intense signal is visible at a chemical shift of  $\delta^{1}H = 0.17$ , next to a smaller signal at  $\delta^{1}H = 0.11$ . Additionally, a singlet of low intensity appears at  $\delta^{1}H = 2.06$  which is near the chemical shift of the Si-H hydrogen atoms of the starting material **101** ( $\delta^{1}H = 2.60$  in C<sub>6</sub>D<sub>6</sub> at 32 °C). The three signals show relative integrals of roughly 1 (2.05) : 36 (0.17) : 12 (0.11). In the shift area expected for the hydrogen atoms of the cyclopentadienyl rings (around

 $\delta^{1}$ H = 4-5), broad featureless signals of low intensity are detected. Similar observations are made in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure 135).



Figure 135: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum after hydride transfer reaction between ferrocene compound **100** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, -80 °C, \* = CD<sub>2</sub>Cl<sub>2</sub>, # = Ph<sub>3</sub>CH).

The spectrum clearly verifies the formation of Ph<sub>3</sub>CH. Additionally, two main signals are visible in the upfield area. The signals appear at  $\delta^{13}C = -0.5$  and 0.9 which is in the shift range that is expected for dimethylsilyl or trimethylsilyl groups. Both signals resonate at chemical shifts that are comparable to the chemical shifts detected for the starting material **101** ( $\delta^{13}C = 1.1$  for SiMe<sub>2</sub>,  $\delta^{13}C = 2.1$  for SiMe<sub>3</sub>, both in C<sub>6</sub>D<sub>6</sub> at 32 °C). Unexpectedly, the detected <sup>13</sup>C NMR signals in the area around  $\delta^{13}C = 70$  are of very low intensity. In this shift range, the signals of the cyclopentadienyl carbon atoms of the ferrocene are expected (Figure 45).

The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum (Figure 136, bottom spectrum) shows three singlets at  $\delta^{29}$ Si = -118.7, -12.5 and -11.6 with a relative integral ratio of 2 : 1 : 4. The most upfield-shifted of these signals resonates at a frequency very similar to the trisilyl-substituted Si-H silicon atom of the starting material **101** (Figure 46,  $\delta^{29}$ Si = -114.2 in C<sub>6</sub>D<sub>6</sub> at 32 °C). The second and third <sup>29</sup>Si signal appear at chemical shifts that are expected for silyl-substituted trimethylsilyl groups.<sup>[170]</sup> For comparison, the trimethylsilyl groups of the starting material **101** show a similar chemical shift (Figure 46,  $\delta^{29}$ Si = -11.9 in C<sub>6</sub>D<sub>6</sub> at 32 °C). Additionally, the detected <sup>29</sup>Si shifts

at  $\delta^{29}Si = -12.5$  and -11.6 are comparable to the observed shift for the cyclopentadienyl-substituted SiMe<sub>2</sub> groups of the starting material **101** (Figure 46,  $\delta^{29}Si = -15.3$  in C<sub>6</sub>D<sub>6</sub> at 32 °C).



Figure 136: <sup>29</sup>Si{<sup>1</sup>H} NMR (bottom) and <sup>29</sup>Si INEPT NMR (top) spectrum after hydride transfer reaction between ferrocene compound **101** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, -80 °C).

In the hydrogen-coupled <sup>29</sup>Si INEPT NMR spectrum (Figure 136, top spectrum), the signal at  $\delta^{29}$ Si = -118.7 splits up with a coupling of <sup>1</sup>*J*<sub>Si,H</sub> = 152 Hz which is nearly identical to the splitting measured for the neutral ferrocene derivative **101** (Figure 44, <sup>1</sup>*J*<sub>H,Si</sub> = 154.4 Hz). The detected splitting verifies its assignment to a trisilyl-substituted silicon atom bearing a hydride as fourth substituent (Si<sub>3</sub>SiH unit). Both other main <sup>29</sup>Si NMR signals do not show a distinct splitting in the hydrogen-coupled <sup>29</sup>Si INEPT NMR spectrum. Interestingly, neither signals in the <sup>29</sup>Si shift range calculated for the Si-H-Si-bridged cation **130** (Table 18) nor experimentally known for **132** (Scheme 66) are visible in the spectrum. For both structures, the characteristic shift of a Si-H-Si bridge around  $\delta^{29}$ Si = 70 to 90 is expected. Additionally, both compounds do not have groups expected to appear at chemical shifts around  $\delta^{29}$ Si = -118.7.

A <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum (Figure 137) was also measured. In the 2D NMR spectrum, a correlation of the upfield-shifted <sup>29</sup>Si signal at  $\delta^{29}$ Si = -118.7 with the signal at  $\delta^{1}$ H = 2.06 is detected. The correlation appears as a doublet and the doublet splitting has the same size as

the  ${}^{1}J_{\text{Si,H}}$  coupling detected in the hydrogen-coupled  ${}^{29}\text{Si}$  NMR spectrum (Figure 136, top spectrum). The visible correlation and its appearance as a doublet in the  ${}^{1}\text{H}, {}^{29}\text{Si}$  HMBC NMR spectrum verifies the assignment of the signal at  $\delta^{1}\text{H} = 2.06$  to a Si-H functionality.



Figure 137:<sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum after hydride transfer reaction between ferrocene **101** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, -80 °C).

Additionally, the signal at  $\delta^{29}$ Si = -118.7 correlates weakly to the singlet at  $\delta^{1}$ H = 0.17. The situation is more complicated for the signals that appear further downfield in the <sup>29</sup>Si domain of the 2D NMR spectrum. Correlations between the signals at  $\delta^{29}$ Si = -12.5 and -11.9 and  $\delta^{1}$ H = 0.11 and 0.17 are visible. Due to the resolution in the <sup>1</sup>H as well as the <sup>29</sup>Si domain of the two-dimensional NMR spectrum, it is not possible to make an exact distinction of the detected correlations. Correlations to any signal in the downfield area around  $\delta^{29}$ Si = 70 to 100 are not visible in the spectrum. This is the NMR shift range where the cationic silicon atoms of silyl cations stabilised by 2e3c Si-H-Si bridges or by coordination to the ferrocene moiety are expected.<sup>[151, 163, 167-168]</sup> Therefore, it seems as if no such group is present in the detected silicon species. The visible NMR signals rather suggests a neutral silicon compound bearing at least one Si-H functionality.

Overall, no ferrocene-based silvl cation is detected in the NMR data. While exchange reactions of substituents are described in the literature for ferrocene-stabilised silvl cations, whereby

different ferrocene-substituted cations are formed,<sup>[168]</sup> the experimentally observed <sup>29</sup>Si NMR shifts do not show any signals in the chemical shift area expected for stabilised silyl cations. The spectra rather suggest decomposition of the ferrocene compound upon formation of a cationic species. Due to overlap of signals in the <sup>1</sup>H NMR spectrum and no sufficient resolution in the 2D NMR spectra, it was not possible to elucidate the structure of the main product. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra suggest that no cyclopentadienyl units and therefore no ferrocene moiety is present after decomposition. A second possibility is the oxidation of the ferrocene unit after cation formation. Thus, a derivative of the paramagnetic ferrocenium cation would be obtained. The formation of a paramagnetic compound could explain the lack of signals and especially the missing signals of the Cp rings in the <sup>1</sup>H as well as <sup>13</sup>C NMR data.

# 3.5. Comparison of H-Bridged OligosilanyIsilyl Mono- and Dications

Three different intramolecularly stabilised silyl monocations **106**, **111** and **113**, one intmolecularly stabilised silyl dication **118** as well as one intermolecularly stabilised silyl cation **127** (Figure 138) were synthesised by hydride transfer reaction of the respective neutral oligosilanes and characterised via NMR spectroscopy (Table 19).



Figure 138: Intra- and intermolecularly hydrogen-bridged silyl cations. Counter anions ([B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>) are omitted.

Hereafter, the NMR spectroscopy data of the cationic silyl structures are compared among themselves and with a selection of other literature-known silyl cations. The special situation of the intramolecularly bridged silyl cations that possess additional free silyl arms, silyl cations **111** and **113**, is discussed in more detail. Thus, the discussion starts with the oligosilanylsilyl cation **106** and then proceeds to the more branched cation **111** and **113**. Subsequently, the dication **118** is investigated in more detail. As a special case, the formation of the intermolecularly bridged silyl cation **127** instead of the formation of an intramolecular 2e3c Si-H-Si bridge is also analysed further.

Silyl cation	$\delta^{1}$ H	δ <sup>13</sup> C	δ <sup>29</sup> Si	<sup>1</sup> <i>J</i> <sub>Si,H</sub> ([Si-H-Si] <sup>+</sup> )
106 <sup>[a]</sup>	0.10 (Si <sup>1</sup> )	-7.7 (Si <sup>2</sup> )	-43.3 (Si <sup>2</sup> )	53 Hz
	0.13 (Si <sup>2</sup> )	-7.1 (Si¹)	-38.1 (Si <sup>1</sup> )	
	0.39 (Si <sup>3</sup> )	-2.5 (Si <sup>3</sup> )	87.1 (Si <sup>3</sup> )	
	0.44 (Si <sup>3</sup> - <u>H</u> -Si <sup>3</sup> ) <sup>[e]</sup>			
111 <sup>[b]</sup>	0.15(Si⁵)	-11.8 (Si¹)	-76.6 (Si <sup>1</sup> )	42 Hz
	0.21 (Si <sup>1</sup> )	-7.0/-5.3 (Si <sup>2</sup> )	-37.8 (Si <sup>2</sup> )	
	0.27 (Si <sup>4</sup> )	-6.8 (Si <sup>5</sup> )	-37.2 (Si <sup>4</sup> )	
	0.37/0.43 (Si <sup>2</sup> )	-4.9 (Si <sup>4</sup> )	-34.8 (Si <sup>5</sup> )	
	0.74 (Si <sup>3</sup> - <u>H</u> -Si <sup>3</sup> ) <sup>[e]</sup>	-1.9/-1.4 (Si <sup>3</sup> )	90.3 (Si <sup>3</sup> )	
	0.80 (Si <sup>3</sup> )			
113 <sup>[b]</sup>	_[f]	_[f]	-124.8 (Si <sup>1</sup> )	31 Hz <sup>[h]</sup>
			-37.1/-35.0 (Si²/Si⁴) <sup>[g]</sup>	
			-35.0/-37.1 (Si²/Si⁴) <sup>[g]</sup>	
			-34.3 (Si <sup>5</sup> ),	
			89.1 (Si <sup>3</sup> )	
118 <sup>[b]</sup>	0.55 (Si <sup>2</sup> )	-3.1 (Si <sup>2</sup> )	-121.4 (Si <sup>1</sup> )	41 Hz
	0.89 (Si <sup>3</sup> )	-2.2 (Si <sup>3</sup> )	-34.4 (Si <sup>2</sup> )	
	0.81 (Si <sup>3</sup> - <u>H</u> -Si <sup>3</sup> ) <sup>[e]</sup>		88.1 (Si <sup>3</sup> )	
127 <sup>[d]</sup>	0.32 (Si <sup>2</sup> , Me)	-2.9 (Si <sup>2</sup> )	-133.2 (Si <sup>1</sup> )	49 Hz
	0.79 (Si <sup>3</sup> )	1.4 (Si <sup>3</sup> )	-34.0 (Si <sup>2</sup> )	
	4.22 (Si², Si- <u>H</u> )		93.1 (Si <sup>3</sup> )	

Table 19: Comparison of the experimental NMR data of intermolecular stabilised silyl cations 106, 111, 113 and118 as well as intermolecularly stabilised silyl cation 127.

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[a] Recorded in  $C_6D_5Cl$  at -40 °C. [b] Recorded in  $CD_2Cl_2$  at -90 °C. [c] Recorded in  $CD_2Cl_2$  at -80 °C. [d] Recorded in 3-fluorotoluene at -80 °C. [e] Assignment due to signals in the 2D NMR data. [f] NMR signals too broad to make an exact assignment. [g] No distinction possible. [h] Detected at -93 °C.

### 3.5.1. Comparison of Intramolecularly Bridged Silyl Monocations and a Dication

When the linear oligosilane HMe<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>H (**89**) is reacted in a hydride transfer reaction with  $[Ph_{3}C][B(C_{6}F_{5})_{4}]$  using chlorobenzene-d<sub>5</sub> as solvent at -40 °C (Scheme 71), the formation of the cyclic silyl cation **106** is detected in the NMR spectra (Chapter 3.4.1).

$$H_{Si} Si_{Si} Si_{Si} H = \frac{[Ph_{3}C][B(C_{6}F_{5})_{4}]}{C_{6}D_{5}Cl, -40 \ ^{\circ}C} = \frac{Si_{Si}^{1}Si_{Si}^{2}}{Si_{H}^{5}Si^{3}}$$
89
$$Si = SiMe_{2} = \frac{106}{[B(C_{6}F_{5})_{4}]}$$

Scheme 71: Synthesis of  $106[B(C_6F_5)_4]$  in chlorobenzene-d<sub>5</sub> by hydride transfer reaction.

Comparison of the NMR spectroscopic data with similar cyclic cation structures bearing 2e3c Si-H-Si bridges (Table 20) shows that the observed chemical shift of the two silicon atoms involved in the 2e3c Si-H-Si bridge appears between the <sup>29</sup>Si shift values reported for the cyclic silyl cation **36** ( $\delta^{29}$ Si = 76.7) and the bicyclic silyl cation **39** ( $\delta^{29}$ Si = 95.3).<sup>[121, 123]</sup> In contrast, the respective silicon atoms of the cyclic silyl cation **35** appear significantly further downfield ( $\delta^{29}$ Si = 108.9).<sup>[122]</sup> The detected <sup>29</sup>Si NMR shift of the 2e3c Si-H-Si bridge of cation **106** also lays between the shift values reported for the acyclic Si-H-Si-bridged silyl cations **31** ( $\delta^{29}$ Si = 84.8) and **32** ( $\delta^{29}$ Si = 94.3).<sup>[125, 152]</sup>

The <sup>1</sup>H atom of the Si-H-Si bridge ( $\delta^{1}$ H = 0.44), whose <sup>1</sup>H NMR shift is indicated in the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of silvl cation **106** (Figure 52), appears at a higher field than detected for the other listed silvl cations (Table 20). Its <sup>1</sup>H NMR shift is also markedly further upfield-shifted than the respective <sup>1</sup>H NMR shifts of the Si-H-Si groups of the silvl monocation **111** ( $\delta^{1}$ H = 0.74) and the silvl dication **118** ( $\delta^{1}$ H = 0.89).

In general, it can be said that depending on the general constitution of the respective silyl cation, the <sup>1</sup>H NMR shifts of the bridging Si-H-Si varies distinctly.

The  ${}^{1}J_{\text{Si,H}}$  coupling constants of the cationic Si-H-Si bridges all show very similar values around  ${}^{1}J_{\text{Si,H}} = 40-50$  Hz. With a value of  ${}^{1}J_{\text{Si,H}} = 53$  Hz, the direct Si-H coupling constant of oligosilanylsilyl cation **106** is slightly larger than reported for the cations **35-36** and **39** (Table 20). Additionally, it is bigger than detected for the intramolecularly Si-H-Si-bridged silyl cation **111** (Table 19,  ${}^{1}J_{\text{Si,H}} = 42$  Hz) and the dicationic species **118** (Table 19,  ${}^{1}J_{\text{Si,H}} = 41$  Hz).

 Table 20: Comparison of spectroscopic data of **106** and different silyl cation bearing 2e3c Si-H-Si bridges.

 Counter anions are omitted.<sup>[121-123, 125, 152]</sup>



 $Si = SiMe_x$ , x = 1-3

Silyl cation	δ¹Η ([Si-H-Si]⁺)	δ <sup>29</sup> Si ([Si-H-Si]⁺)	<sup>1</sup> <i>J</i> <sub>Si,H</sub> ([Si-H-Si] <sup>+</sup> )
106 <sup>[a]</sup>	0.44 <sup>[f]</sup>	87.1	53 Hz
<b>35</b> <sup>[c]</sup>	2.15 (br)	108.9	43 Hz
<b>36</b> <sup>[b]</sup>	1.47 (br)	76.7	39 Hz
<b>39</b> <sup>[d]</sup>	1.10 (br)	95.3	46 Hz
31 <sup>[e]</sup>	-	84.8	-
<b>32</b> <sup>[e]</sup>	2.1	94.3	-

[a] Recorded in C<sub>6</sub>D<sub>5</sub>Cl at -40 °C. [b] Recorded in C<sub>6</sub>D<sub>6</sub> at 27 °C. [c] Recorded in C<sub>6</sub>D<sub>5</sub>Cl at -30 °C. [d] Recorded in C<sub>6</sub>D<sub>5</sub>Cl at -20 °C. [e] Solid state NMR data given. [f] Assignment due to signals in the 2D NMR data.

The silvl cations **106** as well as **36** have a similar molecular framework. Both silicon atoms involved in the 2e3c bridge are connected via three additional silicon atoms (SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>backbone) in cation **106** while the connection is established in cation **36** by three additional carbon atoms (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> backbone). The silicon cations involved in the respective Si-H-Si bridges are therefore either dialkyl-/monosilyl-substituted (cation **106**) or trialkyl-substituted (cation **36**). The experimentally detected <sup>1</sup>*J*<sub>Si,H</sub> coupling constant is around 14 Hz higher in silyl cation **106** than described for cation **36** (<sup>1</sup>*J*<sub>Si,H</sub> = 39 vs. 53 Hz).

Comparison of the computed gas phase structures of cations **106** and **36** (Figure 139 and Table 21) reveal characteristic structural parameters which result from the different constitution of the backbones.



Figure 139: Computed gas phase structures of silyl cation **106** and **36**. Calculations were performed at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H-Si hydrogen atoms are omitted.

In the two computed structures, the respective six-membered rings adopt a chair-like conformation. Only small differences are calculated for the Si-H bond lengths in the Si-H-Si bridges (163 pm in **106** and 164 pm in **36**). In contrast, a significant difference in the Si-H-Si bond angle is visible. These findings again show that the Si-H bond lengths of 2e3c Si-H-Si bridges is rather fixed while the Si-H-Si angle is a more flexible parameter. These observations were already made for various polycyclic Si-H-Si-bridged silyl cations and for the theoretical investigations of the acyclic Si-H-Si-bridged silyl cations 31 and 88 (Chapter 3.1). While the calculated Si-H-Si angle is  $\angle = 158^{\circ}$  in cation **106**, it is  $\angle = 135^{\circ}$  in cation **36**. The more acute angle in 36 results from the alkyl backbone. Thus, the silyl backbone in the calculated structure of cation **106** shows angles of  $\angle = 107^{\circ}$  for Si<sup>1</sup>-Si<sup>2</sup>-Si<sup>3</sup> and of  $\angle = 109^{\circ}$  for Si<sup>2</sup>-Si<sup>1</sup>-Si<sup>2</sup>. Hence, the bond angles in the silvl bridge have only small deviations from a perfectly tetrahedral coordination ( $\angle = 109.5^{\circ}$ ). In contrast, the deviations are more distinct for the cation 36 containing an alkyl backbone. Its bond angles of  $\angle$  = 114° for C<sup>1</sup>-C<sup>2</sup>-Si and of  $\angle$  = 112° for C<sup>2</sup>-C<sup>1</sup>-C<sup>2</sup> show greater distortions from a perfectly tetrahedral arrangement. These results indicate stronger geometric constraints in cation 36 compared to cation 106. As a result of the geometric constraints, a more acute Si-H-Si angle is detected for cation 36. Additionally, the distances of both silicon atoms involved in the 2e3c Si-H-Si bridge differ significantly for both silyl cations. While Si-Si distance of 320 pm is measured in the calculated structure of **106**, the measured distance in the calculated structure of **36** is only 302 pm. The alkyl-bridged silyl cation **36** cannot adopt a more linear Si-H-Si bridge and thus increased Si-Si distance. The already present geometric strain resulting from the alkyl linkage prevents any further linearisation.

With its increased Si-H-Si angle and increased distance between both silicon atoms involved in the Si-H-Si bridge of silyl cation **106**, the structural parameters (bond lengths and angles) of the 2e3c Si-H-Si bond are comparable to the values calculated for the acyclic Si-H-Si-bridged silyl cations [Me<sub>3</sub>Si-H-SiMe<sub>3</sub>]<sup>+</sup> (**31**) and [Et<sub>3</sub>Si-H-SiEt<sub>3</sub>]<sup>+</sup> (**32**) (Table 21).

During the quantum mechanical analysis, different computational methods were investigated. Interestingly, the Si-H-Si bonding angles of the acyclic, Si-H-Si-bridged silyl cations 31 and 32 show a stronger deviation from linearity when the B3LYP method including Grimme's D3 dispersion correction<sup>[194]</sup> (B3LYP-D3) or if D3 dispersion correction with Becke and Johnson dampening<sup>[195-197]</sup> (B3LYP-D3(BJ)) are used. Thus, when plain B3LYP is used, the calculations predict a perfectly linear Si-H-Si bridge for [Me<sub>3</sub>Si-H-SiMe<sub>3</sub><sup>+</sup>] (31). In contrast, the values are calculated as 163° using B3LYP-D3 and 158° using B3LYP-D3(BJ). For the related ethyl-substituted silvl cation,  $[Et_3Si-H-SiEt_3]^+$  (32), the bonding angle is calculated as 172° using B3LYP, 168° using B3LYP-D3 and 164° using B3LYP-D3(BJ). The change of the Si-H-Si angle when different methods are used might be a result of London dispersion interaction which are not accounted for when plain B3LYP is used as method (see chapter 3.1). It can also be seen in the calculated data that the use of M06-2X results in even more acute angles. In contrast, the use of MP2 results in structural data comparable to B3LYP-D3 and B3LYP-D3(BJ). Analogous observations are made for silyl cation **106** for which bonding angles of 170° (B3LYP), 167° (B3LYP-D3), 165° (B3LYP-D3(BJ)), 158° (M06-2X) and 170° (MP2) are calculated. For cation 36, the computed Si-H-Si angles show only minor differences of 140° (B3LYP), 138° (B3LYP-D3), 137° (B3LYP-D3(BJ)), 135° (M06-2X) and 138° (MP2) when the different methods are applied. This observation can be explained by the mentioned constraints inflicted on the structure of silyl cation **36** by the alkyl backbone. Thus, while London dispersion interactions do influence the calculated geometries of the acyclic silvl cations 31 and 32 as well as the cyclic silvl cation 106, the contributions of the dispersion interactions are overcompensated by ring strain effects in silvl cation 36.

