Filippo Stella, MSc

Synthesis, Rearrangement and Further Reactions of Organosilanes and Organostannanes

DOCTORAL THESIS

to achieve the university degree of

Doktor der technischen Wissenschaften

submitted to

Graz University of Technology

Supervisor

Prof. Dr. Christoph Marschner

Institute of Inorganic Chemistry

Graz, February 2016

AFFIDAVIT

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present doctoral thesis.

Date	Signature

This work was financed by
the Fonds zur Förderung der wissenschaftlichen Forschung (FWF)
via the ERA chemistry project I00669,
and was carried out from January 2012 to December 2014
at the Institute for Inorganic Chemistry,
Graz University of Technology.

I would like to heartily thank my Supervisor Prof. Christoph Marschner for the challenging subjects of my Thesis, for the interesting discussions about working and *not*-working chemistry and for giving me the chance to exapand my research through different topics.
I'm in debt with Dott. Judith Baumgartner for solving my crystal structures and for deeply review my dissertation.
I really enjoy these three years in the laboratory and in the office with my colleagues Mohammad, Maggie and Rainer. I have also to thank the previous PhD students I had the chance to meet: Henning, Joahn, Andy and Istvan.
I'm seriously happy to had Lena Albers and Prof. Thomas Müller as partner for the main topic of this work.

I need to thank the Head of Chemical Science Department in Padova (Italy) Paolo Scrimin, who allowed me to take three years from my work to have this wonderful experience.
I want also to remember Prof. Klaus Müller (University of Stuttgart - Germany) that was by chance the first who introduced me to silicon chemistry.

But for sure I want to thanks my wife Claudia for doing *everything* while I was in the lab.

I hope this work will be usefull to the next generation of students.

Thanks you all again!

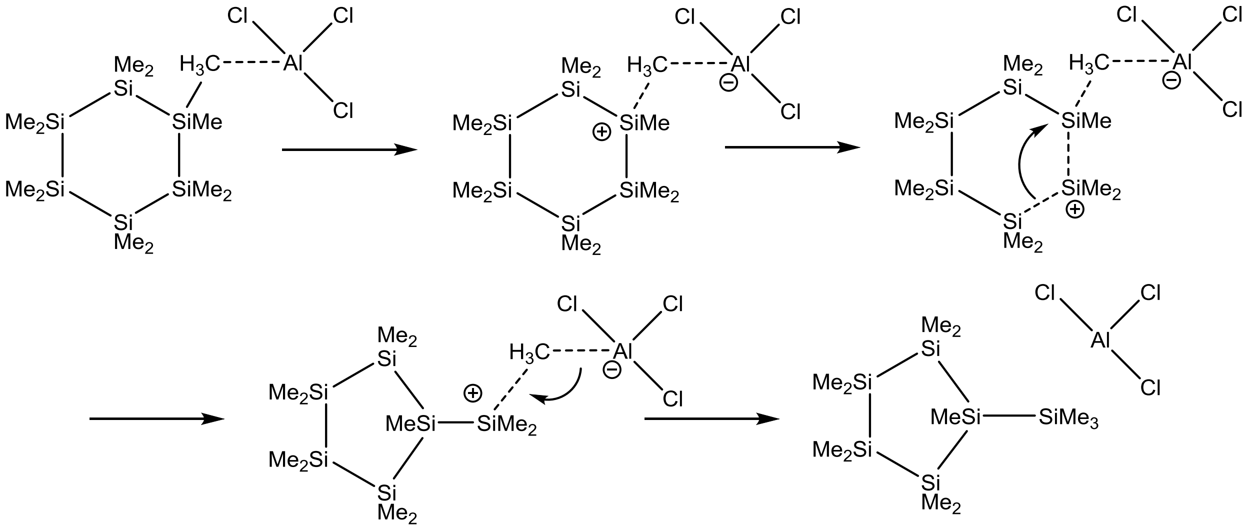
Filippo

INDEX

1. Synthesis and Rearrangement of not Permethylated Oligosilanes with Aluminum Trichloride

1.1 Introduction

From the 1960ies until recent years huge efforts on the synthesis, characterization and isomerization of organosilanes were made by different research groups around the world. In particular, the rearrangement of small permethylated oligosilanes, induced by strong Lewis acids, was explored as a possible route to prepare new molecules otherwise not easily obtained by standard synthetic methods. First, Ishikawa and Kumada studied the rearrangement reactions of dodecamethylcyclohexasilane and small permethylated silicon chains ($Me(Me_2Si)_nMe$, n=4-6), promoted by $AlCl_3$.[1,2,3,4] They observed ring contraction in the case of cyclic substrates (e.g. $(SiMe_2)_6 \rightarrow (SiMe_2)_5SiMe_3$), while in the case of linear polysilanes branched structures were yielded by the rearrangement process (e.g. $Me(Me_2Si)_5Me \rightarrow (Me_3Si)_4Si$). In 1986 Blinka and West went deeper into the investigation on cyclosilane isomers, using wider ring sizes as starting material and verifying which kind of aluminum chloride effectively worked as catalyst for these reactions.[5] The mechanism proposed for the rearrangement involved the formation of a positively charged silicon atom, due to the action of the Lewis acid that coordinates to a methyl group. Then the molecule reorganizes its structure to stabilize the cationic silicon, getting back the methyl group from the catalyst at the end of the process (Scheme 1-1). It is also possible that the cationic intermediate abstracts the methyl group from another molecule of silane, provoking the same reaction pattern.

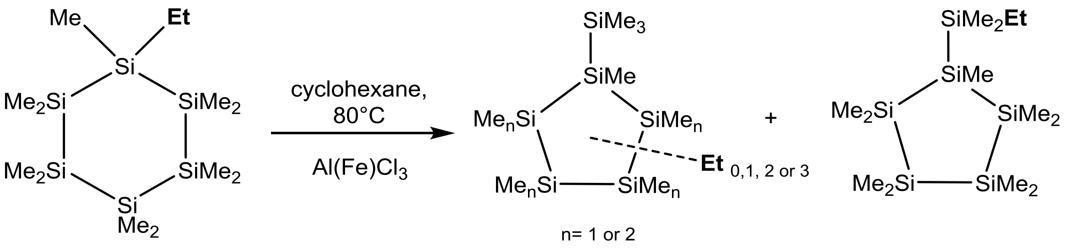


Scheme 1-1: Rearrangement mechanism proposed by Blinka and West.

---

[1] M. Ishikawa, M. Kumada, *J. Chem. Soc., Chem. Commun.*,**1969**, 567–568.
[2] M. Ishikawa, M. Kumada, *J. Chem. Soc., Chem. Commun.*,**1970**, 157.
[3] M. Ishikawa, J. Iyoda, H. Ikeda, K. Kotake, T. Hashimoto, M. Kumada, *J. Am. Chem. Soc.*, **1981**, *103*, 4845–4850.
[4] M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, M. Kumada, *Organometallics*, **1982**, *1*, 317–322.
[5] T.A. Blinka, R. West, *Organometallics*, **1986**, *5*, 128–133.

Another interesting point of West's work concerned the rearrangement of not just permethylated substrates, but small oligosilanes having one or more methyl groups substituted by ethyl groups, as for example undecamethylethylcyclohexasilane (Scheme 2-1).

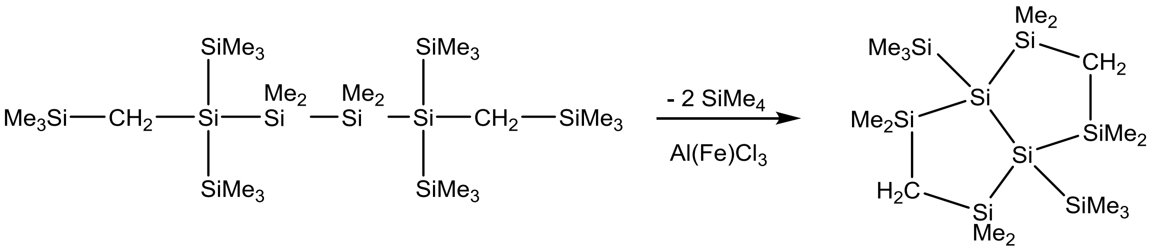


Scheme 2-1: Rearrangement of undecamethylethylcyclohexasilane promoted by 5% w/w $AlCl_3$ cosublimated with $FeCl_3$ (briefly named as $Al(Fe)Cl_3$).

In the reaction shown in Scheme 2-1 a mixture of products was obtained. Anyway, it should be emphasized that the 1-trimethylsilyl-1-ethyl-octamethylcyclopentasilane isomer was not found, as if the presence of the $SiMe_3$ group and the ethyl group both on the same silicon atom was sterically hindered. The varying number of ethyl groups bonded to the rings of the products suggests also that the catalyst could not distinguish between methyl and ethyl groups when it coordinates to the substrate. Alternatively the forming silyl cation might not abstract selectively a methyl group or an ethyl group from the substrate itself. When the isomerization of cyclosilanes as $(Et_2Si)_{n,(n=4-9)}$ or $(EtMeSi)_6$ was attempted, only decomposition (in benzene as solvent) or no reaction (in cyclohexane as solvent) of the starting materials was observed. It was thus stated that "It seems apparent that the $Al(Fe)Cl_3$-catalyzed rearrangement reaction is limited to permethylated polysilanes".

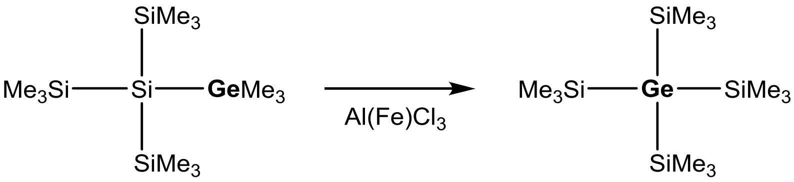
More recently, Marschner and co-workers developed the synthesis of a wide range of small polysilanes[6,7,8] and, especially with Harald Wagner, they studied the rearrangement reactions of branched linear and cyclic permethylated silanes.[9] Some of these substrates are somehow related to the present work, since they contain new functional groups as -(CH_2)- units in their backbone, that differentiate them as starting material from the classical molecules based on $Si_x(Me_3)_y$ structures.

These compounds (when the number of silicon atoms is greater than seven) usually provided clean cyclization reactions together with the formation of tetramethylsilane as by-product (Scheme 3-1).[10]



Scheme 3-1: Rearrangement of 1,4-bis(trimethylsilyl)-1,4-bis(trimethylsilylmethyl)-decamethylhexasilane with 1.1 eq. $Al(Fe)Cl_3$ ($AlCl_3$ cosublimated with $FeCl_3$).

Further studies about the mechanism of these reactions were pursued after the discovery of a special rearrangement given by different substrates functionalized with trimethylgermyl group.[11] In these cases, the process to stabilize the positive charge induced by the Lewis acid catalyst effects the germanium atom migrating towards the center of the neopentasilane structure (Scheme 4-1).



Scheme 4-1: Rearrangement of tris(trimethylsilyl)trimethylgermylsilane with 0.33 eq. of $Al(Fe)Cl_3$.

---

[6] C. Marschner, *Eur. J. Inorg. Chem.*, **1998**, 221-226.

[7] C. Kayser, R. Fischer, J. Baumgartner, C. Marschner, *Organometallics*, **2002**, *21*, 1023-1030.

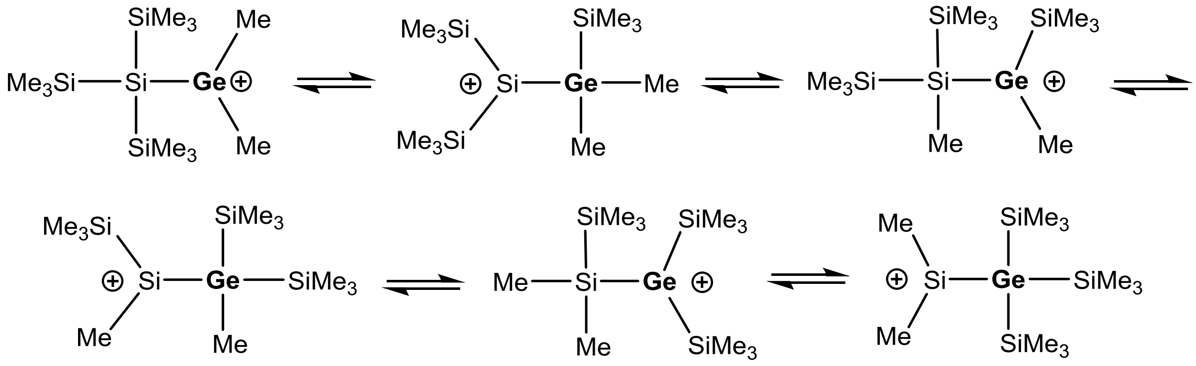
[8] R. Fischer, T. Konopa, S. Ully, J. Baumgartner, C. Marschner, *J. Organomet. Chem.*, **2003**, *685*, 79-92.

[9] H. Wagner, A. Wallner, J. Fischer, M. Flock, J. Baumgartner, C. Marschner, *Organometallics* **2007**, *26*, 6704-6717.

[10] H. Wagner, J. Baumgartner, C. Marschner, P. Poelt, *Organometallics*, **2011**, *30*, 3939-3954.

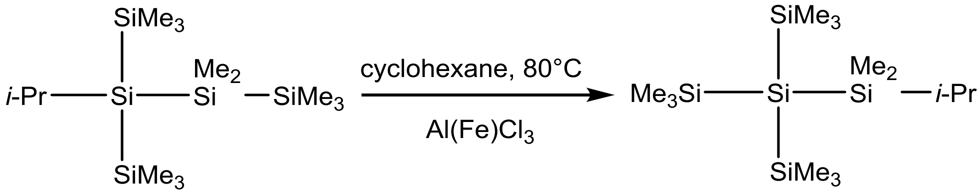
[11] H. Wagner, J. Baumgartner, T. Müller, C. Marschner, *J. Am. Chem. Soc.*, **2009**, *13*, 5022–5023.

Computational calculations carried out by Prof. T. Müller[11] suggested that aluminum trichloride coordinates to the methyl group bonded to the germanium atom, and then the positive charge shifts through the molecule with the pattern depicted in Scheme 5-1.



Scheme 5-1: Calculated rearrangement mechanism of tris(trimethylsilyl)trimethylgermylsilane. ΔG^{298K}(initial state – final state) = -45.7 kJ/mol.

But the preliminary experiments that inspired the main part of this thesis were some rearrangement reactions where the substrates were functionalized with isopropyl group or triisopropylsilyl group (Scheme 6-1):[12]



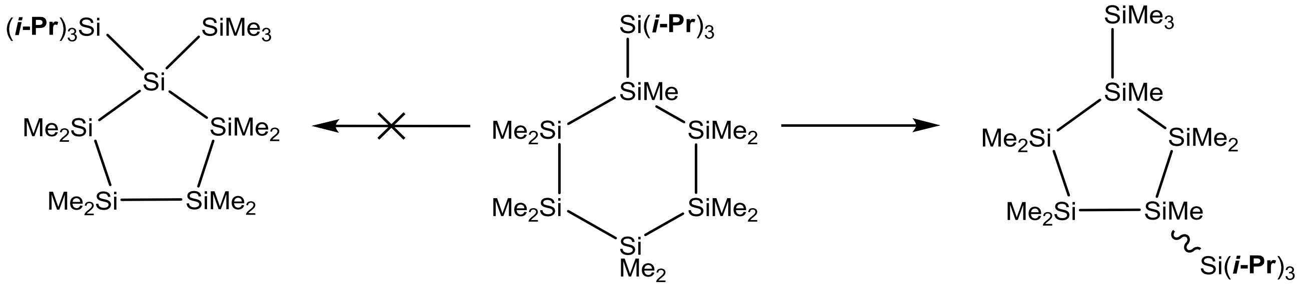
Scheme 6-1: Rearrangement of 1- trimethylsilyl-1-isopropyloctamethyltetrsilane with 0.29 eq. Al(Fe)Cl_3.

As already found for related permethylated molecules, the isomerization of these substrates is driven towards the most highly branched structure. In this case it is the isopropyl group that has to migrate, leaving its position to a $SiMe_3$ group. As a consequence, a quaternary silicon atom and a dimethylisopropylsilyl group are formed.

---

[12] H. Wagner, *research report*, **2009**.

Dodecamethylcyclohexasilane functionalized with a triisopropylsilyl (TIPS) group was isomerized under the same conditions (Scheme 7-1):



Scheme 7-1: Rearrangement of 1-(triisopropylsilyl)undecamethylcyclohexasilane with0.78 eq. of Al(Fe)Cl_3.

In this case, the formation of a quaternary silicon atom was not observed (such as occurring for the case of the isomerization of trimethylsilylundecamethyl-cyclohexasilane). The presence of a sterically more demanding group seems to drive the rearrangement to a product avoiding germinal attachement of the -$SiMe_3$ and the TIPS groups.

1.2 Overview of the thesis

To go further into the study of the rearrangement of not completely permethylated substrates, a number of oligosilanes functionalized with different alkyl groups were prepared. Then, various conditions for the isomerization reactions were explored, either with aluminum trichloride or with the frustrated Lewis pair (trityltetrakis(pentafluorophenyl)borate). Some of the rearranged substances were tried as starting material for subsequent derivatization through treatment with potassium *tert*-butoxide. In fact, beyond the theoretical interest in the feasibility and in the mechanism of these reactions, the new compounds should be used as building blocks for the synthesis of new materials, for example as ligands in organometallic complexes, since they could provide a more shielding structure to protect the metal center, due to the presence of more bulky alkyl groups. These topics are covered in the first three chapters of the thesis.

In chapter 4 some experiments to induce the isomerization of oligomers with triflic acid are described.

Since the formation of a silyl cationic intermediate is the key step for these rearrangement reactions, a series of experiments was carried out for preparing and isolating these extremely reactive species. The associated efforts are presented in chapter 5.

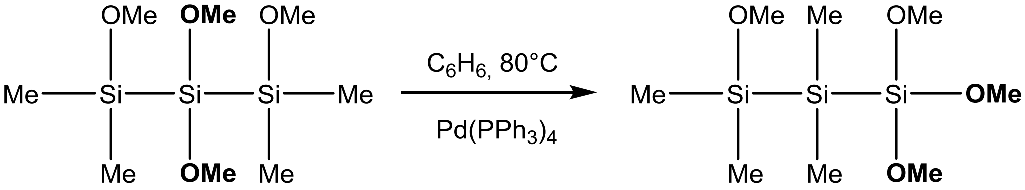
In chapter 6 the chemistry of silylated low valent titanium complexes is discussed: starting from Henning Arp's work,[13] the experience of our research group in this field was pushed slightly forward, with the preparation and characterization of some titanium(II) silyl heterocycles.

An novel organosilylstannane was prepared as a precursor for an oligosilyl cation. Because of its interesting UV properties, a series of similar compounds containing one or two tin atoms (inserted into oligosilane chains) were synthesized. This is discussed in chapter 7.

---

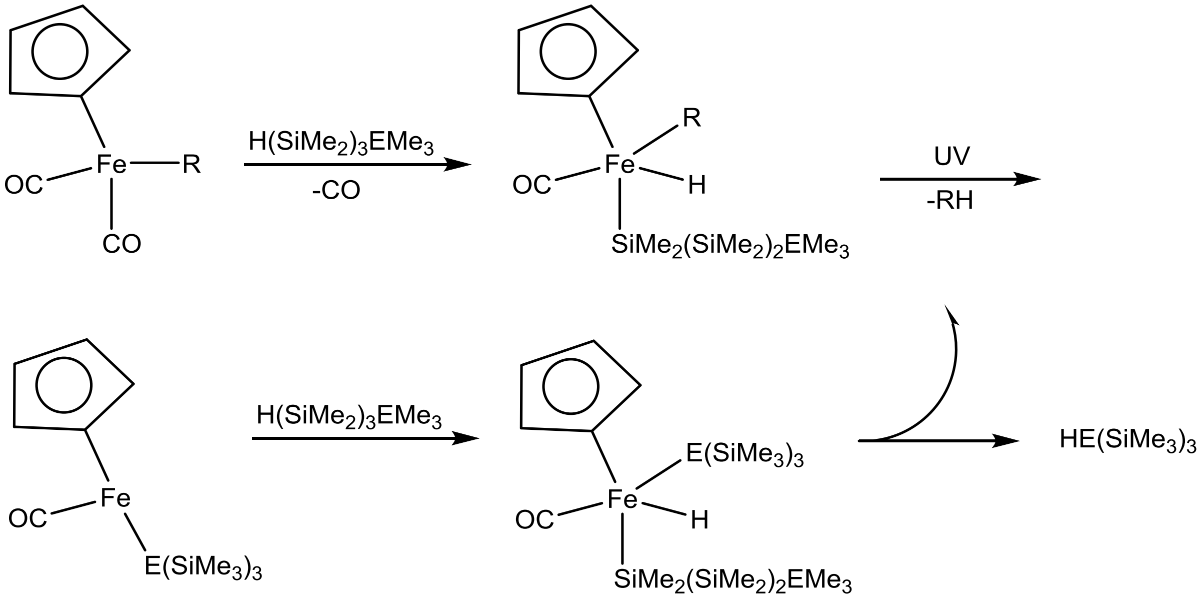
[13] Henning Arp, *Dissertation*, **2009-2012**, Institut für Anorganische Chemie der Technischen Universität Graz.

It is interesting to mention that beyond the work of Kumada, West and later of Marschner, theoretical and experimental studies of the isomerization of polysilanes were only sporadical. Tamao and co-workers observed the skeletal rearrangement of (alkoxy)oligosilanes promoted by a palladium complex, in benzene at 80°C.[14] The authors proposed a mechanism where the catalyst inserts into a silicon-silicon bond and then the migration of an alkoxy group towards the most electropositive silicon atom occurs (Scheme 8-1).



Scheme 8-1: Rearrangement of 1,2,2,3-tetramethoxytetramethyltrisilane with 4% $Pd(PPh_3)_4$, in benzene/80°C.

Pannell and Sharma studied the rearrangement of small oligosilanes and oligosilagermanes using a catalytic amount of a cyclopentadienylcarbonyl iron complex, under UV irradiation (Scheme 9-1).[15,16]



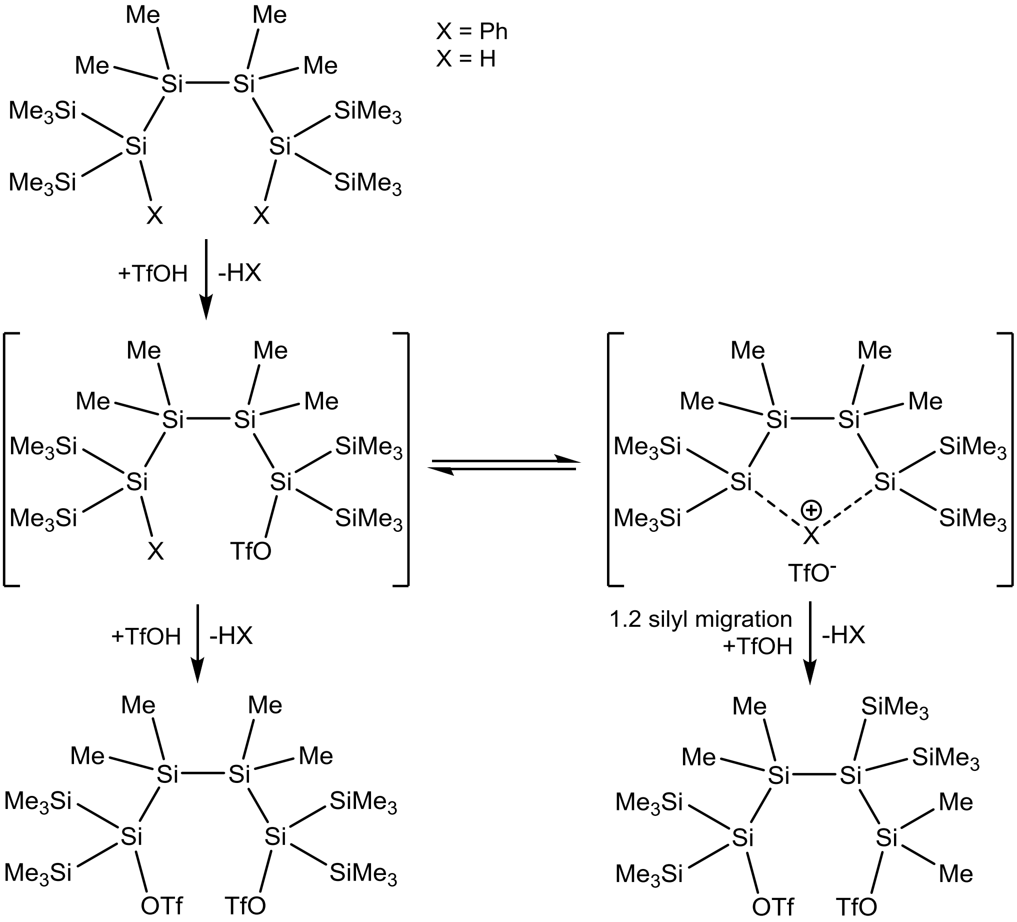
Scheme 9-1: E = Si or Ge. Simplified reaction mechanism.

---

[14] K. Tamao, G. Sun, A. Kawachi, *J. Am. Chem. Soc.*, **1995**, *117*, 8043-8044.
[15] K.H. Pannell, M. Brun, H. Sharma, K. Jones, S. Sharma, *Organometallics*, **1994**, *13*, 1075-1077.
[16] S. Sharma, K.H. Pannell, *Organometallics*, **2000**, *19*, 1225–1231.

Also under these conditions the formation of highly branched molecules is favored and, in the case of linear chains containing one germanium atom, an iron-germanium bond is produced. In this case a neopentasilane type structure with the germanium atom at the center is obtained ($HGe(SiMe_3)_3$).

Krempner and co-workers treated 1,1,4,4-tetrakis(trimethylsilyl)-2,2,2,2-tetramethyltetrasilane* with one/two equivalents of triflic acid. They observed a skeletal rearrangement involving the migration of the methyl groups towards the electropositive silicon atom (Scheme 10-1).[17]



Scheme 10-1: Rearrangement pattern for the substrate of Krempner after treatment with triflic acid.

Even if a silyl triflate is relatively stable (a **Si** – **O**(SO_2)CF_3 bond length of 1.778 Å was reported), the partial positive charge on the silicon atom is enough to promote the alkyl migration, that has as a consequence the formation of a quaternary silicon atom, and of a -$SiMe_2OTf$ group, in which the silicon atom benefits of a better stabilization given by the methyl groups.

---

* This compound will be indicated as **55** in the following chapters

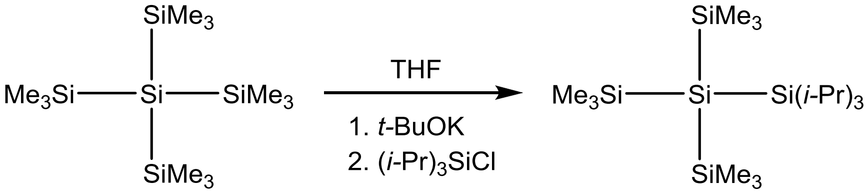
[17] C. Krempner, U. Jäger-Fiedler, C. Mamat, A. Spannenberg, K. Weichert, *New J. Chem.*, **2005**, *29*, 1581-1584.

1.3 Synthesis of the substrates for rearrangement reactions catalyzed by Al(Fe)Cl_3

The functionalization of polysilanes with different types of alkyl groups was already addressed in the past.[18,19,20] One of the main purposes of this work was to synthesize small oligosilanes with one or more sterically high demanding alkyl groups. Then, the rearrangement of these compounds with aluminum trichloride was studied, analyzing how the presence of these bulky substituents influences the isomerization. In most of the cases the starting material for the synthesis of substrates was tetrakis(trimethylsilyl)silane (**1**), prepared according to Gilman's procedure.[21]

1.3.1 Isopropyl derivatives

The first isopropyl derivative was prepared from tetrakis(trimethylsilyl)silane (**1**), as previously reported (Scheme 11-1).[7] The reaction works very well either in DME or in THF, and leads to transparent and quite large crystals, in high yield.



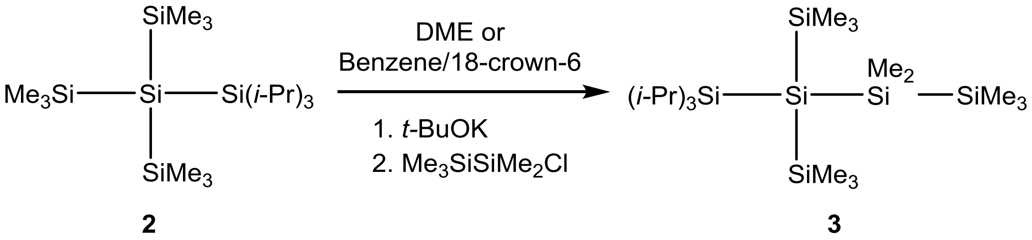
1 **2**

Scheme 11-1: Synthesis of a triisopropylsilyl derivative of **1** through an intermediate silyl anion.

Compound **2** was treated with *t*-BuOK, which selectively removes a $SiMe_3$ group and then the silyl anion thus formed was reacted with pentamethylchlorodisilane (Scheme 12-1). The formation of the anion is difficult in THF (the mixture needs to be heated), while in DME (or in benzene with 18-crown-6) it reacts much faster. It is also possible to react first the silyl anion from **1** with pentamethylchlorodisilane, then forming the silyl anion with *t*-BuOK, and finally react it with the triisopropylchlorosilane, but this route led to lower yield and less pure product (see experimental part).

---

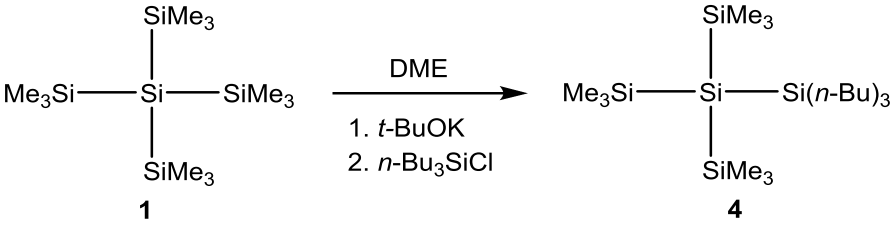
[18] F. K. Cartledge, *Organometallics*, **1983**, *2*, 425-430.
[19] H. Matsumoto, K. Takatsuna, M. Minemura, Y. Nagai, M. Gotob, *J. Chem. Soc., Chem. Comm.*, **1985**, 1365-1368.
[20] U. Herzog, R. West, *Macromolecules*, **1999**, *32*, 2210–2214.
[21] H. Gilman, C. L. Smith, *J. Am. Chem. Soc.*, **1964**, *86*, 1454–1454.



Scheme 12-1: Synthesis of 1,1-bis(trimethylsilyl)-1-(triisopropylsilyl)pentamethyltrisilane (**3**).

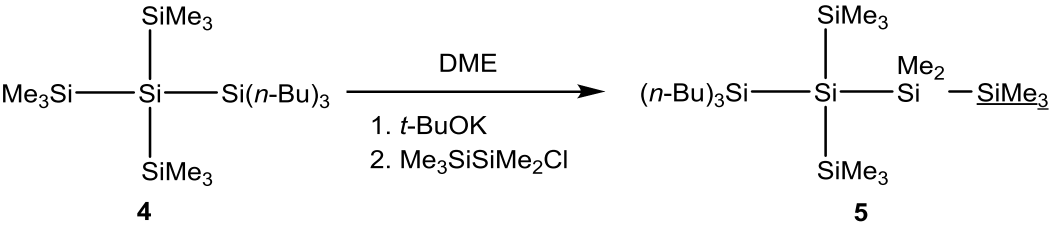
1.3.2. *n*-Butyl derivatives

In the same way as **2**, 1,1,1-tris(trimethylsilyl)tributyldisilane (**4**) was prepared from **1**. The presence of long alkyl chains in the molecule leads to the formation of a product that is a colorless and transparent oil at room temperature (Scheme 13-1).



Scheme 13-1: Synthesis of 1,1,1-tris(trimethylsilyl)tributyldisilane (**4**).

Compound **4** was treated with t-BuOK and the anion thus formed was reacted with pentamethylchlorodisilane (Scheme 14-1). In this way, a hexasilane with four silicon atoms in a row was prepared. As for the triisopropyl derivative **3**, it should be verified if the SiMe$_3$ group allocated in a less hindered position would take part in the planned rearrangement reactions.



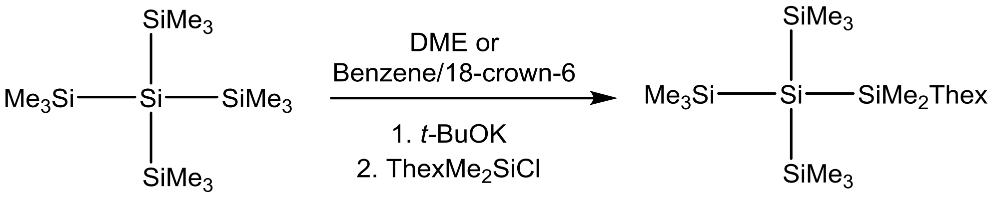
Scheme 14-1: Synthesis of 1,1-bis(trimethylsilyl)-1-(tri-*n*-butylsilyl)pentamethyltrisilane (**5**).

1.3.3. Thexyl derivatives

Another bulky group introduced into these small oligosilanes was the 1,1,2-trimethylpropyl group (named also “thexyl” and indicated as “Thex” in the chemical structures; Scheme 15-1).[22]

---

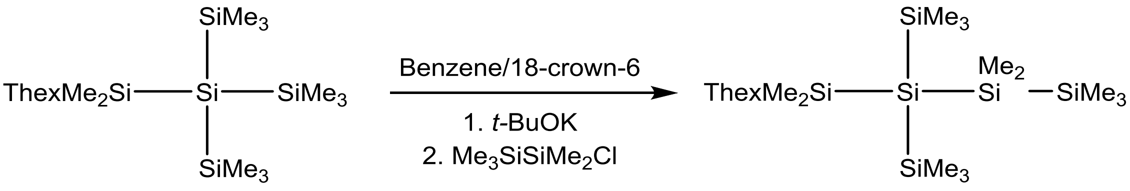
[22] C. Kayser, C. Marschner, *Monatsh. Chem.*, **1999**, *130*, 203-206.



1 **6**

Scheme 15-1: Synthesis of 1,1,1-tris(trimethylsilyl)-2-thexyl-dimethyldisilane (**6**).

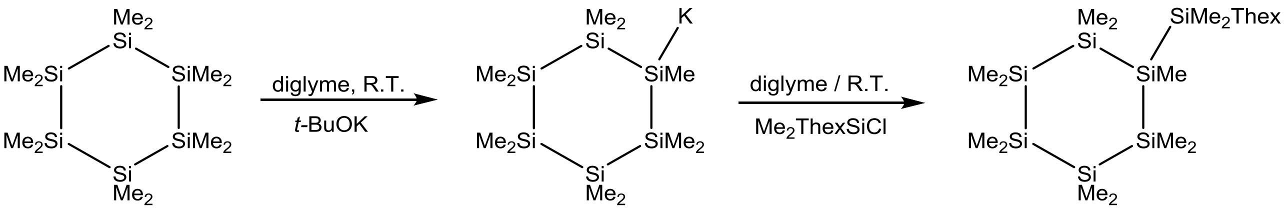
Compound **6** was treated again with *t*-BuOK and the thus formed silyl anion was reacted with pentamethylchlorodisilane to yield **7** (Scheme 16-1).



6 **7**

Scheme 16-1: Synthesis of 1,1-bis(trimethylsilyl)-1-(dimethylthexyl)pentamethyltrisilane (**7**).

The dimethylthexylsilyl group was also used to functionalize dodecamethylcyclohexasilane. Here the silyl anion was prepared according to literature[23] and then reacted with dimethylthexylchlorosilane to give **8** (Scheme 17-1).



8

Scheme 17-1: Synthesis of 1-(dimethylthexylsilyl)undecamethylcyclohexasilane (**8**).

---

[23] F. Uhlig, P. Gspalt, M. Trabi, E. Hengge, *J. Organomet. Chem.*, **1995**, *493*, 33-40.

1.4 Rearrangement reactions catalyzed by $Al(Fe)Cl_3$

All new compounds described (**2**-**8**) were treated with catalytic amounts of aluminum trichloride[*] mostly in dichloromethane (DCM) at room temperature. Wagner reported that under these conditions an undesired chlorination of the final products might occur[24] and that it would be preferable to work in cyclohexane at 80°C. However, the DCM system is easier to prepare and to manage, and the catalyst is completely dissolved in the solvent at room temperature (and, for this reason, it might be more active). As reaction vessels, simple glass vials of 20 mL of volume were used, instead of Schlenk flasks that are necessary to work at the boiling point of cyclohexane. Anyway, in some cases the latter solvent was employed for comparison, but the amount of chlorinated by-products did not decrease dramatically. All reactions were done under nitrogen atmosphere in a dry glove box. The preliminary substrates used are shown again in Figure 1-1.

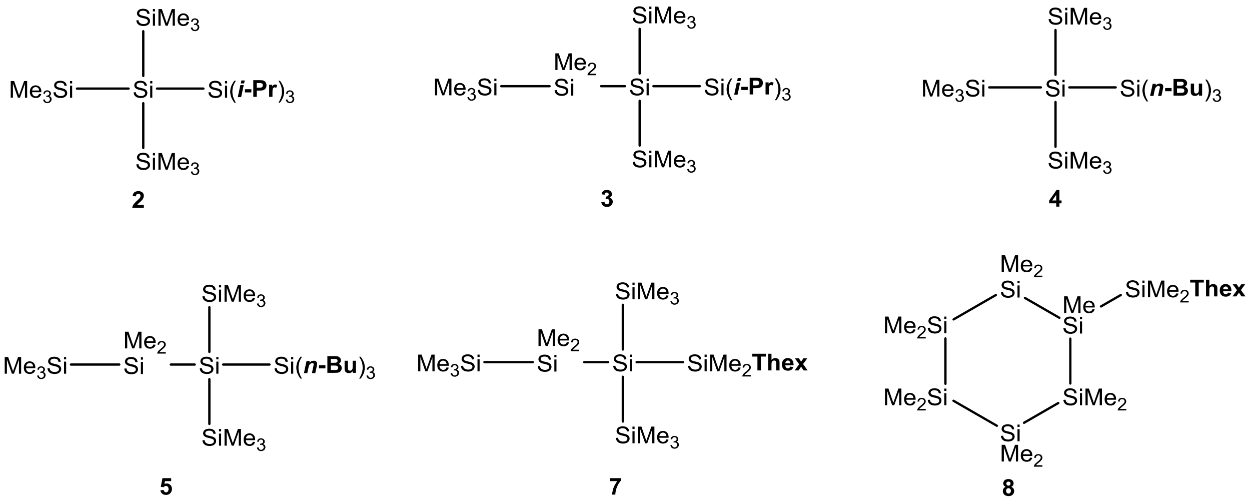


Figure 1-1: Starting compounds for rearrangement reactions.

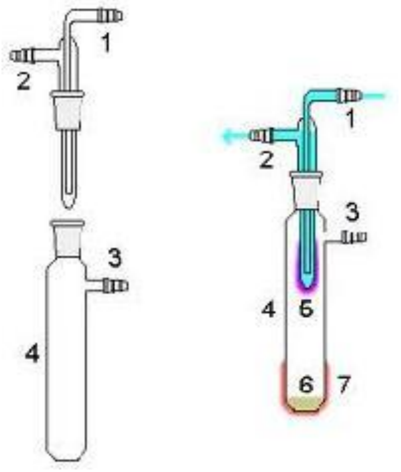
---

[*] Co-sublimated with $FeCl_3$.

[24] H. Wagner, *Dissertation*, **2005-2008**, Institut für Anorganische Chemie der Technischen Universität Graz.

1.4.1 Preparation of the catalyst

The catalyst was prepared subliming commercially available $AlCl_3$ together with ca. 3% w/w of anhydrous $FeCl_3$. The process occurred under vacuum (ca. 1-2 mbar) and at 100°C, for about 1-2 hours (see Figure 2-1). The solid condensed on a water-cooled glass finger inside the flask, and then the sublimated material was scraped and transferred into a glass vial, inside the glove box. The powder presents an intense yellow color, it is coarse but quite homogeneous.

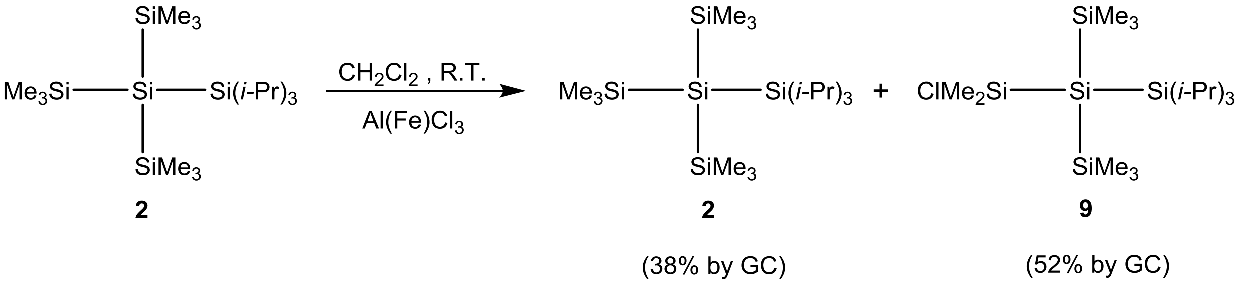


Cold finger distillation system:
1) and 2) water flow lines
3) vacuum connection
4) glass flask
5) condensed/sublimated material
6) starting material
7) external heating

Figure 2-1: Subliming system for the preparation of $Al(Fe)Cl_3$.

1.4.2 Rearrangements of triisopropylsilyl derivatives

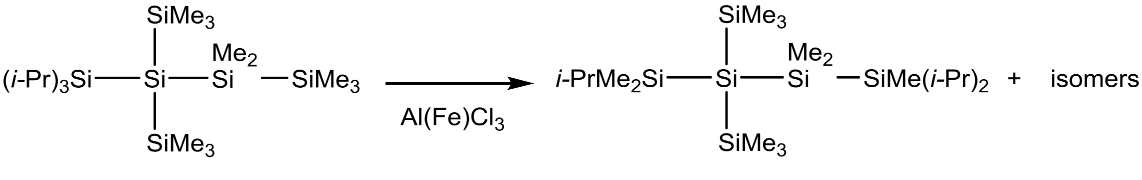
1,1,1-Tris(trimethylsilyl)triisopropyldisilane (**2**) was dissolved in CH_2Cl_2 together with 1 eq. of $Al(Fe)Cl_3$ and the reaction ran for 6 days at room temperature (Scheme 18-1). This large amount of catalyst was employed because for this reaction Wagner reported no conversion using 0.8 eq. of catalyst.[12] Under this condition aluminum trichloride is truly a reagent rather than a catalyst.



Scheme 18-1: Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropyldiisilane (**2**) with 1.0 eq. of $Al(Fe)Cl_3$, 6 days of reaction.

Since the substrate has already a neopentasilane structure, it will not attain a more branched conformation. What was supposed to happen is that the isopropyl groups get involved in the rearrangement process, due to the steric hindrance between these alkyl groups bonded to the same silicon atom: a migration towards a less hindered position was expected. But the previous results of Wagner were confirmed: no rearrangement was observed and the substrate underwent partial chlorination.

Substrate **3** was submitted to four isomerization reactions, under various experimental conditions (a-d, Scheme 19-1):



3

11

Scheme 19-1: Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (**3**), under the following conditions: a) 0.1 eq. catalyst, R.T./CH_2Cl_2, 6 days
b) 0.3 eq. catalyst, R.T./CH_2Cl_2, 6+6 days
c) 0.3 eq. catalyst, 5°C/ CH_2Cl_2, 14 days
d) 0.1 eq. catalyst, 80°C/cyclohexane.

In most of these experiments the reagent was consumed completely to give quite complex mixtures of isomers and also small amounts of **2** as decomposition by-product. The substrate did not truly undergo a skeletal rearrangement (meant as a change of the silicon atoms backbone), but the isopropyl groups were able to shift to different positions along the molecule. In fact in the ^{29}Si NMR spectra the signals from the quaternary silicons (around -130 ppm) and from the dimethylsilylene groups (ca. -36 ppm) indicate that the structure is retained. Then the new peaks in the range of $-5 < \delta < +5$ ppm probe the formation of the diisopropylmethylsilyl group and of the isopropyldimethylsilyl group. The cleanest NMR spectrum was obtained in the case of experiment b) and it is here reported (Figure 3-1).

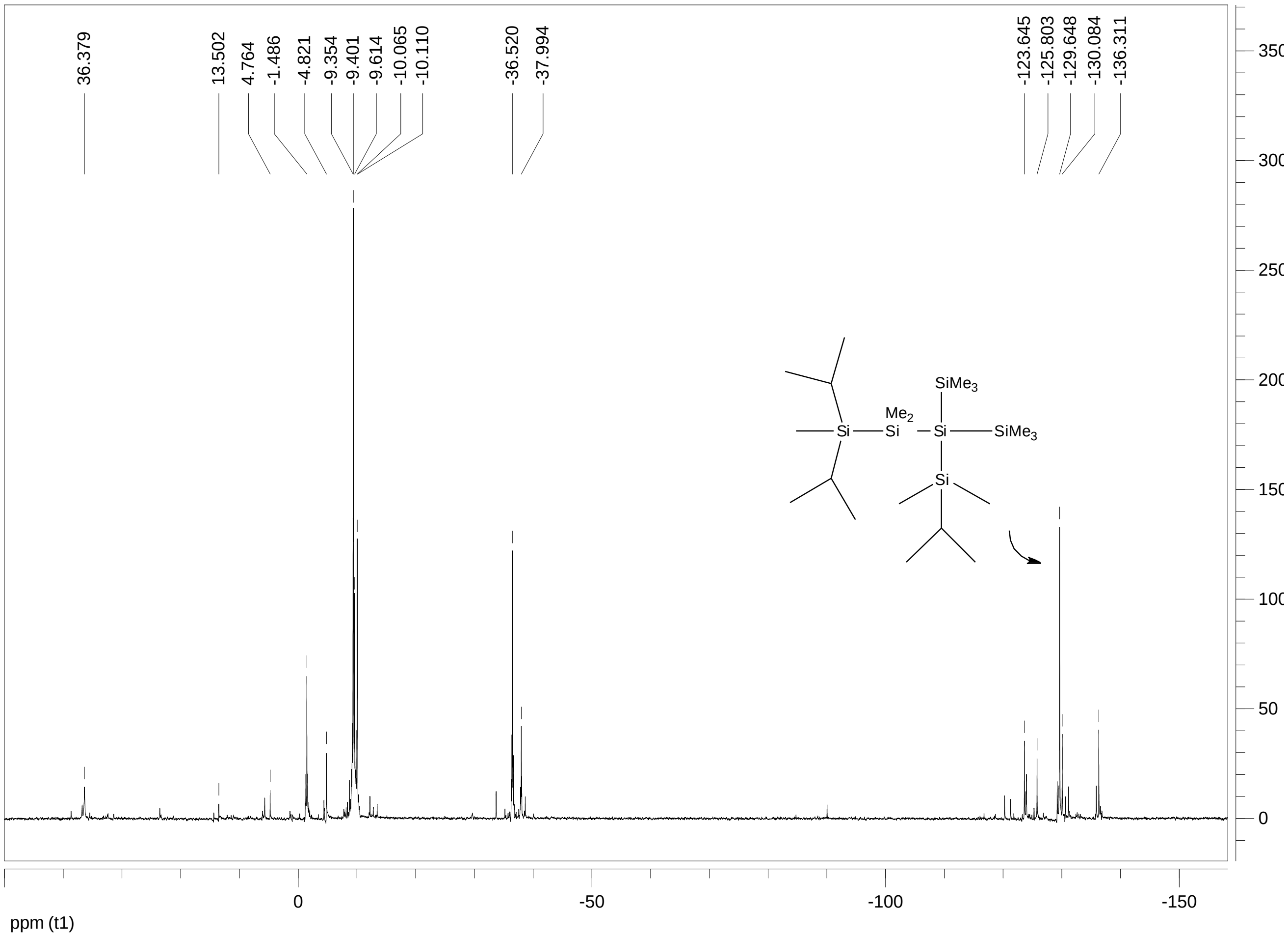


Figure 3-1: ^{29}Si NMR spectrum from the rearrangement of compound **3**, conditions b) Scheme 19-1

The highest peaks can be assigned to product **11** with the quaternary silicon at -129.6 ppm, the -SiMe$_2$- group at -36.5 ppm and the residual trimethylsilyl groups at -9.4 ppm. Regarding the ^{29}Si NMR chemical shifts of the mixed isopropyl/methyl silyl groups in these types of oligosilanes, there are no data in literature. Wagner found the signal of the isopropyldimethylsilyl group (bonded to a quaternary silicon atom) at ca. -1.2 ppm, so the peak at -1.5 ppm could be referred to this function for compound **11**. A signal at -4.8 ppm is supposed to be consistent with the formation of an *i*-Pr$_2$MeSi- group bonded to the dimethylsilylene unit.

The chemical shifts at -136.3 ppm, -10.1 ppm, and 13.5 ppm indicate the formation of **2**, which could also be recovered as large crystals from the worked up reaction mixture. The presence of at least three other signals in the NMR region for the quaternary silicon (-140 to -120 ppm) imply that many isomers were formed, and there is not a single clean rearrangement pattern for this substrate. This behavior could be confirmed by the calculations about the formation energies of all the possible isomers that are virtually generated by this reaction (Figure 4-1).[25]

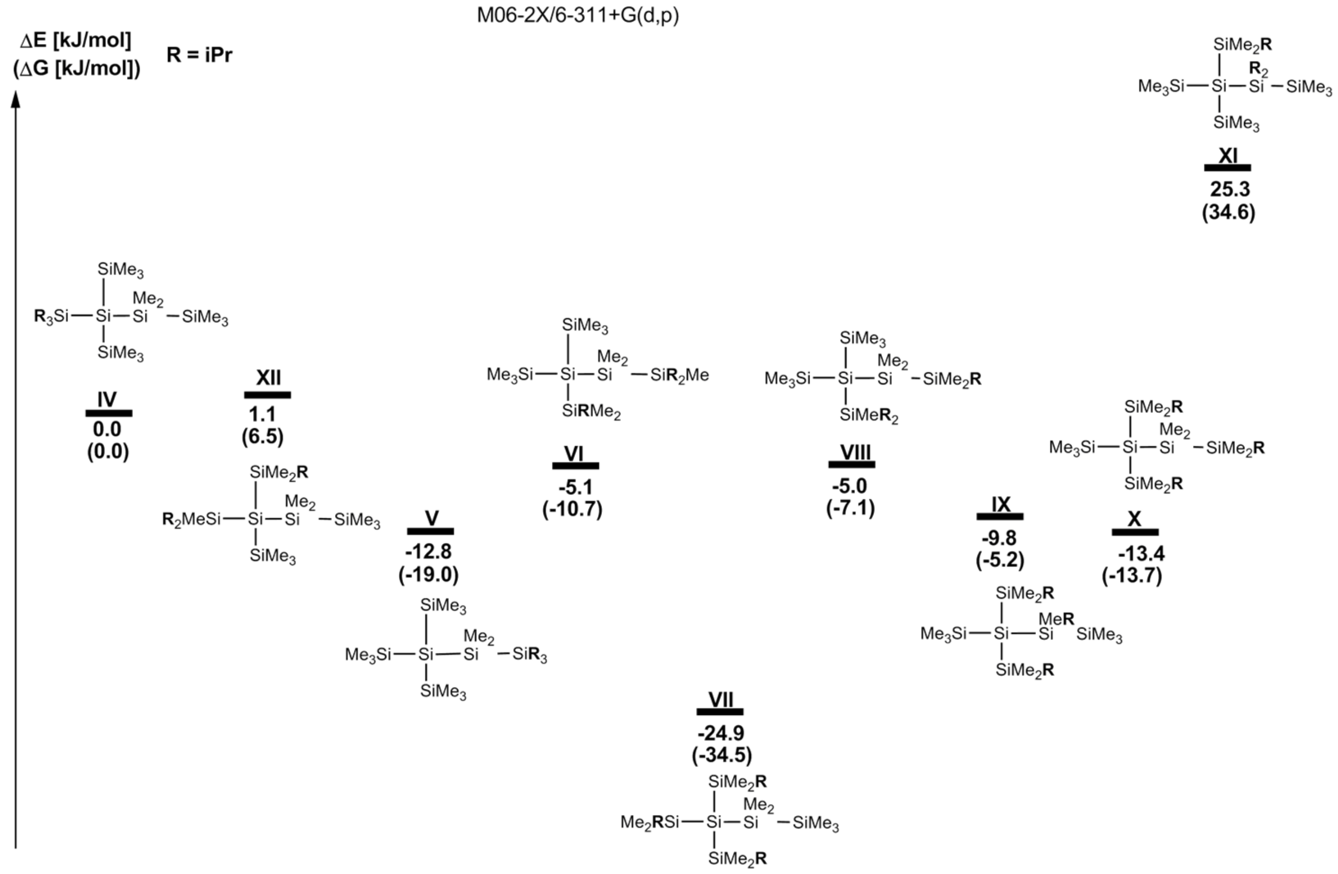
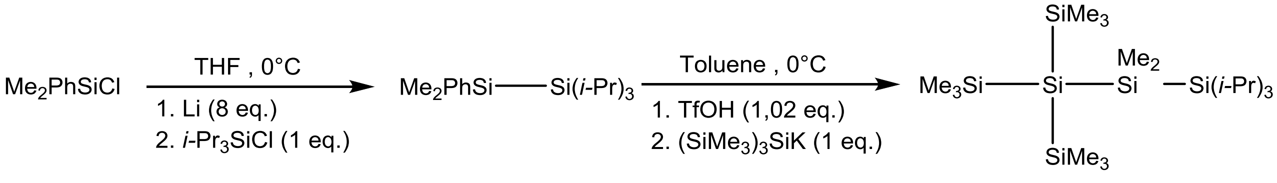


Figure 4-1: Calculated formation energies for all the possible isomers of compound **3**.

---

[25] L. Albers, *research report*, Carl Von Ossietzky Universität (Oldenburg), **2013**.

From this diagram it can be deduced that a rearrangement process is generally allowed, but the energy differences within the possible products are quite low (around 5-10 kJ/mol), and there is not a remarkably favored one. Compound **VII** seems the most stable isomer, but in the NMR spectrum (Figure 3-1) the high intensity of the signals of the $SiMe_3Si_q$ groups suggests that there was not a complete conversion of them into $SiMe_2$*i*-Pr groups. Compound **10** was prepared as described in Scheme 20-1 because it might be one of the resulted isomers.



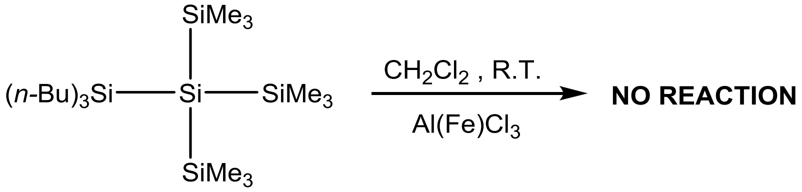
10

Scheme 20-1: Synthesis of 1,1,1-tris(trimethylsilyl)-2,2-dimethyltriisopropyltrisilane (**10**).

While the isopropyl groups enhances the crystallization ability of compound **2**, compound **11** and the other isomers obtained from the rearrangement reaction could not be isolated by this method. It was also not possible to purify the main product by sublimation or quantitative TLC, due to their very similar physical characteristics.

1.4.3 Rearrangement of tributylsilyl derivatives

1,1,1-Tris(trimethylsilyl)tributyldisilane (**4**) was dissolved in CH_2Cl_2 with 0.1 eq. of $Al(Fe)Cl_3$ and the reaction ran for 2 days (Scheme 21-1). No conversion was observed, so other 0.2 eq. of catalyst were added (0.3 eq. in total). After 10 days, no conversion occurred.

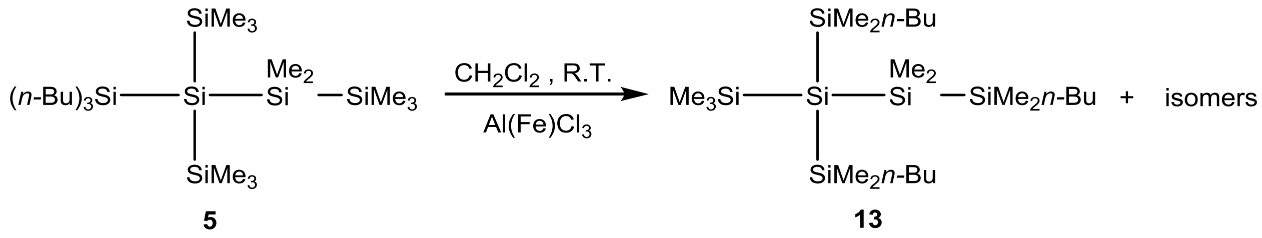


4

Scheme 21-1: Rearrangement attempt of **4** with 0.3 eq. of $Al(Fe)Cl_3$.

As for the isopropylsilyl derivatives, no skeletal rearrangement or alkyl migration was observed.

For compound **5** 0.5 equivalents of catalyst and eight days of stirring were necessary to promote the rearrangement reaction and the complete consumption of the substrate (Scheme 22-1).



Scheme 22-1: Rearrangement of 1,1,1-tributyl-2,2-bis(trimethylsilyl)pentamenthyltetrasilane (**5**).

After the workup, a transparent oil was obtained. Figure 5-1 shows the ^{29}Si NMR spectrum of this reaction.

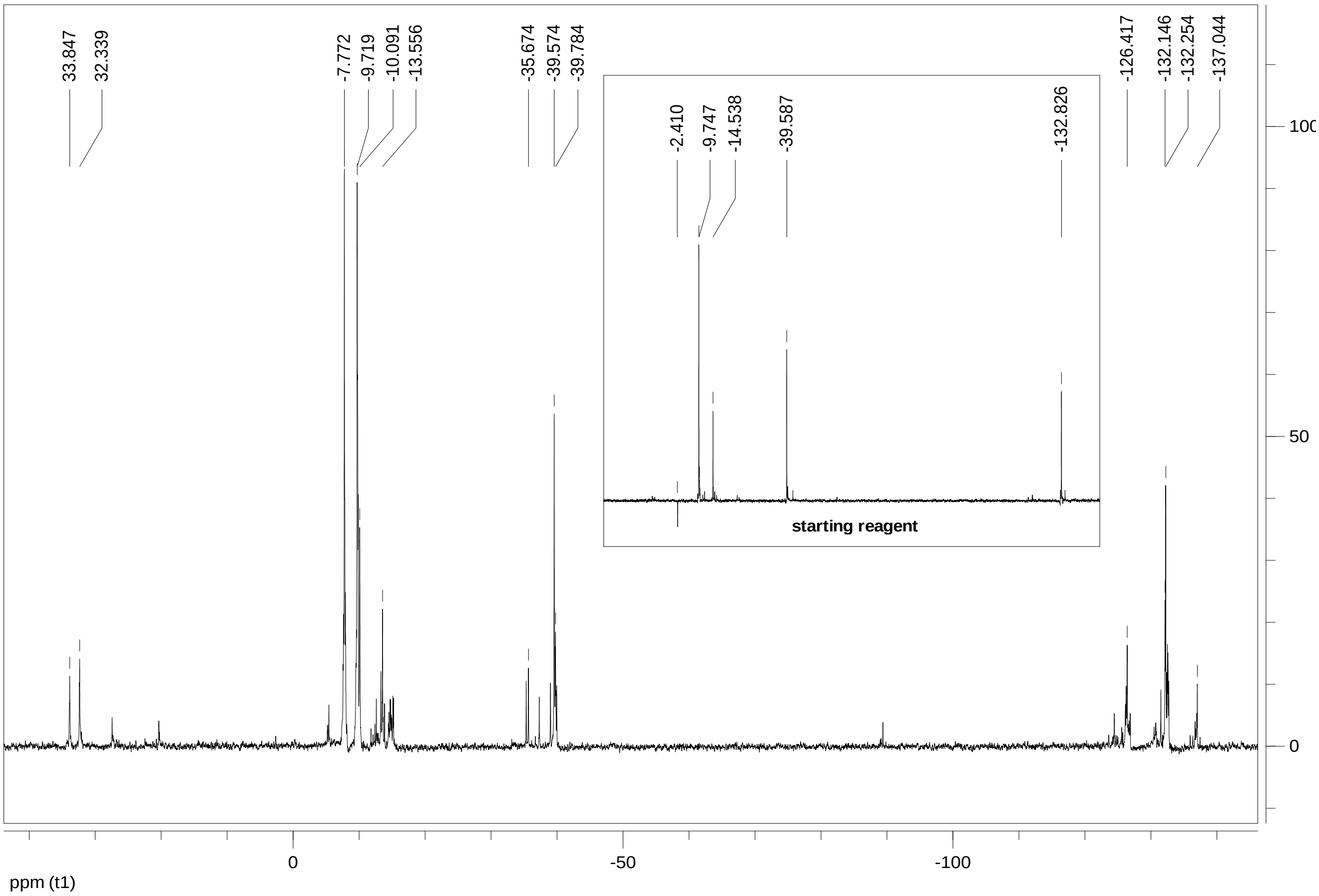


Figure 5-1: ^{29}Si NMR of compound **13** after work up (0.5 eq. of Al(Fe)Cl_3, 8 days of reaction).

Compound **13** seems to be the main product and the chemical shifts might be assigned as shown in Table 1-1:

Silicon atom	**δ (ppm), ^{29}Si NMR**
Si_qSi_4	-132.1
Si_qSiMe_2	-39.5
$SiMe_2SiMe_2$*n*-Bu	-13.5
Si_qSiMe_3	-9.7
Si_qSiMe_2*n*-Bu	-7.7

Table 1-1: ^{29}Si NMR assignment of the main isomerization product **13**, Scheme 22-1.

Compound **5** had a typical signal for the $–SiBu_3$ group at -2 ppm* in the ^{29}Si NMR. This signal was missing in the spectrum in Figure 5-1, suggesting that the starting material reacted completely. Also in this case, there are no references in literature for the ^{29}Si NMR chemical shifts of these types of oligosilanes containing mixed alkyl groups. Generally speaking, replacing one methyl group with another alkyl in a $-SiMe_3$ group leads to a low field shift of the signal of the new $-SiMe_2R$ function (see page 40 for a simple but interesting linear correlation between the number of alkyl groups on a silicon atom and its chemical shift in ^{29}Si NMR). The strong signal at -9.7 ppm indicates that at least one $-SiMe_3$ group is still present in the main product, while the small shift of 1 ppm of the $SiMe_2SiMe_xBu_{3-x}$ group might be due to migration of one butyl group to that position.

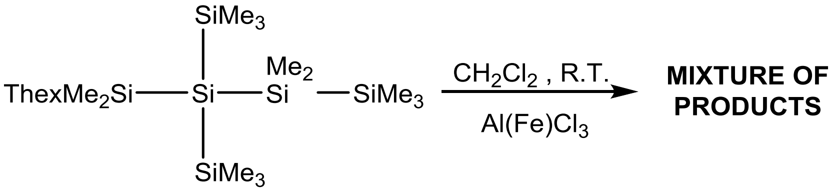
Peaks at around 33 ppm indicate the formation of chlorinated by-products, while some neopentasilane structure were formed and it gives signals at -137.0 ppm and -10.1 ppm.

---

* This signal presents a reversed phase in the INEPT ^{29}Si NMR.

1.4.4 Rearrangement of thexylsilyl derivatives

It required 0.5 equivalents of catalyst and 12 days of stirring to force 1-thexyl-2,2-bis(trimethylsilyl)heptamethyltetrasilane (**7**) to rearrange (Scheme 23-1).



7

Scheme 23-1: Rearrangement of 1-thexly-2,2-bis(trimethylsilyl)heptamethytetrasilane (**7**), with 0.5 eq. of $Al(Fe)Cl_3$.

This effort led to very complicated mixture that still contained some starting material. The ^{29}Si NMR of the reaction solution is here reported (Figure 6-1).

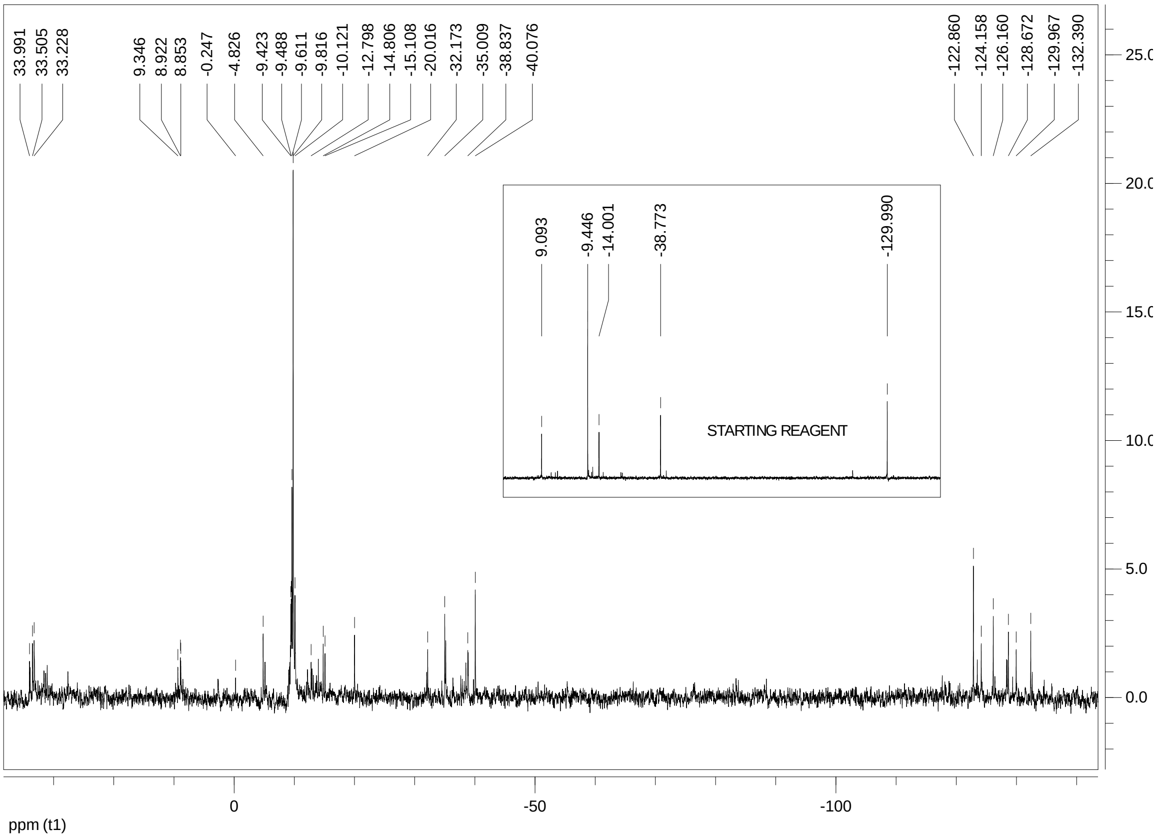
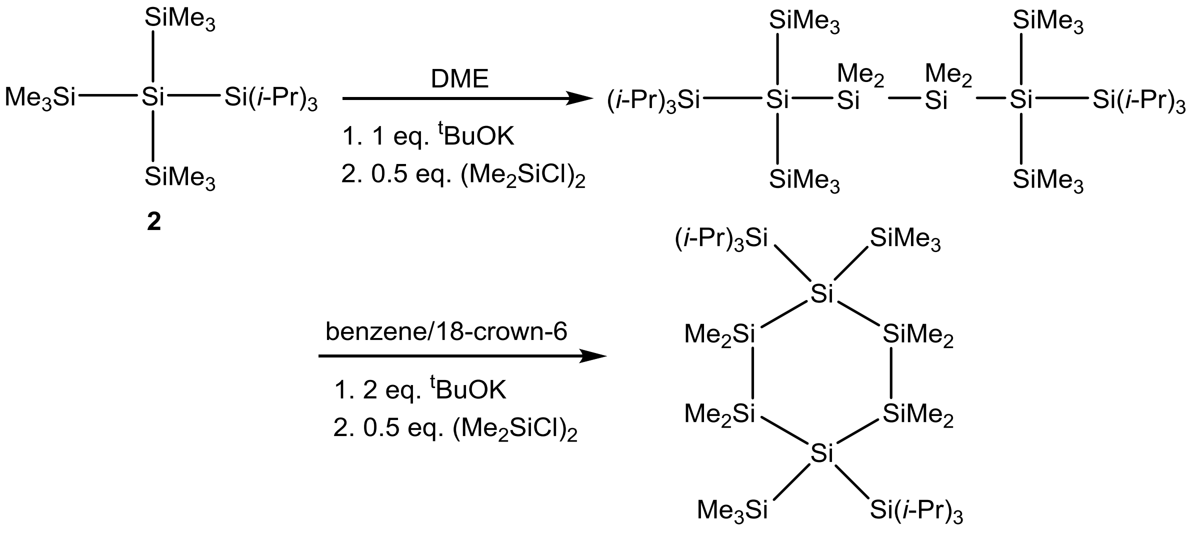


Figure 6-1: ^{29}Si NMR of rearrangement of compound **7**, 0.5 eq. of $Al(Fe)Cl_3$, 12 days of reaction.

In this experiment, the migration of the thexyl group toward the peripheral $–SiMe_2SiMe_3$ silicon atom was expected. But due to the large amount of catalyst employed and the long reaction time (that was necessary to start the reaction), the substrate underwent chlorination (signals around 33 ppm) and partial decomposition (signals from neopentasilane structure: -132.4 ppm and -10.1 ppm).

1.4.5 Synthesis and rearrangement of 1,4-bis(trimethylsilyl)-1,4-bis(triisopropylsilyl)octamethylcyclohexasilane (65)

Compound **65** was prepared to study the behavior of the isopropyl groups during the rearrangement process when the molecular backbone was a cyclic structure. This substrate was synthesized through four steps starting from compound **2** (Scheme 24-1).



2

65 (*cis* + *trans* isomers)

Scheme 24-1: Synthesis of 1,4-bis(trimethylsilyl)-1,4-bis(triisopropylsilyl)octamethylcyclohexasilane (**65**).

The last step of the reactions had not a high yield, but nevertheless it was possible to isolate suitable crystals of both the *cis* and *trans* isomers for X-ray analysis. The crystal structures are shown in Figure 7-1 and in Figure 8-1, respectively.

Selected crystallographic data – (65-*cis*):

Crystal system: monoclinic

Space group: C/c

Goodness-of-fit on F^2	1.298
Bond lengths [Å] and angles [deg]	
Si(1)-Si(4)	2.408(2)
Si(1)-Si(5)	2.380(2)
Si(1)-Si(3)	2.381(2)
Si(2)-Si(3_2)	2.363(2)
Si(5)-Si(1)-Si(4)	113.14(8)
Si(3)-Si(1)-Si(2)	106.93(7)
Si(1)-Si(3)-Si(2_2)	116.74(8)
Si(3)-Si(1)-Si(4)	112.16(8)

Selected crystallographic data – (65-*trans*):

Crystal system: monoclinic

Space group: C2/c

Goodness-of-fit on F^2	1.089
Bond lengths [Å] and angles [deg]	
Si(1)-Si(7)	2.4033(7)
Si(1)-Si(8)	2.33734(8)
Si(1)-Si(2)	2.3613(7)
Si(2)-Si(3)	2.3603(7)
Si(8)-Si(1)-Si(7)	110.29(3)
Si(2)-Si(1)-Si(6)	102.27(3)
Si(2)-Si(3)-Si(4)	117.96(4)
Si(2)-Si(1)-Si(8)	110.43(3)

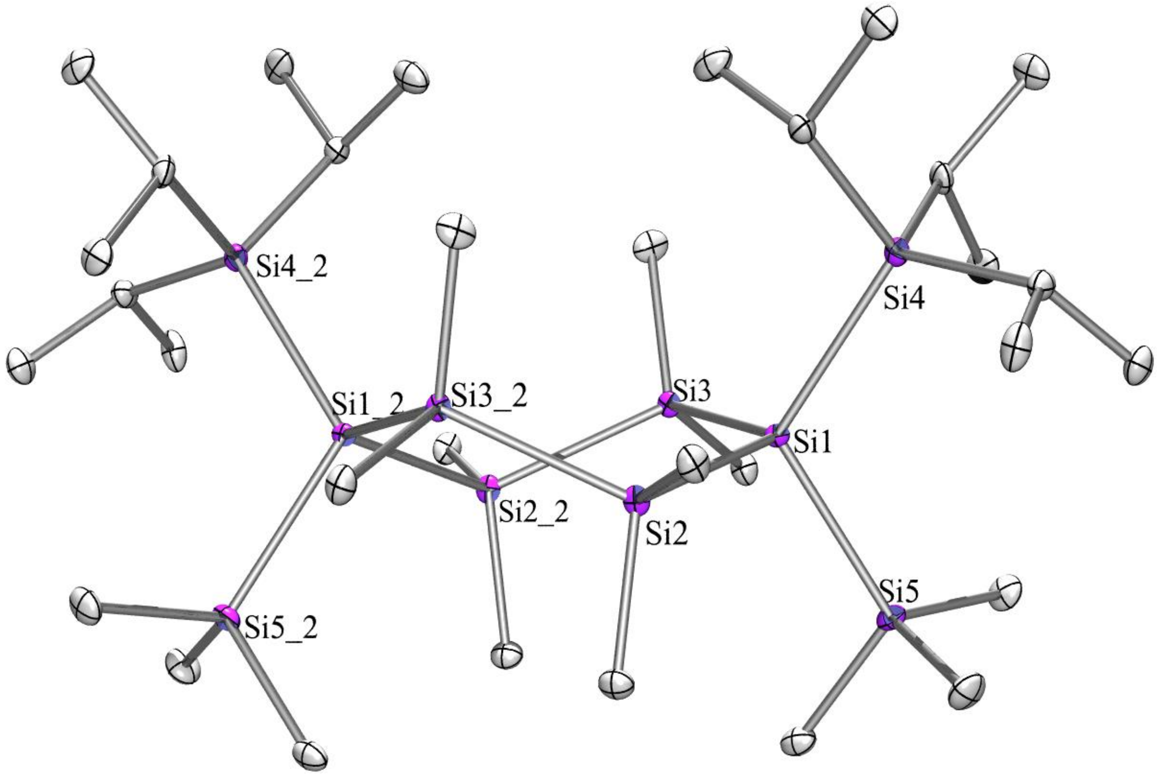


Figure 6-1: Crystal structure of compound **65**, *cis* isomer.

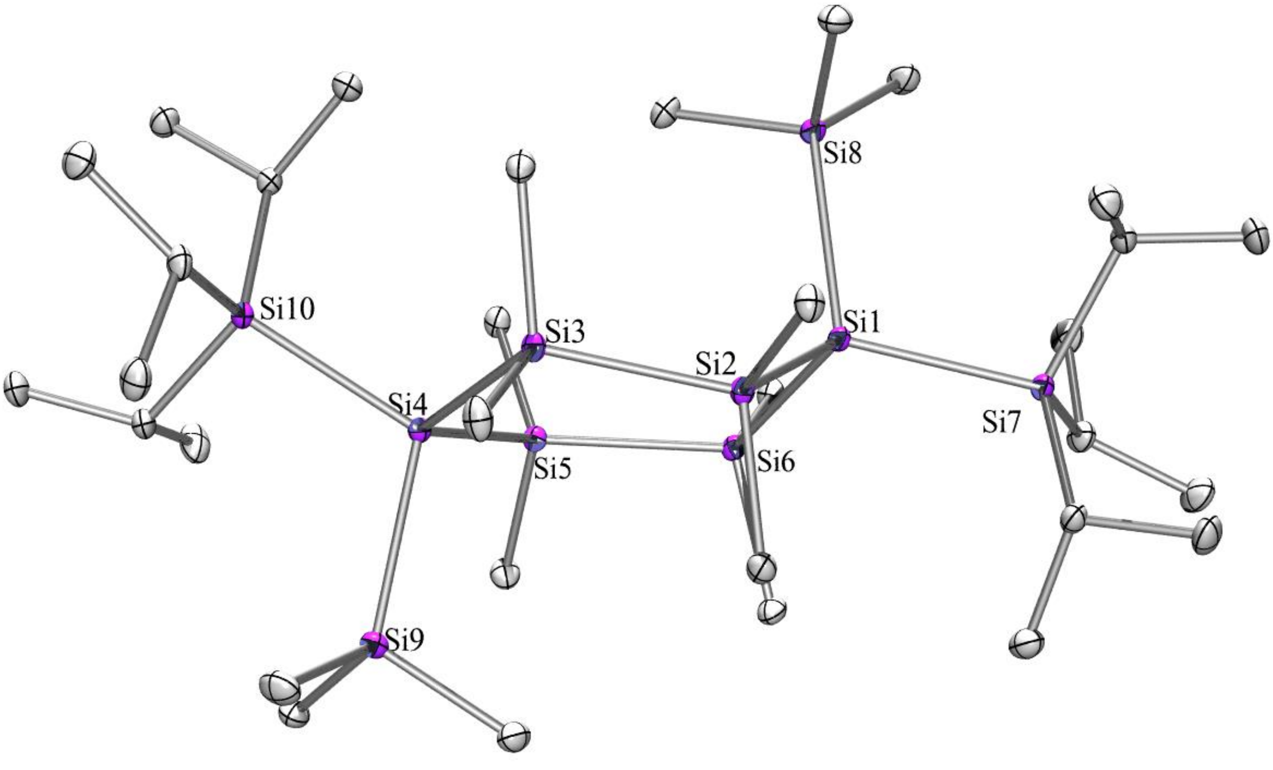


Figure 8-1: Crystal structure of compound **65**, *trans* isomer.