The sum of bond angles around the silicon atoms involved in the bridge do not differ significantly for all calculated structures. All values are around  $\Sigma \angle_{C-Si-C} = 350^{\circ}$  independent of the method that was used during computation.

Cation	Method/6-311+G(d,p)	Si-H [pm]	Si-Si [pm]	Si-H-Si [°]	Σ∠ <sub>C-Si-C</sub> [°]
106	<b>B3LYP</b>	164	327	170	350
	B3LYP-D3	163	325	167	351
	B3LYP-D3(BJ)	162	322	165	351
	M06-2X	163	320	158	350
	MP2	161	321	170	351
36	B3LYP	165	310	140	349
	B3LYP-D3	164	306	138	349
	B3LYP-D3(BJ)	163	304	137	349
	M06-2X	164	302	135	349
	MP2	162	303	138	349
31	B3LYP	164	328	180	348
	B3LYP-D3	163	322	163	349
	B3LYP-D3(BJ)	162	318	158	349
	M06-2X	162	312	148	349
	MP2	161	318	162	349
32	B3LYP	165	329	172	347
	B3LYP-D3	162	323	168	348
	B3LYP-D3(BJ)	162	321	164	349
	M06-2X	162	316	155	348
	MP2	162	320	163	347

Table 21: Comparison of calculated structural parameters of cyclic and acyclic silyl cations containing a 2e3cSi-H-Si bridge using different methods for the structure optimisation.

If one of the central methyl groups of the linear oligosilane **89** is exchanged by a HMe<sub>2</sub>SiMe<sub>2</sub>Si arm the branched oligosilane MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (**90**) results. After hydride transfer reaction with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Scheme 72), the cation **111** is detected (Chapter 3.4.3).



Scheme 72: Synthesis of  $111[B(C_6F_5)_4]$  in dichloromethane-d<sub>2</sub> by hydride transfer reaction.

In general, two possibilities were expected prior to the experiment: Either a static structure without involvement of the newly introduced SiMe<sub>2</sub>SiMe<sub>2</sub>H unit, or alternatively an involvement of the third disilyl unit and thus a possible dynamic behaviour of the cation with its consequences visible in the NMR spectra. The NMR data obtained after hydride transfer reaction indicate a static structure on the NMR time scale (Chapter 3.4.3).

DFT calculations were performed to estimate why an intramolecular hydrogen exchange between the terminal SiMe<sub>2</sub>H group and the cationic SiMe<sub>2</sub>-H-SiMe<sub>2</sub> bridge is not detected by NMR spectroscopy. In course of the possible intramolecular reaction, a transition state **112** is passed through which is characterised by a pentacoordinated silicon atom (Figure 140). The given  $\Delta G^{*183}$  values are pressure-corrected for dichloromethane according to a proposed method by Martin *et al.* (Chapter 7.1).<sup>[222]</sup>



Figure 140: Energetic analysis of the possible intramolecular reaction of silyl cation **111** as well as comparison with the non-bridged silylium ion **134**. The  $\Delta G^{*183}$  values were computed at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H and Si-H-Si hydrogen atoms are omitted in the computed structures.

Proceeding from the transition state **112**, two local minima structures, **111a** and **111b**, were found during DFT calculations by manual displacements of the imaginary frequency by -1 (**111a**) and +1 (**111b**). Both structures show a slight difference in their computed energies and are around  $\Delta G^{*183}$  = -21-23 kJ mol<sup>-1</sup> lower in energy than the transition state **112**.

Additionally, the DFT calculations of different conformers of cation **111** gave another minima structure that has a distinct lower energy (**111**<sup>#</sup>). The conformation **111**<sup>#</sup> is  $\Delta G^{*183} = -31$  kJ mol<sup>-1</sup> lower in energy than the transition state **112**. Hence, the computed total energy barrier of the intramolecular reaction is  $\Delta G^{*183,\ddagger} = 31$  kJ mol<sup>-1</sup>. Additionally, an energetic preference of this structure compared to the non-bridged silylium ion **134** of  $\Delta G^{*183} = -80$  kJ mol<sup>-1</sup> is computed.

If the structure of the lowest energy conformer is analysed in more detail, it can be seen that the conformation of the six-membered ring resembles the classical chair conformation known for cyclohexane derivatives (Figure 141). The computed structural parameter of the 2e3c Si-H-Si bridge of conformer **111**<sup>#</sup> are very akin to the computed values of the cyclic silyl cation **106** which also adopts a chair-like conformation of Si<sub>5</sub>H ring (Table 23).



Figure 141: Computed structure of silyl cation **111**<sup>#</sup> that adopts a conformation with lowest energy. The structure was optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H and Si-H-Si hydrogen atoms are omitted.

For the cation **111**, the large disilyl substituent at Si<sup>1</sup> functions as a conformational anchor and stabilises a conformation of the six-membered ring in which the large substituent is oriented in the equatorial position. In consequence this leads to a multitude of signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. As can also be seen in the computed structure **111**<sup>#</sup>, the SiMe<sub>2</sub>SiMe<sub>2</sub>H unit is turned away from the cationic 2e3c Si-H-Si bridge. Therefore, interactions between both groups do not occur in this conformation.

XRD structures of asymmetric substituted cyclohexasilanes derivatives showed a chair arrangement of the hexacycle.<sup>[55]</sup> Thus, it seems plausible that such an energetic minimum structure is predominantly present in the sample in therefore exclusively detected in the NMR spectra at low temperatures.

Additionally, the NMR data for such a static structure **111<sup>#</sup>** were calculated. The computed <sup>29</sup>Si NMR data agree well with the experimentally observed <sup>29</sup>Si NMR shifts and <sup>1</sup> $J_{H,Si}$  coupling constant (Table 22).

Table 22: Experimental and calculated (*italic*) <sup>29</sup>Si chemical shifts as well as coupling constants of silyl cation **111**<sup>#</sup>. NMR shifts calculated at the M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level of theory. Coupling constant calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level of theory.



Silicon atom	δ <sup>29</sup> Si		<sup>1</sup> <i>J</i> <sub>Si,H</sub> [Hz]	
	exp. <sup>[a]</sup>	calc.	exp. <sup>[a]</sup>	calc.
Si <sup>1</sup>	-76.6	-77		
Si <sup>2</sup>	-37.8	-36		
Si <sup>3</sup>	90.3	98	42	48
Si <sup>4</sup>	-37.2	-34		
Si <sup>5</sup>	-34.8	-34	176	182

[a] NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> at -90 °C, counter anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.

While all NMR spectroscopic data and the respective results of the DFT calculations suggest the static structure of the formed silyl cation **111**, the situation is different for the more branched silyl cation **113** (Scheme 73).



Scheme 73: Synthesis of  $111[B(C_6F_5)_4]$  in dichloromethane-d<sub>2</sub> by hydride transfer reaction.

Its NMR spectroscopic data suggest a dynamic behaviour which is visible by the appearance of broadened signals in the NMR spectra even at -90 °C (Chapter 3.4.3). During this intramolecular process, which passes through a transition state **116**, the Si-H-Si bridge changes place. Calculations on basis of the <sup>29</sup>Si NMR data estimate an energy barrier of  $\Delta G^{\ddagger}(exp.) = 31 \text{ kJ mol}^{-1}$  (Chapter 3.4.4.1). For a more detailed analysis, DFT calculations like

the ones performed for silvl cation **111** (Figure 140) were used. The calculations estimate an energy barrier that is slightly lower in case of silvl cation **113** (Figure 142) than computed for cation **111**. Beginning with the transition state **116**, two minima structures **113a** and **113b** were computed by manual displacement -1 (**113a**) and +1 (**113b**) of the imaginary frequency. Both structures are computed as being  $\Delta G^{*183} = -21-23$  kJ mol<sup>-1</sup> lower in energy than the transition state.



Figure 142: Energetic analysis of the possible intramolecular reaction of silyl cation **113** as well as comparison with the non-bridged silylium ion **135**. The  $\Delta G^{*183}$  values were computed at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H and Si-H-Si hydrogen atoms are omitted in the computed structures.

These differences are comparable to the ones calculated for the Gibbs free energy difference between the transition state **112** and the two local minima conformers **111a** and **111b** (Figure 140). Additionally, a conformer **113**<sup>#</sup> with lower Gibbs free energy was computed. The lowest energy conformer **113**<sup>#</sup> found during DFT calculations is  $\Delta G^{*183} = -27$  kJ mol<sup>-1</sup> lower in energy

than the transition state **116**. Thus, the computed total energy barrier for the postulated intramolecular reaction (Scheme 51) is  $\Delta G^{*183,\ddagger} = 27 \text{ kJ mol}^{-1}$  in case of silyl cation **113**. This value corresponds well to the experimentally estimated value of  $\Delta G^{\ddagger}(exp.) = 31 \text{ kJ mol}^{-1}$ . More importantly, it is lower than the values computed for the comparable process in the case of silyl cation **111** ( $\Delta G^{*183} = 31 \text{ kJ mol}^{-1}$ ). The non-bridged silyl cation **135** could also be optimised and its energy is  $\Delta G^{*183} = 90 \text{ kJ mol}^{-1}$  higher than the value for **113<sup>#</sup>**.

Interestingly, the computed conformation of the lowest energy conformer **113**<sup>#</sup> already shows that one hydrogen-substituted silyl arm is in close vicinity of the 2e3c Si-H-Si bridge (Figure 143).



Figure 143: Computed structure of silyl cation **113**<sup>#</sup> that adopts a topology with lowest energy. The structure was optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H and Si-H-Si hydrogen atoms are omitted.

This observation is important, as the lowest energy conformation of **111**<sup>#</sup> (Figure 141) adopts a conformation in which the hydrogen-bearing silyl arm is turned away from the 2e3c Si-H-Si bridge. Analysis of the preferred conformation can help to clarify while in one case (silyl cation **113**) an intramolecular reaction was observed whereas in the other case (silyl cation **111**) no such reaction was seen in the NMR data. Thus, less conformationally changes are first need in case of **113**<sup>#</sup> compared to **111**<sup>#</sup> to allow interactions between the SiMe<sub>2</sub>SiMe<sub>2</sub>H unit and the cationic 2e3c Si-H-Si bridge. Furthermore, it can be noted that the energetically preferred conformation **113**<sup>#</sup> does not adopt a chair-like conformation of the six-membered ring as computed for **111**<sup>#</sup>. Its structure is rather boat-like. The structural parameters of its 2e3c Si-H-Si bridge also differ from the values computed for **106** and **111**<sup>#</sup> (Table 23). Most notably, its more acute Si-H-Si bridge and the SiMe<sub>2</sub>H group of the disilyl unit that is turned towards it.

Cation	Si-H [pm]	Si-Si [pm]	Si-H-Si [°]	Σ∠ <sub>C-Si-C</sub> [°]
106	163	320	158	350
111#	163	321	161	351
113#	164	313	146	347

Table 23: Comparison of the structural parameters of the 2e3c Si-H-Si bridge of silyl cation 106, 111# and 113#The structures were optimised at the M06-2X/6-311+G(d,p) level of theory.

This close vicinity of the Si-H-Si bridge and one hydrogen-substituted disilyl unit in conformer **113**<sup>#</sup> suggest a possible alternative transition state. Accordingly, a second transition state **136** was found during DFT calculations (Figure 144).



Figure 144: Alternative transition state **136** without pentacoordinated silicon atom. The structure was optimised at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H hydrogen atoms are omitted.

Instead of passing through a transition state **116** with a pentacoordinated silicon atom by antarafacial coordination of two Si-H units to the positive charged silicon centre ( $S_N$ 2-like reaction), the transition state **136** is more akin to a suprafacial coordination of the two Si-H hydrogen atoms and the empty p orbital at Si<sup>+</sup>.



 $Si = SiMe_2$ R = SiMe<sub>2</sub>SiMe<sub>2</sub>H

Figure 145: Schematic representation of the two transition states **116** and **136** that were found during optimisation.

Energetic considerations on the alternative transition state **136** reveal a remarkably higher energy barrier between the lowest energy conformer **113**<sup>#</sup> and **136** (Figure 146,  $\Delta G^{*183,\ddagger} = 65 \text{ kJ mol}^{-1}$ ) compared to the barrier between **113**<sup>#</sup> and transition state **116** (Figure 142,  $\Delta G^{*183,\ddagger} = 27 \text{ kJ mol}^{-1}$ ). As the differences in activation energy are significantly higher, the process involving the S<sub>N</sub>2-like transition state **116** is the more likely cause of the observed behaviour in the NMR spectra.

Additionally, a similar transition state was also found for the cationic species **111**. In this case, the barrier of the reaction between the transition state and the lowest energy conformer **111**<sup>#</sup> was computed as  $\Delta G^{*183,\ddagger} = 67$  kJ mol<sup>-1</sup> which is also remarkably higher than the reaction passing through a transition state **112** with a pentacoordinated silicon atom (Figure 140,  $\Delta G^{*183,\ddagger} = 31$  kJ mol<sup>-1</sup>).

All in all, the quantum chemical findings can explain the different detection of a static silyl cation **111** and the dynamic behaviour for silyl cation **113** in the low-temperature NMR spectra.



Figure 146: Results of the DFT calculation of the alternative intramolecular reaction of silyl cation **113**. The ΔG\*<sup>183</sup> values were computed at the M06-2X/6-311+G(d,p) level of theory. Hydrogen atoms expect Si-H and Si-H-Si hydrogen atoms are omitted in the computed structures.

Silyl cations which are intramolecularly stabilised via 2e3c Si-H-Si bridges and which have at the same time additional Si-H functionalities in the molecular structure are rare. Next to the handful of examples described in this work, the working group around G. I. Nikonov described the synthesis and characterisation of the silyl cations **41** and **42** from the respective silylated benzene derivatives (Scheme 74).<sup>[160]</sup>



Scheme 74: Synthesis of **41**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and **42**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] by hydride transfer reaction of the respective silylated benzene derivatives and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>[160-161]</sup>

For the cationic species **41**, NMR data in the range of -85 to -80 °C suggest a static 2e3c Si-H-Si bridge with the typical reduced Si-H coupling constant ( ${}^{1}J_{H,Si} = 46$  Hz). For the two

neighbouring hydrogen-substituted dimethylsilyl groups in β-position, a coupling of  ${}^{1}J_{H,Si}$  = 119 Hz was observed which is significant lower than for the two hydrogen-substituted silyl groups in γ-position ( ${}^{1}J_{H,Si}$  = 171 Hz). The decrease in the observable coupling was explained by agostic interactions of the Si-H hydrogen atoms of the dimethylsilyl groups in β-position with the silicon atoms of the Si-H bydrogen atoms of the dimethylsilyl groups in  $\beta$ -position with the silicon atoms of the Si-H-Si bridge. In contrast, spectroscopic data of cation **41** at room temperature showed a single signal in the <sup>29</sup>Si NMR data, suggesting a fast intramolecular exchange that results in an averaging of the signals. DFT calculations supported the interpretation of the spectroscopic data. In comparison, agostic interactions characterised by a distinctly decreased Si-H coupling constant are not visible for silyl cation **113**. This can be explained by the marked structural differences of the cations **41** and **111**. The benzene scaffold of cation **41** enforces a structure that does not allow flexibility in the distances between the cationic Si-H-Si unit and the Si-H functionalities of the neighbouring SiMe<sub>2</sub>H groups. However, the acyclic silyl arms in cation **113** enable the central silicon atom to take a tetrahedral coordination which results in a Si-H distances between the formed Si-H-Si bridge and the terminal SiMe<sub>2</sub>H groups that prevents any detectable interaction.

However, if the temperature is raised, coalescence of some of the <sup>29</sup>Si signals becomes visible for silyl cation **113** (Figure 79). This is justified by the intramolecular reaction that results in an alternating 2e3c Si-H-Si bond in silyl cation **113** (Scheme 51). With increasing temperature, the rate of the intramolecular reaction also increases. In the end, it is expected that the process results in an averaging of the four internal dimethylsilyl groups in silyl cation **113** as well as of the terminal SiMe<sub>2</sub>H groups and formed 2e3c Si-H-Si bridge. Thus, the expected <sup>29</sup>Si NMR spectrum would show three signals. Two signals resulting from the averaged signals of the silyl arms and another signal resulting from the central, tetrasilyl-substituted silicon atom. Nonetheless, the averaged signal of the terminal SiMe<sub>2</sub>H groups with the Si-H-Si bridge was not observed in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectra even at -45 °C (Figure 79). While an averaged signal was detected at elevated temperature, it is assigned to the averaged signal of the four internal SiMe<sub>2</sub> groups (Si<sup>2</sup> and Si<sup>4</sup>) of the disilyl units by it chemical shift of  $\delta^{29}Si = -36.6$ . Decomposition occurred before an averaged signal of the [Me<sub>2</sub>Si<sup>3</sup>-H-Si<sup>3</sup>Me<sub>2</sub>]<sup>+</sup> ( $\delta^{29}Si = 89.1$ ) unit and the two Si<sup>5</sup>Me<sub>2</sub>H groups ( $\delta^{29}Si = -34.3$ ) was visible in the <sup>29</sup>Si NMR data.

Nikonov and co-workers furthermore showed that if one of the hydrogen-substituted dimethylsilyl groups of benzene derivative **41** was exchanged by a methyl group, the NMR spectroscopic properties of the obtained cation **42** changed significantly.<sup>[160-161]</sup> For this cation, spectral data suggest a pentacoordinated dimethylsilyl group whose cationic silicon atom is stabilised by both neighbouring SiMe<sub>2</sub>H groups. Therefore, the structural properties of cation **42** are reminiscent of the postulated transition state **116** during the intramolecular reaction of cation **113** (Figure 142). The experimental observation of such a structural element in case of

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cation **42**, support the assumption of the existence of transition state 116 to describe the dynamic behaviour of oligosilarylsilyl cation **113**.

Interestingly, the addition of a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$  to a NMR solution containing the silyl cation **113** results in the formation of a new silyl species, the dication **118** (Scheme 75, reaction a). The formed silyl species was also independently synthesised by the direct reaction of the oligosilane **91** with two equivalents of  $[Ph_3C][B(C_6F_5)_4]$  (Scheme 75, reaction b).

a) Two-step synthesis



b) One-step synthesis



Scheme 75: Synthesis of the dicationic silyl species **118** by either 1) two-step or by b) one-step synthesis. Counter anions  $[B(C_6F_5)_4]$  omitted.

While examples of silyl dications with silicon in its formal oxidation state of +IV are scarce, the facile formation of the dicationic species **118** stands in in strong contrast to other silyl dications described in the literature. Recently, the Oestreich group published the synthesis of a silyl dication **137** after twofold hydride transfer reaction from the silane **138** (Scheme 76).<sup>[150]</sup>



Scheme 76: Synthesis of the silyl dication 137 by hydride transfer reaction and its <sup>29</sup>Si chemical shift.<sup>[150]</sup>

In comparison to oligosilanylsilyl dication **118**, formed silyl cation **137** differs profoundly by means of the stabilisation of the cationic charges at the two silicon atoms. While for dication **118** stabilisation is achieved by the formation of two intramolecular 2e3c Si-H-Si bridges, the dication **137** experiences stabilising effects by the counter anion as can be seen in the NMR data and the crystal structure (Figure 147).<sup>[150]</sup>



Figure 147: Solid state structure of silyl dication 137.[150]

Furthermore, the reaction time for the formation of **137** by the direct reaction of hydrosilane **138** was described as five days at room temperature. In contrast, the formation of dication **118** following one of the two synthesis strategies (Scheme 75) proceeds within minutes or even seconds at -90 to -80 °C. It must be noted that the Oestreich group was also successful in synthesising different dications **139** and **140** as their contact ion pairs starting from different regioisomers of naphthalene-based hydrosilanes **141** and **142** (Scheme 77).





Scheme 77: Synthesis of naphthalene-based silyl dications 139 and 140.[150]

Another example for a dicationic silvl species is the reaction of the cationic naphthylsilvl species **40** which was reacted with an additional equivalent of  $[Ph_3C][B(C_6F_5)_4)]$  to obtain the dicationic silvl species **143** as described by Müller and co-workers.<sup>[135]</sup> The reaction was described to proceed over the course of 9 h at 75 °C and did not result in the formation of the dicationic species **143** but instead in the formation of the fluorine-bridged monocation **144**. The detection of the fluorine-bridged **144** was explained by the intermediate formation of the dicationic species **143** which under the reaction conditions directly reacts with the counter anion  $[B(C_6F_5)_4)]^-$  (Scheme 78).



Scheme 78: Attempted synthesis of dicationic silyl species **143** by hydride transfer reaction of the hydrogen-bridged monocation **40** and follow-up reaction with the counter anion which results in the detection of the fluorine-bridged monocation **144**.<sup>[135]</sup>

In contrast, the facile formation of silvl dication **118** shows that the first hydride transfer reaction does not influence the second hydride transfer reaction. This can be explained by the molecular structure, which is on the one hand less sterically demanding, and on the other hand helps to ensure that both positive charges are quite far separate in the molecule. The facile formation of the dication also shows the high utility of intramolecular 2e3c Si-H-Si bonds to stabilise otherwise elusive silvl cationic and dicationic species.

While there are no other examples of silyl dications with 2e3c Si-H-Si bridges in the literature yet, Sorensen and co-workers described the structurally comparable µ-hydrido-bridged carbodication **145** already in 1993 (Scheme 79).<sup>[233]</sup>



Scheme 79: Synthesis of carbodication 145.<sup>[233]</sup> The counter anion is omitted.

The cation was synthesised from its respective diol **146** which was added at low temperatures, as a its solution in dichloromethane- $d_2$ , to a solution of 1 : 1 FSO<sub>3</sub>H·SbF<sub>5</sub> (magic acid) in

SO<sub>2</sub>CIF. The formed carbodication was investigated via low temperature <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The spectroscopic data revealed a highly symmetric structure with three signals in the <sup>1</sup>H NMR spectrum and four signals in its <sup>13</sup>C NMR data (Table 24).

Unit	$\delta^{1}$ H (rel. integral)	δ <sup>13</sup> C	<sup>1</sup> <i>J</i> <sub>С,Н</sub> [Hz]
CH₃	2.53 (8H)	29.5	130 Hz
C-H-C	-4.89 (2H)	160.1	t, 20 Hz
CH <sub>2</sub>	2.23 (24H)	50.5	not given
Central C	-	45.8	-

Table 24: <sup>1</sup>H and <sup>13</sup>C NMR data of carbodication 145 (CD<sub>2</sub>Cl<sub>2</sub>, -93 °C).<sup>[233]</sup>

Interestingly, the C-H-C carbon atoms ( $\delta^{13}$ C = 160.1) gave no doublet in the hydrogen-coupled <sup>13</sup>C NMR spectrum. Instead, a triplet with a coupling of <sup>1</sup>*J*<sub>C,H</sub> = 20 Hz was detected in the <sup>13</sup>C NMR spectrum. As an explanation, the authors postulated a very rapid exchange for the bridging units in carbodication **145**. The exchange was expected to proceed via small concentrations of non-bridged cation species.

In contrast, a doublet is observed for the oligosilanylsilyl dication **118** in the hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 98). According to that observation, it can be concluded that no intramolecular exchange reaction happens for silyl dication **118**. The NMR spectra of silyl dication **118** are consistent with two static 2e3c Si-H-Si bonds as seen by the sharp <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR signals the doublet for the Si-H-Si silicon atoms in the hydrogen-coupled <sup>29</sup>Si NMR spectrum.

It must be noted that for the carbodication **145** the non-bridged cation species would involve tertiary cationic carbon centres, a known structural motif that was also observed experimentally.<sup>[175, 234]</sup> In contrast, non-bridged variations of silyl dication **118** would involve [(Silyl)Me<sub>2</sub>Si]<sup>+</sup> end groups in their acyclic forms. Such structural motifs have not been observed experimentally in dichloromethane yet and are energetically highly disfavoured (Figure 92).

### 3.5.2. Formation of an Intermolecularly Stabilised Silyl Cation and its Properties

The hydride transfer reaction using  $Si(SiMe_2H)_4$  (**100**) did not result in the formation of the intramolecularly stabilised silyl cation **126**. While the reaction in dichloromethane-d<sub>2</sub> resulted in the formation  $Si(SiMe_2CI)_4$  (**93**), the reaction using chlorobenzene-d<sub>5</sub> indicated decomposition (Chapter 3.4.6.1). In contrast, cation formation was detected when

3-fluorotoluene was used as a solvent (Chapter 3.4.6). In this case, instead of the formation of the intramolecular substituted oligosilane **126**, the formation of the intermolecularly stabilised cationic silyl species **127** is visible in the NMR spectra (Scheme 80),



Scheme 80: Synthesis of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in 3-Fluorotoluene.

This stands in strong contrast to the oligosilanylsilyl cations **106**, **111** and **113** and the oligosilanylsilyl dication **118** as all four are stabilised by intramolecular 2e3c Si-H-Si bridges. In general, the stabilisation resulting from an intramolecular 2e3c Si-H-Si bond is expected to be favoured compared to an intermolecular stabilisation due to entropic effect. The preference for the formation of silyl cation **127** instead of **126** likely results from the energetically strongly disfavoured four-membered ring structure (Table 15) that is present in the structure of silyl cation **126**. Therefore, the destabilising effects of the ring strain seems to overcompensate the otherwise unfavourable entropic effects associated with the formation of cation **127**. As a result, an intermolecular instead of an intramolecular 2e3c Si-H-Si bridge is formed.

To further investigate this working hypothesis, additional quantum chemical calculations were performed. At first, the structures of cations **126** and **127** were optimised. Furthermore, the structures of the non-bridged silvlium ion **147** as well as  $Si(SiMe_2H)_4$  (**100**) and the silvl cations **148-150** stabilised by coordination of 3-fluorotoluene were optimised (Figure 148). The structures were optimised at the M06-2X/6-311+G(d,p) level of theory and energetic minima were found for all described compounds.

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Figure 148: Neutral silane **100** and cationic silyl species that were examined by quantum mechanical methods to explain the formation of the intramolecularly stabilised silyl cation **127**.

If the calculated energy of the non-bridged silvlium ion **147** is compared with the intramolecularly bridged silvl cation **126**, energetic preferences of  $\Delta E = -43 \text{ kJ mol}^{-1}$  and  $\Delta G^{*193} = -41 \text{ kJ mol}^{-1}$  are calculated after formation of the 2e3c Si-H-Si bridge (Scheme 81).



Scheme 81: Computed reaction of silylium ion **147** to the intramolecularly stabilised silyl cation **126**. The values for  $\Delta E$  and  $\Delta G^{*193}$  were calculated at the M06-2X/6-311+G(d,p) level of theory.

This value is also significantly lower than the comparable differences between silvl cation **111** (Figure 140,  $\Delta G^{*183} = -80 \text{ kJ mol}^{-1}$ ) or silvl cation **113** (Figure 142,  $\Delta G^{*183} = -90 \text{ kJ mol}^{-1}$ ) and their respective non-bridged silvlium ions **134** and **135**. The quite low energetic difference between bridged silvl cations **126** and non-bridged silvlium ion **147** fits well to the calculated energies of an isodesmic reaction which involved the formation of a comparable model system (Scheme 58). In its case, a value of  $\Delta E = 51 \text{ kJ mol}^{-1}$  for the energetically disfavoured Si-H-Si-bridged structure compared to its non-bridged relative was computed (Table 15).

Further evidence for the formation of the intermolecular stabilised silyl cation **127** results from the computed reaction between the intramolecularly stabilised silyl cation **126** with the neutral silane **100** to form **127** (Scheme 82). The calculations reveal a highly exothermic ( $\Delta E = -96 \text{ kJ mol}^{-1}$ ) reaction upon formation of the intramolecularly stabilised silyl cation. More importantly, the reaction is still significantly exergonic ( $\Delta G^{*193} = -55 \text{ kJ mol}^{-1}$ ), albeit entropically disfavoured. This result shows that the formation of the intramolecularly stabilised silyl species **126** even if the entropic effects are considered.



Scheme 82: Computed reaction between **126** and **100** resulting in the formation of **127**. The values for for  $\Delta E$  and  $\Delta G^{*193}$  were calculated at the M06-2X/6-311+G(d,p) level of theory.

In aryl solvents, stabilisation due to the formation of silylated arenium ions or by coordination of the halogen-substituted solvent is possible.<sup>[85]</sup> To estimate the likelihood of such a reaction with the solvent, quantum mechanical calculation for the formation of fluoronium-stabilised silyl cation **148** and the arenium-stabilised silyl cations **149-150** from the intramolecularly stabilised silyl cation **124** and the solvent molecules were executed (Scheme 83). The calculations reveal the reaction to be significantly less exothermic (**148**:  $\Delta E = -51 \text{ kJ mol}^{-1}$ , **149** and **150**: -63 kJ mol<sup>-1</sup>) than the formation of the intermolecularly bridged silyl cation **127** (Scheme 82,  $\Delta E = -96 \text{ kJ mol}^{-1}$ ). Even though entropically disfavoured, analysis of the Gibbs free energies marks the formation of the fluoronium ions **148** ( $\Delta G^{*193} = -15 \text{ kJ mol}^{-1}$ ) as well as the formation of the two arenium ions **149** ( $\Delta G^{*193} = -25 \text{ kJ mol}^{-1}$ ) and **150** ( $\Delta G^{*193} = -28 \text{ kJ mol}^{-1}$ ) as still exergonic. Nonetheless, all reactions with the solvent are less exergonic than the formation of the intermolecularly bridged cation **126** and neutral silane **100** (Scheme 82,  $\Delta G^{*193} = -55 \text{ kJ mol}^{-1}$ ).

These results support the assumption that no silyl cation stabilised by coordination of 3-fluorotoluene is formed after hydride abstraction, but that the formation of the intermolecular stabilised silyl cation **127** occurs.

Interestingly, comparison of the three different investigated coordination modes between 3-fluorotoluene and the silyl cation show that the coordination of the fluorine substituent,

whereby fluoronium ion **148** is formed, is energetically disfavoured compared to the formation of arenium ions **149** (*para*-position) and **150** (*ortho*-position).

Formation of fluoronium ion:





Formation of arenium ions:



126

149



Scheme 83: Formation of the fluoronium ion **148** and arenium ions **149-150** from the intramolecularly stabilised silyl cation **126** and 3-fluorotoluene. The values for  $\Delta G^{*193}$  and  $\Delta E$  were calculated at the M06-2X/6-311+G(d,p) level of theory.

The formation of the fluoronium cation **148** was also ruled out on basis of the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum in which no splitting of the downfield-shifted signal due to <sup>29</sup>Si,<sup>19</sup>F coupling is visible (Figure 119), while a splitting of this signal is visible in the hydrogen-coupled <sup>29</sup>Si NMR spectrum (Figure 120).

These findings are furthermore represented by the hypothetical reactions of the intermolecular stabilised silyl cation **127** with 3-fluoroluene whereby the free silane **100** and either fluoronium ion **148** or the arenium ions **149-150** are formed (Scheme 84).


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Scheme 84: Computed reactions of intermolecular stabilised silyl cation **127** with 3-fluorotoluene. The values for  $\Delta G^{*193}$  and  $\Delta E$  were calculated at the M06-2X/6-311+G(d,p) level of theory.

Independent of which of the three solvent-stabilised cations is formed after reaction of **127** with 3-fluorotoluene, all reactions were calculated to be significantly endotherm ( $\Delta E = 32-45 \text{ kJ mol}^{-1}$ ) as well as endergonic ( $\Delta G^{*193} = 27-41 \text{ kJ mol}^{-1}$ ) and therefore unlikely to occur.

All in all, the preference of the intermolecularly stabilised cation **127** compared to its intramolecularly stabilised relative **126** or any of the solvent-stabilised silyl cations **148-149** can be verified by the results of the DFT calculations.

## 4. Summary and Outlook

In this work, the hydrogen-substituted oligosilanes **90** and **91** as well as the phenyl-substituted oligosilane **92** were synthesised (Figure 149).



Figure 149: Neutral oligosilanes that were synthesised and characterised in this work.

All three silanes were characterised by NMR and IR spectroscopy as well as elemental analysis (EA) and high-resolution mass spectrometry (HRMS). Furthermore, the molecular structure of the phenyl-substituted oligosilane **92** was elucidated by XRD analysis.

An exchange reaction between silanides and fluorosilanes, which was previously described by the Marschner group to synthesise various oligosilanes,<sup>[68]</sup> was used for the synthesis of oligosilane **92**. In this case, the exchange reaction between potassium silanide **12** and an excess of fluorosilane **94** yielded the oligosilane **92** in high yields and good purity prior to purification (Figure 150). By the successful synthesis of **92** following Marschner's protocol, the range of applicable substrates for the exchange reaction could be extended to FMe<sub>2</sub>SiSiMe<sub>2</sub>Ph (**94**).



Figure 150: Synthesis of phenyl-substituted silane 92.

Subsequently, the silane **92** was reacted with triflic acid whereby it was transformed to the corresponding oligosilanylsilyl tetratriflate. By reaction with Li[AlH<sub>4</sub>], the hydrogen-substituted oligosilane **91** was successfully obtained. In a similar way, the hydrosilane **90** was obtained from its phenyl-substituted precursor.

The branched oligosilanes **90-91** and the linear oligosilane **89** were successfully converted to their respective silyl monocations **106** (Chapter 3.4.1), **111** (Chapter 3.4.3) and **113** (Chapter

3.4.4) by hydride transfer reaction with  $[Ph_3C][B(C_6F_5)_4]$  (Figure 151). All oligosilanylsilyl cations were characterised by NMR spectroscopy.



Figure 151: Intramolecularly Si-H-Si-bridged silyl cations that were synthesised and characterised in this work.

The silvl cation **106** showed a static behaviour in the NMR spectra ( $C_6D_5CI$ , -40 °C) with a characteristic, downfield-shifted <sup>29</sup>Si NMR signal and <sup>1</sup> $J_{Si,H}$  coupling constant of the cationic 2e3c Si-H-Si bridge.

A static behaviour in the NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>, -90 °C) was also observed for the silyl cation **111**. While the detected <sup>29</sup>Si NMR shift and <sup>1</sup>*J*<sub>Si,H</sub> coupling were similar to the values detected for cation **106**, the <sup>1</sup>H and <sup>13</sup>C NMR data differed significantly. In case of **111**, the methyl groups at the formed six-membered ring were shown to be magnetically inequivalent. These was explained by the asymmetric substitution at the central silicon atom. Due to its substitution with a methyl group and SiMe<sub>2</sub>SiMe<sub>2</sub>H unit, the methyl groups in *syn*- and *anti*-position relative to the SiMe<sub>2</sub>SiMe<sub>2</sub>H unit could be distinguished by NMR spectroscopy. No interaction of the hydrogen-substituted disilyl unit with the 2e3c Si-H-Si bridge was detected in the NMR data. The results of DFT calculations predicted **111** to adopt an energetically preferred, chair-like conformation in which the hydrogen-substituted disilyl unit is in an equatorial position (Chapter 3.5). The results of the DFT calculations supported the absence of any detectable interactions between the SiMe<sub>2</sub>SiMe<sub>2</sub>H moiety and the cationic 2e3c Si-H-Si bridge in the NMR spectra.

In contrast, a dynamic behaviour was observed in the NMR spectra ( $CD_2Cl_2$ , various temperatures) of silyl cation **113**. By VT NMR experiments, a strong dependency between temperature and line broadening of the NMR signals was detected. While the <sup>29</sup>Si NMR spectra at temperatures above -93° did not allow for the detection of the <sup>1</sup>*J*<sub>Si,H</sub> coupling constant of the downfield-shifted <sup>29</sup>Si NMR signal of the 2e3c Si-H-Si bridge, it was possible to detect the splitting at -93 °C. This was attributed to an intramolecular reaction which was slowed down by the decreased temperature so that detection on the NMR time scale became possible. By DFT calculations, a reaction mechanism which explains the temperature-dependent NMR signals of silyl cation **113** was found (Chapter 3.5). The intramolecular process was shown to

proceed via a transition state with pentacoordinated silicon atom and a small energy barrier of  $\Delta G^{*183,\ddagger} = 27 \text{ kJ mol}^{-1}$  was computed.

Additionally, the intramolecularly stabilised dication **118** was obtained by twofold hydride transfer reaction of oligosilane **91** with  $[Ph_3C][B(C_6F_5)_4]$  (Chapter 3.4.5). The dication could be synthesised by direct reaction of one equivalent of oligosilane **91** with two equivalents of  $[Ph_3C][B(C_6F_5)_4]$  (Figure 152, path a). Alternatively, it was obtained by first generating the monocation **113** and subsequent reaction with a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$  (Figure 152, path b).



Figure 152: Two synthetic approaches to obtain the Si-H-Si-bridged silyl dication 118.

In both cases, it was shown that the second hydride abstraction happened nearly instantly. In comparison to monocation **113**, the dication **118** showed quite sharp signals in the <sup>1</sup>H,<sup>13</sup>C{<sup>1</sup>H} as well as <sup>29</sup>Si{<sup>1</sup>H} NMR spectra and the dication could be completely characterised by low-temperature NMR spectroscopy. Its <sup>29</sup>Si NMR spectrum showed the characteristic chemical shift and splitting of cationic 2e3c Si-H-Si bridges, and a highly symmetric structure of dication **118** was derived from the NMR data.

In contrast to the intramolecularly Si-H-Si-bridged silyl cations, the intermolecularly stabilised silyl cation **127** was obtained when oligosilane **100** was reacted with different amounts of  $[Ph_3C][B(C_6F_5)_4]$  at low temperatures (Figure 153). In its case, the use of 3-fluorotoluene was shown to be the solvent of choice and the formation of the intramolecularly bridged species **127** was independent of the amount  $[Ph_3C][B(C_6F_5)_4]$  used (Chapter 3.4.6). The formation of

**127** instead of the intramolecularly bridged cation **126** was reasoned on basis of ring strain effects. Despite being entropically disfavoured, the destabilising ring strain effects contribute to the formation of cation **127**. Additionally, DFT calculations revealed that the formation of the intermolecular Si-H-Si bridge is also favoured compared to different solvent complexes with 3-fluorotoluene (Chapter 3.5.2).



Figure 153: Formation of the intermolecularly Si-H-Si-bridged silyl cation **127** instead of the intramolecularly bridged silyl cation **126**.

Furthermore, the oligosilanylsilyl cations **113** and **127** as well as the oligosilanylsilyl dication **118** were reacted with tributyltin deuteride to trap the reactive cationic species whereby the deuterated silanes **117** (Chapter 3.4.4.2), **123** (Chapter 3.4.5.2) and **128** (Chapter 3.4.6.2) were formed (Figure 154).



Figure 154: Deuterated oligosilanes that were obtained after trapping reaction of the respective cations with tributyltin deuteride.

While the trapping of the dication **118** was associated with several side-products, all side-products were identified by GCMS and could be traced back to the silyl dication.

The previously unknown 1,1'-silyl-substituted ferrocene derivatives **101** and **103** (Figure 155) were also synthesised in this work and both compounds were characterised by NMR and IR spectroscopy, EA and HRMS as well as XRD analysis (Chapter 3.3).



Figure 155: The 1,1'-silyl substituted ferrocene derivatives 101 and 103 that were synthesised in this work.

Additional attempts were performed to obtain a cationic species by reacting the synthesised ferrocene derivative **101** with  $[Ph_3C][B(C_6F_5)_4]$  (Figure 156). Neither a Si-H-Si-bridged cationic species nor a cationic silvl species stabilised by coordination to the ferrocene moiety could by observed in the NMR spectra (Chapter 3.4.7.2). Albeit the hydride abstraction was successful (detection of Ph<sub>3</sub>CH), the spectra indicated decomposition. Most notably, unexpectedly weak signals for the Cp rings of the ferrocene were detected in the <sup>1</sup>H and <sup>13</sup>C NMR data. Although these observations could be explained by the formation of paramagnetic ferrocenium cations due to oxidation of the ferrocene moiety after cation formation, the exact process was not elucidated during this thesis.



Figure 156: Hydride transfer reaction between ferrocene derivative and **101** resulting in unidentified products.

In addition to the results with an experimental focus, further quantum mechanical studies were performed. Polycyclic Si-H-Si-bridged oligosilanylsilyl cations with various ring sizes as well as their corresponding non-bridged silylium ions were investigated (Chapter 3.1.1). The results showed that a certain size of the rings is needed so that the formation of the bridged cation is preferred compared to the non-bridged silylium ions. The results also showed that the Si-H bond lengths of the 2e3c Si-H-Si bridges is confined to a very narrow range around 160 pm. Next to the quantum mechanical investigations of 2e3c Si-H-Si bridges in polycyclic systems, the general properties of 2e3c Si-H-Si bridges were investigated by analysis of two acyclic model systems [H<sub>3</sub>Si-H-SiH<sub>3</sub>]<sup>+</sup> (**88**) and [Me<sub>3</sub>Si-H-SiMe<sub>3</sub>]<sup>+</sup> (**31**) (Chapter 3.1.3). By comparison of different DFT and *ab initio* methods, it was detected that the Si-H-Si angles of both systems became more acute if methods were applied that include London dispersion interaction. Based

on this result, the conclusion was drawn that attractive London dispersion interaction contribute to the arrangement of the Si-H-Si unit of bridged silyl cations.

In future studies, the results of the quantum mechanical calculations of Si-H-Si-bridged polycyclic silyl compounds can be used to determine before the experiment how the polycyclic systems need to be designed so that cation generation is possible.

Furthermore, it can be tried to crystallise the Si-H-Si-bridged silyl cations. Especially the structure of the bridged dication **118** is of interest as it is the first example of an oligosilanylsilyl dication with two intramolecular Si-H-Si bridges. For crystallisation attempts, it might be advisable to use another counter anion. For example, *closo*-(car)borates can be tried as they have a higher tendency to crystallise than the respective  $[B(C_6F_5)_4]$  salts (Chapter 1.3.2).

Another worthwhile field of investigation is the use of the oligosilane **91** as an anionic building block. First preliminary results, that were not include in this work, show that the reaction with potassium *tert*-butylate results in the formation of silanide **151** (Scheme 85).



Scheme 85: Formation of silanide 151 by reaction of 91 with potassium tert-butylate.

If the synthesis of silanide **151** is successful, the extensively investigated reactivity of  $(Me_3Si)_3SiK (12)^{[50, 54, 56, 60, 73]}$  can be transferred to **151**. On this way, the Si(SiMe\_2SiMe\_2H)\_3 unit can be introduced with its potential in follow-up reactions, e.g. hydrosilylation or dehydrocoupling reactions.