In respect of similar compounds (1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane – Figure 9-1,[26] and 1,4-bis(trimethylsilyl)-1,4-bis(dimethyl*tert*burtylsilyl)octamethylcyclohexasilane – Figure 10-1[8]) the silicon-silicon bonds Si(1)-Si(4) and Si(1)-Si(7) were slightly elongated. In the case of compound **65** the Si(1)-Si(4) and Si(1)-Si(7) bond lengths were ca. 2.40 Å, while for the cited compounds bond distances of 2.35 Å[8] and 2.39 Å[26] were reported, respectively). Due to the higher steric hindrance of the triisopropylsilyl group in comparison with that one of the trimethylsilyl groups and the dimethyltertbutyl groups, in the case of the **65-*cis*** isomer, also the Si(1)-Si(5) bond lengths were slightly increased.

On the other hand, bond lengths and angles of the silicon rings of both isomers of compound **65** were not strongly affected by the presence of the triisopropylsilyl substituents.

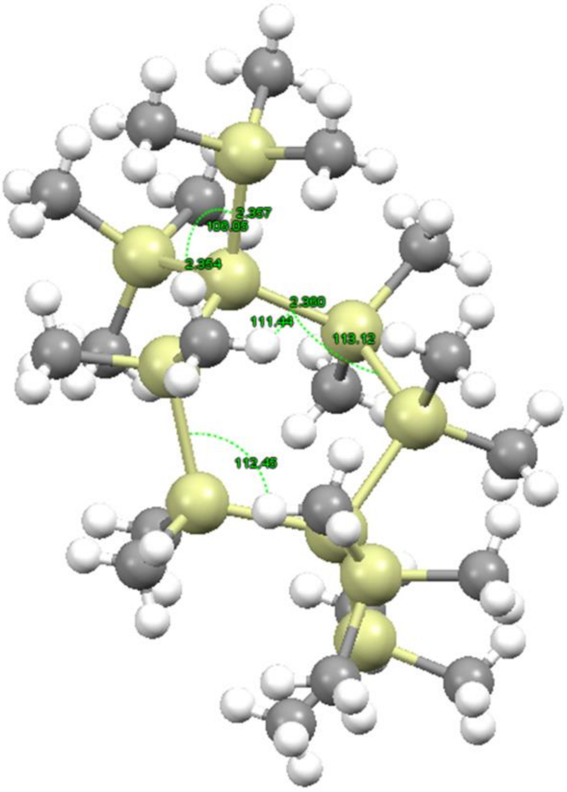


Figure 9-1:
1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane[26]

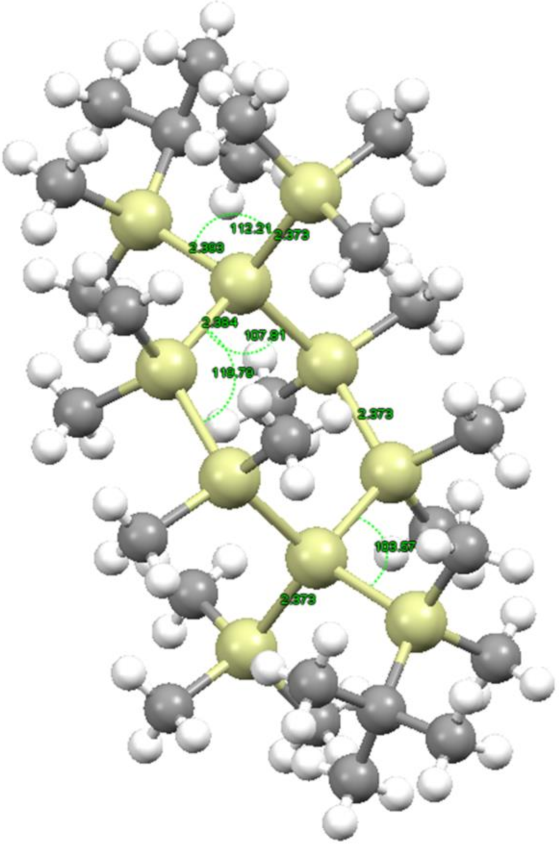


Figure 10-1:
1,4-bis(trimethylsilyl)-1,4-bis(dimethyl*tert*burtylsilyl)
octamethylcyclohexasilane[8]

---

[26] R.Fischer, T.Konopa, S.Ully, A.Wallner, J.Baumgartner, C.Marschner, *Organosilicon Chem.:From Mol.to Mater.*, **2005**, *6*, 355-360.

The ^{29}Si NMR spectrum of the product, acquired before crystallization, already showed the presence of the two isomers (Figure 11-1).

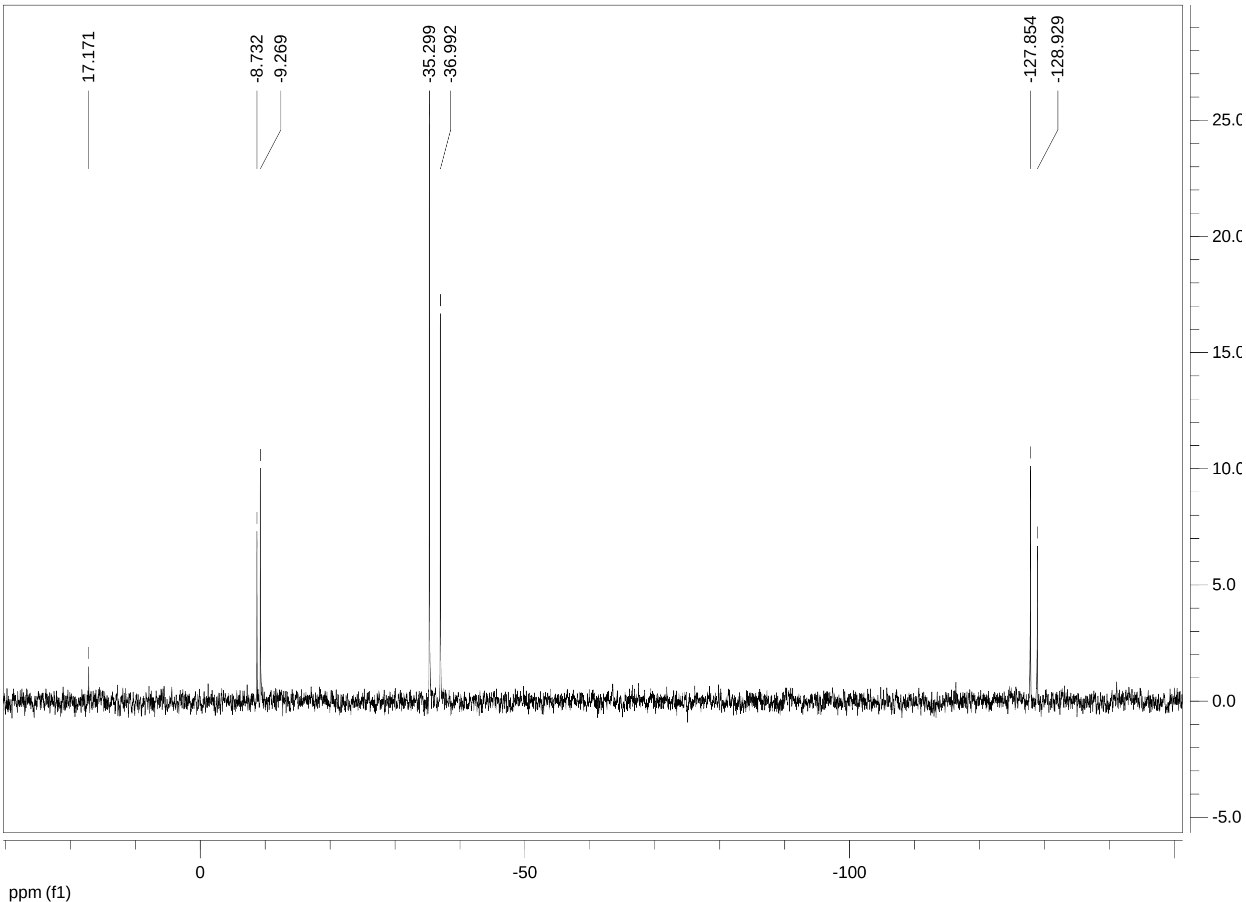
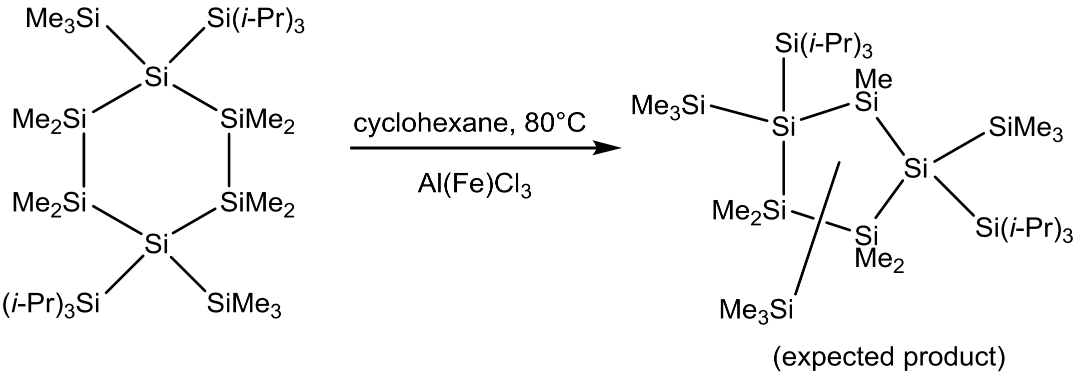


Figure 11-1: ^{29}Si NMR spectrum of the worked up product **65** (*cis* and *trans* isomer mixture). Just one signal for the triisopropylsilyl groups was visible.

A small amount of compound **65** was treated with Al(Fe)Cl_3, in cyclohexane at 80°C (Scheme 25-1). A ring contraction was expected, together with the migration of the isopropyl groups.[10,11]



Scheme 25-1: Rearrangement of 1,4-bis(trimethylsilyl)-1,4-bis(triisopropylsilyl)octamethylcyclohexasilane (**65**), with aluminum trichloride.

However, a quite complex mixture was generated (see ^{29}Si NMR spectrum in Figure 12-1).

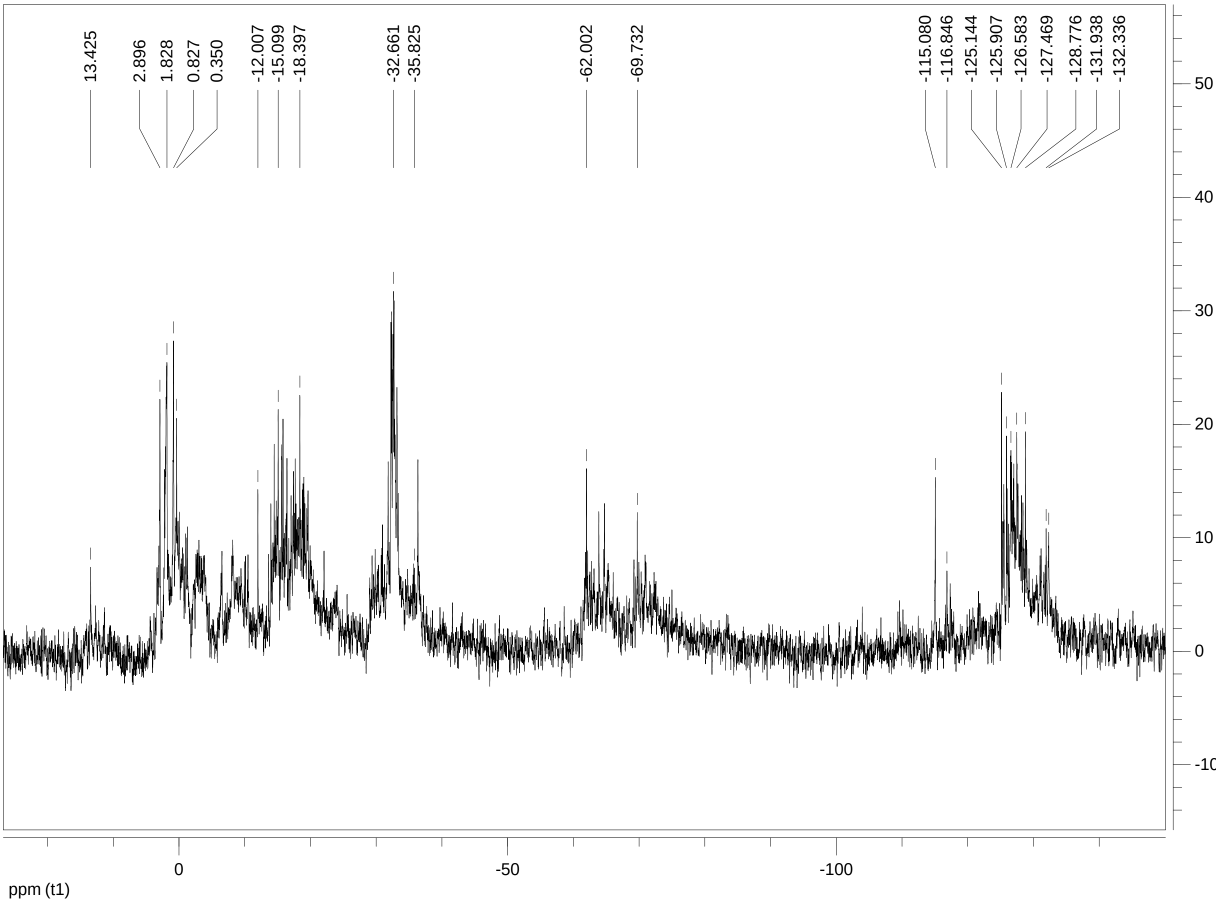


Figure 12-1: ^{29}Si NMR spectrum of the reaction mixture from the rearrangement of compound **65**.

At least eight types of quaternary silicon atom were formed (peaks between -133 and -125 ppm). In addition, the signals around -70 ppm could indicate the formation of tertiary silicon atoms in thew structure (R*Si*Si_3). The peaks in the range of 0-3 ppm suggested the formation of silyl groups carrying both methyl and isopropyl groups.

2. Synthesis and Rearrangement of not Permethylated Oligosilanes with Trityl Tetrakis(pentafluorophenyl) Borate

2.1 Rearrangement reactions catalyzed by trityltetrakis(pentafluorophenyl) borate – TTPFPB

The main conclusions arising from the previous isomerization reactions, carried out with aluminum trichloride as catalyst, could be summarized as follow (Table 1-2):

Advantages	**Disadvantages**
Catalyst easily available	Always chlorinated by-products are forming
Low cost of commercial $AlCl_3$	Some reactions did not work at all
Quick and easy handling of the reactions in CH_2Cl_2	Some reactions required a large amount of “catalyst” and a long reaction time

Table 1-2: Comparison between aluminum trichloride (on the left) and the trityl borate salt (on the right) as catalysts for the rearrangement reactions.

The chance that the substrate undergoes chlorination, because of a methyl-chloride exchange with aluminum trichloride, can be suppressed employing not halogenated Lewis acid. Chlorine is not a strong base but the transient silyl cation is so reactive that it does not differentiate sufficiently between a methyl group and a halogen atom to quench its electron deficiency. Often this problem was by-passed by treating the reaction mixture with methyl lithium, replacing in this way all the chlorinated sites with a methyl group.[4] But for the reactions presented here, this procedure might be risky, because different types of alkyl groups are involved in the process and it is not said that aluminum trichloride coordinates just the methyl groups or maybe also the isopropyl or the butyl groups.

Andreas Wallner in this research group and Lena Albers in our partner group at Carl von Ossietzky Universität Oldenburg, started to work using a different type of Lewis acid, a trityl cation with a very bulky and hindered counter-anion, the triphenyl carbenium tetrakis(pentafluorophenyl)borate (TTPFPB). This frustrated Lewis pair provides a very low basicity from the anionic side, while the Ph_3C^+ carbenium ion is quite reactive and can easily coordinate bases as phosphine and amines[27] and it is widely used as initiator, catalyst, and co-catalyst in the polymerization of olefins.[28,29,30,31]

---

[27] L. Cabrera, G.C. Welch, J.D. Masuda, P. Wei, S.W. Douglas, *Inorg. Chim. Acta*., **2006**, *359*, 3066-3071.
[28] A. F. Johnson, D.A. Pearce, *J. Polym. S.*, Polymer Symposia, **1976**, *56*, 57-69.
[29] J. Wang, H. Li, N. Guo, L. Li, C.L. Stern, T.J. Marks, *Organometallics*, **2004**, *23*, 5112-5114.
[30] S.W. Ewart, M.J. Sarsfield, W.F. Edan, M.C. Baird, *J.Organomet. Chem*., **1999**, *579*, 106-113.

First experiments using this Lewis acid for the rearrangement of permethylated oligosilanes and oligogermanes were quite promising:[32] the same reaction patterns were observed as in the rearrangements with aluminum chloride, but with lower molecular amounts of catalyst and a cleaner set of products because of the absence of chlorinated by-products. In these experiments the TTPFPB salt is not really a catalyst, since it is consumed to give CH_3CPh_3. It acts as a starter for the reaction: it removes a methyl group from the substrate, generating an oligosilylcation that performs the skeletal rearrangement. Then, the thus formed cationic intermediate can abstract a methyl group from another molecule of substrate, giving a neutral rearranged species and a new intermediate that will isomerizes again and continue the process. The reaction usually proceeds till all the starting material has been rearranged.

This catalyst was employed on different substrates, using first CH_2Cl_2 as solvent at room temperature, and then cyclohexane at 80°C.

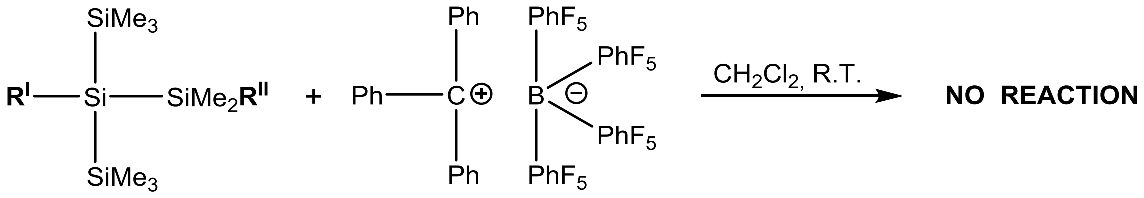
---

[31] T. Tsutomu; K. Takenoya, *Reactive & Functional Polymers*, **1996**, *30*, 251-260.

[32] L. Albers, A. Wallner, J. Baumgartner, C. Marschner, T. Müller, *poster Eur. Silicon Days - Lyon*, **2012**.

2.2 Rearrangements of oligosilanes using CH_2Cl_2 as solvent

TTPFPB is completely soluble in dichloromethane, giving a bright orange solution. The substrates previously prepared were submitted to the rearrangement process, but no reaction occurred under these conditions (Scheme 1-2, see experimental part):



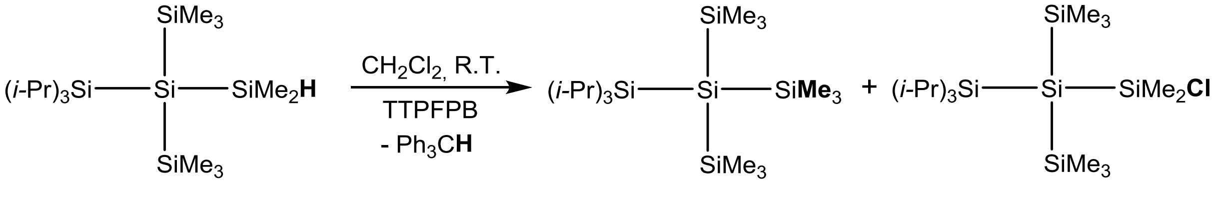
R^{I} = Si(*i*-Pr)$_3$, Si(*n*-Bu)$_3$ or SiMe$_2$Thex
R^{II} = Me or SiMe$_3$

Scheme 1-2: General scheme reaction for rearrangement of substrates **2**, **3**, **4**, **5** and **7**; 0.05 – 0.4 eq. of TTPFPB, until 10 days of stirring.

It is possible that the solvent it is too strongly coordinated to the trityl cation, reducing its activity and thus preventing the abstraction of a methyl group from the substrate. In fact, during the preparation of the catalyst itself, TTPFPB cannot be crystallized/precipitated directly from dichloromethane, because a dense oil is always forming. The interactions between the chlorinated solvent and the trityl salt can be avoided by using large amount of pentane (or other hydrocarbons) and applying sonication to destroy the CH_2Cl_2/trityl complex to obtain the pure borate salt.

2.2.1 Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane (14)

In order to promote the reactivity of the substrate, one methyl group of substrate **2** was substituted by a hydrogen atom (see experimental part): due to its higher electronegativity, the hydrogen of **14** behaves as a hydride and it should be easily abstracted by the catalyst to form triphenyl methane. A silyl cation is thus generated and the isomerization of the molecule could then start (Scheme 2-2).



14 **2** **9**

Scheme 2-2: Rearrangement reaction promoted by a hydride abstraction, in dichloromethane, at room temperature, 0.1 eq. of TTPFPB, 3 days.

With 0.1 eq. of catalyst and after 3 days the starting material was completely consumed. Surprisingly, a mixture of products was obtained, which was extremely similar to that one obtained from the rearrangement of **2** with aluminum trichloride (Scheme 18-1).

Hydride abstraction from the reagent can be performed in dichloromethane, but then the intermediate silylcation does not undergo any rearrangement: it removes a methyl group from another molecule of substrate, or a chloride from the solvent (the only source of chlorine in the reaction mixture). The NMR of the reaction mixture is shown in Figure 1-2.

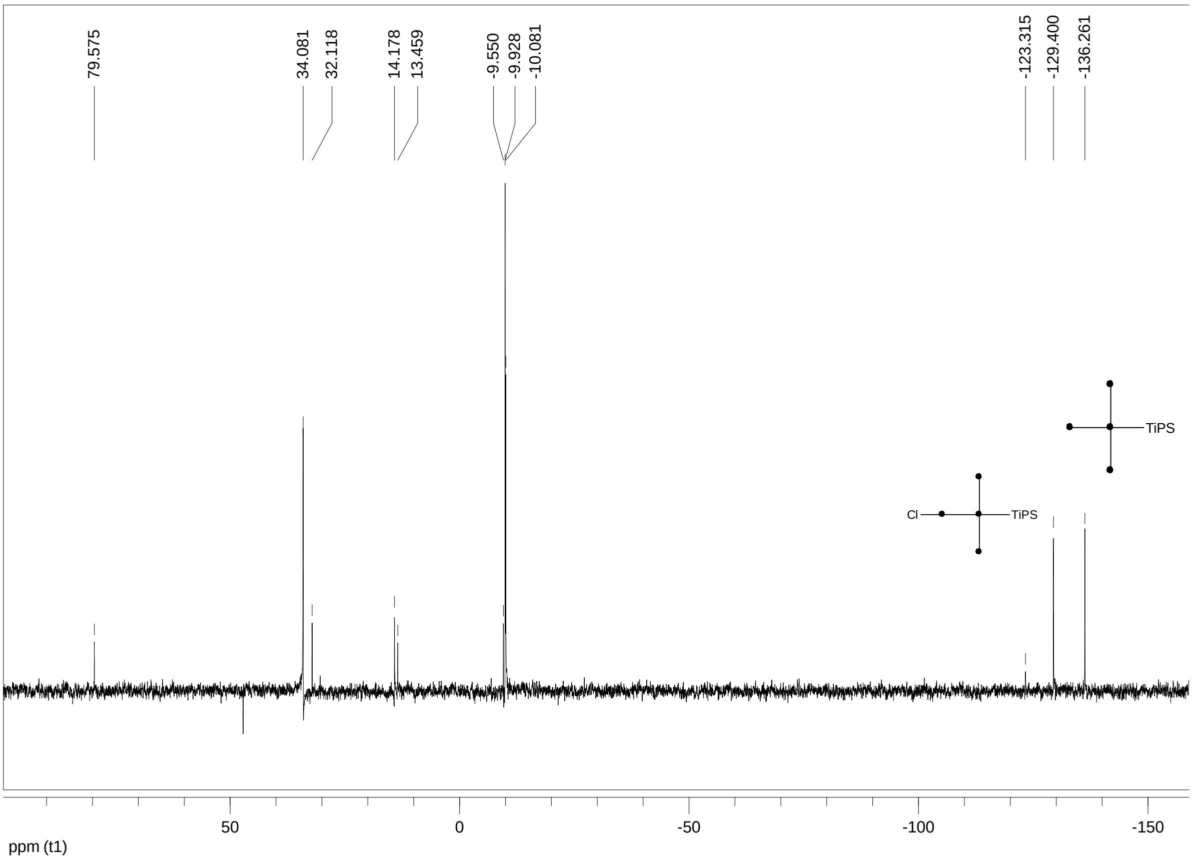


Figure 1-2: ^{29}Si NMR of the rearrangement of compound **14** with TTPFPB. TIPS = -Si(*i*-Pr)$_3$.

The products resulting from this reaction were formed almost in the same amount. Compound **2** presents its typical signals in the ^{29}Si NMR spectrum at -136.2 ppm, -10.0 ppm and 13.4 ppm. Chlorinated derivative **9** has chemical shifts at -129.4 ppm, -9.9 ppm, 14.1 ppm, and 34.0 ppm. Peaks at -123.3 ppm, -9.5 ppm and 32.1 ppm might be due to subsequent chlorination of **9**. A small signal at 79.5 ppm it is in the common range of a silyl cation species,[33] and it might be given by a small amount of intermediate still present in solution.

---

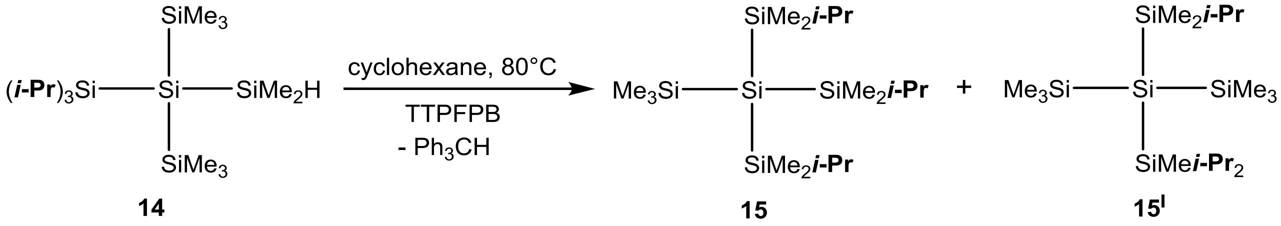
[33] J.B. Lambert, S. Zhang, S.M. Ciro, *Organometallics*, **1994**, *13*, 2430-2443.

2.3 Rearrangement of oligosilanes with TTPFPB in cyclohexane as solvent

To avoid any source of chlorine that rapidly reacts with the forming silyl cation, dichloromethane was substituted by cyclohexane. This hydrocarbon provides very good solubility for the substrates, but usually it requires working with Schlenk flasks at 80°C, the boiling point of this solvent. Interestingly, at the beginning of these reactions, the catalyst is completely suspended in the reaction mixture. However, after some hours of stirring, the yellow powder of TTPFPB goes into solution, and the reaction mixture becomes quite clear and palely yellow.

2.3.1 Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane (14)

The reaction shown in Scheme 2-2 was repeated in cyclohexane at 80°C, with 0.1 equivalent of catalyst (Scheme 3-2). After 4 days of reaction, the starting material was completely consumed (absence of the typical signal for the -$SiMe_2H$ group at ca. -30 ppm). The work up led to a dense and transparent oil. The ^{29}Si NMR spectrum of this material is reported in Figure 2-2.



Scheme 3-2: Rearrangement reaction promoted by a hydride abstraction, in cyclohexane at 80°C,0.1 eq. of TTPFPB, 4 days.

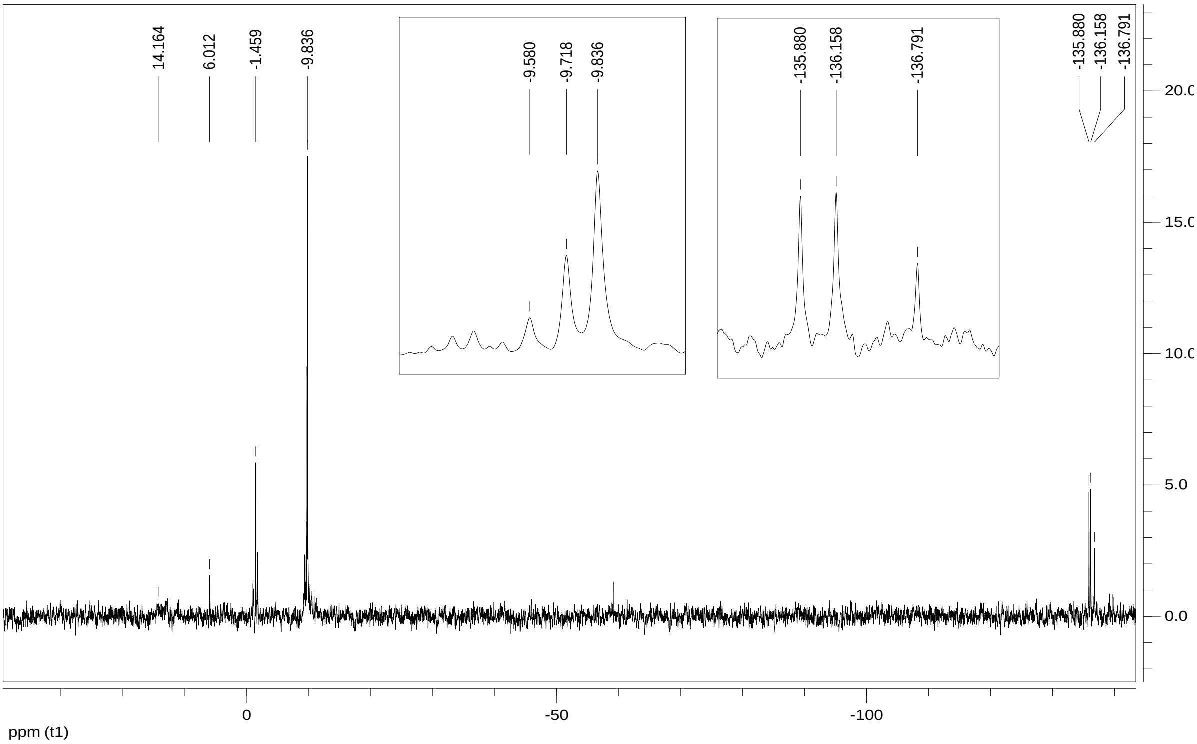


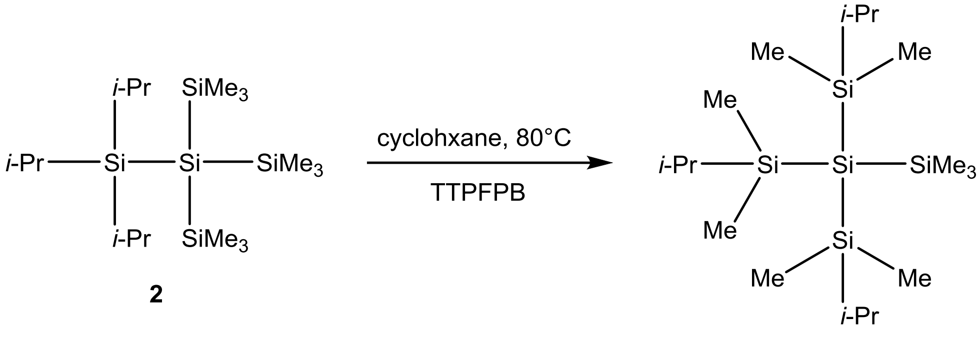
Figure 2-2: ^{29}Si NMR of *i*-$Pr_3Si(Me_3Si)_2SiMe_2H$ (**14**) treated with 0.1 eq. TTPFPB, in cyclohexane/80°C, for 4 days.

Three signals in the quaternary silicon region of the spectrum implies that three main products are present in the mixture. Compound **2** was formed (peaks at -135.9 ppm, -9.8 ppm and 14.1 ppm, respectively Si_q, -$SiMe_3$ group and -Si(*i*-Pr)$_3$ group) but also two new products that show unusual chemical shifts, due to the rearrangement process. Signals at -136.8 ppm, -9.5 ppm and -1.4 ppm can be assigned to compound **15**, where the isopropyl groups are completely spread through the molecule. The isopropyldimethylsilyl group can be detected at -1.4 ppm in the ^{29}Si NMR spectrum.

It is also interesting to observe the middle step of the isomerization, compound **15^{I}**. In this case only one isopropyl group has migrated, exchanging with a methyl group: signal at 6.0 ppm should be referred to the diisopropylmethylsilyl group (the signal from *i*-$PrMe_2Si$- of **15^{I}** it is probably too close to that one of compound **15** to be solved; the quaternary silicon atom has a chemical shift at -136.1 ppm, confirmed by subsequent experiments).

2.3.2 Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropyl disilane (2)

The isomerization of substrate **2** was repeated in cyclohexane at 80°C (Scheme 4-2).



Scheme 4-2: Rearrangement reaction of 1,1,1-tris(trimethylsilyl)triisopropyl disilane (**2**), 0.1 eq. of TTPFPB, 5 days, ca. 200 mg of substrate.

The reaction was quite clean, with a complete conversion of the starting material. The main product was compound **15**, but a small amount of "intermediate" **15^I** was formed too (see ^{29}Si NMR spectrum in Figure 3-2).

After the work up, a glassy semi-transparent solid mass was isolated. It was not possible to isolate single crystals for X-ray analysis, despite a number of attempts using different techniques (slow evaporation of the solvent – acetone, dichloromethane, ethylacetate, pentane/isopropanol mixtures; double vial crystallization with cyclohexane as solvent and acetone as antisolvent; precipitation at low temperature in different solvents; solvents layering crystallization). The isopropyl groups are heavier than the methyl groups and usually they confer good crystallization ability to the products as in the case of compound **2**. However, in the case of compound **15** the symmetric distribution of the isopropyl groups gives the molecules no preferential ways to aggregate during crystallization. Therefore, an amorphous solid was obtained. For comparison, tetrakis(trimethylsilyl)silane (**1**), that is completely symmetric, crystallizes as thin needles that but the structure of **1** was determined by high resolution X-ray analysis only using a synchrotron light source.[34]

---

[34] R.E. Dinnebier, W.A. Dollase, X. Helluy, J. Kummerlen, A. Sebald, M.U Schmidt, S. Pagola, P.W. Stephens, S. Van Smaalen, *Acta Crystall. B Stru.*, **1999**, *B55*, 1014-1029.

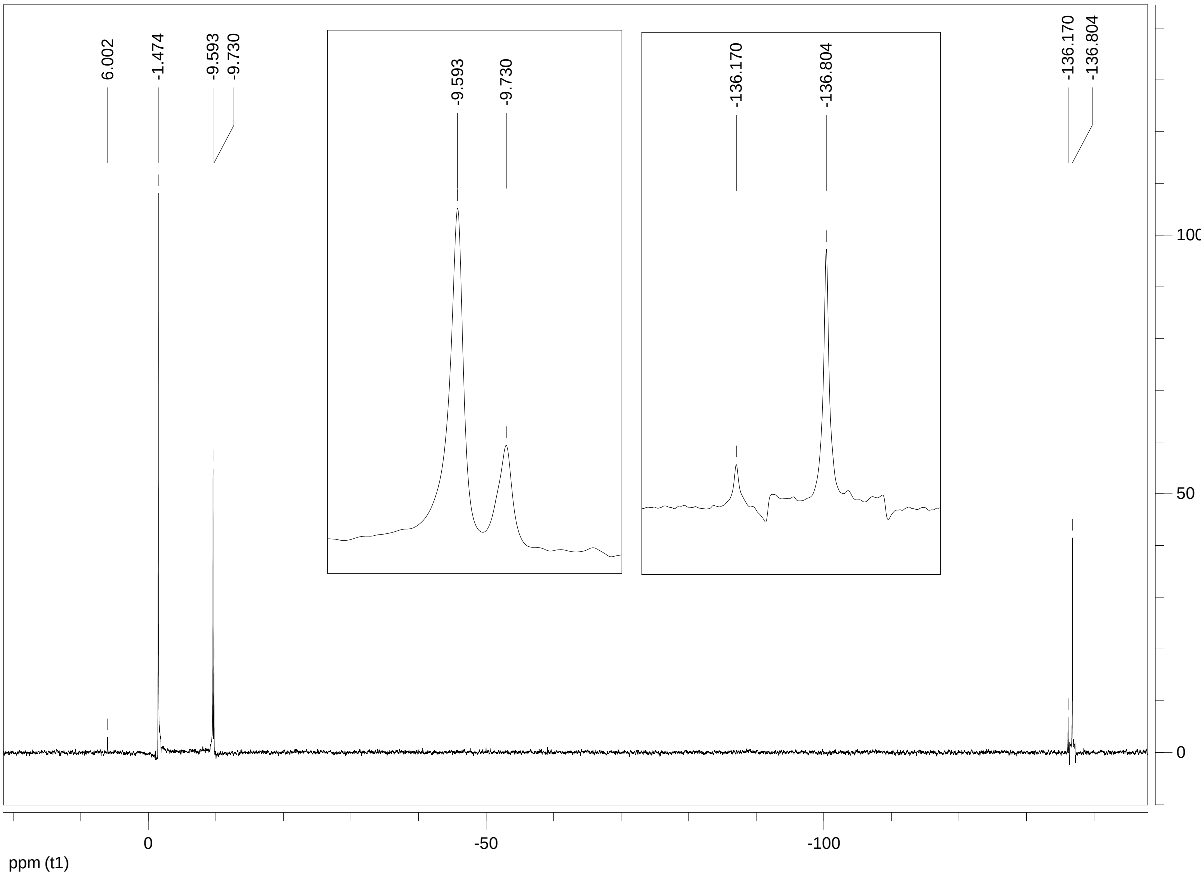


Figure 3-2: ^{29}Si NMR rearrangement of *i*-$Pr_3Si(Me_3Si)_3Si$ (**2**), 0.1 eq. of TTPFPB, 5 days of reaction.

This reaction was repeated in a larger scale, starting with ca. 1 gram of substrate and 0.01 equivalents of TTPFPB. The reaction worked in the same manner, but as before an amount of catalyst of 0.1 eq. had to be added for complete conversion.

The rearrangement was repeated also with Al(Fe)Cl_3 as catalyst, in cyclohexane at 80°C. The reaction did not work in CH_2Cl_2 at room temperature, but surprisingly it worked under the “classical” reaction conditions. The spectrum was less clean than the one shown here (there were some chlorinated by-products), but it was possible to observe the chemical shifts of the mixed methyl and isopropyl groups on the same silicon atom (6.0 ppm and -1.4 ppm). Al(Fe)Cl_3 worked better at 80°C in chlorobenzene as solvent: a small fraction of chlorinated substrate and an almost complete conversion were obtained.

Also for this reaction, the formation energies of the isomerized products were calculated by Lena Albers in our partner group at Carl von Ossietzky Universität Oldenburg (Figure 4-2).[25] These calculations show that the rearrangement process is thermodynamically favored, but with a ΔG value for compound **15**^{I} slightly more negative than the one for **15**, which is in contrast to our experimental results. Probably the steric interactions were underestimated, and the reaction from **15**^{I}/**II** to **15**/**III** should be still favored.

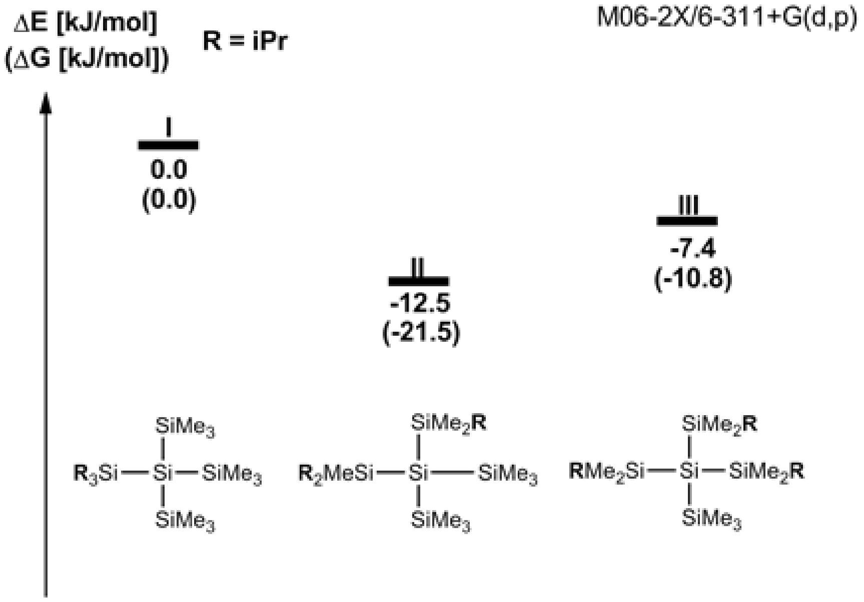


Figure 4-2: Calculated formation energies for products **15**^{I}/**II** and **15**/**III** in respect to the starting material **2**.

The reaction mechanism might be represented as in Figure 5-2. Substrate **2** is activated by the catalyst and a positive charge is induced/generated in the molecule. The abstraction of an isopropyl group by TTPFPB seems not likely, since it is possible to detect by GC/MS the by-product Me-CPh_3 in the case of methyl abstraction, but not the by-product *i*-Pr-CPh_3.[25] Then one isopropyl migrates to the tri-substituted silyl cation, thus forming a [*i*-Pr $_2Si^+$] fragment in the molecule. The better electron-donating behavior of the isopropyl group in respect to the methyl group probably drives the isomerization in this direction. The new cationic species could abstract a methyl group from another molecule of substrate, thus producing **15^I** and concluding the process, or it could undergo internal migration of a methyl group, forming again a [-Me_2Si^+] fragment and a -SiMe*i*-Pr_2 group. One of these two isopropyl groups shifts to the silyl cation, and a -$SiMe_2$*i*-Pr is once again formed together with a [-Me*i*-PrSi$^+$] unit. The latter group could now remove a methyl from the substrate, or it could undergo a further internal methyl migration (from a -$SiMe_3$ group) and then finally produce **15** by the reaction with the starting material itself.

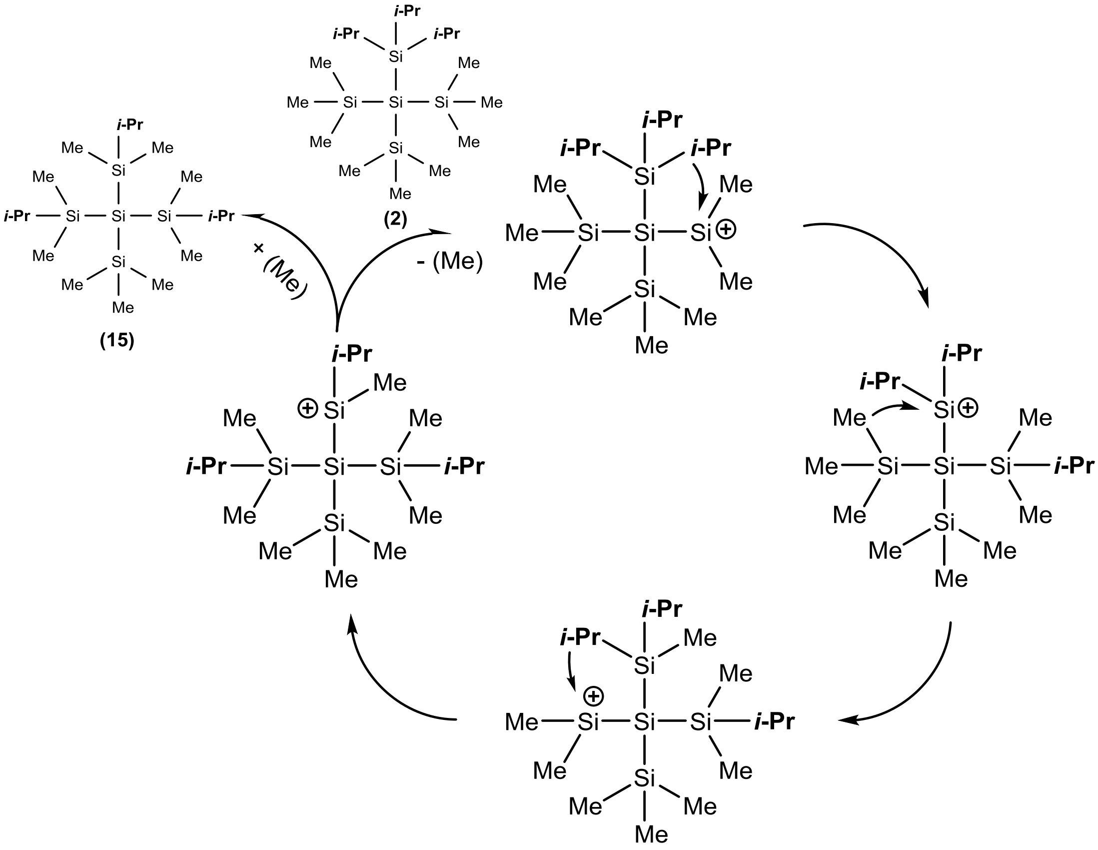
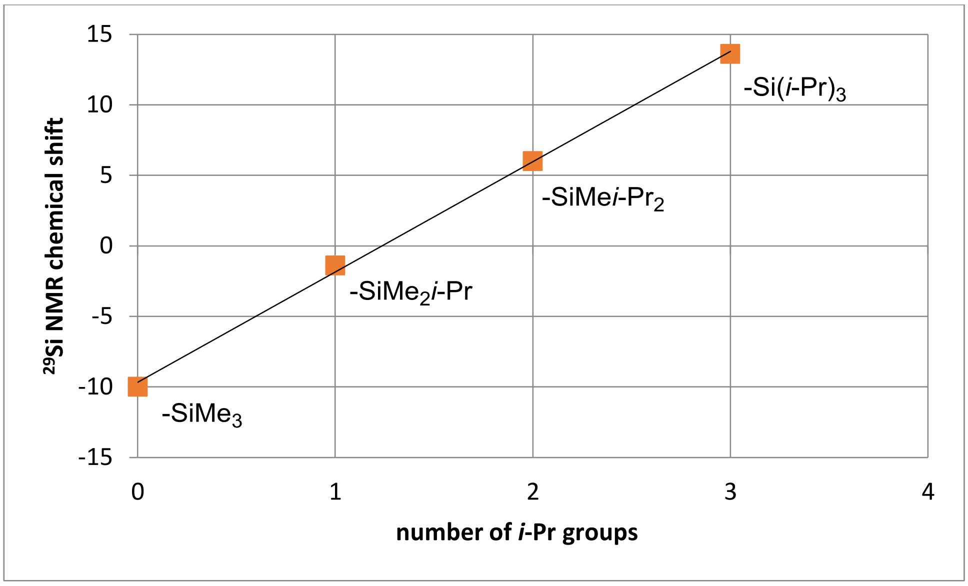


Figure 5-2: Proposed mechanism for reaction described in Scheme 4-2.

A simple but useful investigation about the ^{29}Si NMR chemical shifts of the -SiMe$_n$*i*-Pr$_{3-n}$ groups of the isomerized compounds was pursued looking for some relationship between the number of isopropyl groups bonded to the silicon atom and the behavior of the signals in the silicon NMR spectrum. A good linear correlation was found, considering also the chemical shift of the -SiMe$_3$ group (Figure 6-2):



Nr. of *i*-Pr groups	**δ^{29}Si NMR**
0	-10.0
1	-1.4
2	6.0
3	13.6

$y = 7.82x - 9.68$

$R = 0.9994$

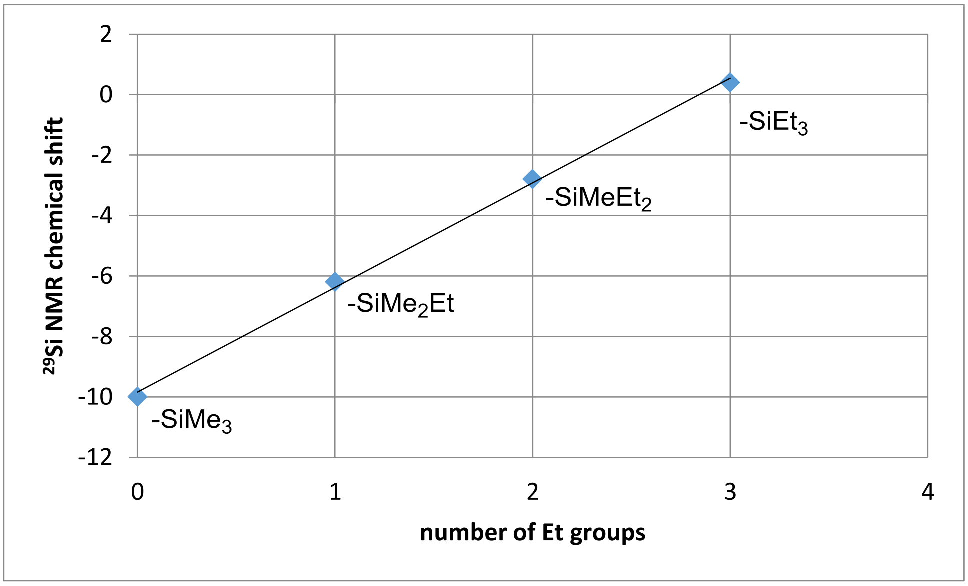
Figure 6-2: Linear correlation between -SiMe$_n$*i*-Pr$_{3-n}$ groups and their ^{29}Si NMR chemical shift.

As already stated, the presence of alkyl groups different from methyl bonded to a silicon atom always determines a low field shift of the signals in the ^{29}Si NMR spectrum. The more these alkyl groups are bulky and branched, the more this shift is pronounced.[35,36] In this case, the displacement of the methyl groups by an increasing number isopropyl groups provides a particularly regular shift of the NMR signals (relative to that silicon atom), that somehow can support spectra interpretation.

---

[35] N. Wiberg, W. Niedermayer, H. Nöth, J. Knizek, W. Ponikwar, K. Polborn, *Z. Naturforsch.*, **2000**, *55b*, 389-405.
[36] Y. Apeloig, M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, K. Klinkhammer, *Organometallics*, **1997**, *16*, 1265-1269.

In addition, a series of oligosilanes containing mixed ethyl and methyl groups bonded to the silicon atoms was prepared by Matsumoto et al. and characterized by ^{29}Si NMR.[37] These data are here reported as they show a good linear correlation and the same trend observed for the NMR chemical shifts of the -SiMe$_n$*i*-Pr$_{3-n}$ groups (Figure 7-2).



Nr. of Et groups	**δ^{29}Si NMR**
0	-10.0
1	-6.2
2	-2.8
3	0.4

$y = 3.46x – 9.84$

$R = 0.9992$

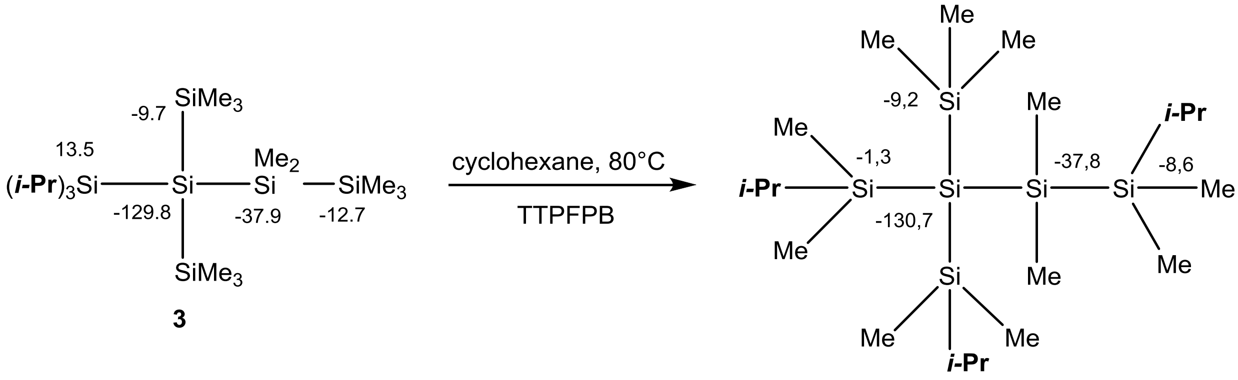
Figure 7-2: The compounds prepared in the cited paper were $(Et_3Si)_4Si$, $(Et_2MeSi)_4Si$, and $(EtMe_2Si)_4Si$.

---

[37] S. Kyushin, H. Sakurai, T. Betsuyaku, H. Matsumoto, *Organometallics*, **1997**, *16*, 5386–5388.

2.3.3 Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (3)

Also this isomerization was repeated in cyclohexane at 80°C in the presence of TTPFPB. The amount of catalyst was increased from 0.01 to 0.07 equivalents, to complete the conversion of the starting material (after 10 days, Scheme 5-2). In respect to the experiment shown in Scheme 19-1, the reaction pattern was slightly different and it nearly led to a single product. The ^{29}Si NMR spectrum (Figure 8-2) seems consistent with the structure of compound **12**. One -SiMe$_3$ is still present in the molecule (δ = -9.2 ppm). The intensity of the signal of the -SiMe$_2$*i*-Pr is higher than that one of the-SiMe$_3$ group, so there are two groups of this type bonded directly to the quaternary silicon atom (δ = -1.3 ppm). An unusual signal at -8.6 ppm suggests that only one isopropyl group migrated to the peripheral -SiMe$_3$, while in the previous experiment with Al(Fe)Cl$_3$ the peak at -4.8 ppm might be referred to the -SiMe(*i*-Pr)$_2$ bonded to the SiMe$_2$ unit.



Scheme 5-2: Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (**3**) with 0.07 eq. TTPFPB, 10 days of reaction. ^{29}Si NMR chemical shifts are reported (ppm).

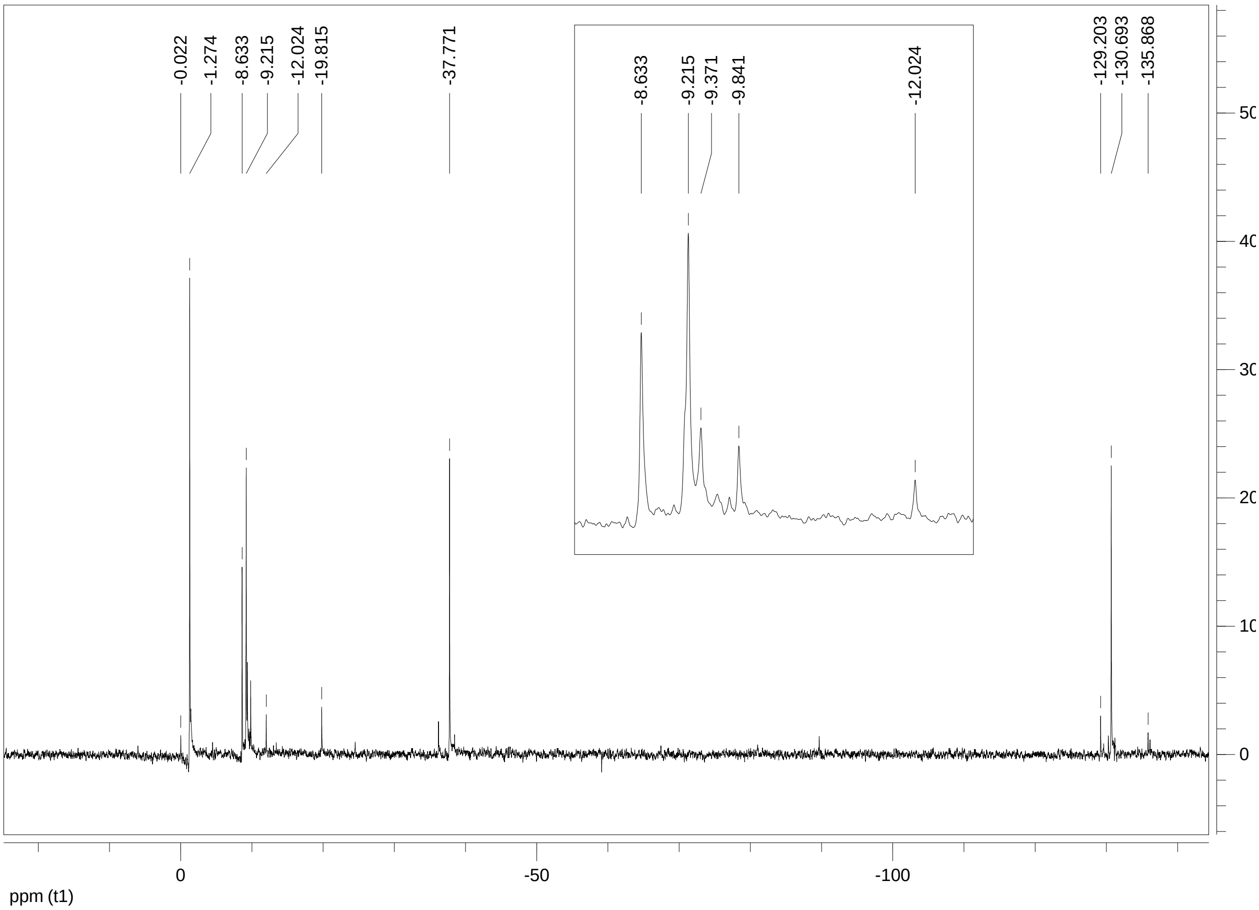


Figure 8-2: ^{29}Si NMR, rearrangement of compound **3**, 0.07 eq. of TTPFPB, 10 days of reaction.

This result is only partially in agreement with the distribution energies of the possible isomers shown in Figure 4-1. The formation of compound **X** (number **12** in our numbering) is thermodynamically favored in respect of the starting material, but product **VII** shows even lower ΔG and ΔE calculated values (Figure 9-2).

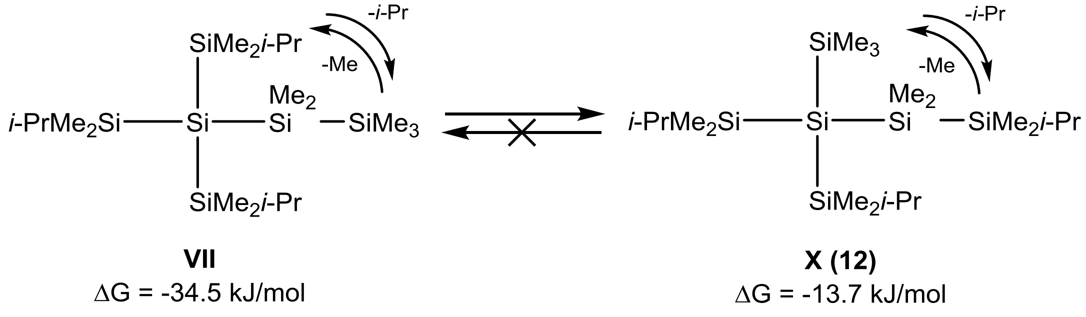
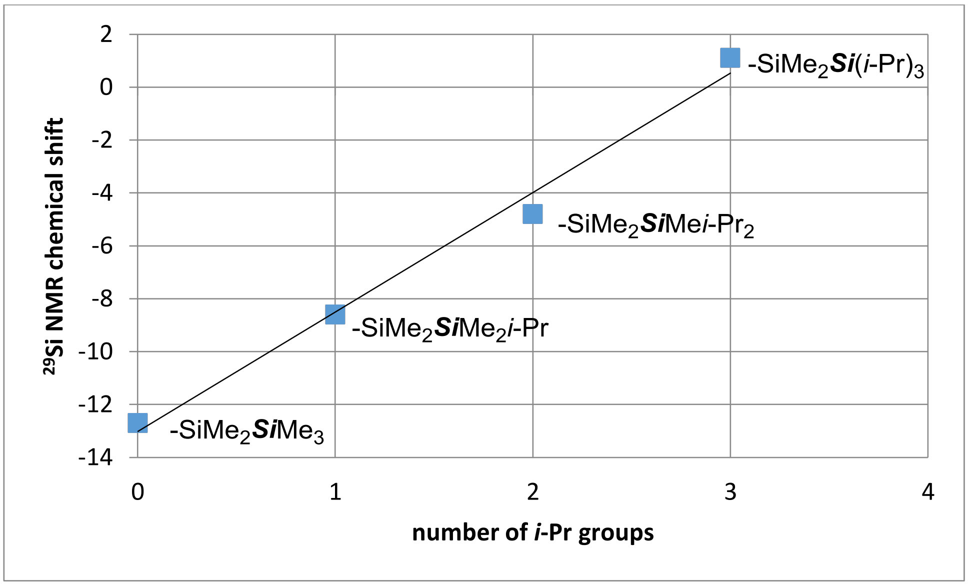


Figure 9-2: Comparison between calculated ΔG formation energies of isomers **VII** and the observed product **X/12** (complete distribution in Figure 4-1).

One possible explanation is that **VII** was probably formed during the reaction, but then the rearrangement continued and led to **X**. At this point, the isopropyl group was not able to migrate back, because of the steric hindrance provided by the isopropyl groups still present at the core of the structure.

To verify the correct interpretation of the spectrum for the isomerization of **3**, a possible correlation between the ^{29}Si NMR signals for the $SiMe_2SiMe_n$*i*-Pr_{3-n} groups was investigated (Figure 10-2).



Nr. of *i*-Pr groups	**δ^{29}Si NMR**
0	-12,7
1	-8,6
2	-4,8
3	1,1

$y = 4.52x – 13.03$

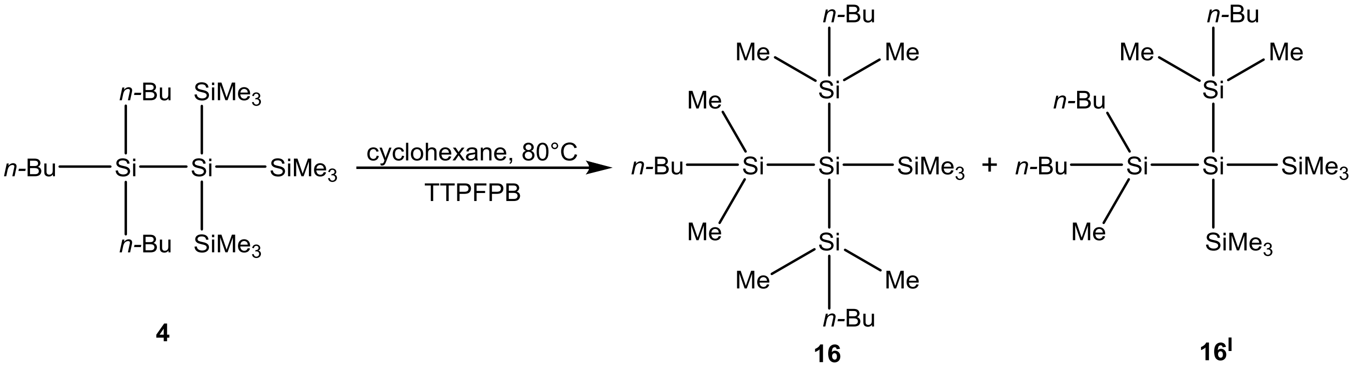
R = 0.995

Figure 10-2: linear correlation between the number n of the isopropyl groups in the $SiMe_2SiMe_{3-n}$*i*-Pr_n fragment, and their respective ^{29}Si NMR chemical shifts.

The least squares method gives again a good correlation between the numbers of the isopropyl groups bonded to the selected silicon atom and the ^{29}Si NMR chemical shift.

2.3.4 Rearrangement of 1,1,1-tris(trimethylsilyl)tributyldisilane (4)

The tributylsilyl derivative of tetrakis(trimethylsilyl)silane (**4**) was rearranged in cyclohexane at 80°C, with 0.2 eq. of TTPFPB, over a period of 5 days (Scheme 6-2). The expected product **16** was obtained quantitatively as a colorless oil.



Scheme 6-2: Rearrangement of 1,1,1 -tris(trimethylsilyl)tributyldisilane (**4**).

As for the rearrangement of compound **2**, also in this case the migration of the alkyl groups is almost complete. Calculations[25] showed that **16** should be the favored product, with 9.8 kJ/mol of ΔG gained energy in respect of **4** (Figure 11-2).

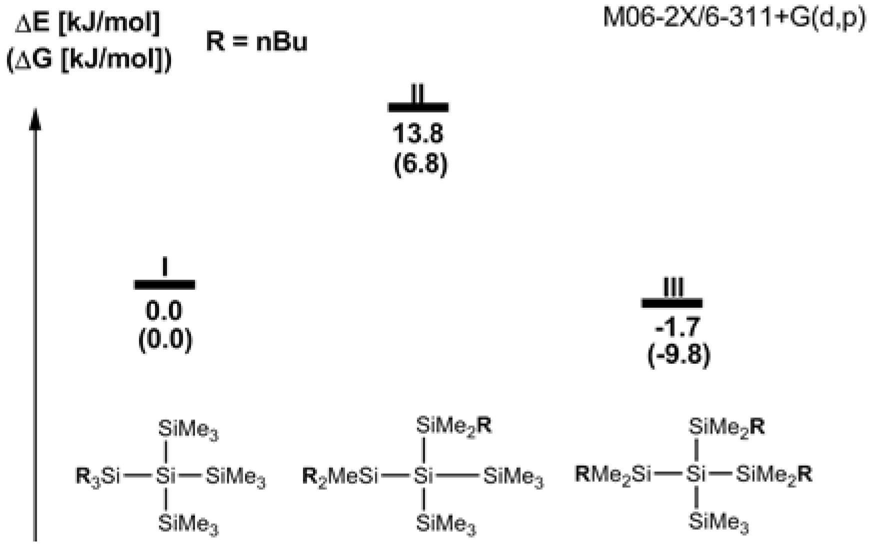


Figure 11-2: Calculated formation energies for products **16^{I}/II** and **16/III** in respect of the starting material **2**.

In the ^{29}Si NMR spectrum (Figure 12-2), the typical reversed signal at -2.1 ppm of the tributylsilyl group disappeared. The chemical shift at -7.8 ppm indicates the formation of butyldimethylsilyl groups, while the peak at -5.2 ppm (together with those at -136.8 ppm and at ca. -9.9 ppm, not visible) is due to the residual -SiMeBu$_2$ groups of the not completely rearranged substrate. In addition, the higher intensity of the signals at -7.8 ppm involves a higher numbers of silicon atoms of this type in respect of the -SiMe$_3$ group at -9.9 ppm.

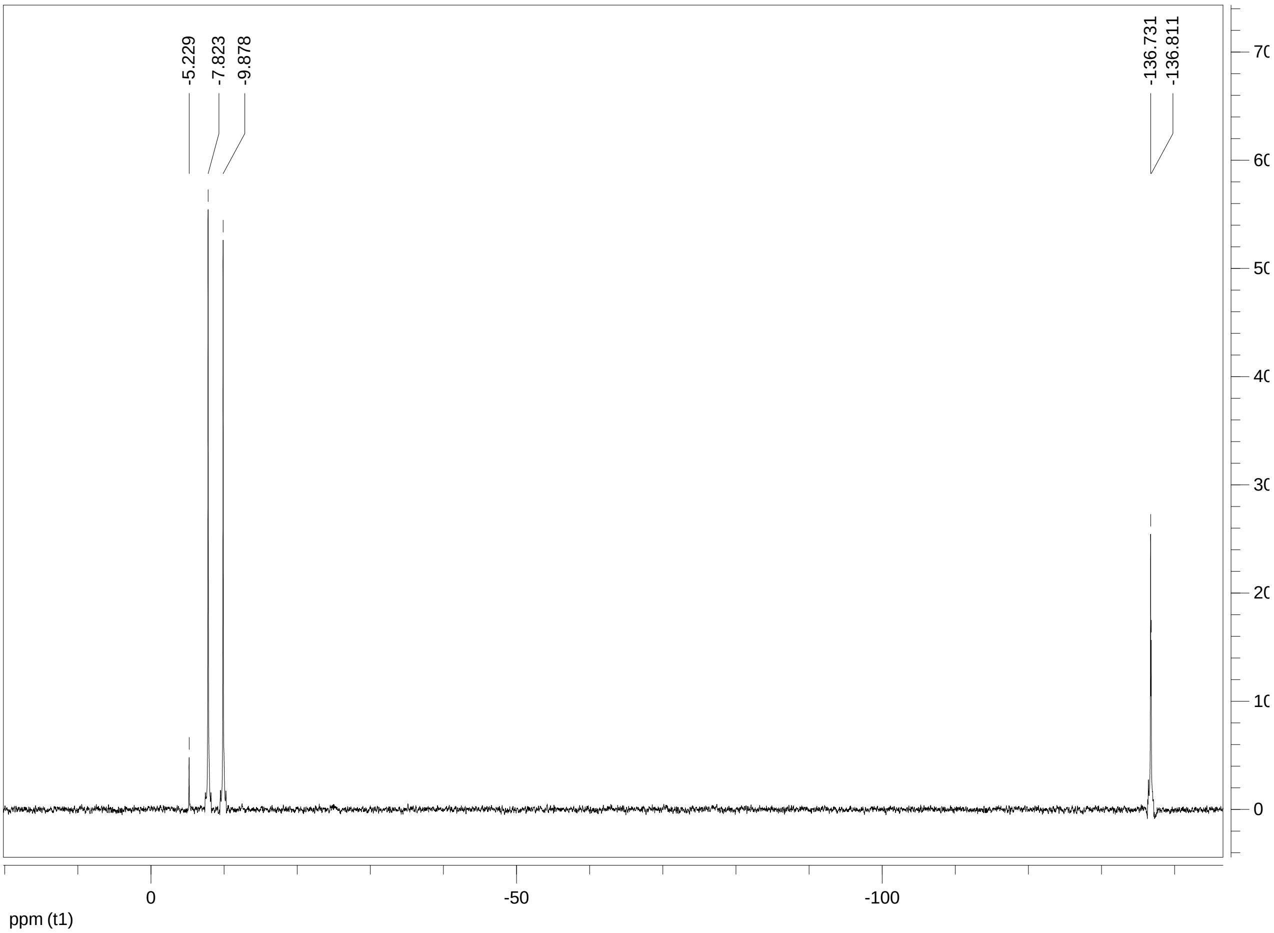
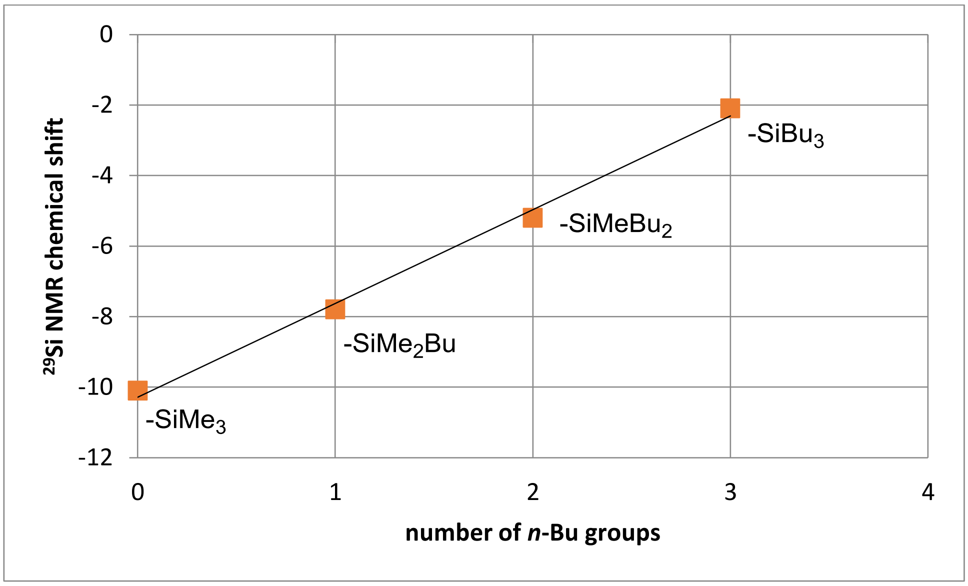


Figure 12-2: ^{29}Si NMR spectrum of 1,1,1-trimethyl-2,2,2-(dimethylbutylsilyl)disilane (**16**).

Even in this case, the chemical shifts of the $–SiMe_n(n\text{-}Bu)_{3-n}$ groups fit quite well with a linear regression straight line (Figure 13-2).



Nr. of ***n*-Bu** **groups**	**δ^{29}Si NMR**
0	-10.1
1	-7.8
2	-5.2
3	-2.1

y = 2.66x – 10.29

R = 0.998

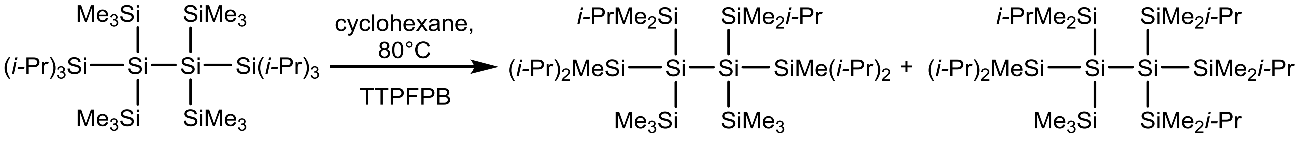
Figure 13-2: Linear correlation between the number n of the *n*-butyl groups in the $SiMe_{(3-n)}n\text{-}Bu_n$ fragments, and their respective ^{29}Si NMR chemical shifts.

2.4 Synthesis and rearrangement of new substrates functionalized with different alkyl groups

The previous results were quite promising and encouraged to explore the isomerization reactions of new oligosilanes, having higher number of silicon atoms in the structure, different alkyl groups in the same molecule, or containing germanium and tin atoms as well. The preparation of all these substances is described in the experimental part, while in the following chapters the reaction pattern and the spectroscopic data are discussed.

2.4.1 Rearrangement of 1,1,1,4,4,4-hexaisopropyl-2,2,3,3-tetrakis(trimethylsilyl)hexasilane (17)

Compound **17** was prepared from hexakis(trimethylsilyl)disilane, as previously reported.[38] The isomerization required 0.2 eq. of TTPFPB and 10 days of reaction to start (Scheme 7-2). After three more days, the mixture was worked up, leading a semisolid colorless material. The ^{29}NMR spectrum of this compound is shown in Figure 14-2.



17

Scheme 7-2: Rearrangement of 1,1,1,4,4,4-hexaisopropyl-2,2,3,3-tetrakis(trimethylsilyl)disilane (**17**) with 0.2 eq. of TTPFPB, 13 days; more probable isomers represented.

---

[38] Roland Fischer, *Dissertation*, **2001-2005**, Institut für Anorganische Chemie der Technischen Universität Graz.

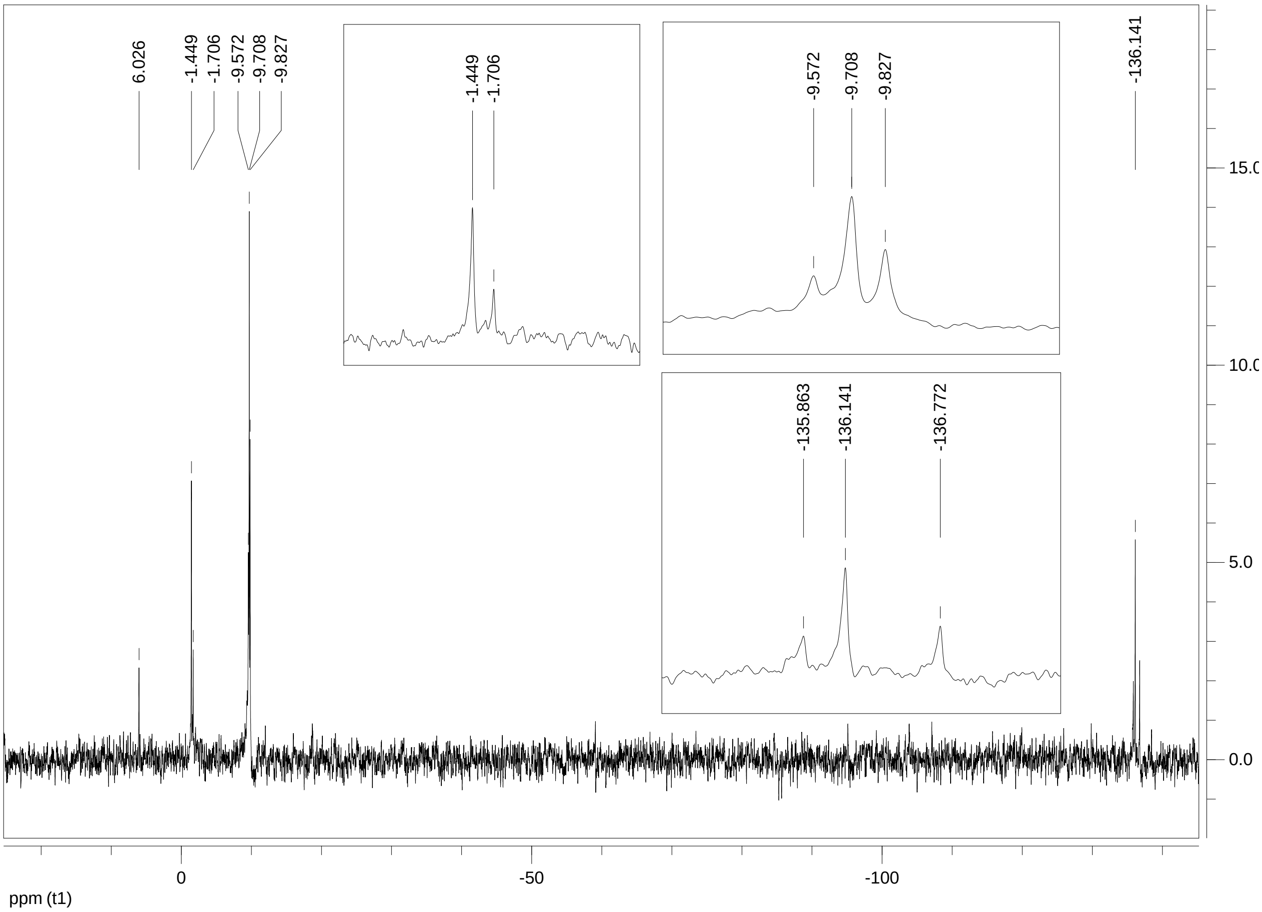
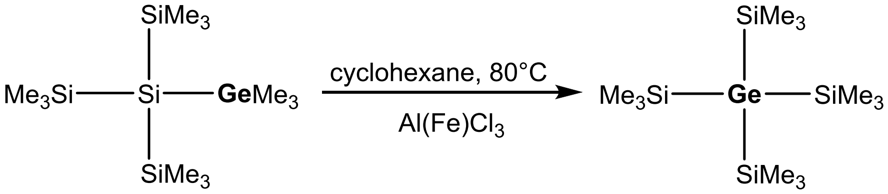


Figure 14-2: ^{29}Si NMR from rearrangement of (i-Pr$_3$Si)(Me$_3$Si)$_2$SiSi(Me$_3$Si)$_2$(i-Pr$_3$Si) (**17**) with TTPFPB.