# 5. Experimental Section

## 5.1. General Aspects

All reactions in which air- and moisture-sensitive compounds were used, common Schlenk techniques were applied. As protective gas nitrogen 5.0 was used. If reactions were carried out in a glove box, nitrogen 5.0 was also used as protective gas. Non-deuterated solvents were dried prior to use and freshly distilled. For THF, *n*-hexane, *n*-pentane and diethyl ether sodium-potassium alloy was used as drying agent. Toluene was dried using sodium metal. Deuterated NMR solvents (dichloromethane-d<sub>2</sub>, chlorobenzene-d<sub>5</sub>) and the non-deuterated 3-fluorotoluene were dried over 4 Å molecular sieve. All glassware was heated in an oven at 160 °C, evacuated while hot and then flushed with nitrogen before use.

Lithium rod used for the formation of lithium silanides was first hammered to small slices which were directly cut with a scissor into the prepared reaction vessel which contained a layer of anhydrous *n*-hexane. Subsequently, the oxide layer was removed by reacting it with trimethylchlorosilane (Me<sub>3</sub>SiCl).<sup>[83]</sup> Chlorosilane and solvents were removed and lithium slices were washed with *n*-hexane. The activated lithium was than used for the synthesis of the respective lithium silanides.

Triflic acid, dichlorodimethylsilane and chlorotrimethylsilane were distilled prior to use and stored under nitrogen atmosphere.

Tributyltin deuteride,  $(n-Bu)_3$ SnD was prepared from  $(n-Bu)_3$ SnCl and Li[AlD<sub>4</sub>],<sup>[235]</sup> and the tin deuteride was distilled prior of use.

The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  was synthesised according to a slightly modified literature procedure.<sup>[119, 236]</sup>

Triethylammonium chloride ([HNEt<sub>3</sub>]Cl) was dried prior to use by heating under vacuum (120-150 °C at 0.1-1 Pa) for 5 h.

## NMR Spectroscopy

All NMR spectra were recorded on a Bruker Fourier 300, a Bruker Avance DRX 500, a Bruker Avance III 500 or a Bruker Avance III HD 500 XWB spectrometer.

<sup>1</sup>H NMR spectra were referenced to the residual protons of the deuterated solvent as internal reference. <sup>13</sup>C NMR spectra were referenced to the central line of the solvent signal when deuterated solvents were applied. If reactions were carried out in non-deuterated solvents, except 3-fluorotoluene, the NMR spectrum was referenced to the corresponding signals of the deuterated solvent which was used in a capillary (Table 25). In case of 3-fluorotoluene, the

signals were calibrated against the <sup>1</sup>H and <sup>13</sup>C NMR shifts of its methyl group relative to tetramethylsilane (TMS) used as an internal standard in neat 3-fluorotoluene.

Solvent	$\delta^{_1}H^{_{[a]}}$	δ <sup>13</sup> C
Acetone-d <sub>6</sub>	2.05	29.8
Benzene-d <sub>6</sub>	7.16	128.1
Chlorobenzene-d₅	6.96	134.2
Chloroform-d <sub>3</sub>	7.26	77.2
Dichloromethane-d <sub>2</sub>	5.32	53.9
Toluene-d <sub>8</sub>	2.08	20.4
Water-d <sub>2</sub>	4.79	-
3-Fluorotoluene <sup>[b]</sup>	2.13	21.0

Table 25: NMR chemical shifts of solvents used as reference.<sup>[223]</sup>

[a] NMR shift of the residual protons of the deuterated solvents (except 3-fluorotoluene). [b] NMR shifts referenced versus CH<sub>3</sub> group of neat 3-fluorotoluene using TMS as internal standard (TMS:  $\delta^{1}H = 0.00$ ,  $\delta^{13}C = 0.0$ ).

Other heteronuclear NMR spectra (<sup>11</sup>B, <sup>19</sup>F, <sup>29</sup>Si) were calibrated against external standards (Table 26).

NMR Nucleus	External Standard	Reference
<sup>11</sup> B	$BF_3{\cdot}OEt_2$	0.0
<sup>19</sup> F	CFCI₃	0.0
<sup>29</sup> Si	Me <sub>2</sub> HSiCI	11.1 <sup>[a]</sup>

Table 26: External standard used for calibration of heteronuclear NMR spectra.

[a] Referenced vs. TMS ( $\delta^{29}$ Si = 0.0)

All NMR spectra were analysed and modified using the Mestrelab MestReNova NMR software (Version 9.1.0-14011). The FIDs (free induction decay) of the heteronuclear 1D NMR spectra were folded with an exponential function using the window function routine of the NMR software and the exponential factors (em) of em = 2.00-10.00. For 1D <sup>1</sup>H NMR spectra, em = 0.30 was used. If other em or gauss multiplications (gm) were used, it is specified beneath the respective spectra. The <sup>29</sup>Si and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded with a relaxation delay of D1 = 10 s, while D1 = 3 s was used for <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectra. The <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectra. The <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectra were obtained using values of J = 8 Hz, n = 6 for SiMe<sub>2</sub> groups or J = 9 Hz, n = 9 for SiMe<sub>3</sub> groups. The <sup>1</sup>H,<sup>29</sup>Si HMQC spectra and <sup>1</sup>H,<sup>29</sup>Si HMBC spectra were obtained for J = 180 Hz and J = 8 Hz, respectively. <sup>1</sup>H,<sup>13</sup>C HMQC spectra and <sup>1</sup>H, <sup>13</sup>C

HMBC spectra were obtained using settings for J = 145 Hz and J = 8 Hz, respectively. The 2D NMR spectra were processed using window functions of sine square 0.00° in both dimensions for <sup>1</sup>H,<sup>13</sup>C HMQC and <sup>1</sup>H,<sup>29</sup>Si HMQC/HMBC. For <sup>1</sup>H,<sup>1</sup>H COSY NMR spectra and <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectra windows function of sine bell 0.00° in both dimensions were used. Deviating processing settings are marked beneath the respective 2D NMR spectra.

## **IR Spectroscopy**

Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

## Gas Chromatography-Mass Spectrometry (GCMS)

GCMS data were obtained on an Agilent 7890B with Agilent 5977B GC/MSD detection unit (stationary phase: HP-5MS UI column, length 30 m, diameter 0.25 mm, film thickness  $0.25 \ \mu$ m).

Two different temperature programs were used:

- T<sub>initial</sub> = 50°C for 3 min, then heating with 40°C/min to T<sub>end</sub> = 280 °C, staying at this temperature for 8.5 min; injector temperature: 280 °C; detector: EI with 70 eV.
- T<sub>initial</sub> = 50°C for 3 min, then heating with 30°C/min to T<sub>end</sub> = 250 °C, staying at this temperature for 8 min; injector temperature: 250 °C; detector: EI with 70 eV.

For mass peaks with different isotope patters, the mass of the isotope constitution with highest probability is given.

## High-Resolution Mass Spectrometry (HRMS)

High resolution mass spectra were measured on a Finnigan-LCQ or a Finnigan-MAT95 mass spectrometer using electron ionisation (EI).

## Elemental Analysis (EA)

Elemental analyses were accomplished by combustion analyses (C, H, N, S) using a Euro EA Element Analyzer with EuroVector equipment.

## **XRD Analysis**

Single crystal X-ray analyses were performed on a Bruker Apex 2 with Mo K $\alpha$ -radiation ( $\lambda$  = 71.073 pm). Molecular structures were solved using SHELXS,<sup>[237]</sup> and refined with SHELXL<sup>[238]</sup> and OLEX2-GUI.<sup>[239]</sup> The XRD structures were visualised with Crystal Impact Diamond 4.6.4.

### 5.2. Synthesis of Starting Materials

#### Synthesis of PhMe<sub>2</sub>SiSiMe<sub>2</sub>H (151)<sup>[240]</sup>

HSiCl + PhSiLi THF, -20 °C to r.t., 16 h 16 - LiCl 151  $Si = SiMe_2$ 

Lithium dimethylphenylsilanide, PhMe<sub>2</sub>SiLi (**16**),<sup>[83]</sup> was prepared by reduction of dimethylphenylchlorosilane (PhMe<sub>2</sub>SiCl, 1.00 equiv., 111.7 mmol) with Li slices (4.00 equiv., 446.7 mmol) in THF (100 mL). After a reaction time of 16 h, the formation of silanide **16** was verified by <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectroscopy and the red solution of **16** was carefully added via PTFE canula to a cooled solution (T = -20°C) of dimethylchlorosilane (HMe<sub>2</sub>SiCl, 1.20 equiv., 134.0 mmol) in THF (120 mL) during 1.5 h. The decolouration of the solution as well as the formation of salts were observed in course of the addition. After complete addition, the slightly red reaction mixture was stirred for 16 h at room temperature. The next day, the colour of the suspension had completely faded. The solvent and volatile components were removed *in vacuo* followed by distillation under reduced pressure (35-42 °C at 8.4 Pa). The product **151** was obtained after distillation as a colourless liquid in 65% yield (72.1 mmol).

Analytical data of 16

<sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (THF/D<sub>2</sub>O lock, 99.31 MHz, 305.0 K): -27.5 (s, <u>Si</u>Me<sub>2</sub>).

Analytical data of 151

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K): 0.09 (d, 6H,  ${}^{3}J_{H.H} = 4.5$  Hz, Si<u>Me</u><sub>2</sub>H), 0.32 (s, 6H, Si<u>Me</u><sub>2</sub>Ph), 4.00 (sept, 1H,  ${}^{3}J_{H,H} = 4.5$  Hz,  ${}^{1}J_{H,Si} = 174.6$  Hz, SiMe<sub>2</sub>H), 7.15-7.21 (m, 3H, Aryl-<u>H</u>), 7.44-7.46 (m, 2H, Aryl-<u>H</u>).  ${}^{29}$ Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -39.4 (s, <u>Si</u>Me<sub>2</sub>H,  ${}^{1}J_{Si,Si} = 86$  Hz), -21.1 (s, <u>Si</u>Me<sub>2</sub>Ph,  ${}^{1}J_{Si,Si} = 86$  Hz).



Figure 158: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **151 (**C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).

### Synthesis of PhMe<sub>2</sub>SiSiMe<sub>2</sub>Cl (152)



For the chlorination of PhMe<sub>2</sub>SiSiMe<sub>2</sub>H (**151**) to obtain PhMe<sub>2</sub>SiSiMe<sub>2</sub>Cl (**152**), the reaction of hydrogen-substituted silanes with trichloro*iso*cyanuric acid (TCCA) was used.<sup>[21]</sup> The distilled hydrogen-substituted silane **151** (1.00 equiv., 69.72 mmol) was dissolved in THF (100 mL). The resulting solution was cooled to -20 °C and TCCA (0.35 equiv., 24.40 mmol) was added in small portions. After complete addition, a colourless suspension was obtained. After 10 min, the cooling bath was removed, and the reaction was stirred for 45 min at room temperature. The solvent was removed under reduced pressure. The residue was redissolved in *n*-pentane and the salts filtered off via a D4 frit. The solvent was again removed from the filtrate under reduced pressure. The chlorosilane **152** was obtained as a colourless oil in 92% yield (64.32 mmol).

Spectroscopic data were in accordance with literature.<sup>[241]</sup>

### Analytical data of 152

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.14 MHz, 295.5 K): 0.30 (s, 6H, Si<u>Me<sub>2</sub></u>), 0.33 (s, 6H, Si<u>Me<sub>2</sub></u>), 7.15-7.19 (m, 3H, Aryl-<u>H</u>), 7.39-7.7.42 (m, 2H, Aryl-<u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (THF/D<sub>2</sub>O lock, 99.31 MHz, 298.2 K): -21.8 (s, <u>Si</u>Me<sub>2</sub>Ph), 22.2 (s, <u>Si</u>Me<sub>2</sub>Cl).



Figure 160: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **152** (THF/D<sub>2</sub>O lock, 99.31 MHz. 298.2 K).

#### Synthesis of PhMe<sub>2</sub>SiSiMe<sub>2</sub>F (94)

CISi-SiPh 
$$\xrightarrow{ZnF_2}$$
 FSi-SiPh  
**152**  $Si = SiMe_2$  **94**

The chlorosilane **152** (1.00 equiv., 70.78 mmol) was dissolved in diethyl ether (150 mL) and the resulting solution was cooled via ice bath. Anhydrous zinc(II) fluoride (0.60 equiv., 42.47 mmol) was added and the suspension was stirred for 16 hours. In course of this reaction time, the bath warmed up to room temperature. The following day, the previously colourless suspension had changed its colour and the formation of a brownish, glue-like substance was observed. The solvent was removed under pressure and *n*-pentane was added to the residue. The resulting suspension was filtered via a D4 frit and a small layer of kieselgur. After removal of the solvent, the fluorosilane **94** was obtained in 89% yield (62.66 mmol) as a slightly yellow liquid.

#### Analytical data of 94

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.45 MHz, 300.0 K): 0.19 (d, 6H,  ${}^{3}J_{H,F} = 8.7$  Hz, Si<u>Me</u><sub>2</sub>F), 0.30 (s, 6H, Si<u>Me</u><sub>2</sub>Ph), 7.15-7.20 (m, 3H, Aryl-<u>H</u>), 7.42-7.44 (m, 2H, Aryl-<u>H</u>).  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125.85 MHz, 300.0 K): -4.2 (d,  ${}^{3}J_{C,F} = 1$  Hz,  ${}^{1}J_{C,Si} = 46$  Hz, Si<u>Me</u><sub>2</sub>Ph), 0.6 (d,  ${}^{2}J_{C,F} = 12$  Hz,  ${}^{1}J_{C,Si} = 49$  Hz, Si<u>Me</u><sub>2</sub>F), 128.4 (s, Aryl-C), 129.2 (s, Aryl-C), 134.2 (s, Aryl-C), 137.6 (d,  ${}^{3}J_{C,F} = 2.1$  Hz, Aryl-C). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 470.84 MHz, 300.0 K): -175.28 (sept,  ${}^{3}J_{F,H} = 8.7$  Hz,  ${}^{1}J_{F,Si} = 308.3$  Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99.42 MHz, 300.0 K): -25.3 (d,  ${}^{2}J_{Si,F} = 27$  Hz), 33.5 (d,  ${}^{2}J_{Si,F} = 308$  Hz).



Figure 162:  $^{13}C\{^{1}H\}$  NMR spectrum of 94 (C\_6D\_6, 125.85 MHz, 300.0 K).



Figure 164:  ${}^{29}Si{}^{1}H$  NMR spectrum of **94** (C<sub>6</sub>D<sub>6</sub>, 99.42 MHz, 300.0 K).

#### Synthesis of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>4</sub> (92)



In a glove box, tetrakis(trimethylsilyl)silane (1)<sup>[12]</sup> (1.00 equiv., 11.77 mmol) was dissolved in THF (20 mL) and potassium t-butylate (1.05 equiv., 12.36 mmol) was added to the stirred solution. The resulting red solution was stirred overnight and the quantitative formation of potassium tris(trimethylsilyl)silanide, (Me<sub>3</sub>Si)<sub>3</sub>SiK (12), <sup>[50]</sup> was confirmed by <sup>29</sup>Si{1H} INEPT NMR spectroscopy. The solution containing the silanide 12 was subsequently added to a stirred solution of fluorosilane 94 (6.00 equiv., 70.62 mmol) in toluene (100 mL). The reaction mixture was stirred for 7 days during which time the progress of the reaction was monitored via <sup>29</sup>Si<sup>1</sup>H INEPT NMR spectroscopy. During the reaction, the addition of one additional equivalent of potassium t-butylate was needed. The addition was necessary as termination of the reaction can happen if KF gets eliminated instead of Me<sub>3</sub>SiF.<sup>[68]</sup> In this case, addition of new potassium t-butylate restarts the reaction as a new silyl anion is formed which can then react further with the fluorosilane 94. Subsequently, the product mixture was taken from the glove box. Solvents and volatile components (e.g. excess fluorosilane 94) were removed under reduced pressure. The solid residue was redissolved in *n*-hexane and filtered via a D4 frit. The solvent was again removed, and the obtained solid residue was recrystallised from acetone at -20 °C. The oligosilane 92 was obtained as a colourless solid in 86% yield (10.09 mmol). Crystals suitable for X-ray diffraction were also obtained by crystallisation from acetone at -20 °C.

#### Analytical data of 92

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.87 MHz, 305.0 K): 0.21 (s, 24H, Si<u>Me</u><sub>2</sub>). 0.51 (s, 24H, Si<u>Me</u><sub>2</sub>Ph), 7.39-7.41 (m, 12H, Aryl-C<sub>meta</sub> and Aryl-C<sub>ipso</sub>), 7.49-7.51 (m, 8H, Aryl-C<sub>ortho</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125.71 MHz, 305.0 K): -1.7 (s, Si<u>Me</u><sub>2</sub>Ph, <sup>1</sup>J<sub>C,Si</sub> = 46 Hz), 0.6 (s, Si<u>Me</u><sub>2</sub>, <sup>1</sup>J<sub>C,Si</sub> = 37 Hz), 127.8 (s, Aryl-C<sub>para</sub>), 128.5 (Aryl-C<sub>meta</sub>), 134.3 (s, Aryl-C<sub>ortho</sub>), 139.7 (s, Aryl-C<sub>ipso</sub>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (CDCl<sub>3</sub>, 99.31 MHz, 305.0 K): -105.1 (s, <u>Si</u>Si<sub>4</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 38 Hz), -38.2 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 38 Hz, <sup>1</sup>J<sub>Si,Si</sub> = 74 Hz), -16.8 (s, <u>Si</u>Me<sub>2</sub>Ph, <sup>1</sup>J<sub>Si,Si</sub> = 74 Hz).

HRMS (m/z) found/calculated for C<sub>40</sub>H<sub>68</sub>Si<sub>9</sub>: 800.3234/800.3239.

EA (%) found/calculated for C<sub>40</sub>H<sub>68</sub>Si<sub>9</sub>: C 59.47/59.92, H 9.43/8.55.

IR (cm<sup>-1</sup>): 3065 (w), 3046 (w), 3019 (w), 2949 (w), 2894 (w), 1486 (w), 1426 (m), 1403 (w), 1299 (w), 1241 (s), 1067 (m), 998 (w), 829 (s), 772 (s), 730 (s), 696 (s), 650 (s), 633 (s).



Figure 165 <sup>1</sup>H NMR spectrum of **92** (CDCI<sub>3</sub>, 499.87 MHz, 305.0 K).







Figure 168: <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum of **92** (CDCl<sub>3</sub>, 499.87 MHz, 305.0 K).



Figure 169: <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of **92** (CDCl<sub>3</sub>, 499.87 MHz, 305.0 K).



Figure 171:Excerpt of the <sup>1</sup>H, <sup>29</sup>Si HMQC NMR spectrum of **92** (CDCl<sub>3</sub>, 499.87 MHz, 305.0 K). Expansion shows the correlations of the hydrogen atoms in *ortho*-position of the four phenyl substituents.







Figure 173: ATR IR spectrum of 92.

## Synthesis of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub> (91)

## Synthesis of triflate 95



The phenyl-substituted oligosilane **92** (1.00 equiv., 10.09 mmol) was dissolved in *n*-pentane (60 mL). The stirred solution was cooled via ice bath and triflic acid was added via Hamilton syringe to the cooled solution. After addition of the triflic acid, the reaction mixture was stirred for one hour in the cooling bath. Subsequently, the bath was removed and stirring was continued for 2.5 h at room temperature. A sample was taken an analysed via NMR spectroscopy. The quantitative formation of the silyl triflate **95** was observed.

### Analytical data of 95

<sup>1</sup>H NMR (*n*-pentane/D<sub>2</sub>O lock, 499.87 MHz, 305.0 K): 0.49 (s, 24H, Si<u>Me<sub>2</sub></u>), 0.68 (s, 24H, Si<u>Me<sub>2</sub></u>). <sup>19</sup>F{<sup>1</sup>H} NMR (*n*-pentane/D<sub>2</sub>O lock, 470.30 MHz, 305.1 K): -77.21. <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (*n*-pentane/D<sub>2</sub>O lock, 99.31 MHz, 305.0 K): -113.1 (s, <u>Si</u>Si<sub>4</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 43 Hz), -37.2 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 43 Hz, <sup>1</sup>J<sub>Si,Si</sub> = 85 Hz), 44.5 (s, <u>Si</u>Me<sub>2</sub>OTf, <sup>1</sup>J<sub>Si,Si</sub> = 85 Hz).









## Transformation silyl triflate 95 to hydrosilanes 91



Subsequently, *n*-pentane was removed and the silyl triflate **95** was redissolved in diethyl ether (50 mL). The triflate-containing solution was added to a cooled solution of lithium aluminium hydride (4.00 equiv., 40.36 mmol) in diethyl ether via PTFE canula. The resulting suspension was stirred for 16 h. Afterwards, the solvent and volatile components were removed under reduced pressure and n-pentane (80 mL) was added to the residue. The suspension was filtered via a D4 frit and the salts were washed with additional *n*-pentane (100 mL). The solvent was again removed from the filtrate to yield oligosilane **91** in 94% yield (9.47 mmol), relative to **92**, as a colourless oil.

Analytical data of 91

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K): 0.25 (d, 24H,  ${}^{3}J_{H,H} = 4.5$  Hz, Si<u>Me</u><sub>2</sub>H). 0.43 (s, 24H, Si<u>Me</u><sub>2</sub>), 4.11 (sept, 4H,  ${}^{3}J_{H,H} = 4.5$  Hz,  ${}^{1}J_{H,Si} = 178.0$  Hz.  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.0 K): -5.4 (s, Si<u>Me</u><sub>2</sub>H,  ${}^{1}J_{C,Si} = 43$  Hz), -0.5 (s, Si<u>Me</u><sub>2</sub>,  ${}^{1}J_{C,Si} = 38$  Hz).  ${}^{29}Si{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -119.2 (s, <u>Si</u>Si<sub>4</sub>), -38.3 (s, <u>Si</u>Me<sub>2</sub>), -34.1 (s, <u>Si</u>Me<sub>2</sub>H).  ${}^{29}Si{}^{1}H{}$  INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -119.2 (s, <u>Si</u>Si<sub>4</sub>,  ${}^{1}J_{Si,Si} = 42$  Hz), -38.3 (s, <u>Si</u>Me<sub>2</sub>,  ${}^{1}J_{Si,Si} = 42$  Hz,  ${}^{1}J_{Si,Si} = 74$  Hz), -34.1 (s, <u>Si</u>Me<sub>2</sub>H,  ${}^{1}J_{Si,Si} = 74$  Hz).

HRMS (m/z) found/calculated for  $C_{40}H_{68}Si_9$ : 496.1987/496.1981.

EA (%) found/calculated for C<sub>40</sub>H<sub>68</sub>Si<sub>9</sub>: C 33.43/38.64, H 9.684/10.54.

IR (cm<sup>-1</sup>): 2957 (w), 2896 (w), 2108 (m), 1404 (w), 1247 (m) 1019 (s), 907 (m), 877 (s), 827 (s), 785 (s), 733 (m), 696 (m), 663 (s), 636 (m).







Figure 179: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 180: Excerpt of the  ${}^{1}$ H, ${}^{13}$ C HMBC NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 181: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).



Figure 182: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).







Figure 184: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of **91** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 185: ATR IR spectrum of 91.

#### Synthesis of Me<sub>2</sub>Si(SiMe<sub>2</sub>Ph)<sub>2</sub> (98)

SiCl<sub>2</sub> 
$$2 PhSiLi (16)$$
  
THF/n-hexane, 0 °C to r.t., 22 h  
- 2 LiCl 98  
Si = SiMe<sub>2</sub>

Dimethyldichlorosilane (1.00 equiv., 0.07 mol) was dissolved in *n*-hexane (150 mL) and cooled to 0 °C. A solution of silanide **16** (2.00 equiv., 0.14 mol) in THF (150 mL) was added during 1.5 h to the stirred solution. The reaction was stirred for 4.5 h while gradually warming-up of the cooling bath. The bath was removed and stirring was continued for 16 h at room temperature. The solvents and volatile components were removed under reduced pressure and *n*-hexane (100 mL) was added to the residue. The resulting suspension was filtered via a D4 frit and filtered salts were washed with *n*-hexane (2 x 40 mL). The solvent was again removed to give a brownish oil. After distillation (22 °C at 4.6 Pa) the product **98** was obtained as a colourless oil in 65% yield (45.55 mmol).

Spectroscopic data were in accordance with literature.<sup>[240, 242]</sup>

### Analytical data of 98

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K): 0.17 (s, 6H, Si<u>Me<sub>2</sub></u>), 0.33 (s, 12 H, Si<u>Me<sub>2</sub></u>H), 7.20-7.25 (m, 6H, Aryl-<u>H</u>), 7.41-7.44 (m, 4H, Aryl-<u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -48.1 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup> $J_{Si,Si}$  = 73 Hz), -18.7 (s, <u>Si</u>Me<sub>2</sub>Ph, <sup>1</sup> $J_{Si,Si}$  = 73 Hz).



Figure 187: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **98** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).

#### Synthesis of Me<sub>2</sub>Si(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>2</sub> (99)

PhSi 
$$Si$$
 SiPh  
98  
 $Si = SiMe_2$   
 $Si = SiMe_2$ 

The trisilane **98** (1.00 equiv., 9.13 mmol) was dissolved in *n*-pentane (35 mL) and cooled to 0 °C. Triflic acid (2.05 equiv., 18.71 mmol) was added via Hamilton syringe to the stirred solution. Stirring was continued for 10 min at 0 °C and subsequently for 2 h at room temperature. A solution of silanide **16** (2.20 equiv., 20.08 mmol) in toluene (50 mL) was added at room temperature during 40 min to the solution of the silyl triflate in *n*-pentane. The formation of salts was observed during addition of the silanide. After complete addition, the resulting suspension was stirred for 16 h at room temperature. The following day, the reaction was quenched by addition of HCI/H<sub>2</sub>O (100 mL). The organic layer was separated, and the aqueous layer extracted with *n*-pentane (2 x 50 mL). The combined organic phases were dried with sodium sulphate, filtered and the solvents and volatile components were removed under reduced pressure. A yellow solid was obtained from which pure silane **99** was isolated after crystallisation from ethanol at -70 °C in 28% yield (2.56 mmol).

Spectroscopic data were in accordance with literature.[243]

### Analytical data of 99

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.87 MHz, 305.0 K): -0.02 (s, 6H, Si<u>Me</u><sub>2</sub>), 0.08 (s, 12H, Si<u>Me</u><sub>2</sub>), 0.36 (s, 12H, Si<u>Me</u><sub>2</sub>), 7.30-7.34 (m, 6H, Aryl-<u>H</u>), 7.41-7.44 (m, 4H, Aryl-<u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -43.3 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup> $J_{Si,Si} = 61$  Hz, <sup>1</sup> $J_{Si,Si} = 72$  Hz), -40.3 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup> $J_{Si,Si} = 61$  Hz), -18.2 (s, <u>Si</u>Me<sub>2</sub>Ph, <sup>1</sup> $J_{Si,Si} = 72$  Hz).



Figure 189: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **99** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).

#### Synthesis of Me<sub>2</sub>Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>2</sub> (89)



The pentasilane **99** (1.00 equiv., 5.91 mmol) was dissolved in *n*-pentane (20 mL) and cooled to 0 °C. Triflic acid (2.05 equiv., 12.12 mmol) was added via Hamilton syringe to the stirred solution. The reaction mixture was stirred for 10 min in the cooling bath and for additional 2 h at room temperature. The solvent and volatile components were removed under reduced pressure and the formed silyl triflate was redissolved in diethyl ether (20 mL). The solution was then added to a cooled suspension of lithium aluminium hydride (2.00 equiv., 11.82 mmol) in diethyl ether (30 mL). After complete addition, the suspension was stirred for 3 d at room temperature. Subsequently, the solvent was again removed under reduced pressure and the residue redissolved in *n*-pentane (50 mL). The suspension was filtered via a D4 frit and the solvent was again removed under residue, oligosilane **89** was isolated via Kugelrohr distillation (70 °C at 3 x 10<sup>-2</sup> mbar) in 33% yield (1.96 mmol). Small amounts of impurities were still present which could not be separated. Trials to purify the oligosilane **89** by column chromatography on silica gel using *n*-hexane as eluent indicated decomposition of the silane.

Spectroscopic data were in accordance with literature.[211]

### Analytical data of 89

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K): 0.19 (d, 12H, Si<u>Me<sub>2</sub></u>H, <sup>3</sup>*J*<sub>H,H</sub> = 4.5 Hz), 0.23 (s, 12H, Si<u>Me<sub>2</sub></u>), 0.25 (s, 6H, Si<u>Me<sub>2</sub></u>), 4.05 (sept, 2H, SiMe<sub>2</sub><u>H</u>, <sup>3</sup>*J*<sub>H,H</sub> = 4.5 Hz, <sup>1</sup>*J*<sub>H,Si</sub> = 174.3 Hz). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -43.6 (s, <u>Si</u>Me<sub>2</sub>), -41.2 (s, <u>Si</u>Me<sub>2</sub>), -36.6 (s, <u>Si</u>Me<sub>2</sub>H).




## Synthesis of MeSi(SiMe<sub>2</sub>Ph)<sub>3</sub> (96)

SiCl<sub>3</sub> 
$$3 PhSiLi (16)$$
  
THF/n-hexane, 0 °C to r.t., 16 h  
- 3 LiCl  
Si = SiMe<sub>x</sub>, x = 1 or 2  
 $3 PhSi < Si - SiPh$   
SiPh  
96

The silanide **16** was freshly prepared from PhMe<sub>2</sub>SiCl (3.00 equiv., 0.12 mol) and Li slices (9.00 equiv., 0.36 mol) in THF (120 mL). The silanide-containing red solution was then added at 0 °C to a solution of trichloromethylsilane (1.00 equiv., 0.04 mol) in *n*-hexane (150 mL) during 1.5 h. The resulting suspension was stirred for 16 h. Subsequently, the reaction was quenched by addition to HCl/H<sub>2</sub>O (150 mL). The organic phase was separated, and the aqueous phase extracted with *n*-hexane (2 x 80 mL). The combined organic layers were dried with sodium sulphate. After aqueous work-up as described for oligosilane **99**, the oligosilane **96** was obtained as a colourless solid in 41% yield (0.16 mol).

Spectroscopic data were in accordance with literature.[207]

## Analytical data of 96

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 304.9 K): 0.11 (s, 3H, Si<u>Me</u>), 0.12 (s., 18H. Si<u>Me</u>), 7.17-7.21 (m, 15H, Aryl-<u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -86.2 (s, <u>Si</u>Me, <sup>1</sup>J<sub>Si,Si</sub> = 62 Hz), -15.7 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 62 Hz).



Figure 193: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **96** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).

# Synthesis of MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>3</sub> (97)

PhSi 
$$\stackrel{Si-SiPh}{SiPh}$$
  
 $\begin{array}{c}
1) 3 HOTf / n-pentane, 0 °C to r.t., 3.5 h \\
2) 3 PhSiLi (16) / toluene, r.t., 16 h \\
1) - 3 PhH \\
2) - 3 LiOTf \\
96 \\
Si = SiMe_x, x = 1 or 2 \\
\end{array}$ 
PhSi  $\stackrel{Si-Si-Si-SiPh}{Si}$ 
PhSi  $\stackrel{Si-Si-Si-SiPh}{Si}$ 
PhSi  $\stackrel{Si-Si-Si-SiPh}{Si}$ 

The oligosilane **96** (1.00 equiv., 8.91 mmol) was dissolved in in *n*-pentane (40 mL) and cooled to 0 °C. Triflic acid (3.10 equiv., 27.62 mmol) was added via Hamilton syringe to the stirred solution. The resulting mixture was stirred for 10 min in the cooling bath and then 2 h at room temperature. A solution of silanide **16** (3.30 equiv., 29.41 mmol) in toluene (50 mL) was added during 40 min. The resulting suspension was stirred for 16 h at room temperature. After aqueous work-up consisting of quenching with HCl/H<sub>2</sub>O, extracting of the aqueous phase with *n*-pentane (2 x 30 mL), drying of the organic layers over sodium sulphate followed by filtration and removal of volatile components under reduced pressure, a slightly yellow oil was obtained. After filtration over silica using *n*-hexane as eluent, the silane **97** was obtained in 21% yield (1.87 mmol).

Spectroscopic data were in accordance with literature.[207]

Analytical data of 97

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.87 MHz, 296.0 K): 0.05 (s, 3H, Si<u>Me</u>), 0.05 (s, 18H, Si<u>Me<sub>2</sub></u>), 0.35 (s, 18H, Si<u>Me<sub>2</sub></u>), 7.28-7.30 (m, 9H, Aryl-<u>H</u>), 7.38-7.40 (m, 6H, Aryl-<u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 296.0 K): -72.1 (s, <u>Si</u>Me, <sup>1</sup> $J_{Si,Si}$  = 49 Hz), -39.9 (s, <u>Si</u>Me<sub>2</sub>, <sup>1</sup> $J_{Si,Si}$  = 49 Hz, <sup>1</sup> $J_{Si,Si}$  = 73 Hz), -17.4 (s, <u>Si</u>Me<sub>2</sub>Ph, <sup>1</sup> $J_{Si,Si}$  = 73 Hz).



Figure 195: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **97** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 296.0 K).

# Synthesis of MeSi(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>3</sub> (90)

### Synthesis of chlorine-substituted oligosilane 153

The oligosilane **97** (1.00 equiv., 2.89 mmol) was dissolved in *n*-pentane (30 mL) and cooled to 0 °C. Subsequently, triflic acid (3.05 equiv., 8.81 mmol) was added via Hamilton syringe to the stirred solution. The reaction mixture was stirred for 15 min in the cooling bath. Afterwards, the cooling bath was removed and stirring was continued for additional 3 h at room temperature. The solvent and volatile components were removed under reduced pressure. The residue was redissolved in diethyl ether (20 mL) and added to a cooled suspension of [HNEt<sub>3</sub>]Cl (6.00 equiv., 17.33 mmol) in diethyl ether (20 mL). The resulting suspension was stirred for 16 h at room temperature. An NMR sample was taken to observe the progress of the reaction. As the <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum showed the complete conversion to the chlorosilane **153**, the reaction mixture was filtered. The chlorosilane **153** was used without further purification.

## Analytical data of 153

<sup>1</sup>H NMR (THF/D<sub>2</sub>O lock, 499.87 MHz, 300.4 K): 1.09 (s, 18H, Si<u>Me</u><sub>2</sub>), 1.10 (s, 3H, Si<u>Me</u>), 1.26 (s, 18H, Si<u>Me</u><sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (THF/D<sub>2</sub>O lock, 99.31 MHz, 300.4 K): -75.4 (s, <u>Si</u>Me), -37.2 (s, <u>Si</u>Me<sub>2</sub>), 26.5 (s, <u>Si</u>Me<sub>2</sub>Cl).





## Synthesis of hydrogen-substituted oligosilane 90

$$\begin{array}{c} \text{CISi} \overbrace{Si}^{Si} \overbrace{Si}^{Si} \stackrel{SiCl}{i} \\ Si \\ \text{CISi}^{i} \\ 153 \end{array} \xrightarrow{Si} \begin{array}{c} 3 \text{ Li}[\text{AIH}_4] \\ \hline \text{Et}_2\text{O}, 0 \ ^\circ\text{C} \text{ to r.t., 16 h} \\ Si \\ Si \\ \text{Si} \\ \text{S$$

The solution containing the chlorosilane **90** (1.00 equiv., 2.61 mmol) in diethyl ether (20 mL) was added to a cooled suspension of lithium aluminium hydride (3.00 equiv., 7.83 mmol) in diethyl ether (20 mL). The suspension was subsequently stirred for 16 h at room temperature. The next day, the solvent and volatile components were removed under reduced pressure and the residue was redissolved in *n*-pentane (50 mL). The suspension was filtered via a D4 frit. After removal of the solvent, a colourless liquid was obtained. Analytical data showed the product **90** as well as small amounts of undisclosed impurities. The product was therefore obtained as a slightly impure colourless oil in 64% yield (1.58 mmol). Further purification via distillation or column chromatography was not possible. Trials to purify the oligosilane **90** by column chromatography on silica gel using *n*-hexane as eluent indicated decomposition of the silane.

## Analytical data of 90

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K): 0.22 (d, 18H, Si<u>Me</u><sub>2</sub>H, <sup>3</sup>J<sub>H,H</sub> = 4.4 Hz), 0.31 (s, 3H, Si<u>Me</u>), 0.33 (s, 18H, Si<u>Me</u><sub>2</sub>), 4.08 (sept, 3H, SiMe<sub>2</sub><u>H</u>, <sup>3</sup>J<sub>H,H</sub> = 4.4 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.1 K): -10.0 (s, Si<u>Me</u>, <sup>1</sup>J<sub>C,Si</sub> = 33 Hz), -5.6 (s. Si<u>Me</u><sub>2</sub>H, <sup>1</sup>J<sub>C,Si</sub> = 44 Hz), -3.3 (s, Si<u>Me</u><sub>2</sub>, <sup>1</sup>J<sub>C,Si</sub> = 38 Hz). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -76.9 (s, <u>Si</u>Me, <sup>1</sup>J<sub>Si,Si</sub> = 52 Hz), -40.3 (s, SiMe<sub>2</sub>, <sup>1</sup>J<sub>Si,Si</sub> = 52 Hz), -35.3 (s, SiMe<sub>2</sub>H).

HRMS (m/z) found/calculated for C<sub>13</sub>H<sub>42</sub>Si<sub>7</sub>: 394.1667/394.1666.

IR (cm<sup>-1</sup>): 2953 (m), 2894 (w), 2097 (m), 1407 (w), 1247 (m), 1025 (m), 908 (w), 874 (s), 830 (s), 800 (s), 769 (s), 732 (s), 661 (s), 636 (m).







Figure 200: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K).



Figure 201: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMBC NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K).



Figure 202: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).



Figure 203: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC spectrum of **90** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K).



Figure 205: ATR IR spectrum of 90.

## Synthesis of (Me<sub>3</sub>Si)<sub>3</sub>SiSiMe<sub>2</sub>Ph (154)



The phenyl-substituted oligosilane **154** was synthesised by a slightly modified literature protocol.<sup>[50]</sup> The silanide **12** was generated by reacting Si(SiMe<sub>3</sub>)<sub>4</sub> (**1**, 1.00 equiv., 15.02 mmol) with potassium *t*-butylate (1.05 equiv., 15.77 mmol) in THF (12 mL).<sup>[50]</sup> After complete formation of the silanide **12**, the solvent was removed, and the residue was redissolved in toluene (60 mL). The silanide-containing solution was then added at -10 °C to a stirred solution of PhMe<sub>2</sub>SiCl (1.05 equiv., 15.77 mmol) in toluene (100 mL) over a period of 2.5 h. Afterwards, the reaction mixture was stirred for 16 h while warming up to room temperature. Toluene and volatile components were removed *in vacuo*, and *n*-pentane (100 mL) was added. The resulting suspension was filtered via a D4 frit and the solvent was again removed under reduced pressure. The obtained solid was recrystallised from ethanol at -20 °C to give **154** as a colourless solid in 83% yield (12.51 mmol).

The NMR spectroscopic data were in accordance with literature.<sup>[50]</sup>

## Analytical data of 154

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.14 MHz, 295.6 K): 0.23 (s, 27H, Si<u>Me<sub>3</sub></u>). 0.53 (s, Si<u>Me<sub>2</sub></u>), 7.19-7.24 (m, 3H, Aryl-<u>H</u>), 7.55-7.58 (2H, Aryl-<u>H</u>).



Figure 206: <sup>1</sup>H NMR spectrum of **154** ( $C_6D_6$ , 300.14 MHz, 295.6 K, \* =  $C_6D_5H$ ).



#### Synthesis of 1,1'-silyl-substituted ferrocene 103

The ferrocene derivative 103 was synthesised in three steps starting from the phenylsubstituted oligosilane 154. In the first step of the reaction scheme, the silvl triflate 155 was obtained by reacting 154 (1.00 equiv., 6.03 mmol) with triflic acid (1.03 equiv., 6.21 mmol) in 10 mL *n*-pentane at 0 °C. After complete addition of the triflic acid, stirring was continued for 10 min at 0 °C. Subsequently, the cooling bath was removed, and the reaction mixture was stirred for 2 h at room temperature. The formation of the silvl triflate **155** was verified by <sup>29</sup>Si NMR spectroscopy. In a separate Schlenk tube, LiCp (1.10 equiv., 6.64 mmol) was dissolved in Et<sub>2</sub>O (50 mL) and cooled to -78° C. The triflate-containing reaction mixture in *n*-pentane was added over a period of 15 min to this ethereal solution. After complete addition, the reaction mixture was stirred for 16 h while gradually warming up to room temperature. Subsequently, the solvent and volatile components of the reaction mixture containing oligosilane 104 were removed under reduced pressure and n-pentane (20 mL) was added. The resulting suspension was filtered via a D4 frit and the salts were washed with n-pentane (20 mL). The solvent was again removed and the obtained solid was redissolved in THF (60 mL). The solution was cooled to -78 °C and n-BuLi (1.00 equiv., 6.03 mmol) was added as its solution n-hexane. The reaction mixture was stirred for 30 min at -78 °C and then for additional 30 min at room temperature. Subsequently, anhydrous FeBr<sub>2</sub> was added and stirring was continued for 16 h at room temperature. The reaction mixture was then slowly added to a mixture of *n*-pentane/2 M H<sub>2</sub>SO<sub>4</sub>/ice. The organic layer was separated, and the aqueous layer was extracted with *n*-pentane ( $3 \times 50 \text{ mL}$ ). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was again removed under reduced pressure. The silyl-substituted ferrocene compound **103** was obtained as a red solid in 81% yield (2.45 mmol).

Analytical data of 155

<sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (*n*-pentane/D<sub>2</sub>O lock, 99.31 MHz, 305.0 K): -132.3 (s, <u>Si</u>Si<sub>4</sub>), -9.5 (s, <u>Si</u>Me<sub>2</sub>), 53.2 (s, <u>Si</u>Me<sub>2</sub>OTf).



Figure 207: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of triflate **155** (*n*-pentane/D<sub>2</sub>O lock, 99.31 MHz, 305.0 K).

#### Analytical data of 103

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.2 K): 0.26 (s, 54H. Si<u>Me<sub>3</sub></u>), 0.59 (s, 12H. Si<u>Me<sub>2</sub></u>), 4.11 (s, 4H,  $\beta$ -<u>H<sub>Cp</sub></u>), 4.29 (s, 4H,  $\gamma$ -<u>H<sub>Cp</sub></u>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.0 K): 1.8 (s, Si<u>Me<sub>2</sub></u>), 3.1 (s, Si<u>Me<sub>3</sub></u>), 71.4 (s,  $\gamma$ -<u>C<sub>Cp</sub></u>), 73.6 (s,  $\beta$ -<u>C<sub>Cp</sub></u>), 74.6 (s,  $\alpha$ -<u>C<sub>Cp</sub></u>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -133.0 (s, <u>SiSi<sub>4</sub></u>), -13.7 (s, <u>SiMe<sub>2</sub></u>), -10.0 (s, <u>SiMe<sub>3</sub></u>).

HRMS (m/z) found/calculated for  $C_{32}H_{74}FeSi_{10}$ : 794.2833/794.2827.

EA (%) found/calculated for  $C_{32}H_{74}FeSi_{10}$ : C 47.84/48.31, H 9.39/9.38.