The peaks of the trimethylsilyl groups were still present in the ^{29}Si NMR spectrum (-9.5 ppm, -9.7 ppm, -9.8 ppm). It means that a partial spreading of the isopropyl groups occurred. Starting material seems consumed (missing of the signals at -136.3, -10.1 and 13.6 ppm). Chemical shifts at -1.4 ppm and -1.7 ppm suggest that two types of dimethylisopropyl groups were formed in the mixture, while the signal at 6.0 ppm implies that diisopropylmethylsilyl group did not complete the rearrangement pattern as in the case of product **15**. Products represented in Scheme 7-2 seem the most consistent with the ^{29}Si NMR data.

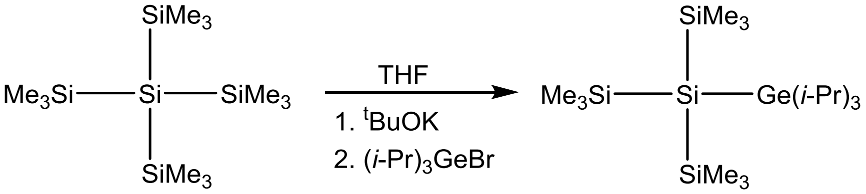
2.4.2 Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropylgermylsilane (18)

Wagner discovered[11] that organosilicon compounds having trimethylgermyl groups on the periphery of the molecule, could be rearranged by Al(Fe)lCl$_3$ and this isomerization involves the "shuttling" of the germanium atom towards the center of the molecule, with the formation of new silicon-germanium bonds (Scheme 8-2).



Scheme 8-2: Rearrangement of 1,1,1-tris(trimethylsilyl)trimethylgermylsilane.

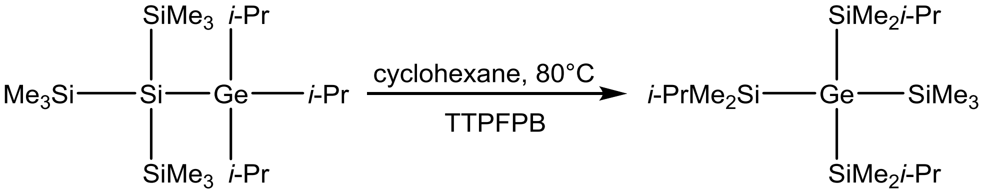
The question was if this rearrangement is still possible when the germanium atom is surrounded by more bulky alkyl groups. The triisopropylgermyl derivative of tetrakis(trimethylsilyl)silane **18** was prepared (Scheme 9-2). It crystallizes quite well and together with the ^{29}Si NMR silicon spectrum (Figure 15-2) also its crystal structure is reported (Figure 16-2).



1 **18**

Scheme 9-2: Synthesis of 1,1,1-tris(trimethylsilyl)trimethylgermylsilane (**18**).

The rearrangement was performed in cyclohexane at 80°C, with 0.05 eq. of TTPFPB (Scheme 10-2). After 3 days the reagent was consumed and the reaction mixture was worked up in the usual manner. The product is a glassy colorless solid. The ^{29}Si NMR spectrum is shown in Figure 17-2.



18 **19**

Scheme 10-2: Rearrangement of 1,1,1-tris(trimethylsilyl)trimethylgermylsilane (**18**) with 0.05 eq. of TTPFPB, 3 days of reaction.

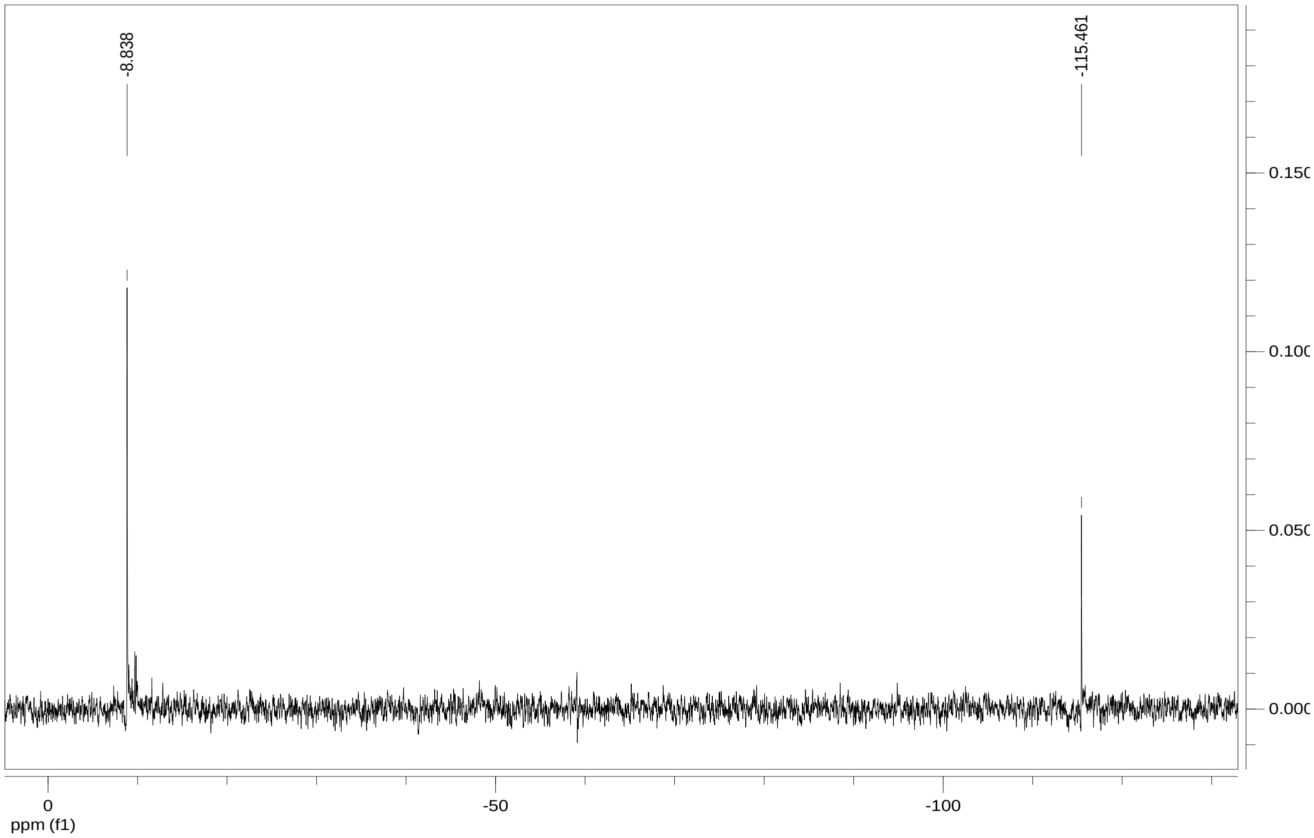
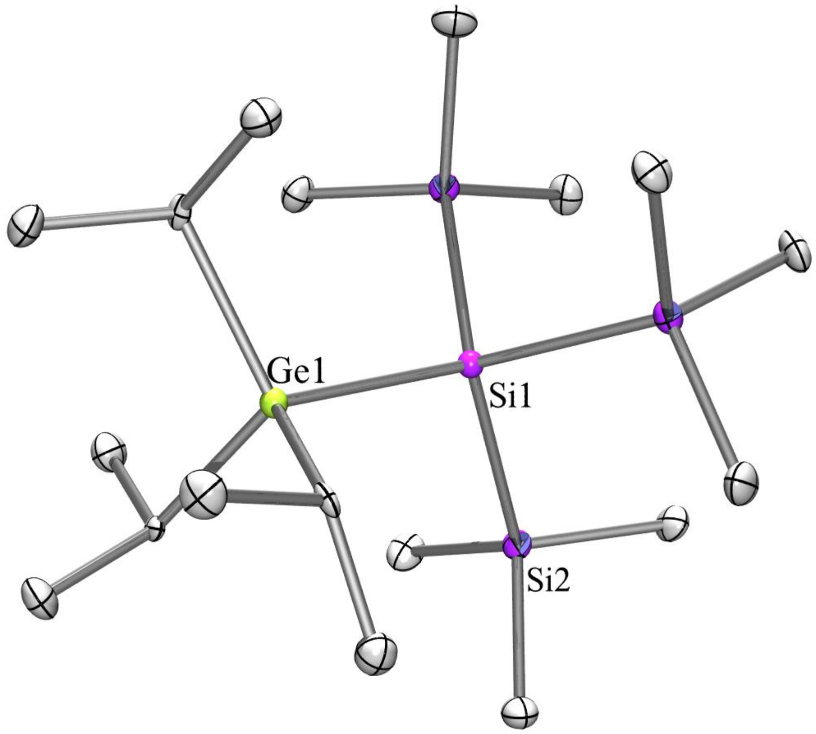


Figure 15-2: ^{29}Si NMR spectrum of compound **18**: δ(Si_q) = -115.4 ppm, δ($SiMe_3$) = -8.8 ppm.



Selected crystallographic data:

Crystal system:hexagonal

Space group: R3

Goodness-of-fit on F^2	1.054
Bond lengths [Å] and angles [deg]	
Ge(1)-C(4)	2.035(2)
Ge(1)-Si(1)	2.4148(12)
Si(2)-C(1)	1.878(3)
Si(2)-Si(1)	2.3621(8)
C(4)#1-Ge(1)-C(4)	110.26(6)
C(4)-Ge(1)-Si(1)	108.67(6)
C(3)-Si(2)-C(1)	107.46(12)
Si(2)#1-Si(1)-Si(2)	106.41(3)

Figure 16-2: Crystal structure of $(Me_3Si)_3Si(i\text{-}Pr_3Ge)$ (**18**).

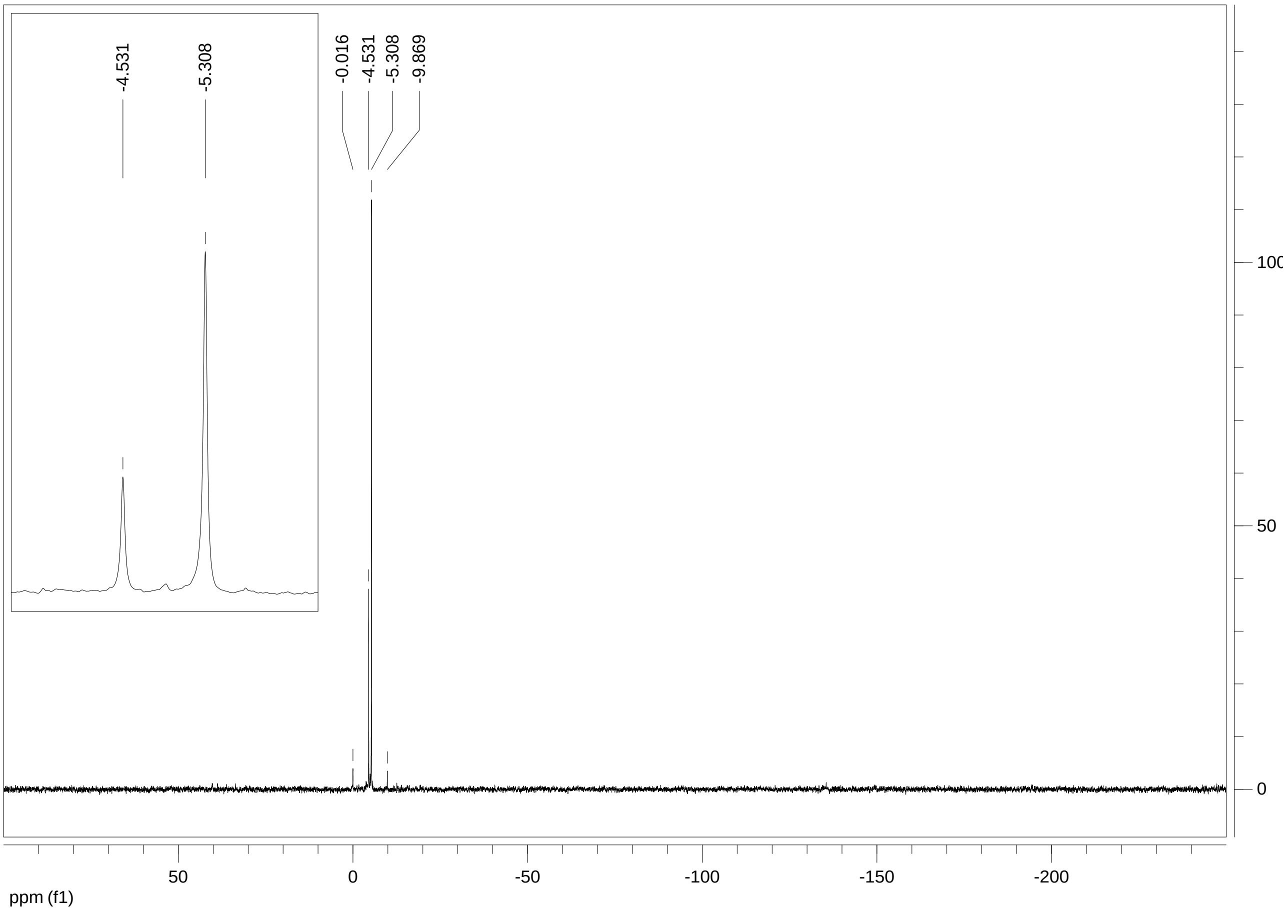
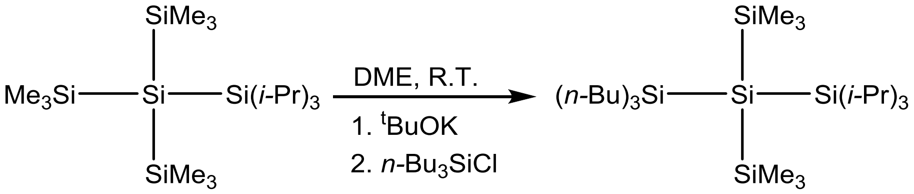


Figure 17-2: ^{29}Si NMR spectrum of the rearrangement product **19**, from the reaction of $(Me_3Si)_3Si(i\text{-}Pr_3Ge)$ (**18**) with TTPFPB.

The signal at -115.4 ppm of the starting reagent disappeared, meaning that there is no more a quaternary silicon atom in the molecule. Instead of one signal for trimethylsilyl groups, there is one signal at -5.3 ppm (for one trimethylsilyl group – this value is typical when $-SiMe_3$ groups are bonded to germanium (IV) atom, see cited reference[11]), and there is another signal at -4.5 ppm (for the three dimethylisopropylsilyl groups).

2.4.3 Rearrangement of 1,1,1-triisopropyl-3,3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (24)

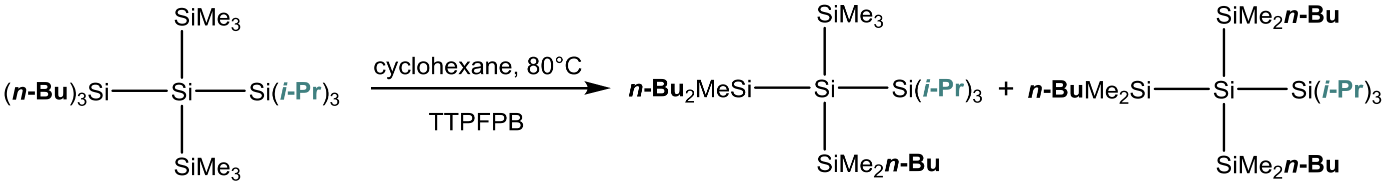
To compare the mobility of the isopropyl and the *n*-butyl groups when they are located in the same molecule, compound **24** was prepared as shown in Scheme 11-2:



2 **24**

Scheme 11-2: Synthesis of 1,1,1-triisopropyl-3,3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (**24**).

The isomerization took place in cyclohexane at 80°C, with 0.1 eq. of TTPFPB (Scheme 12-2). After 3 days, the starting material was consumed. The usual work up led to a transparent oil. The ^{29}Si NMR spectrum of this material is shown in Figure 18-2.



24 **25** **26**

Scheme 12-2: Rearrangement of 1,1,1-triisopropyl-3,3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (**24**).

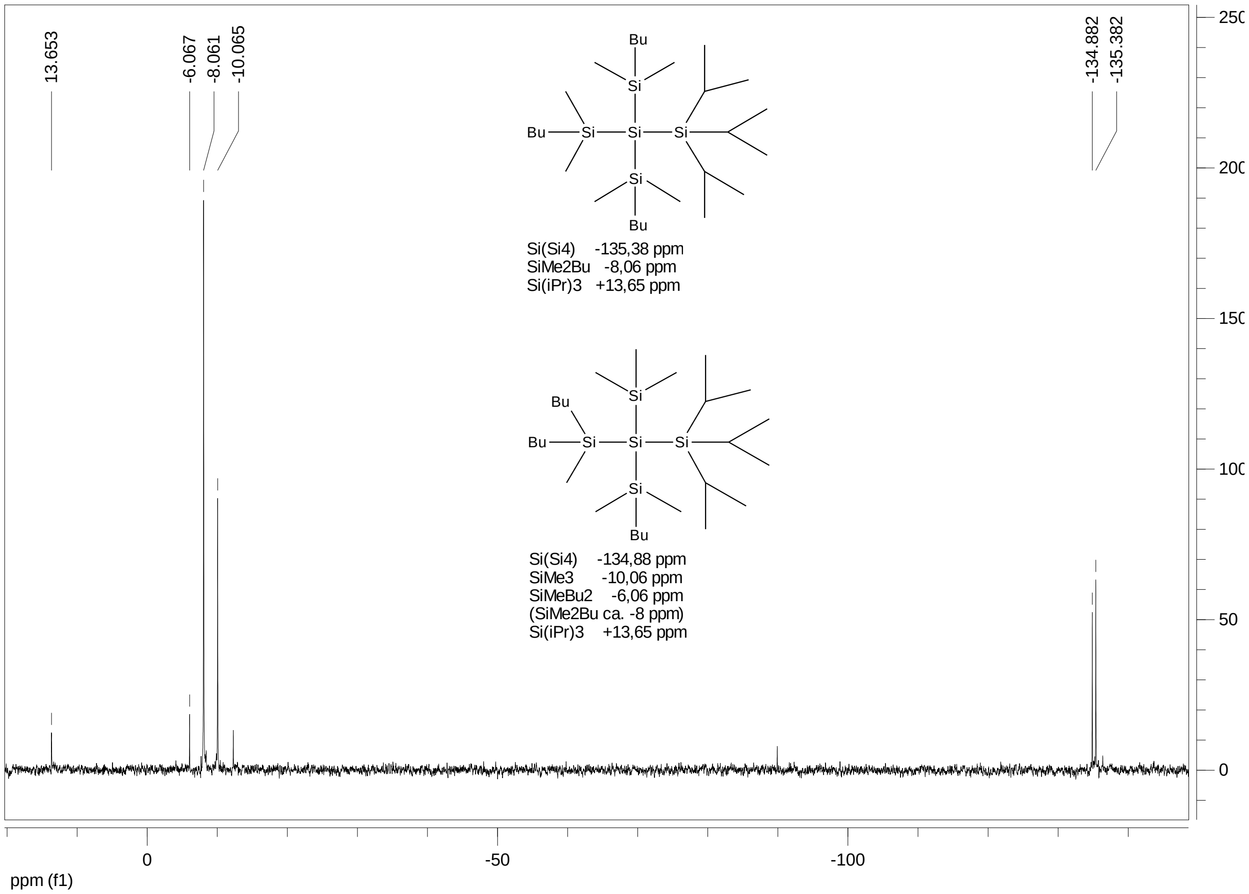
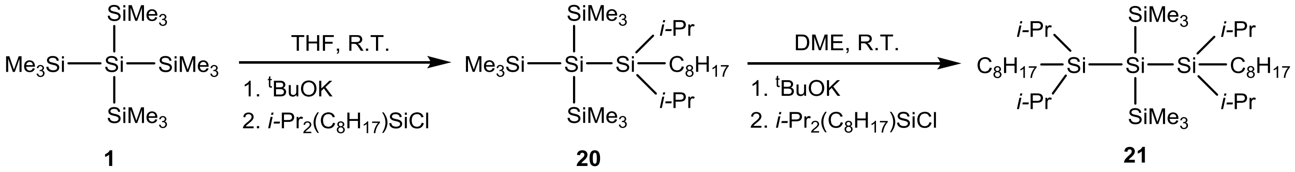


Figure 18-2: ^{29}Si NMR spectrum of the mixture of products **25** and **26**, from the rearrangement of 1,1,1-triisopropyl-3,3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (**24**) with TTPFPB.

The absence of the reversed phase peak at ca. -2.0 ppm indicates that the tributylsilyl group took part in the isomerization process, while the signal at 13.8 ppm shows that the triisopropylsilyl group stayed untouched. Also the absence of the usual chemical shifts at 6.0 ppm and -1.3 ppm suggests that there was no migration of the isopropyl groups. Two products are present in the final mixture (two signals at -134.8 ppm and -135.3 ppm, for $SiSi_4$). For compound **26** the rearrangement involved a complete migration of the butyl groups ($-SiMe_2$*n*-Bu, δ = -8.0 ppm), while for compound **25** this spreading occurred only partially (-SiMe*n*-Bu_2, δ = -6.0 ppm, and one residual $-SiMe_3$ at -10.0 ppm). Even if the butyl groups are heavier than isopropyls, their minor hindrance probably favors a faster exchange with methyl groups. Once the $-SiMe_2$*n*-Bu group is formed, it does not accept a further alkyl migration, so that the isopropyl groups seem locked to their initial position.

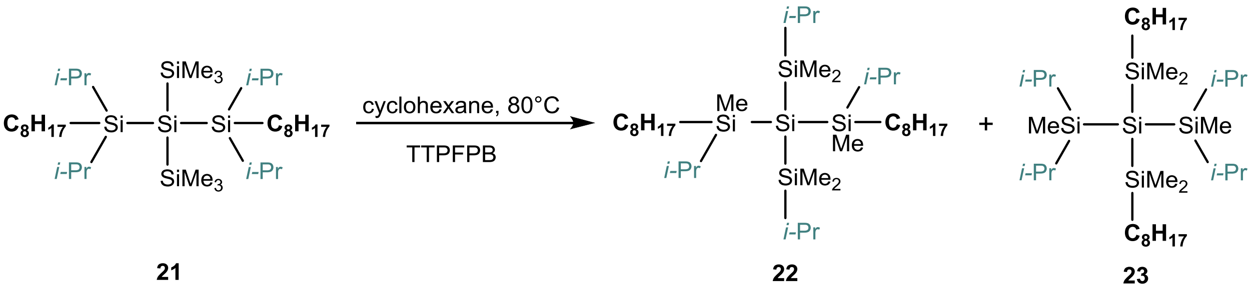
2.4.4 Rearrangement of 1,1,3,3-tetraisopropyl-1,3-dioctyl-2,2-bis(trimethylsilyl)trisilane (21)

In a similar experiment, compound **21** was prepared with two pre-formed silyl groups carrying different alkyl units (Scheme 13-2):

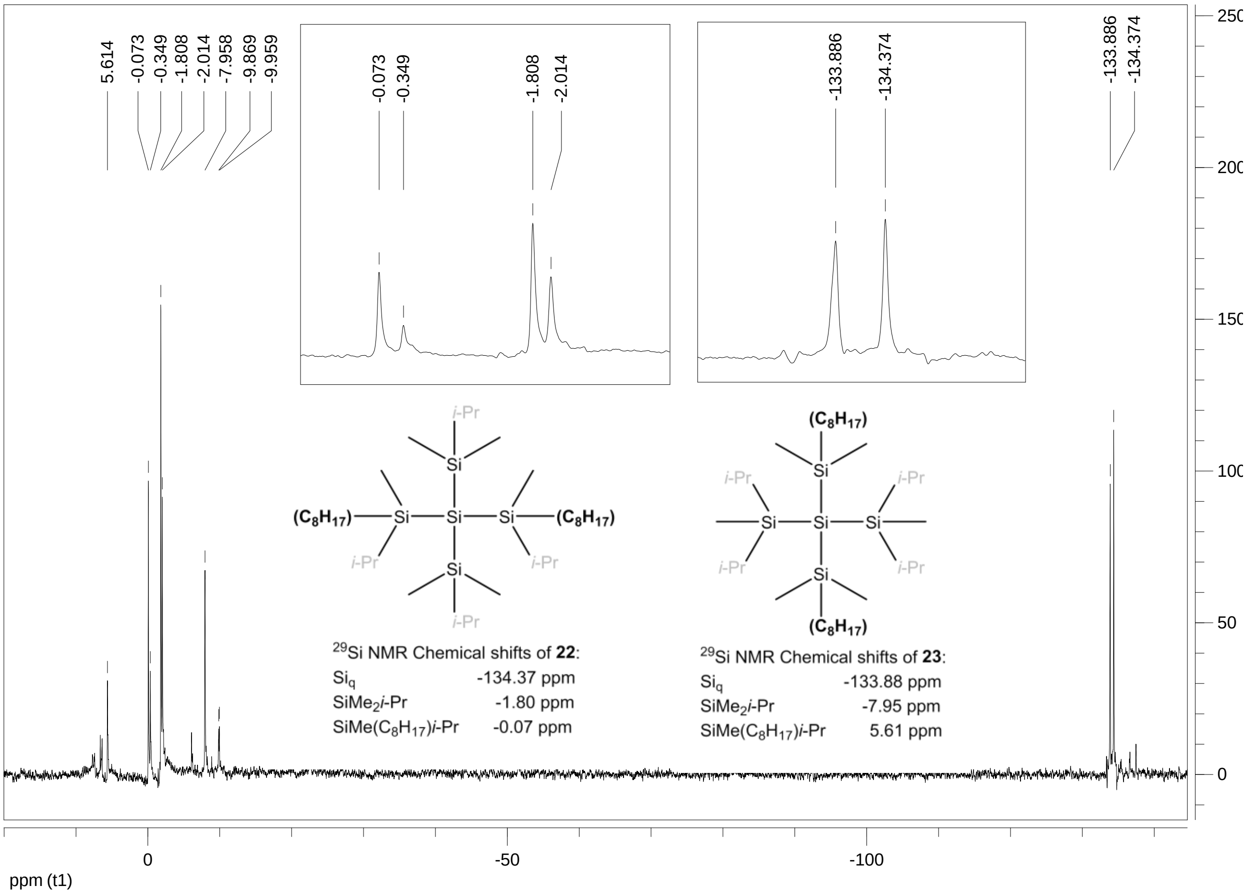


Scheme 13-2: Synthesis of 1,1,3,3-tetraisopropyl-1,3-dioctyl-2,2-bis(trimethylsilyl)trisilane (**21**).

The rearrangement reaction required 0.05 eq. of catalyst to be completed. The starting material was converted into two main products (Scheme 14-2) identified by ^{29}Si NMR spectroscopy (Figure 19-2).



Scheme 14-2: Rearrangement of 1,1,3,3-tetraisopropyl-1,3-dioctyl-2,2-bis(trimethylsilyl)trisilane (**21**).



^{29}Si NMR Chemical shifts of **22**:

Si_q	-134.37 ppm
$SiMe_2$*i*-Pr	-1.80 ppm
$SiMe(C_8H_{17})$*i*-Pr	-0.07 ppm

^{29}Si NMR Chemical shifts of **23**:

Si_q	-133.88 ppm
$SiMe_2$*i*-Pr	-7.95 ppm
$SiMe(C_8H_{17})$*i*-Pr	5.61 ppm

Figure 19-2: ^{29}Si NMR spectrum of the mixture of products of **22** and 23, from the rearrangement of 1,1,3,3-tetraisopropyl-1,3-dioctyl-2,2-bis(trimethylsilyl)trisilane (**21**) with TTPFPB.

The lack of signal at ca. 8 ppm indicates that the diisopropyloctylsilyl groups completely took part in the rearrangement process. Nevertheless, there are still some by-products having intact -$SiMe_3$ groups (small peaks at -9.9 ppm). The first main compound **22** underwent the migration of two isopropyl groups: as a consequence, two dimethylisopropylsilyl groups (δ(^{29}Si NMR) = -1.8 ppm) and two isopropylmethyloctylsilyl groups (δ(^{29}Si NMR) = -0.1 ppm) were formed. In the case of compound **23**, the octyl groups were migrating, exchanging with the methyl groups of the -$SiMe_3$. As a result, two -$SiMe(i\text{-}Pr)_2$ groups (δ(^{29}Si NMR) = 5.6 ppm) and two -$SiMe_2$(octyl) groups (δ(^{29}Si NMR) = -7.9 ppm) were generated.

Other isomers are probably present in the mixture (for example, the completely asymmetric compound ($SiMe_2$*i*-Pr)($SiMe_2$Octyl)(SiMe*i*-Pr_2)(SiMe*i*-PrOctyl)Si, and those ones still carrying -$SiMe_3$ groups, Figure 20-2). Regrettably, a complete identification of all products in the mixture was not possible. Mass spectroscopy is in this case was not helpful, as during electron ionization of the sample the fragments could always recombine and give rise to false signals in the spectrum.

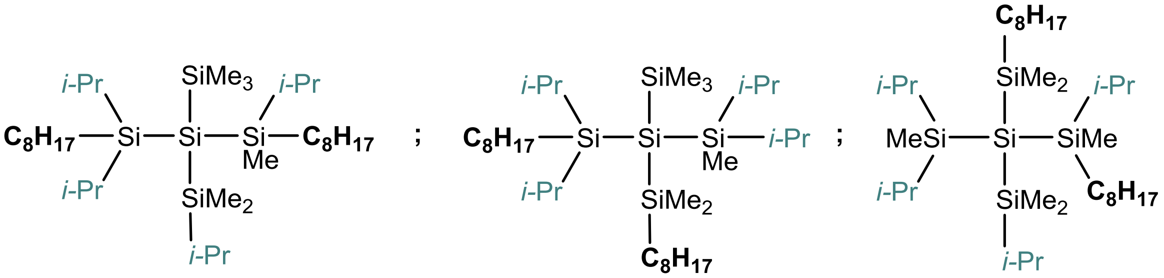
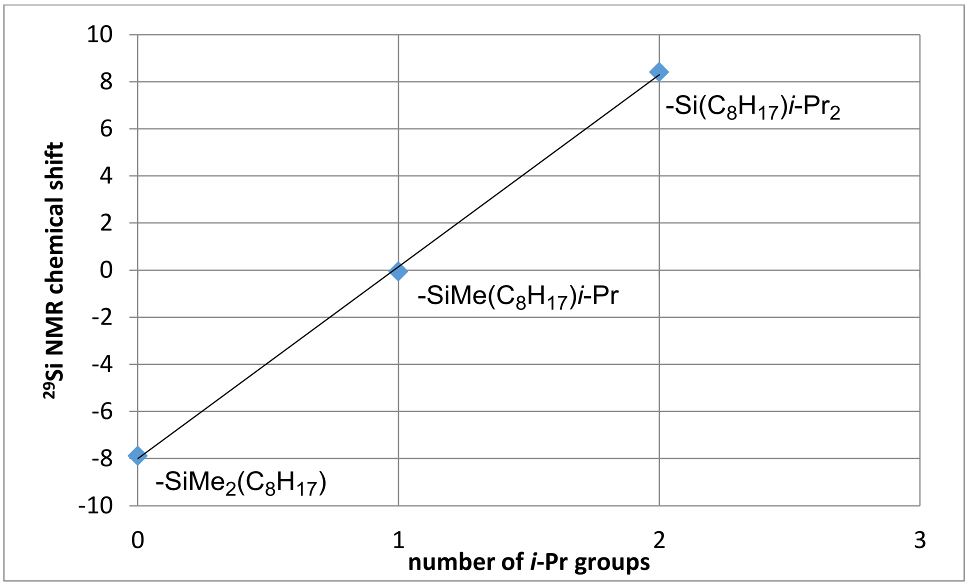


Figure 20-2: Other possible isomers from rearrangement presented in Scheme 14-2.

Nevertheless, linear correlation of the ^{29}Si NMR chemical shifts of the -Si(Octyl)Me_x*i*-Pr_{2-x} groups works quite well (Figure 21-2, but in this case, only three points are available):



Nr. of *i*-Pr groups	δ^{29}Si NMR
0	-7.9
1	-0.07
2	8.4

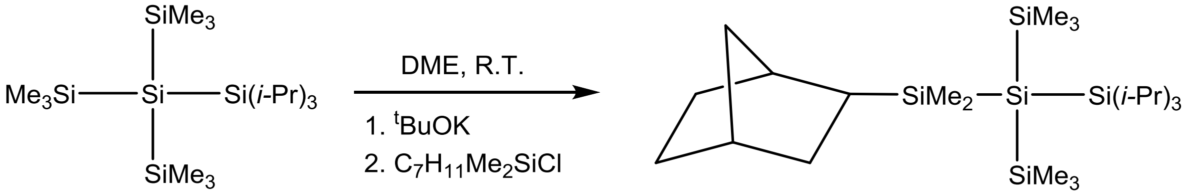
$y = 8.15x – 8.01$

$R = 0.999$

Figure 21-2: Linear correlation between the number n of the isopropyl groups in the Si(C_8H_{17})Me_{2-n}*i*-Pr_n fragments, and their respective ^{29}Si NMR chemical shifts.

2.4.5 Rearrangement of 1-(2-norbornyl)-1,1-dimethyl-2,2-bis(trimethylsilyl)-triisopropyltrisilane (33)

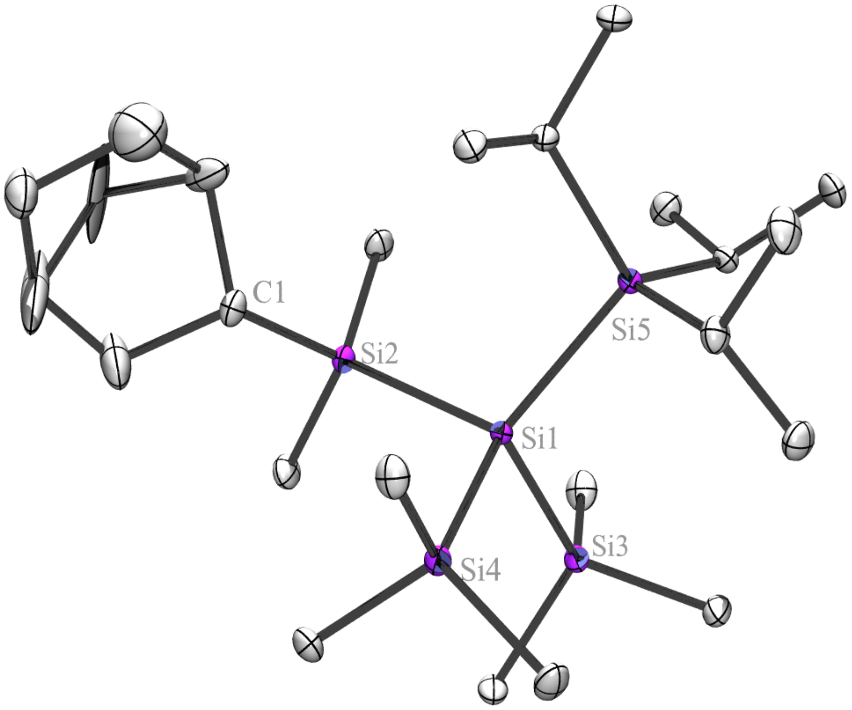
In order to improve the crystallization of **15**, a rigid and bulky alkyl group was introduced in compound **2** (Scheme 15-2):



2 **33**

Scheme 15-2: Synthesis of 1-(2-norbornyl)-1,1-dimethyl-2,2-bis(trimethylsilyl)triisopropyltrisilane (**33**).

The product crystallizes very well as colorless plates. The crystal structure is shown in Figure 22-2:



Selected crystallographic data:

Crystal system: monoclinic

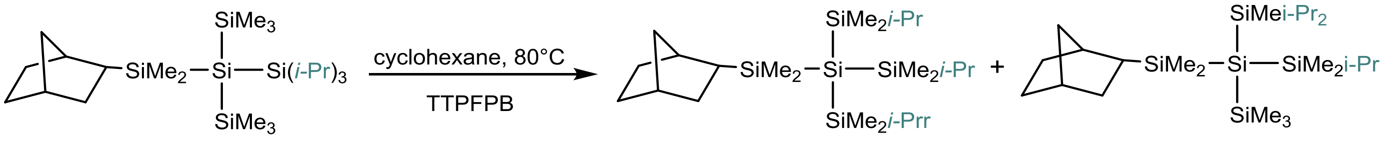
Space group: P2(1)/c

Goodness-of-fit on F^2 1.043

Bond lengths [Å] and angles [deg]	
C(16)-Si(5)	1.904(3)
C(1)-Si(2)	1.914(3)
Si(1)-Si(2)	2.3761(14)
Si(1)-Si(5)	2.3857(11)
Si(1)-Si(3)	2.3652(11)
Si(4)-Si(1)-Si(2)	106.26(4)
Si(3)-Si(1)-Si(5)	112.88(4)
Si(4)-Si(1)-Si(3)	104.76(4)
C(1)-Si(2)-Si(1)	110.44(10)

Figure 22-2: Crystal structure of compound **33**.

This substrate was mixed with 0.1 eq. of catalyst in cyclohexane and then heated at 80°C (Scheme 16-2).



33 **34** **34^I**

Scheme 16-2: Rearrangement of 1-(2-norbornyl)-1,1-dimethyl-2,2-bis(trimethylsilyl)triisopropyltrisilane (**33**).

It was necessary to employ 0.3 equivalent of TTPFPB and then the reaction continued for ten days to complete the conversion of the starting material. In Figure 23-2 the ^{29}Si NMR spectrum of the worked up product is presented:

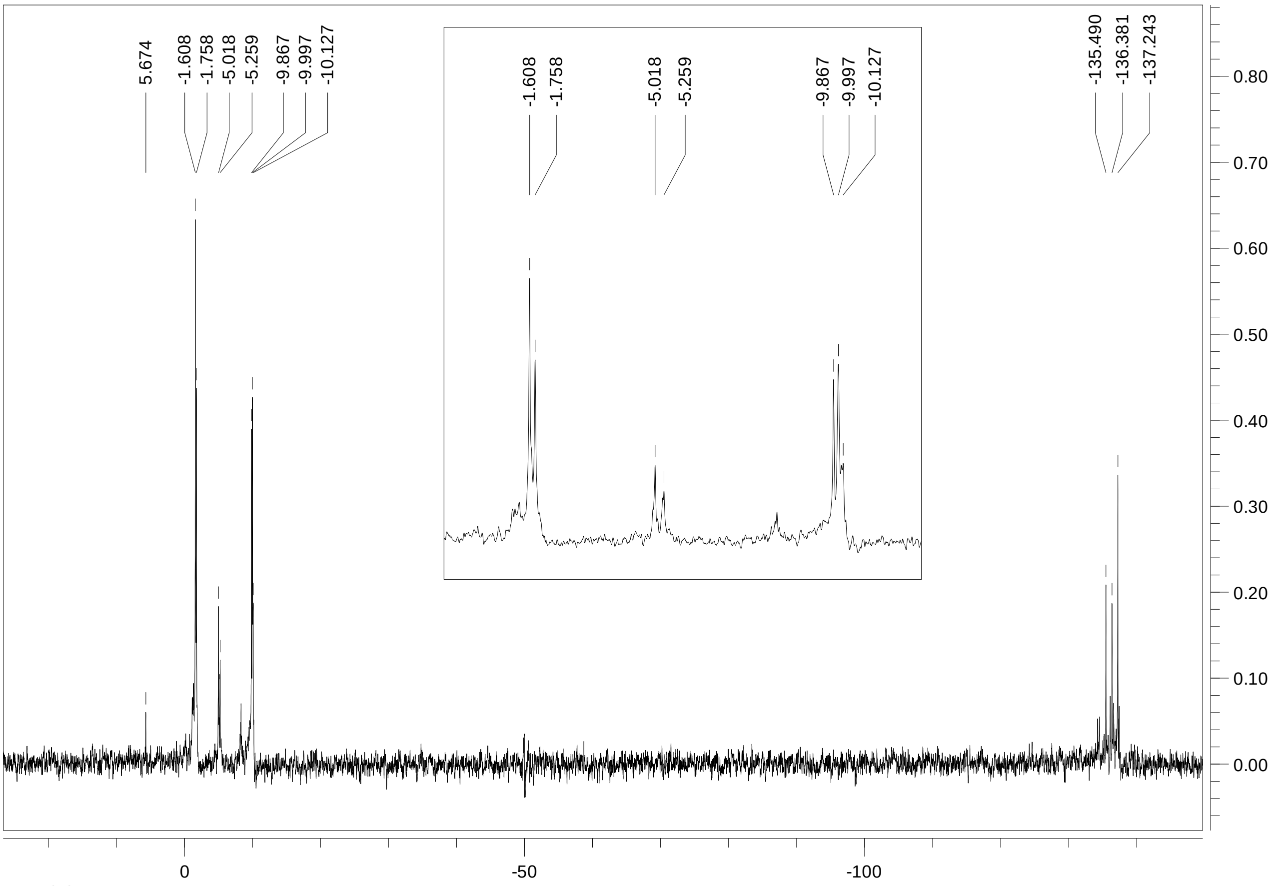
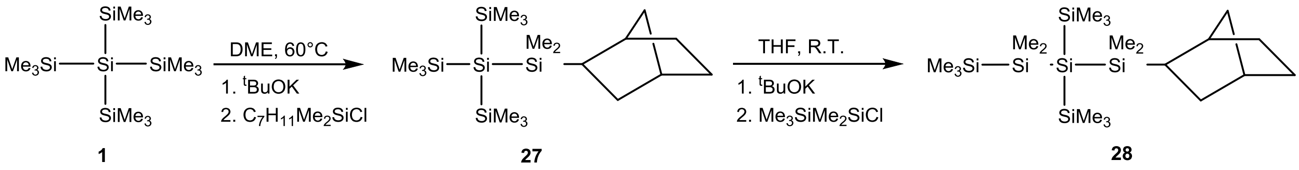


Figure 23-2: ^{29}Si NMR spectrum from the rearrangement of compound **33** after the work-up.

The final mixture contains at least three different molecules, because of the three main peaks in the region of -130 to -140 ppm. The signals at -1.6 ppm and -1.7 ppm could be assigned to the -SiMe$_2$*i*-Pr groups and those ones at -5.0 and -5.2 ppm to the -SiMe$_2$C$_7$H$_{11}$ groups. Together with the peak at 5.6 ppm (-SiMe*i*-Pr$_2$ group) and 10.1 ppm (-SiMe$_3$ group), these signals might be due to the formation of the two isomers **34** and **34**^{I}, respectively. Here the steric influence of the norbornyl group causes a relevant change in the chemical environment of the silicon atoms, favoring the chemical shifts resolution (as an example, the -SiMe$_2$*i*-Pr groups in compounds **15** and **15**^{I} cannot be distinguished in the ^{29}Si NMR spectrum). There are still visible some -SiMe$_3$ groups (ca. -9.9 ppm), and that suggests the presence of some residual starting material or some decomposition of by-products. Unfortunately, crystallization of these products from acetone or dichloromethane did not work.

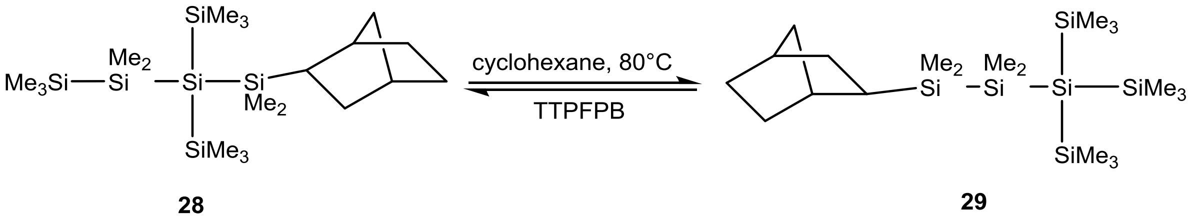
2.4.6. Rearrangement of 1-(2-norbornyl)-2,2-bis(trimethylsilyl)heptamethyltetrasilane (28)

To have a simpler system in respect of compounds **3** and **5**, to increase the chances of crystallization of the isomerized products and to verify if large bulky alkyl groups could migrate across the molecule despite of their steric hindrance, a 2-norbornyl group was introduced in compound **28** (Scheme 17-2).



Scheme 17-2: Synthesis of 1-(2-norbornyl)-2,2-bis(trimethylsilyl)heptamethyltetrasilane (**28**).

The isomerization ran under the usual conditions (cyclohexane, 80°C, 0.1 eq. of TTPFPB – Scheme 18-2). After five days, only one product of isomerization was observed, but ca. 50% of starting material was still present in solution (see the ^{29}Si NMR spectrum of the reaction mixture, Figure 24-2).



ca. 50% of conversion

Scheme 18-2: Rearrangement of compound **28**, reaction mixture after 7 days, 0.2 eq. of catalyst.

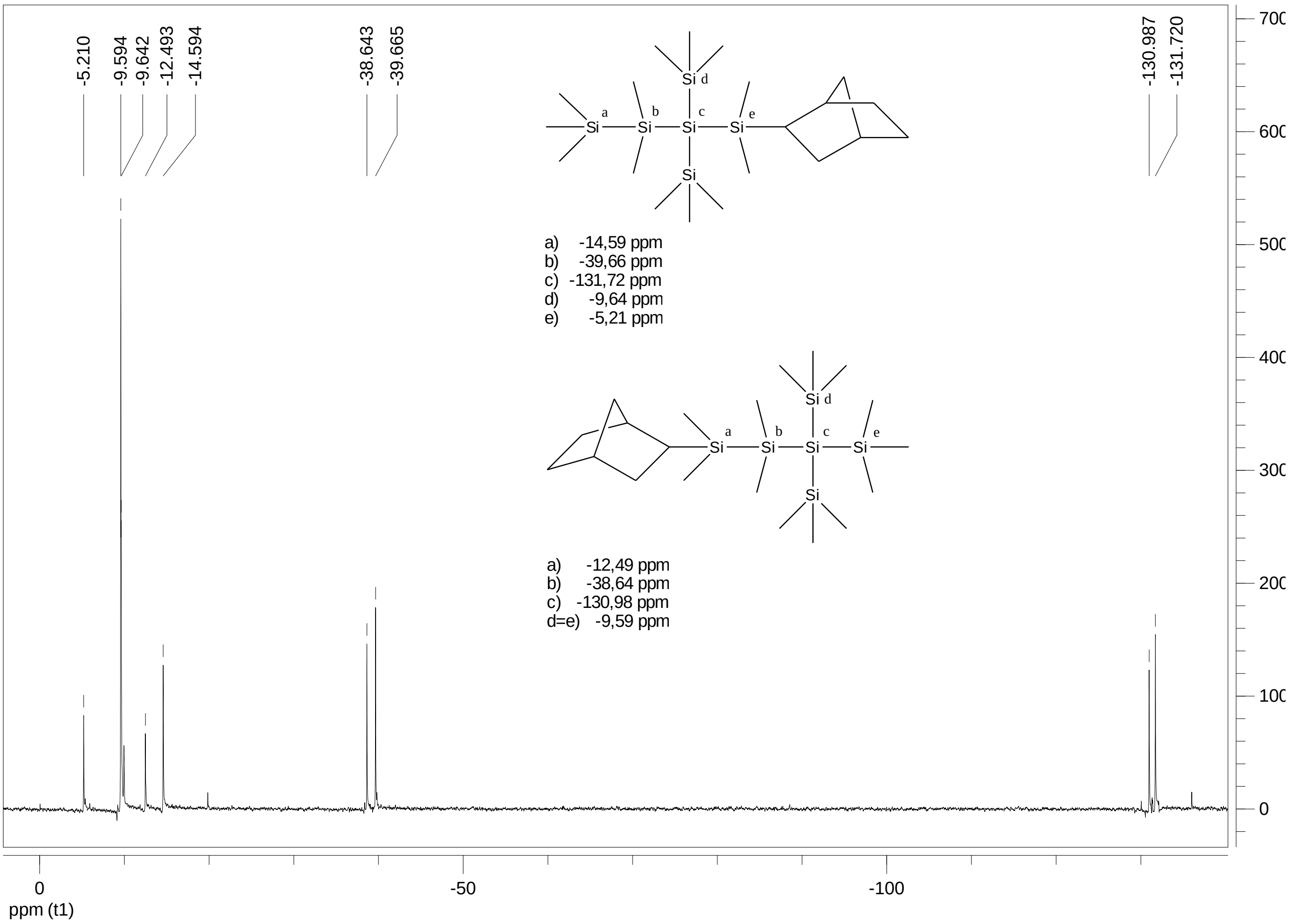
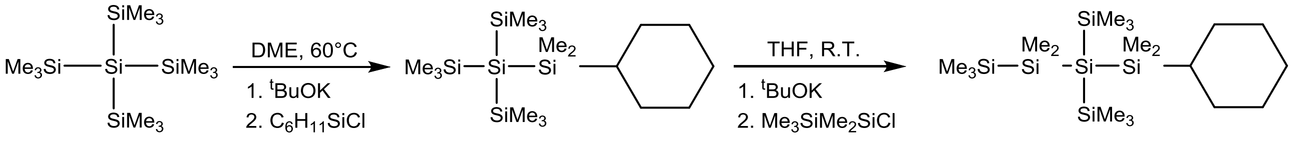


Figure 24-2: ^{29}Si NMR spectrum on the reaction mixture containing compounds **28** and **29**, from the rearrangement of 1-(2-norbornyl)-2,2-bis(trimethylsilyl)heptamethyltetrasilane (**28**) with TTPFPB.

At this point, 0.1 eq. of catalyst were added but after three days of stirring the reaction did not go forward. After one week with 0.2 equivalent of TTPFPB, the situation was the same. It seems that when the amounts of reagent and product reach the 1:1 proportion, the catalyst could promote indiscriminately the migration of the norbornyl group towards the peripheral $SiMe_2$-$SiMe_3$ group, or the back-migration of the alkyl group towards its original position. An equilibrium state was achieved.

2.4.7 Rearrangement of 1-cyclohexyl-2,2-bis(trimethylsilyl)heptamethyltetrasilane (31)

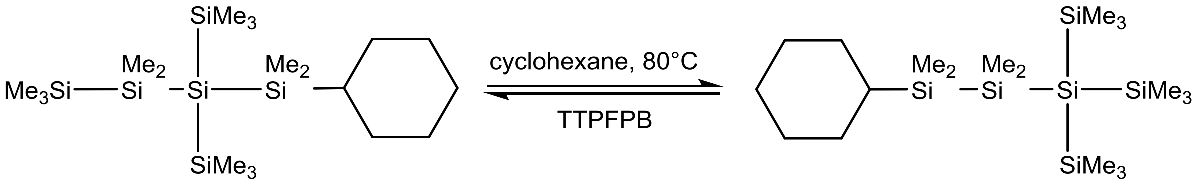
In a similar experiment as in chapter 2.4.6, here a cyclohexyl group was introduced in compound **31**, Scheme 19-2.



1 **30** **31**

Scheme 19-2: Synthesis of 1-cyclohexyl-2,2-bis(trimethylsilyl)heptamethyltetrasilane (**31**).

This substrate was treated with 0.1 eq. of TTPFPB in cyclohexane at 80°C (Scheme 20-2).



31 **32**

ca. 50% of conversion

Scheme 20-2: Rearrangement of of compound **31**, reaction mixture after 3 days, 0.2 eq. of catalyst.

After three days of reaction, only half of conversion was detected by ^{29}Si NMR (see Figure 25-2). Because most of the catalyst was not in solution, instead of adding more TTPFPB, some drops of chlorobenzene were added, to dissolved completely the trityl salt into the reaction mixture and to verify if the action of the catalyst might be then improved. However, after ca. 12 h. the ^{29}Si NMR spectrum was basically the same.

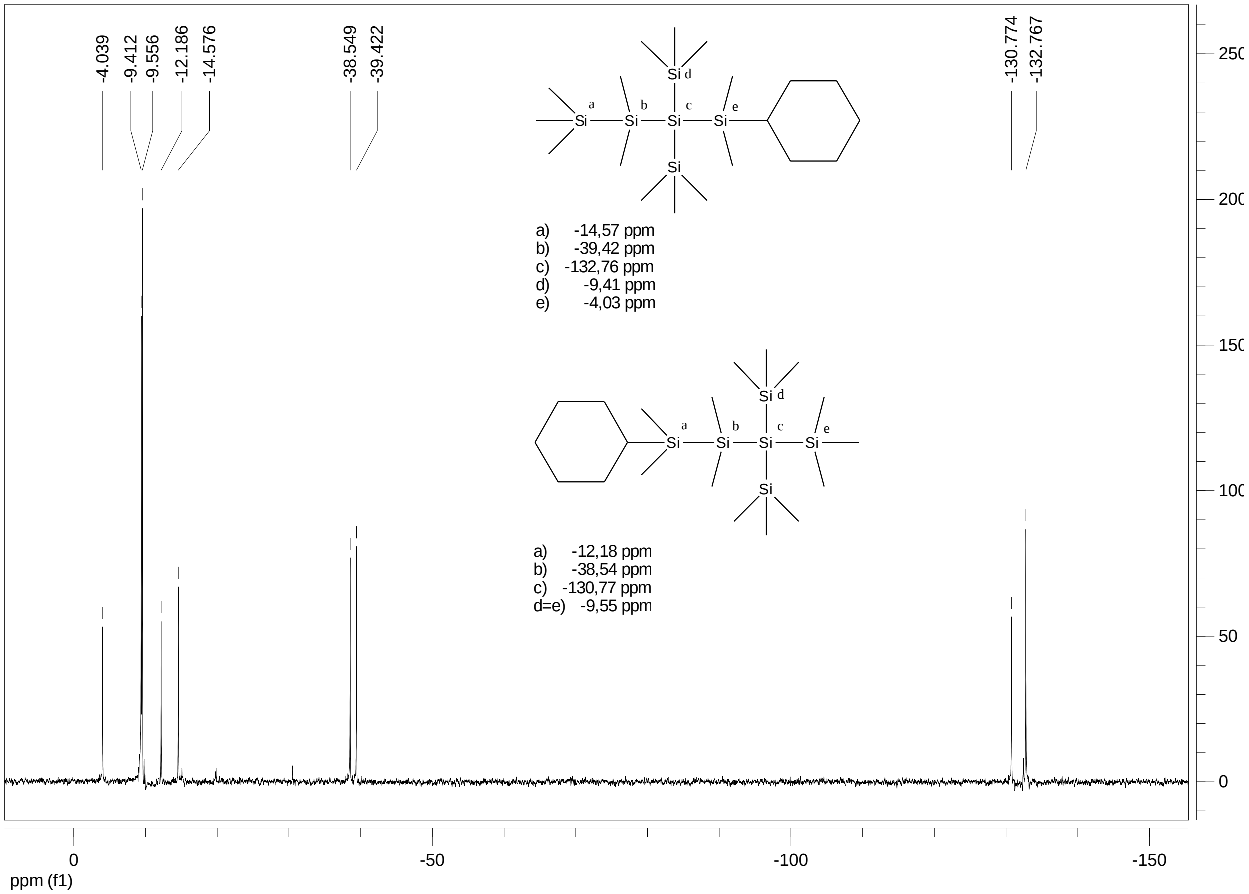


Figure 25-2: ^{29}Si NMR spectrum of the reaction mixture containing compounds **31** and **32**, from the rearrangement of 1-cyclohexyl-2,2-bis(trimethylsilyl)heptamethyltetrasilane (**31**) with TTPFPB.

As it was found in the previous experiment, it can be argue that the starting material and the rearranged product are energetically very similar, and so it is possible that they reach an equilibrium in which the catalyst simply converts one compound into the other with no selectivity.

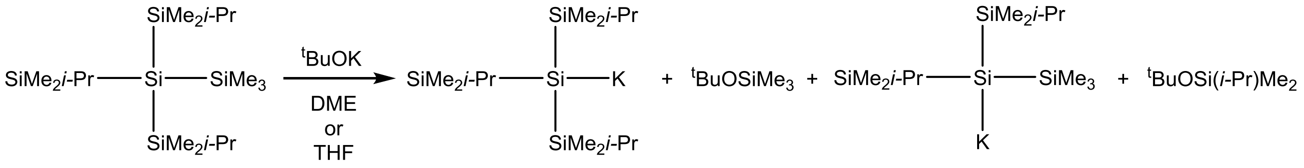
3. Reaction
with
Isomerized Substrates

3.1 Derivatization of isomerized substrates

The isomerization of oligosilanes functionalized with different types of alkyl groups, should allow to produce a wide set of small polysilanes having different steric hindrance. Then, it would be possible to use these compounds as starting material to synthesize, for example, ligands for complexation of transition metals, in which the bulky structure of the new silanes could protect and stabilized the metal center in a more efficient way than a simple permethylated ligand could do.

3.1.1 Synthesis of 1,1,1-tris(dimethylisopropylsilyl)silyl potassium in DME or THF

Compound **15** was treated with one equivalent of *t*-BuOK to verify the selectivity of the reaction in respect of the abstraction of a trimethylsilyl group by the base (Scheme 1-3):



15

Scheme 1-3: Synthesis of silyl anions from compound **15,** 1.03 eq. of *t*-BuOK, at room temperature.

As shown in the ^{29}Si NMR spectrum (Figure 1-3), the *tert*-butoxide was able to abstract indiscriminately a -$SiMe_3$ group and a dimethylisopropylsilyl group (two signals at 6.8 ppm and 13.6 ppm, from the two silyl ethers). In this way, two different silyl anions were formed, almost in the same amount (two peaks in the typical range for the anion Si_3Si-K, at -207 ppm and -210 ppm).

Because in DME the potassium base is very active, the experiment was repeated in THF, but the same results were achieved (two anionic products, in a slightly different ratio).

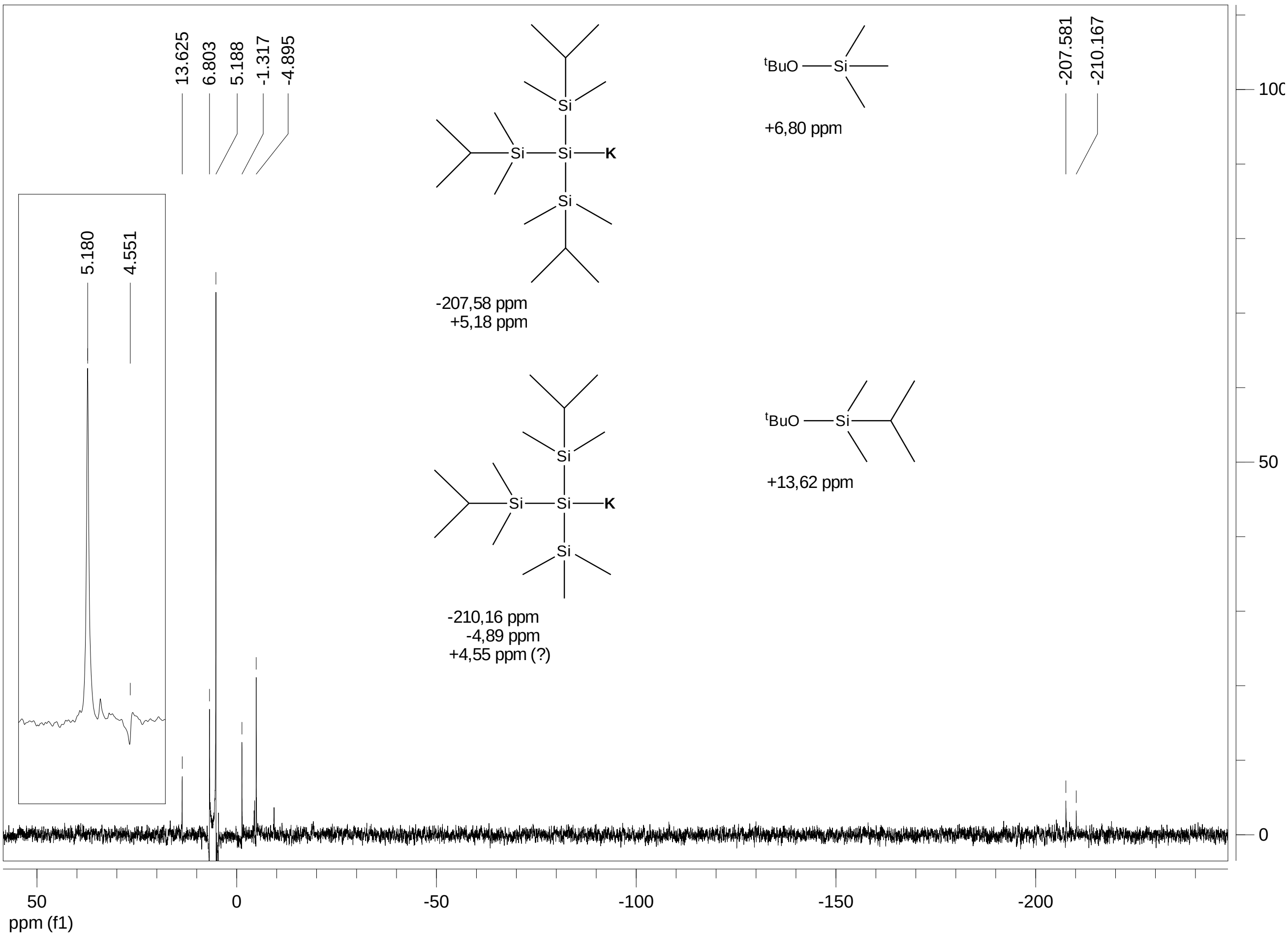
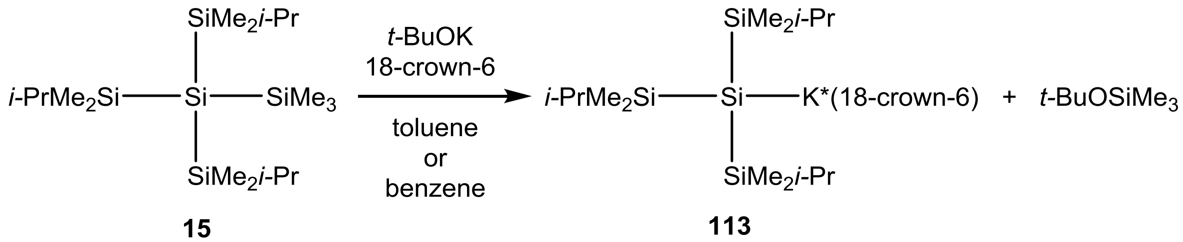


Figure 1-3: ^{29}Si NMR spectrum of the reaction mixture after treatment of compound **15** with ^{t}BuOK in DME (D_2O capillary).

This unexpected behavior of the substrate could represent a problem, because any attempt to derivatize the molecule it will always lead to a mixture of products that are very similar, with comparable sublimation points and solubility. It would be very hard to separate them by chromatography or crystallization processes.

3.1.2 Synthesis of 1,1,1-tris(dimethylisopropylsilyl)silyl potassium in toluene/18-crown-6

Nevertheless, the reaction of compound **15** with *t*-BuOK was tried also in toluene as solvent, in the presence of an equimolecular amount of 18-crown-6 (Scheme 2-3). Usually under these conditions the base is extremely reactive, because the potassium cation is trapped in the crown ether molecule and the *tert*-butanolate is nearly “free” in solution. Then no particular selectivity was expected.



15 **113**

Scheme 2-3: Synthesis of tris(dimethylisopropylsilyl)silyl potassium (**113**).

Surprisingly, *tert*-butoxide was able to abstract selectively only a trimethylsilyl group from the reagent, leading to a quite clean product in the reaction mixture (see ^{29}Si NMR spectrum in Figure 2-3). There are still some residual signals in the spectrum because it is the reagent itself that always contains a small quantity of partially rearranged product **15^{I}** that could not be purified.

Probably the reaction proceeds so fast that the potassium base reacts only with the less hindered silyl group, and only the kinetic product is obtained.

In addition, the brilliant scarlet red color of the solution suggests that the silyl anion has formed. The reaction works also in benzene. However, slow evaporation of this solvent led to a microcrystalline precipitate, not suitable to be analyzed by X-ray diffraction analysis.

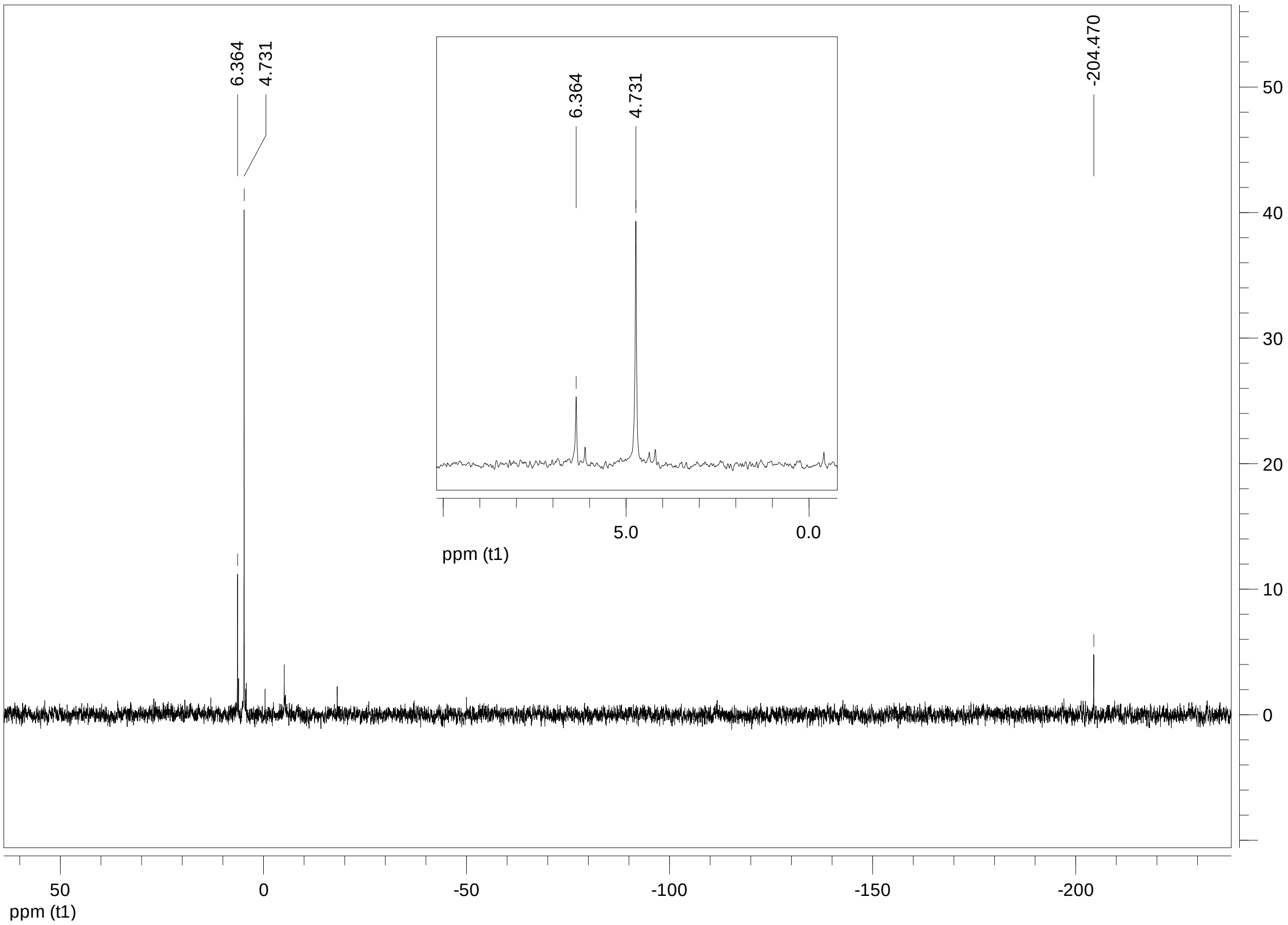


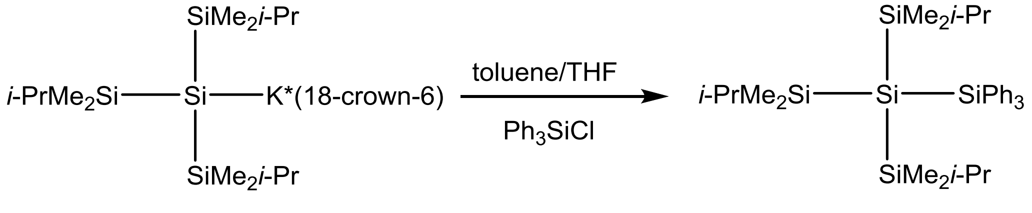
Figure 2-3: ^{29}Si NMR spectrum of the reaction mixture containing the oligosilyl potassium **113**.

Storing a toluene solution of **113** at -60°C led to an amorphous sticky solid from which no crystals could be isolated. From one side it might be acceptable that compound **15** is not a good candidate to precipitate in large crystals, because of its high symmetry that does not help the crystal growth. But from another side, usually silyl anions crystallize well directly from the reaction mixture, especially in the presence of crown ether. In the case of **113**, the presence of the isopropyl groups probably increases deeply the solubility of the silyl anion, and the solvent retained in the precipitating solid causes disorder during the crystal growth.

Then, subsequent reactions with this silyl anion were pursued to confirm indirectly the formation of anion **113**.

3.1.3 Synthesis of 1,1,1-tris(dimethylisopropylsilyl)triphenyldisilane (114)

To improve the crystallization ability of the final product, anion **113** was reacted with triphenylsilylchloride (Scheme 3-3), where the relative heavy and large phenyl groups should promote the crystal growth.



113 **114**

Scheme 3-3: Synthesis of ,1,1-tris(dimethylisopropylsilyl)triphenyldisilane (**114**).

It is quite evident that from the ^{29}Si NMR the expected product was formed (Figure 3-3), but subsequent attempts to crystallize **114** poorly failed. It was only possible to isolate some crystals of the by-product $Ph_3SiOSiPh_3$, probably generated during the aqueous work up.

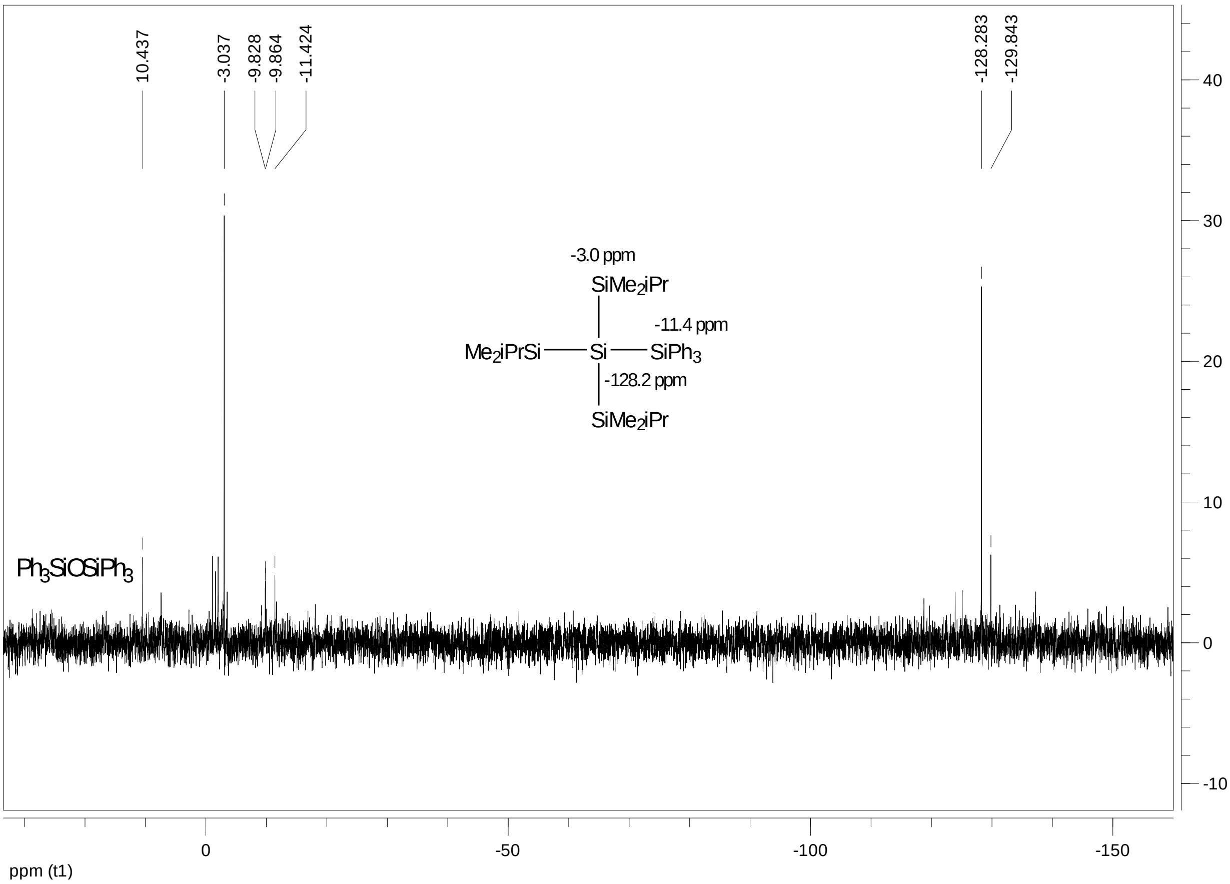
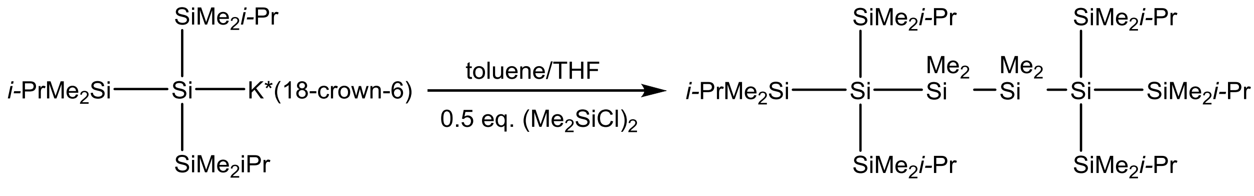


Figure 3-3: ^{29}Si NMR spectrum of the worked up product **114**.

3.1.4 Synthesis of 1,1,1,4,4,4-hexakis(dimethylisopropylsilyl)tetramethyltetrasilane (115)

Compound **115** (Scheme 4-3) might be an interesting starting material for further derivatization reactions as the synthesis of cyclosilanes or as the preparation of complexes with transition metals, that were previously prepared starting from the permethylated analogous (**70**).[8,39,40]



113 **115**

Scheme 4-3: Synthesis of 1,1,1,4,4,4-hexakis(dimethylisopropylsilyl)tetramethyltetrasilane (**115**).

The ^{29}Si NMR of the reaction mixture (Figure 4-3) is consistent with the expected product: the formation of the quaternary silicon atom is confirmed by the signal at -131.8 ppm; there is one signal for the -$SiMe_2$ groups at -36.0 ppm and one for the isopropyldimethylsilyl group at-1.2 ppm (peak at 6.5 ppm represents the by-product trimethylsilyl-*tert*-butyl-ether).

After the work up, the complete evaporation of the solvent surprisingly led to a very dense and transparent oil. Subsequent crystallization attempts from dichloromethane or pentane/acetone mixtures produced extremely thin plates co-crystallizing into each other. This material was then not suitable to be mounted on the X-ray diffractometer.

---

[39] C. Kayser, G. Kickelbick, C. Marschner, *Angew. Chem. Int. Edit.*, **2002**, *41*, 989-992.

[40] H. Arp, M. Zirngast, C. Marschner, J. Baumgartner, K. Rasmussen, P. Zark, T. Müller, *Organometallics*, **2012**, *31*, 4309–4319.

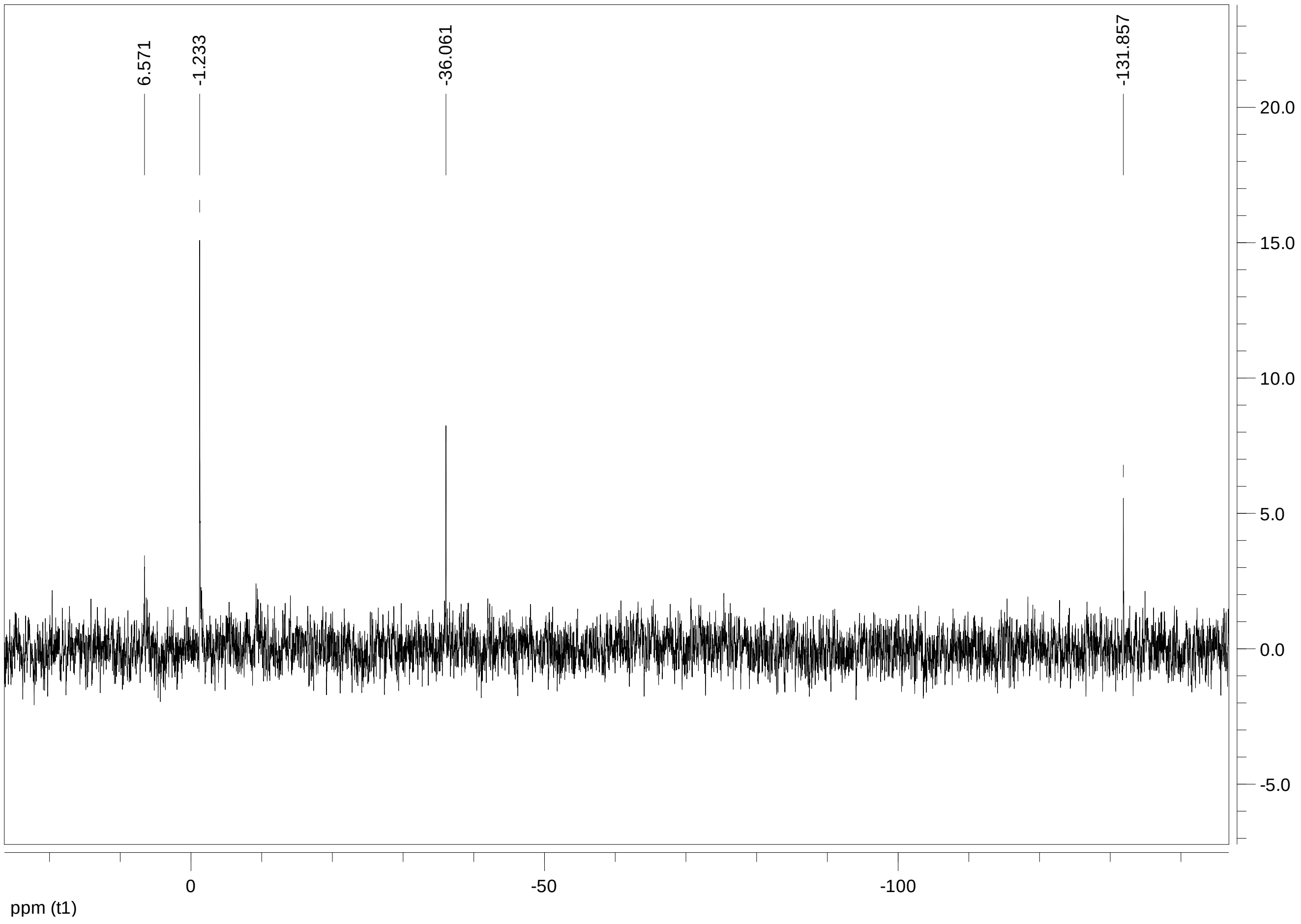


Figure 4-3: ^{29}Si NMR spectrum of the reaction mixture containing compound **115**.

4. Synthesis and Rearrangement of Oligosilyl Triflates

4.1 Rearrangement induced by triflic acid

The main step of the rearrangement reactions (both with Al(Fe)Cl_3 and TTPFPB) is the formation of a transient silyl cation. This unstable species undergoes an internal migration of its functional groups, trying to stabilize the positive charge on a silicon atom.

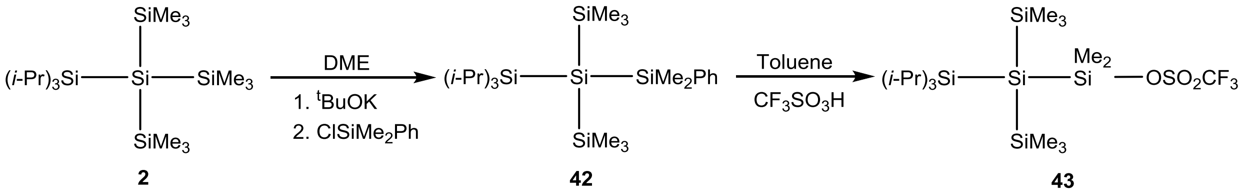
It is possible to induce a partial positive charge on the silicon atom by forming a silyl triflate. Usually, a phenyl group is introduced into the polysilane, and then it is cleaved off by triflic acid.[41] Silyl triflates can react *in situ*, for example with a silyl anion or a hydride. As already mentioned,[17] Krempner and co-workers observed the rearrangement of polysilanes treated with triflic acid. Our question is if the formed silyl triflate could induce a rearrangement process in some of the substrates previously prepared.

---

[41] A. R. Bassindale and T. J. Stout, *J. Organomet. Chem*., **1984**, *271*, C1-C3.

4.1.1 Synthesis and rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilyl triflate

A dimethylphenylsilyl group was introduced in compound **2** via reaction with *tert*-butanolate and subsequent coupling with dimethylphenylsilylchloride (Scheme 1-4). Then product **42** was treated with 1 equivalent of triflic acid to obtain the silyl triflate **43** by elimination of the phenyl group as benzene. The ^{29}Si NMR spectrum of this compound is shown in Figure 1-4.



Scheme 1-4: Synthesis of oligosilyl triflate **43**.

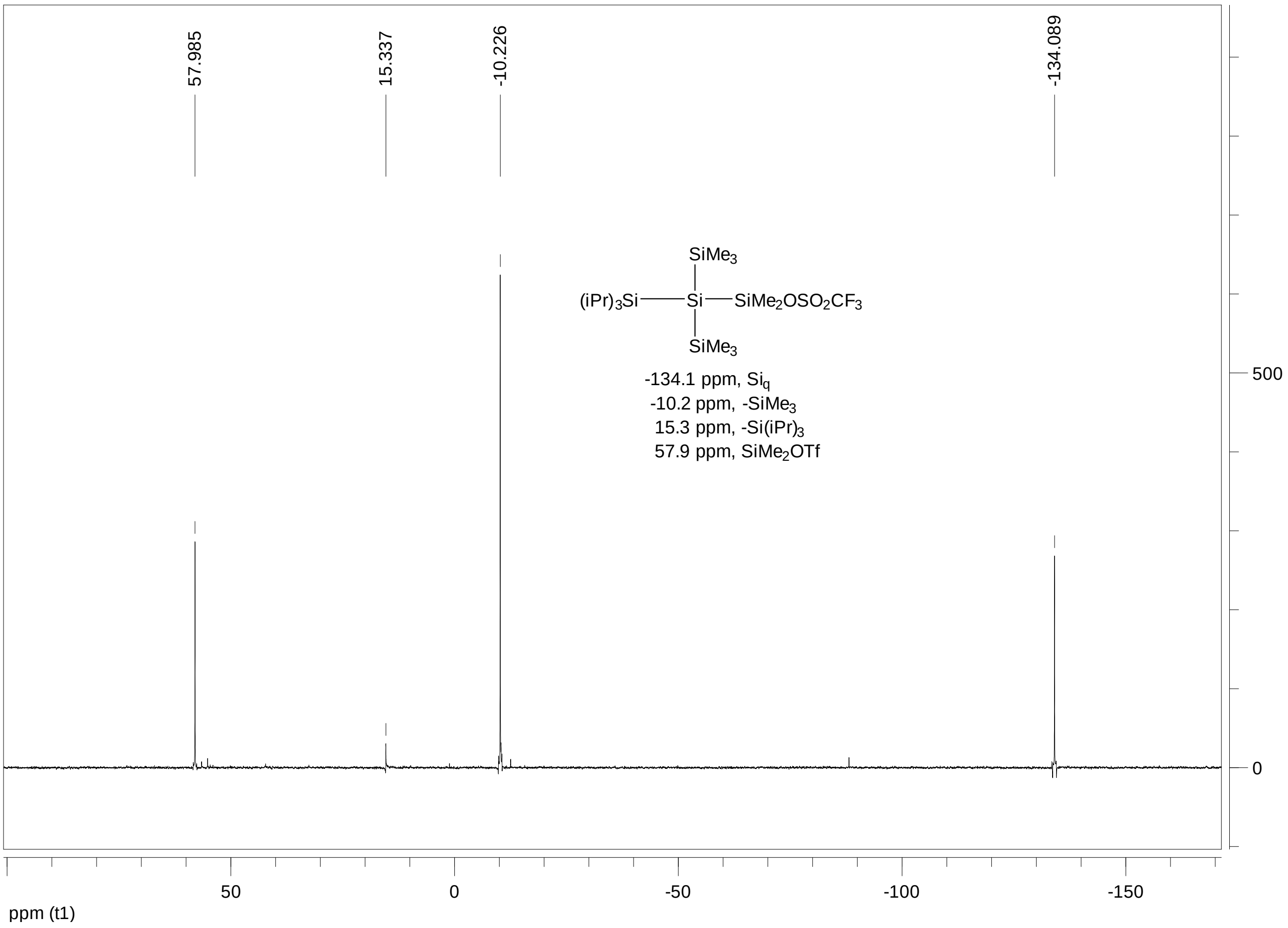


Figure 1-4: ^{29}Si NMR spectrum of compound **43**.

The silyl triflate **43** was stable at room temperature (in toluene or dichloromethane under nitrogen atmosphere). The signal at 15.3 ppm (Figure 1-4) indicated that the triisopropylsilyl group remained intact and no sign of mixed isopropyl/methyl silyl group could be detected (signals should rise in the range of -2 to 6 ppm). The temperature was increased to 60°C and the formation of new products was observed, but after a number of days the starting triflate **43** was still the main compound in the reaction mixture (Figure 2-4). Peaks at -88.3 ppm and -13.1 ppm might be due to tris(trimethylsilyl)methylsilane. The signal at -142.7 ppm was quite uncommon for a quaternary silicon atom and together with the peaks at -9.9 ppm (-SiMe$_3$) and 53.2 ppm (-SiMe$_2$OTf) they could not be assigned to a defined structure.

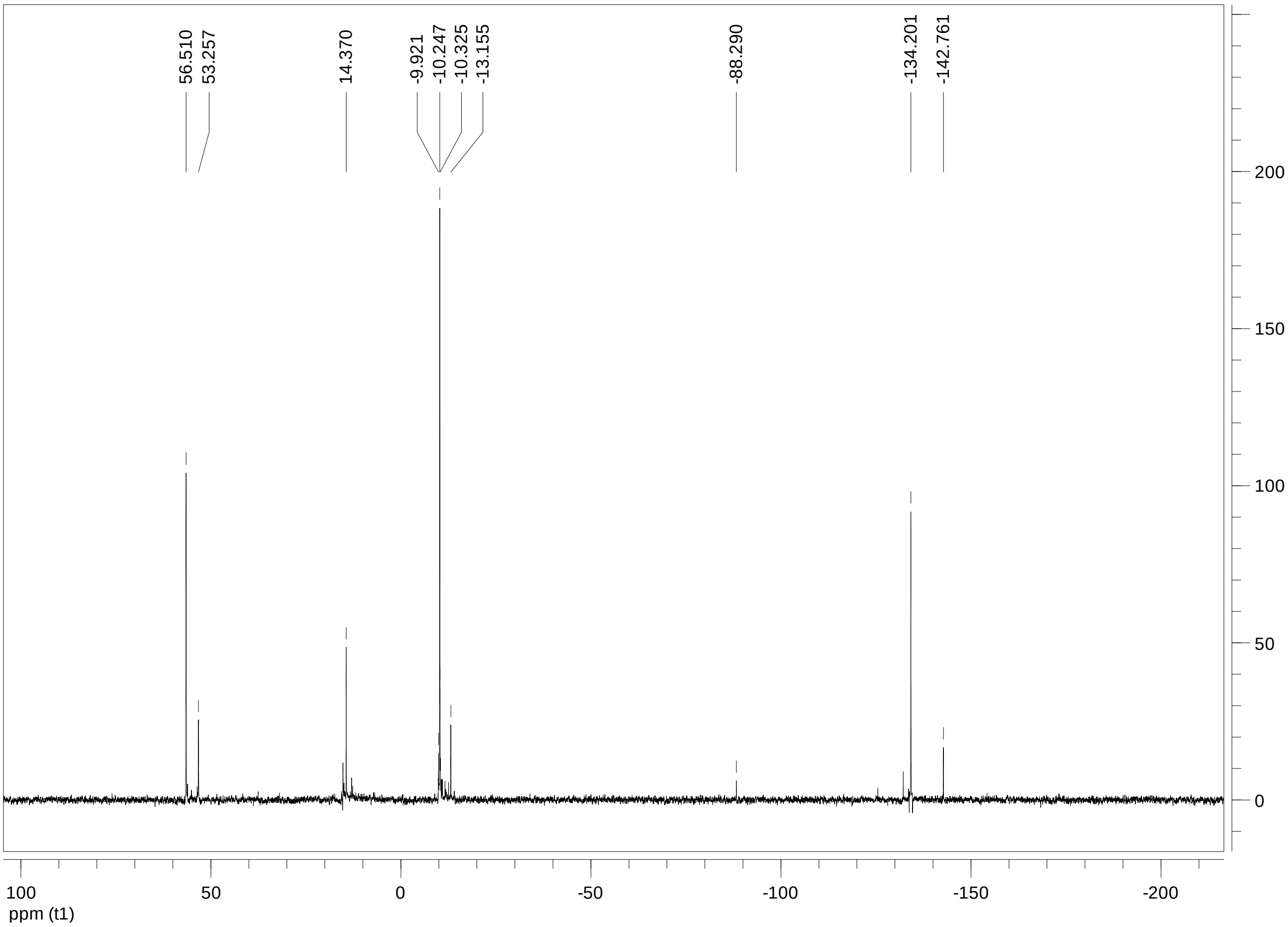
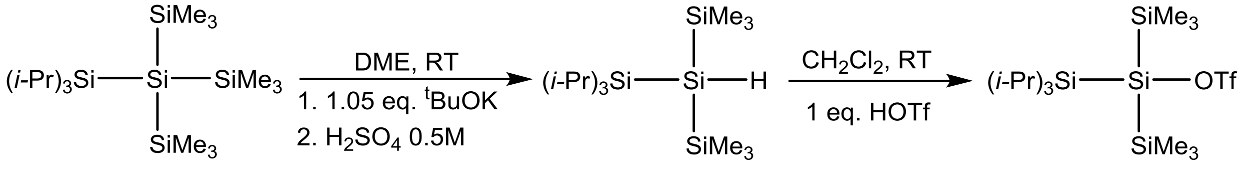


Figure 2-4: ^{29}Si NMR spectrum of **43** during heating (toluene as solvent).

4.1.2 Synthesis and rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)disilyl triflate (45)

Substrate **45**[42] should be more inclined to start a rearrangement process, because in this case a methyl group should move to the tertiary silicon atom, as already observed.[17] The synthesis is shown in Scheme 2-4, and the ^{29}Si NMR spectrum in Figure 3-4.



2 **44** **45**

Scheme 2-4: Synthesis of trisilylsilyl triflate **45** via the reaction of a H-oligosilane with triflic acid.

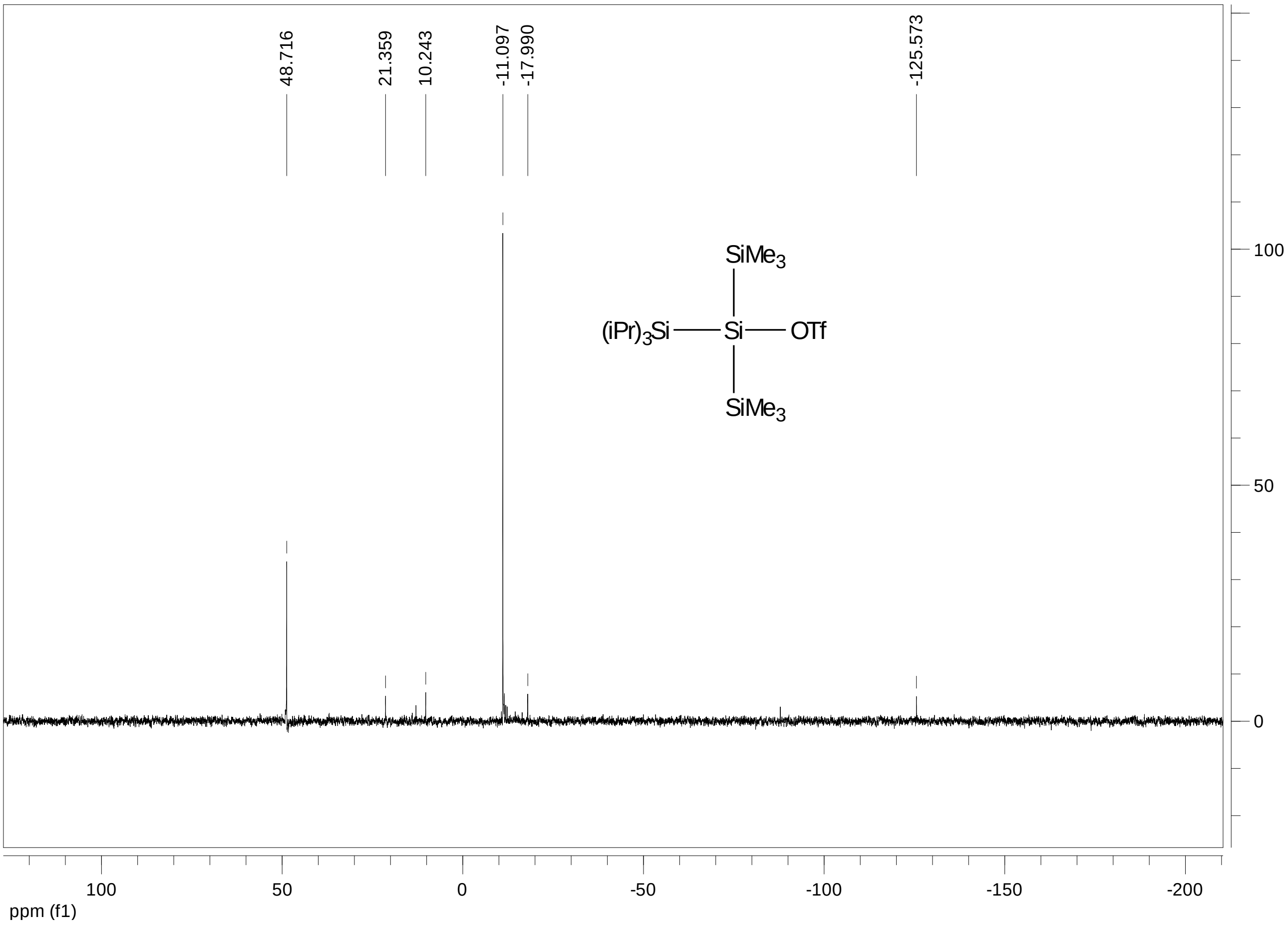
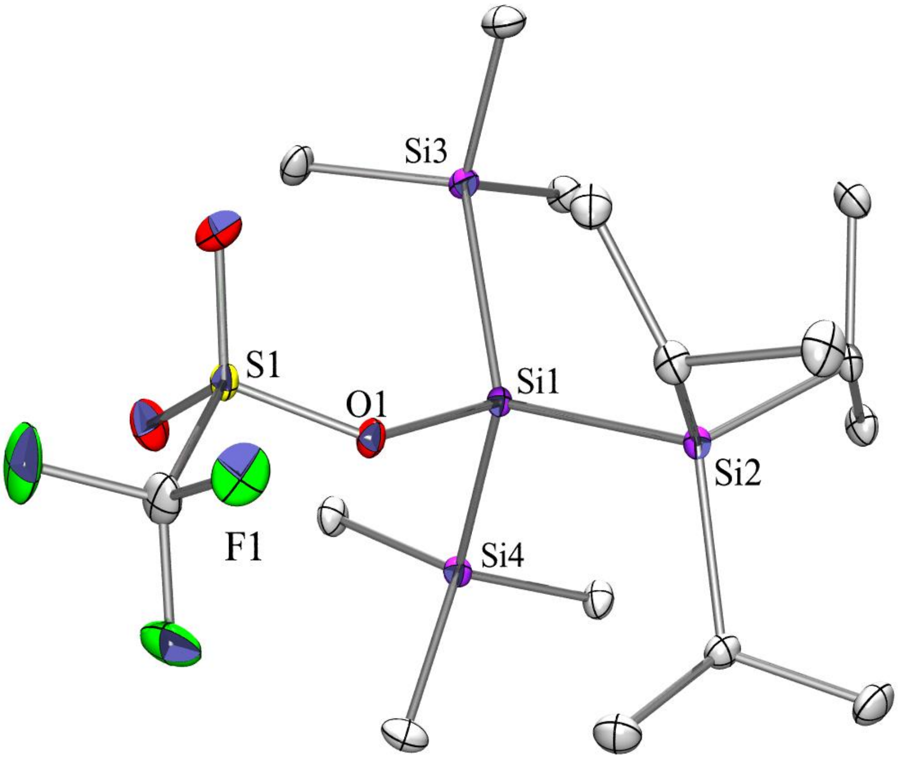


Figure 3-4: ^{29}Si NMR spectrum of the reaction mixture containing product **45**.

---

[42] M. Zirngast, M. Flock, J. Baumgartner, C. Marschner, *J. Am. Chem. Soc.,* **2008**, *130*, 17460-17470.

The signal of the Si-OTf silicon atom was at 48.7 ppm and the two $-SiMe_3$ groups gave a peak at -11.1 ppm. The triisopropylsilyl group (signal at 21.4 ppm) did not undergo a rearrangement process, as revealed by the crystal structure of compound **45** (Figure 4-4)



Selected crystallographic data:

Crystal system: monoclinic. Space group: P2(1)/n. Goodness-of-fit on F^2 = 1.115. Bond lengths [Å] and angles [deg]: Si(1)-Si(2) 2.3850(7); Si(1)-O(1) 1.7939(13); S(1)-O(1) 1.5149(12); Si(2)-Si(1)-O(1) 97.92(4); Si(1)-O(1)-S(1) 131.39 (7)

Figure 4-4: Crystal structure of compound **45**.

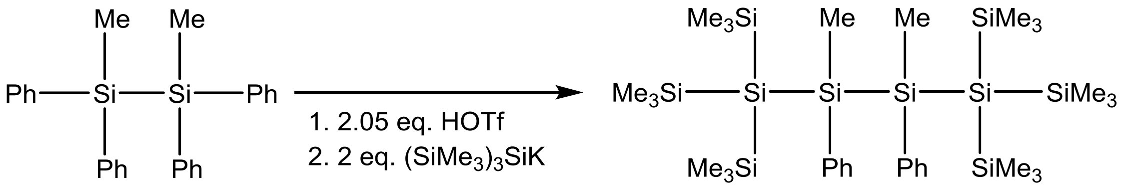
The silicon-oxygen bond was slightly longer but in the same range of similar types of silyl triflates (Si-O = 1.760 Å, CCDC 187811; Si-O =1.743, CCDC 187810).[43] Also the Si-O-S angle in compound **45** (131.39°) was consistent with the cited structures (132.21° for CCDC 187811 and 129.06° for CCDC 187810).

---

[43] A.Asadi, A.G.Avent, C.Eaborn, M.S.Hill, P.B.Hitchcock, M.M.Meehan, J.D.Smith, *Organometallics*, **2002**, *21*, 2183-2188.

4.1.3 Synthesis of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,3-diphenyl-dimethyltetrasilane (46)

During a numbers of attempts to prepare 1,2-bis(hypersilyl)tetraphenyldisilane (see chapter 7), it was possible to obtain product **46** starting from 1,2-dimethyl-tetraphenyldisilane (Scheme 3-4). This compound had two phenyl groups in an unusual position that could be treated with triflic acid to investigate the rearrangement process.



46

Scheme 3-4: Synthesis of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,3-diphenyl-dimethyltetrasilane (**46**).

It was possible to confirm the formation of the new silicon-silicon bonds by the rise of the signal at -30 ppm in the ^{29}Si NMR (Figure 5-4).

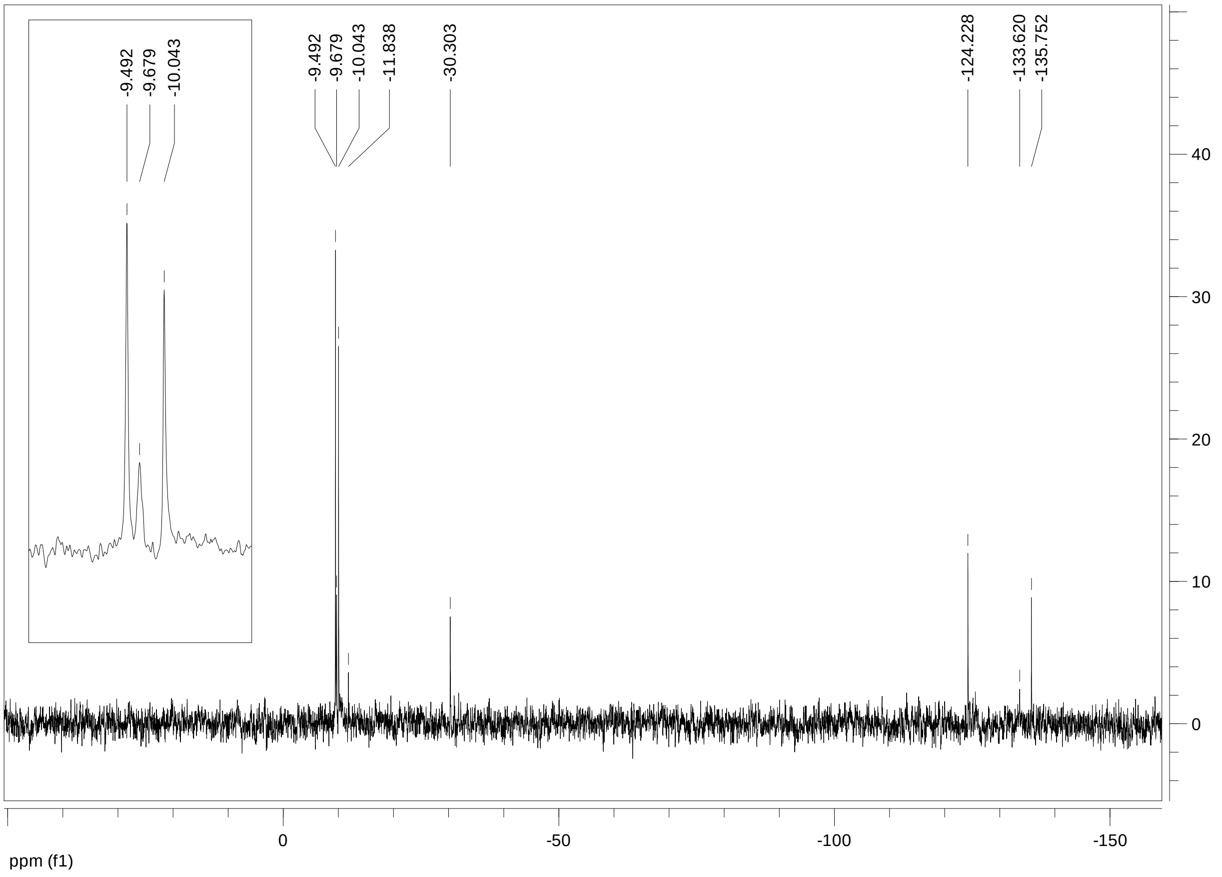
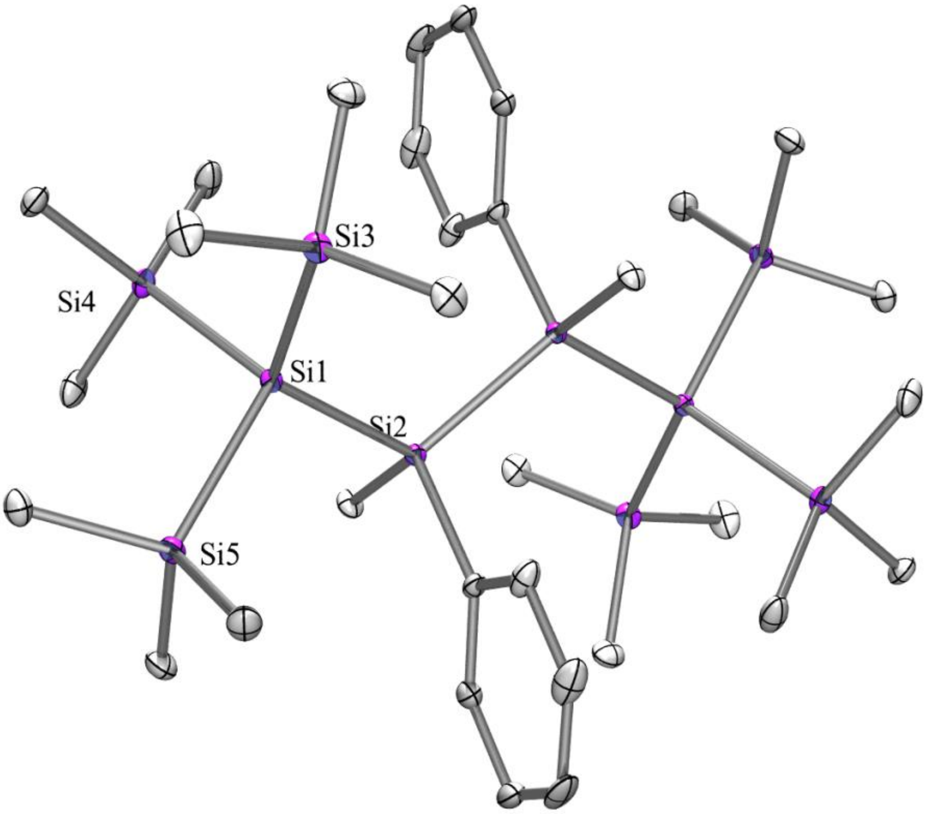


Figure 5-4: ^{29}Si NMR spectrum of compound **46** after the workup.

In the ^{29}Si NMR spectrum signals of compound **46** appeared at δ (ppm) = -124.2, -30.3, -9.5. The remaining signals were due to some tetrakis(trimethylsilyl)silane (**1**) (δ (ppm) = -135.7, -10.0), that crystallized together with the main product. Nevertheless, it was possible to isolate some pure crystals and determined the crystal structure by X-ray analysis (Figure 6-4).



Selected crystallographic data:

Crystal system: monoclinic

Space group: P2(1)/n

Goodness-of-fit on F^2 1.269

Bond lengths [Å] and angles [deg]

Si(1)-Si(2)	2.3762 (11)
Si(1)-Si(3)	2.3543 (12)
S(1)-C(9)	1.875 (3)
Si(2)-Si(2)#	2.3665 (16)
Si(2)-Si(1)-Si(3)	118.47 (4)
C(1)-Si(2)-Si(1)	106.57 (10)

Figure 6-4: Crystal structure of compound **46**.

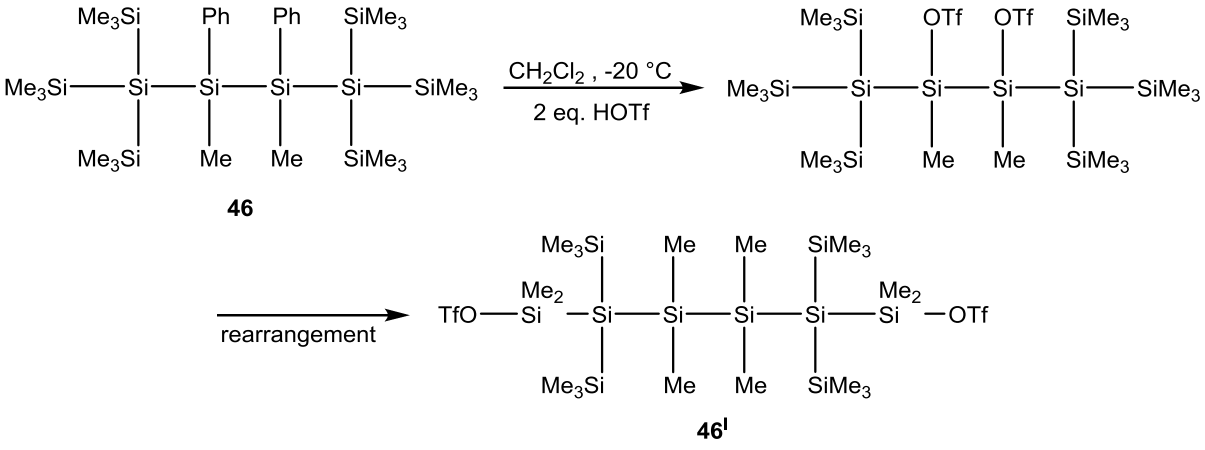
This structure was compared with that one of 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (**70**).[44] Compound **46** presented an internal silicon-silicon bond Si(2)-Si(2)# slightly shorter by ca. 0.01 Å than in **70**. The Si(1)-Si(3) bond was nearly the same (0.007 Å of difference), while the Si(1)-Si(2) bond was longer by ca. 0.03 Å than the respective bond of the permethylated analogous **70**.

---

[44] S.M. Whittaker, M. Brun, F. Cervantes-Lee, K.H. Pannell, *J. Organomet. Chem.*, **1995**, *499*, 247-252.

4.1.4 Rearrangement of compound 46 by treatment with triflic acid

Compound **46** was treated with 2 equivalents of triflic acid to verify if a rearrangement would occur (Scheme 4-4). The migration of a -$SiMe_3$ group or a methyl group and a subsequent exchange with the triflate group was expected.



Scheme 4-4: Rearrangement of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,3-diphenyl-dimethyltetrasilane (**46**).

In the ^{29}Si NMR spectrum the peaks at ca. -30 ppm for the -$SiMe_2$- groups confirmed this reaction path (Figure 7-4). The group of signals at -130.8 ppm, -29.9 ppm, -9.7 ppm and 53.9 ppm could correspond to the major product **46^{I}**. The remaining signals suggested the formation of asymmetric by-products, which could not be identify. Crystallization attempts to isolate the main product from the reaction mixture failed (storage at low temperature and slow evaporation of the solvent).

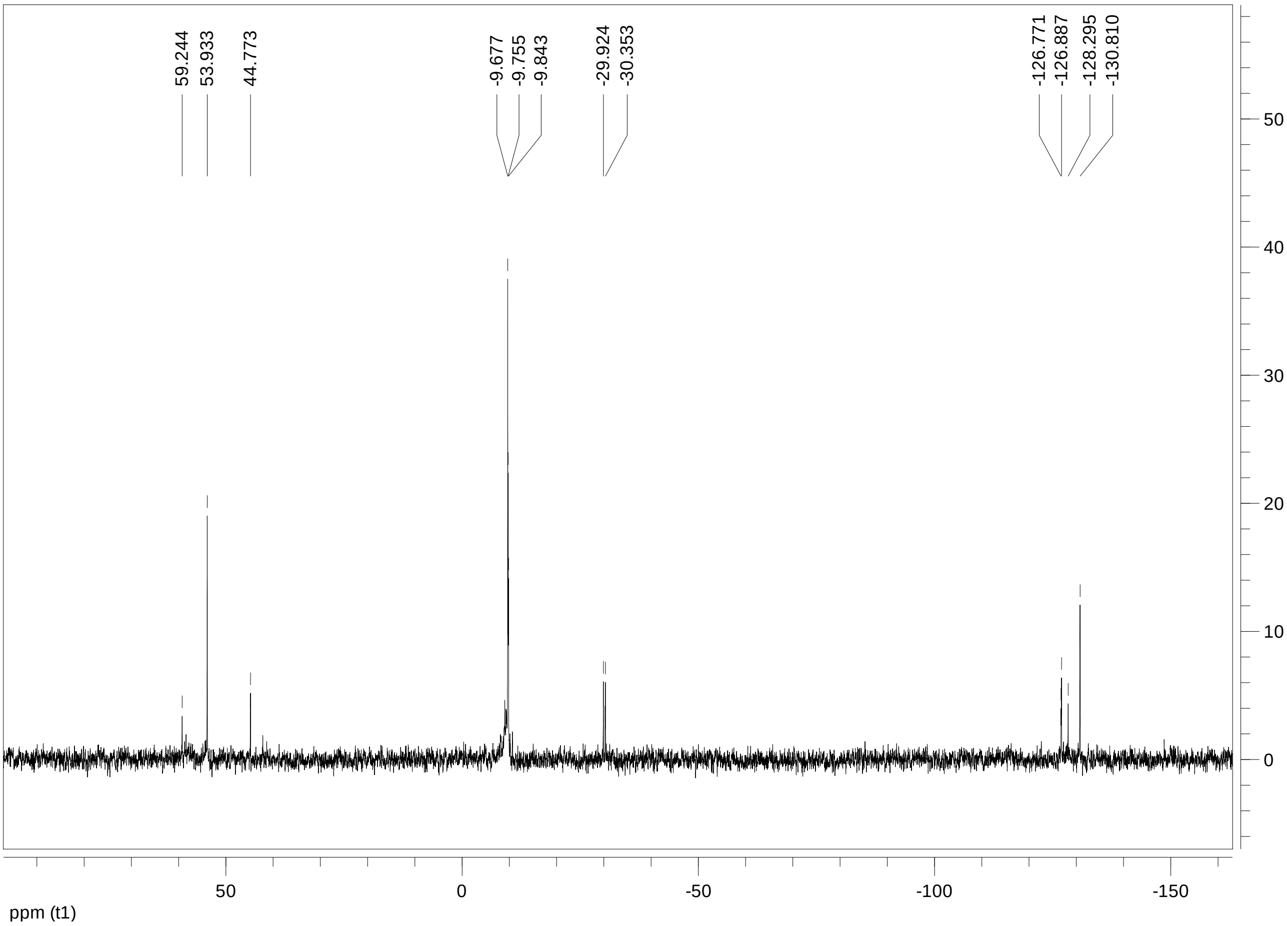
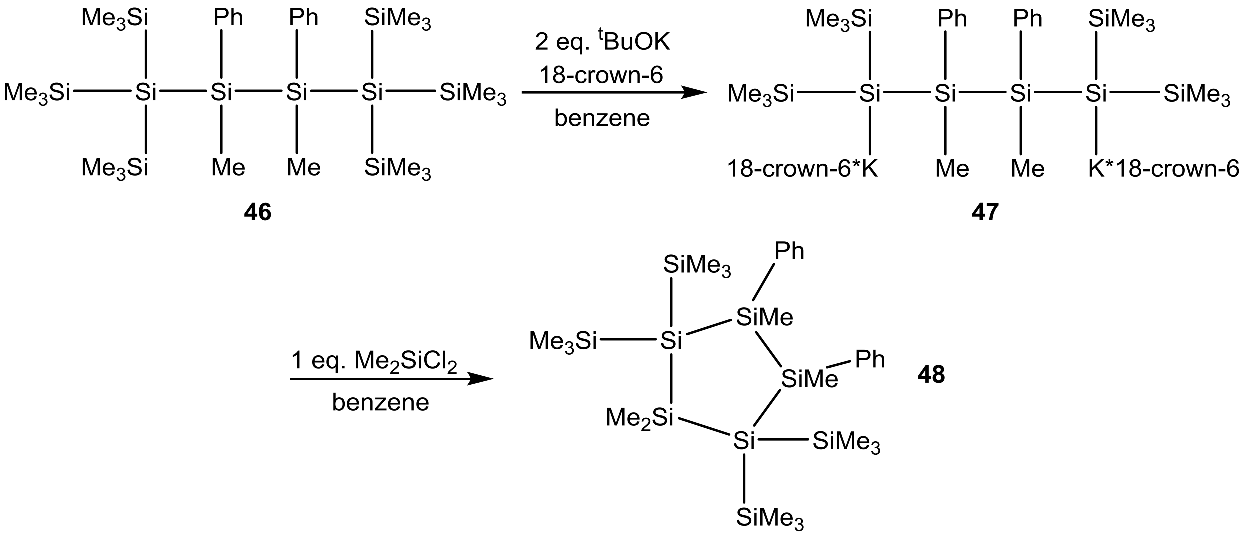


Figure 7-4: ^{29}Si NMR spectrum of the reaction mixture of the rearrangement of compound **46.**

4.1.5 Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-2,3-diphenyltetramethylcyclopentasilane (48)

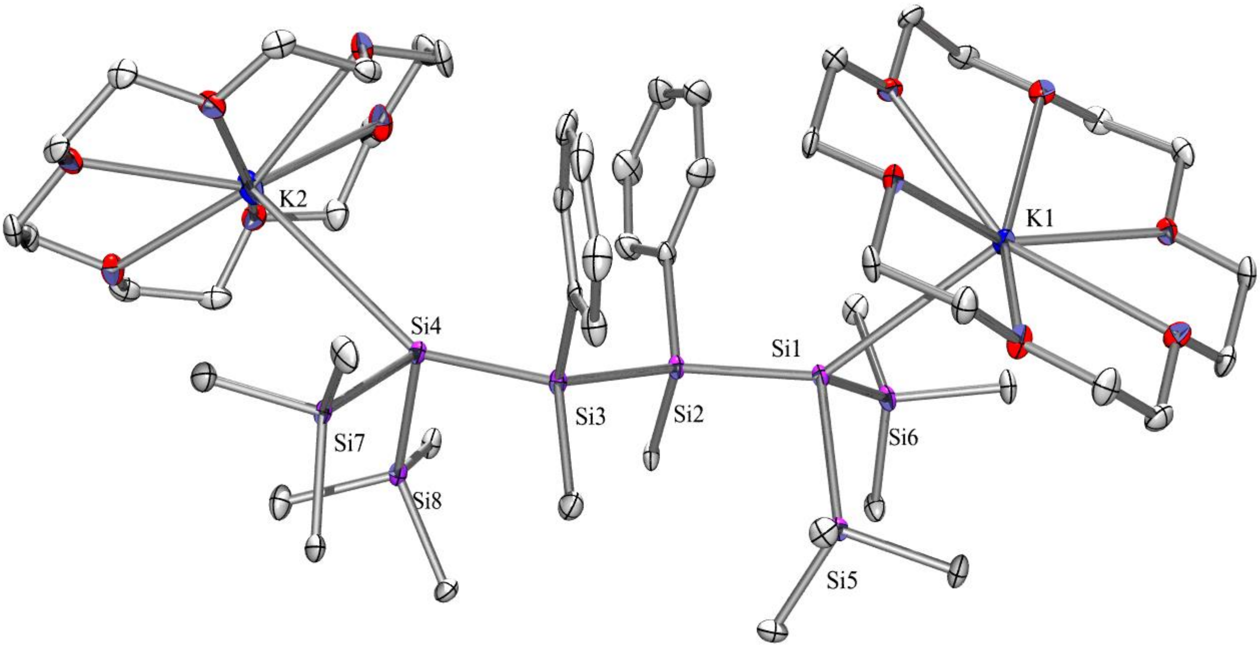
Compound **46** was treated with 2 equivalents of *t*-BuOK and then reacted with 1 equivalent of Me_2SiCl_2 (Scheme 5-4).



Scheme 5-4: Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-2,3-diphenyltetramethylcyclopentasilane (**48**).

The selective abstraction of a $-SiMe_3$ group from substrate **46** by potassium *tert*-butanolate was not obvious. In the cited paper,[6] the author found that in the presence of a dimethylphenylsilyl group, the base could easily attack the phenylated silicon atom. Thus led to the formation of tris(trimethylsilyl)silyl potassium and bis(trimethylsilyl)(dimethylphenylsilyl)silyl potassium in a 1:1 ratio.

The intermediate silyl dipotassium salt **47** could be isolated as 18-crown-6 complex and structurally characterized by X-ray analysis (Figure 8-4).



Selected crystallographic data: Crystal system: monoclinic; Space group: Cc; Goodness-of-fit on F^2: 1.147; Bond lengths [Å]: Si(1)-Si(2) 2.360 (2); Si(2)-Si(3) 2.3734 (17); Si(1)-K(1) 3.5079 (19); Angles [deg]: Si(1)-Si(2)-Si(3) 117.41 (7); K(1)-Si(1)-Si(2) 106.57 (10)

Figure 8-4: Crystal structure of compound **47**.

The Si(2)-Si(3) and the Si(1)-Si(2) bonds have basically the same length of the corresponding silicon-silicon bonds in the starting material **46**. The Si(1)-K(1) bond length is consistent with that one of other silyl potassium salts, previously measured.[7]

The cyclopentasilane (**48**) exhibited a double signal set in the ^{29}Si NMR spectrum (Figure 9-4) because of two possible structural isomers (phenyls groups in *cis* and *trans* position in respect of the ring plane). Also this compound was crystallized and characterized by X-ray analysis (Figure 10-4).

The silicon-silicon bond lengths were quite similar to the ones of 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane,[45] all in the range of 2.340 to 2.380 Å. For example, Si(4)-Si(5) = 2.350 Å (average value) in the case of the permethylated structure. The internal angles of the ring were also comparable, all between 100 to 112°.

---

[45] T. A. Blinka, R. West, *Organometallics,* **1986**, *5*, 133-139.

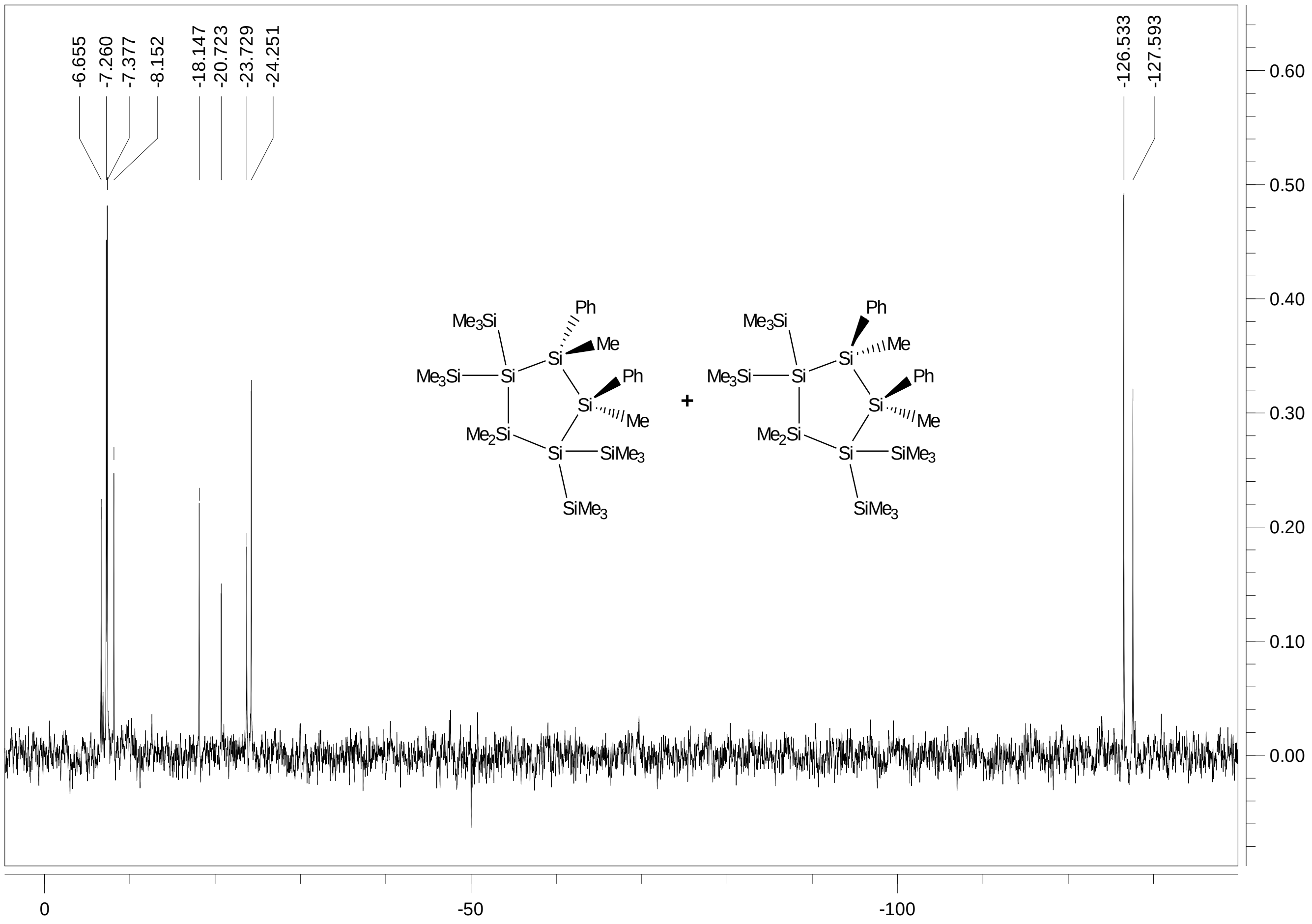
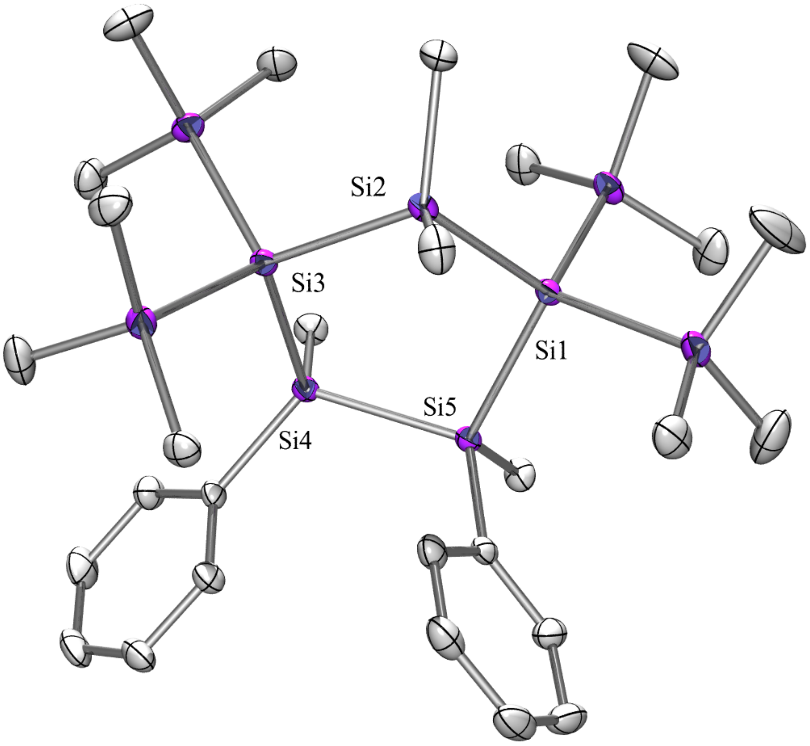


Figure 9-4: ^{29}Si NMR spectrum of the two isomers of compound **48**.



Selected crystallographic data:

Crystal system: monoclinic

Space group: P2(1)/c

Goodness-of-fit on F^2 1.025

Bond lengths [Å] and angles [deg]

Si(4)-Si(5) 2.3570 (9)

Si(1)-Si(2) 2.3684 (10)

S(1)-Si(5) 2.3632 (8)

Si(1)-Si(2)-Si(3) 107.73 (3)

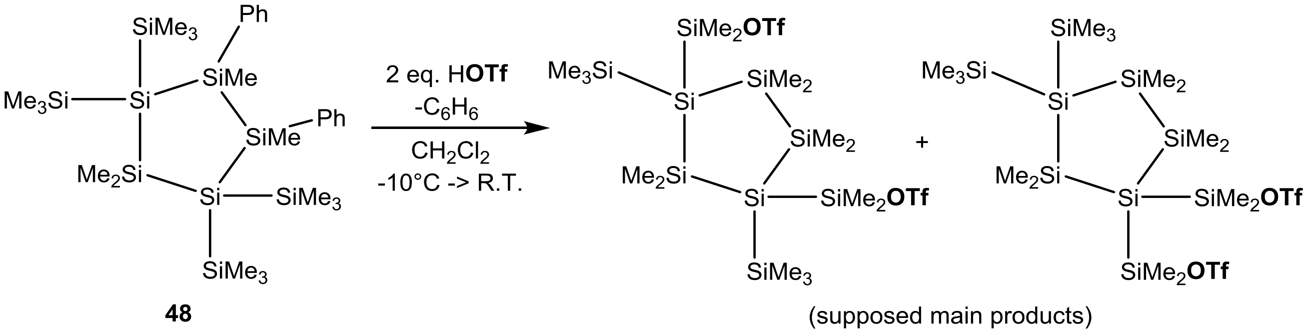
Si(2)-Si(1)-Si(5) 104.09 (3)

Si(5)-Si(4)-Si(3) 107.18 (4)

Figure 10-4: Crystal structure of compound **48** (cis-isomer).

4.1.6 Rearrangement of compound 48 through treatment with triflic acid

Cyclopentasilane **48** was reacted with 2 equivalents of triflic acid, to investigate the rearrangement process in a cyclic structure. As pointed out in the previous experiment with the linear substrate (Scheme 4-4), the methyl groups of the -$SiMe_3$ should migrate to positions 4 and 5 of the ring, and exchanging with the forming triflates (Scheme 6-4).



Scheme 6-4: Rearrangement of 1,1,4,4-tetrakis(trimethylsily)-2,3-diphenyl-tetramethylcyclopentasilane (**48**).

The ^{29}Si NMR spectrum of the reaction mixture is shown in Figure 11-4 and attempts were done to figure out the main products. First, the signals at -18 to -20 of the -SiMePh- fragments were not detected in the spectrum. Then the triflate groups migrated after their formation, and two -$SiMe_2$- units were formed. There were four peaks that might be assigned to these groups, as they might belong to asymmetric structures. Anyway, for the -$SiMe_2$- in position 2 of the ring, only two peaks appeared, at -22.4 ppm and -22.7 ppm. In addition, only two signals for the silyltriflate groups were detected. These signals were quite low-field shifted (usually silyltriflates give ^{29}Si NMR chemical shift at ca. 50 ppm), and from integration they had a ratio of 2:1. Regarding the NMR region of the quaternary silicon atoms, one main signal appeared at -129.5 ppm, and two smaller ones very close to each other were detected at -130.6 ppm. It might be possible that only two main products were formed, and that the high number of signals in the -$SiMe_3$ and -$SiMe_2$- regions was due to the different positions of the silyltriflate groups in the molecules. As a conclusion, two possible structures were supposed and they are depicted in Scheme 6-4.

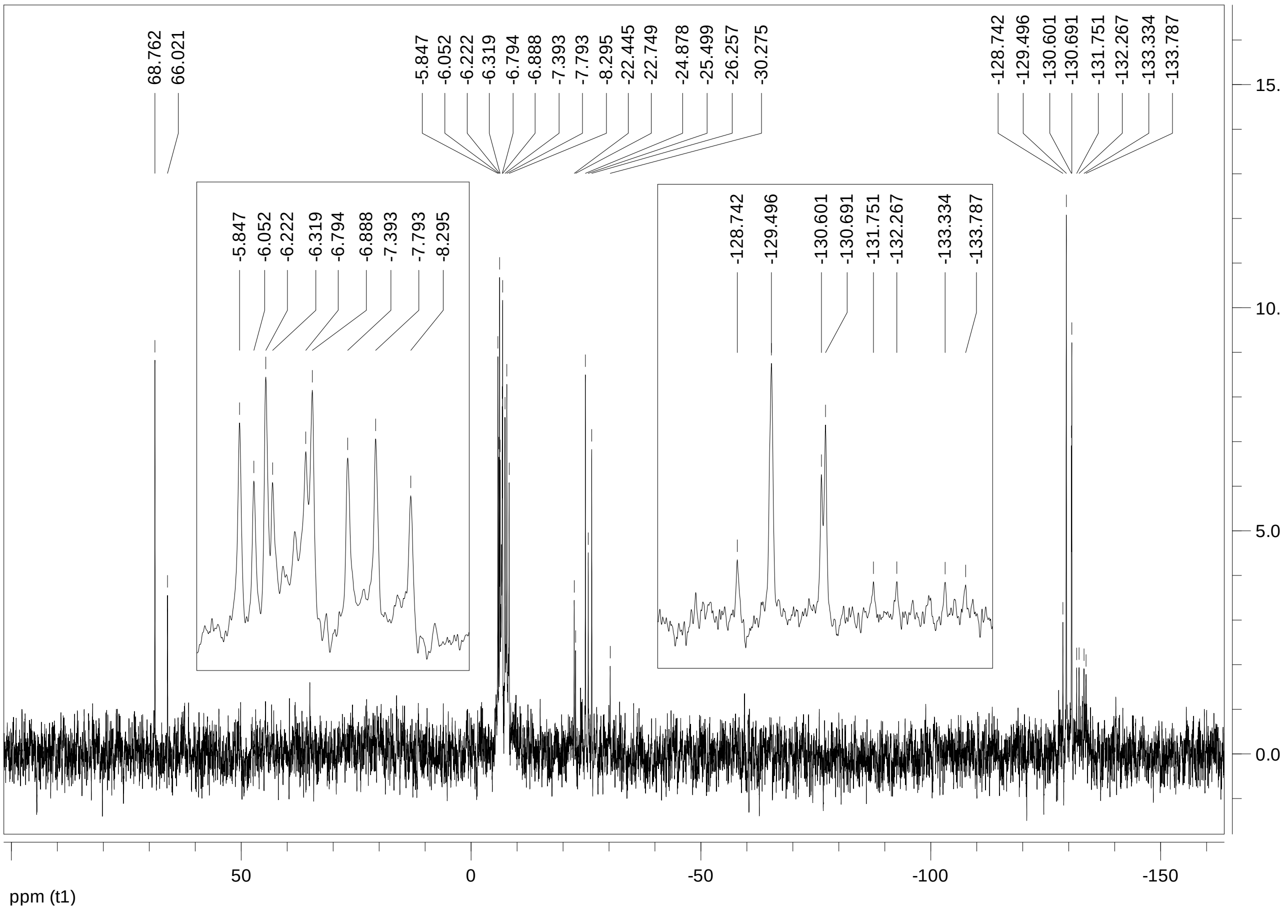


Figure 11-4: ^{29}Si NMR spectrum of the reaction mixture of the rearramngement of compound **48**.

5. From Catalytic to Stoichiometric Amount of TTPFPB:

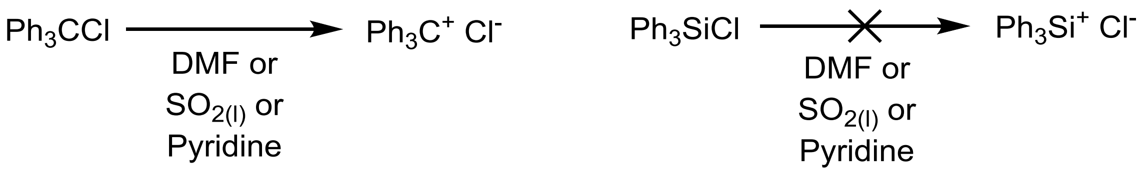
the Oligosilyl Cation

5.1 Introduction

The first successful attempt to prepare a carbenium ion was pursued by Merling,[46] at the end of the nineteenth century. The product of the reaction between cycloheptatriene and bromine was later characterized by Doering and Knox,[47] who demonstrated the formation of a C_7 aromatic ring containing a delocalized positive charge. But other examples of carbocation were observed at the beginning of 1900, rising from the reaction of triphenylmethanol and concentrated sulfuric acid, or by mixing triphenylmethylchloride with aluminum trichloride.[48,49]

Regarding organosilicon compounds, the first pioneering studies and experiments to obtain a silyl cation were carried on from the early 1950ies.[50] But scientists soon discovered that was not possible to repeat the same types of reactions for preparing carbocations with organosilicon substrates.

While dissolving Ph_3CCl in a very polar solvent it is sufficient to generate the salt $[Ph_3C^+][Cl^-]$, the same procedure leaves intact the corresponding chlorosilane Ph_3SiCl (Scheme 1-5):



$$Ph_3CCl \xrightarrow[\text{DMF or } SO_{2(l)} \text{ or Pyridine}]{} Ph_3C^+\ Cl^- \qquad Ph_3SiCl \xrightarrow[\text{DMF or } SO_{2(l)} \text{ or Pyridine}]{\times} Ph_3Si^+\ Cl^-$$

Scheme 1-5: Different behavior of triphenylmethylchloride and triphenylsilylchloride in polar solvents.

---

[46] G. Merling, *Chem. Ber.*, **1891**, *24*, 3108-3126.
[47] W. von E. Doering, L. H. Knox, *J. Am. Chem. Soc.*, **1954**, *76*, 3203–3206.
[48] J. F. Norris, *Org. Synth.,* **1925**, *4*, 81.
[49] M. Gomberg, *J. Am. Chem. Soc.*, **1902**, *24*, 597–628.
[50] If not otherwise specified, the examples in the text are derived from this review: R. J. P. Corriu, M. Henner, *J. Organomet. Chem.,* **1974**, *74*, 1-28.

At an early stage, the ion character of the solutions of these compounds was estimated by electric conductivity measurements. For example, solution of silyl perchlorate in polar solvents revealed the presence of ions.[51] However, deeper investigations showed that the cationic species were adducts of the solvent strongly coordinated to silicon, rather than “free” silylium ions.[52]

During the following years, it was possible to identify the supposed silyl cation by NMR techniques. In Table 1-5 are resumed some ^{29}Si NMR chemical shifts of various silyl derivatives in which the silicon atom presents a light positive charge:[53]

Organosilane	**δ ^{29}Si (ppm)**
$(CH_3)_3Si\text{-}OSO_2CF_3$	44.6
$(CH_3)_3Si\text{-}OClO_3$	43.4
$(CH_3)_3Si\text{-}OOCF_3$	34.3
$[(CH_3)_3Si]_2SO_4$	33.7
$(CH_3)_3Si\text{-}Cl$	32.5
$(CH_3)_3Si\text{-}F$	30.5
$(CH_3)_3Si\text{-}Br$	26.4
$(CH_3)_3Si\text{-}OOCH_3$	22.0
$[(CH_3)_3Si]_3PO_4$	20.0
$(CH_3)_3Si\text{-}S(C_6H_5)$	15.3
$(CH_3)_3Si\text{-}I$	8.6

When the electron density on the silicon atom decreases, because of the substituent effect, a low-field shift is observed in the ^{29}Si NMR spectrum. However, this shift is relatively small: for example, between silyl chloride and silyl triflate there are only 12 ppm difference in the chemical shifts.

Table 1-5: Electron draining substituent effect on the ^{29}Si NMR chemical shift.

In the case of $(CH_3)_3C\text{-}Cl$, $(CH_3)_3C\text{-}OSO_2CF_3$ and $(CH_3)_3C\text{-}OClO_3$, ^{13}C NMR chemical shifts are respectively 70 ppm, 90 ppm and 105 ppm,[54] while free carbenium ion usually shows a chemical shift above 200 ppm.[55]

---

[51] J.B. Lambert, J. A. McConnell, W. J. Jr. Schulz, *J. Am. Chem. Soc.*, **1986**, *108*, 2482−2484.

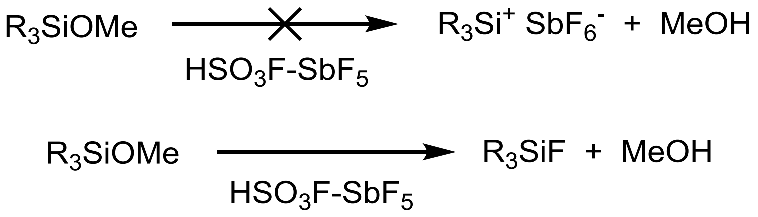
[52] Z. Xie, D. J. Liston, T. Jelínek, V. Mitro, R. Bau, C. A. Reed, *J. Chem. Soc., Chem. Commun.*, **1993**, 384−386.

[53] H. C. Marsmann, H. G. Horn, *Z. Naturforsch.*, **1972**, *27b*, 1448-1451.

[54] Predicted NMR data calculated using Advanced Chemistry Development, Inc. (ACD/Labs) Software V11.01 (© 1994-2015 ACD/Labs).

[55] G. A. Olah, G. K. Surya Prakash, G. Liang, *J. Org. Chem.*, **1977**, *42*, 2666-2671.

Treating alkoxysilanes or siloxane with $HSO_3F\text{-}SbF_5$ (extremely acidic conditions) does not lead to the silylium ion, and the alkoxy group is simply replaced by a fluorine atom (Scheme 2-5).



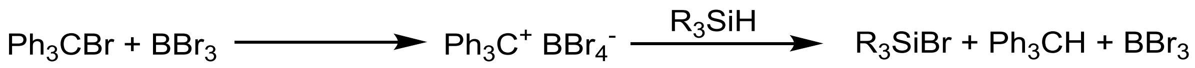
$$R_3SiOMe \xrightarrow[HSO_3F\text{-}SbF_5]{\times} R_3Si^+\ SbF_6^- + MeOH$$

$$R_3SiOMe \xrightarrow[HSO_3F\text{-}SbF_5]{} R_3SiF + MeOH$$

Scheme 2-5: Reaction of an alkoxysilane with super acid $HSO_3F\text{-}SbF_5$.

It is possible to prepare stable carbenium salt by mixing Ar_3CX (Ar = usually Ph; X = Cl, Br, I) with BX_3. The same reaction does not work with the corresponding triarylsilyl bromide or chloride.[50,56]

From a series of experiments by Corey and West on the hydrogen-halogen exchange between silanes and triphenylmethyl halides,[56] -it was taking a foothold the idea to react a pre-formed carbocation with an organosilanes containing a hydride group. Because of different electronegativity between silicon and hydrogen (1.9 against 2.2), the latter is slightly negatively charged, and the abstraction of $[H^-]$ should be favored. C-H bond are also stronger than Si-H bond (see Table 2-5). However, the reactions proceeded further and a halide was abstracted in turn by the forming silyl cation, from the starting counter anion (Scheme 3-5).



$$Ph_3CBr + BBr_3 \longrightarrow Ph_3C^+\ BBr_4^- \xrightarrow{R_3SiH} R_3SiBr + Ph_3CH + BBr_3$$

Scheme 3-5: Hydride abstraction from an H-Silane by a pre-formed carbocation.

Nevertheless, this concept was developed afterwards, and it became the starting point to achieve an isolable and “free” (or almost free) silyl cation.

---

[56] J. Y. Corey, R. West, *J. Am. Chem. Soc.*, **1963**, *85*, 2430-2433.

Before proceeding with the explanation of the main historical steps in the silylium ion chemistry, it is necessary to underline the most important differences between carbon and silicon, and why there is such a diverse behavior in the reactions shown above.

First, silicon and carbon hold different Pauling electronegativity: respectively 1.90 and 2.55. This could suggest that silicon atom is more "electropositive", and it could better allocate a positive charge. On the other hand, as in organosilanes silicon is bonded to carbon atoms, the latter drain electron density from the silicon atom. Then carbons are not really helping the silicon atom to sustain a forming positive charge, on the contrary they make the silicon atom even more desperate in the need to fulfill the octet rule.
As silicon is under carbon in the periodic table, it is bigger (atomic radius C = 77 pm, atomic radius Si = 111 pm). That implies silicon-carbon bonds are longer than carbon-carbon bonds, and also there is a worse overlapping between the *p* or *d* orbitals of silicon and the *p* orbitals of carbon (silicon is usually *sp*^{3} hybridized, but it can use 3*d* orbitals to interact with the *p*-electrons of an aryl substituent). The silylium ion is supposed to have a *sp*^{2} hybridisation, with the positive charge allocated in an empty 3*p* orbital. But even in this case, longer nuclei distance and smaller 2p/3p overlapping do not favor charge redistribution by resonance (Figure 1-5).[57]

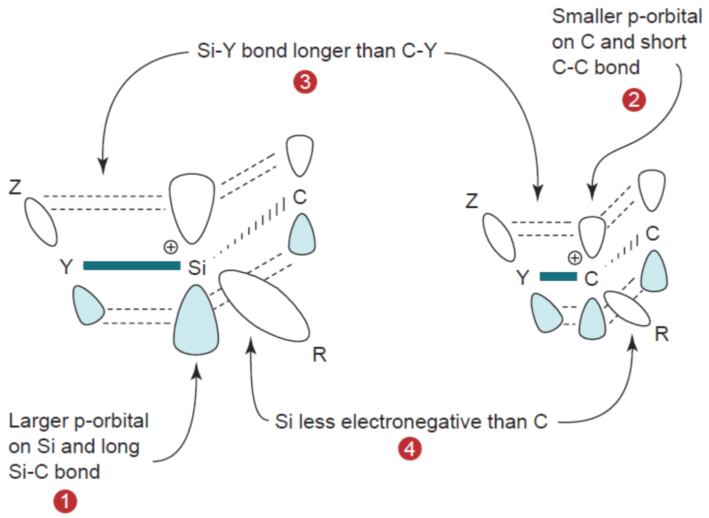


Figure 1-5: "The vacant *p* (1) orbital holding most of the positive charge on R_3Si^+ is larger than the corresponding orbital (2) on R_3C^+, and the Si-C bond is longer than the C-C bond. Si-C π-bonding is therefore weaker than C-C π-bonding (1,2). Donation of σ-electron density to Si from adjacent Y-Z bonds is diminished relative to C by the longer Si-Y bond (3). The Si atom of R_3Si^+ is less able to attract the electron pair that it shares with an attached R group than is the C atom of R_3C^+ because of the lower electronegativity of Si (4)".[57]

---

[57] P. P. Gaspar, *Science*, **2002**, *297*, 785-786.

Surprisingly, silicon is able to make stronger bonds than carbon with oxygen and halogens. This fact is due to the presence of empty 3*d* orbitals at the silicon atom, but in this case these orbitals can accept an entire lone pair from oxygen, sulphur, fluorine and all the other halogens. Then a partial π bond is formed, and the atoms show a slight double bond character (Figure 2-5).

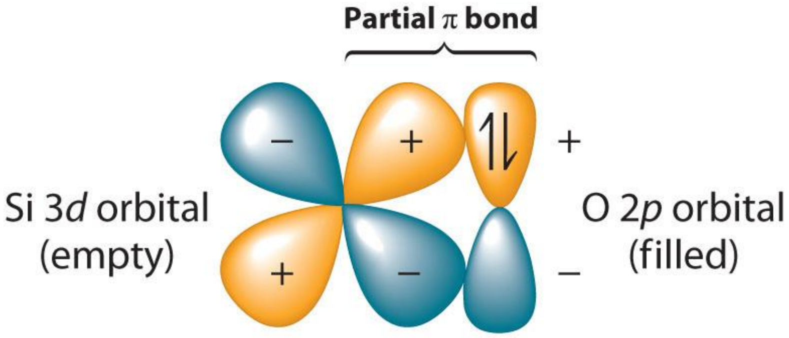


Figure 2-5: Representation of the overlapping between Si 3*d* orbitals and O 2*p* orbitals.

In Table 2-5 common C-X and Si-X bond lengths and bond energies are reported for comparison:

C-X	**Bond length (pm)**	***Bond energie (kJ/mol)***	**Si-X**	**Bond length (pm)**	***Bond energie (kJ/mol)***
C-C	154	*346*	Si-Si	233	*222*
C-H	109	*411*	Si-H	148	*318*
C-O	143	*358*	Si-O	163	*452*
C=O	120	*799*	Si=O	150	*799*
C-F	135	*485*	Si-F	160	*565*
C-Cl	177	*327*	Si-Cl	202	*381*
C-Br	194	*285*	Si-Br	215	*310*
			Si-C	185	*318*

Table 2-5: Literature data(*) for some common molecular fragments containing carbon and silicon. With 565 kJ/mol the Si-F bond is the strongest single bond known.

(*) Reference: Huheey, pps. A-21 to A-34; T.L. Cottrell, "*The Strengths of Chemical Bonds*," 2nd ed., Butterworths, London, **1958**; B. deB. Darwent, "*National Standard Reference Data Series*," National Bureau of Standards, No. 31, Washington, DC, **1970**; S.W. Benson, *J. Chem. Educ.*, **1965**, *42*, 502-518.

In summary, silicon is inclined to form strong covalent bonds with oxygen and halogens: whenever a neat (or almost neat) positive charge is induce at the silicon atom in the presence of water, air, oxygenated solvents, chlorinated solvents or halides, the silicon substrate may react to give alkoxy silanes, siloxane or silyl halides.

Anyway, the past misconceptions and failures contributed to improve the reaction conditions and the general approach to the "silylium ion problem".[58,59] As already stated, a Corey-type reaction (Scheme 3-5) was the mostly examined experiment and it was usually performed between a silane as R_3SiH and a carbocation as $Ph_3C^+X^-$. But after the work of Kulhmann and Lambert on trivalent tin cation, at the beginning of the Nineties,[60] aromatic solvents were employed instead of chlorinated or ethereal solvents, SO_2, DMF, acetonitrile or other polar or very polar solvents. Benzene and relative aromatics easily dissolve the substrate, the by-product Ph_3CH and eventually the carbenium salt (depending on the counter anion X^-). In addition, because of aromatic rings are highly polarizable, they can provide stabilization to the forming silyl cation. If the trityl salt was not soluble in benzene, two distinct phases could be observed, where the upper one could be called the *nonpolar phase* (containing triphenylmethane and residual silane) and the lower phase could be called the *polar phase*, as it contained the silyl anion salt.

---

[58] J. B. Lambert, Y. Zhao, S. Zhang, *J. Phys. Org. Chem.*, **2001**, *14*, 370-379, and cited papers therein.
[59] C. A. Reed, *Acc. Chem. Res.*, **1998**, *31*, 325–332.
[60] J. B. Lambert, B. Kuhlmann, *J. Chem. Soc., Chem. Commun.*, **1992**, 931-932.

Then, the choice of a sufficiently stable and not-coordinating counter anion was under investigation. Anions as BF_4^- and $B(Ph)_4^-$ were tried again by Lambert and collaborators,[51] but only fluorosilane and phenylsilane were obtained in high yield, respectively (Scheme 4-5).

$$R_3SiH + Ph_3C^+ BF_4^- \xrightarrow{\qquad} R_3SiF + Ph_3CH + BF_3$$

$$R_3SiH + Ph_3C^+ B(Ph)_4^- \xrightarrow{\qquad} R_3SiPh + Ph_3CH + B(Ph)_3$$

Scheme 4-5: Reaction attempts of an H-Silane with the trityl cation and different borate counteranions.

The turning point was reached by two separate works by Marks[61] and Chien,[62] who reported the methyl abstraction from a zirconium complex carried out by perfluorophenyl borates. Marks employed $B(C_6F_5)_3$ to coordinate the methanide anion and break the Zr-CH_3 bond.[51] But this approach did not work in the case of Si-CH_3, probably because the Si-C bond is too strong in respect to the Zr-C bond.

Chien performed a similar reaction.[51] However, to remove the methyl group, the Zr-CH_3 complex was treated with trityl tetrakis(pentafluorophenyl)borate, often indicated as TTPFPB, $[Ph_3C^+B(C_6F_5)_4^-]$. Combining the latter experiment with the Corey reaction,[56] the so long sought silyl cation was finally prepared by the group of Lambert (Scheme 5-5).[63]

$$R_3SiH + Ph_3C^+ B(C_6F_5)_4^- \xrightarrow[\text{benzene}]{\qquad} R_3Si^+ B(C_6F_5)_4^- + Ph_3CH$$

Scheme 5-5: Formation of the silylium ion by removal of a hydride with a trityl perfluorophenylborate salt.
R = -Me, -Et, -*i*-Pr, -*i*Bu, -Me*i*-Pr_2, -Hex, -$MePh_2$, -$SiMe_3$.

The TTPFPB provided a well disperse negative charge, strong B-C and C-F bonds, a rather good solubility in aromatic solvents (it is sparingly soluble in toluene but completely soluble in chlorobenzene) and a fairly easy preparation procedure.

Subsequently, the first crystal structure of a silyl cation was again proposed by Lambert in 1994 (Figure 3-5).[64]

---

[61] X. Yang, C. L. Stern, T. J. Marks, *Organometallics*, **1991**, *10*, 840-842.

[62] J. C. W. Chien, W. M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.*, **1991**, *113*, 8570-8571.

[63] J. B. Lambert, S. Zhang, Chem. Soc., *Chem. Commun.*, **1993**, 383-384.

[64] J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics*, **1994**, *13*, 2430-2443.

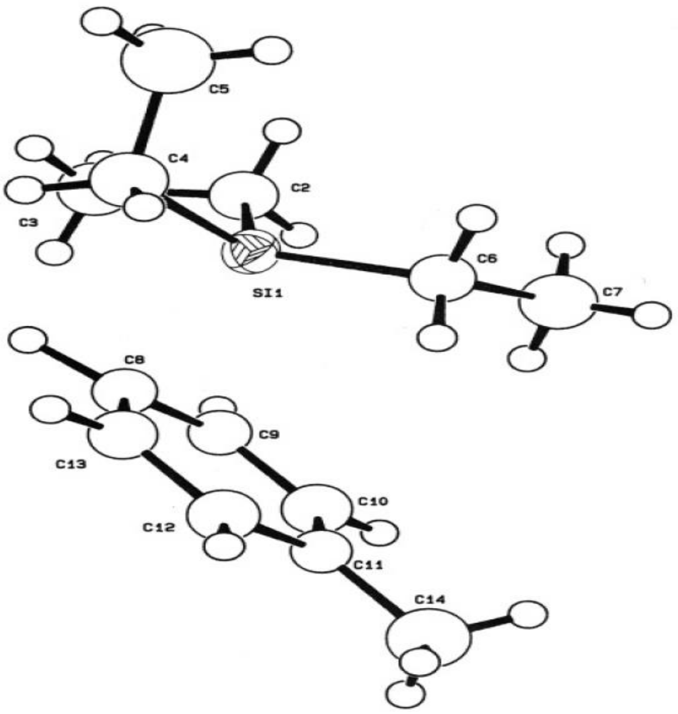


Figure 3-5: Crystal structure of the trivalent Et_3Si^+,[64] coordinating a toluene molecule (counter anion omitted for clarity). Main crystallographic data: Si(1)-C(2) = 1.85 Å; Si(1)-C(8) = 2.18 Å; C(2)-Si(1)-C(4) ≈ 113°.