IR (cm<sup>-1</sup>): 3100 (vw), 2952 (w), 2894 (w), 2058 (w), 1241 (m), 1159 (m), 1034 (w), 818 (s), 792 (s), 755 (s), 686 (m), 622 (m).



Figure 208: <sup>1</sup>H NMR spectrum of **103** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.2 K,  $* = C_6D_5H$ ).







Figure 211: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of **103** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 212: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **103** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).



Figure 213: Excerpt of the  ${}^{1}$ H, ${}^{29}$ Si HMBC NMR spectrum of **103** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 214: ATR IR spectrum of 103,



#### Synthesis of 1,1'-silyl-substituted ferrocene derivative 101

18-crown-6 (18cr6) = 1,4,7,10,13,16-hexaoxacyclooctadecane

The ferrocene compound **103** (1.00 equiv., 2.39 mmol) and 18-crown-6 ether (2.05 equiv., 4.90 mmol) were put in a Schlenk tube and evacuated for 30 min. The Schlenk tube was flushed with nitrogen and benzene (40 mL) was added. Subsequently, potassium *t*-butylate (2.10 equiv., 5.01 mmol) was added to the stirred solution at room temperature. Stirring was continued for 16 h and an NMR sample was taken to verify the formation of the dianion **105** by <sup>29</sup>{<sup>1</sup>H} INEPT NMR spectroscopy. The dianion-containing solution was then added via syringe to a mixture of *n*-pentane/2 M H<sub>2</sub>SO<sub>4</sub>/ice at 0 °C. After 5 min stirring at 0 °C, stirring was continued for 20 min at room temperature. The organic layer was separated, and the aqueous layer was extracted with Et<sub>2</sub>O (3 x 40 mL). The combined organic phases were then dried over Na<sub>2</sub>SO<sub>4</sub> and the solvents and volatile components were removed under reduced pressure. To further purify the raw product, it was filtered over silica gel using *n*-pentane. The ferrocene derivative **101** was obtained as a red solid in 76% yield (1.81 mmol). Crystallisation from degassed *i*-propanol at -20 °C gave crystals that were suitable for XRD analysis.

#### Analytical data of 105

<sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (benzene/D<sub>2</sub>O lock, 99.31 MHz, 305.0 K): -185.5 (s, Si<sub>3</sub>SiK), -5.7 (s, SiMe<sub>2</sub>), -4.8 (s, SiMe<sub>3</sub>).



 $# = Me_3SiOt-Bu$ ).

# Analytical data of **101**

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K): 0.22 (s, 36H, Si<u>Me<sub>3</sub></u>), 0.55 (s, 12H, Si<u>Me<sub>2</sub></u>), 2.60 (s, 2H, Si-<u>H</u>, <sup>1</sup>J<sub>H,Si</sub> = 154.4 MHz), 4.07 (pseudo-t,4H,  $\beta$ -<u>H</u><sub>Cp</sub>), 4.29 (pseudo-t,4H,  $\gamma$ -<u>H</u><sub>Cp</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.0 K): 1.1 (s, Si<u>Me<sub>2</sub></u>), 2.1 (s, Si<u>Me<sub>3</sub></u>), 71.5 (s,  $\gamma$ -<u>C</u><sub>Cp</sub>), 73.4 (s,  $\beta$ -<u>C</u><sub>Cp</sub>), 73.6 (s,  $\alpha$ -<u>C</u><sub>Cp</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -114.2 (s, <u>Si</u>Si<sub>4</sub>), -15.3 (s, <u>Si</u>Me<sub>2</sub>), -11.9 (s, <u>Si</u>Me<sub>3</sub>).

HRMS (m/z) found/calculated for C<sub>26</sub>H<sub>58</sub>FeSi<sub>8</sub>: 650.1652/650.2042.

EA (%) found/calculated for  $C_{26}H_{58}FeSi_8$ : C 49.24/47.95, H 9.12/8.98.

IR (cm<sup>-1</sup>): 3100 (vw), 2953 (m), 2893 (w), 2056 (m), 1420 (w), 1423 (s), 1160 (m), 1034 (m), 831 (s), 795 (s), 755 (s), 689 (s), 607 (s).



Figure 217:  ${}^{13}C{}^{1}H$  NMR spectrum of **101** (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.0 K, \* = C<sub>6</sub>D<sub>6</sub>).



Figure 218: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **101** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K)



Figure 219: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMBC NMR spectrum of **101** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 220: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **101** (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K).



Figure 221: Excerpt of the  ${}^{1}$ H, ${}^{29}$ Si HMBC NMR spectrum of **101** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 222: ATR IR spectrum of 101.

# 5.3. Preparation of Silyl Cations

## General Procedure for the Synthesis of Silyl Cations

All hydride transfer reactions of hydrogen-substituted silanes performed as NMR experiments following the same protocol. The specified amount of trityl salt was directly weighted into an NMR tube which was then evacuated for 30 minutes and gently flushed with nitrogen. The trityl salt was dissolved in the NMR tube in the respective solvent and the resulting solution was cooled to the temperature needed for the NMR experiment using a cooling bath. Subsequently, the hydrogen-substituted silane was slowly added as solution in the used solvent via syringe. The addition proceeded slowly so that the silane-containing solution cooled down while it went down on the glass walls of the cooled NMR tube. Hence, a biphasic mixture is obtained. The bottom layer containing the trityl salt and an upper layer containing the hydrogen-substituted silane. The NMR tube was sealed, removed from the cooling bath, and thoroughly mixed. The mixing proceeded as fast as possible so that a warming-up of the reaction mixture was minimised. Directly after mixing, the NMR tube was put back into the cooling bath, transferred into the precooled spectrometer and directly measured. In cases were 3-fluorotoluene was used as non-deuterated solvent, a glass capillary filled with acetone-d<sub>6</sub> was also added to the NMR tube prior to mixing. The handling of the NMR tubes was performed in specially designed glassware that allowed for the evacuation of the NMR tube and the subsequent handling under nitrogen. To guarantee a good thermal conduction between cooling bath and the solution in the NMR tube, the room between the glassware and the inlying NMR tube was filled with nhexane.

## Synthesis of 106[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

$$H_{Si}^{Si}_{Si}^{Si}_{Si}^{H} \xrightarrow{[Ph_{3}C][B(C_{6}F_{5})_{4}]}_{C_{6}D_{5}Cl, -40 \ ^{\circ}C} \xrightarrow{Si}_{Si}^{Si}_{H}^{Si} [B(C_{6}F_{5})_{4}]}_{H}^{F}$$

$$89 \qquad 5i = SiMe_{2}$$

$$Si_{Si}^{Si}_{H}^{Si} = SiMe_{2}$$

٦.

The general procedure was applied for the synthesis of the monocation **106** in chlorobenzene-d<sub>5</sub>. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.06 mmol), was dissolved in chlorobenzene-d<sub>5</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, the solution of silane **89** (1.00 equiv., 0.06 mol) in chlorobenzene-d<sub>5</sub> (0.3 mL) was slowly added at -40 °C via syringe.

Analytical data of 106[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K): 0.10 (s, 6H, Si<u>Me</u><sub>2</sub>), 0.13 (s, 12H, Si<u>Me</u><sub>2</sub>), 0.39 (d, 12H,  ${}^{3}J_{H,Si} = 1.9$  Hz, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 160.38 MHz, 233.1 K): -16.0 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 470.28 MHz, 233.1 K): -165.40 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -161.42 (m, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -131.89 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 125.71 MHz, 233.0 K): -7.7 (s, Si<u>Me</u><sub>2</sub>), -7.1 (s, Si<u>Me</u><sub>2</sub>), -2.5 (s, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), 124.6 (bs, C<sub>*ipso*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 136.0-136.0 (m, Cortho and Cmeta, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 148.8 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>*para*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, 233.0 K): -38.1 (s, <sup>1</sup>J<sub>Si,Si</sub> = 64 Hz, <u>Si</u>Me<sub>2</sub>), -43.3 (s, <sup>1</sup>J<sub>Si,Si</sub> = 58 Hz, <sup>1</sup>J<sub>Si,Si</sub> = 64 Hz, <u>Si</u>Me<sub>2</sub>), 87.1 (s, <sup>1</sup>J<sub>Si,Si</sub> = 58 Hz, <u>Si</u>-H-<u>Si</u>). <sup>29</sup>Si INEPT NMR (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, 233.0 K): -38.1 (m, <u>Si</u>Me<sub>2</sub>), 87.1 (dm, <sup>1</sup>J<sub>Si,H</sub> = 53 Hz, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>).



Figure 223: <sup>1</sup>H NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K, \* = C<sub>6</sub>HD<sub>4</sub>Cl, # = Ph<sub>3</sub>CH).



Figure 224: Excerpt of the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K, spectrum processed using sine bell 0.00° in F1 and sine bell 28.00° in F2 dimension).



(C<sub>6</sub>D<sub>5</sub>Cl, 125.71 MHz, 233.0 K, \* = C<sub>6</sub>D<sub>5</sub>Cl, # = Ph<sub>3</sub>CH, \$ = [B(<u>C</u><sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>)



Figure 226: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMQC NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K).



Figure 227: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K).



Figure 228:  ${}^{29}Si{}^{1}H$  NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]









Figure 231: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (C<sub>6</sub>D<sub>5</sub>Cl, 499.87 MHz, 233.0 K,).



Figure 233: Excerpt of the <sup>13</sup>C NMR spectrum of **106**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] showing the NMR signals of the counter anion (C<sub>6</sub>D<sub>5</sub>Cl, 125.71 MHz, 233.0 K, \* = C<sub>6</sub>D<sub>5</sub>Cl, # = Ph<sub>3</sub>CH)



## Synthesis of 110[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



The general procedure was applied for the synthesis of the silyl cation in dichloromethane- $d_2$ . The trityl salt, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1.00 equiv., 0.11 mmol), was dissolved in dichloromethane- $d_2$  (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **89** (1.00 equiv., 0.11 mol) in dichloromethane- $d_2$  (0.3 mL) was slowly added at -80 °C via syringe. The NMR spectra showed a mixture containing hydrogen-bridged silyl cation **106** and a second set of signals suggesting the formation of chlorine-bridged silyl cation **110**. The NMR sample was taken out of the spectrometer, warmed-up and mixed again. The recorded spectra showed signals in accordance with the quantitative formation of chlorine-bridged silyl cation **110**. Analytical data of  $110[B(C_6F_5)_4]$ 

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 192.9 K): 0.32 (s, 6H, Si<u>Me<sub>2</sub></u>), 0.36 (s, 12H, Si<u>Me<sub>2</sub></u>), 0.89 (s, 12H, <u>Me<sub>2</sub>Si-Cl-SiMe<sub>2</sub></u>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 193.0 K): -7.7 (s, Si<u>Me<sub>2</sub></u>), -7.5 (s, Si<u>Me<sub>2</sub></u>), 3.1 (s, <u>Me<sub>2</sub>Si-Cl-SiMe<sub>2</sub></u>), 122.8 (bs, C<sub>*ipso*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 134.7-138.5 (m, C<sub>ortho</sub> and C<sub>meta</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 147.2 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>*para*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>11</sup>B{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 160.38, 193.1 K): -17.1 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 470.30, 193.1 K): -166.14 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -162.20 (m, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -133.35 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.3 K): -44.2 (s, <u>Si</u>Me<sub>2</sub>), -40.2 (s, <u>Si</u>Me<sub>2</sub>), 94.8 (s, Me<sub>2</sub><u>Si</u>-Cl-<u>Si</u>Me<sub>2</sub>). <sup>29</sup>Si INEPT NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.3 K): -44.2 (m, <u>Si</u>Me<sub>2</sub>), -40.2 (m, <u>Si</u>Me<sub>2</sub>), 94.8 (m, Me<sub>2</sub><u>Si</u>-Cl-<u>Si</u>Me<sub>2</sub>).
















(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.3 K, # = unidentified side-products).



Figure 241:  ${}^{11}B{}^{1}H{}$  spectrum after formation of **110**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 160.38, 193.1 K).





### Synthesis of 111[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



The general procedure was applied for the synthesis of the monocation **111** in dichloromethane-d<sub>2</sub>. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.09 mmol), was dissolved in dichloromethane-d<sub>2</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **90** (1.00 equiv., 0.09 mol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added at -80 °C via syringe.

Analytical data of 111[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K): 0.15 (s, 6H, Si<u>Me</u><sub>2</sub>H), 0.21 (s, 3H, Si<u>Me</u>) 0.27 (s, 6H, Si<u>Me</u><sub>2</sub>), 0.37 (s, 6H, ring-Si<u>Me</u><sub>2</sub>), 0.43 (s, 6H, ring-Si<u>Me</u><sub>2</sub>), 0.74 (s, Me<sub>2</sub>Si-<u>H</u>-SiMe<sub>2</sub>), 0.80 (s, 12H, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), 3.71 (s, 1H, SiMe<sub>2</sub><u>H</u>) <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 183.1 K): -17.1 (s, [<u>B</u>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 470.28 MHz, 183.1 K): -166.02 (bs, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -162.06 (bs, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -133.34 (bs, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.0 K): -11.8 (s, Si<u>Me</u>), -7.0 (s, ring-Si<u>Me</u><sub>2</sub>), -6.8 (s, Si<u>Me</u><sub>2</sub>H), -5.3 (s, ring-Si<u>Me</u><sub>2</sub>), -4.9 (s, Si<u>Me</u><sub>2</sub>), -1.9 (s, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), -1.4 (s, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), 122.4 (bs, C<sub>*ipso*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 134.4-138.2 (m, C<sub>ortho</sub> and C<sub>*meta*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 146.9 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>*para*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -34.8 (s, <u>Si</u>Me<sub>2</sub>H), 90.3 (s, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>), -37.8 (s, ring-<u>Si</u>Me<sub>2</sub>), -37.2 (s, <u>Si</u>Me<sub>2</sub>), -34.8 (s, <u>Si</u>Me<sub>2</sub>H), 90.3 (s, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>), -34.8 (d, <sup>1</sup>J<sub>Si,H</sub> = 176 Hz, <u>Si</u>Me<sub>2</sub>H), 90.3 (d, J<sub>Si,H</sub> = 42 Hz, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>).



Figure 244: <sup>1</sup>H NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K, \* CDHCl<sub>2</sub>,  $# = Ph_3CH$ ).







Figure 247: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K).



Figure 248: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMBC NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K).



side-products).



Figure 251: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K, optimised for J = 45 Hz).



Figure 252: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K).



Figure 253:  ${}^{11}B{}^{1}H$  NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 183.1 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.0 K, # = Ph<sub>3</sub>CH).



Figure 255: <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of **111**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 470.28 MHz, 183.1 K).

## Synthesis of 113[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]



The general procedure was applied for the synthesis of the monocation **113** in dichloromethane-d<sub>2</sub>. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.12 mmol), was dissolved in dichloromethane-d<sub>2</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of oligosilane **91** (1.00 equiv., 0.12 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added at -90 °C via syringe.

#### Analytical data of $113[B(C_6F_5)_4]$ at -(92-93) °C

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 180.0 K): 0.17, 0.32, 0.40, 0.46, 0.80, 3.72 (no assignment possible). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 181.0 K): -6.7, -3.0, -2.2, -1.6, 0.0 (no assignment possible), 122.4 (bs,  $C_{ipso}$ , [B( $\underline{C}_{6}F_{5}$ )<sub>4</sub>]<sup>-</sup>), 134.4-138.2 (m,  $C_{ortho}$  and  $C_{meta}$ , [B( $\underline{C}_{6}F_{5}$ )<sub>4</sub>]<sup>-</sup>), 146.9 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz,  $C_{para}$ , [B( $\underline{C}_{6}F_{5}$ )<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 180.0 K): -124.8 (s,  $\underline{Si}Si_4$ ), -37.2 (bs,  $\underline{Si}Me_2$ ), -35.1 (bs,  $\underline{Si}Me_2$ ), -34.2 (d, <sup>1</sup>J<sub>Si,H</sub> = 170-180 Hz,  $\underline{Si}Me_2$ H), 89.0 (d, <sup>1</sup>J<sub>Si,H</sub> = 31 Hz, Me<sub>2</sub>Si-H-SiMe<sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 181.1 K): -17.1 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 470.27 MHz, 181.0 K): -166.07 (s, [B(C<sub>6</sub>E<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -162.08 (s, [B(C<sub>6</sub>E<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -133.35 (s, [B(C<sub>6</sub>E<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 180.0 K): -124.8 (s, SiSi<sub>4</sub>), -37.1 (bs, <u>Si</u>Me<sub>2</sub>), -35.0 (bs, <u>Si</u>Me<sub>2</sub>), -34.3 (d, <sup>1</sup>J<sub>Si,H</sub> = 170 Hz, <u>Si</u>Me<sub>2</sub>H), 89.1 (d, <sup>1</sup>J<sub>Si,H</sub> = 31 Hz, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>).

Analytical data of 113[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -90 °C

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K): 0.21, 0.36, 0.47, 0.81 (no assignment possible). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.0 K): -6.7, -3.0, -2.3, -1.6, 0.1 (no assignment possible), 122.4 (bs, C<sub>ipso</sub>, [B(<u>C</u><sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 134.4-138.2 (m, C<sub>ortho</sub> and C<sub>meta</sub>, [B(<u>C</u><sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 146.9 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>para</sub>, [B(<u>C</u><sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): -124.8 (s, <u>Si</u>Si<sub>4</sub>), -37.1 (s, <u>Si</u>Me<sub>2</sub>), -35.0 (s, <u>Si</u>Me<sub>2</sub>), -34.3 (s, <u>Si</u>Me<sub>2</sub>H), 89.1 (s, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): -124.8 (s, SiSi<sub>4</sub>), -37.1 (bs, <u>Si</u>Me<sub>2</sub>), -35.0 (bs, <u>Si</u>Me<sub>2</sub>), -34.3 (d, <sup>1</sup>J<sub>Si,H</sub> = 170-180 Hz, <u>Si</u>Me<sub>2</sub>H), 89.1 (bs, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>). Analytical data of 113[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -75 °C

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 198.0 K): 0.41 (no assignment possible). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 198.0 K): -2.4 (no assignment possible). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 198.0 K): -124.8 (s, <u>Si</u>Si<sub>4</sub>). -36.6 (s, <u>Si</u>Me<sub>2</sub>), 89.1 (bs, Me<sub>2</sub>Si-H-SiMe<sub>2</sub>).

Analytical data of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -(30-33) °C:

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 243.0 K): 0.47, 0.56, 2.87 (no assignment possible). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 243.0 K): -3.8, -1.8 (no assignment possible), 123.3 (bs, C<sub>*ipso*</sub>,  $[B(\underline{C}_{6}F_{5})_{4}]^{-}$ ), 135.0-139.1 (m, C<sub>ortho</sub> and C<sub>meta</sub>,  $[B(\underline{C}_{6}F_{5})_{4}]^{-}$ ), 147.8 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>*para*</sub>,  $[B(\underline{C}_{6}F_{5})_{4}]^{-}$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 240.0 K): -124.8 (s, <u>Si</u>Si<sub>4</sub>). -37.6 (s, <u>Si</u>Me<sub>2</sub>).



Figure 256: <sup>1</sup>H NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).



Figure 257: Excerpt of the  ${}^{1}H,{}^{1}H$  COSY NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.0 K, \* = CD<sub>2</sub>Cl<sub>2</sub>, # = Ph<sub>3</sub>CH, \$ = [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>).



 $(CD_2Cl_2, 99.31 \text{ MHz}, 183.0 \text{ K} \# = \text{hydrolysis products } 114[B(C_6F_5)_4] \text{ and } 115[B(C_6F_5)_4]).$ 



Figure 262:  ${}^{13}C{}^{1}H$  NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 181.0 K, \* = CD<sub>2</sub>Cl<sub>2</sub>, # = Ph<sub>3</sub>CH).







Figure 265: <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 179.9 K, optimised for J = 50 Hz). No correlation of the downfield-shifted signal of the [Me<sub>2</sub>Si-H-SiMe<sub>2</sub>] unit is detectable.







Figure 267: Excerpt of the <sup>13</sup>C NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] showing the NMR signals of the counter anion (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 181.0 K,  $\# = Ph_3CH$ ).



Figure 268:  ${}^{19}F{}^{1}H$  NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 470.27 MHz, 181.0 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 198.0 K, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH, \$ = [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>).



Figure 271: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 198.0 K)



Figure 272: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 198.0 K, # = hydrolysis product **115**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).



 $\label{eq:constraint} \begin{array}{l} \mbox{Figure 274: $^{13}C\{^{1}H\}$ NMR spectrum of $$113[B(C_6F_5)_4]$ (CD_2Cl_2, 125.71 MHz, 243.0 K, $^* = CDHCl_2, $$# = Ph_3CH, $$ = [B(C_6F_5)_4]^{-}$. \end{array}$ 







Figure 278: <sup>1</sup>H, <sup>29</sup>Si HMBC NMR spectrum of the NMR sample containing **113**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at r.t. (CD<sub>2</sub>Cl<sub>2</sub>, 499,87 MHz, 305.0 K)





## Synthesis of the dication $118[B(C_6F_5)_4]_2$

# 

One-step synthesis procedure

The general procedure was applied for the synthesis of the dication **118** in dichloromethane-d<sub>2</sub>. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (2.00 equiv., 88 µmol), was dissolved in dichloromethane-d<sub>2</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **91** (1.00 equiv., 44 µmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added at -80 °C via syringe.