Some NMR data by Lambert are here reported (Table 3-5) and they will be later discussed.[64]

$\mathbf{R}_3Si^+B(C_6F_5)_4^-$	δ ^{29}Si NMR (ppm)	$\mathbf{R}_3Si^+B(C_6F_5)_4^-$	δ ^{29}Si NMR (ppm)
R = Me	83.6 (benzene)	R = $MePh_2$	73.6 (benzene)
R = Et	92.3 (benzene) 81.8 (toluene) 36.7 (acetonitrile)	R = Me*i*-Pr_2	96.9 (benzene) 41.9 (acetonitrile) 44.3 (pyridine/C_6D_6)
R = *i*-Pr	107.5 (benzene)	R = $SiMe_3$	111.1 (benzene) 96.1 (toluene)

Table 3-5: Silylium ion ^{29}Si NMR data from Lambert's paper.[64] The solvent is specified in brackets.

Nevertheless, the choice of the counter anion was not unique, and at the same time as Lambert the research group of C. A. Reed reported the synthesis and the characterization of a triisopropylsilyl cation supported by a hexabrominated *closo*-carborane $Br_6CB_{11}H_6^-$.[65] Brominated and chlorinated carborane are extremely robust and inert clusters, that probably provide the least nucleophilicity nowadays known.[66,67] The crystal structure of Reed's silylium ion is here shown (Figure 4-5).

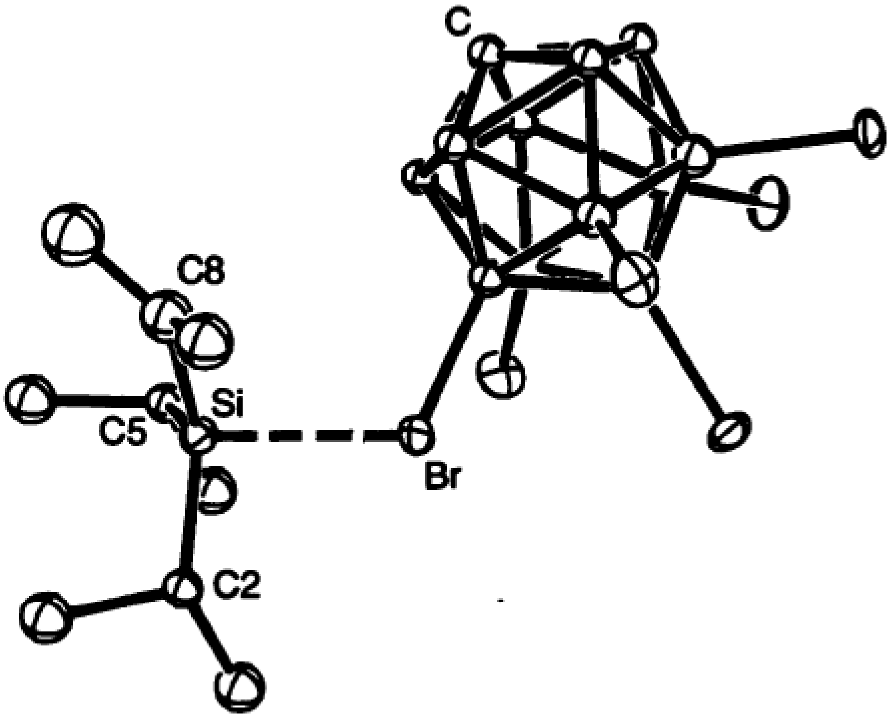


Figure 4-5: Crystal structure of [*i*-Pr_3Si^+][*closo*-7,8,9,10,11,12-Br_6-$CB_{11}H_6^-$].[65] Main crystallographic data: Si(1)-C(2) = 1.86 Å; Si(1)-Br = 2.48 Å; C(2)-Si(1)-C(5)' ≈ 120°; average C-Si-C' angle = 117°.

The ^{29}Si NMR revealed a chemical shift of 105 ppm for a toluene solution of this compound, and a chemical shift of 109 ppm in the case of solid state NMR.[65] These values are quite similar to those ones reported by Lambert (Table 3-5).[64]

---

[65] C. A. Reed, Z. Xie, R. Bau, A. Benesi, *Science*, **1993**, *262*, 402-404.

[66] Z. Xie, J. Manning, R.W. Reed, R. Mathur, P.D.W. Boyd, A. Benesi, C.A. Reed, *J. Am. Chem. Soc.*, **1996**, *118*, 2922–2928.

[67] C. A. Reed, *Acc. Chem. Res.*, **1998**, *31*, 133-139.

Because of the *not* extremely long distance between the silicon atom and the bromine atom, the “pure” cationic character of the silylium ion might be objected. The same counts for the structure shown in Figure 3-5, where the *para*-carbon of the toluene molecule is even closer to the silicon. In the latter case, Pauling calculated that about 35% of the positive charge was transferred to the aromatic ring.[68] But most of all, Pauling, Müller and others provided computational calculations about the theoretical ^{29}Si NMR chemical shift of a completely “naked” silyl cation, which should be comprised between 200 and 400 ppm, depending on the alkyl/aryl substituents and on the computational methods.[69,70,71] For example, the signal of a “free” Et_3Si^+ ion should appear at 354.6 ppm. On the other hand, calculations work very well when a molecule of the solvent or any type of nucleophiles (aromatics, alkanes and even a rare gas) are placed at van der Waals distance from the R_3Si^+ fragment (around 2.10 Å for silicon atom), causing a dramatic high-field shift of the NMR signals.[59]

One of the few examples for which calculated NMR chemical shifts and experimental data were in a good agreement it was the Mes_3Si^+ cation (Mes = mesityl, 2,4,6-trimethylphenyl; counter anion $B(C_6F_5)_4^-$), reported by Lambert in 1997.[72] In that case, the *ortho*-methyl groups provided sufficient steric hindrance to avoid any coordination of aromatic solvents to the silicon center, and at the same time the methyl groups themselves could not be in turn coordinated by the silyl cation, because of their geometry. The ^{29}Si NMR of the reaction mixture showed a single signal at 225.5 ppm. The theoretical value was calculated by Müller as 230.1 ppm.[69] However, the adding of small polar solvent as acetonitrile caused significant high-field shift of the NMR signal, as CH_3CN was able to move around the *o*-methyl groups barrier and it could form the adduct with silylium ion ($\delta(^{29}Si)$ = 37 ppm).

---

[68] L. Pauling*, Science,* **1994**, *263*, 983-984.

[69] T. Müller, Y. Zhao, J. B. Lambert, *Organometallics*, **1998**, *17*, 278–280.

[70] T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem*., **2007**, *119*, 6462-6465.

[71] G. A. Olah, L. D. Field, *Organometallics*, **1982**, *1*, 1485-1487.

[72] J. B. Lambert,Y. Zhao, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400−401.

Few years later, Lambert together with Reed (finally!) prepared again the trimesitylsilyl cation, but using a carborane cluster as counter anion. It was possible to crystallize the silyl salt and characterized it by NMR in the solid state and in solution (Figure 5-5).[73]

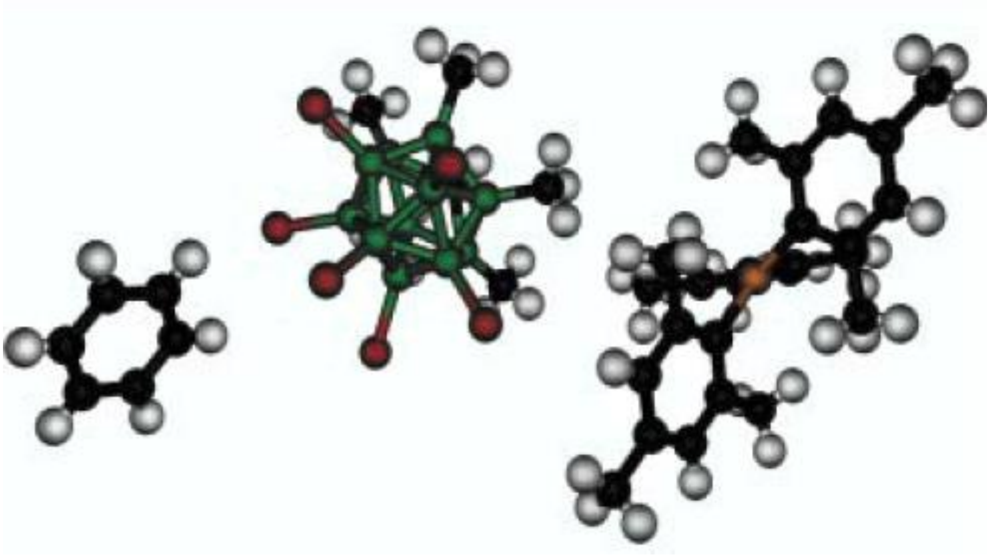


Figure 5-5: Crystal structure of [Mes_3Si^+][$H\text{-}CB_{11}Me_5Br_6^-$]$\cdot C_6H_6$ (green, B; red, Br; black, C; gray, H; brown, Si).[73] Main crystallographic data: average Si-C = 1.817 Å; average C-Si-C' angle ≈ 120°.

Here, molecules of the solvent and of the anion are at least 6 Å away from the silicon center. In addition, the agostic interactions with the *o*-methyl groups of the mesityl substituents can be neglected. As a consequence, the ^{29}Si NMR chemical shifts in liquid phase and in solid state are very similar, respectively 225.5 ppm and 226.7 ppm, and the calculated value is in-between 220 and 230 ppm, depending on the applied computational method. Finally, this compound was the first one that could be characterized as a "free" silylium ion by both crystallographic and spectroscopic techniques.

---

[73] K. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science*, **2002**, *297*, 825-827.

Very recently Krossing and co-workers pursued a different approach to a silylium-like species, reacting trimethylsilylfluoride with an *in situ* prepared perfluro-*tert*-butoxy aluminate (Scheme 6-5).[74]

$$Me_3SiF + AlEt_3 + 3HOR^F \xrightarrow[\text{hexane}]{} Me_3Si\text{-}F\text{-}Al(OR^F)_3 + 3C_2H_4$$

Scheme 6-5: Synthesis of a silyl cation having a fluoride-aluminate adduct as counter anion ($R^F = C(CF_3)_3$).

The latter compound[74] presented a Si-F bond length elongated only by 0.14 Å in respect to the trimethylsilylfluoride. But the ^{29}Si NMR chemical shift was quite consistent with the examples previously mentioned, and that's suggested the cationic character of the silicon atom ($^{29Si}\delta$(MAS) = 84.6 ppm). In addition, the reactivity studies[74] showed the ability of this silyl salt to form adduct with phosphines or to react with alcohols or silanols to form $Me_3SiO(H)\text{-}Al(OR^F)_3$ adducts. The crystal structure of this atypical silylium ion is here shown (Figure 6-5).

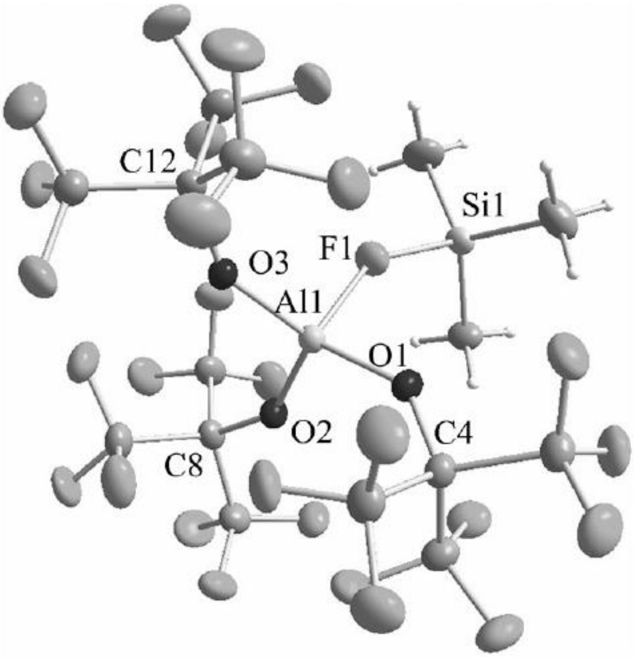


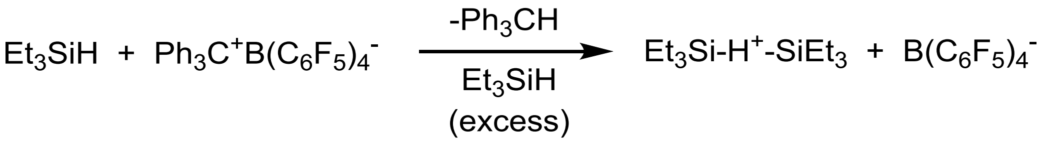
Figure 6-5: Crystal structure of $[Me_3Si\text{-}F\text{-}Al(OR^F)_3]$.[74]
Main crystallographic data: Si-F = 1.744 Å; Al-F=1.803; average C-Si-C' angle ≈ 115°.

---

[74] M. Rohde, L. O. Müller, D. Himmel, H. Scherer, I. Krossing, *Chem. Eur. J.*, **2014**, *20*, 1218–1222.

While in the Nineties preparation methods of the silylium ions species were going to be standardized, after 2000 these extremely reactive molecules started to be used for both stoichiometric[75] and catalytic reactions.[76]

But the debate around the true nature of the silyl cation remains still lively. In 2011, Nava and Reed went deeper inside the apparently “simple” Corey reaction, and by ATR-IR measurements they discovered that when the silyl cation was prepared with an excess of silane, a hydride bridged disilyl cation was formed (Scheme 7-5).[77]



$$Et_3SiH + Ph_3C^+B(C_6F_5)_4^- \xrightarrow[\substack{Et_3SiH \\ (excess)}]{-Ph_3CH} Et_3Si\text{-}H^+\text{-}SiEt_3 + B(C_6F_5)_4^-$$

Scheme 7-5: Synthesis of the silane-silylium ion adduct.

If only one equivalent of trityl cation was employed, only half equivalent of the bridged silyl cation was generated, while only half equivalent of carbocation was consumed. Adding some coordinating solvent as benzene or ether to the reaction mixture, it caused the displacement of the silane and the formation of the [Et_3Si^+-solvent] adduct. To remove the silane molecule was not possible under high vacuum, and heating the remaining solid provoked decomposition of the anion (with the formation of $B(C_6F_5)_3$). However, the silane adduct reacted effectively as a silyl cation, and the by-product silane remained innocently in solution or it evaporated from the reaction mixture. But attention should be paid planning a reaction involving these species. In fact, one mole of triethylsilane plus one mole of TTPFPB generates half mole of [$Et_3Si\text{-}H^+\text{-}SiEt_3$] and half mole of Ph_3CH. Half mole of TTPFPB will remain unreacted in solution.

---

[75] C. A. Reed, *Acc. Chem. Res.*, **2010**, *43*, 121–128.
[76] H. F. T. Klare, M. Oestreich, *DaltonTrans.*, **2010**, *39*, 9176–9184.
[77] M. Nava, C. A. Reed, *Organometallics*, **2011**, *30*, 4798–4800.

After a couple of years, Heinekey and his collaborators were able to crystallize the silane adduct from a chlorobenzene/alkane solution (Figure 7-5).[78]

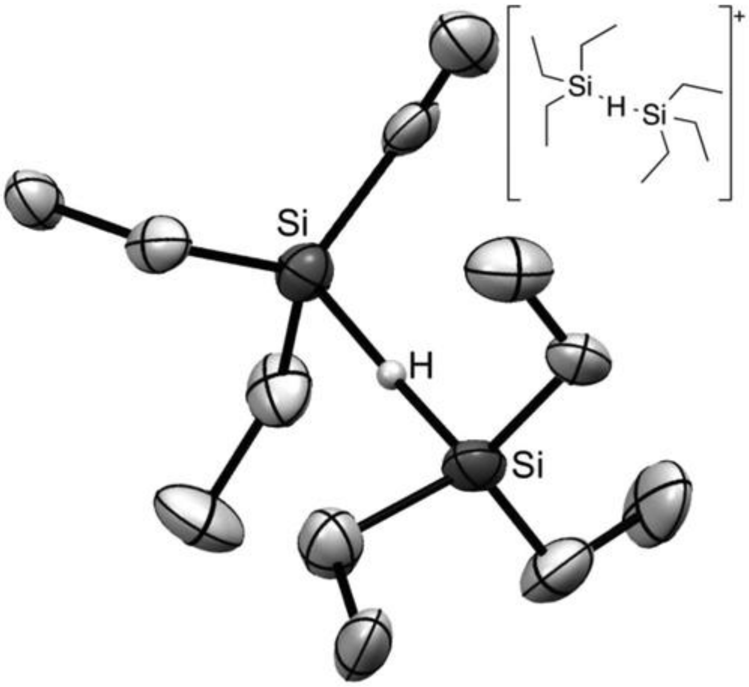


Figure 7-5: Crystal structure of $[Et_3Si\text{-}H^+\text{-}SiEt_3][B(C_6F_5)_4^-]$.[78]
Main crystallographic data: Si-Si' = 3.217 Å; average C-Si-C' angle ≈ 116°.

The ^{29}Si NMR chemical shift[78] of the adduct was measured in fluorobenzene by ^{29}Si-^{1}H HMQC. The spectrum revealed that the silane was a stronger ligand for the silyl cation, with a high field shifted signal at 57 ppm, and that the fluorobenzene adduct was not forming (or forming in a small amount).

---

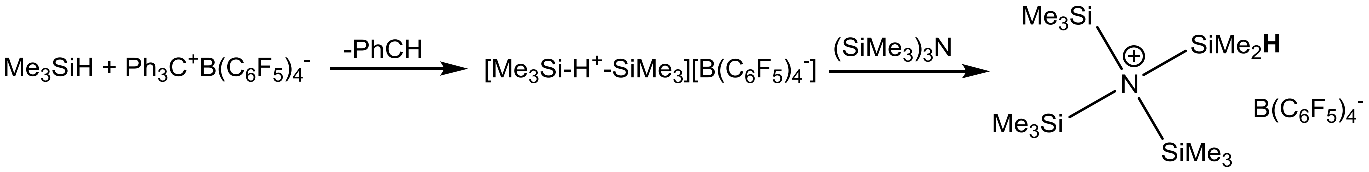
[78] S. J. Connelly , W. Kaminsky, D. M. Heinekey, *Organometallics*, **2013**, *32*, 7478–7481.

More, if the silylium ion solution was prepared in neat solution of Et_3SiD (deuterated silane), the addition of toluene or benzene caused hydrogen evolution (Scheme 8-5).[78]

$$Et_3Si\text{-}D^+\text{-}SiEt_3 + C_6H_6 \longrightarrow Et_4Si + HD_{(g)} + \text{unknown oily phase}$$

Scheme 8-5: Hydrogen evolution during the formation of the $[Et_3Si(benzene)]^+$ adduct.[78]

But the Corey reaction had still some hidden special features. In fact, during various attempts to synthesize the first tetrakis(trimethylsilyl)ammonium cation, Villinger and his group obtained the unexpected $[(Me_3Si)_3NSi(H)Me_2]^+$.[79] A trimethylsilyl cation was prepared with the standard procedure and then it was reacted with tris(trimethylsilyl)amine (Scheme 9-5).



Scheme 9-5: Synthesis of the tris(trimethylsilyl)dimethysilylammonium borate salt.[79]

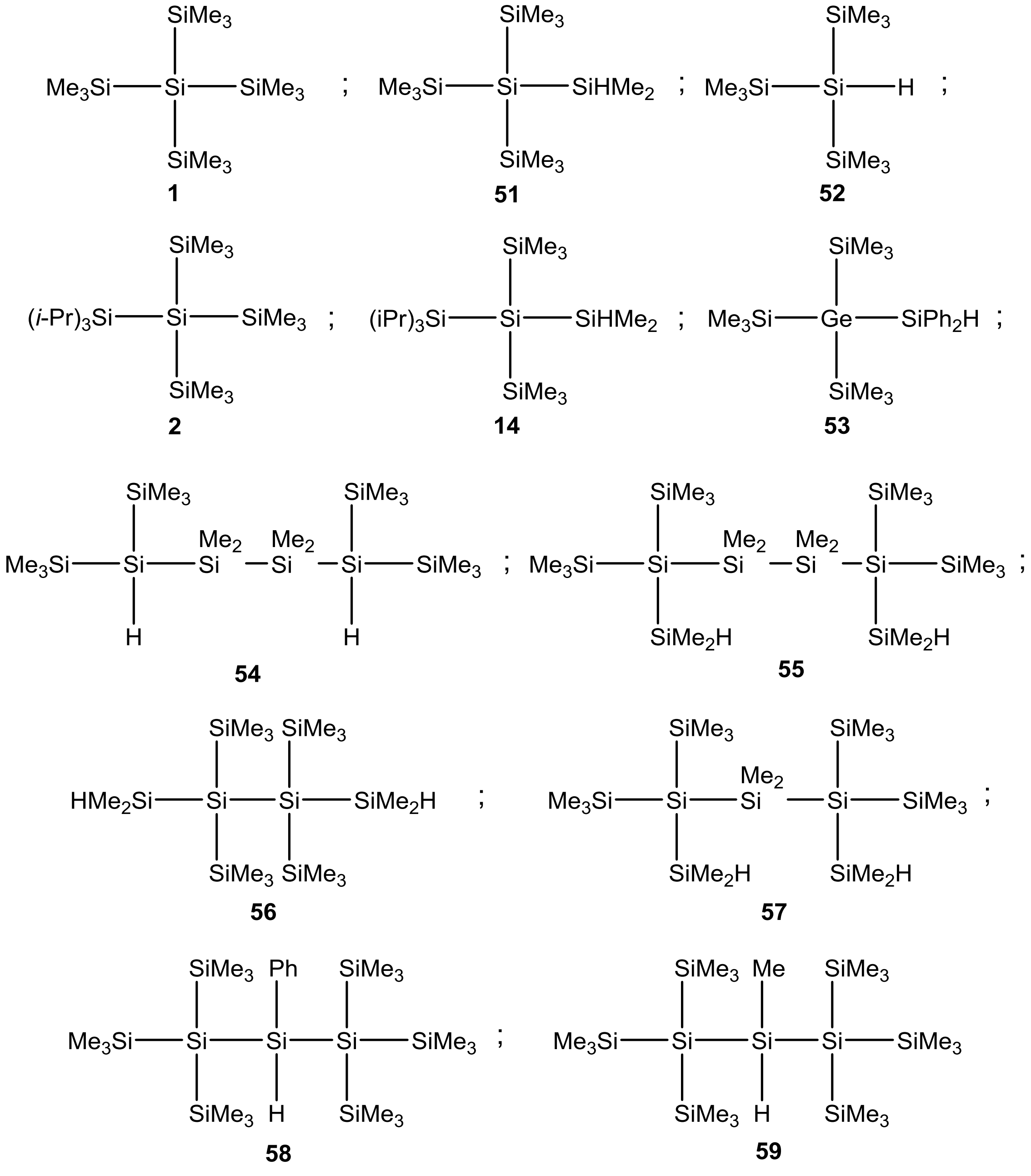
The presence of the $–SiMe_2H$ group was then explained by the scrambling of the methyl groups during the preparation of the silylium ion. Indeed, in a separate experiment, an excess of Me_3SiH was treated with 3%(mol) of TTPFPB for 12 hours.[79] That led to a mixture of products containing Me_4Si, Me_3SiH, Me_2SiH_2 and $MeSiH_3$. This rearrangement was also observed in the case of triethylsilane.[79] As a consequence, during the reaction presented in Scheme 9-5, the active species $[Me_3Si\text{-}H^+\text{-}SiMe_2H]$ was formed and then the $[SiMe_2H^+]$ fragment (less sterically hindered) reacted with the amine.

---

[79] R. Labbow, F. Reiß, A. Schulz, A. Villinger, *Organometallics*, **2014**, *33*, 3223–3226.

5.2 Substrates for stoichiometric reactions with trityl tetrakis(tetraperfluorophenyl)borate (TTPFPB)

A series of small oligosilanes, with the number of silicon atoms between 4 and 10, was treated with half or one equivalent of TTPFPB, under different reaction conditions (Figure 8-5). Some of these compounds were already known; the others were prepared on purpose for this type of experiments (see experimental part for synthesis details).



1 ; **51** ; **52** ; **2** ; **14** ; **53** ; **54** ; **55** ; **56** ; **57** ; **58** ; **59**

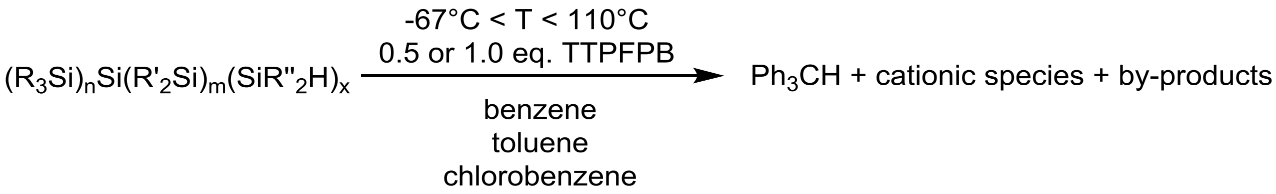
Figure 8-5: Oligosilanes to be employed for equimolecular reactions with TTPFPB.

5.3 General experimental conditions

Most of these compounds contained a Si-H functional group that should be suitable for the abstraction of a hydride by the trityl cation. However, in some experiments the reactivity of permethylated substrates was investigated.

Usually the reactions were done in a small glass vial or on in an NMR tube, with a sufficient amount of starting material to have visible signals in the NMR spectrum. Different solvents were tested for each experiment, and if no reaction occurred at room temperature, its value was increased to the boiling point of the solvent in use. In some cases low temperature conditions were adopted to prevent the rearrangement process and to stabilize the forming silyl cation.

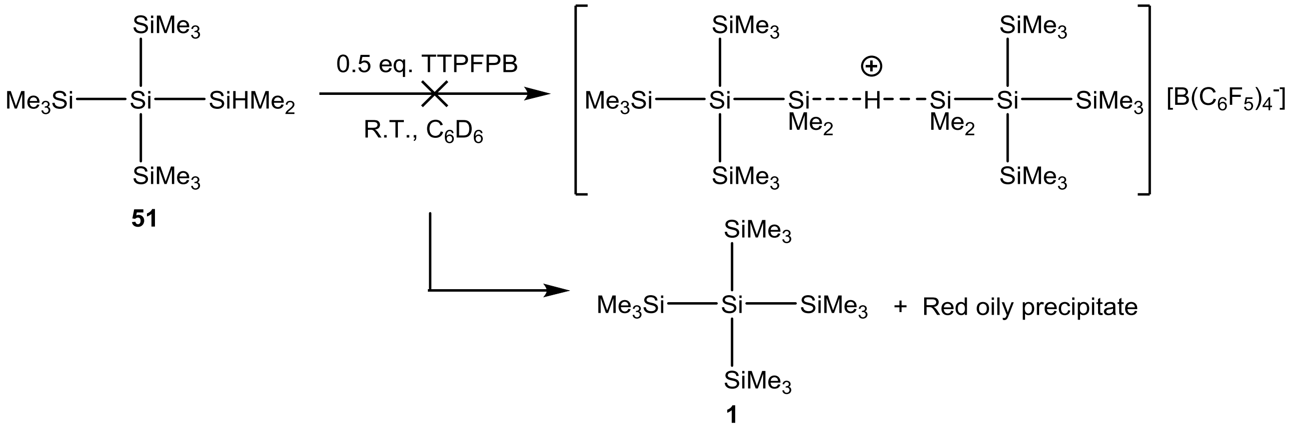
The generally Corey-type reactions is described in Scheme 10-5:



Scheme 10-5: General equimolecular reaction between oligosilanes and trityl borate salt. The mentioned solvents are the most used ones. R, R'= Me or *i*-Pr; R''= Me, Cl, Ph.

5.3.1 Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) in benzene as solvent at room temperature

In the first experiment half equivalent of TTPFPB was employed. The idea was that two oligosilyl cation might be bridged by a proton, as it was found with smaller substrates (Scheme 11-5).[77,78]

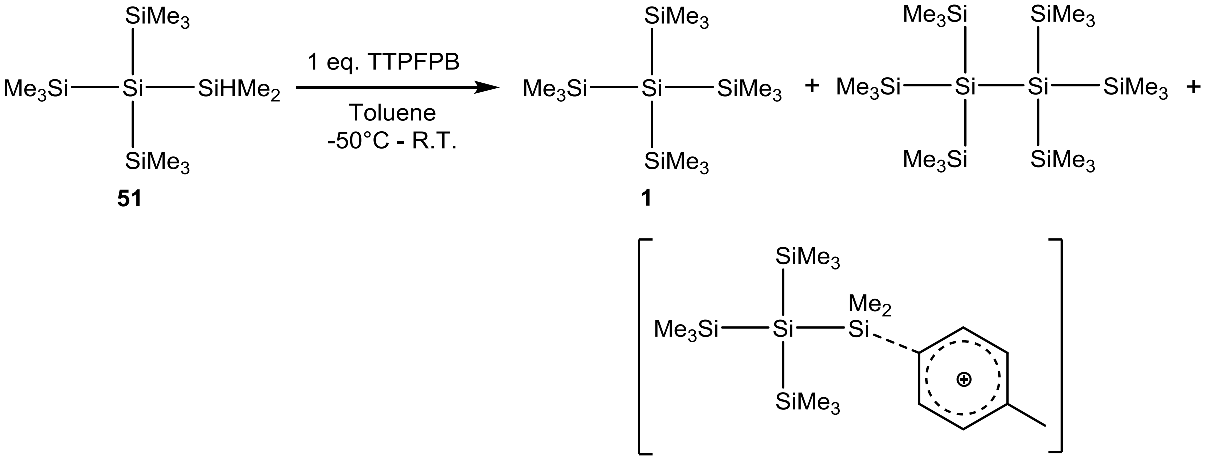


Scheme 11-5: Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane with 0.5 equivalent of trityl cation. After 3 hours, only pure tetrakis(trimethylsilyl)silane (**1**) was detected in solution.

After mixing the reagents, two liquid phases were formed. Tetrakis(trimethylsilyl)silane (**1**) was found by ^{29}Si NMR in the upper phase after 3 hours of stirring, while no signals could be detected in the lower dark red oily phase. The solvent was dried and the residue washed with pentane. Then a small amount of chlorobenzene was added and the solution was stored at -67°C. However, no crystals formation could be observed, even after weeks. Double vial precipitation was also tried, using pentane as precipitating solvent, but only a dense red oil was obtained.

5.3.2 Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) in toluene as solvent at low temperature

The previous reaction was repeated in toluene with 1 equivalent of TTPFPB. It was started at -50°C and then the mixture was slowly coming back to room temperature (Scheme 12-5).



Scheme 12-5: Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane with 1 equivalent of trityl cation. Products detected by ^{29}Si NMR after dissolution in chlorobenzene.

The solution showed an upper liquid phase and a lower red oily phase. After one hour, the solvent was removed and the oily red residue was dissolved in a small amount of chlorobenzene. The ^{29}Si NMR spectrum of the solution was then acquired (Figure 9-5). Three products were present in the mixture:

- tetrakis(trimethylsilyl)silane, δ(^{29}Si, ppm) = -136.2; -10.4
- hexakis(trimethylsilyl)disilane, δ(^{29}Si, ppm) = -132.3; -9.9
- $[(SiMe_3)_3SiMe_2Si(toluene)^+][B(C_6F_5)_4^-]$, δ(^{29}Si, ppm) = -132.2; -9.55; 44.7.

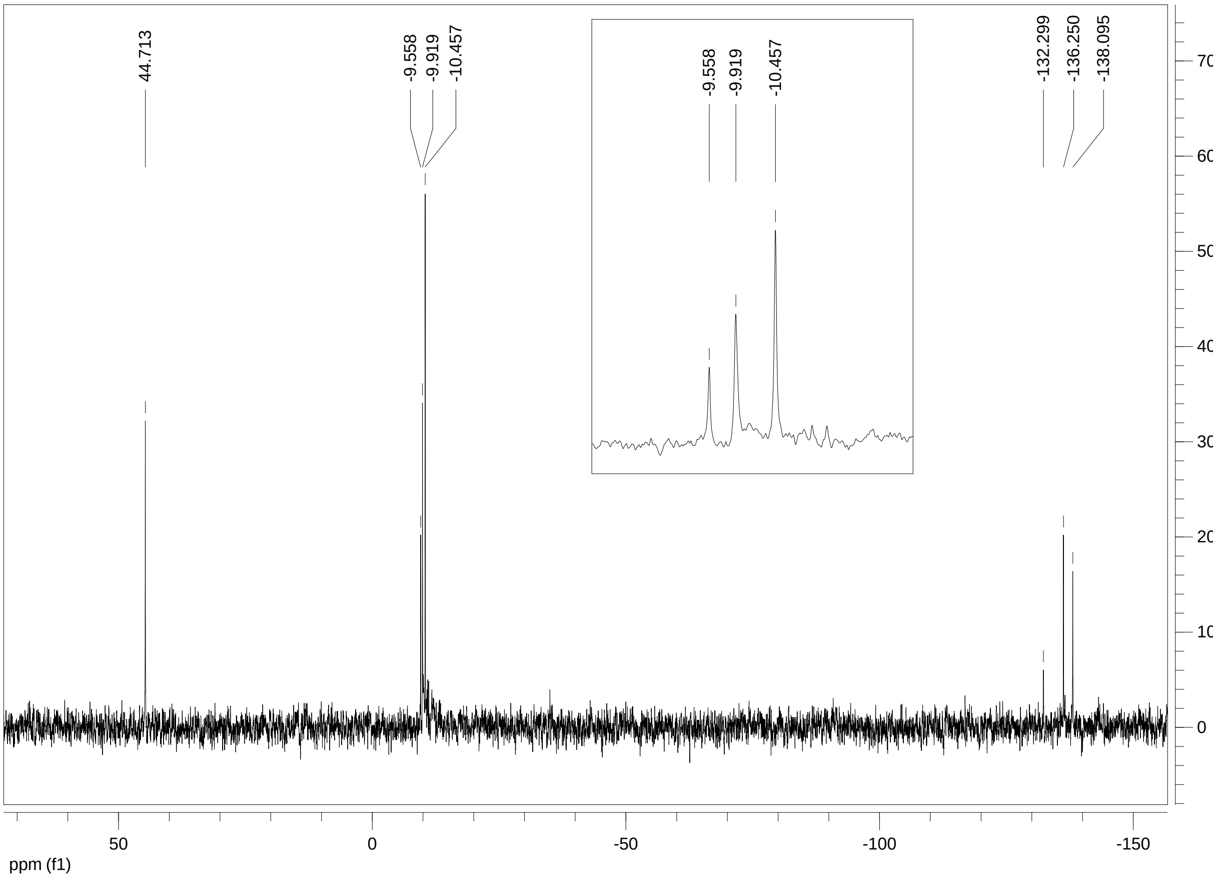


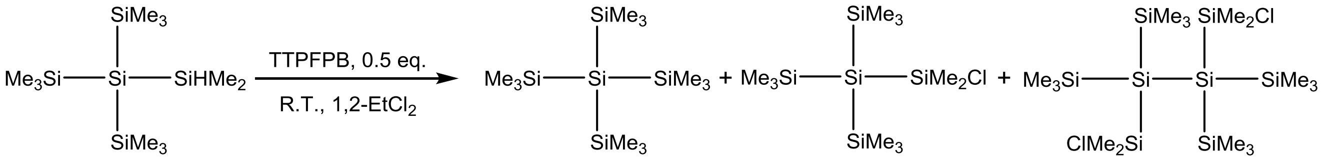
Figure 9-5: ^{29}Si NMR spectrum of the reaction mixture containing **1**, hexakis(trimethylsilyl)disilane, and a presumed cationic species.

The ^{29}Si NMR chemical shift of the silylium-like species was not extremely downfield shifted. The cationic silicon might be coordinated to a toluene molecule forming an adduct. But, as already anticipated, the NMR signal should occur at 80 ppm, as for $[R_3Si(toluene)^+][B(C_6F_5)_4^-]$. In this case, it could also be that the hydrogen bridged silyl cation was formed, because a chemical shift around 58 ppm was reported for $[Et_3Si\text{-}H^+\text{-}SiEt_3][B(C_6F_5)_4^-]$.[78]

The volume of the solution was reduced and then it was stored at -67°C. However, no crystallization occurred, neither after adding pentane and taking again the sample at low temperature.

5.3.3 Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) in 1,2-dichloroethane as solvent at room temperature

Searching for a solvent that could stabilize the forming silyl cation at room temperature, in this experiment 1,2-dichloroethane was employed (Scheme 13-5). This solvent was already used by Oestreich to prepare a ferrocenyl stabilized silyl cation.[80]



51

1

Scheme 13-5: Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane with 0.5 equivalent of trityl cation, and 1,2-dichloroethane as solvent.

After adding the solvent to the reagents, an intense bubbling was observed. The ^{29}Si NMR revealed that a clean decomposition reaction occurred, that led to tetrakis(trimethylsilyl)silane (**1**) and chlorinated by-products (Figure 10-5). Three different signals from the quaternary silicon atoms of the three products could be identified. On the other hand, the chemical shifts of the –SiMe$_3$ groups were very close to each other and they collapsed in one single signal. But the ^{1}H NMR showed five clear peaks, each one due to one of the five types of methyl group, and this confirmed the previous interpretation (Figure 11-5).

1,2-dichloroethane was decomposed by the forming silyl cation (with formation and evolution of ethane), which showed that it cannot be used in this type of reactions.

---

[80] K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.*, **2011**, *133*, 12442–12444.

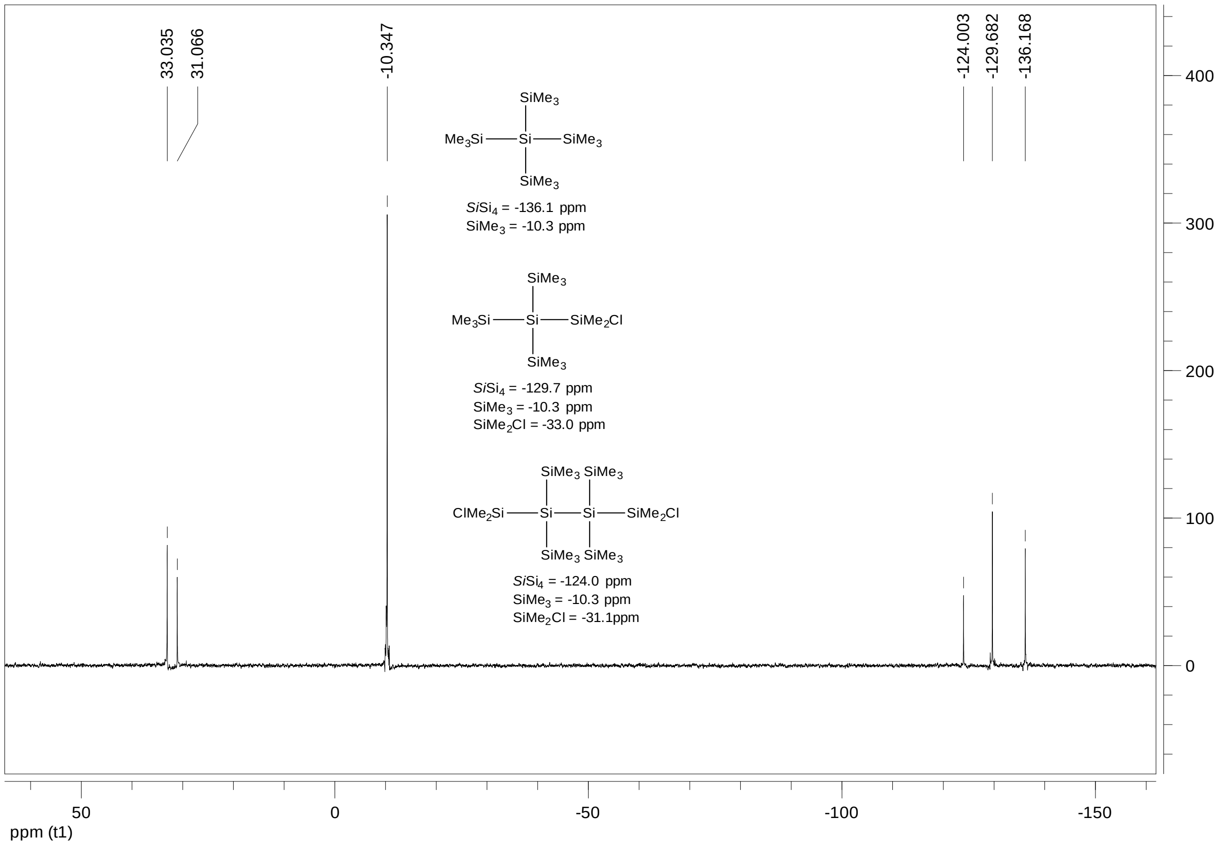


Figure 10-5: ^{29}Si NMR of the reaction mixture after treatment of **51** with TTPFPB in 1,2-dichloroethane.

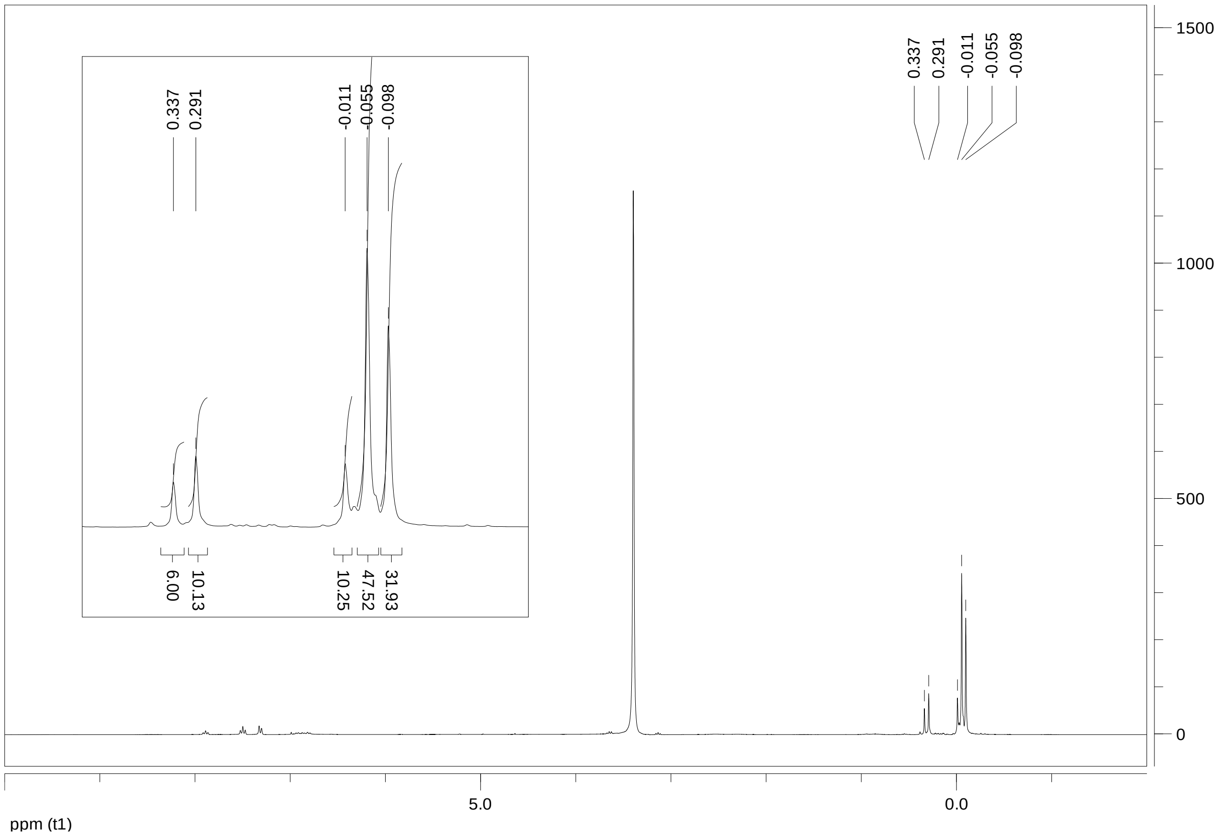
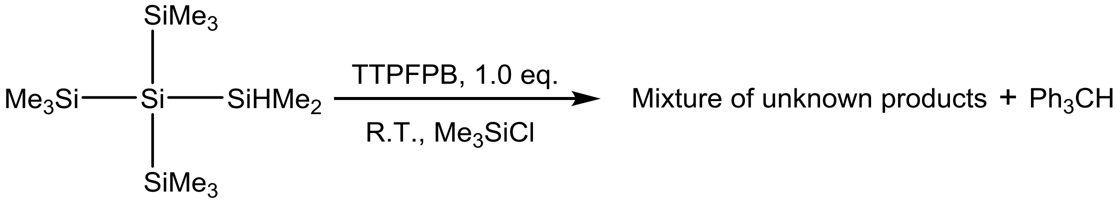


Figure 11-5: ^{1}H NMR of the reaction mixture after treatment of **51** with TTPFPB in 1,2-dichloroethane. Integrals are not correct as products are not exactly in the same amount.

5.3.4 Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) in trimethylchlorosilane at room temperature

Villinger and co-workers prepared a series of bissilylated halonium ions,[81] treating a pre-formed silyl cation [$Me_3Si^+B(C_6F_5)_4^-$] with different silyl halides (Me_3SiF, Me_3SiCl, etc.). The halogen formed a bridge between two silicon atoms, sharing its electron density with them and formally assuming a positive charge.

With this idea, the reaction was done in trimethylchlorosilane, to verify if the solvent could stabilize the forming silylium ion in the same way (Scheme 14-5).



51

Scheme 14-5: Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane with 1.0 equivalent of trityl cation, and trimethylchlorosilane as solvent.

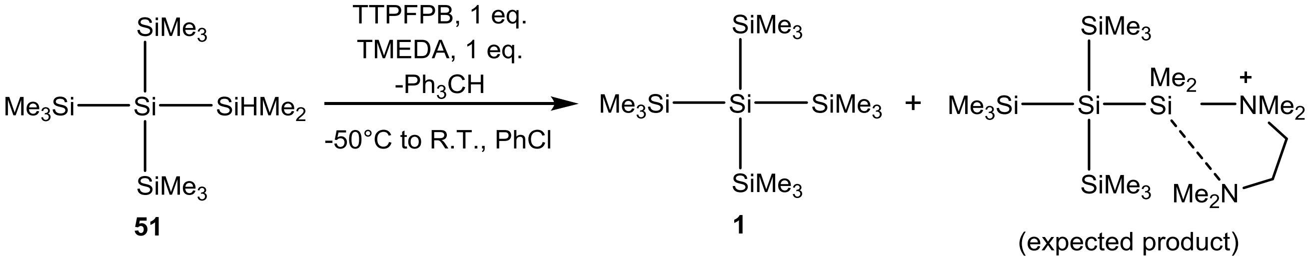
The trityl salt was not completely soluble in trimethylsilylchloride, as it formed a deep red solution with a supernatant yellow solid. No significant change was determined by the addition of the substrate to this suspension. After one hour of stirring, the ^{29}Si NMR spectrum showed the formation of a small amount of chlorinated byproduct, but no signal of a silyl cation. The solvent was dried and the residue washed with pentane. The remaining semi-solid material was dissolved in chlorobenzene, but no signal in the ^{29}Si NMR spectrum could be detected.

---

[81] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem. Inter. Ed.*, **2009**, *48*, 7444-7447

5.3.5. Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) in the presence of TMEDA at low temperature

To stabilize the forming silyl cation, a strong and robust base as TMEDA (tetramethylethylenediamine) was added to the reaction mixture (Scheme 15-5).



Scheme 15-5: Reaction of 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane with 1.0 equivalent of trityl cation, in the presence of TMEDA.

After four hours of reaction, the substrate was still present in a large amount (^{29}Si NMR chemical shifts: -137.2, -33.9, -10.0 ppm). The reaction mixture contained also some tetrakis(trimethylsilyl)silane (**1**) (^{29}Si NMR: -136.2 ppm, -10.4 ppm). Nevertheless, two very small signals in the typical region of a silyl cation were detected (^{29}Si NMR: 65.0 ppm and 64.0 ppm). These peaks might correspond to those ones at -135.2 ppm and -9.4 ppm. However, the conversion was extremely small (Figure 12-5).

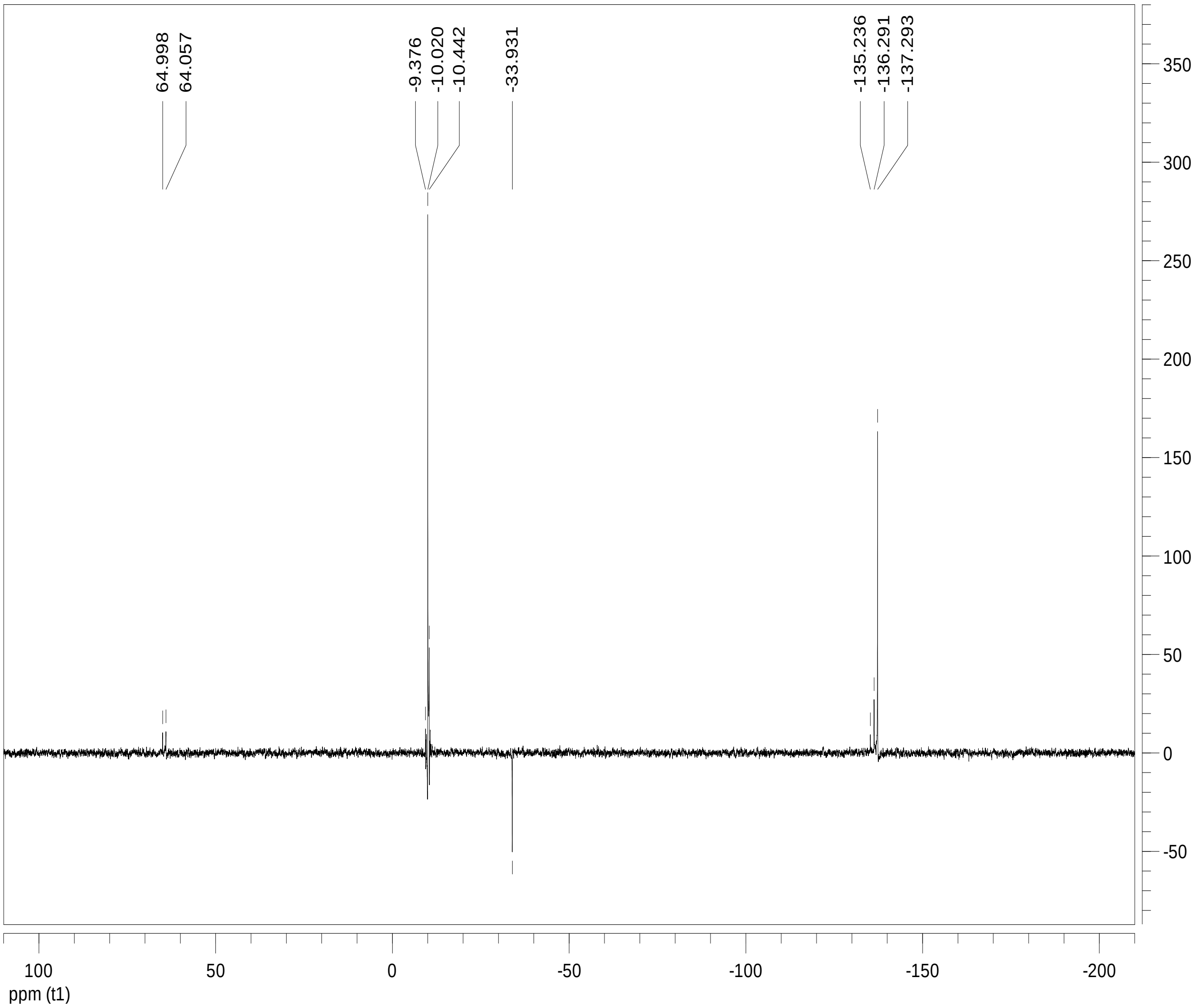
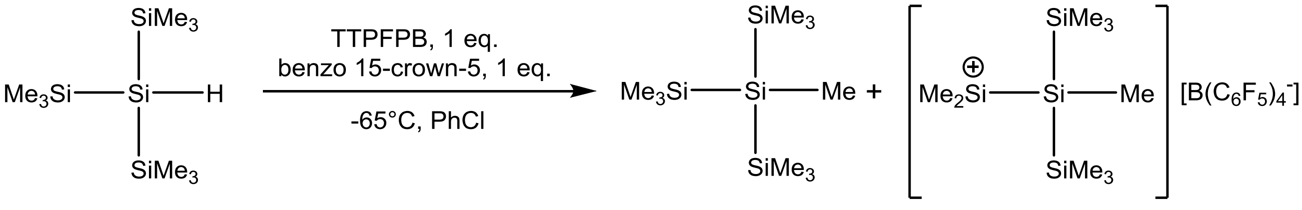


Figure 12-5: ^{29}Si NMR at room temperature of the reaction mixture after treatment of **51** with TTPFPB in the presence of TMEDA.

After 12 hours of stirring, the ^{29}Si NMR spectrum of the reaction mixture showed almost a baseline. In the reaction vial a kind of semi-solid substance was in suspension. The solvent was dried and the residue was washed with pentane, but afterwards it was not possible to dissolve this material completely with chlorobenzene neither with dichloromethane. The pentane used to wash the residue was evaporated and a white crystalline solid was collected. The ^{29}Si NMR of this material revealed a quite high amount of the starting material and the ^{1}H NMR also the presence of triphenylmethane.

5.3.6. Reaction of tris(trimethylsilyl)silane (52) in the presence of crown ether

Because the silicon atom is relatively small, during a hydride abstraction the forming silyl cation might be coordinated and stabilized by a crown ether molecule (Scheme 16-5). However, possible decomposition of the carbon-oxygen bonds should be kept in account.



52

Scheme 16-5: Reaction of tris(trimethylsilyl)silane with 1.0 equivalent of trityl cation, in the presence of benzo,15-crown-5.

Chlorobenzene was pre-cooled at around -65°C and after mixing the reagents with the solvent, the vial was stored at -67°C. After 12 hours, the solution was clear and it had an intense violet color. The ^{29}Si NMR spectrum was acquired at room temperature and is here shown (Figure 13-5).

Signals at -88.6 ppm and -13.1 ppm derived from the rearrangement by-product $(SiMe_3)_3SiMe$ (^{29}Si NMR of the pure material measured in chlorobenzene: -88.63 ppm, *Si*Si$_3$; -13.12 ppm, $SiMe_3$). For the expected product signals might be assigned as:

-89.4 ppm, for -*Si*Si$_3$;

-11.5 ppm, for -$SiMe_3$;

108.4 ppm, for [-$SiMe_2^+$].

The other peaks in the spectrum could derive from oxygenated silicon fragments (26.3 ppm and 11.2 ppm), and/or from side products generated by chloride or fluoride abstraction respectively from the solvent or from the counter anion (-15.5 ppm). Even if an intense signal was present in the silylium ion region, it was not possible to verify only with the NMR spectra if this signal was due to a [Me_2Si^+-solvent] adduct or to a [Me_2Si-crown-ether] complex.

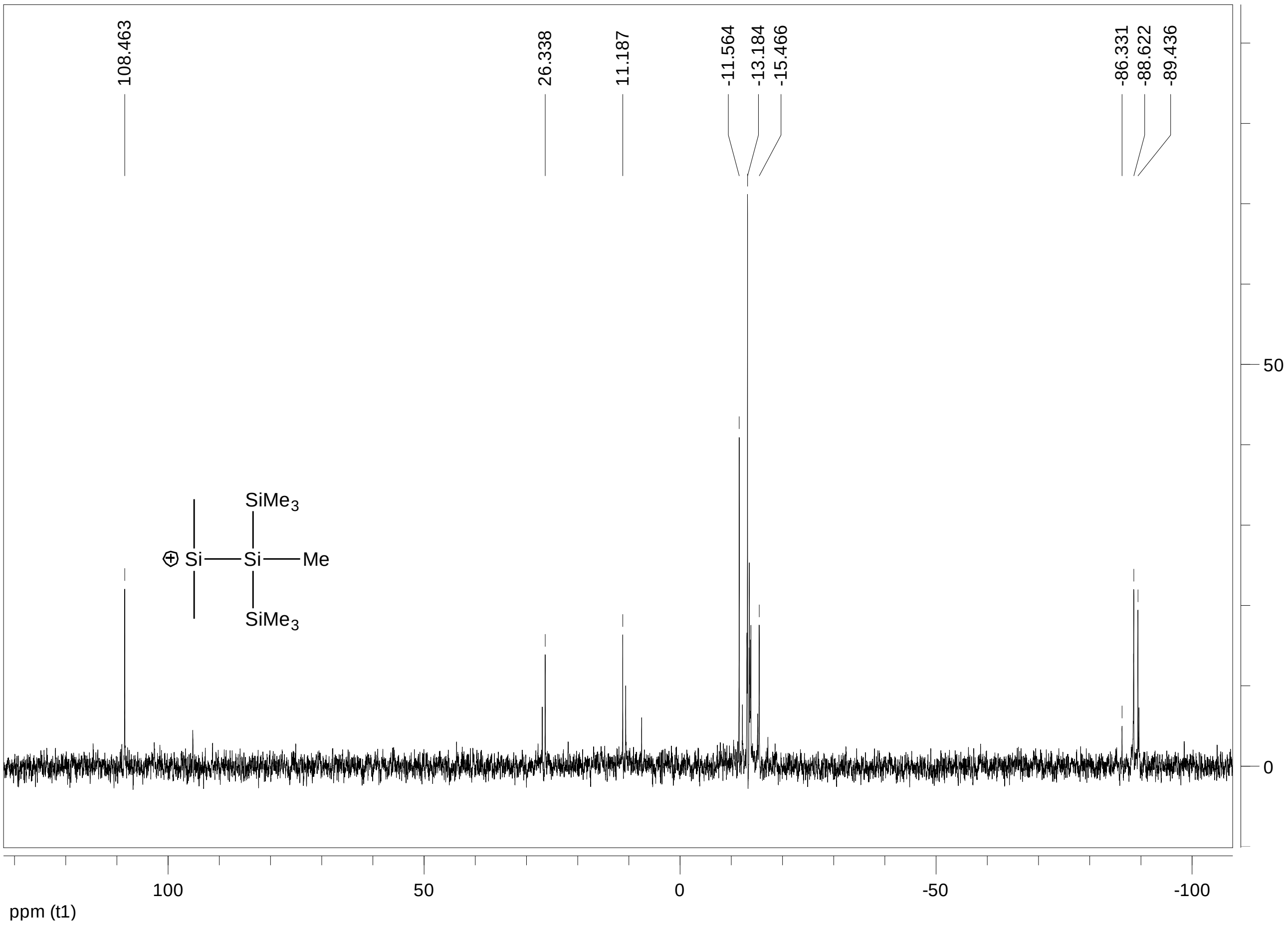


Figure 13-5: ^{29}Si NMR of the reaction mixture after treatment of **52** with TTPFPB in the presence of benzo,15-crown-5 (acquired at room temperature).

The ^{1}H NMR was even less clear, and only the major by-product $(SiMe_3)_3SiMe$ could be recognized (-0.18 ppm and -0.29 ppm). It was also possible to fairly compare the integrals of the protons of the $–SiMe_3$ groups: ^{29}Si NMR spectrum suggested that the by-product and the oligosilyl cation were present approximately in the same quantity, and these proportions seemed to be reflected in the ^{1}H NMR (-0.18 ppm, 27H; -0.23 ppm, ca. 18H, Figure 14-5).

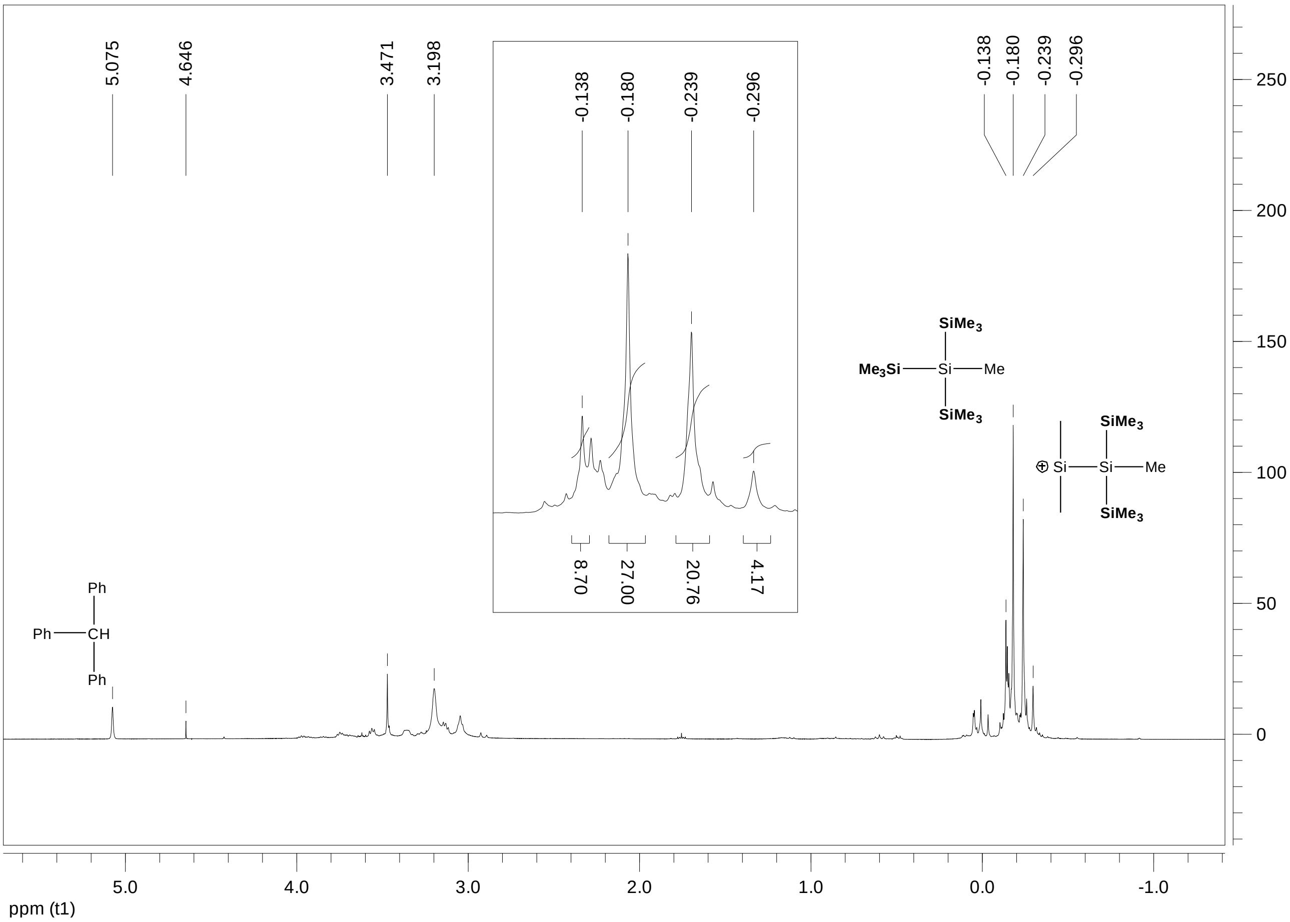
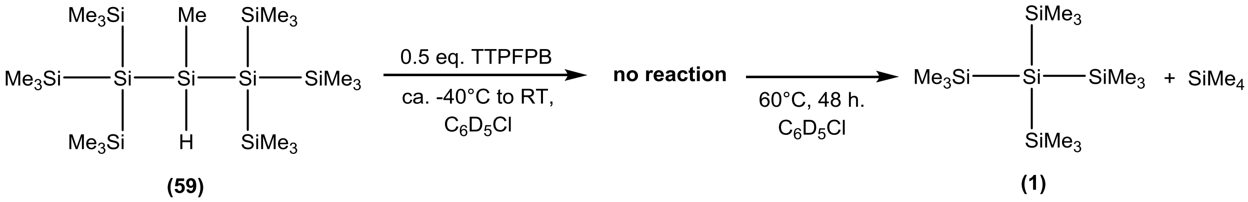


Figure 14-5: ^{1}H NMR of the reaction mixture after treatment of **52** with TTPFPB in the presence of benzo,15-crown-5 (acquired at room temperature).

Part of the solution was layered with pentane in an NMR tube (ca. 1:4 vol.). After some days, a kind of dark solid settled. Another portion of the solution was mixed with pentane and stored at -67°C. Also in this case some pseudo-crystalline precipitate could be observed. Anyway, it was not possible to mount these materials on the X-ray diffractometer due to their deliquescent behavior.

5.3.7. Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-methylsilane (59), chlorobenzene as solvent

The substrate was prepared via a modified procedure originally reported by Gross et al. (see experimental part).[82] A hydride abstraction from this molecule should give rise to a silyl cation having six -$SiMe_3$ groups in β position, which should stabilize the positive charge, as previously stated. The reaction was done in deuterated chlorobenzene, with 0.5 equivalent of trityl salt, starting at -30°C and then slowly increasing the temperature (Scheme 17-5).



Scheme 17-5: Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-methylsilane (**59**) with 0.5 equivalent of trityl cation, *d*-chlorobenzene as solvent.

Surprisingly, no reaction occurred, even after stirring the mixture for 12 hours at room temperature (Figure 15-5). Probably the hydrogen atom was too sterically hindered by the trimethylsilyl groups, and the trityl cation could not approach it for a hydride abstraction.

---

[82] T. Gross, H. Reinke and H. Oehme, *Can. J. Chem.*, **2000**, *78*, 1399-1404

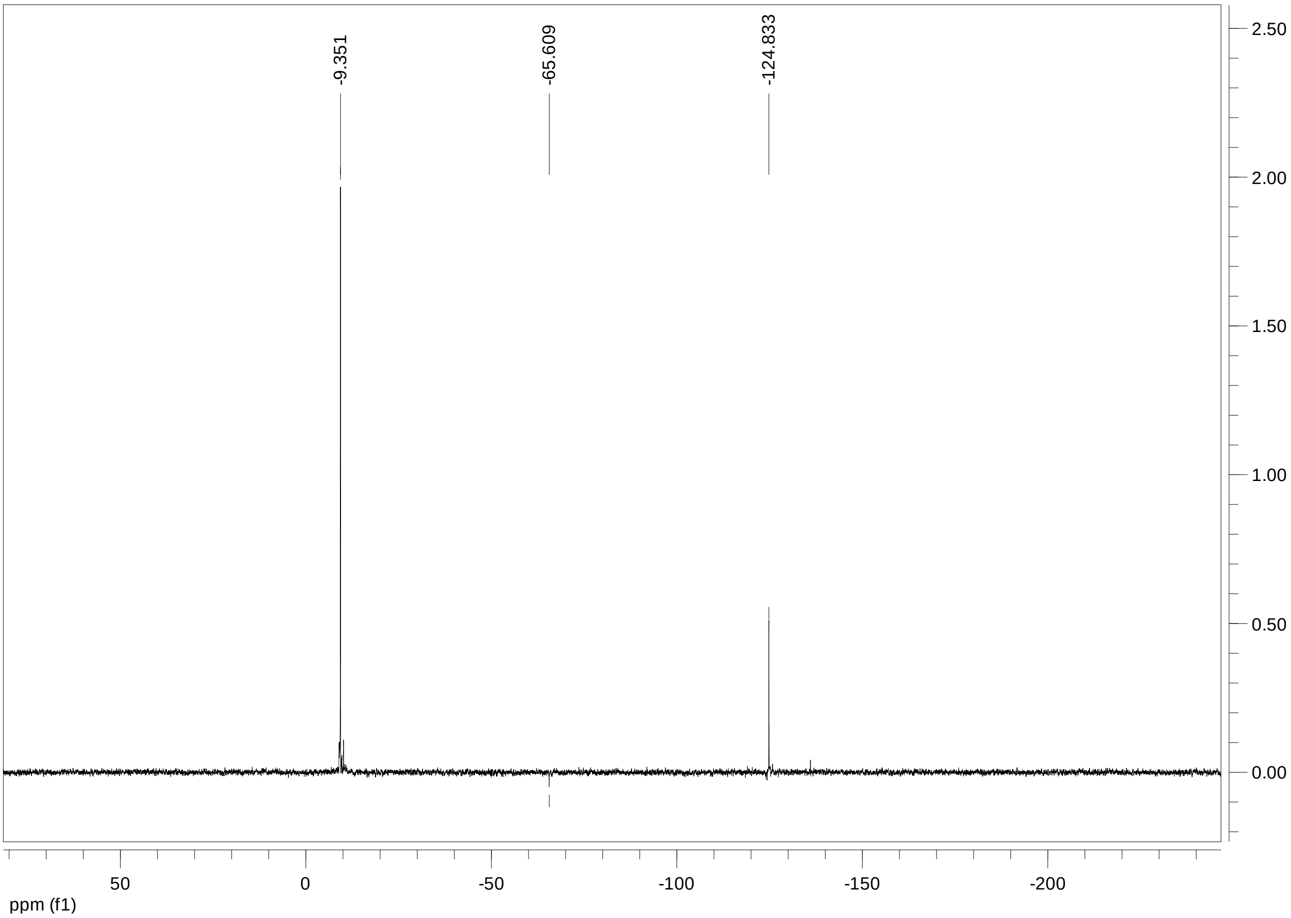


Figure 15-5: ^{29}Si NMR of the reaction mixture at R.T., after 12 h. of stirring.
Only starting material **59** was detected.

Increasing the temperature to 60°C and stirring the mixture for other 48 hours, finally forced compound **59** to react with the trityl borate. The ^{29}Si NMR showed that the starting material was completely consumed, but it was mostly converted into tetrakis(trimethylsilyl)silane (**1**) and tetramethylsilane. Anyway, weak signals at -135.0 ppm, -7.5 ppm and 47.0 ppm could suggest the formation of a cationic species.

This reaction was repeated employing 1.0 equivalent of TTPFPB and carrying out the reaction from R.T. to 80°C. The outcome was more or less the same, but the ^{29}Si NMR spectrum was clearer (Figure 16-5).

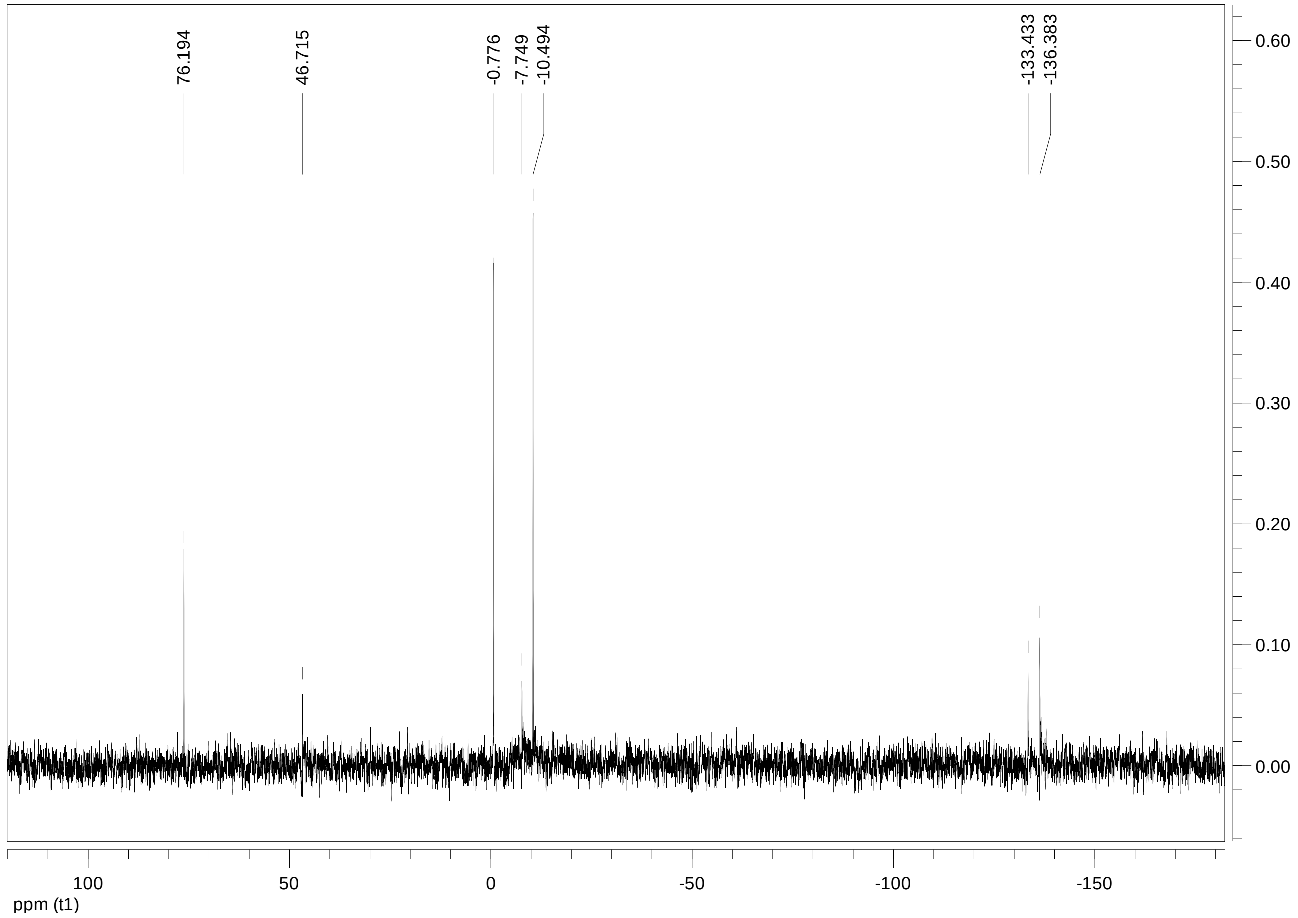


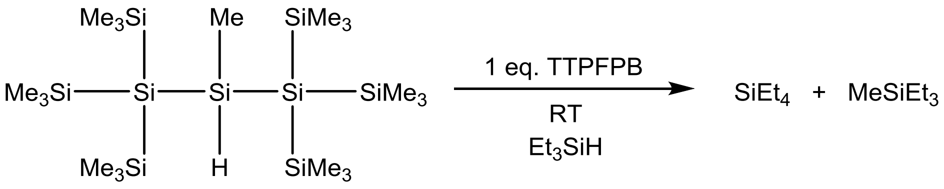
Figure 16-5: ^{29}Si NMR of the reaction mixture after 12 h. of stirring at 80°C (compound **59** treated with 1 eq. TTPFPB).

Main products were still tetrakis(trimethylsilyl)silane (**1**) (δ = -136.4, -10.5 ppm) and probably tetramethylsilane (δ = -0.8 ppm). The cationic species could be identified by the chemical shifts at -133.4 ppm (Si*Si*$_q$), -7.7 ppm (SiMe$_3$) and 46.7 ppm (Me$_2$Si$^+$). The latter value might be due to the solvent adduct of the silylium ion or again to its H bridged form.

The signal at 76.2 ppm is often emerging in the NMR spectra acquired in these types of reaction mixtures: it might be assigned to [Me$_3$Si$^+$][B(C$_6$F$_5$)$_4$$^-$], but until now it was not possible to isolate it.

5.3.8. Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-methylsilane (59), triethylsilane as solvent

As already discussed in the introduction chapter, an excess of Et_3SiH treated with TTPFPB leads to the formation of $[Et_3Si\text{-}H^+\text{-}SiEt_3][B(C_6F_5)_4^-]$. This species is more reactive than the trityl cation itself, therefore it was prepared *in situ* and reacted with substrate **59** (Scheme 18-5). The idea was that this silane could stabilize the oligosilyl cation by the formation of an H-bridged adduct.



59

Scheme 18-5: Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-methylsilane (**59**) with 1 equivalent of trityl cation, triethylsilane as solvent.

After 24 hours of stirring, the ^{29}Si NMR showed the signals of the solvent and two by-products (tetraethylsilane, δ = 7.9 ppm; methyltriethylsilane, δ = 6.8 ppm). No sign of the starting material or an ionic species could be detected in the solution (Figure 17-5).

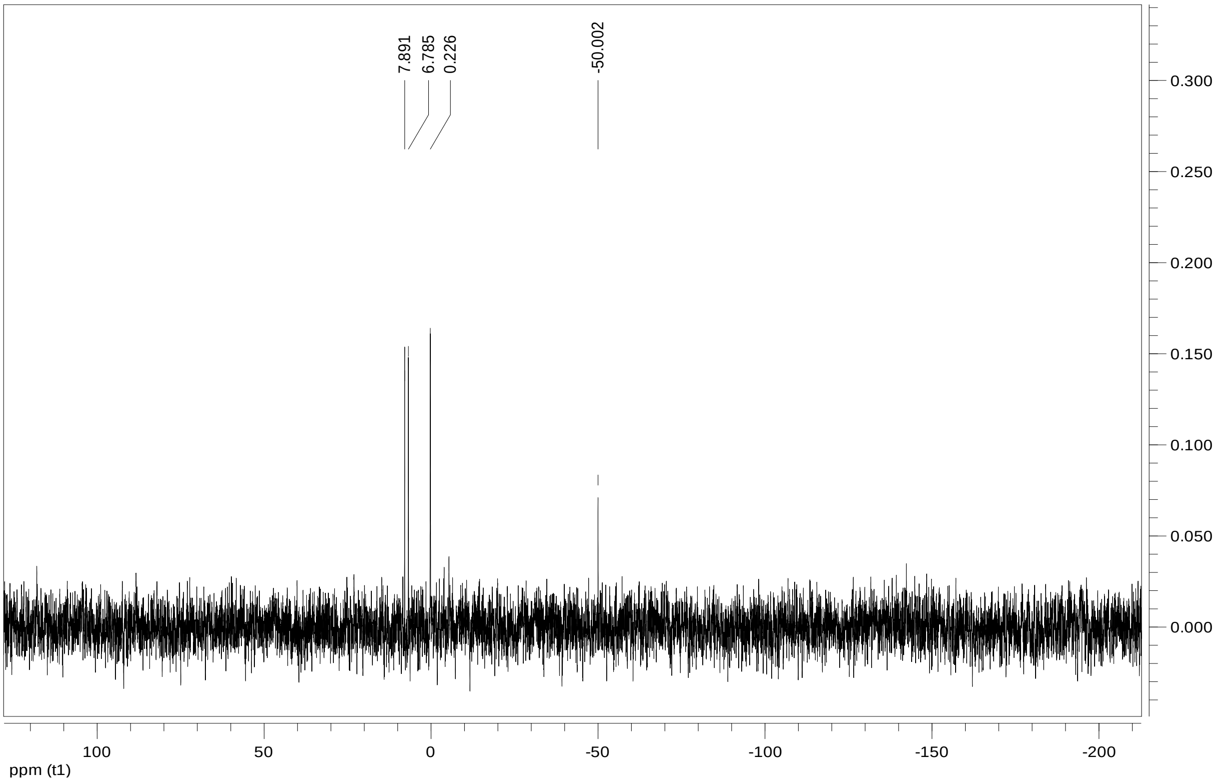
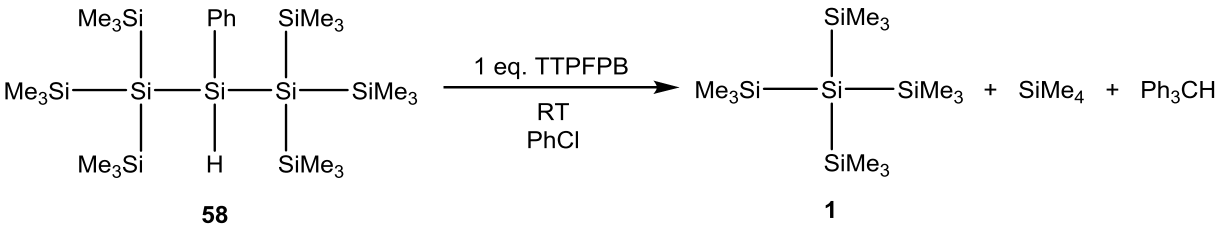


Figure 17-5: ^{29}Si NMR of the reaction mixture (compound **59** treated with TTPFPB in triethylsilane as solvent). Peak at -50 ppm is an artifact.

5.3.9. Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-phenylsilane (58), chlorobenzene as solvent

Substrate **58** was previously reported by Gross et al..[82] It is quite similar to compound **59**, but the influence given by the phenyl group to the forming silyl cation should be investigated. Compound **58** was treated with 1 equivalent of TTPFPB in chlorobenzene at room temperature (Scheme 19-5).



Scheme 19-5: Reaction of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2-phenylsilane (**58**) with 1 equivalent of trityl cation, chlorobenzene as solvent.

The ^{29}Si NMR spectrum showed the formation of tetrakis(trimethylsilyl)silane (**1**) (δ = -136.4, -10.5 ppm) and tetramethylsilane (δ = -0.8 ppm) (Figure 18-5). There was only a very weak signal in the silyl cation region at 67.5 ppm, which could not be identified.

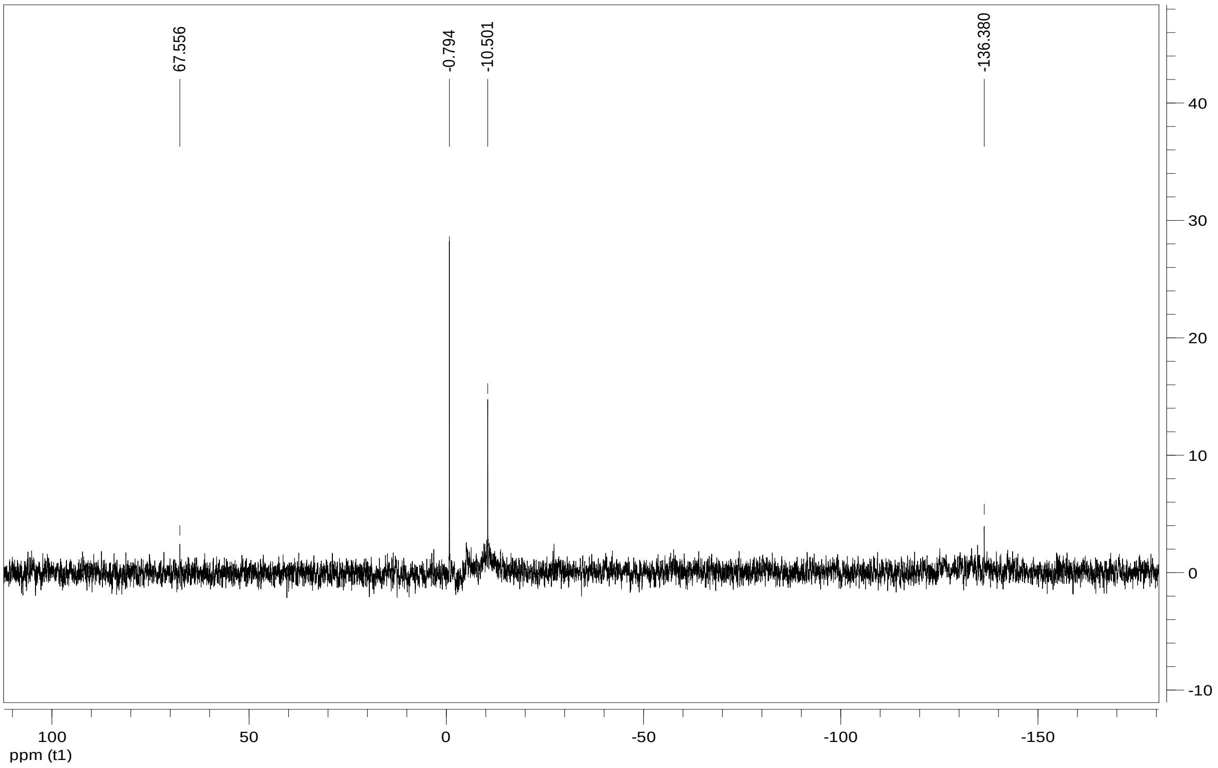
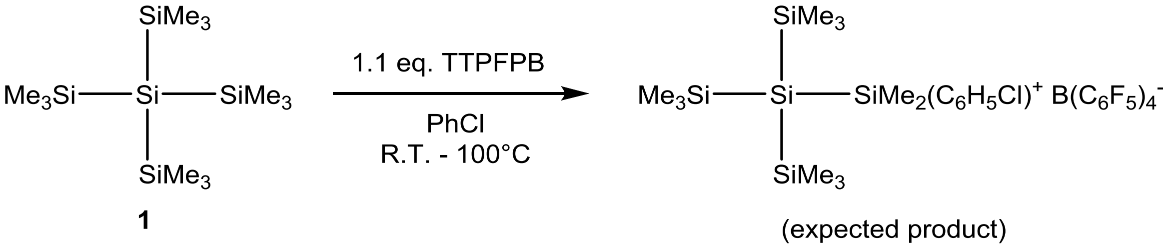


Figure 18-5: ^{29}Si NMR of the reaction mixture of compound **58** treated with TTPFPB in chlorobenzene.

5.3.10. Reaction of tetrakis(trimethylsilyl)silane (1), in chlorobenzene

The stochiometric reaction between compound **1** and TTPFPB was done in chlorobenzene and started at room temperature (Scheme 20-5).



Scheme 20-5: Reaction of tetrakis(trimethylsilyl)silane (**1**) with 1.1 equivalent of trityl cation, chlorobenzene as solvent.

After 12 hours of stirring at room temperature, no sign of a reaction was detected by ^{29}Si NMR. The temperature was then increased as follow (Table 4-5):

Reaction time	Temperature	Conversion
12 hours	R.T. (ca. 30° in the glove box)	0 %
+5 hours	60 °C	0 %
+12 hours	80 °C	0 %
+48 hours	100°C	Very small conversion

Table 4-5: Reaction conditions for experiment in Scheme 20-5.

After the last temperature increment, the ^{29}Si NMR spectrum was acquired (Figure 19-5). The starting material was almost intact and unreacted. Nevertheless, a cationic species was synthesized and it could be identified by the signals at 80.7 ppm (-Me_2Si^+), -7.7 ppm (-$SiMe_3$ groups) and -133.3 ppm (Si_q).

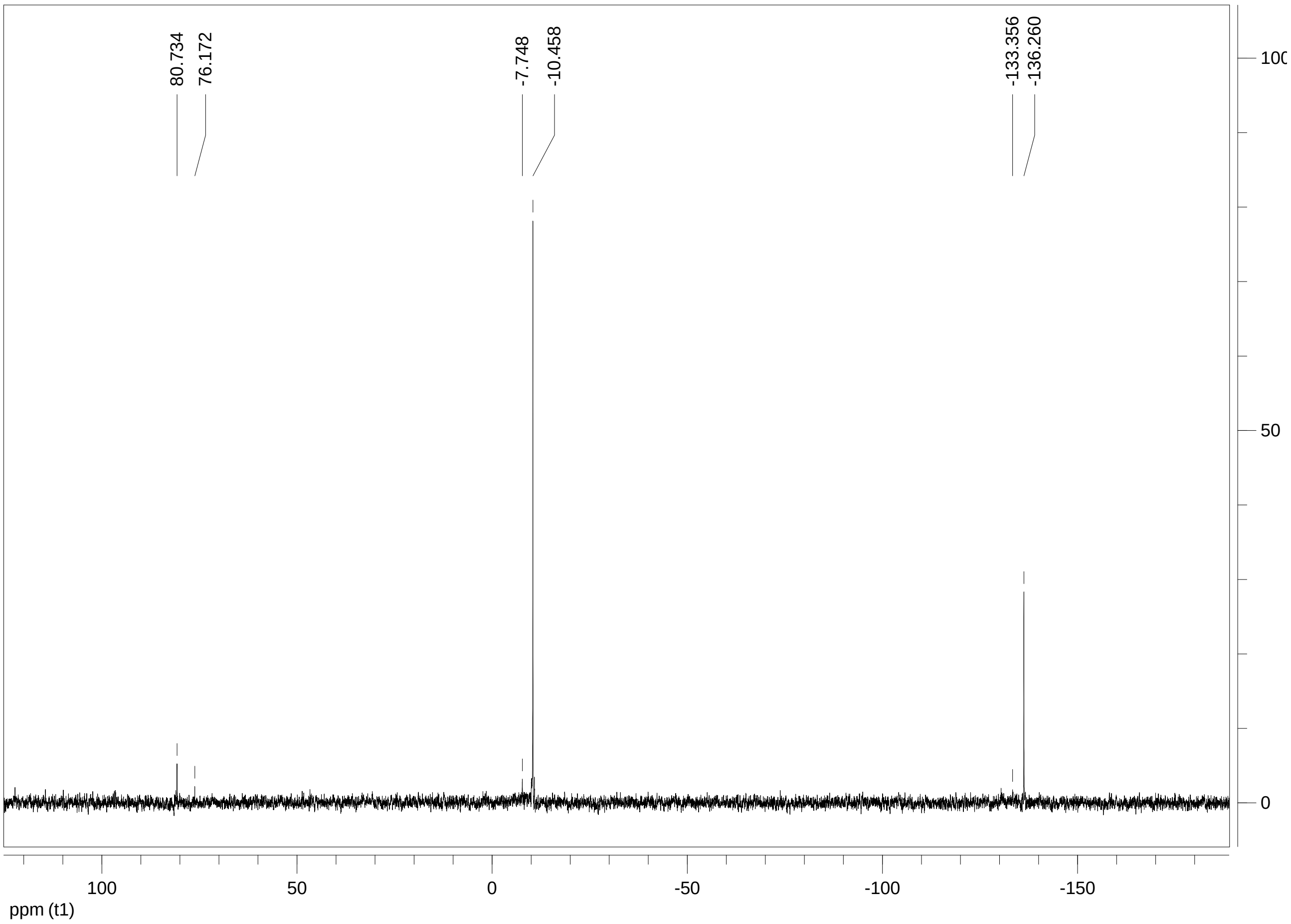


Figure 19-5: ^{29}Si NMR of the reaction mixture of compound **1** treated with TTPFPB, after about 80 hours of reaction.

Anyway, the conversion was too small: tetrakis(trimethylsilyl)silane (**1**) seemed not to be a good starting material for the formation of a oligosilyl cation, at least under these experimental conditions.

These reaction was repeated with 1,1,1-triisopropyl-tris(trimethylsilyl)disilane (**2**) as substrate, in cyclohexane at 80°C and in chlorobenzene at 110°C. No reaction was observed in the first case, while decomposition (very noisy ^{29}Si NMR spectrum with no signals for the -SiMe$_3$ groups) and also polymerization (broad signals in the ^{1}H NMR) occurred in the second experiment.

5.3.11. Reaction of tetrakis(trimethylsilyl)silane (1) with $[Et_3Si^+][B(C_6F_5)_4^-]$

Because tetrakis(trimethylsilyl)silane (**1**) showed a low reactivity towards the trityl salt, a triethylsilyl cation was prepared *in situ* and was then reacted with compound **1** (Scheme 21-5).

$$\mathrm{Et_3SiH} \xrightarrow[\text{-50°C to R.T., PhCl}]{\text{TTPFPB, 1 eq.}} [\mathrm{Et_3Si^+}][\mathrm{B(C_6F_5)_4^-}] \xrightarrow[\text{-50°C to R.T., PhCl}]{\mathrm{(SiMe_3)_4Si}\text{, 1 eq.}} \text{unknown polymer}$$

Scheme 21-5: Reaction of tetrakis(trimethylsilyl)silane (**1**) with 1.0 equivalent of triethylsilyl cation, chlorobenzene as solvent.

After ca. 5 hours of reaction, the ^{29}Si NMR showed just a baseline, while in the proton spectrum very broad signals were detected, suggesting that a kind of polymerization occurred (Figure 20-5).

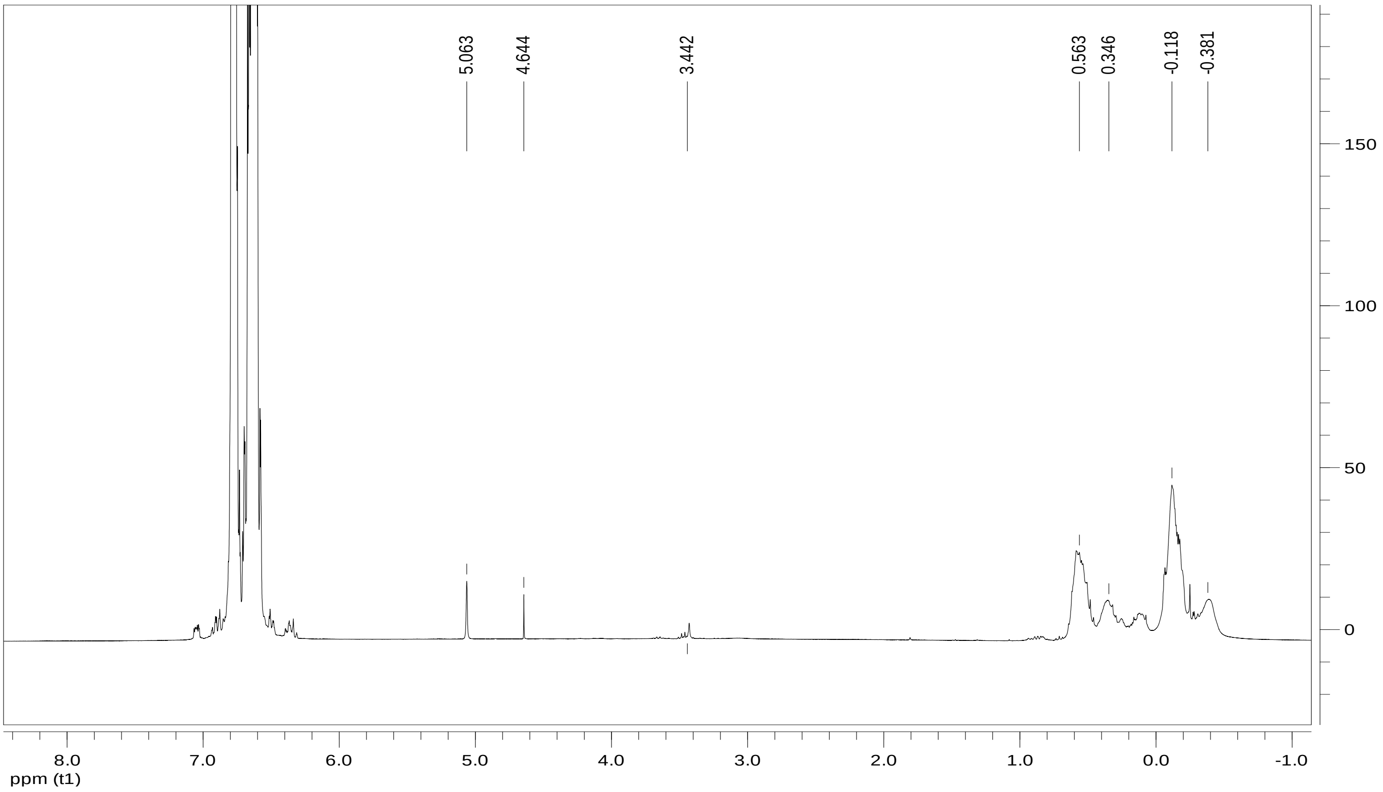


Figure 20-5: ^{1}H NMR at room temperature of the reaction mixture of compound **1** treated with $[Et_3Si^+]$, after 5 hours of reaction.

The ^{19}F NMR spectrum showed two groups of signals, one for tetrakis(pentafluorophenyl) borate and one for tris(pentafluorophenyl)borane (Figure 21-5).

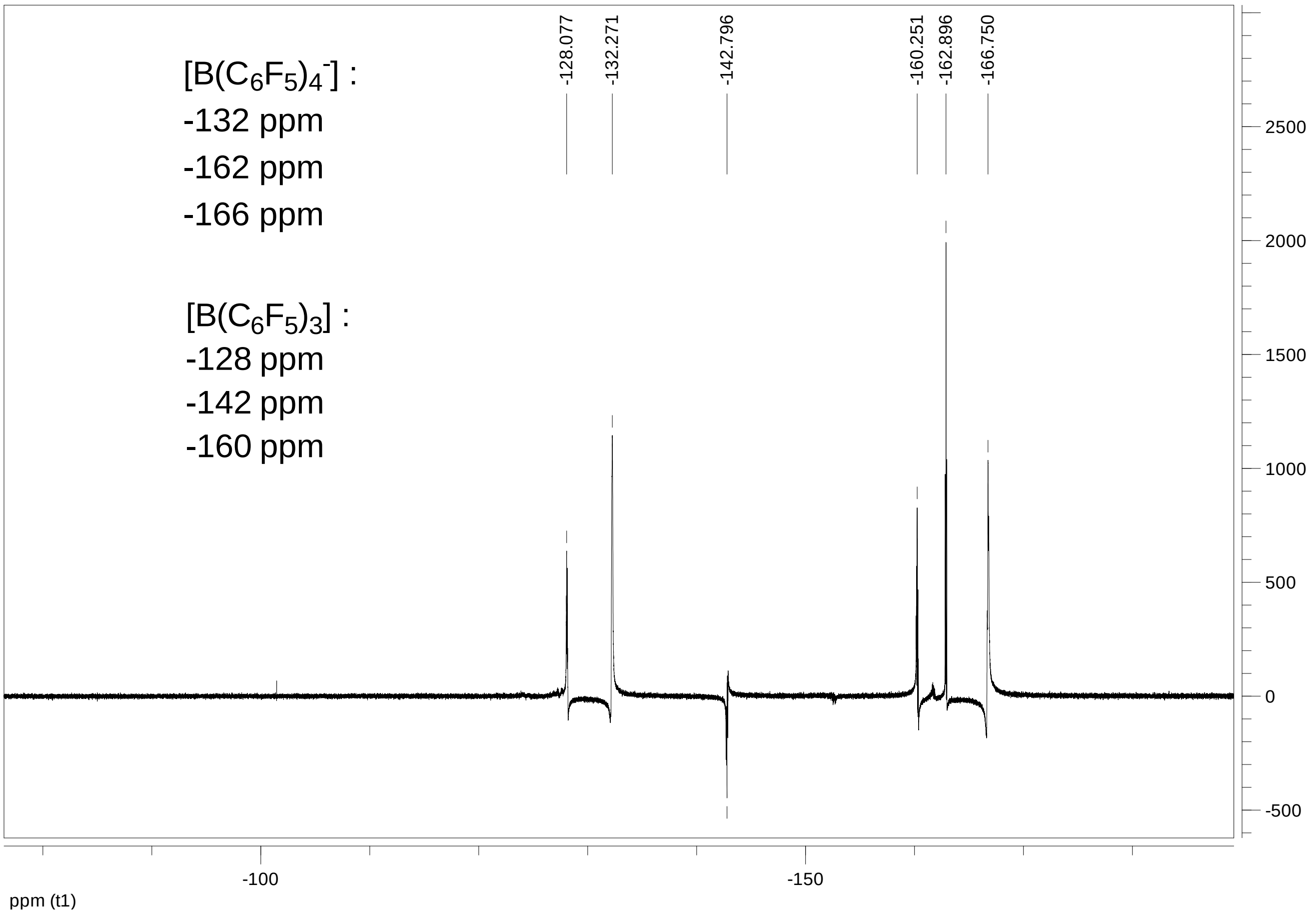
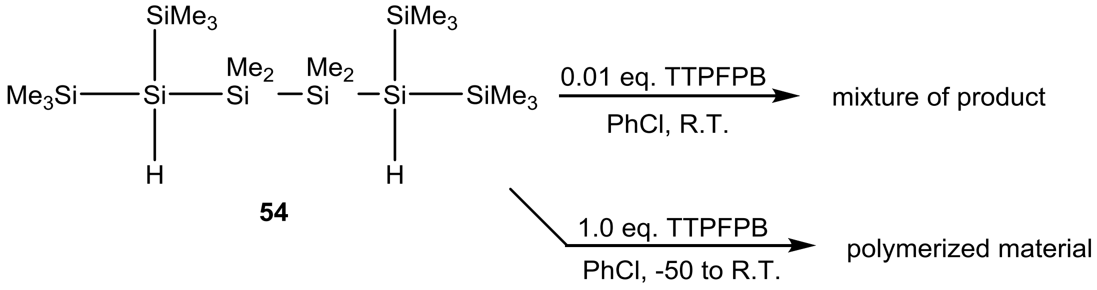


Figure 21-5: ^{19}F NMR at room temperature of the reaction mixture of compound **1** treated with $[Et_3Si^+]$, after 5 hours of reaction.

5.3.12. Reactions with 1,1,4,4-tetra(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane (54)

Compound **54** was treated with 0.01 and with 1.0 eq. of TTPFPB in two different experiments (Scheme 22-5). The first one was intended to find the rearrangement pattern of the molecule, while the second one could lead to an oligosilyl cation, as observed with similar substrates having two H groups in their structure.[83]



54

Scheme 22-5: Reaction of 1,1,4,4-tetra(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane (**54**) with 0.01 and 1.0 equivalent of trityl cation, chlorobenzene as solvent.

In the first reaction the starting material was completely consumed, but many products were detected in ^{29}Si NMR spectrum (numbers of peaks in the range of -120 ÷ -140 ppm, see Figure 23-5). Some types of silicon atoms were identified and it might be argued that the following compounds were present in solution (Figure 22-5):

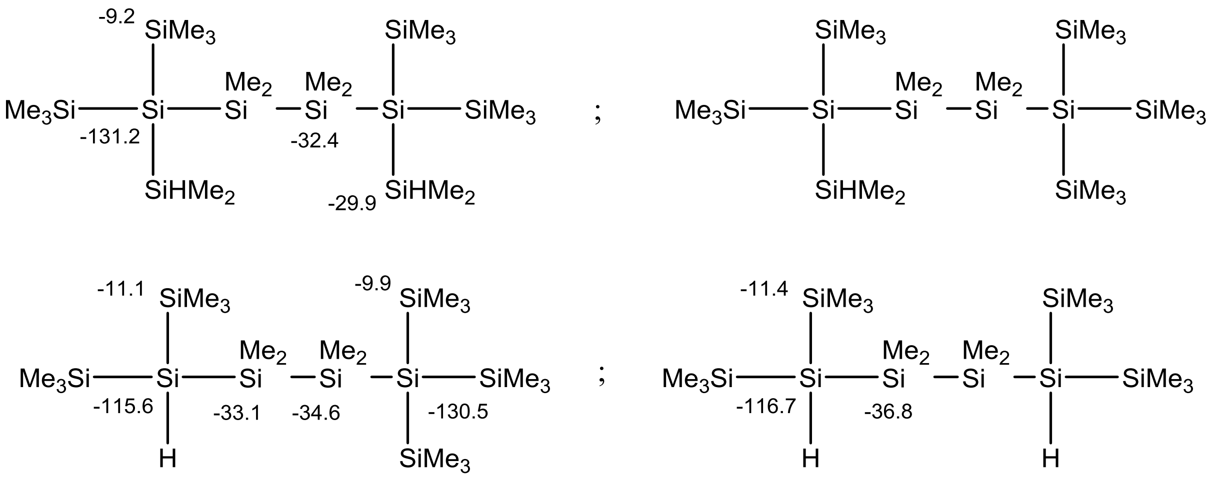


Figure 22-5: possible products and ^{29}Si NMR chemical shifts (if known).

---

[83] Lena Albers, **2013**, *Research report* and *Poster presentation*, ISOS XVII **2014** (Berlin)

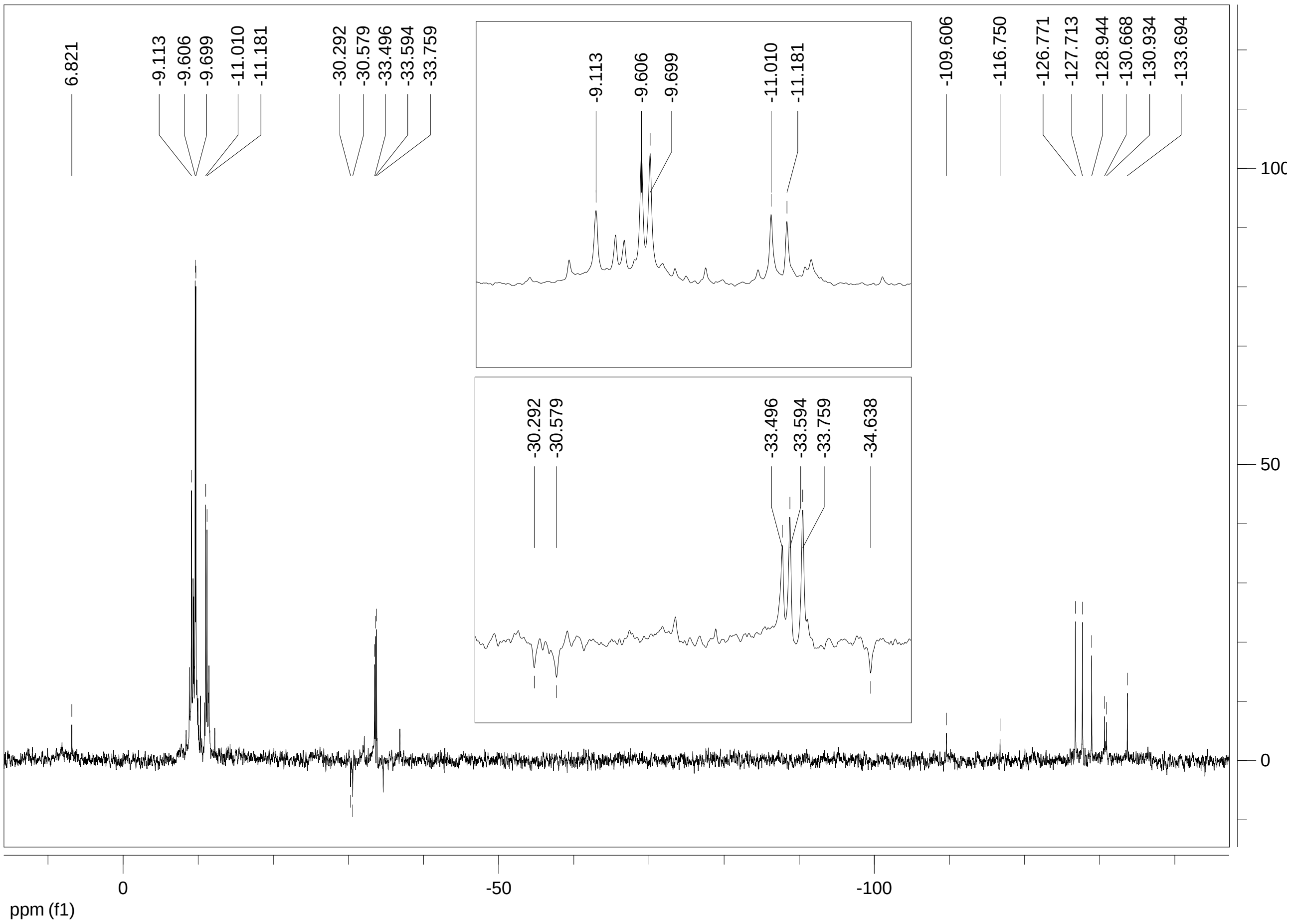


Figure 23-5: ^{29}Si NMR spectrum of the reaction mixture of compound **54** treated with a catalytic amount of TTPFPB.

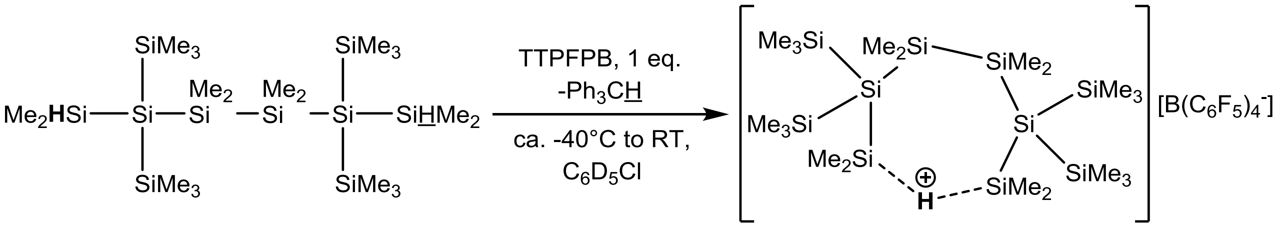
At least, it was possible to exclude the formation of tertiary silicon atoms of the type “Si$_3$*Si*Me” because of the absence of peaks between -80 and -90 ppm. In addition, the downfield shift of the signals ofthe quaternary silicon atoms (ca. -127 ppm) indicated the formation of crowded and maybe cyclic structures.

The GC/MS of the product spectrum was even more unclear and it presented many signals for isomers in the range of 480 and 539 of molecular weight.

In the second experiment, equimolecular amounts of TTPFPB and substrate were reacted. The reaction started at -50°C and was allowed to come back to room temperature (in about 6 hours). Then the volume of the solvent was reduced and some pentane was layered over the chlorobenzene solution. The resulting biphasic system was put in the fridge at -67°C. The day after a semisolid precipitate was found in the vial, collected on a glass plate and observed at the microscope: it seemed to be a polymerized material. Due to the small amount of starting material employed, it was not possible to acquire an NMR spectrum of the upper solution.

5.3.13. Reaction with 2,2,5,5-tetrakis(trimethylsilyl)-3,3,4,4-tetramethyl-1,1,6,6-tetramethylhexasilane (55) at low temperature

Compound **55** was treated with 1 equivalent of TTPFPB. In principle a rearrangement should not occur, as the abstraction of a hydride would generate a [≡$SiMe_2Si^+$] fragment, the most stable one as established by isomerization experiments. In addition, by removing only one hydride from the molecule, the forming silyl cation should be bridged by the remaining H group, to have an intramolecular stabilization (Scheme 23-5).



55

68

Scheme 23-5: Reaction of 2,2,5,5-tetrakis(trimethylsilyl)-3,3,4,4-tetramethyl-1,1,6,6-tetramethylhexasilane (**55**) with 1.0 equivalent of trityl cation, *d*-chlorobenzene as solvent.

Reagents were mixed at ca. -40°C in deuterated chlorobenze as solvent, to have better NMR spectra. Because at this temperature the reaction mixture was still solid, the first NMR spectrum was acquired at about -30°C (Figure 24-5). Then the temperature was increased by 5 degree every 15 minutes, acquiring the NMR spectrum each time. The ^{29}Si NMR spectrum was quite stable as the temperature was under -15°C, then decomposition/rearrangement started and a numbers of peaks appeared in the spectrum at room temperature (Figure 25-5). This series of signals was quite similar to that one of the reaction with substrate **54** (Figure 23-5). Indeed, when a higher temperature provoked the ring opening a –$SiMe_2H$ group is formed again and this group could also take part in a rearrangement process.

However, after four hours at room temperature, no signals in the silicon NMR spectrum could be detected in the reaction mixture.

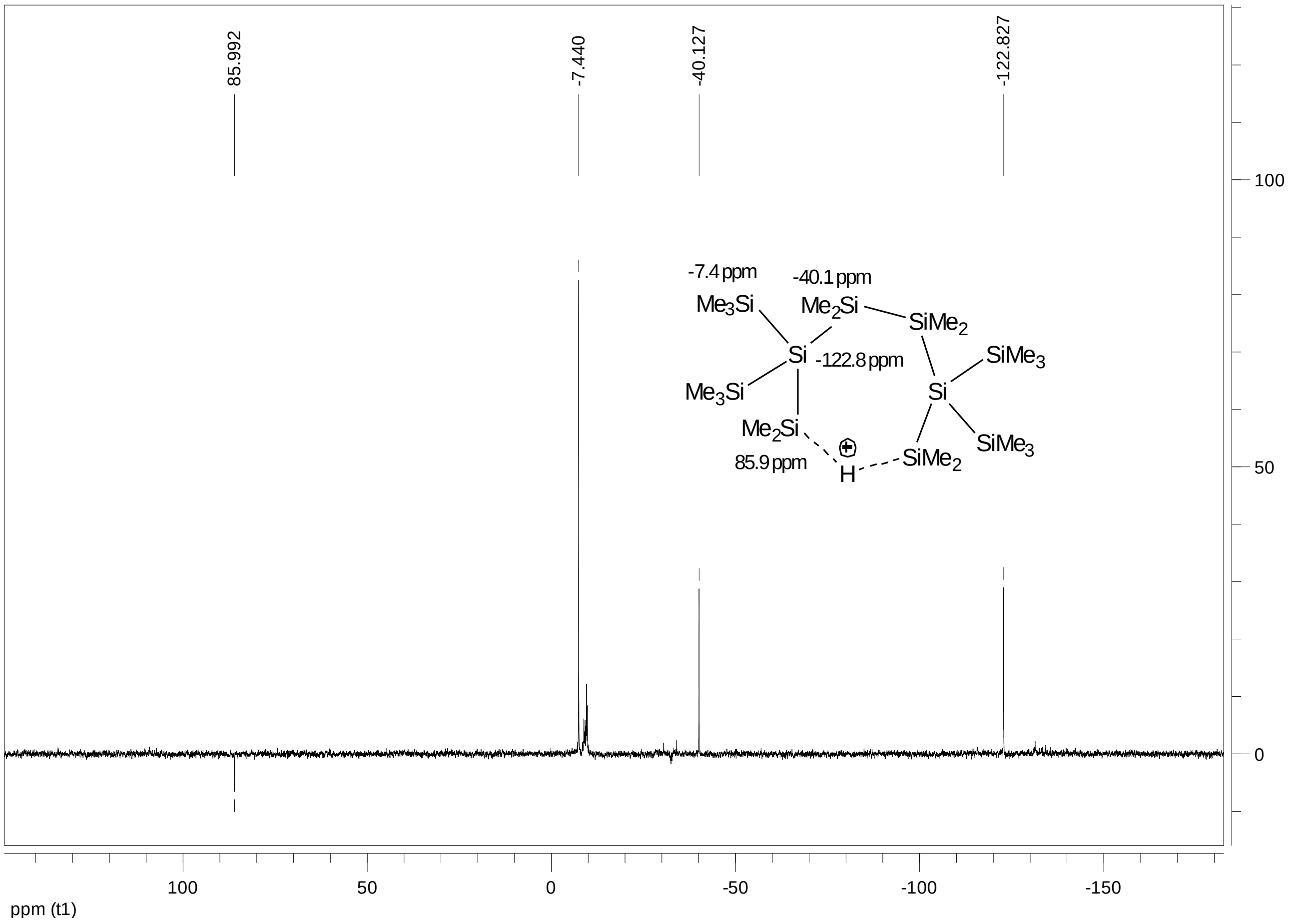


Figure 24-5: ^{29}Si NMR of compound **68** in the reaction mixture at -30°C.

The spectrum in Figure 24-5 revealed a quite clean reaction. There were four main signals, each in the expected range of the spectrum for those types of silicon atoms. The -SiMe$_3$ groups had the typical chemical shift as when they are present in cyclic structure (for comparison, see the pictures shown below, Figure 26-5). The -SiMe$_2$-groups in the backbone had a δ < -35 ppm, which is normal in ring structures not strongly strained. The quaternary silicon atoms (*Si*Si$_4$) signal is quite low-field shifted, but this might also be due to the proximity of the silyl cation (anyway, in the molecule with seven silicon atoms in the ring the Si$_q$ gives signal at -118 ppm) . Finally, at ca. 86 ppm there should be the peak from the [Me$_2$Si-H$^+$-SiMe$_2$] group. It had a reversed phase, as often it happens in the INEPT NMR sequence for the -Me$_2$SiH groups. The signal then disappeared as the temperature increased.

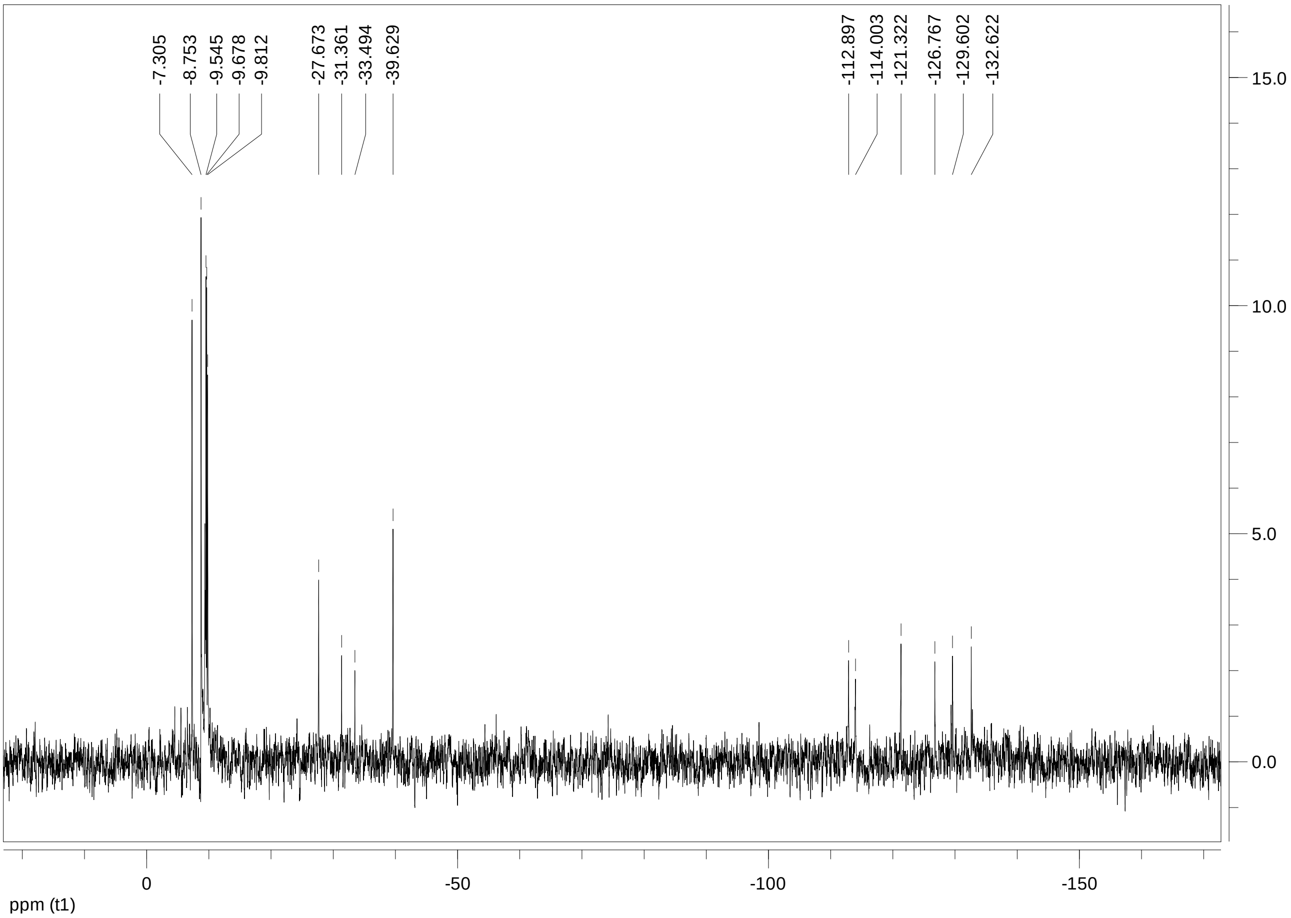


Figure 25-5: ^{29}Si NMR of the reaction mixture at +5°C: different products were formed due to the rearrangement of compound **55**.

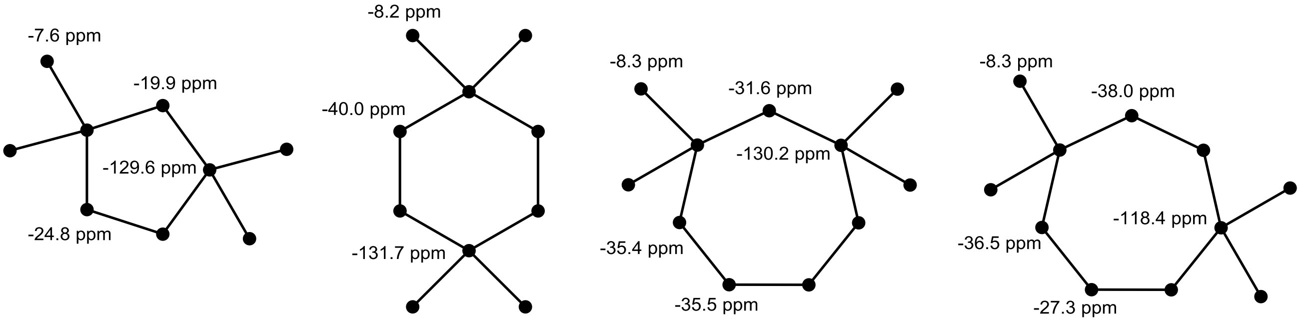


Figure 26-5: Typical ^{29}Si NMR chemical shifts of silicon ring structures.

In the ^{1}H NMR (Figure 27-5) there were four main signals for the methyl groups between 0.0 and 0.5 ppm. Probably there was diasterotopicity of some groups of proton that were in the upside and downside in respect to the backbone plane of the molecule. But because of partial overlapping and not correct integration of the peaks, it was not possible to figure out a correct assignment of the chemical shifts.

The bridging proton showed a broad signal at ca. 2.0 ppm. Heinekey reported a value of 2.1 ppm for [Et_3Si-H^+-$SiEt_3$],[78] but this measure anyway depended on the amount of triethylsilane in solution.

Finally, there is the signal of the by-product triphenylmethane at 5.3 ppm.

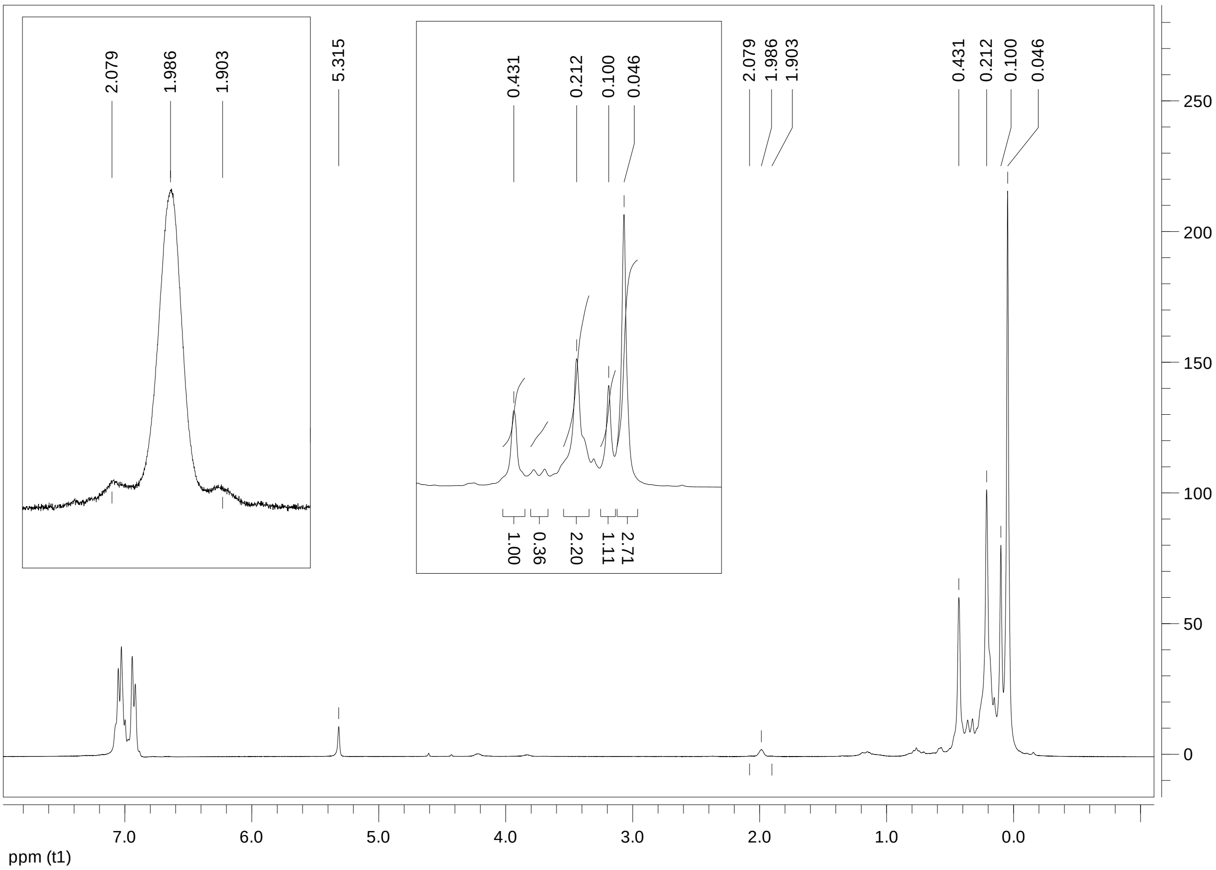


Figure 27-5: ^{1}H NMR of compound **68** in the reaction mixture at -30°C.

In a separate experiment the same results were obtained, and in addition the s2pul ^{29}Si NMR was acquired (^{1}H-coupled ^{29}Si NMR, Figure 28-5).

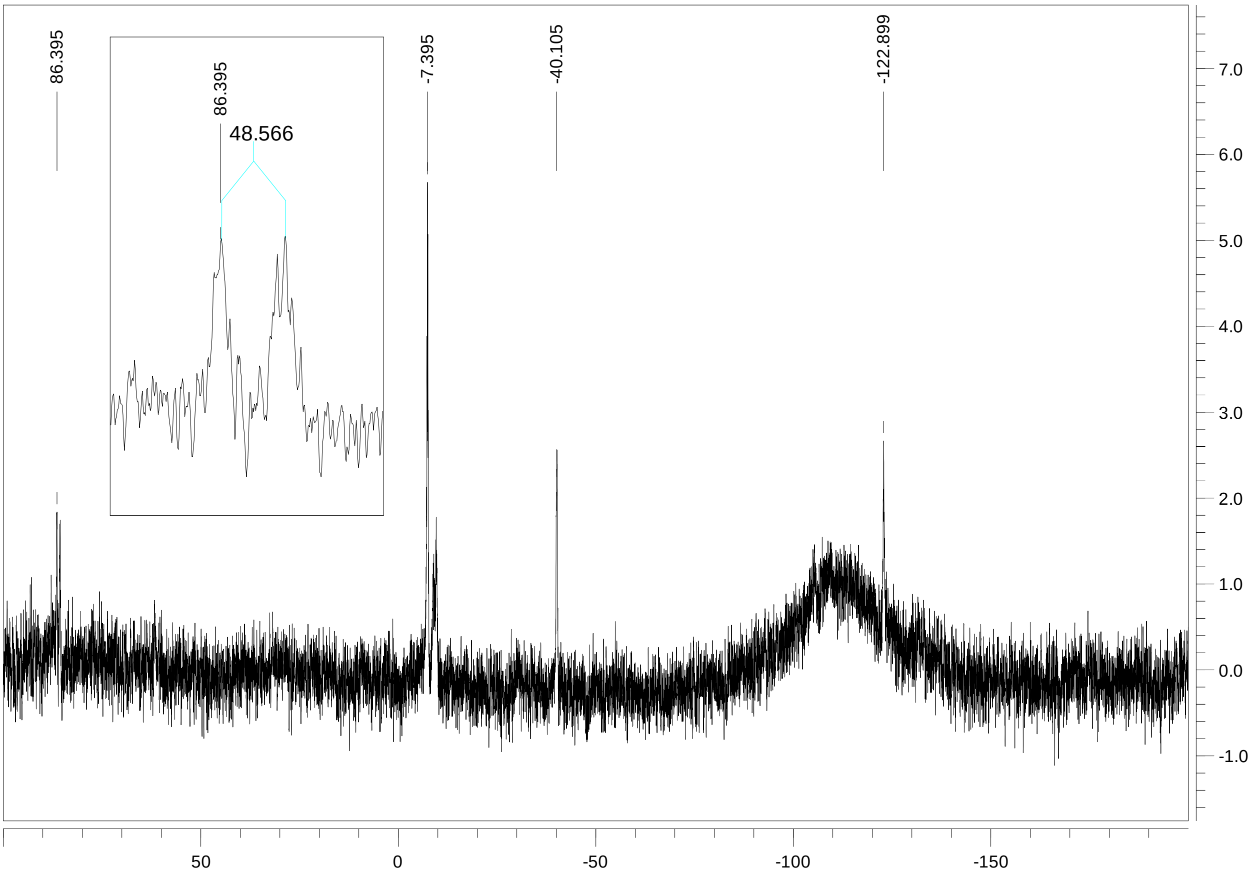


Figure 28-5: ^{1}H-coupled ^{29}Si NMR of compound **68** in the reaction mixture at -30°C.

The spectrum was quite noisy and the signals were broad because of the coupling between silicon and protons of the relative methyl groups. But a clear coupling for the [Me_2Si-H^+] fragment could be observed: a doublet of septets (broad) was detected, as expected. The coupling constant was measured as $^{1}J_{SiH}$ = 48.6 Hz, that could be reasonable for this kind of structure ($^{1}J_{SiH}$ = 40 Hz for Heinekey's adduct; $^{1}J_{SiH}$ = 117 Hz for free triethylsilane; $^{1}J_{SiH}$ = 177.8 Hz for compound **55**).

As it was not possible to crystallize compound **68**, its structure was calculated by Lena Albers and it is here shown (Figure 29-5).[83]

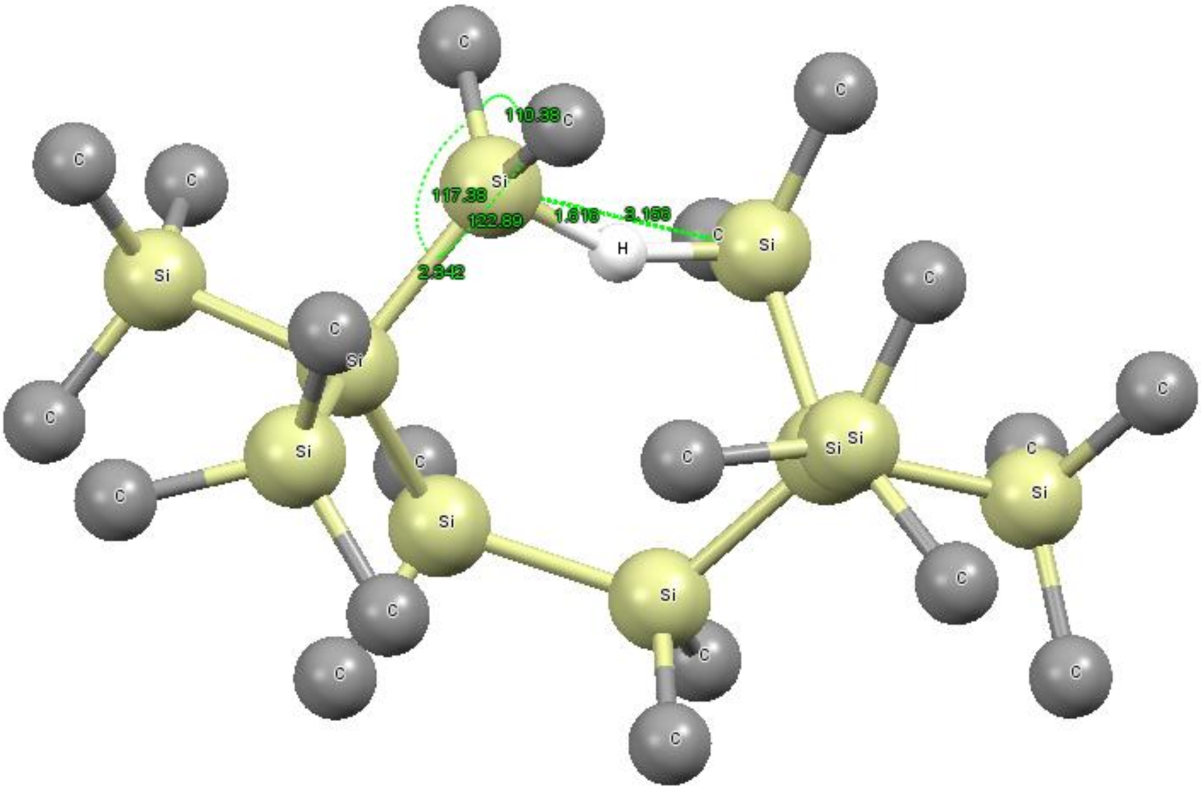


Figure 29-5: Calculated structure for compound **68**. Bond length in Å.
Hydrogen atoms hidden for clarity, except the bridging one.

The Si-H bond was measured as 1.616 Å, while the silicon atoms of the bridged system [Si-H$^+$Si] had a distance of 3.156 Å (Heinekey measured a Si-Si distance of 3.217 Å for [Et$_3$Si-H$^+$SiEt$_3$],[78] 0.06 Å more than that one of compound **68**. This difference could be consistent with an "open" linear system in comparison with the observed "close" seven members ring. The sum of the angles at the cationic silicons is ∑C–*Si*$^+$–Si = 350.6°, while a mean value of 348.3° was measured for ∑C–Si–C in Heinekey structure.[78] Finally, the Si-H-Si angle was quite distant from linearity, and it was calculated as 154.3°.

For the structure in Figure 29-5 also NMR chemical shifts were calculated.[83] Two computational methods were applied. Data are shown in Table 5-5.

-R_3Si fragments compound 68	**Experimental δ(^{29}Si), $^{1}J_{SiH}$**	**Calculated δ(^{29}Si), $^{1}J_{SiH}$** M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p)	**Calculated δ(^{29}Si), $^{1}J_{SiH}$** B3LYP/IGLOIII//M06-2X/6-311+G(d,p)
[*Si*-H$^+$-*Si*]	85.9 ppm, 48 Hz	84.6 ppm, 40 Hz	100.7 ppm, 48 Hz
-*Si*Me$_3$	-7.4 ppm	-6.0 ppm	-1.3 ppm
-*Si*Me$_2$-	-40.1 ppm	-37.4 ppm	-32.2 ppm
Si$_4$*Si*	-122.8 ppm	-126.0 ppm	-113.5 ppm

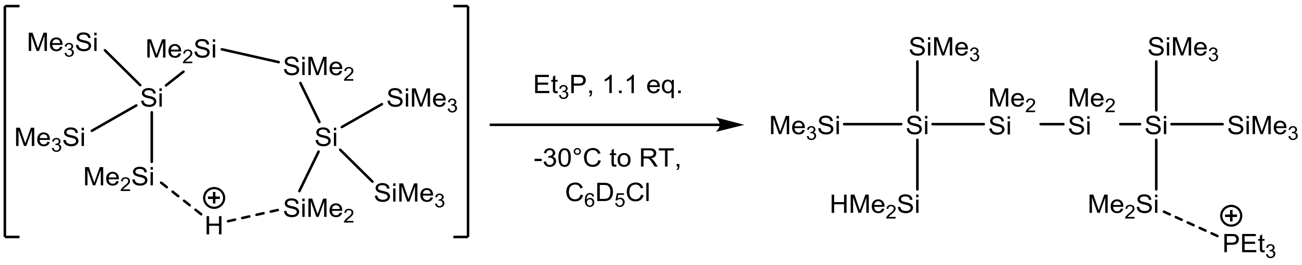
Table 5-5: Experimental and calculated NMR data for compound **68**.

The chemical shifts fit quite well with those ones calculated by the M06-L method, while the coupling constant was better in agreement with B3LYP. These differences between the two theoretical methods are known[*], and then it is possible to assert that the proposed interpretation of the NMR spectra was correct and that compound **68** was obtained.

---

[*] By the experience of L. Albers and of Prof. Müller group, M06-L method and B3LYP method have, quite always, only a partial agreement with the NMR experimental data. It is not the place here to go into deep discussion about theoretical chemistry, but a short explanation could be given as follow. The main criteria why the IGLOIII basis sets fits so well with J_{SiH} calculation it is that it takes more *s* orbital functions into account. For the coupling constant it is important to describe the core electrons in a detailed manner. For example, the 6-31G(d,p) basis set uses only 4*s* and 1*p* function. On the contrary, IGLOIII uses 6*s* and 2*p* function. The many *s* functions are also a reason for the huge size of the calculations and it need much memory and time to calculate with this basis set. The reason why the M06-L method works much better for the chemical shift calculations than the B3LYP it is because B3LYP calculates a HOMO-LUMO difference which is always too small. But this is important for the NMR shift, because a HOMO-LUMO difference results in a too much deshielded chemical shift. It is always very difficult to explain why DFT calculations (density functional methods) are good for several systems, because they are based on experiments and they are not *ab initio* calculation. B3LYP also has difficulties in describing molecular orbitals. Both methods, M06-2X and M06-L, are very good in describing MOs and include dispersion energies. That is why they are more detailed than B3LYP. For theoretical details about the basis sets and orbital functions, see: F. Jensen, *J. Chem. Theory Comput.*, **2008**, *4*, 719-727.

Since the oligosilyl cation was stable only at low temperature, and since crystallization attempts by layering pentane at -30°C did not afford any suitable crystals for X-ray diffraction analysis, the reaction mixture was treated with a strong Lewis base (Scheme 24-5). Similar adducts were already synthesized by Ashley and co-workers through the reaction of [i-Pr_3Si^+][$B(C_6F_5)_4^-$] with t-Bu_3P in chlorobenzene: the [i-Pr_3Si-$P(t$-$Bu)_3^+$] adduct seemed more stable and treatable than the precursor, but it still retained a good reactivity.[84]



68

69

Scheme 24-5: Reaction of oligosilyl cation from compound **55** with 1.1 equivalent of triethylphosphine, d-chlorobenzene as solvent.

The outcome of this reaction would confirm previous NMR spectra interpretation and it maybe could offer more crystallization chances to the final product. Indeed the ^{29}Si NMR seemed consistent with the expected product (Figure 31-5). The proposed NMR assignments are shown in Figure 30-5.

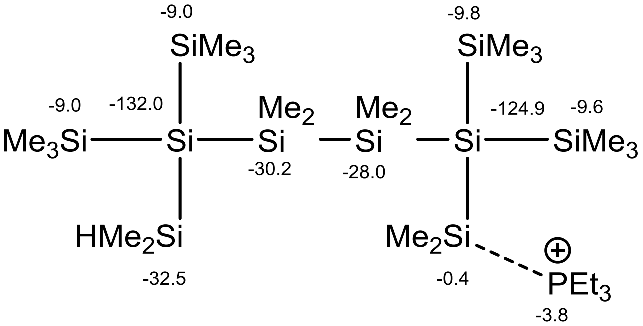


Figure 30-5: ^{29}Si and ^{31}P NMR chemical shifts (in ppm) of compound **69**.

---

[84] T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt, A. E. Ashley, *Chem. Comm.*, **2014**, *50*, 12753-12756.

Since the cyclic structure of **68** was opened by the attack of the phosphine, the symmetry of the cationic species was lost. Two different signals for the quaternary silicon atoms and two for the -SiMe$_2$ groups appeared in the ^{29}Si NMR spectrum. Also the back formation of the -SiMe$_2$H group indicated that in the starting material a hydrogen was still present in the structure. The -SiMe$_3$ region was more complicated, as probably the NMR signals were affected by spatial interactions with the phosphine group or even with the counter anion.

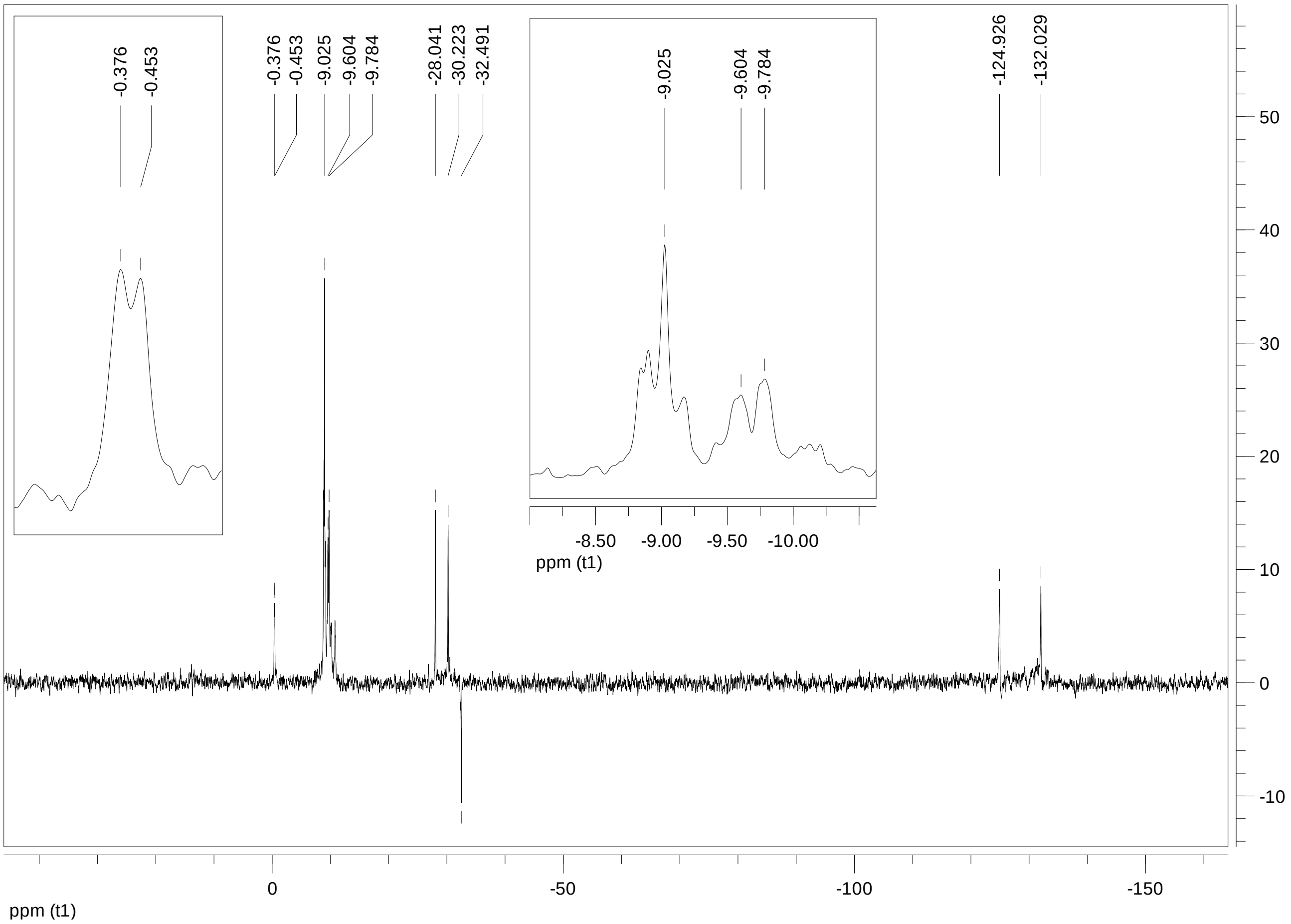


Figure 31-5: ^{29}Si NMR of compound **69** in the reaction mixture, after phosphine addition.

Finally, an unusual peak at ca. -0.4 ppm was detected. At first sight, these signal could be assigned to the silyl phosphonium group [Me_2Si-PEt_3^+]. But similar adducts usually maintain a significant downfield shift in the ^{29}Si NMR (δ = 43.1 ppm for [*i*-Pr_3*Si*-P(*t*-$Bu)_3^+$][$B(C_6F_5)_4^-$];[84] δ = 16.6 ppm for [Me_3*Si*-PPh_3^+][F-Al($OR^F)_3^-$][74]).

In addition, the signal should appear as doublet, because of the coupling Si-P, with a $^1J_{SiP}$ ≈ 20 to 40 Hz. But here a $^1J_{SiP}$ = 4.5 Hz was measured, as if phosphorus were not directly bonded to silicon.

Müller and his collaborators reported the synthesis and characterization of various silylium ion/phosphine Lewis pair: depending on the substituents of the silicon and of the phosphorus atoms, acid/base adducts or frustrated Lewis pair could form.[85] In the case of [$(Me_5C_6)_3Si$-PEt_3^+], the ^{29}Si NMR was measured at -1.9 ppm, extremely highfield shifted regarding the starting material [$(Me_5C_6)_3Si^+$][$B(C_6F_5)^-$] (δ(^{29}Si) = 216.2 ppm).[86] In that case, the value of coupling constant $^1J_{SiP}$ was 41.2 Hz.

There are not many other examples in literature reporting silyl cation adducts with phosphine. And the cited ones were only partially in agreement with the proposed interpretation of the NMR spectra. It could be that traces of impurities (ethereal solvents, water) in the liquid triethylphosphine formed an oxonium salt with compound **68**, and subsequently the oxidized derivative reacted with the phosphine. That would explain the low value for $^1J_{SiP}$. On the other hand, the abstraction of an ethyl groups by the cationic silicon from Et_3P could be considered as a remote side reaction. The signal of a -$SiMe_2Et$ group should appear in the range of -5.0 to -7.0 ppm.

---

[85] M. Reißmann, A. Schäfer, S. Jung , T. Müller, *Organometallics*, **2013**, *32*, 6736–6744.

[86] A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.*, **2011**, *50*, 12636 –12638.

The ^{31}P NMR showed one intense signal for the supposed product at -3.8 ppm, plus a small peak due to the excess of phosphine at -21.6 ppm (Figure 32-5).

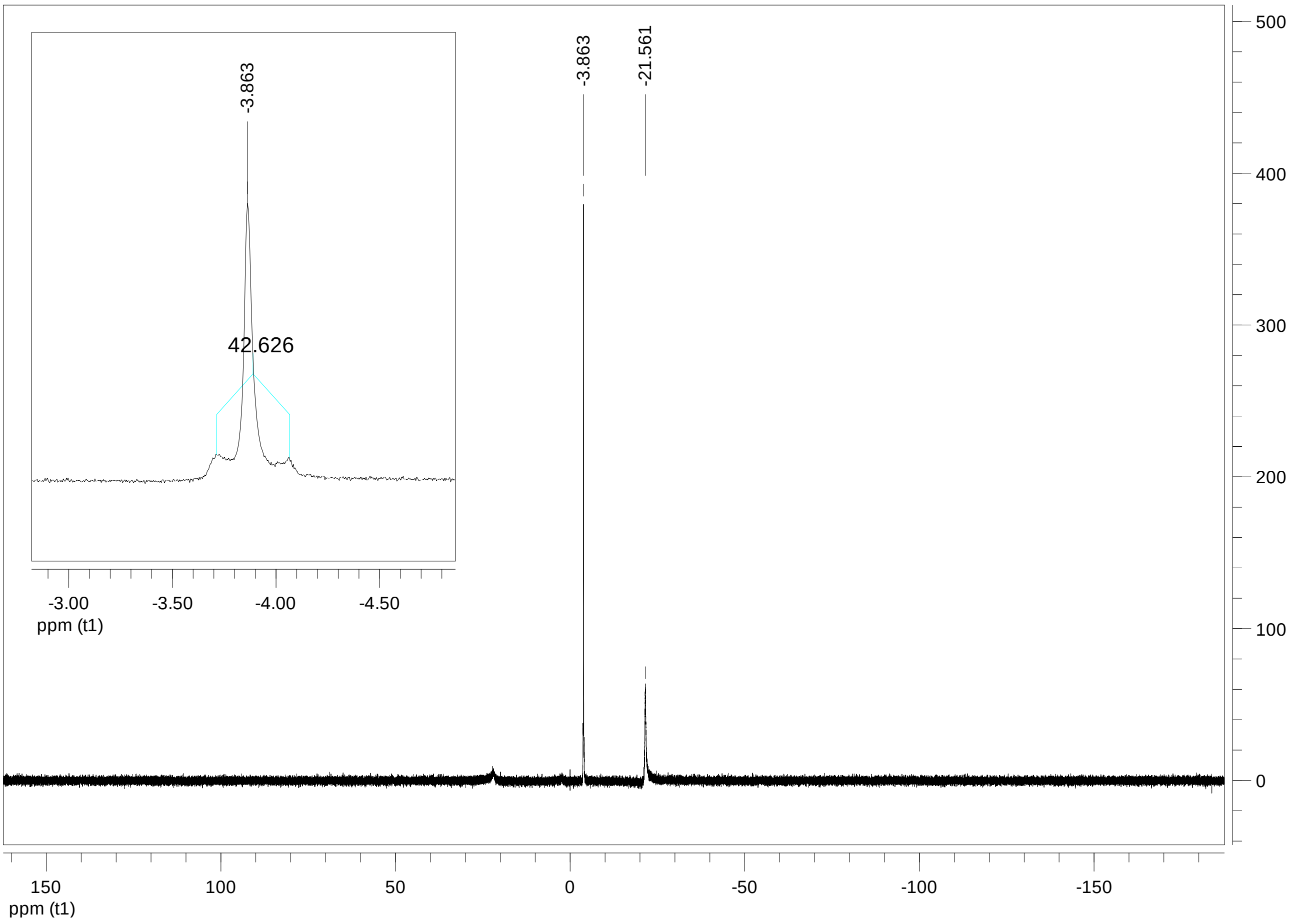


Figure 32-5: ^{31}P NMR of compound **69** in the reaction mixture, after phosphine addition.

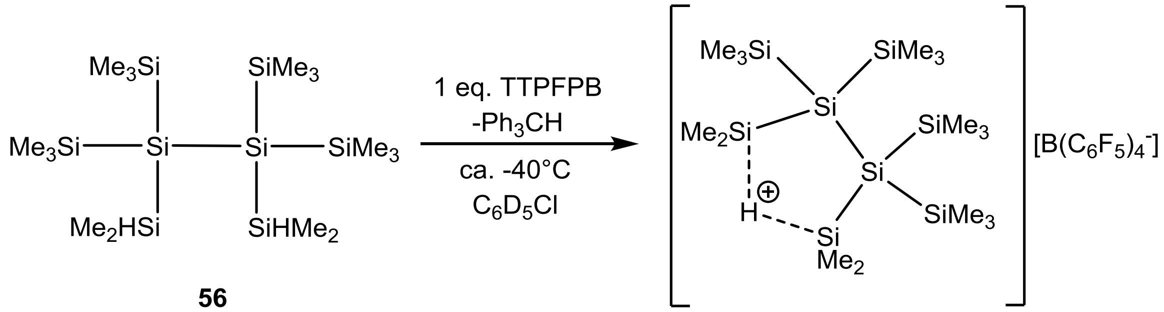
Ashley reported for [i-Pr$_3$*Si*-P(t-Bu)$_3^+$][B(C$_6$F$_5$)$_4^-$] a δ(^{31}P) = -2.8 ppm, less than 3 ppm downfield shifted in respect to free tri*tert*-butylphosphine NMR signal.[84] While Krossing reported for [Me$_3$*Si*-PPh$_3^+$][F-Al(OR^F)$_3^-$] a δ(^{31}P) = 57.3 ppm, surprisingly a signal 6 ppm highfield shifted in respect to free triphenylphosphine.[74] Müller's adduct was prepared with Et$_3$P, and a δ(^{31}P) = -4.3 ppm was measured.[85]

The ^{31}P NMR signal of compound **69** was comparable with those ones of the trialkylphosphine adducts synthesized by Ashley and Müller,[84,85] and this could confirm the formation of the desired product.

As a marginal note, the satellite bands at the main peak in the ^{31}P NMR (Figure 32-5, expanded box) showed a coupling constant with ^{13}C nuclei measured as 42.6 Hz. For the free triethylphosphine $^{1}J_{PC}$ = 14.0 Hz.[87] A larger $^{1}J_{PC}$ value is usually a sign of how much the phosphorus atom is acting as a ligand and sharing its lone pair electron. In other words, the ^{31}P-^{13}C coupling constant variation could suggest how the coordination number of phosphorus is changing (as an example, $^{1}J_{PC}$ = 104.0 Hz for $Ph_3P{=}O$).[88] In the case of compound **69**, the quite high value of the $^{1}J_{PC}$ could indicate that phosphorus atom is interacting with the cationic silicon and donating its electron density.

5.3.14. Reaction with 2,2,3,3-tetrakis(trimethylsilyl)-1,1,4,4-tetramethyltetrasilane (56) – low temperature experiment

The same type of experiment as escribed for **55** at low temperature was repeated with substrate **56**, Scheme 25-5. Usually cyclosilanes with five silicon atoms in the ring are very stable and crystallize well.



56

71

Scheme 25-5: Reaction of 2,2,3,3-tetrakis(trimethylsilyl)-1,1,4,4-tetramethyltetrasilane (**56**) with 1.0 equivalent of trityl cation, *d*-chlorobenzene as solvent.

First ^{29}Si NMR spectrum was acquired at -30°C (Figure 33-5): the reaction was not clean as the previous one, but anyway the signals of the expected compound at -120.6 ppm, -6.4 ppm and 109.1 ppm are the most intense. In Table 6-5 these data are presented together with the calculated NMR chemical shifts: as for compound **68**, a fairly good fitting was observed with a difference between the experimental and the calculated values not greater than 5 ppm. In the reaction mixture there was still some unreacted starting material (δ(^{29}Si) = -136.6 ppm, -30.0 ppm, -8.8 ppm).

---

[87] B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 30-34.

[88] Y. S. Varshavskii, T. G. Cherkasova, M. R. Gal'ding, V. A. Gindin, I. S. Podkorytov, O. V. Sizova, S. N. Smirnov, A. B. Nikol'skii, *Russ. J. Gen. Chem.*, **2013**, *83*, 567-569.

Rising the temperature to -25°C a small decomposition was detected. Then the NMR tube solution was recombined with that one in the Schlenk flask, kept at -30°C to -40°C and layered with dry pentane. After ca. 6 hours, the system has been left slowly coming back to room temperature. Unfortunately, just a red dense oily mass separated from the solvent mixture. Probably, the only way to try to obtain crystals from the reaction solution it is to carry all the process below -30°C, including the crystallization procedure.