## Analytical data of 118[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K): 0.55 (s, 24H, Si<u>Me<sub>2</sub></u>), 0.81 (m, Me<sub>2</sub>Si-<u>H</u>-SiMe<sub>2</sub>), 0.89 (s, 24H, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub></u>). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 193.0 K): -17.1 (s, [<u>B</u>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 470.27 MHz, 193.0 K): -166.12 (s, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -162.24 (s, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -133.27 (s, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 193.0 K): -3.1 (s, Si<u>Me<sub>2</sub></u>), -2.2 (s, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>), 122.5 (bs, C<sub>*ipso*</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 134.5-138.3 (m, C<sub>ortho</sub> and C<sub>meta</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), 147.1 (d, <sup>1</sup>J<sub>C,F</sub> = 240.8 Hz, C<sub>para</sub>, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.0 K): -121.4 (s, <u>Si</u>Si<sub>4</sub>), -34.4 (s, <u>Si</u>Me<sub>2</sub>), 88.1 (s, Me<sub>2</sub><u>Si-H-Si</u>Me<sub>2</sub>). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.0 K): -121.4 (s, <u>Si</u>Si<sub>4</sub>), -34.4 (m, <u>Si</u>Me<sub>2</sub>), 88.1 (dm, <sup>1</sup>J<sub>Si,H</sub> = 41 Hz, Me<sub>2</sub><u>Si-H-Si</u>Me<sub>2</sub>).</u>



Figure 282: <sup>1</sup>H, <sup>1</sup>H COSY NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K).



Figure 284: Excerpt of the <sup>1</sup>H, <sup>13</sup>C HMQC NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K).



Figure 285: Excerpt of the <sup>1</sup>H,<sup>13</sup>C HMBC NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K, \* = *n*-hexane, # = unidentified side-product).



 $(CD_2CI_2, 99.31 \text{ MHz}, 193.0 \text{ K}, \# = hydrolysis product 122[B(C_6F_5)_4]_2).$ 



122[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>).



Figure 288: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K, optimised for J = 50 Hz, spectrum processed using sine square 0.00° and sine square II with -30% and 50% in F1 and sine square 4.00° and sine square II with -5% and 50% in F2).









Figure 291: Excerpt of the <sup>13</sup>C{<sup>1</sup>H] NMR spectrum of **118**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> showing the NMR signals of the counter anion (CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 193.0 K,  $\# = Ph_3CH$ ).



#### Two-step synthesis procedure



For the first step of the two-step reaction scheme, the monocation **113** was obtained as described above for the one-step synthesis of **113**. A solution of silane **91** (1.00 equiv., 0.09 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added via syringe at -80 °C to the cooled NMR tube containing a solution of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.09 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL). After mixing, the reaction mixture was analysed by NMR spectroscopy. After verification that the monocation **113** was formed, the sample was again removed from the NMR spectrometer and a second equivalent of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.09 mmol) dissolved in dichloromethane-d<sub>2</sub> (0.2 mL) was added. The resulting reaction mixture was mixed and returned to the NMR spectrometer. The formation of the dication **118** was verified by NMR spectroscopy.

See above for NMR spectroscopic data of  $113[B(C_6F_5)_4]$  and  $118[B(C_6F_5)_4]_2$ .



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 190.0 K, # = hydrolysis product 115)



 $(CD_2CI_2, 125.71 \text{ MHz}, 190.0 \text{ K}, * = CDHCI_2, # = Ph_3CH, \$ = [B(C_6F_5)_4]^{-}).$ 



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.0 K, # = hydrolysis products).



Figure 299: <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum after addition of a second equivalent [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K, optimised for J= 45 Hz).



(CD<sub>2</sub>Cl<sub>2</sub>, 160.38 MHz, 193.0 K).




(CD<sub>2</sub>Cl<sub>2</sub>, 470.27 MHz, 193.0 K).

# Hydride transfer reactions of Si(SiMe<sub>2</sub>H)<sub>4</sub> (100) with $[Ph_3C][B(C_6F_5)_4]$

Hydride transfer reactions between Si(SiMe<sub>2</sub>H)<sub>4</sub> (**100**) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were performed under different conditions.

HSi, SiH HSI, Solvent, T - n Ph<sub>3</sub>CH n = 0.5, 1 or 2 Si = SiMe<sub>2</sub> Solvents = CD<sub>2</sub>Cl<sub>2</sub> (T = -90 °C) C<sub>6</sub>D<sub>5</sub>Cl (T = -40 °C) 3-F-toluene (T = -80 °C)

In course of the hydride transfer reaction, variable stoichiometries for the ratio  $Si(SiMe_2H)_4$ :  $[Ph_3C][B(C_6F_5)_4] = 1 : 0.5, 1 : 1 \text{ or } 1 : 2 \text{ were tried as well as different solvents}$  and temperatures: Dichloromethane-d<sub>2</sub> at -90 °C, chlorobenzene-d<sub>5</sub> at -40 °C, and 3-fluorotoluene at -80 °C.

 $127[B(C_6F_5)_4]$  in 3-fluorotoluene at -80 °C (Silane 100 :  $[Ph_3C][B(C_6F_5)_4] = 1 : 1)$ 



The general procedure was applied for the hydride transfer reaction between equimolar amounts of pentasilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  in 3-fluorotoluene. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.08 mmol), was dissolved in 3-fluorotoluene (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **100** (1.00 equiv., 0.08 mmol) in 3-fluorotoluene (0.3 mL) was slowly added at -80 °C via syringe. The NMR tube was additionally equipped with a capillary filled with acetone-d<sub>6</sub>. The obtained NMR spectra showed the clean formation of one product. Analysis of the spectroscopic data revealed the formation

of the intermolecular stabilised silyl cation **127** instead of the intramolecularly stabilised silyl cation **126**.

Analytical data of 127[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, 192.9 K): 0.32 (s, 36H, Si<u>Me<sub>2</sub></u>H), 0.79 (s, 12H, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>), 4.22 (s, 6H, SiMe<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 125.71 MHz, 193.0 K): -2.9 (s, Si<u>Me<sub>2</sub></u>H), 1.4 (s, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>), <sup>13</sup>C signals of [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> not assigned. <sup>11</sup>B{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 160.38 MHz, 193.1 K): -17.5 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 470.28 MHz, 193.1 K): -167.02 (bs, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -163.02 (bs, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -133.35 (bs, [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, 193.0 K): -133.2 (s, <u>Si</u>Si<sub>4</sub>), -34.0 (s, <u>Si</u>Me<sub>2</sub>H) 93.1 (s, Me<sub>2</sub><u>Si-H-Si</u>Me<sub>2</sub>). <sup>29</sup>Si NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 99.31 MHz, 193.0 K): -133.2 (s, <u>Si</u>Si<sub>4</sub>), -34.0 (d, <sup>1</sup>J<sub>Si,H</sub> = 185 Hz, <u>Si</u>Me<sub>2</sub>H) 93.1 (d, <sup>1</sup>J<sub>Si,H</sub> = 49 Hz, Me<sub>2</sub><u>Si-H-Si</u>Me<sub>2</sub>).</u></u>



Figure 303: <sup>1</sup>H NMR spectrum of  $127[B(C_6F_5)_4]$ (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, 192.9 K, \* = 3-fluorotoluene).



Figure 304: Excerpt of the <sup>1</sup>H,<sup>1</sup>H COSY NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, 192.9 K, spectrum processed using sine square 0.00° and sine square II with 0.0% and 50.0% in F1 and sine square 3.00° and sine square II with 0.0% and 50.0% in F2, \* = 3-fluorotoluene).



Figure 305:  ${}^{13}C{}^{1}H$  NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

(3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 125.71 MHz, 193.0 K, # = 3-fluorotoluene and (CD<sub>3</sub>)<sub>2</sub>CO, \* = Ph<sub>3</sub>CH).



(3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, 192.9 K).







Figure 310: Excerpt of the <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO lock, 499.87 MHz, 193.0 K, optimised for J = 180 Hz, spectrum processed using sine square 0.00° in F1 and sine square 0.00° and sine square II with 0.0% and 50.0% in F2).









127[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in 3-fluorotoluene at -80 °C (Silane 100 : [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] = 1 : 2)

**-** .

The reaction was performed analogously to the procedure described above for a 1 : 1 stoichiometry of pentasilane **100** and trityl salt. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (2.00 equiv., 0.08 mmol), was dissolved in 3-fluorotoluene (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **100** (1.00 equiv., 0.04 mmol) in 3-fluorotoluene (0.3 mL) was slowly added at -80 °C via syringe. The NMR tube was additionally equipped with a capillary filled with the NMR solvent acetone-d<sub>6</sub>. The NMR spectra indicated the formation of the intermolecular bridged silyl cation **127**.

Analytical data of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 499.87 MHz, 193.0 K): 0.32 (s, Si<u>Me</u><sub>2</sub>H), 0.79 (s, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), 4.23 (s, SiMe<sub>2</sub><u>H</u>). <sup>29</sup>Si{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 99.31 MHz, 193.0 K): -133.3 (s, <u>Si</u>Si<sub>4</sub>), -33.9 (s, <u>Si</u>Me<sub>2</sub>H) 93.1 (s, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>).





127[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in 3-fluorotoluene at -80 °C (Silane : [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] = 1 : 0.5)

$$HSi SiH = \frac{0.5 [Ph_3C][B(C_6F_5)_4]}{3 - Fluorotoluene/(CD_3)_2CO, -80 °C} \xrightarrow{HSi} \frac{SiH}{HSi Si - Si - Si - Si - Si - SiH} + \frac{Si}{HSi} \frac{SiH}{SiH} + \frac{Si}{SiH} \frac{SiH}{SiH} + \frac{Si}{SiH} \frac{SiH}{SiH} + \frac{Si}{SiH} \frac{SiH}{Si} \frac{SiH}{SiH} + \frac{Si}{SiH} \frac{SiH}{Si} \frac{SiH}{Si} + \frac{Si}{SiH} \frac{SiH}{Si} \frac{SiH}{Si} + \frac{Si}{SiH} \frac{SiH}{Si} \frac{SiH}{Si} + \frac{Si}{Si} \frac{SiH}{Si} \frac{SiH}{Si} + \frac{Si}{Si} \frac{SiH}{Si} \frac{SiH}{S$$

The general procedure was applied for the hydride transfer reaction between equimolar amounts of pentasilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  in 3-fluorotoluene in a 1 : 0.5 stoichiometry. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.07 mmol), was dissolved in 3-fluorotoluene (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **100** (1.00 equiv., 0.14 mmol) in 3-fluorotoluene (0.3 mL) was slowly added at -80 °C via syringe. The NMR tube was additionally equipped with a capillary filled with the NMR solvent acetone-d<sub>6</sub>. The recorded NMR spectra showed the formation of the intermolecular bridged silyl cation **127** which was also obtained after the reaction of equimolar amounts silane and trityl salt.

Analytical data of **127**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 499.87 MHz, 193.0 K): 0.32 (bs, Si<u>Me</u><sub>2</sub>H), -0.76 (bs, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>), 4.23 (bs, SiMe<sub>2</sub><u>H</u>). <sup>13</sup>C{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 125.71 MHz, 193.0 K): -2.9 (s, Si<u>Me</u><sub>2</sub>H), 1.4 (s, <u>Me</u><sub>2</sub>Si-H-Si<u>Me</u><sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 99.31 MHz, 193.0 K): -133.3 (bs, <u>Si</u>Si<sub>4</sub>), -34.0 (bs, <u>Si</u>Me<sub>2</sub>H) 93.1 (bs, Me<sub>2</sub><u>Si</u>-H-<u>Si</u>Me<sub>2</sub>).







Figure 318: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **127** (3-fluorotoluene/(CD<sub>3</sub>)<sub>2</sub>CO, 99.31 MHz, 193.0 K).

 $127[B(C_6F_5)_4]$  in dichloromethane-d<sub>2</sub> at -80 °C (Silane 100 : [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] = 1 : 0.5)



The general procedure was applied for the hydride transfer reaction between pentasilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  in dichloromethane-d<sub>2</sub>. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.07 mmol), was dissolved in dichloromethane-d<sub>2</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **100** (1.00 equiv., 0.07 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added at -90 °C via syringe. The spectroscopic data showed the formation of one main product which was correlated to the intermolecular stabilised silyl cation **127** (compare reactions in 3-fluorotoluene).

#### Analytical data of 127[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K): No signals assigned. <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): -133.0 (bs, <u>Si</u>Si<sub>4</sub>), -32.6 (s, <u>Si</u>Me<sub>2</sub>H), -93.9 (bs, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): -133.0 (s, <u>Si</u>Si<sub>4</sub>), -32.6 (s, <u>Si</u>Me<sub>2</sub>H), 93.9 (bs, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 182.9 K): -132.7 (bs, <u>Si</u>Si<sub>4</sub>), -32.6 (d, <sup>1</sup>*J*<sub>Si,H</sub> = 185 MHz, <u>Si</u>Me<sub>2</sub>H), -94.0 (bm, <u>Me<sub>2</sub>Si-H-SiMe<sub>2</sub>).</u></u></u>



Figure 319: <sup>1</sup>H NMR spectrum after hydride abstraction of **100** with 0.5 equiv. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in CDC<sub>2</sub>Cl<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K, \* = CDHCl<sub>2</sub>, Ph<sub>3</sub>CH).



Figure 320: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum after hydride abstraction of **100** with 0.5 equiv. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in CDC<sub>2</sub>Cl<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K).









The general procedure was applied for the hydride transfer reaction between pentasilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  in dichloromethane. The trityl salt,  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.13 mmol), was dissolved in dichloromethane-d<sub>2</sub> (0.3 mL) in an NMR tube and cooled down. Subsequently, a solution of silane **100** (1.00 equiv., 0.13 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was slowly added at -90 °C via syringe. Instead of the formation of the expected silyl cation **126**, the NMR spectra showed a multitude of signals from which no structure could be elucidated. After renewed mixing of the NMR sample accompanied by a slight warming of the sample resulted in the formation of the chlorosilane Si(SiMe<sub>2</sub>Cl)<sub>4</sub> (**93**). Next to left-over trityl cation, the decomposition of the Ph<sub>3</sub>CH formed during hydride transfer reaction was visible in the NMR data. The analytical data (NMR spectra and GCMS) fitted to the chlorosilane **93**.<sup>[244]</sup>

# Analytical data of 93

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.4 K): 0.69 (s, Si<u>Me</u><sub>2</sub>Cl). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.14 MHz, 293.6 K): 0.79 (s, Si<u>Me</u><sub>2</sub>Cl). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.6 K): 5.3 (s, Si<u>Me</u><sub>2</sub>Cl). <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): 28.7 (s, <u>Si</u>Me<sub>2</sub>Cl), -117.2 (s, <u>Si</u>Si<sub>4</sub>). <sup>29</sup>Si INEPT NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K): 28.7 (m, <u>Si</u>Me<sub>2</sub>Cl), -117.2 (bs, <u>Si</u>Si<sub>4</sub>).

Mass required for  $C_8H_{24}Cl_4Si_5$  (**93**): 399.95. Mass found: 387.00 (7) [M<sup>+</sup> -CH<sub>3</sub>], 367.00 (10) [M<sup>+</sup> -C<sub>2</sub>H<sub>6</sub>], 309.00 (35) [M<sup>+</sup> -C<sub>2</sub>H<sub>6</sub>ClSi], 272.1 (100) [M<sup>+</sup> -C<sub>2</sub>H<sub>6</sub>Cl<sub>2</sub>Si], 174.1 (56) [M<sup>+</sup> -C<sub>2</sub>H<sub>6</sub>Cl<sub>3</sub>Si], 93.00 (39) [C<sub>2</sub>H<sub>6</sub>ClSi<sup>+</sup>].



Figure 323:  $^{29}Si\{^{1}H\}$  NMR spectrum after hydride abstraction of 100 before renewed mixing (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 183.6 K, \* = CD<sub>2</sub>Cl<sub>2</sub>)



(CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.0 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K).



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.0 K).







Figure 332: GCMS of the reaction mixture and MS spectrum of the main component 93.

#### Formation of 93 in dichloromethane-d<sub>2</sub> at -90 °C (Silane 100 : $[Ph_3C][B(C_6F_5)_4] = 1 : 2)$

The same reaction was attempted with a ratio **100** :  $[Ph_3C][B(C_6F_5)_4] = 1 : 2$ . A solution of the pentasilane **100** (1.00 equiv., 0.06 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) was added to an NMR tube containing the solution of  $[Ph_3C][B(C_6F_5)_4]$  (2.00 equiv., 0.12 mmol) in dichloromethane-d<sub>2</sub> (0.3 mL) at -80 °C. The spectroscopic data did not show significant differences compared to the reaction using a 1 : 1 ratio except for more left-over trityl cation. The mixture was also removed from the NMR spectrometer, newly mixed, and returned to the spectrometer. The same formation of the chlorosilane Si(SiMe\_2Cl)\_4 (**93**) as well as the decomposition of Ph<sub>3</sub>CH were observed.

For the spectroscopic data of chlorosilane  $Si(SiMe_2Cl)_4$  (93) see reaction with 1 : 1 stoichiometry.



(CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 183.1 K, \* = CDHCl<sub>2</sub>).



(CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 183.1 K).

Reaction in chlorobenzene-d₅ at -40 °C, Silane 100 : [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] = 1 : 1



The general procedure was applied for the hydride transfer reaction between pentasilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  in chlorobenzene. Subsequently, a solution of silane **100** (1.00 equiv., 0.09 mmol) in chlorobenzene-d<sub>5</sub> (0.3 mL) was added at -40 °C to an NMR tube containing a cooled solution of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.09 mmol) in chlorobenzene-d<sub>5</sub> (0.3 mL). The reaction mixture was examined by NMR spectroscopy. The NMR spectra indicated decomposition. No structure could be elucidated from the spectroscopic data.





0

-50

-100

-150

-200

50

100

200

150

# Reaction of 1,1-silyl-subsituted ferrocene 101 with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

The hydride transfer reaction of ferrocene derivative **101** was tried in dichloromethane- $d_2$  at - 80 °C as well as chlorobenzene- $d_5$  at -40 °C. Under both conditions, it was not possible to identify any ferrocene-stabilised or Si-H-Si-stabilised silyl cation. The spectra rather suggested decomposition of the formed cationic silyl species. No product identification was possible in both cases.



# Hydride transfer reaction of 101 and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene-d<sub>5</sub> at -40 °C

In a Schlenk tube, the ferrocene derivative **101** (1.00 equiv., 0.10 mmol) was dissolved in chlorobenzene-d<sub>5</sub> (0.4 mL) and thoroughly mixed with a vortex mixer. The solution was then slowly added at -40 °C to a NMR tube containing a solution of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.10 mmol) in chlorobenzene-d<sub>5</sub> (0.4 mL). The combined solutions were mixed and directly measured via NMR spectroscopy. While the NMR data showed the formation of  $Ph_3CH$ , no signal of a ferrocene-based silyl cation was detected.



Figure 339: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum after hydride abstraction of **101** (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, 233.0 K).



Figure 340: <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum after hydride abstraction of **101** (C<sub>6</sub>D<sub>5</sub>Cl, 99.31 MHz, 233.0 K).

# Hydride transfer reaction of 101 and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in dichloromethane-d<sub>2</sub> at -80 °C

At -80 °C, a solution of the ferrocene derivative **101** (1.00 equiv., 0.10 mmol) in dichloromethane- $d_2$  (0.4 mL) was added via syringe to a NMR tube containing a solution of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv., 0.10 mmol) in dichloromethane- $d_2$  (0.2 mL). The resulting mixture was thoroughly mixed, transferred in a precooled NMR spectrometer and analysed by NMR spectroscopy. No ferrocene-stabilised or Si-H-Si-bridged silyl cation were detected in the NMR spectroscopic data. It was not possible to identify the main component visible in the NMR spectra.



(CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz, 193.0 K, \* = CDHCl<sub>2</sub>, # = Ph<sub>3</sub>CH).



Figure 344: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum after hydride abstraction of **101** (CD<sub>2</sub>Cl<sub>2</sub>, 99.31 MHz, 193.0 K).







Figure 346: <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum after hydride abstraction of **101** (CD<sub>2</sub>Cl<sub>2</sub>, 499.87 MHz, 193.0 K).





# 5.4. Trapping Reactions

#### Trapping of the monocation of Si(SiMe<sub>2</sub>SiMe<sub>2</sub>H)<sub>4</sub>



The trapping reaction of silvl cation 113 was performed in toluene as its use generated a biphasic mixture with an upper phase containing non-polar components and a bottom phase containing polar components. A proton sponge, 2,6-di-t-butyl-4-methylpyridine, was used in the trapping reaction. The trityl salt (1.00 equiv., 0.15 mmol) as well as the pyridine derivative (1.00 equiv., 0.15 mmol) were dissolved in toluene (0.4 mL) and cooled to -40 °C. The oligosilane 91 (1.00 equiv., 0.15 mmol) was added as its solution in toluene (0.6 mL) via PTFE canula. The bottom layer of the reaction mixture became very sticky after addition of the silane. The biphasic mixture was stirred for 10 min at -40 °C. The trapping reagent, *n*-Bu<sub>3</sub>SnD (1.00 equiv., 0.15 mmol), was added via Hamilton syringe. Stirring was continued until the bath reached -20 °C at which temperature the bottom layer became liquid again. Stirring was continued for additional 5 min to guarantee a complete mixing of all components. Subsequently, the upper layer was removed via syringe. The bottom layer was washed with toluene (2 x 1 mL). The combined non-polar phases were combined, and the solvent and volatile components removed under reduced pressure. The residue was redissolved in benzene-d<sub>6</sub> (0.6 mL) and analysed by NMR spectroscopy. The NMR sample was afterwards also used for GCMS analysis. The deuterated oligosilane **117** was detected and analysed by NMR spectroscopy as well as by GCMS in the non-polar phase after trapping. The bottom layer, containing the polar components was also, was also analysed by NMR spectroscopy. Therefore, the solvent and volatile components were removed under reduced pressure and the residue was redissolved in chlorobenzene- $d_5$ . No silv species were detected in the polar phase while one tin component was detected as the main component in the <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum. By its chemical shift and the reaction conditions, the tin component was identified as  $[(n-Bu_3)Sn][B(C_6F_5)_4]$ .

Analytical data of 117 (non-polar phase):

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K): 0.34 (6H, Si<u>Me</u><sub>2</sub>D), 0.35 (d, 18H, <sup>3</sup>J<sub>H,H</sub> = 4.4 Hz, Si<u>Me</u><sub>2</sub>H), 4.22 (sept, 3H, <sup>3</sup>J<sub>H,H</sub> = 4.4 Hz, <sup>1</sup>J<sub>H,Si</sub> = 178.0 Hz SiMe<sub>2</sub>H).<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.71 MHz, 305.0 K): -5.5 (s, Si<u>Me</u><sub>2</sub>D), -5.4 (s. Si<u>Me</u><sub>2</sub>H), -0.5 (s, Si<u>Me</u><sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -119.2 (t, <u>Si</u>Si<sub>4</sub>, <sup>3</sup>J<sub>Si,D</sub> = 2 Hz), -38.4 (t, <sup>2</sup>J<sub>Si,D</sub> = 2 Hz, <u>Si</u>Me<sub>2</sub>SiMe<sub>2</sub>D), -38.3 (s, <u>Si</u>Me<sub>2</sub>SiMe<sub>2</sub>H), -34.6 (t, <sup>1</sup>J<sub>Si,D</sub> = 27 Hz, <u>Si</u>Me<sub>2</sub>D), -34.0 (s, <u>Si</u>Me<sub>2</sub>H). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -119.3 (t, 1Si, <u>Si</u>Si<sub>4</sub>, <sup>3</sup>J<sub>Si,D</sub> = 2 Hz), -38.4 (bs, 1Si), -38.3 (s, <u>Si</u>Me<sub>2</sub>SiMe<sub>2</sub>H), -34.6 (t, 1Si, <sup>1</sup>J<sub>Si,D</sub> = 27 Hz, <u>Si</u>Me<sub>2</sub>D), -34.1 (s, 3Si, <u>Si</u>Me<sub>2</sub>H).

Mass required for  $C_{16}H_{51}DSi_9$  (**117**): 497.21. Mass found (%): 438.20 (25) [M<sup>+</sup> -C<sub>2</sub>H<sub>7</sub>Si], 381.20 (4) [M<sup>+</sup> -C<sub>4</sub>H<sub>13</sub>Si<sub>2</sub>], 364.10 (8) [M<sup>+</sup> -C<sub>5</sub>H<sub>17</sub>DSi<sub>2</sub>], 321.1 (6) [M<sup>+</sup> -C<sub>6</sub>H<sub>20</sub>DSi<sub>3</sub>], 289.1 (100) [M<sup>+</sup> -C<sub>8</sub>H<sub>26</sub>DSi<sub>3</sub>], 59.0 (8) [C<sub>2</sub>H<sub>7</sub>Si]<sup>+</sup>.

# Analytical data polar phase:

<sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>5</sub>Cl/D<sub>2</sub>O lock, 160.38 MHz, 305.0 K): -16.3 (s, [<u>B</u>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>5</sub>Cl/D<sub>2</sub>O lock, 470.28 MHz, 305.0 K): -166.67 (m, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -162.80 (t, <sup>3</sup>J<sub>F,F</sub> = 20.6 Hz, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>), -131.98 (m, [B(C<sub>6</sub><u>F</u><sub>5</sub>)<sub>4</sub>]<sup>-</sup>). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>5</sub>Cl/D<sub>2</sub>O lock, 186.42 MHz, 305.0 K): 213.8 ([*n*-Bu<sub>3</sub>Sn(C<sub>6</sub>H<sub>5</sub>Cl)]<sup>+</sup>).







Figure 351:  ${}^{1}$ H, ${}^{13}$ C HMQC NMR spectrum of **117** in the non-polar phase after trapping reaction (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).














Figure 355:  ${}^{1}$ H, ${}^{29}$ Si HMQC NMR spectrum of **117** in the non-polar phase after trapping reaction (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 356:  ${}^{1}$ H, ${}^{29}$ Si HMBC NMR spectrum of 117 in the non-polar phase after trapping reaction (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).



Figure 357: GCMS of the non-polar phase and mass spectrum of 117 (Rt = 10.6 min).



200	150	100	50	0	-50	-100	-150	-200	

Figure 358: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of the polar phase after trapping of silyl cation **113** with tributyltin deuteride ( $C_6H_5CI/D_2O$  lock, 99.31 MHz, 305.0 K).



Figure 359: <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum of the polar phase after trapping of silyl cation **113** with tributyltin deuteride  $(C_6H_5Cl/D_2O \text{ lock}, 186.42 \text{ MHz}, 305.0 \text{ K}).$ 



Figure 360: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of the polar phase after trapping of silyl cation **113** with tributyltin deuteride  $(C_6H_5Cl/D_2O \text{ lock}, 160.38 \text{ MHz}, 305.0 \text{ K}).$ 



Figure 361: <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of the polar phase after trapping of silyl cation **113** with tributyltin deuteride  $(C_6H_5CI/D_2O \text{ lock}, 470.28 \text{ MHz}, 305.0 \text{ K}).$ 

### Trapping of the dication 118



In contrast to the trapping reaction of monocation **113** the solvent was changed from toluene to 3-fluorotoluene. The change in solvent was necessary as no stirring of the very sticky polar phase of the biphasic mixture after generation of dication **119** was possible in toluene. The oligosilane **91** (1.00 equiv., 0.08 mmol) was dissolved in 3-fluorotoluene (0.5 mL). The resulting solution was added at -80 °C to a stirred solution of  $[Ph_3C][B(C_6F_5)_4]$  (2.00 equiv., 0.16 mmol) in 3-fluorotoluene (0.5 mL). The mixture was stirred for 15 min at -80 °C to ensure complete reaction of the trityl salt with the silane **91**. Tributyltin deuteride (2.00 equiv., 0.16 mmol) was subsequently added via Hamilton syringe to the cooled solution. Stirring was

continued for additional 10 min and *n*-hexane (3.0 mL) was added. Two phases as well as a solid formed after addition of the alkane. The upper phase was removed, filtered via syringe filter, and the volatile components were removed under reduced pressure. The residue was examined by GCMS and NMR spectroscopy.

Mass required for  $C_{16}H_{50}D_2Si_9$  (**123**): 498.21. Mass found (%): 439.20 (24) [M<sup>+</sup> -C<sub>2</sub>H<sub>7</sub>Si], 290.0 (100) [M<sup>+</sup> -C<sub>8</sub>H<sub>26</sub>DSi<sub>3</sub>], 73.00 (71) [C<sub>3</sub>H<sub>9</sub>Si]<sup>+</sup>, 59.00 (11) [CH<sub>7</sub>Si]<sup>+</sup>.

Mass required for  $C_{16}H_{48}O_2Si_9$  (**124**): 524.16. Mass found: 524.20 (100) [M]<sup>+</sup>, 509.16 (10) [M<sup>+</sup> -CH<sub>3</sub>], 451.10 (48) [M<sup>+</sup> -C<sub>3</sub>H<sub>9</sub>Si], 377.0 (58) [M<sup>+</sup> -C<sub>5</sub>H<sub>15</sub>OSi<sub>2</sub>], 147.0 (34) [C<sub>5</sub>H<sub>15</sub>OSi<sub>2</sub>]<sup>+</sup>, 73.00 (62) [C<sub>3</sub>H<sub>9</sub>Si]<sup>+</sup>, 59.00 (3) [CH<sub>7</sub>Si]<sup>+</sup>.

Mass required for  $C_{16}H_{59}DOSi_9$  (**125**): 511.18. Mass found (%): 511.20 (8) [M]<sup>+</sup>, 452.12 (29) [M<sup>+</sup> -C<sub>2</sub>H<sub>7</sub>Si], 377.10 (100) [M<sup>+</sup> -C<sub>5</sub>H<sub>26</sub>DSi<sub>2</sub>], 319.00 (95) [M<sup>+</sup> -C<sub>7</sub>H<sub>32</sub>DSi<sub>3</sub>], 147.0 (45) [C<sub>5</sub>H<sub>15</sub>OSi<sub>2</sub>]<sup>+</sup>, 73.00 (70) [C<sub>3</sub>H<sub>9</sub>Si]<sup>+</sup>, 59.00 (7) [CH<sub>7</sub>Si]<sup>+</sup>.



Figure 362: <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR spectrum of the trapping products of dication **118** and tributyltin deuteride in 3-fluorotoluene (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 32 °C).







Figure 364: GCMS data after trapping reaction and mass spectrum of **124** ( $R_t = 11.1$  min).



60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 m/z

Figure 365: GCMS data after trapping reaction and mass spectrum of 125 (Rt = 11.9 min).

#### Trapping reaction of the cation of Si(SiMe<sub>2</sub>H)<sub>4</sub>



The cation formed after hydride reaction of oligosilane **100** and  $[Ph_3C][B(C_6F_5)_4]$  was reacted with deuterated tributyltin deuteride using 3-fluorotoluene as a solvent. For the trapping reaction, the silane **100** (1.00 equiv, 0.13 mmol) was dissolved in the solvent (0.4 mL). The resulting solution was then added to a solution of  $[Ph_3C][B(C_6F_5)_4]$  (1.00 equiv, 0.13 mmol) in 3-fluorotoluene (0.4 mL) at -80 °C. The resulting reaction mixture was stirred for 5 min at -80 °C. Subsequently, tributyltin deuteride (1.00 equiv, 0.13 mmol) was added via Hamilton syringe to the stirred solution. After 5 min of stirring, *n*-hexane was added to the reaction mixture. Upon addition the formation of a solid as well as the formation of two phases occurred. The upper phase was separated, filtered via syringe filter, and the volatile components were removed under reduced pressure. The residue was examined by GCMS and NMR spectroscopy.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.1 K): 0.27 (6H, Si<u>Me<sub>2</sub></u>D), 0.28 (d, 18H,  ${}^{3}J_{H,H} = 4.4$  Hz, Si<u>Me<sub>2</sub></u>H), 4.29 (sept, 3H,  ${}^{3}J_{H,H} = 4.4$  Hz). <sup>29</sup>Si{<sup>1</sup>H} INEPT NMR (C<sub>6</sub>D<sub>6</sub>, 99.31 MHz, 305.0 K): -140.3 (s, <u>Si</u>Si<sub>4</sub>), -33.9 (t, <u>Si</u>Me<sub>2</sub>D,  ${}^{1}J_{Si,D} = 28$  Hz), -33.5 (s, <u>Si</u>Me<sub>2</sub>H).

Mass required for  $C_8H_{27}DSi_5$  (**128**): 265.11. Mass found (%): 250.10 (2) [M<sup>+</sup> -Me], 204.10 (100) [M<sup>+</sup> -C<sub>2</sub>H<sub>7</sub>DSi], 73.00 (28) [C<sub>3</sub>H<sub>9</sub>Si]<sup>+</sup>, 59.00 (11) [CH<sub>7</sub>Si]<sup>+</sup>.



Figure 366: <sup>1</sup>H NMR spectrum of the deuterated oligosilane **128** ( $C_6D_6$ , 499.87 MHz, 305.1 K, # = 3-fluorotoluene and *n*-hexane).



Figure 368: <sup>1</sup>H,<sup>29</sup>Si HMQC NMR spectrum of the deuterated oligosilane **128** (C<sub>6</sub>D<sub>6</sub>, 499.87 MHz, 305.0 K).





50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 m/z



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# 7. Appendix

## 7.1. Computational Details

All quantum chemical calculations were carried out using the Gaussian 16 package.<sup>[245]</sup> If not noted otherwise, structure optimisations were performed using the M06-2X<sup>[201]</sup> functional in combination with the 6-311+G(d,p) basis set as implemented in Gaussian 16. For the iron-containing ferrocene derivatives a generated basis set consisting of 6-311+G(d,p) for Si, C and H and def2tzvpd<sup>[246]</sup> for Fe was used. NMR chemical shift calculations of the optimised structures were performed using the GIAO method<sup>[247-248]</sup> as implemented in Gaussian 16. The M06-L functional along with the 6-311G(2d,p) basis were used for the GIAO NMR calculations, while Si-H coupling constants were computed using the B3LYP<sup>[249-250]</sup> method in combination with the IGLOIII basis set.<sup>[251]</sup>

The values for the Gibbs free energy  $\Delta G$  were first computed at physical parameters of 298 K and 1 atm. A correction of the data computed at 298 K and 1 atm, that was proposed by Martin and co-workers,<sup>[222]</sup> was subsequently applied using Gaussian's *freqchk* utility. According to the equation p = nVRT and the respective density of the used solvent the different pressure corrections at different temperatures were used (Table 27). Corrected values are marked with an additional asterisk ( $\Delta G^*$ ).

Solvent	Density [kg m <sup>-3</sup> ]	Temperature [K (°C)]	Calculated Pressure [MPa]
Chlorobenzene	1327	233 (-40)	23.81
Dichloromethane	1110	183 (-90)	19.15
3-Fluorotoluene	9991	193 (-80)	14.49

Table 27: Pressure corrections applied for the Gibbs free energy values  $\Delta G^{\star}.$ 

All computations were performed at the HPC Cluster CARL, located at the University of Oldenburg (Germany) and funded by the DFG through its Major Research Instrumentation Programme (INST 184/157-1 FUGG) and the Ministry of Science and Culture (MWK) of the Lower Saxony State.

## 7.2. List of Abbreviations

BCS	Barlett-Condon-Schneider (Hydride Transfer Reaction)
CPMAS	Cross Polarised Magic Angle Spinning (Solid State NMR)
DEPT	Distortionless Enhancement by Polarization Transfer (NMR)
DFT	Density Functional Theory (Quantum Mechanics)
EA	Elemental Analysis
EI	Electron Ionisation (MS Ionisation Method)
EN	Electronegativity
GCMS	Gas Chromatography–Mass Spectrometry
em	Exponential Multiplication (NMR Data Processing)
gm	Gauss Multiplication (NMR Data Processing)
HMBC	Heteronuclear Multiple Bond Correlation (2D NMR)
HMQC	Heteronuclear Multiple Quantum Coherence (2D NMR)
HRMS	High-Resolution Mass Spectrometry
INEPT	Insensitive Nuclei Enhanced by Polarisation Transfer (NMR)
ATR IR	Attenuated Total Reflection Infrared Spectroscopy
LB	Lewis Base
LG	Leaving Group
Mes	Mesityl (2,4,6-Trimethylphenyl)
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
OTf	Triflate
TCCA	Trichloroisocyanuric Acid
TMS	Tetramethylsilane (NMR Standard)
WCA	Weakly-Coordinating Acids
XRD	X-Ray Diffraction
bm	Broad Multiplet (NMR)
bs	Broad Singlet (NMR)
d	Doublet (NMR)
r.t.	Room Temperature
S	Singlet (NMR)
sep	Septet (NMR)
t	Triplet (NMR)
XS	Excess

# 7.3. Crystallographic Data

Crystal data and structure refinement for S	i(SiMe <sub>2</sub> HSiMe <sub>2</sub> Ph) <sub>4</sub> ( <b>92</b> ).			
Identification code	jpn58			
Empirical formula	C40 H68 Si9			
Formula weight	801.75			
Temperature	100(2) K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	P21			
Unit cell dimensions	a = 9.7333(4) Å	a = 90°.		
	b = 16.2667(6) Å	b = 93.2627(19)°.		
	c = 15.3868(6) Å	g = 90°.		
Volume	2432.22(16) Å <sup>3</sup>			
Z	2			
Density (calculated)	1.095 Mg/m <sup>3</sup>			
Absorption coefficient	0.271 mm <sup>-1</sup>			
F(000)	868			
Crystal size	0.400 x 0.350 x 0.150 mm	n <sup>3</sup>		
Theta range for data collection	1.326 to 36.318°			
Index ranges	-16<=h<=16, -27<=k<=27	′, -25<=l<=25		
Reflections collected	151138			
Independent reflections	23590 (R(int) = 0.0247)			
Observed reflections $(I > 2(I))$	22329			
Completeness to theta = 36.318°	100.0 %			
Absorption correction	Semi-empirical from equiv	valents		
Max. and min. transmission	1.0000 and 0.9676			
Refinement method	Full-matrix least-squares	on F <sup>2</sup>		
Data / restraints / parameters	23590 / 1 / 483			
Goodness-of-fit on F <sup>2</sup>	1.013			
Final R indices (I>2sigma(I))	R1 = 0.0230, wR2 = 0.05	73		
R indices (all data)	R1 = 0.0258, wR2 = 0.05	88		
Absolute structure parameter	0.001(9)			
Extinction coefficient	n/a			
Largest diff. peak and hole	0.375 and -0.216 e.Å <sup>-3</sup>			

Crystal data and structure refinement for fe	rrocene derivative <b>101</b> .			
Identification code	jpn205			
Empirical formula	C26 H58 Fe Si8			
Formula weight	651.29			
Temperature	130(2) K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	P2 <sub>1</sub> /c			
Unit cell dimensions	a = 9.8632(5) Å	a = 90°.		
	b = 6.4391(3) Å	b = 90.3708(12)°.		
	c = 30.2758(16) Å	g = 90°.		
Volume	1922.78(17) Å <sup>3</sup>			
Z	2			
Density (calculated)	1.125 Mg/m <sup>3</sup>			
Absorption coefficient	0.656 mm <sup>-1</sup>			
F(000)	704			
Crystal size	0.360 x 0.160 x 0.030 mm	3 <sub>1</sub> 3		
Theta range for data collection	1.345 to 33.727°			
Index ranges	-15<=h<=15, -10<=k<=10	), -47<=l<=47		
Reflections collected	59346			
Independent reflections	7679 (R(int) = 0.0547)			
Observed reflections (I > 2(I))	6017			
Completeness to theta = 33.727°	100.0 %			
Absorption correction	Semi-empirical from equivalents			
Max. and min. transmission	1.0000 and 0.9048			
Refinement method	Full-matrix least-squares	on F <sup>2</sup>		
Data / restraints / parameters	7679 / 0 / 172			
Goodness-of-fit on F <sup>2</sup>	1.037			
Final R indices (I>2sigma(I))	R1 = 0.0356, wR2 = 0.079	93		
R indices (all data)	R1 = 0.0542, wR2 = 0.08	71		
Extinction coefficient	n/a			
Largest diff. peak and hole	0.641 and -0.390 e.Å <sup>-3</sup>			

Crystal data and structure refinement for fe	rrocene derivative <b>103</b> .	
Identification code	jpn124	
Empirical formula	C35 H81 Fe Si10	
Formula weight	838.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5639(12) Å	$a = 76.646(2)^{\circ}$ .
	b = 14.8727(19) Å	b = 82.574(2)°.
	c = 18.462(2) Å	$g = 87.480(2)^{\circ}.$
Volume	2533.4(6) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.100 Mg/m <sup>3</sup>	
Absorption coefficient	0.556 mm <sup>-1</sup>	
F(000)	914	
Crystal size	0.300 x 0.200 x 0.060 mm	3 <sub>1</sub> 3
Theta range for data collection	1.407 to 32.031°	
Index ranges	-14<=h<=14, -22<=k<=22	, -27<=l<=27
Reflections collected	88374	
Independent reflections	17641 (R(int) = 0.0631)	
Observed reflections $(I > 2(I))$	12556	
Completeness to theta = 32.031°	100.0 %	
Absorption correction	Semi-empirical from equiv	valents
Max. and min. transmission	1.0000 and 0.8297	
Refinement method	Full-matrix least-squares	on F <sup>2</sup>
Data / restraints / parameters	17641 / 0 / 438	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices (I>2sigma(I))	R1 = 0.0393, wR2 = 0.090	06
R indices (all data)	R1 = 0.0702, wR2 = 0.102	29
Extinction coefficient	n/a	
Largest diff. peak and hole	0.441 and -0.636 e.Å <sup>-3</sup>	

## 7.4. Curriculum Vitae

Akademischer Werdegang	
Okt. 2016 – Juni 2021	Carl von Ossietzky Universität Oldenburg Promotion, Abschlussziel: Dr. rer. nat.
	Thema der Arbeit:
	Si-H-Si Stabilised Oligosilanylsilyl Cations and Dications with Multiple Si-H Functionalities
	– Syntheses and Analysis by NMR Spectroscopy and Quantum Mechanical Methods
Okt. 2013 – April 2016	Carl von Ossietzky Universität Oldenburg Studium, Abschlussziel: M.Sc. Chemie (Note: 1.15)
	Thema der Arbeit:
	Synthesestudien zu H-substituierten Silastaffanen
Okt. 2010 – April 2013	Carl von Ossietzky Universität Oldenburg Studium, Abschlussziel: B.Sc. Chemie (Note: 1.47)
	Thema der Arbeit:
	Trimesinsäure als Baustein mehrkerniger Titanocenkomplexe

Publikationen/ Konferenzbeiträge	
2018	9th European Silicon Days (Saarbrücken), Posterpräsentation
	21. Norddeutsches Doktorandenkolloquium (Braunschweig), Posterpräsentation
2017	22 <sup>nd</sup> European Conference on Organometallic Chemistry (Amsterdam): Posterpräsentation
	GDCh-Wissenschaftsforum Chemie (Berlin), Posterpräsentation
	Agichem (Göttingen), Posterpräsentation
2015	L. H. Lühning, C. Brahms, J. P. Nimoth, M. Schmidtmann und S. Doye, Z. anorg. allg. Chem. 2015, 641, 2071–2082.
Kenntnisse	
Wiss. Software	NMR software Bruker Topspin und Mestrelab Mnova
	Gaussian/GaussView
	OriginLab Origin
	LaTeX
Sprachen	Deutsch: Muttersprache
	Englisch: Fließend in Word und Schrift

Interessen

Lesen, Kochen, Joggen, Rad fahren/reisen und am Rad basteln

Französisch: Grundständig