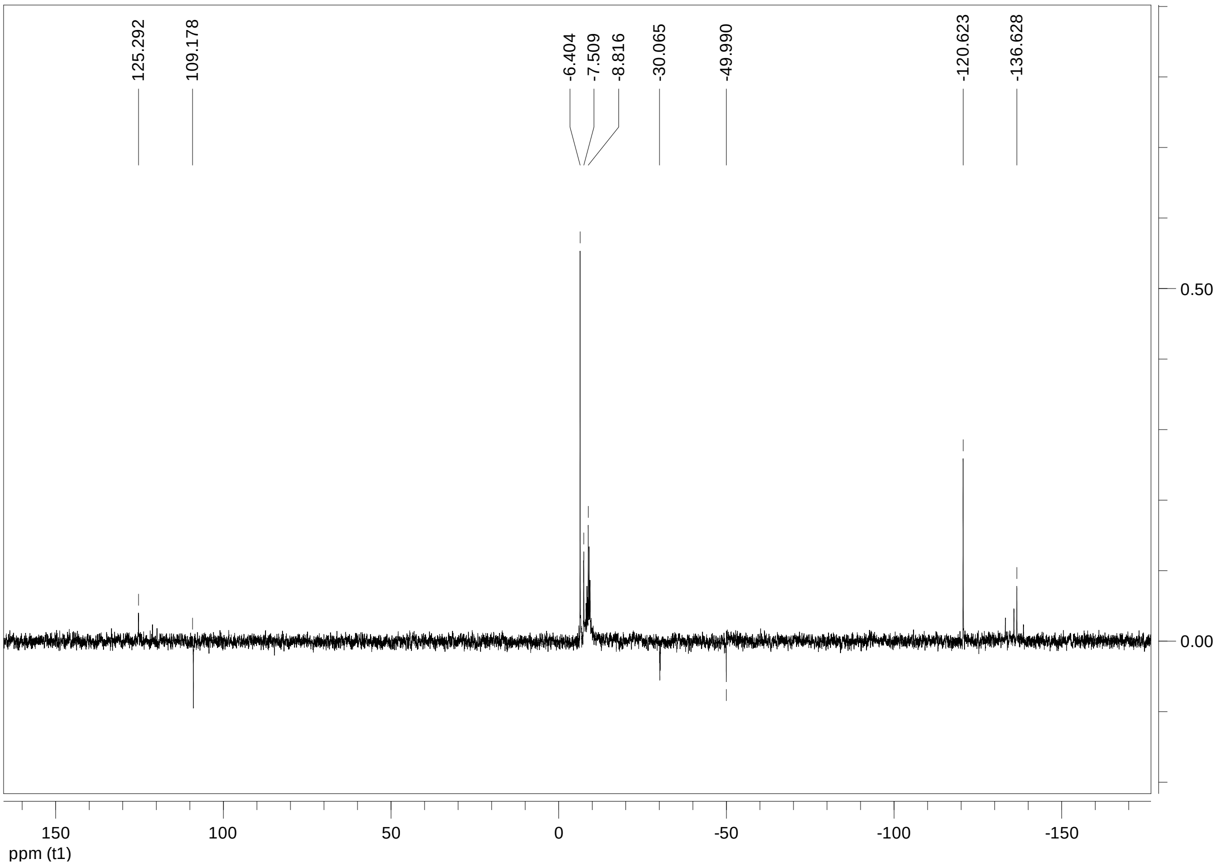


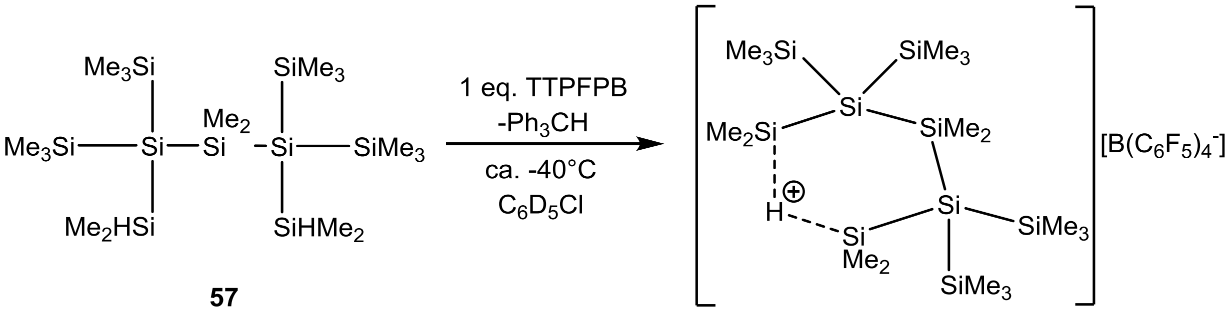
Figure 33-5: ^{29}Si NMR of the reaction mixture of compound **71**, at -30°C.

-R_3Si fragments compound 71	Experimental δ(^{29}Si), $^{1}J_{SiH}$	Calculated δ(^{29}Si), $^{1}J_{SiH}$ M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p)
[*Si*-H^+-*Si*]	109.2 ppm, 48 Hz	105.9 ppm, 40 Hz*
-*Si*Me_3	-6.4 ppm	-5.0 ppm
Si_4*Si*	-120.6 ppm	-124.8 ppm

Table 6-5: Experimental and calculated NMR data for compound **71**.
(*) Calculated with B3LYP/IGLOIII//M06-2X/6-311+G(d,p).

5.3.15. Reaction with 1,1,4,4-tetrakis(trimethylsilyl)-1,1,3,3,5,5-hexamethylpentasilane (57), low temperature experiment

Substrate **57** was reacted with 1 equivalent of TTPFPB, with the aim to form a six members ring containing a bridging hydrogen (Scheme 26-5).



57

72

Scheme 26-5: Reaction of 2,2,3,3-tetrakis(trimethylsilyl)-1,1,4,4-tetramethyltetrasilane (**56**) with 1.0 equivalent of trityl cation, *d*-chlorobenzene as solvent.

After 15 minutes of reaction, the ^{29}Si NMR was acquired. The desired product was forming, but there was still some starting material in the reaction mixture, and already some decomposition/rearrangement was proceeding (Figure 34-5). Also the ^{19}F NMR showed the formation of $B(C_6F_5)_3$, typical decomposition product of the borate counteranion. In Table 7-5 the experimental data are compared with the calculated NMR chemical shifts. In this case a good fitting was observed only for the cationic silicon and the -$SiMe_3$ groups.

After NMR measurement, the solution was treated with one equivalent of triphenylphosphine. In this case the formation of a single product (as for reaction in Scheme 24-5) was not observed, but a number of signals appeared in the ^{29}Si NMR. The presence of four peaks at ca. -20 ppm (-$SiMe_2$- groups) indicated the formation of four products at least, to which might correspond the eight peaks in the quaternary silicon region (probably asymmetric structures were generated). The ^{31}P NMR showed one main signal at 7.5 ppm (δ = -5.8 ppm for free Ph_3P in chlorobenzene), which appeared as a doublet, but with a coupling constant of 3.5 Hz only. A minor signal was detected at 4.1 ppm. The decay of the phosphine should be kept in account, and this case the abstraction of a phenyl group by the silyl cation could take place.

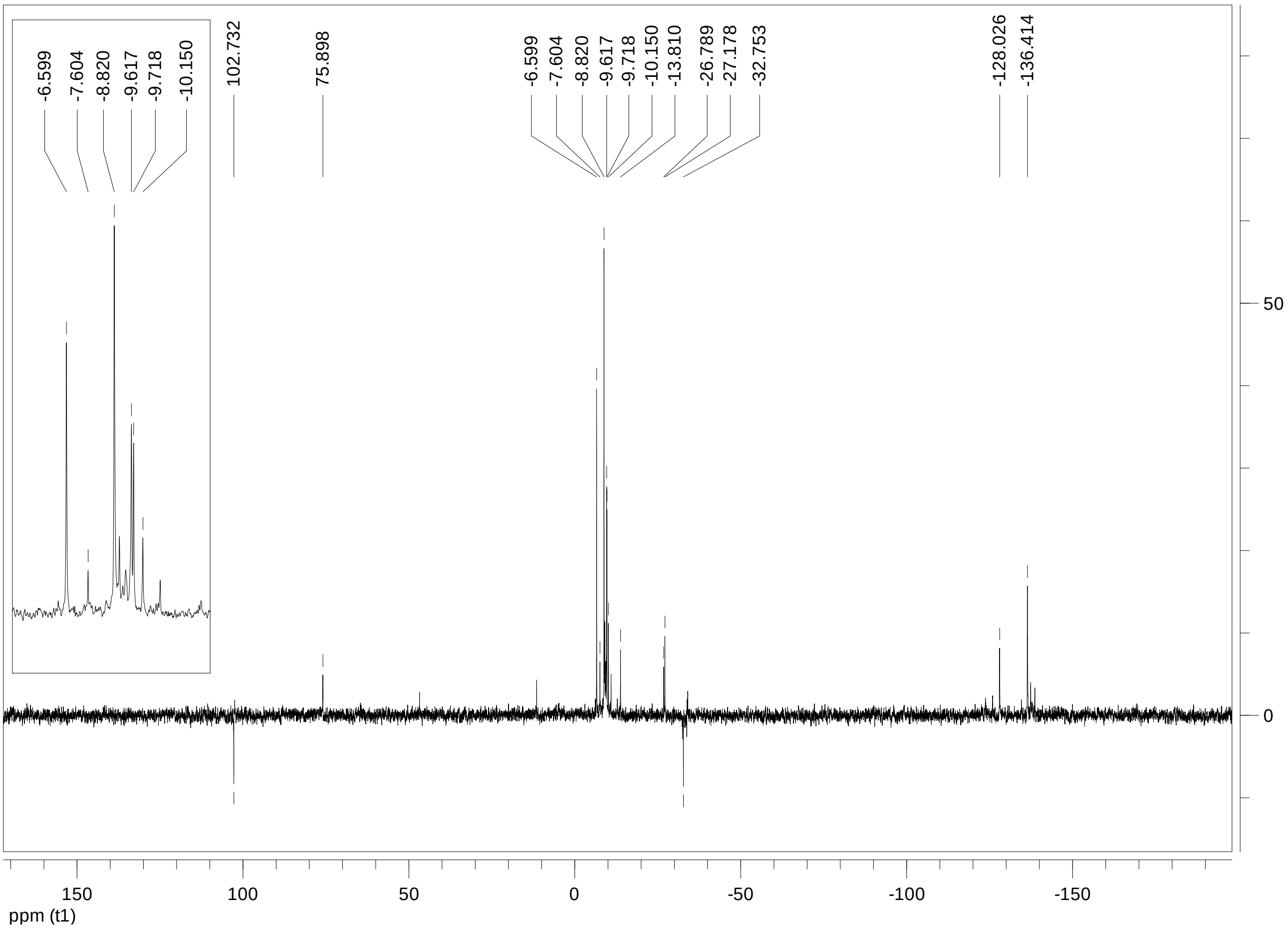


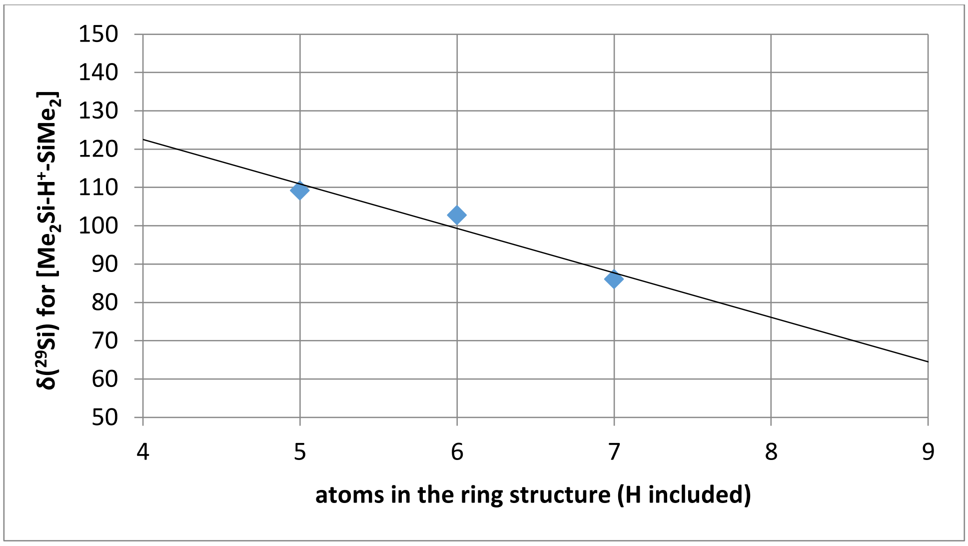
Figure 34-5: ^{29}Si NMR of the reaction mixture of compound **72**, at -30°C.

-R$_3$Si fragments compound 72	**Experimental δ(^{29}Si), $^1J_{SiH}$**	**Calculated δ(^{29}Si), $^1J_{SiH}$** M06-L/6-311G(2d,p)//M06-2X/6-311+G(d,p)
[*Si*-H$^+$-*Si*]	102.7 ppm, 48 Hz	104.3 ppm, 45 Hz*
-*Si*Me$_3$	-6.6 ppm	-6.8 ppm
-*Si*Me$_2$-	-26.8 ppm	-14.1 ppm
Si$_4$*Si*	-128.0 ppm	-142.6 ppm

Table 7-5: Experimental and calculated NMR data for compound **72**.
(*) Calculated with B3LYP/IGLOIII//M06-2X/6-311+G(d,p).

5.3.16 Correlation between the chemical shifts of the silyl cation fragment and the ring constraint.

As already shown, the [Et_3Si-H^+-$SiEt_3$] adducts had a linear and open conformation (Si-H-Si angle ≈ 177°).[78] But in the case of compounds **69**, **71** and **72**, rings were forming. Then, the cationic silicon atoms were not completely “free” to generate stable H-bridged structures, and the rings should shrink to allow the formation of these intramolecular adducts. The possibility for the starting linear substrate to “close” itself as a ring it was related to the number of silicon atoms in the backbone: as this numbers increased, the silicon was less forced to modify its bond angles from their ideal value of 109°. As a consequence, larger molecules should provide better stabilization to the [Si-H^+-Si] system, and this fact was put in evidence by the ^{29}Si NMR chemical shifts of the cationic species. A simple attempt to correlate NMR chemical shifts with the number of atoms in the ring structures was tried (Figure 35-5).



Nr. of atoms	δ ^{29}Si NMR
5	109.2
6	102.7
7	86.0

$y = -11.6x+168.9$

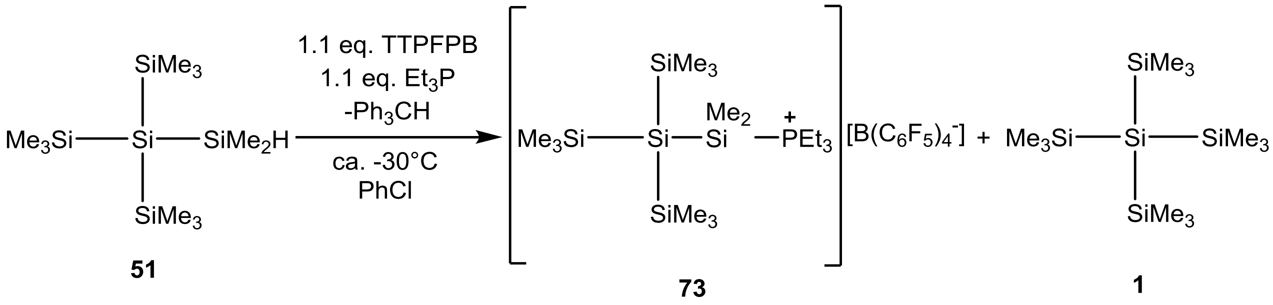
$R = -0.9692$

Figure 35-5: Correlation between ^{29}Si NMR chemical shifts (silyl cation fragments) and the number of atoms in the ring structures of compounds **69**, **71** and **72**.

As expected, smaller rings presented low-field shifted signals for the [Me_2Si-H^+-$SiMe_2$] fragments and that indicated a higher cationic character of the silylium ion. The linear correlation had an acceptable value for R, but at least another set of data δ(^{29}Si)/(nr. of atoms in the ring) would be desirable.

5.3.17. Reaction of compound 51 in the presence of Et_3P, at low temperature

The experiment involving the formation of a silyl-phosphonium adduct was repeated starting from 1,1,1-tris(trimethylsilyl)dimethyldisilane (**51**) as substrate (Scheme 27-5).



Scheme 27-5: Reaction of 1,1,1-tris(trimethylsilyl)dimethyldisilane (**51**) with a slight excess of trityl cation and triethylphosphine, chlorobenzene as solvent.

All the reagents were kept at ca. -30°C and quickly mixed with the solvent in this order: oligosilane, TTPFPB and finally triethylphosphine. As it was known from previous experiments, with mono H-silane (**51**) the formation of tetrakis(trimethylsilyl)silane (**1**) was the preferred reaction path. Nevertheless, adding immediately the phosphine ligand, it might be possible that the adduct was formed. In a separate experiment, the trityl salt and Et_3P were mixed in chlorobenzene and then added to compound **51**. But the trityl cation was forming itself an adduct with the phosphine, $[Ph_3C\text{-}PEt_3^+]$, that was not reactive enough to abstract a hydride from the oligosilyl substrate. In Figure 36-5 the ^{29}Si NMR of the reaction mixture is shown: compound **1** was formed anyway, but the other signals seemed to belong to the expected product **73**. There are pairs of very close peaks at -130.8 ppm (Si_q), -9.5 ppm ($SiMe_3$) and -0.1 ppm ($Me_2Si\text{-}PEt_3$). These signals could resemble doublets, but the eventual coupling constants would be quite low ($^{1\text{-}3}J_{SiP} \approx 3$ to 5 Hz), at least for the $^1J_{SiP}$. In addition, the value of $^3J_{SiP}$ would be greater than the value of $^1J_{SiP}$. It might be more reasonable that two isomers were synthesized and that they had slightly different spatial conformations. In the ^{31}P NMR spectrum three signals were detected (Figure 37-5): two intense ones at -4.0 ppm and 45.2 ppm, and a small peak at 22 ppm (probably the TTPFPB-Et_3P adduct).

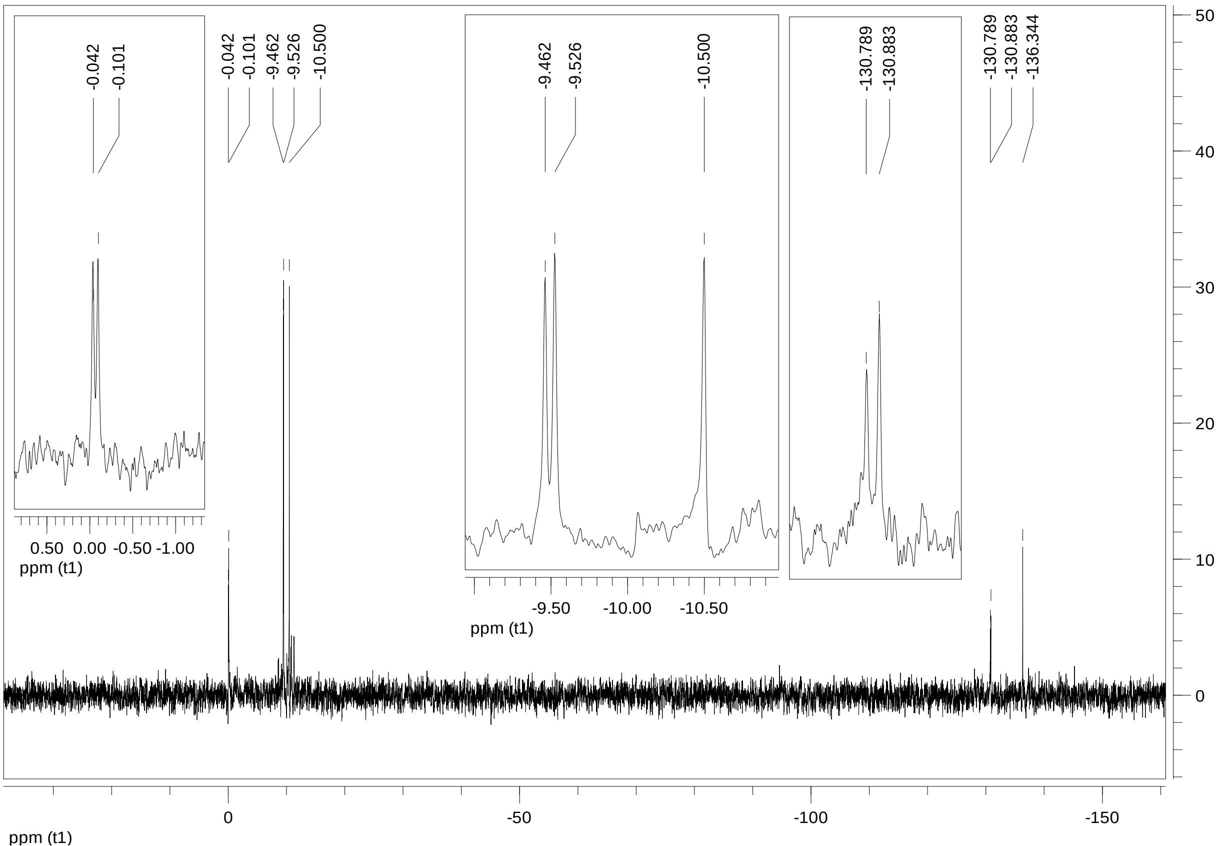


Figure 36-5: ^{29}Si NMR of the reaction mixture of compound **51** treated with TTPFPB in the presence of Et$_3$P.

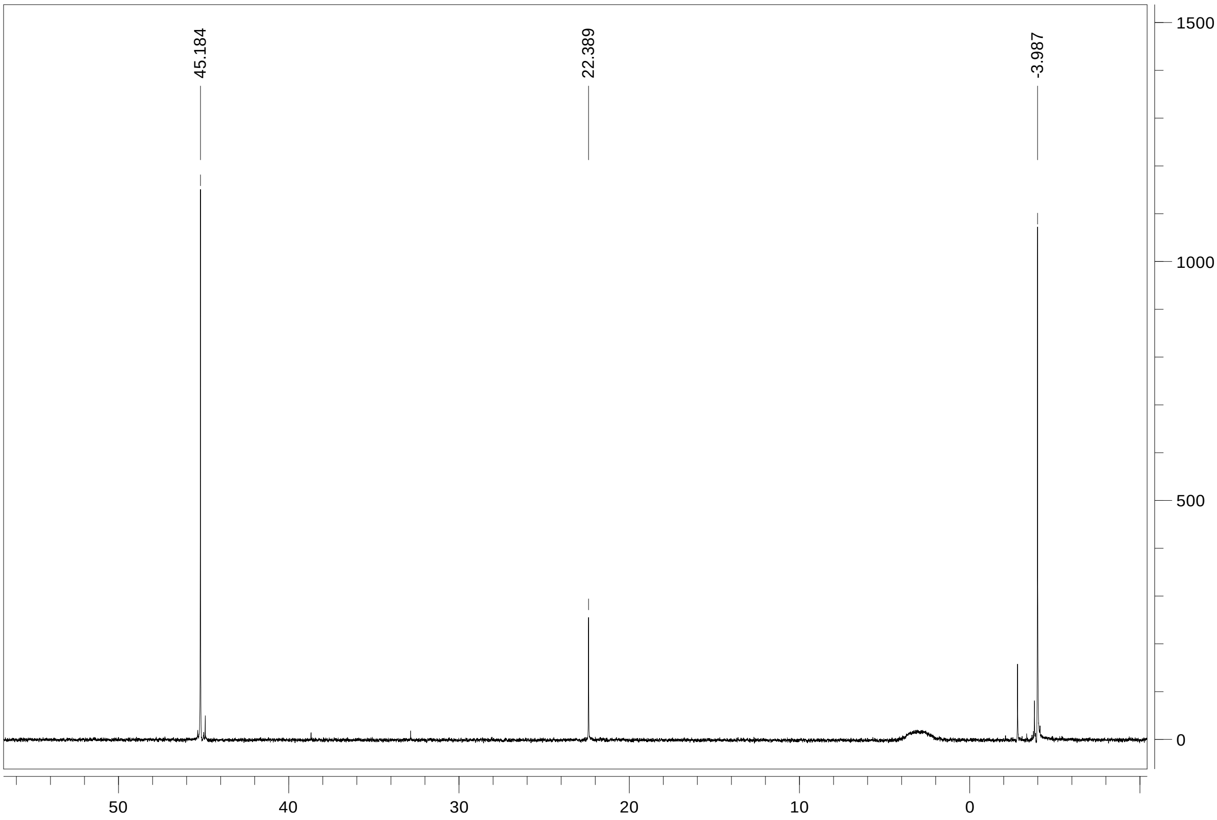


Figure 37-5: ^{31}P NMR of the reaction mixture of compound **51** treated with TTPFPB in the presence of Et$_3$P.

No more Et_3P was present in solution, so the starting amount of phosphorus was somehow splitted in two different compounds, in a comparable ratio.

A gHMBC (^{29}Si-^{1}H) NMR spectrum was also acquired (Figure 38-5). This spectrum showed at least that the signals at -130.8 ppm and -9.5 ppm were correlated and they corresponded to silicon atoms of the same molecule. On the other hand, it suggested that the peak at ca. -0.1 ppm could be due to another molecule or molecular fragment.

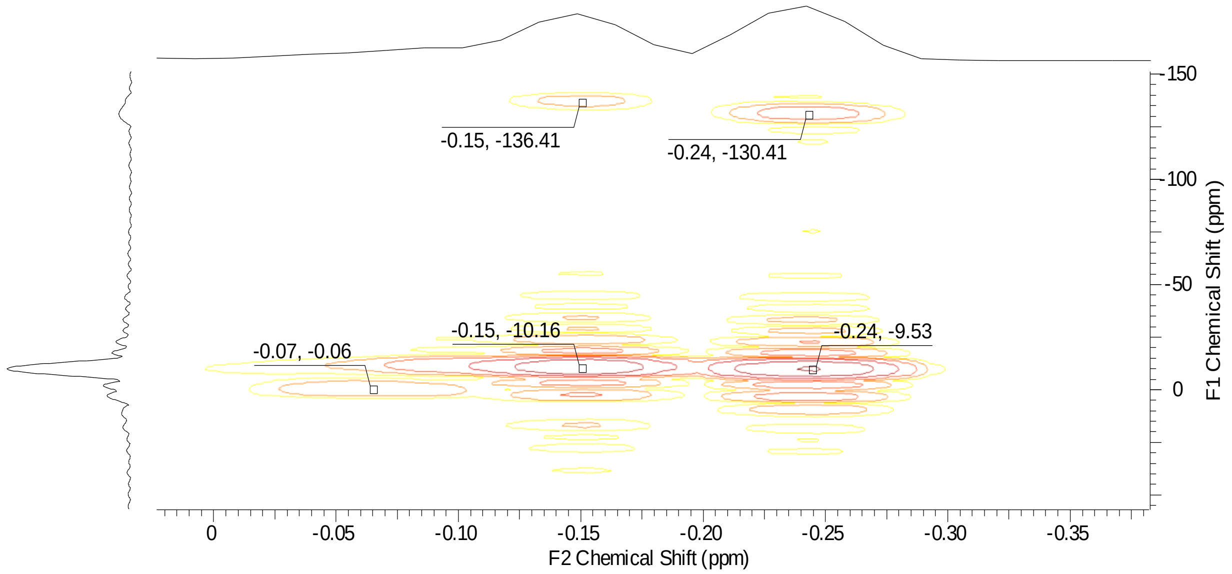
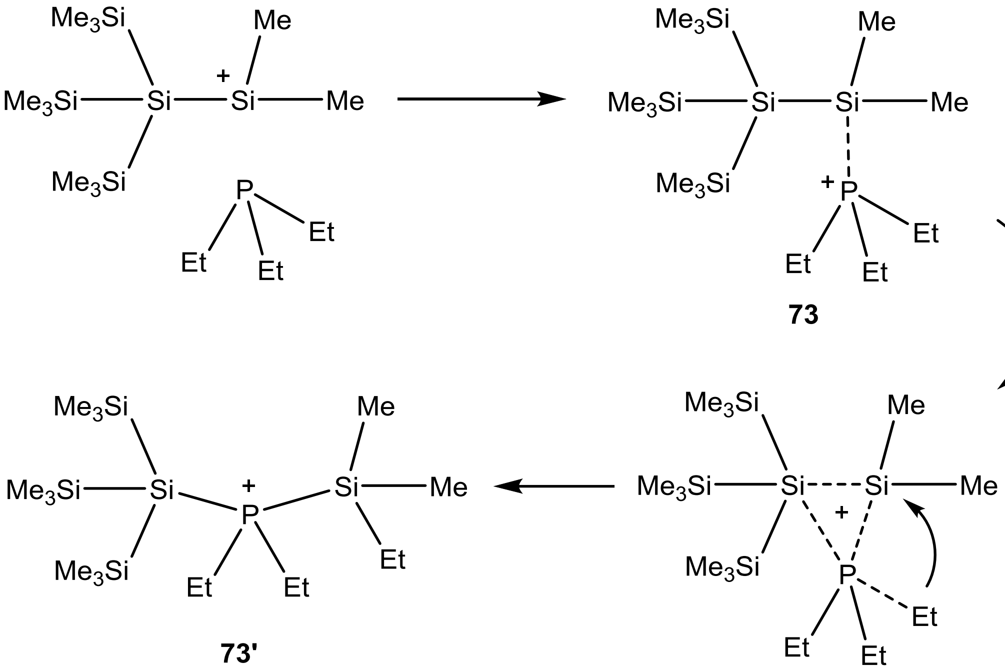


Figure 38-5: gHMBC ^{1}H-^{29}Si NMR of the reaction mixture of compound **51** treated with TTPFPB in the presence of Et_3P (F1=^{29}Si; F2=^{1}H).

To explain what appeared in these NMR spectra, it could be argued that during or after the formation of the silyl-phosphonium adduct, the latter underwent an internal rearrangement (Scheme 28-5). This process should be considered also for the reaction presented in Scheme 24-5.

The final product of the following reaction path could satisfy NMR spectra interpretations because:

- it would be reasonable to have from the hypersilyl fragment two coupling constant measured as $^{1}J_{SiP}$ = 5.4 Hz and $^{2}J_{SiP}$ = 3.8 Hz, and one as $^{1}J_{SiP}$ = 3.3 Hz from the dimethylethylsilyl group. This would explain the presence of the three doublets in the ^{29}Si NMR spectrum, with quite similar J_{SiP}
- the NMR signals of the hypersilyl fragment were correlated in the HMBC spectrum, while the signal of the –$SiEtMe_2$ group resulted isolated
- both signals from $(SiMe_3)_3$*Si* and from Me_2Et*Si* were down-field shifted by ca. 6 ppm from their standard values (respectively -136 ppm and -6 ppm)

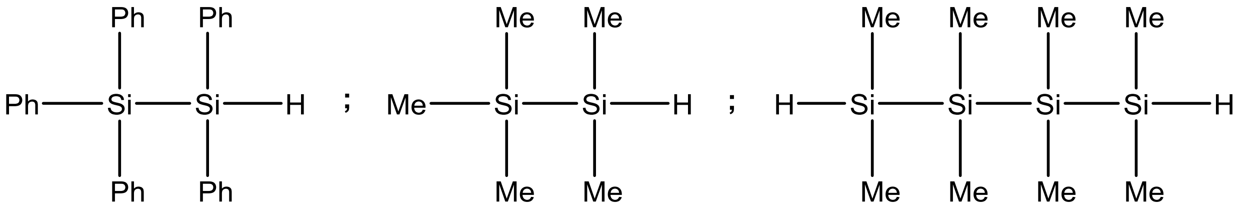


Scheme 28-5: Proposed mechanism to correlate the NMR spectra with a representative product.

However, this reaction pattern did not solve the presence of the two main signals in the ^{31}P NMR. The peak at ca. -4 ppm was comparable to the observed signal for compound **69**. But the peak at ca. 42 ppm was strongly down-field shifted, and it could only be explained by some decomposition reactions that involved some impurities or decomposition products of the trityl borate salt.

5.4 Approach to the silyl cation through smaller oligosilanes

As the first isolated silyl cation was prepared from a very simple molecule (Et_3SiH), some reactions were tried with very small oligosilanes (Figure 39-5).



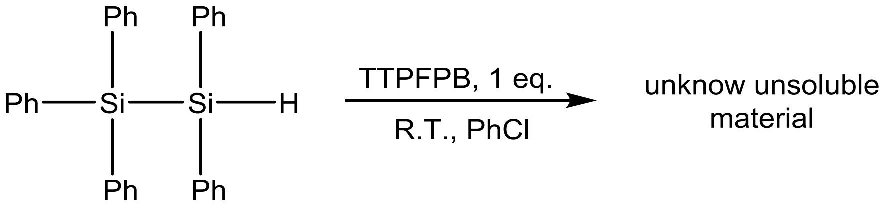
60 **61** **63**

Figure 39-5: Substrates containing few atoms of silicon and one or two hydrogen atoms.

Monosilanes have been reacted with 1 equivalent or half equivalent of TTPFPB. Compound **63** was treated with 1 equivalent of trityl borate salt to verify the formation of a hydrogen-bridged ring.

5.4.1. Attempt to prepare a silyl cation from pentaphenyldisilane (60)

The reaction was pursued on NMR tube scale. The reagents were mixed at room temperature in chlorobenzene (Scheme 29-5):



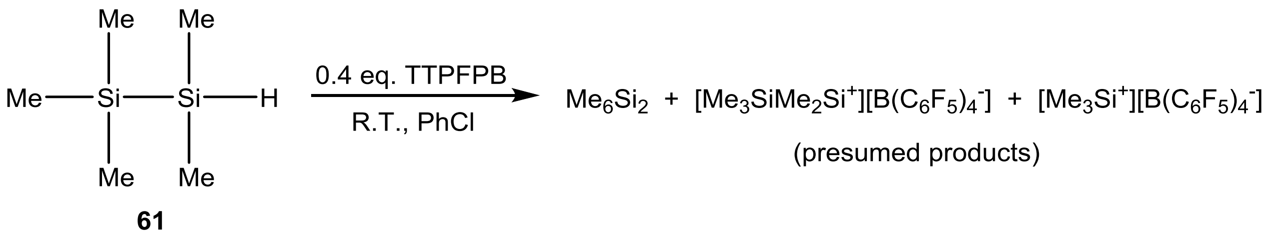
60

Scheme 29-5: Reaction of pentaphenyldisilane with 1 equivalent of trityl cation.

The mixture (an orange suspension) was stirred overnight. The NMR spectra were collected for both ^{29}Si and ^{1}H, but in the first case no signal was detected, while for the proton NMR only the solvent was visible together with a very small amount of triphenylmethane. In addition, the ^{19}F NMR revealed that the counteranion $[B(C_6F_5)_4^-]$ was completely converted into $B(C_6F_5)_3$.

5.4.2. Attempt to prepare a silyl cation from pentamethyldisilane (61)

In this experiment, the substrate was treated with TTPFPB in substoichiometric amounts (Scheme 30-5). The reaction mixture remained colorless until ca. half of the TTPFPB solution was dropped in, and then turned red. No bubbling was observed.



Scheme 30-5: Reaction of pentamethylsilane with less than half equivalent of trityl cation.

With only two silicon atoms in the starting material, a numbers of signals were observed in the ^{29}Si NMR of the reaction mixture (Figure 40-5). Compound **61** was completely consumed (no sign of the –$SiMe_2H$ group at -39 ppm, with the characteristic reversed phase). Hexamethyldisilane was considered as possible product, but it usually showed a chemical shift of ca. -20 ppm, then probably it was not forming in this reaction. The peak at -18.5 ppm was anyway due to a Me_3*Si*Si fragment. But it was not clear if this signal was correlated to the one at 76.3 ppm or to the one at ca. 50 ppm.

By experience, the signal at 76.3 ppm should indicate the formation of the $[Me_3Si^+][B(C_6F_5)_4^-]$ species. Then peaks at 51.9 ppm and -18.5 ppm could be assigned to $[Me_3SiMe_2Si^+][B(C_6F_5)_4^-]$. However, ^{19}F NMR revealed serious decomposition of the borate counter anion, and other by-products could form as $Me_3Si(C_6F_5)$ (peak at 1.5 ppm).[89]

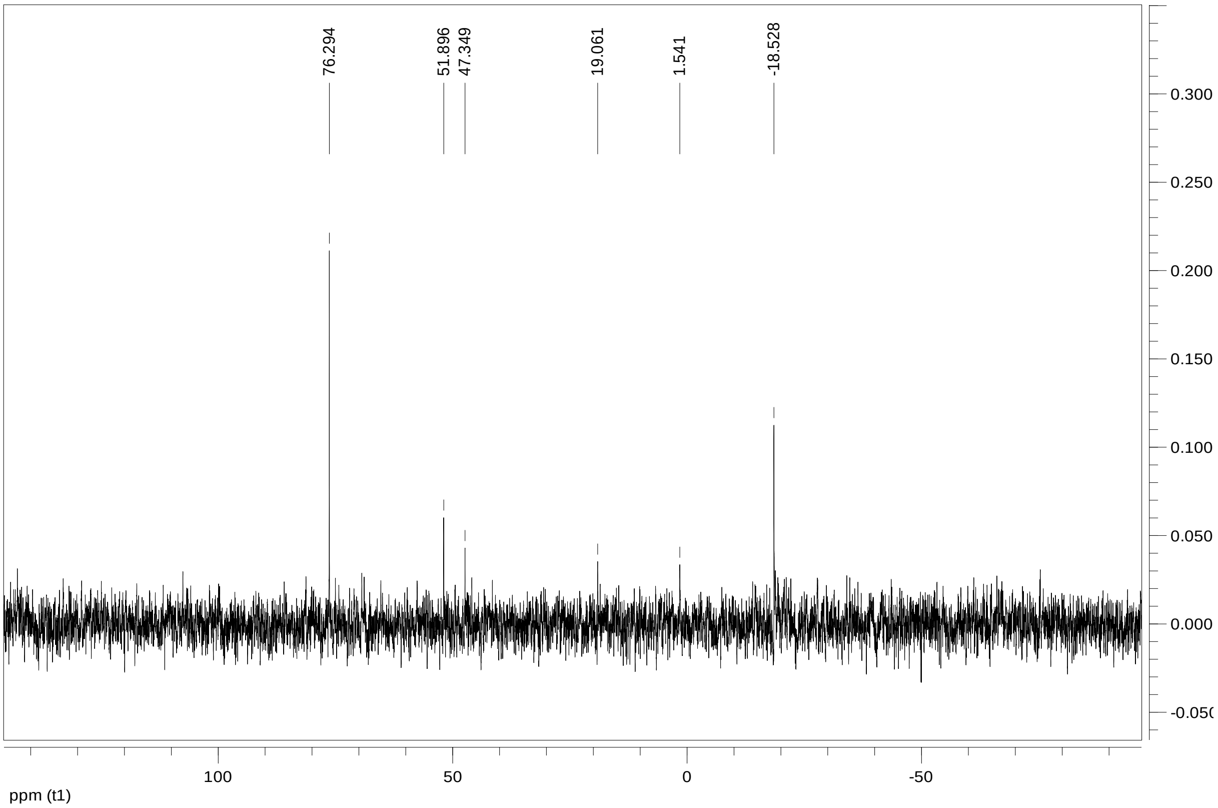


Figure 40-5: ^{29}Si NMR of the reaction mixture of compound **61** treated with half equivalent of TTPFPB ($^{29Si}\delta$(**61**) = -39.2 ppm, -18.6 ppm).

The reaction was repeated under the same conditions, but adding TTPFPB in two steps and checking the NMR spectra after every addition. Until the reaction mixture was colorless, the ^{29}Si NMR showed a number of peaks (Figure 41-5), but no starting material. The second addition gave a pale red solution and it seemed to lead the reaction to one single product, hexamethyldisilane (δ = -20.3 ppm).

---

[89] J. P. Kintzinger, H. Marsmann, *NMR Basic Principles and Progess, Oxygen-17 and Silicon-29*, Springer-Verlag, **1981**, 161.

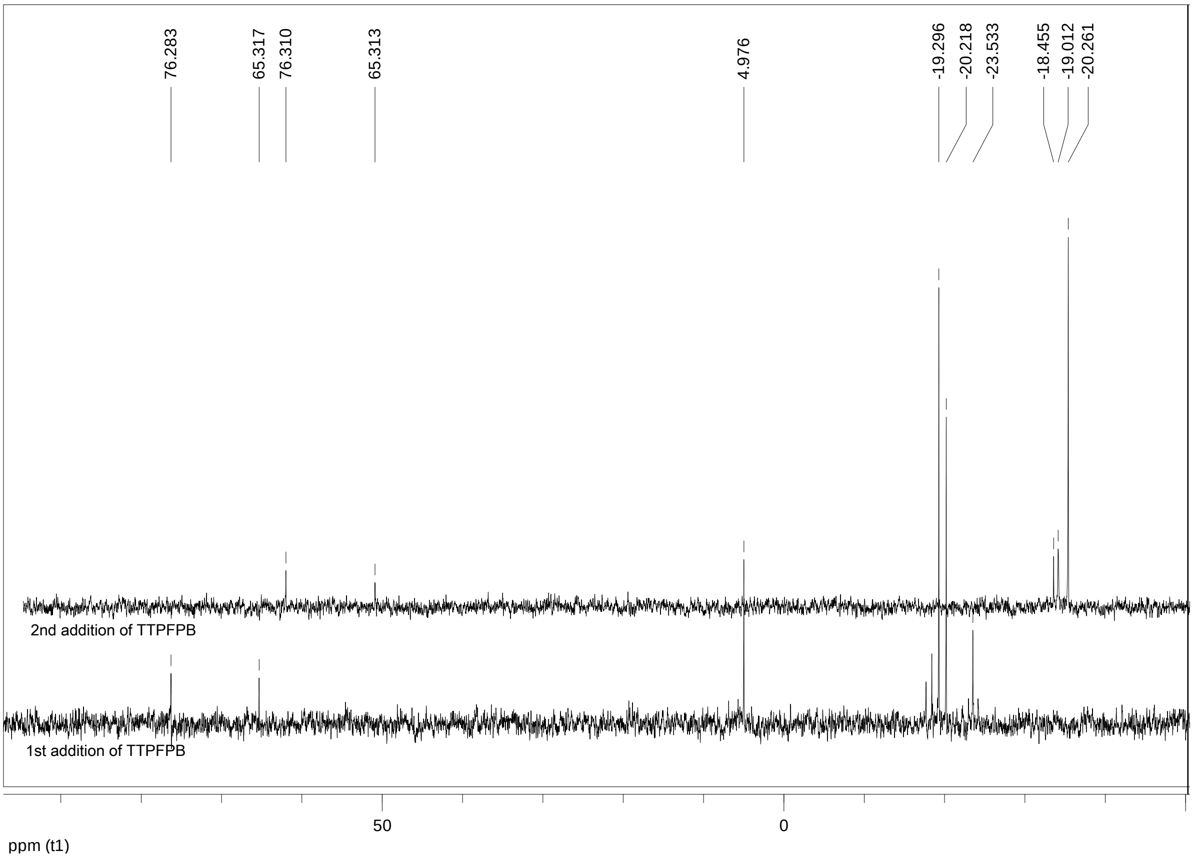
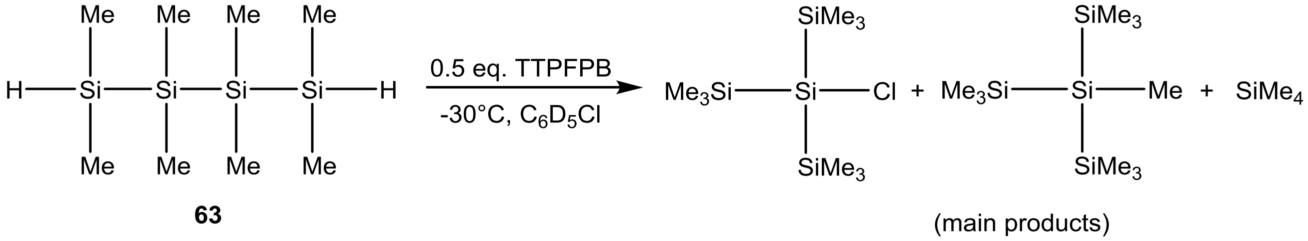


Figure 41-5: ^{29}Si NMR of the reaction mixture of compound **61** treated with two additions of TTPFPB.

5.4.3. Attempt to prepare a silyl cation from octamethyltetrasilane (63)

Compound **63** was treated with half equivalent of TTPFPB in deuterated chlorobenzene at -30°C (Scheme 31-5).



Scheme 31-5: Reaction of octamethyltetrasilane with 0.5 equivalents of trytil cation.

The ^{29}Si NMR acquired at -30°C showed different compounds, mainly some rearrangement branched products that usually derive from linear polysilanes (Figure 42-5).

The peaks at -12.9 ppm and -11.9 ppm seemed to indicate the presence of 1,1,1-tris(trimethylsilyl)chlorosilane, as if the forming silyl cation was able to abstract a chlorine from the solvent. Also 1,1,1-tris(trimethylsilyl)methylsilane (δ = -89.3 ppm, -12.1 ppm) and tetramethylsilane (δ = -0.3 ppm) were synthesized. Weak signals of cationic silyl species were visible at around 60 ppm, but they were not identified.

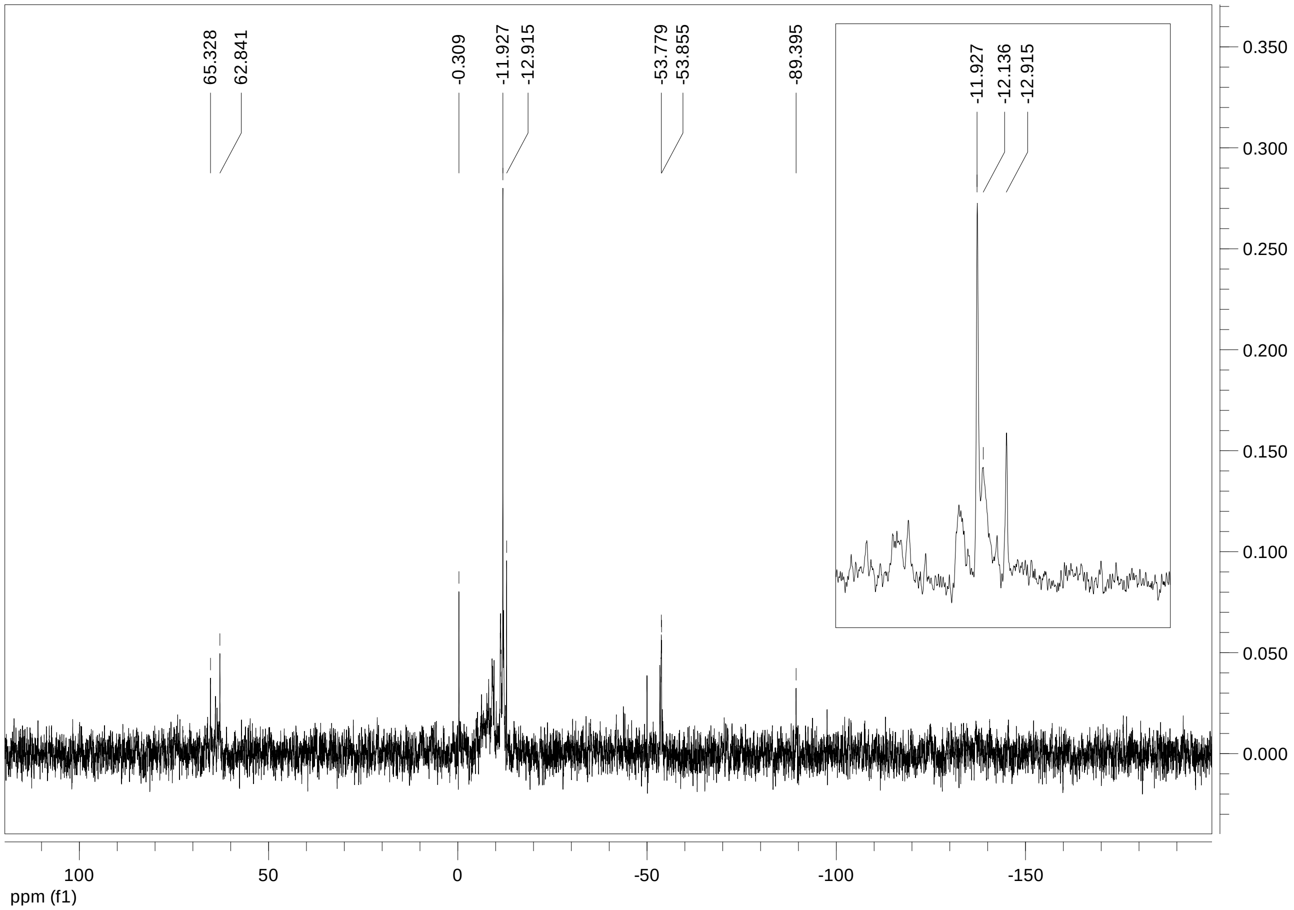


Figure 42-5: ^{29}Si NMR of the reaction mixture of compound **63** treated with half equivalent of TTPFPB, at -30°C (^{29Si}δ(**63**) = -36.8 ppm, -44.8 ppm).

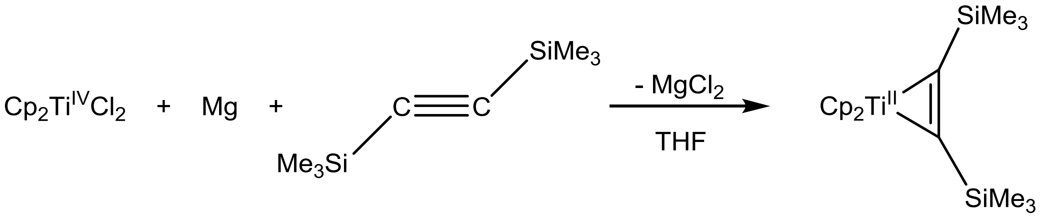
6. Bissilylated Metallocene of the Group 4 Elements in the Oxidation State +2

6.1 Introduction

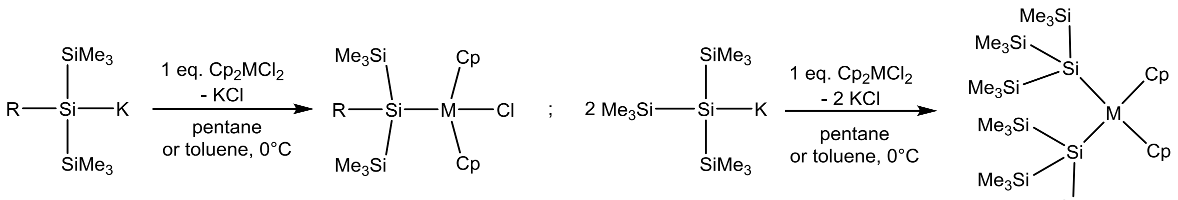
The organometallic chemistry of the elements of group 4 (titanium, zirconium and hafnium) is essentially based on the bis(cyclopentadienyl) complexes of these transition metals. After the first structural characterization of zirconocene dichloride (Cp_2ZrCl_2) by Wilkinson in 1954,[90] an extremely wide, manifold and complex new branch in organometallic chemistry developed.[91]

In the last decade, our group has studied the reactivity of these metallocenes towards oligosilyl anions, where the metal center was usually in the oxidation state +4, but also +3 and +2.[13,22,40,92,93,94,95] In addition, the coordination chemistry of some silylated germylenes, stannylenes, and plumbylenes to group 4 metallocenes was investigated.[96,97] In Figure 1-6 and Figure 2-6 some examples related to the cited papers are shown.

For the synthesis of silylated metallocenes in a low valence state, the *Rosenthal reagent* was employed as substrate for the reactions.[98] This compound is a bis(trimethylsilyl)acetylene complex of bis(cyclopentadienyl) titanium or zirconium in the oxidation state +2, and it is easily prepared from the respective metallocenes dichloride by reduction with magnesium (Scheme 1-6):



Scheme 1-6: Standard procedure for the synthesis of the Rosenthal reagent (titanium complex).



Kayser et al., 1999.
M = Zr or Hf
R = H, $SiMe_3$, $SiMe_2{}^tBu$, $SiMe_2$texyl, $SiMe_2$Hyp

Kayser et al., 2003.
M = Zr or Hf

---

[90] G. Wilkinson, J. M. Birmingham, *J. Am. Chem. Soc.*, **1954**, *76*, 4281–4284.

[91] For a comprehensive study about titanium and zirconium coordination chemistry, see I. Marek, (Ed.), *Titanium and Zirconium in Organic Synthesis*, Wiley-VHC, Weinheim, **2002**.

[92] C. Kayser, D. Frank, J. Baumgartner, C. Marschner, *J. Organomet. Chem.*, **2003**, *667*, 149-153.

[93] R. Fischer, M. Zirngast, J. Baumgartner, C. Marschner, *J. Am. Chem. Soc.* **2005**, *127*, 70-71.

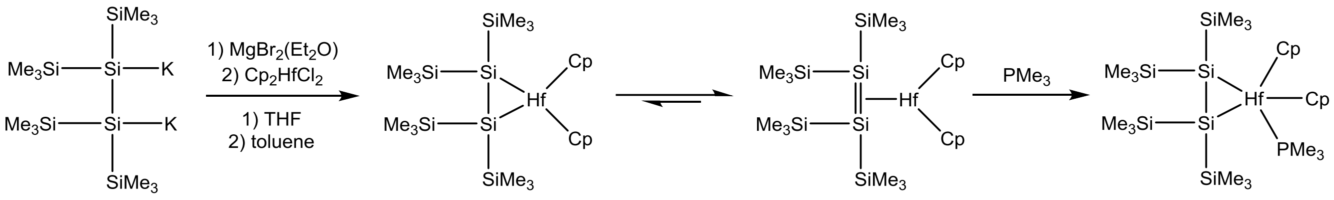
[94] M. Zirngast, U. Flörke, J. Baumgartner, C. Marschner, *Chem. Commun.*, **2009**, 5538-5540.

[95] M. Zirngast, M. Flock, J. Baumgartner, C. Marschner, *J. Am. Chem. Soc.*, **2009**, *131*, 15952-15962.

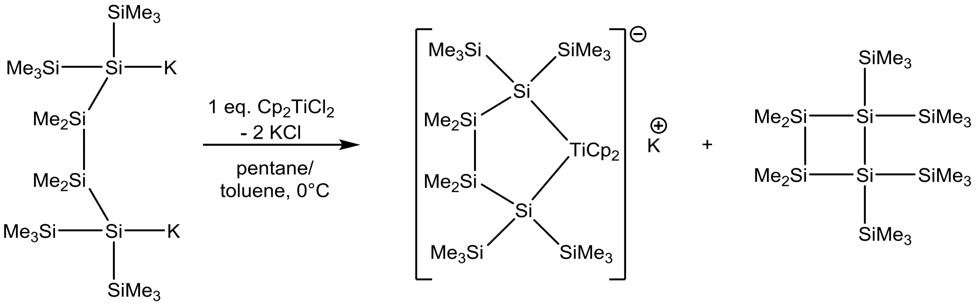
[96] H. Arp, C. Marschner, J. Baumgartner, P. Zark, T. Müller, *J. Am. Chem. Soc.*, **2012**, *134*, 10864-10875.

[97] J. Hlina, J. Baumgartner, C. Marschner, P. Zark, T. Müller, *Organometallics*, **2013**, *32*, 3300-3308.

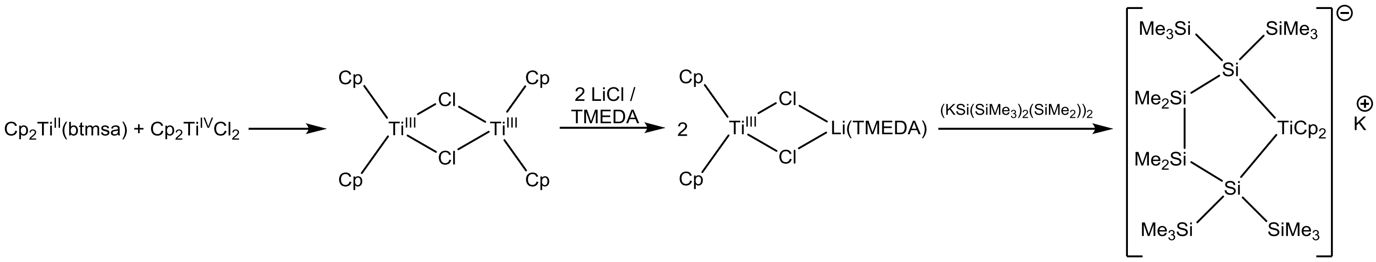
[98] U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics*, **2003,** *22,* 884-900.



Fischer et al., 2005.

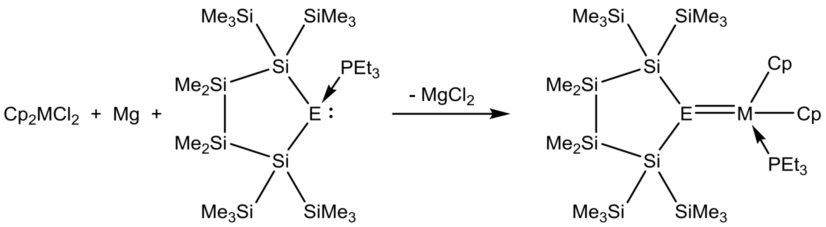


Zirngast et al., 2009.

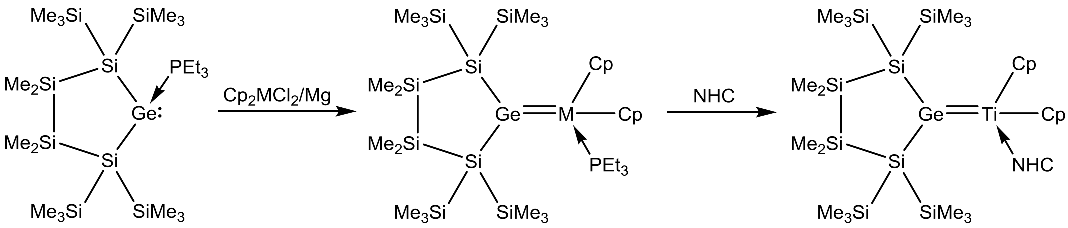


Arp et al., 2012.

Figure 1-6: Selected oligosilyl metallocene of the 4th group prepared by our group in the recent years. All these compounds were characterized by X-ray spectroscopy.



Arp et al., 2012
M = Ti, Zr, Hf ; E = Sn, Pb



Hlina et al., 2013
M = Ti, Zr, Hf

Figure 2-6: Selected coordination complexes of the 4th group metallocenes with germylenes, stannylenes, and plumbylenes, prepared by our group in the recent years. Also all these compounds were characterized by X-ray spectroscopy.

In the present work, other sources of low valent titanium and zirconium were considered. However, compounds as $Cl_2Ti(dmpe)_2$[99] or $Cl_2Ti(py)_4(THF)$[100] needed expensive ligands (dmpe = 1,2-(dimethylphosphino)ethane) or harsh condition (KC_8 as reducing agent) to be prepared, and they had the tendency to form insoluble polymers during the preparation. In addition, these complexes are unstable in respect to moisture, light and impurities. The Rosenthal reagent is a very good compromise for reactivity and stability, and the presence of the $SiMe_3$ group in the ligand allows monitoring the reactions course also by ^{29}Si NMR.

On the other hand, while metallocene dichloride underwent the transmetallation reaction with the silyl anions through chloride-silanide exchange and subsequent formation of KCl, in the case of Cp_2Ti(*btmsa*) this route was not possible. The cyclopentadienyl ligands were strongly coordinated to the metal center, and their displacement by the attack of silyl anion was not obvious. In the following chapters, the synthesis of various oligosilanyl metallocenes in the oxidation state +2 and the optimization of the reaction conditions are presented. Then, the NMR and crystal data of the desired product are discussed.

---

[99] G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett, M. B. Hursthouse , *J. Chem. Soc., Dalton Trans.*, **1985**, 1339-1348.

[100] M. A. Araya, F. A. Cotton, J. H. Matonic, C. A. Murillo, *Inorg. Chem.*, **1995**, *34*, 5424-5428.

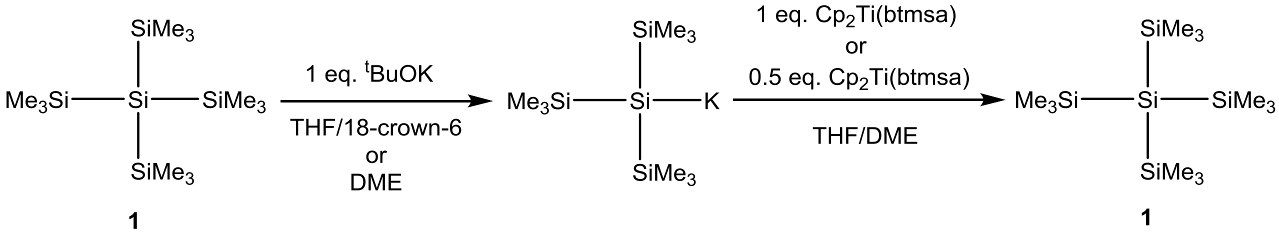
6.2 Synthesis of titanocene(II)-oligosilyl complexes

The Rosenthal reagent was prepared from titanocene dichloride in THF, in the presence of slight excess of magnesium flakes and bis(trimethylsilyl)acetylene (*btmsa*). The product was ready after overnight stirring at room temperature, and the reaction mixture was checked by ^{1}H and ^{29}Si NMR. Adding pentane caused precipitation of $MgCl_2$. Filtration and evaporation of the solvent gave the desired starting material.

The oligosilyl anions were prepared in different manners and then usually dropped into a toluene, benzene, or ethereal solution of the titanium(II) complex.

6.2.1 Reaction between Rosenthal reagent and tris(trimethylsilyl)silyl potassium

Tris(trimethylsilyl)silyl potassium anion was reacted under different conditions with the titanium(II) precursor (Scheme 2-6):



Scheme 2-6: Synthetic attempt of a tris(trimethylsilyl)silyl titanocene(II) complex.

The silyl anion was prepared in THF in the presence of 18-crown-6, to favor the crystallization of the product if it retained the potassium cation. However, the reaction with one or half equivalent of Rosenthal reagent gave only tetrakis(trimethylsilyl)silane (**1**) almost pure. The experiment was repeated with DME as solvent, but the same result was obtained. More, the ^{29}Si NMR spectrum of the reaction mixture showed that after 48 hours of stirring still some unreacted silyl anion was in solution (signals at -193.0 ppm and -4.2 ppm, Figure 3-6).

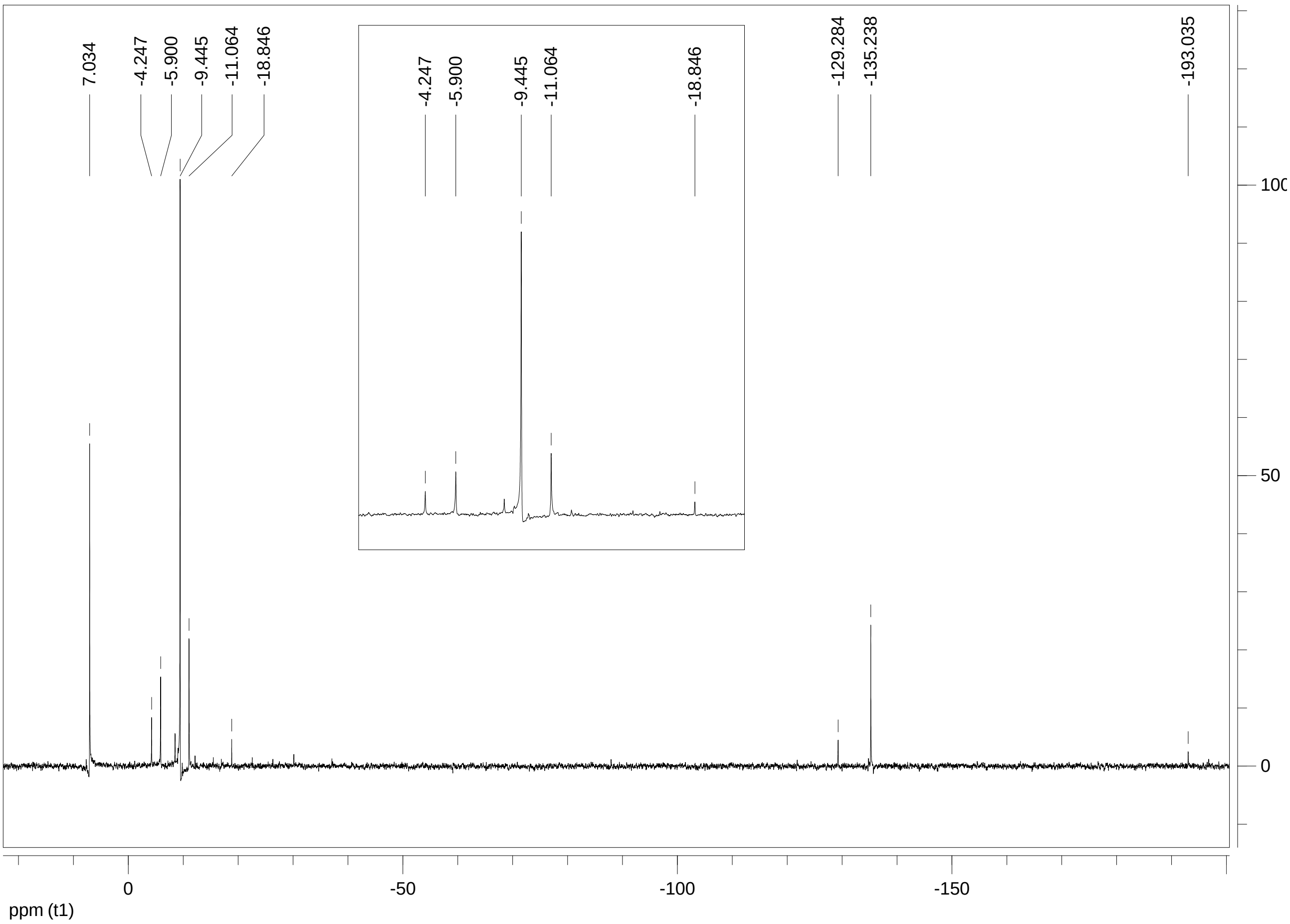
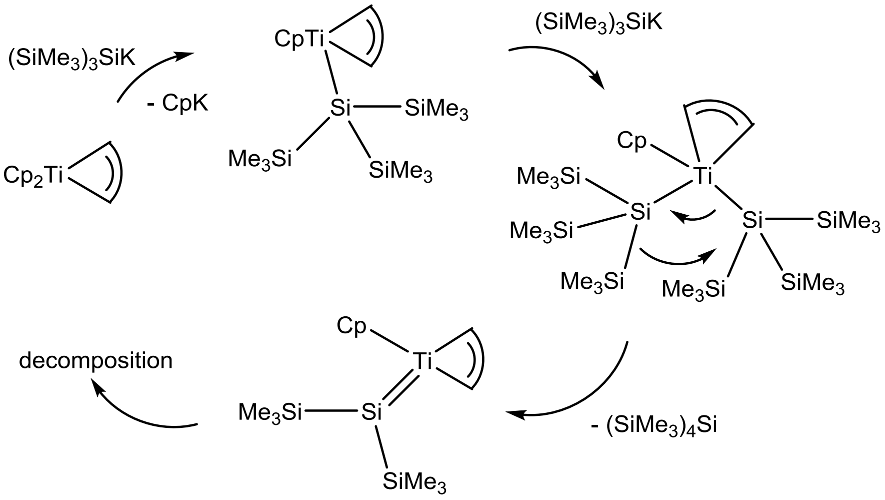


Figure 3-6: ^{29}Si NMR spectrum of the reaction mixture of silyl anion from **1** and the Rosenthal reagent.

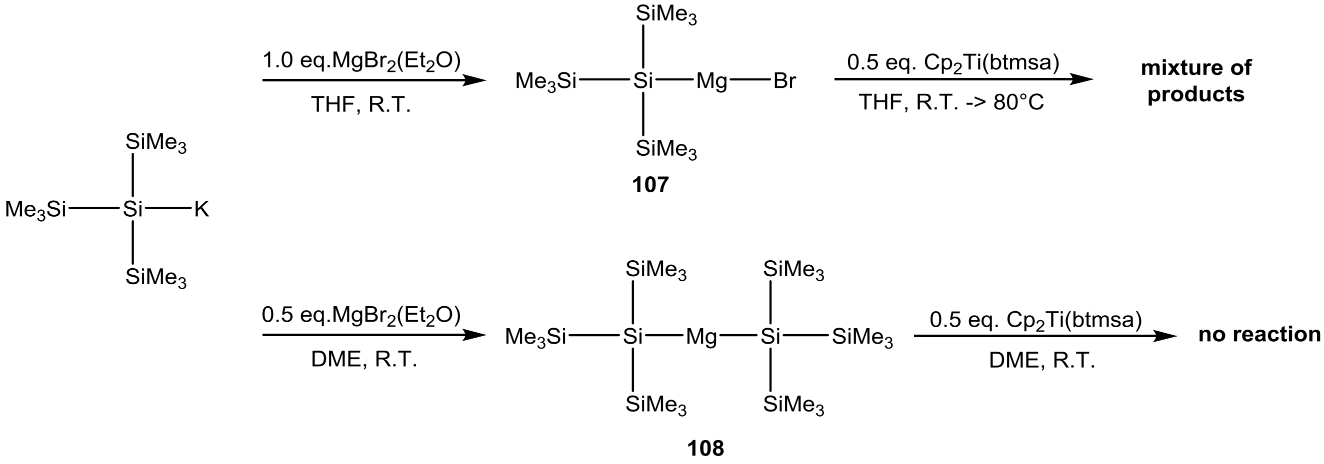
To explain this reaction's outcome, the following mechanism is proposed (Scheme 3-6):



Scheme 3-6: Supposed mechanism that led to the formation of tetrakis(trimethylsilyl)silane (**1**).

As the silyl potassium anion could be too reactive towards the Rosenthal reagent, a milder silyl ion was attempted, prepared by transmetalation with magnesium bromide etherate. This derivative is easy to obtain and was successfully used in the past in the formation of silicon-transition metal complexes.[94,101]

The hypersilyl magnesium bromide salt and the bis(hypersilyl) magnesium salt were reacted with the Rosenthal reagent, under different conditions, but also in these cases the reaction did not proceed (Scheme 4-6).



Scheme 4-6: Reactions between hypersilyl magnesium and the Rosenthal reagent.

The ^{29}Si NMR spectrum of the first reaction shown in the scheme above, it revealed that some silyl magnesium anion was still present in the solution (-170 ppm, -7 ppm), even after 48 hours at 80°C. Also in this case the formation of tetrakis(trimethylsilyl)silane (**1**) and tris(trimethylsilyl)silane was observed (Figure 4-6).

---

[101] W. Gaderbauer, M. Zirngast, J. Baumgartner, C. Marschner, T. D. Tilley, *Organometallics,* **2006**, *25*, 2599-2606.

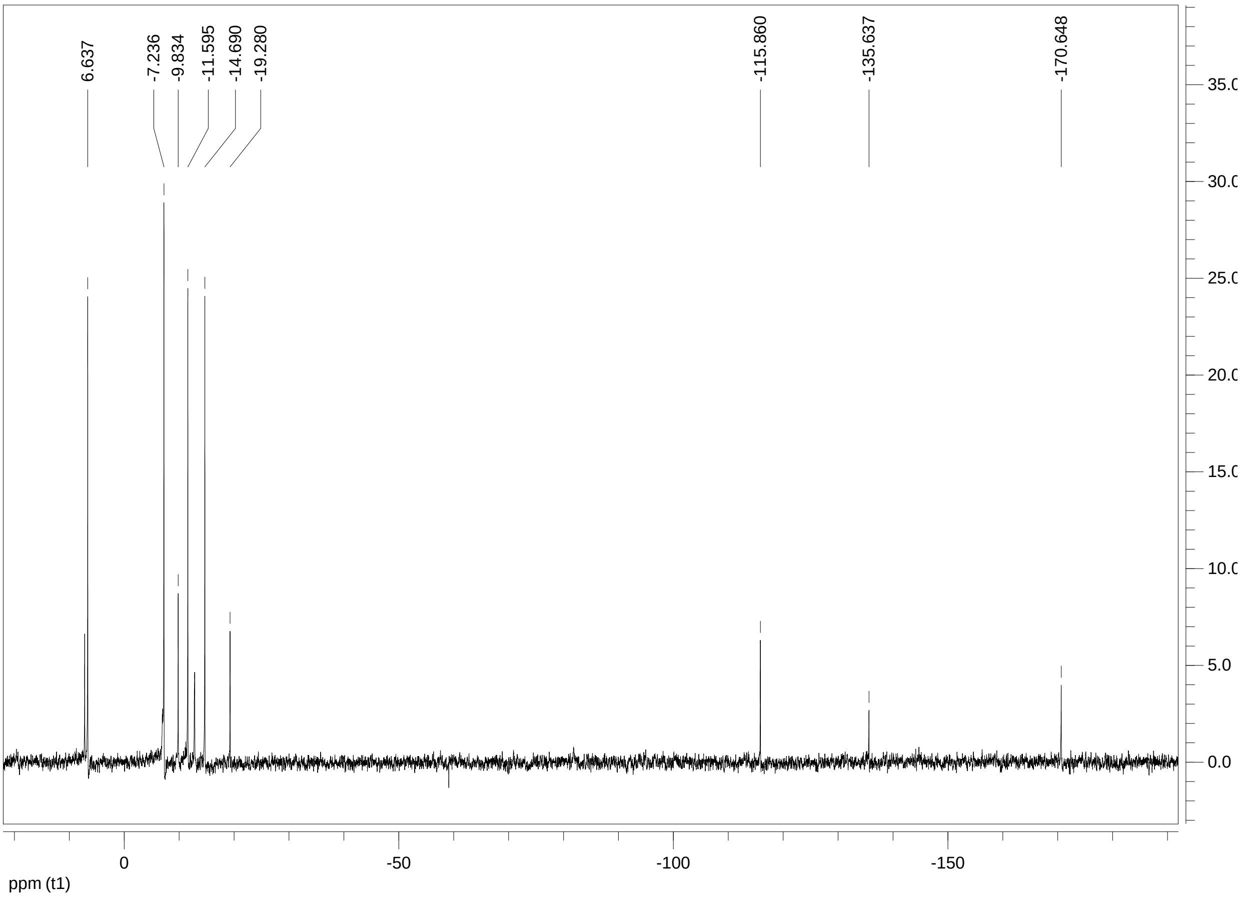
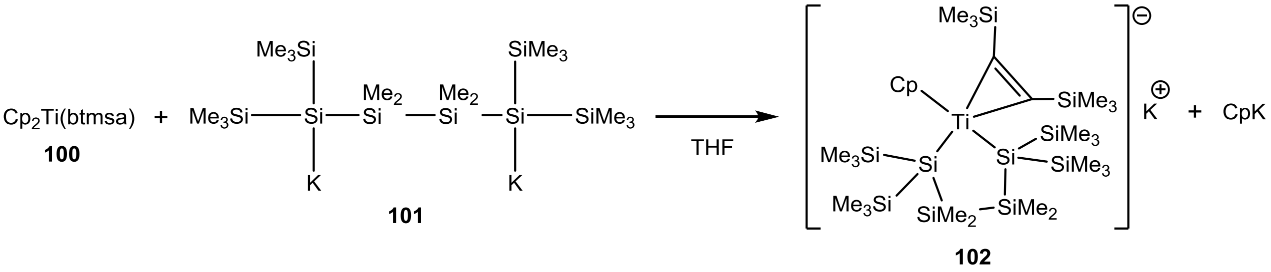


Figure 4-6: ^{29}Si NMR spectrum from the reaction between the hypersilyl magnesium salt and the Rosenthal reagent.

6.2.2. Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)pentacyclo(tetramethyl)disilyl cyclopentadienyltitanium(II) bis(trimethylsilyl)acetylene complex (102)

This oligosilyl titanium heterocycle was initially prepared following the procedure reported by Henning Arp (Scheme 5-6),[96] but without using 18-crown-6 during the synthesis of the dipotassium disilyl anion **101**. In fact, crown ether might negatively affect the crystallization process, causing disorder during crystal aggregation. Arp already obtained some crystals of compound **102**, but they were not of a satisfactory quality.



Scheme 5-6: Reaction between the Rosenthal reagent and dipotassium disilyl anion **101**.

Dianion **101** was ready after 3 days of reaction. Then it was added to a THF solution of the Rosenthal reagent and after 1 hour of reaction the mixture was worked up. In Figure 5-6, the ^{29}Si NMR spectrum of the semisolid material obtained is shown.

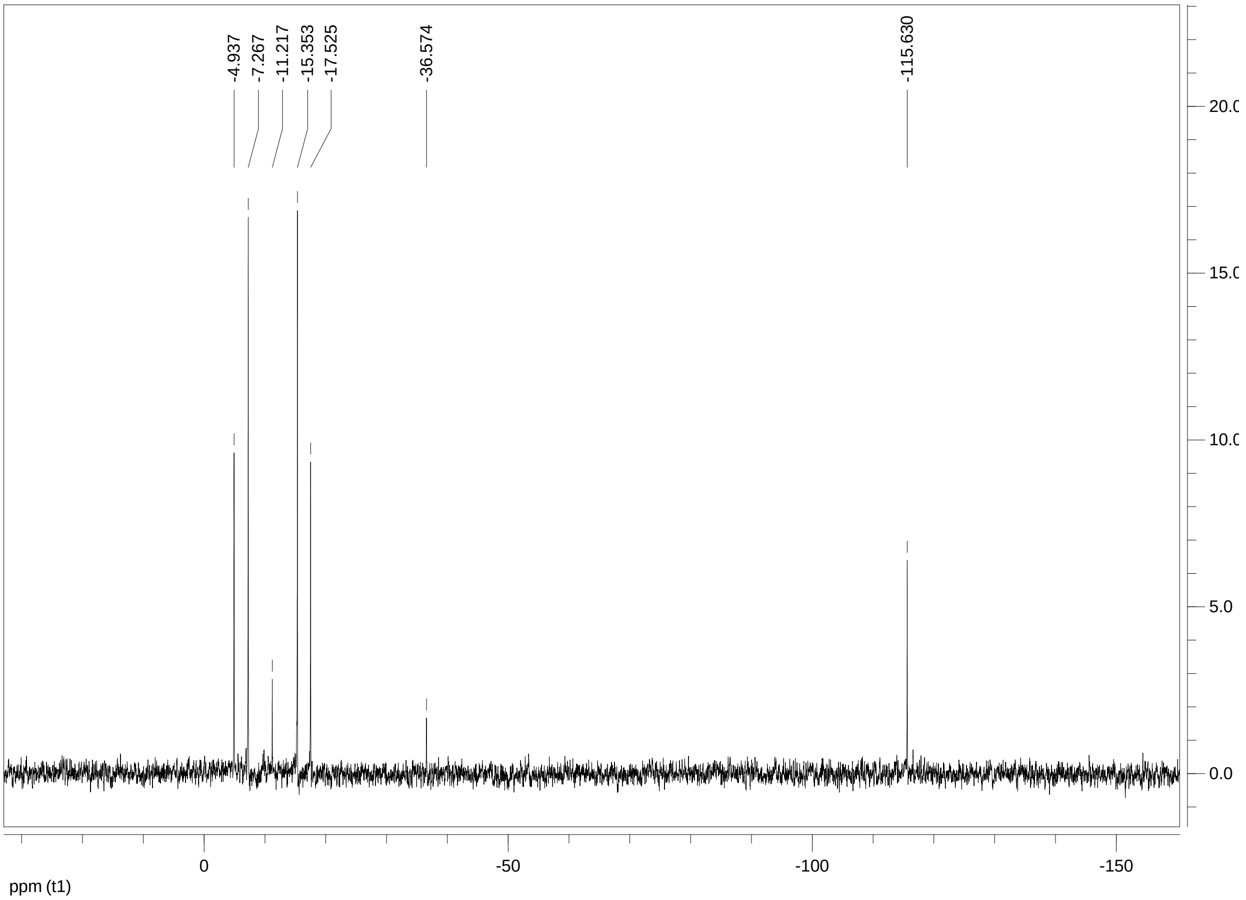


Figure 5-6: ^{29}Si NMR of product **102** after the work up.

The reaction seemed quite clean and all the signals of the expected product could be identified. The peak at -115.6 ppm was due to the quaternary silicon atoms bonded to the titanium atom (see for example Qiu et al.[102] for some comparable ^{29}Si NMR data on M*Si*Si$_3$, M=Zr, Hf, Ta). The signal at -17.5 ppm belonged to the -SiMe$_2$- groups of the formed ring. It was quite downfield-shifted in respect to the silyl dianion **101** that usually appeared at ca. -24 ppm. In similar oligosilyl heterocycles containing zirconium(IV) or hafnium(IV), -SiMe$_2$- groups gave the NMR signals at around -28 ppm.[39] At -15.3 ppm there was the signal of the -SiMe$_3$ of the *btmsa* ligand, and at -7.2 ppm and -4.9 ppm two peaks for the -SiMe$_3$ groups bonded to the ring were detected thus indicated that the structure in solution was not symmetric along the plane of the ring.

---

[102] H. Qiu, H. Cai, J. B. Woods, Z. Wu, T. Chen, X. Yu, Z. Xue, *Organometallics*, **2005**, *24*, 4190–4197.

For comparison, the ^{1}H NMR spectrum of compound **102** (Figure 6-6) and the one reported by Arp in his dissertation (Figure 7-6) are shown.[13]

In the proton spectrum two signals from the Cp groups were visible (one from the Ti-Cp fragment at 6.4 ppm, one from the KCp, 5.8 ppm). Some residual THF seemed to be involved in the formation of the complex (3.4 ppm and 1.4 ppm, broad signals instead of the classical multiplets). Two peaks between 0.4 and 0.6 ppm for the trimethylsilyl groups were present, as in Arp´s spectrum, and the integration fitted quite well. Unfortunately, some residual pentane did not let alow to observe the signal of *btmsa* (also some THF was retained in the forming semisolid mass, that never really reached a crystalline state).

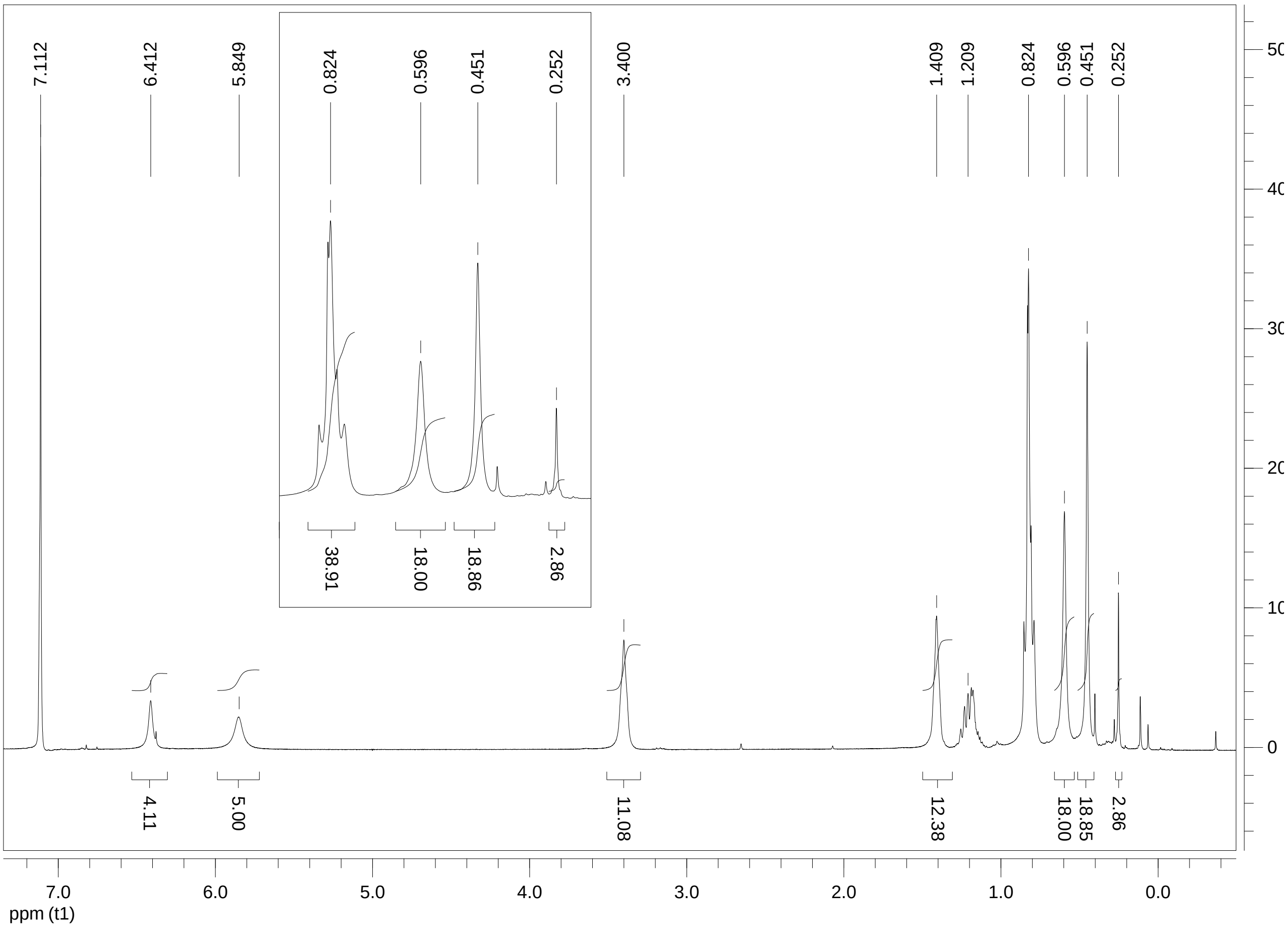


Figure 6-6: ^{1}H NMR of the product **102** after the work up in C_6D_6 (still some residue of pentane).

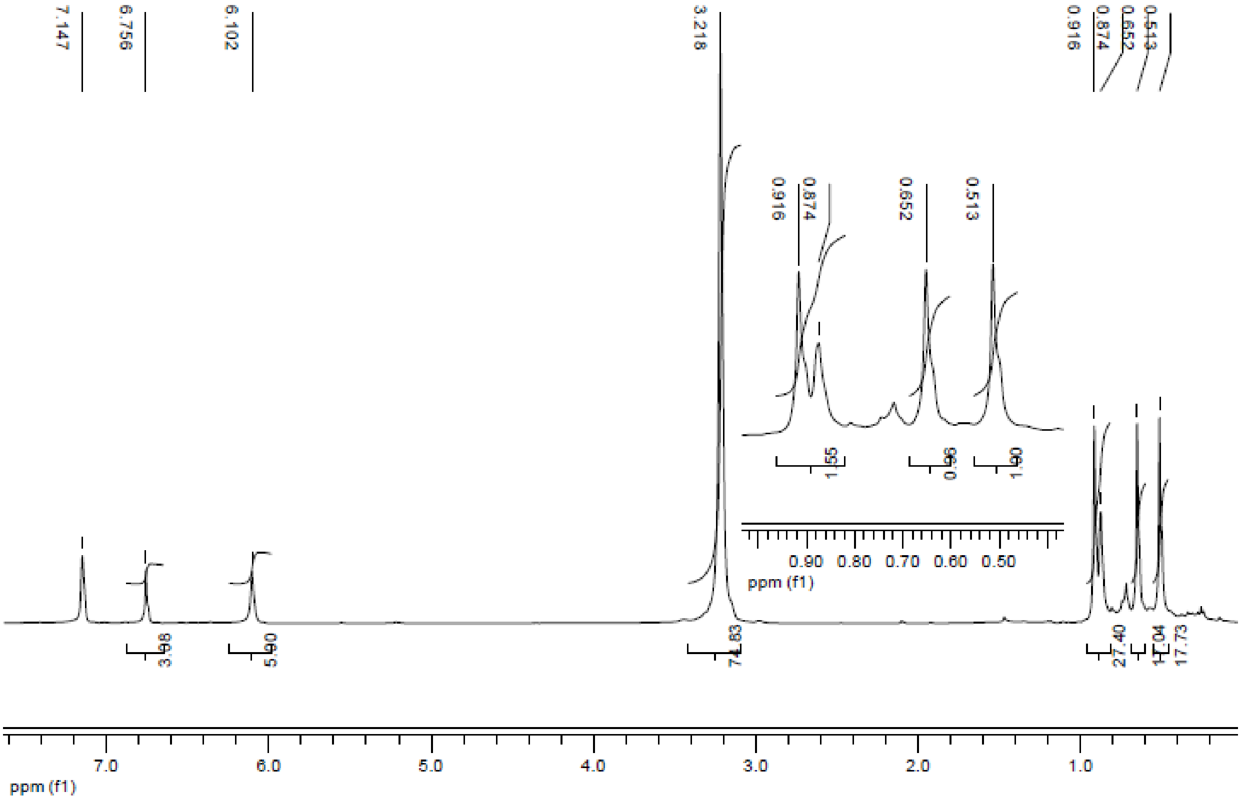


Figure 7-6: ^{1}H NMR reported in Arp´s dissertation for complex **102**.[13]

After storing a pentane/toluene solution of compound **102** at low temperature, it was possible to recover some semi-crystalline material for X-ray analysis. However, the quality of the structure was not better than that one found by Arp,[13] and even if it could be considered another proof for the formation of the desired product, it could not be used for a discussion of the structural parameters (Figure 9-6). Nevertheless, this structure confirmed the ^{29}Si NMR spectrum interpretation, as two different types of –SiMe$_3$ could be found, depending on the position in respect to the Cp group. More, one cyclopentadienyl group effectively left the complex forming CpK (that was also crystallized from the reaction mixture).

A better ^{1}H NMR spectrum was acquired when the disilyl dianion **101** was prepared in DME (see the following chapters) – Figure 8-6. The spectrum shows again two signals for the protons of the trimethylsilyl groups, two very close signals for the dimethylsilyl groups and one signal for the trimethysilyl groups of *btmsa*.

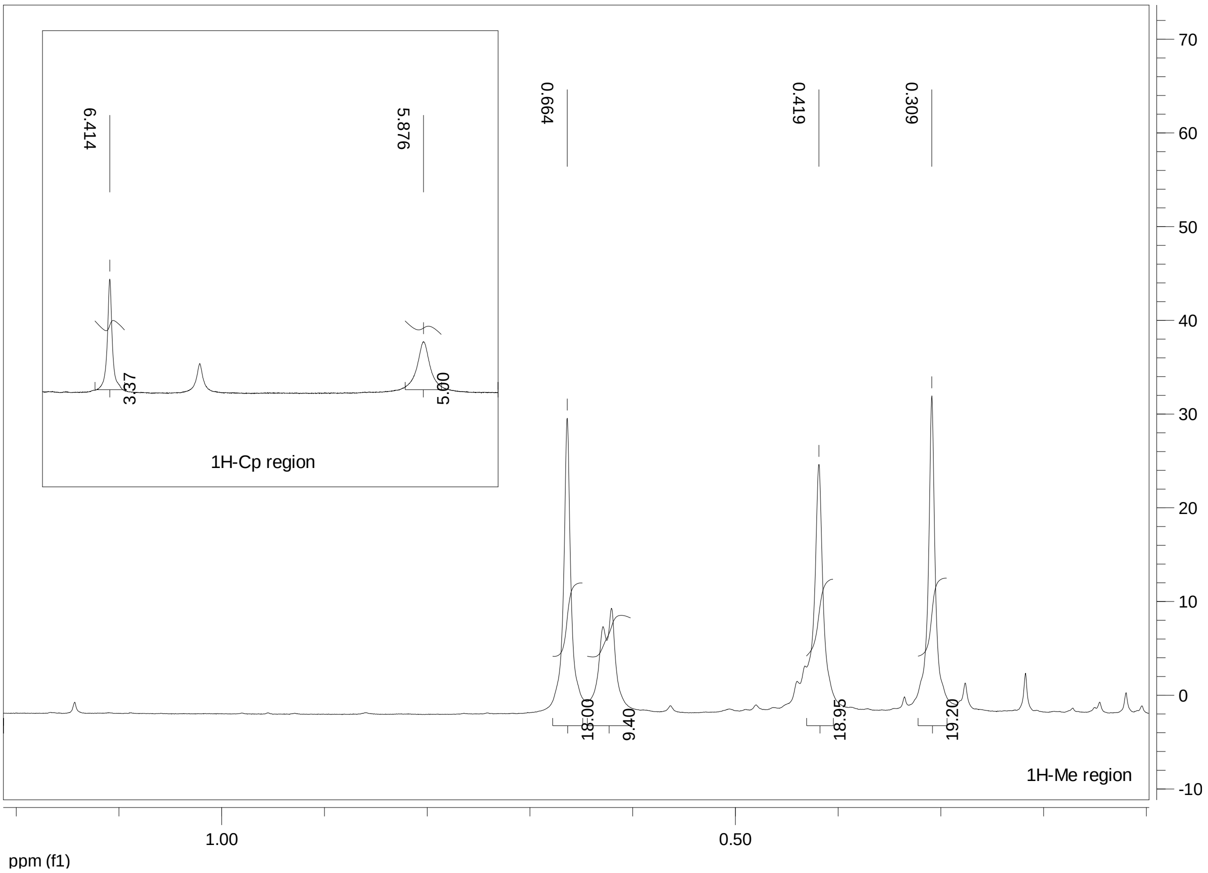


Figure 8-6: ^{1}H NMR of the product **102** in DME/toluene.

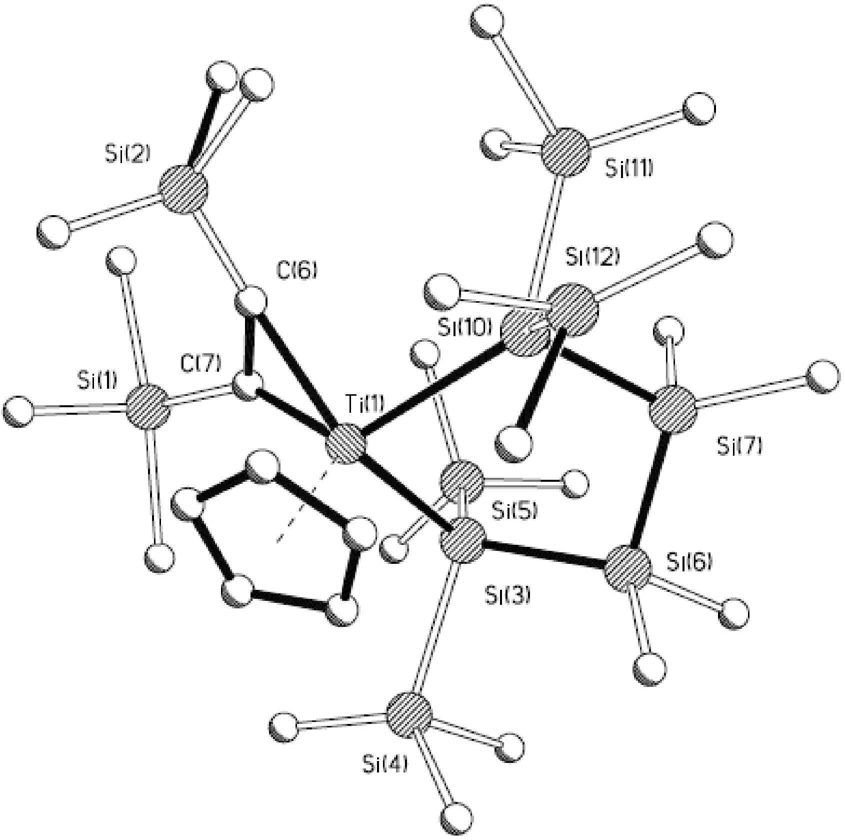
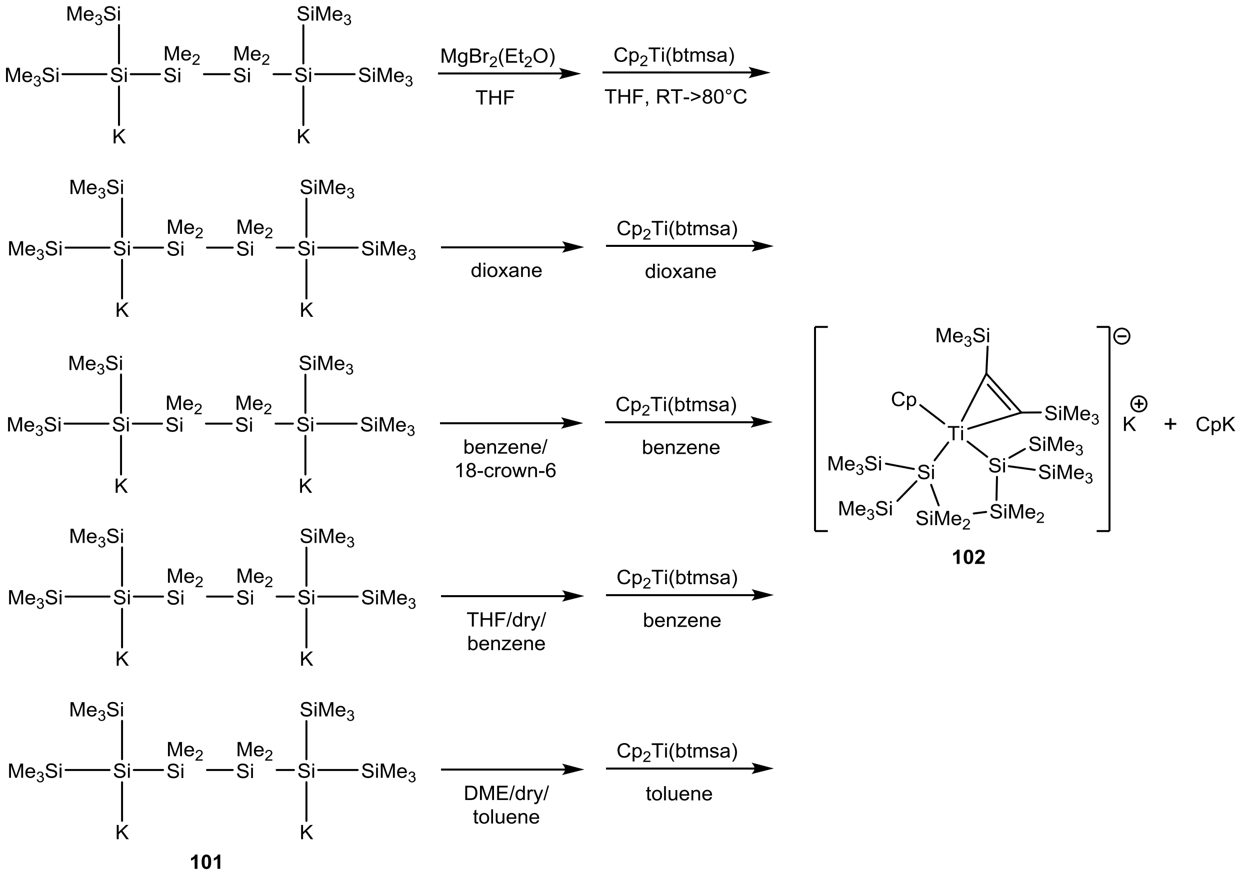


Figure 9-6: Low quality crystal structure of **102** reported by Arp in his dissertation.[13]

A number of experiments were pursued to optimize the reaction conditions (in terms of purity and yield) and most of all to have the right environment in solution that could favor good crystal precipitation. These series of reactions are summarized in Scheme 6-6:



Scheme 6-6: Reactions between the Rosenthal reagent and dipotassium disilyl anion **101**. The first arrow refers to the conditions under which the disilyl dianions were prepared.

While the transmetalation through $MgBr_2$ did not lead to a clean outcome, the subsequent experiments gave almost the same results as for the reaction presented in Scheme 5-6. The preparation of dianion **101** in benzene/crown-ether and the following reaction with the titanocene in benzene gave a quite clear ^{29}Si NMR spectrum, with the same groups of signals but with an interesting difference in the chemical shift of the quaternary silicon atoms (Figure 9-6).

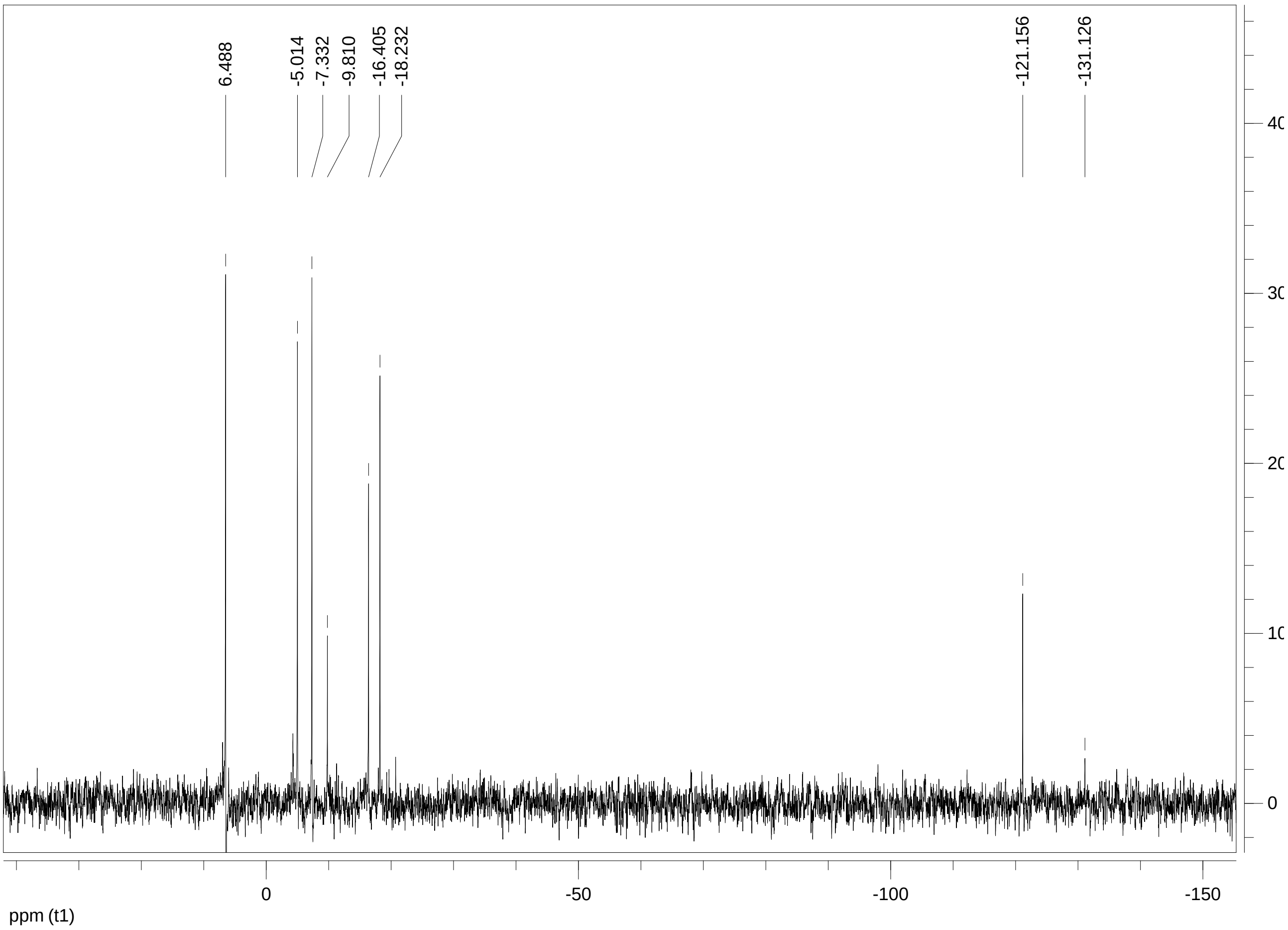


Figure 9-6: ^{29}Si NMR spectrum of the reaction between the Rosenthal reagent and disilyl dianion **101**, in benzene and in the precence of 18-crown-6.

A small amount of hexakis(trimethylsilyl)disilane was formed (signals at -131.1 ppm and -9.8 ppm). The peaks of the -SiMe$_3$ groups and of the -SiMe$_2$- groups had almost the same chemical shifts as the compound prepared in THF (see Figure 5-6). On the other hand, in this case the signal for the quaternary silicon atoms bonded to the titanium atom was 5 ppm high-field shifted. This phenomenon could reflect the electronic situation at the metal center: perhaps in the absence of a coordinating solvent as THF, the titanium atom could share more electron density with the silicon atom, and then the silicon resulted more shielded in the NMR analysis.

Nevertheless, the cleanest reactions were obtained under the last conditions shown in Scheme 6-6: the disilyl dianion **101** was prepared in THF or DME, and then the ethereal solvents were completely removed. The residue was dissolved in benzene or toluene and added to a benzene or toluene solution of the Rosenthal reagent. The ^{29}Si NMR of compound **102** derived from dianion **101** prepared in THF is here presented (Figure 10-6).

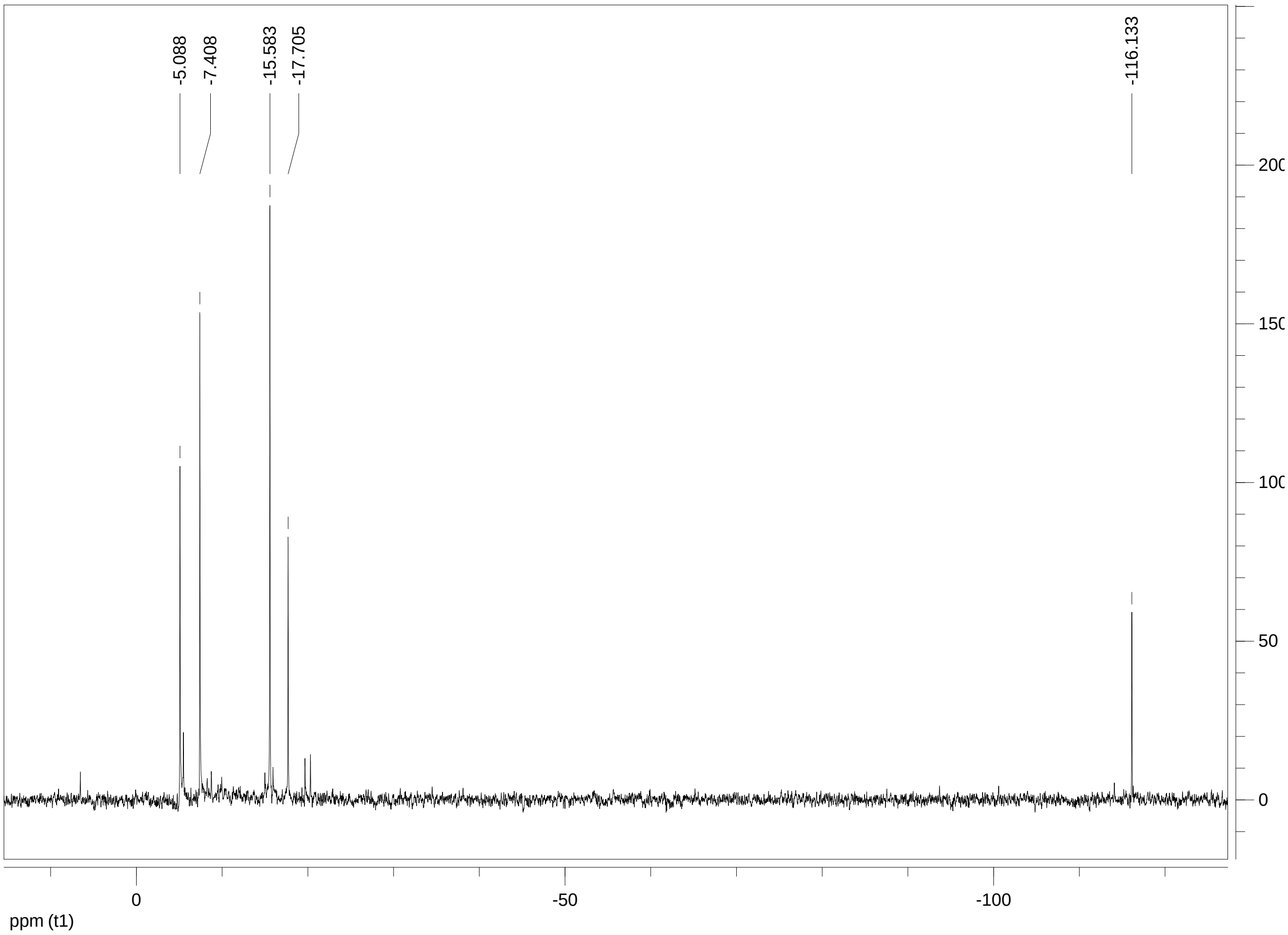


Figure 10-6: ^{29}Si NMR of the reaction between the Rosenthal reagent and the disilyl dianion **101** prepared in THF, dried and dissolved in benzene.

All the chemical shifts were in the same range (± 1 ppm) in respect to the product synthesized completely in THF. In fact, it was not possible to eliminate completely the ethereal solvent from the dianion **101** as it is strongly coordinated to the potassium cations.

For comparison, also the ^{29}Si NMR of the outcome of the reaction between the Rosenthal reagent and the disilyl dianion prepared in DME is here shown (Figure 11-6).

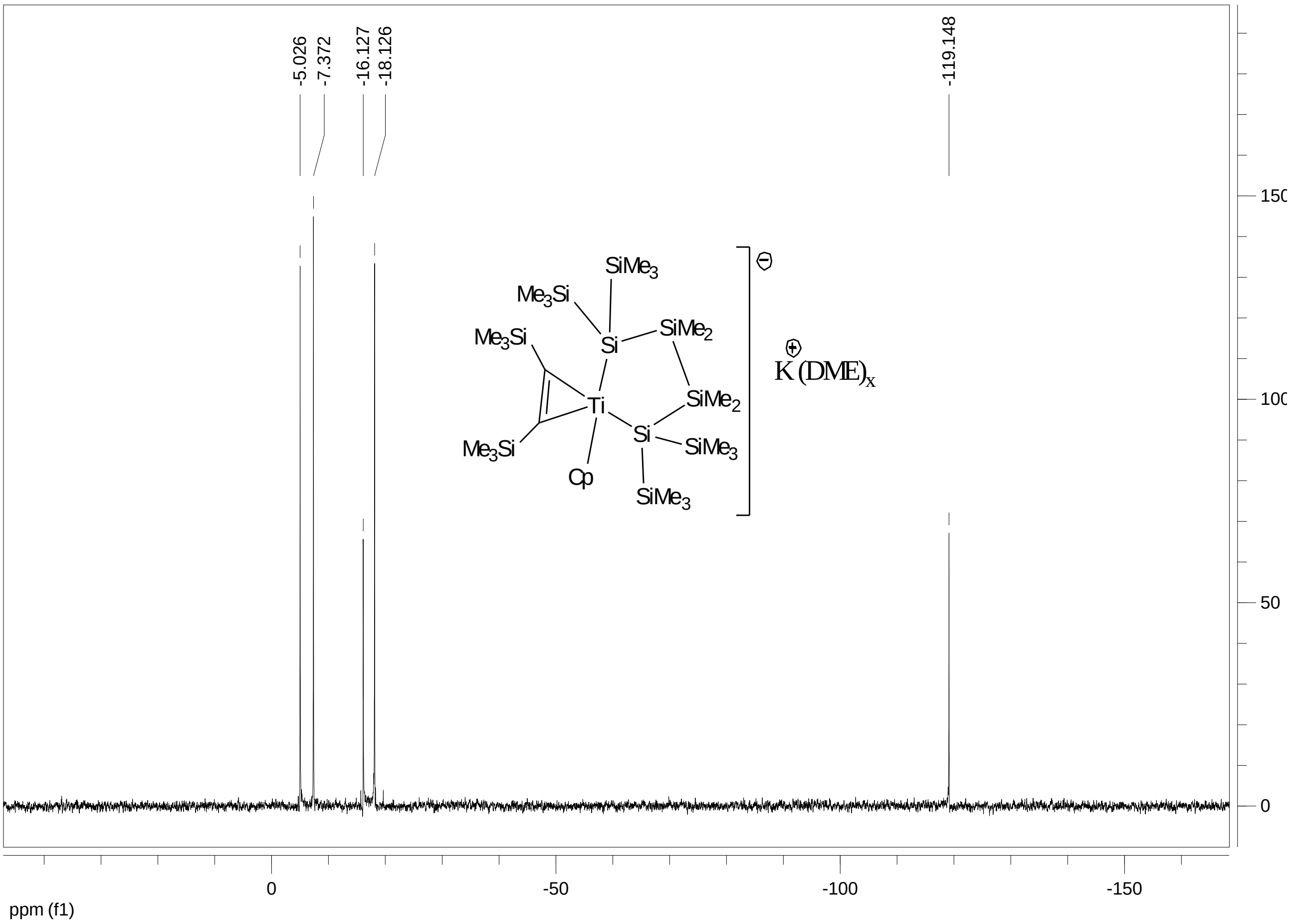


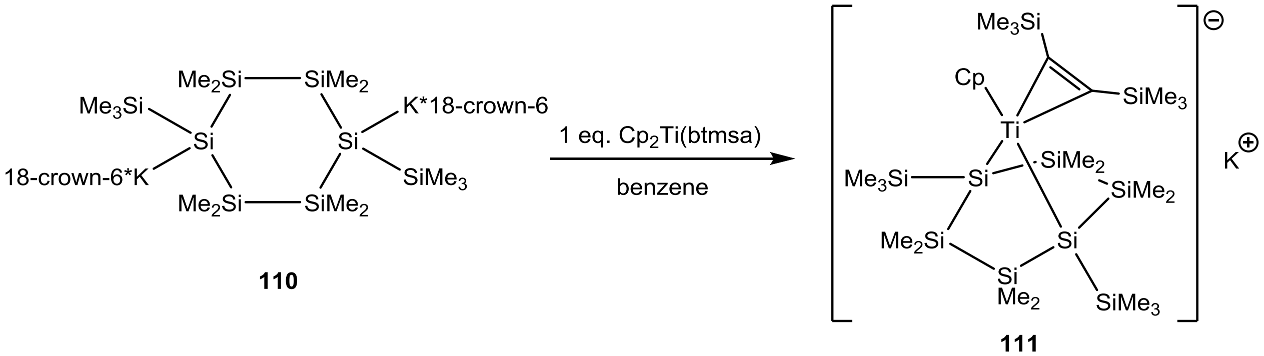
Figure 11-6: ^{29}Si NMR of the reaction between the Rosenthal reagent and the disilyl dianion **101** prepared in DME, dried and dissolved in benzene.

The reaction was very clean and a beautiful ^{29}Si NMR spectrum was already obtained from the mixture before the work up. The peaks for the -SiMe$_3$ groups and the -SiMe$_2$- were detected in the usual range, while the quaternary silicon atoms revealed a high-field shift of about 3 ppm in respect to the product obtained in the benzene/THF system.

Also the ^{1}H NMR was quite clean and well solved with consistent values for the peaks integration. Despite the absence of impurities and by-products all attempts to crystallize this product failed. Slow evaporation of the solvent, double vial crystallization (toluene/pentane) and storage of the solution at low temperature, all these methods only led to a semi-solid deliquescent black mass.

6.2.3. Reactions between the Rosenthal reagent and 1,4-bis(trimethylsilyl)-2,2,3,3,5,5,6,6-octamethylcyclohexasilyl dipotassium (110)

With the idea to have a more rigid structure that could favor the crystallization of the complex, the Rosenthal reagent was reacted with a disilyl potassium dianion prepared from 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (Scheme 7-6):



111

Scheme 7-6: Reaction between the Rosenthal reagent and a hexacyclodisilyl dipotassium anion **110**.

The reaction proceeded rather smoothly and a good ^{29}Si NMR was acquired (Figure 12-6). The silicon atom bonded to the metallic center was detected at -101.8 ppm. There are no similar known oligosilyl bicyclic complexes to compare to this value. The chemical shift was remarkably down-field shifted probably because of the ring strain. The signals of the dimethylsilyl groups appeared at -23.3 ppm and -27.6 ppm, indicating that the product might possess an asymmetric structure. There was some free *btmsa* (-19.6 ppm) and a peak of the acetylene ligand bonded to the titanium atom (-17.6 ppm). Finally, only one signal for the two -SiMe$_3$ at -5.6 ppm was assigned. No sign of unreacted disilyl dianion was found (no signals between -180 and -200 ppm).

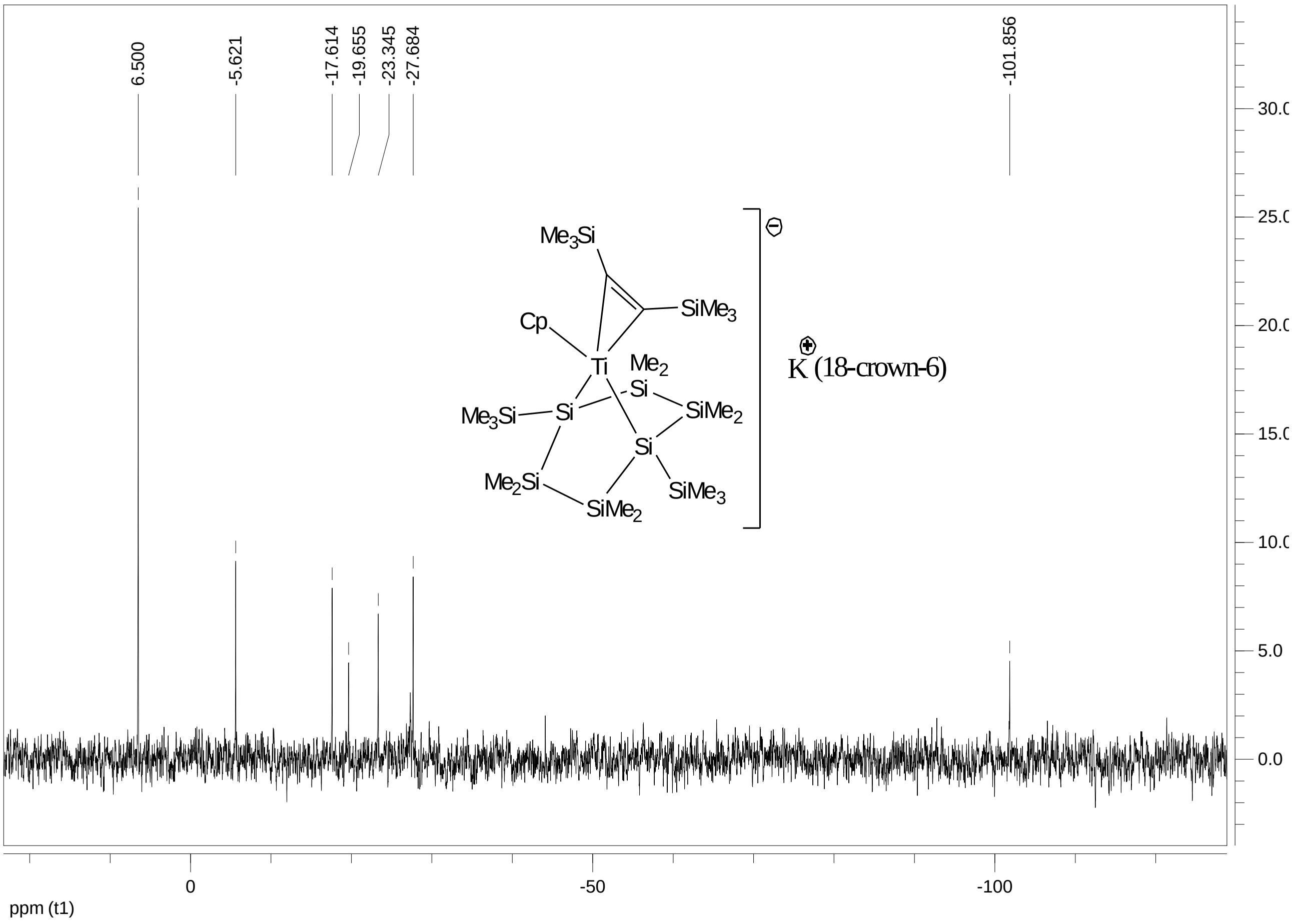


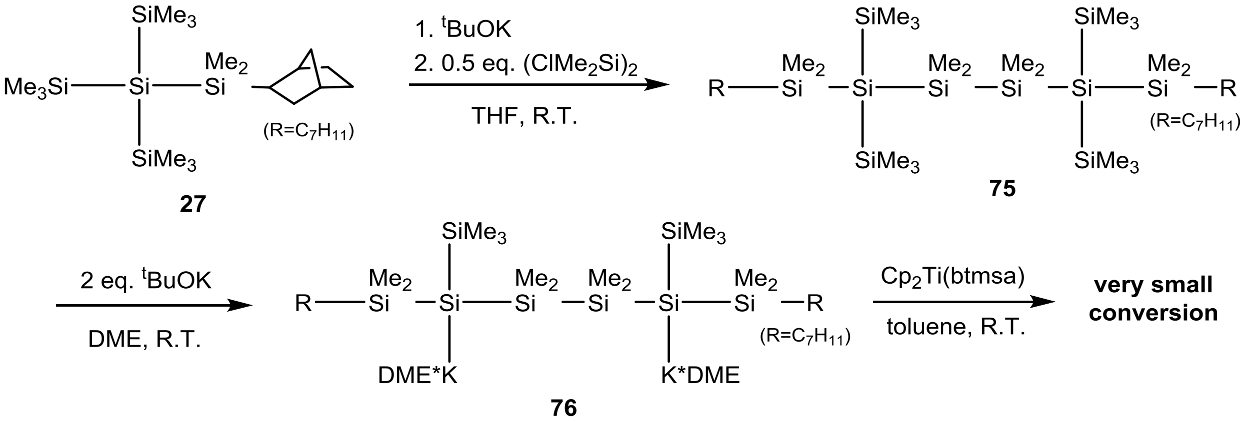
Figure 12-6: ^{29}Si NMR of the reaction mixture of compound **111** after ca. 12 hours.

After adding few milliliters of pentane, decanting the insoluble material, removing and drying the solution, a small fraction of the solid product was dissolved in benzene in a NMR tube (0.5 mL) and layered with ca. 2-3 mL of pentane. The remaining material was dissolved in a 50÷50 pentane/toluene mixture and stored at -67°C. After some days, very small transparent crystals appeared in the NMR tube, but the crystallographic analysis revealed that it was the cyclopentadienyl potassium salt.

No crystal formed at low temperature. The solvent was slowly evaporated and very small but brilliant dark red particles were recovered. It was possible to identify this compound by crystallographic analysis as that one reported in the NMR spectrum above. However, the structure was not well solved, due to the poor quality of the crystals.

6.2.4. Reactions between the Rosenthal reagent and 1,4-bis(trimethylsilyl)-1,4-bis(dimethylnorbornylsilyl)-2,2,3,3-tetramethyldisilyl dipotassium (76)

In order to improve crystallization chances of the oligosilyl titanium complex, compound **70** was functionalized with two norbornyl groups and then treated with two equivalents of *t*-BuOK. The disilyl dianion thus prepared was then reacted with the Rosenthal reagent (Scheme 8-6).



Scheme 8-6: Reaction between the Rosenthal reagent and oligosilyl dianion **76** functionalized with two norbornyl groups.

The bulky norbornyl groups should also confer to the forming complex a greater solubility in nonpolar solvent (like pentane), from which it might be possible to crystallize the final product at low temperature. The disilyl dianion **76** was formed with a clean reaction (see ^{29}Si NMR in Figure 13-6).

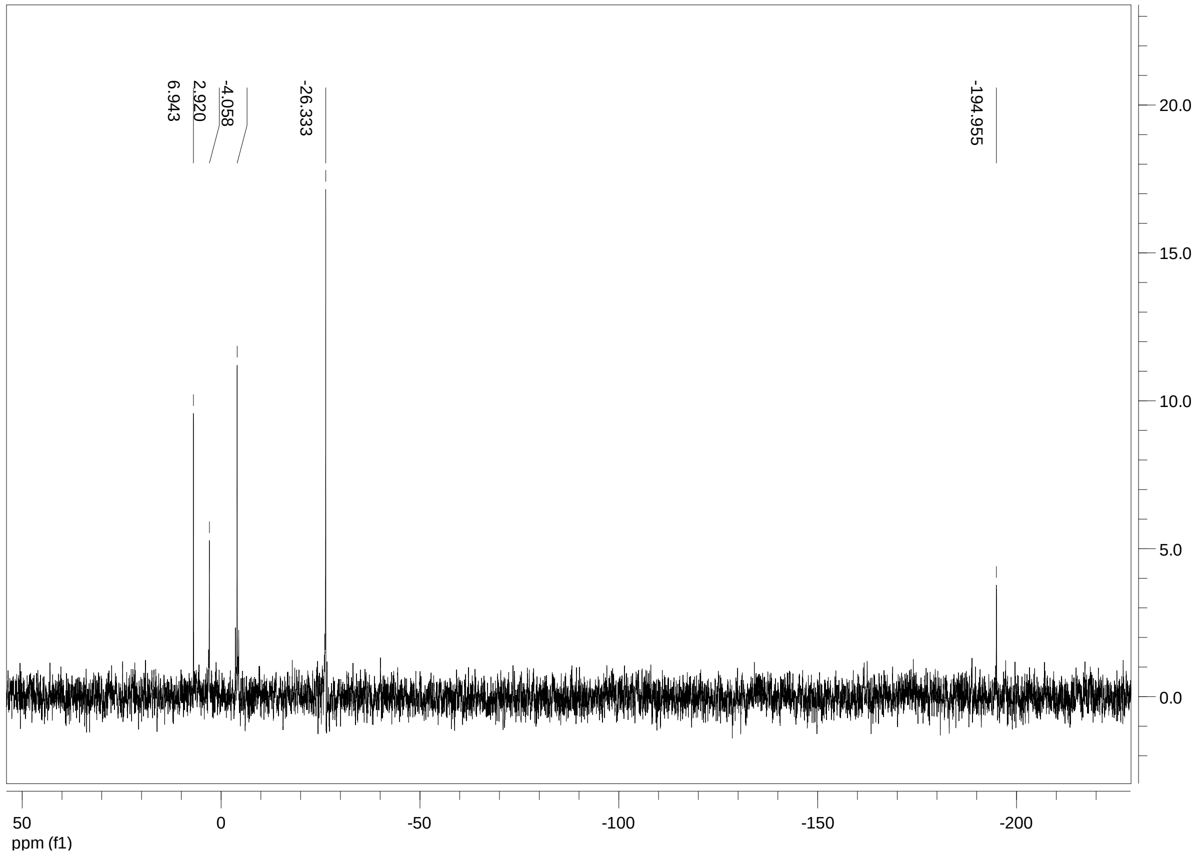


Figure 13-6: ^{29}Si NMR of the disilyl dianion **76** in DME.

The DME solution of **76** was dried, the residue was dissolved in toluene and this solution was slowly dropped into a toluene solution of the Rosenthal reagent. However, in this case the reaction needed 48 hours to have complete consumption of the disilyl dianion **76**. The ^{29}Si NMR spectrum acquired after this time was not as clean as the previous ones, it was quite noisy and the peaks of the forming titanium complex could not be assigned with certainity (Figure 14-6).

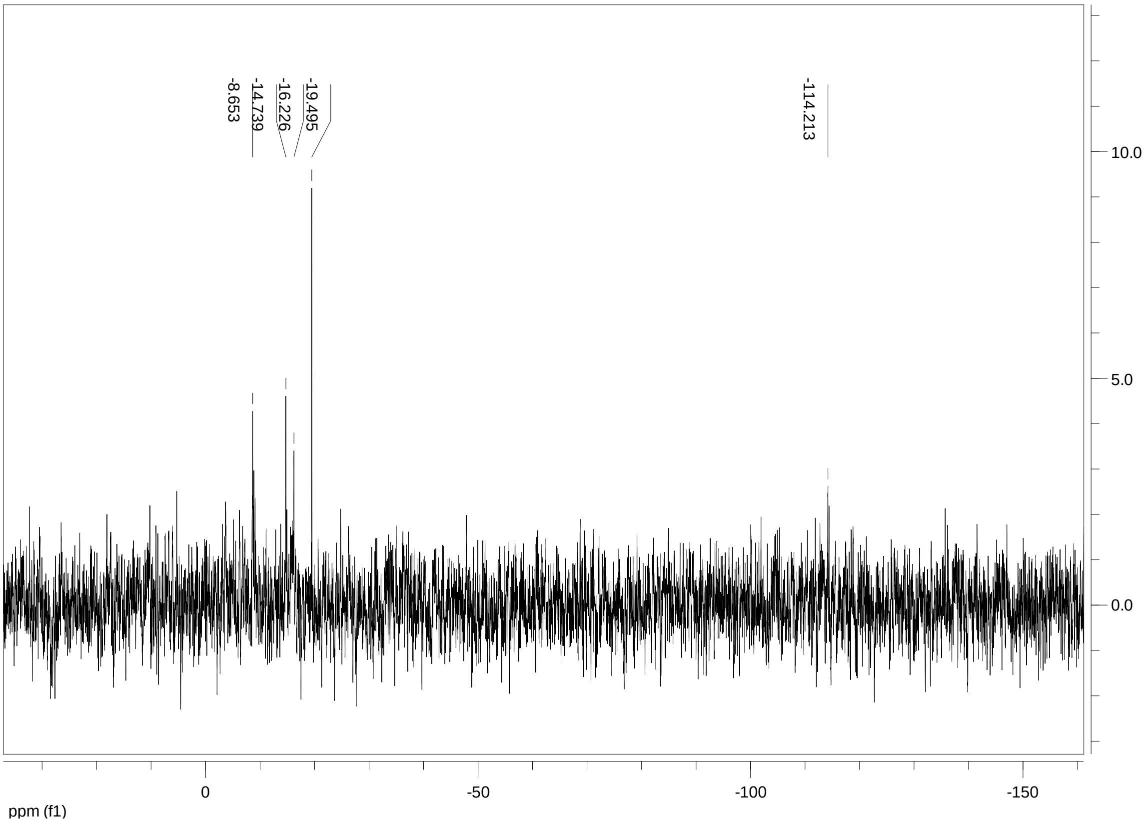


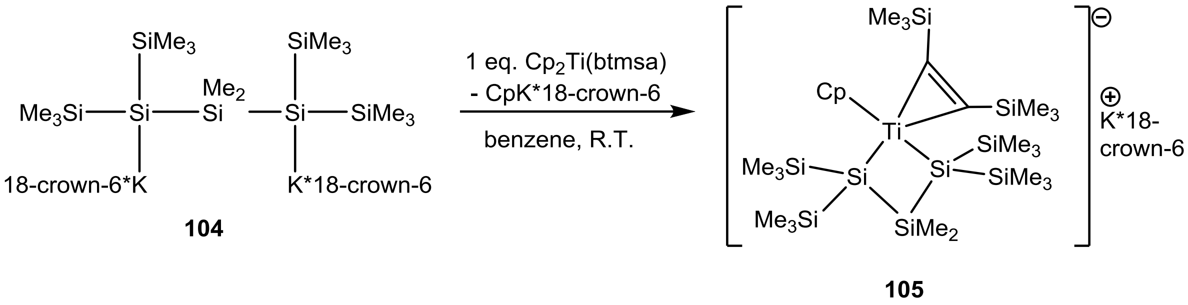
Figure 14-6: ^{29}Si NMR of the reaction mixture of disilyl anion **76** after adding the Rosenthal reagent (in toluene, after 48 hours).

Probably the steric hindrance of the oligosilyl dianion did not favor the attack of the silanide to the titanium atom.

By extraction of the solid with pentane, a clear red solution was obtained, but after evaporation of the solvent only few drops of a reddish oil remained in the vial. The residue from the first extraction was dissolved in a small amount of toluene and stored at -67°C, but no crystals precipitated.

6.2.5. Reactions between Rosenthal reagent and 1,3-dipotassium-1,1,3,3 – tetrakis(trimethylsilyl)-2,2-dimethyltrisilane (104).

To verify if smaller oligosilyl dianions could give more crystallization chance, compound **104** was prepared from hexakis(trimethylsilyl)-2,2-dimethyltrisilane (**71**) in toluene in the presence of 18-crown-6 and then it was reacted with Rosenthal reagent in toluene (Scheme 9-6).



Scheme 9-6: Reaction between Rosenthal reagent and 1,3-dipotassium oligosilyl anion **104** in benzene/18-crown-6.

After six hours of stirring at room temperature, the dianion was completely consumed. The ^{29}Si NMR spectrum of the reaction mixture was acquired (Figure 15-6), and it could be considered as fairly clean, with the main signals assignable to the expected product **105**. Peaks at -123.0 ppm (*Si*Si_4), -18.4 ppm (*btmsa*), -4.5 ppm and -5.9 ppm (Si*Si*Me_3) seemed consistent with the respective signals of compound **102** and they were in their common detection range. But the peak of the -$SiMe_2$- group was surprisingly high-field shifted at ca. -60 ppm, about -40 ppm out of the usual value for this type of silicon fragment. In the case of complex **102**, the dimethylsilyl groups were found at ca. -16 ppm, ca. 10 ppm low-field shifted in respect to the standard value. In similar structures, as in 1,1,3,3-tetrakis(trimethylsilyl)tetramethylcyclotetrasilane[103] or 1,1-dicyclopentadienyl-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)-1-zirconacyclotetrasilane,[104] the -$SiMe_2$- groups were not affected by the high ring strain and their ^{29}NMR signals were detected in the usual range of -20 to -25 ppm.

---

[103] A. Wallner, J. Hlina, T. Konopa, H. Wagner, J. Baumgartner, C. Marschner, U. Flörke, *Organometallics*, **2010**, *29*, 2660-2675.

[104] R. Fischer, D. Frank, W. Gaderbauer, C. Kayser, C. Mechtler, J. Baumgartner, C. Marschner, *Organometallics*, **2003**, *22*, 3723-3731.

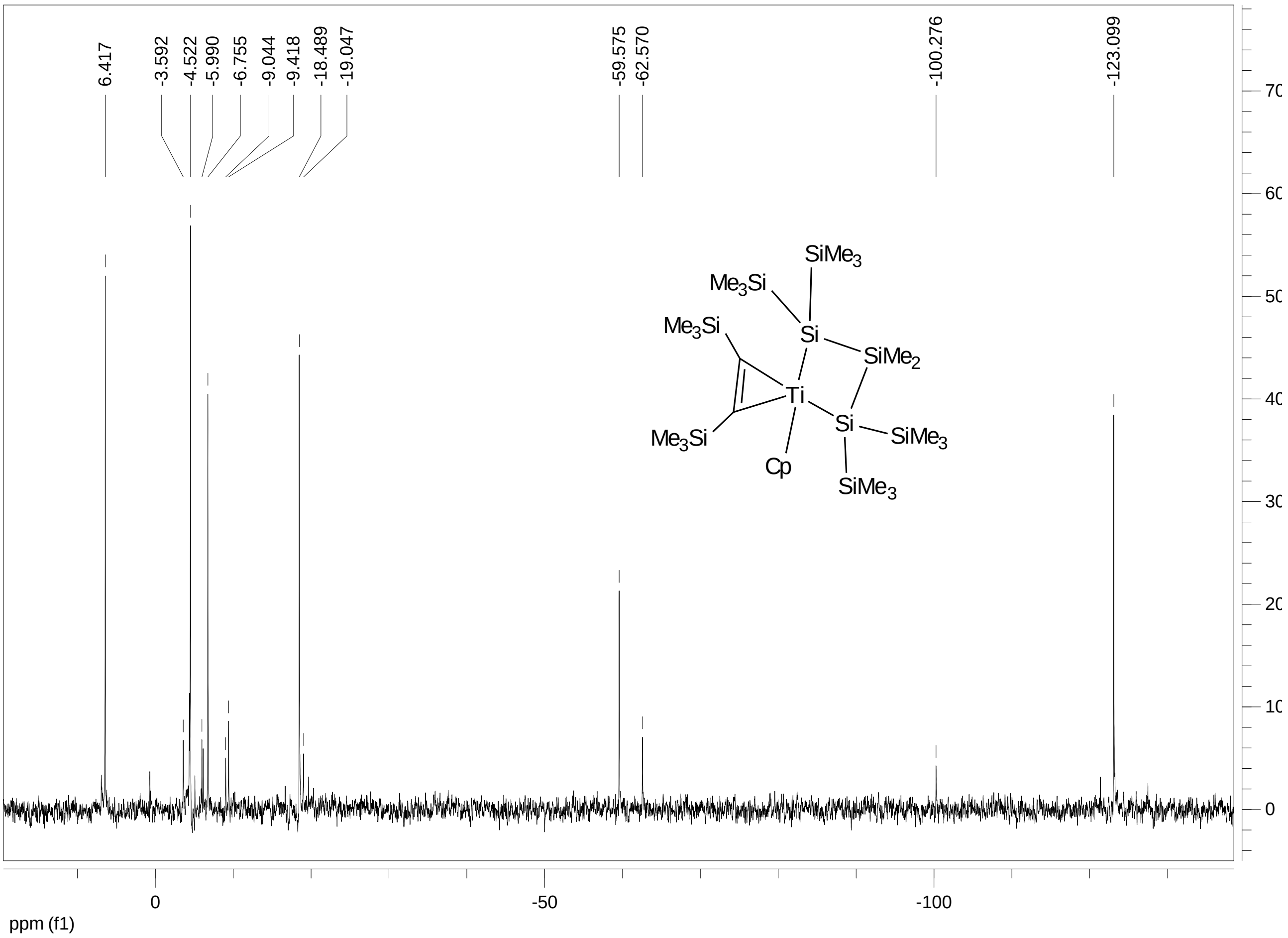
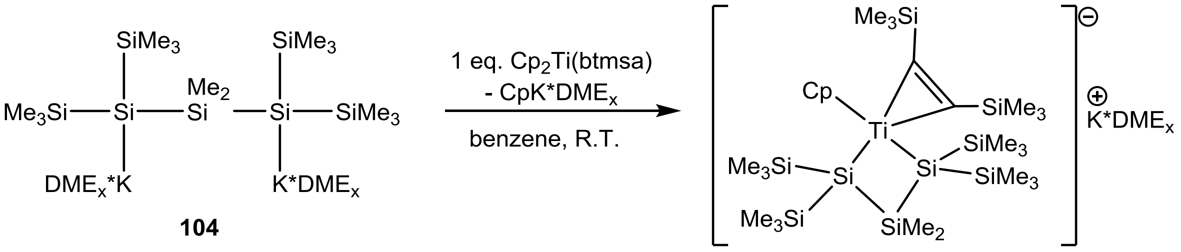


Figure 15-6: ^{29}Si NMR of the reaction mixture of disilyl anion **104** (prepared in toluene/crown ether) with the Rosenthal reagent.

The solution was dried and the remaining oily product was dissolved in a small amount of toluene and stored at -67°C, but no crystal precipitation occurred.

6.2.6. Reactions between Rosenthal reagent and 1,3-dipotassium-1,1,3,3-tetrakis(trimethylsilyl)-2,2-dimethyltrisilane (104), in DME/toluene

The previous experiment was repeated preparing the silyl dianion **104** in DME; then this solvent was dried and the potassium salt was dissolved in benzene. This mixture was slowly dropped into a benzene solution of the Rosenthal reagent (Scheme 10-6).



104

105

Scheme 10-6: Reaction between the Rosenthal reagent and 1,3-dipotassium oligosilyl anion **104** in toluene/DME.

The reaction ran 6 hours at room temperature and then the ^{29}NMR silicon spectrum was acquired (Figure 16-6). In respect to the previous experiment, a cleaner reaction mixture was obtained, containing almost exclusively the expected product **105**. The NMR data were also confirmed, only the quaternary silicon atom was detected at -120.9 ppm with a light down-field shift of 3 ppm, probably due to the solvent effect.

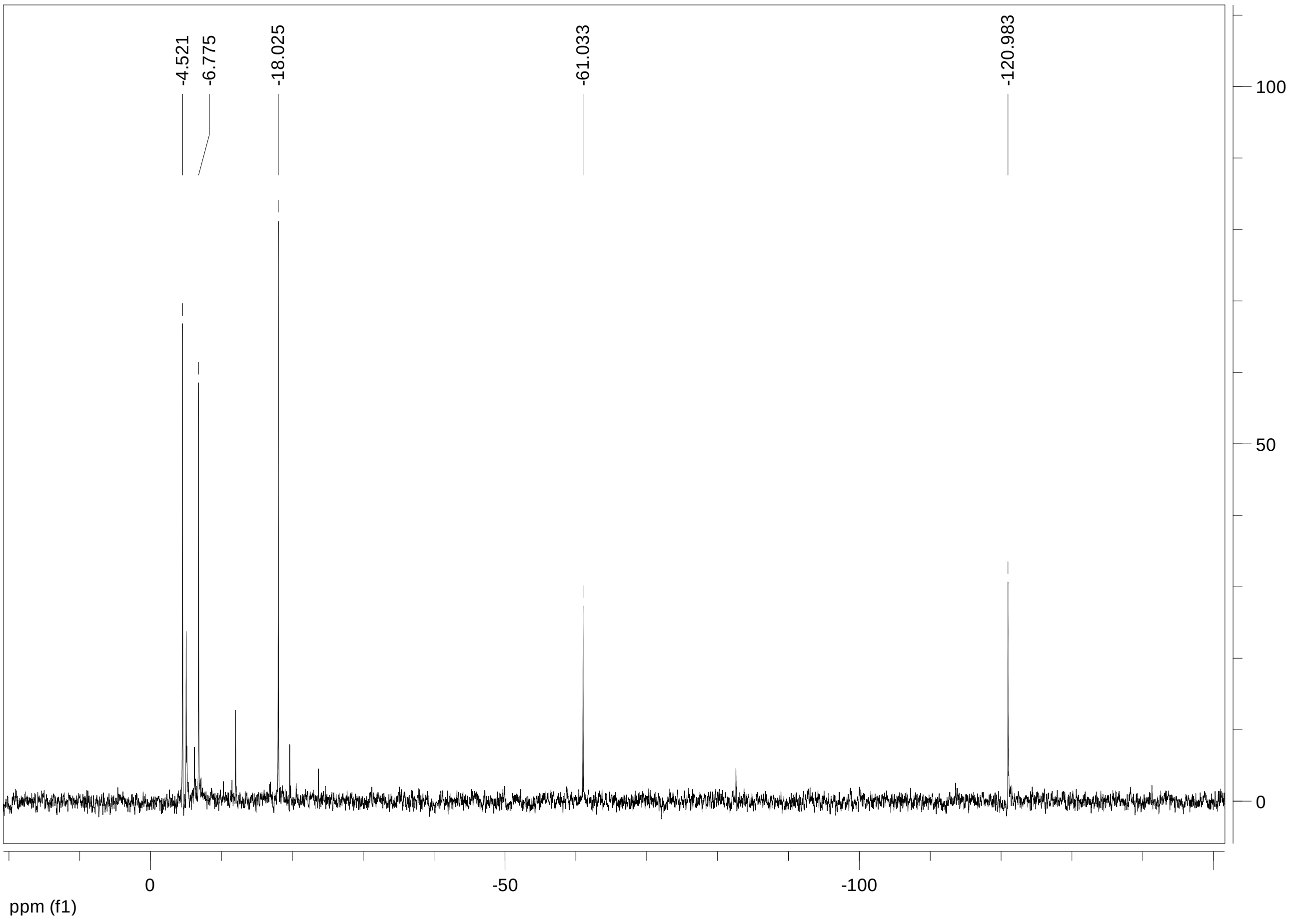


Figure 16-6: ^{29}Si NMR spectrum of the reaction of disilyl anion **104** (prepared in toluene/DME) with the Rosenthal reagent.

Finally, during this experiment it was possible to obtained fairly good crystals for X-ray spectroscopy, from a pentane/toluene solution of the compound stored for several weeks at -67°C (Figure 17-6 and 18-6).

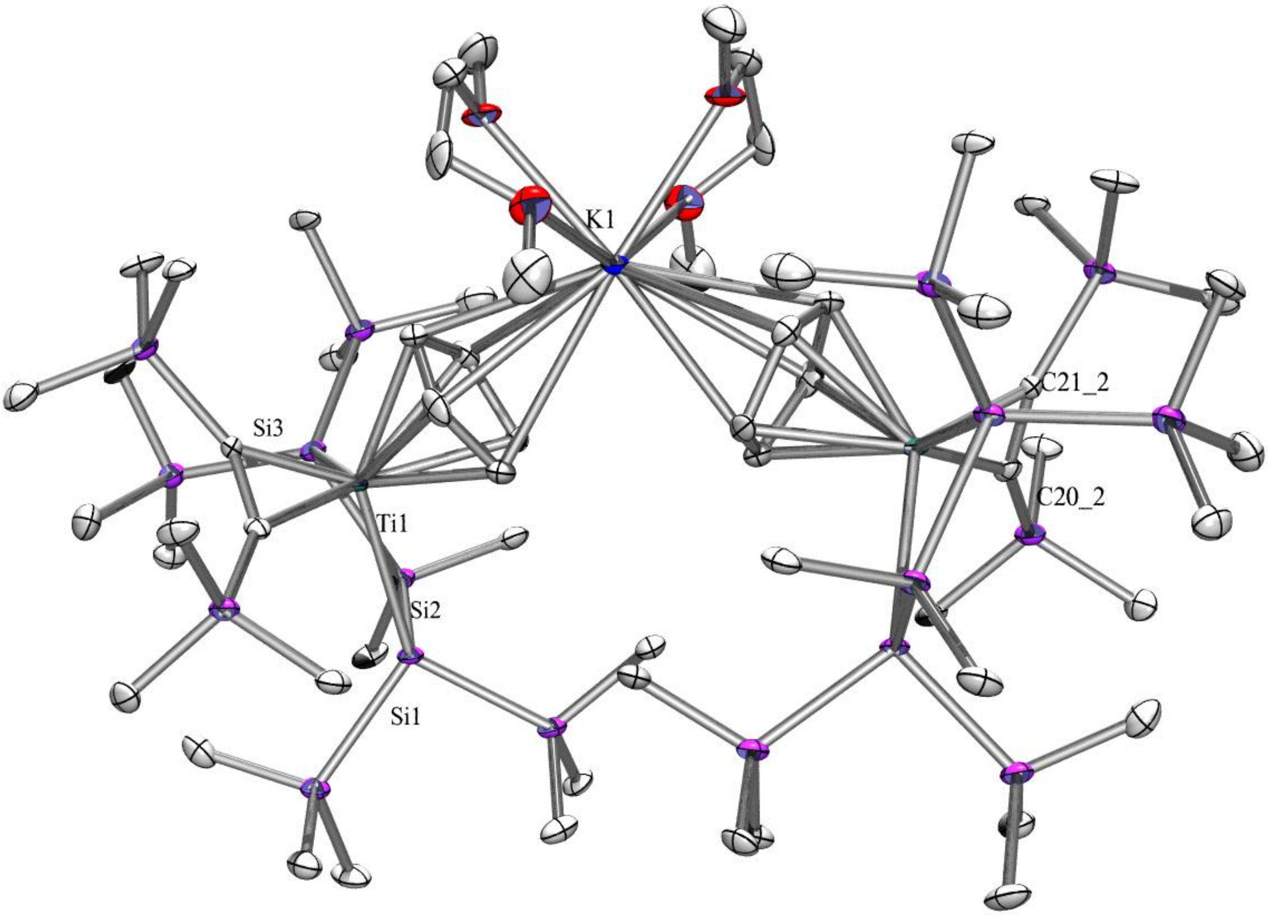
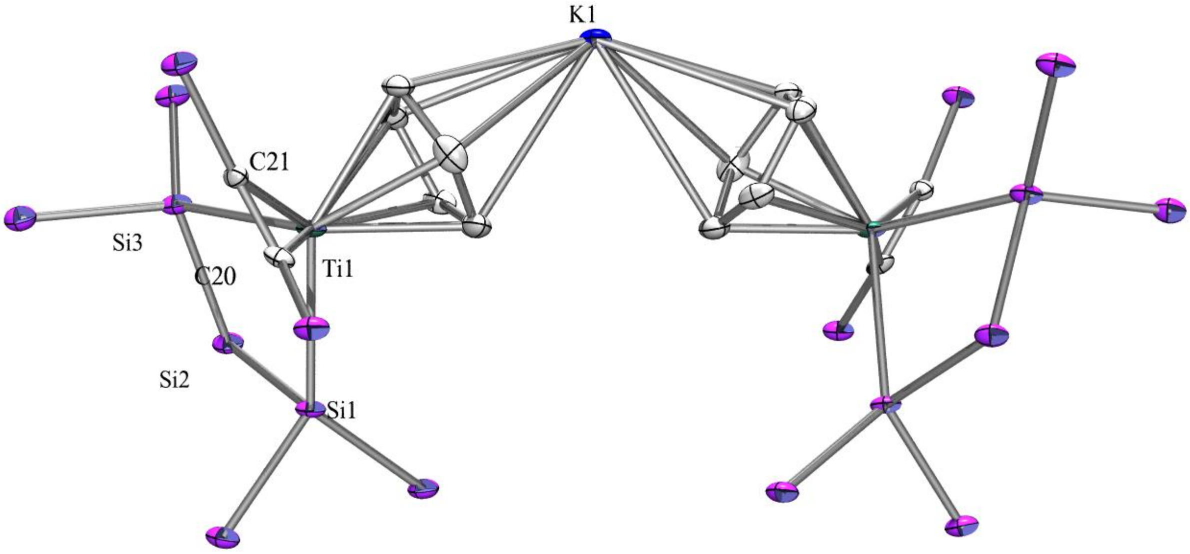


Figure 17-6: Crystal structure of compound **105**, hydrogen atoms omitted.

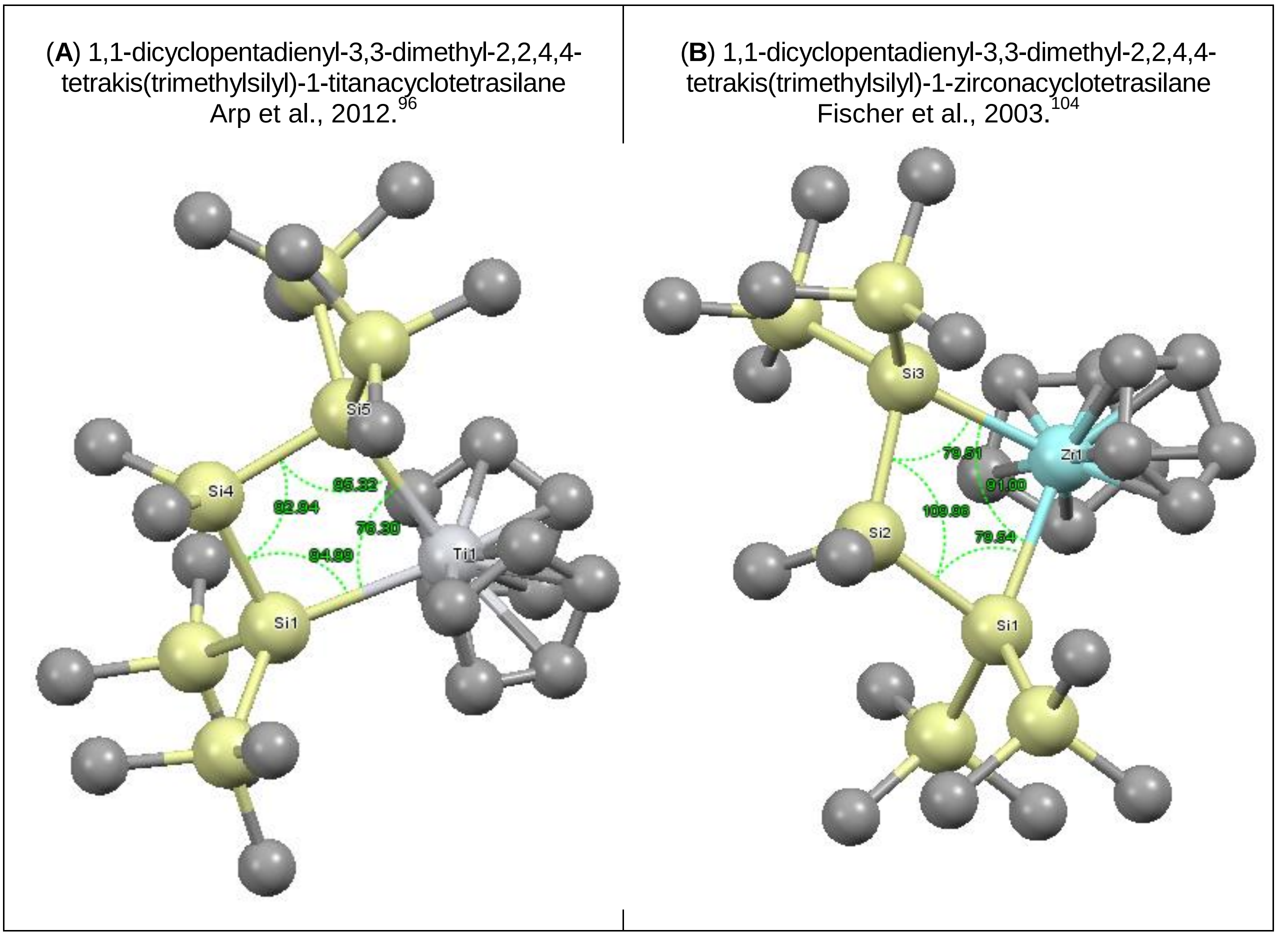


Selected crystallographic data: Crystal system: monoclinic; Space group: C2/c; Goodness-of-fit on F^2: 0.800; Bond lengths [Å]: Ti(1)-Si(1) 2.723(2); Ti(1)-Si(3) 2.722(2); Ti(1)-C(21) 2.019(6); Ti(1)-C(20) 2.046 (6); Si(1)-Si(2) 2.365(3); Si(2)-Si(3) 2.364(2); Angles [deg]: C(21)-Ti(1)-C(20) 37.4(2); Si(3)-Ti(1)-Si(1) 83.51(6); Si(3)-Si(2)-Si(1) 100.15(9); Si(2)-Si(1)-Ti(1) 85.41(7); Si(2)-Si(3)-Ti(1) 85.44(7)

Figure 18-6: Crystal structure of compound **105**, hydrogen and carbon atoms (of the heterocycle) omitted.

The structure confirmed that a cyclopentadienyl group was driven out by the incoming disilanide, with the consequent formation of CpK. The second potassium cation coordinated two Cp groups of two molecules of the complex and a dimer was formed. In addition, two molecules of solvent (DME) were retained by the potassium.

Also the presence of two different signals for the -SiMe$_3$ groups in the ^{29}Si NMR spectrum could be now justified, as four trimethylsilyl fragments were orientated towards the core of the dimer, and the other four were directed outside.



(**A**) 1,1-dicyclopentadienyl-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)-1-titanacyclotetrasilane
Arp et al., 2012.[96]

(**B**) 1,1-dicyclopentadienyl-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)-1-zirconacyclotetrasilane
Fischer et al., 2003.[104]

Figure 19-6: Crystal structures of a titanium(III) oligosilyl complex (**A**, left) and of a zirconium(IV) oligosilyl complex (**B**, right), prepared with dianion **104**, reported for comparison (hydrogen hidden).

In Figure 19-6 two similar structures of an oligosilyl titanocene (**A**) and an oligosilyl zirconocene (**B**) are reported to compare some structural data. The ligands situation around the metal center was obviously different from compound **105**, but at least the backbone of silicon atoms was the same in all these complexes. In Table 1-6 the main crystallographic values are collected.

Bond lengths [Å] and angles [deg]	Compound **105** [CpTi^{II}(*btmsa*)(**104**)$^-$]*K$^+$	Compound **A** [Cp$_2$Ti^{III}(**104**)$^-$]*K$^+$	Compound **B** [Cp$_2$Zr^{IV}(**104**)]
Si - M	2.722	2.769	2.749
Si - Si	2.364	2.359	2.395
Si’ - M	3.320 (calc.)	3.795	3.302
Si - M - Si	83.51	76.30	91.00
Si - Si’ - Si	100.15	92.94	109.96

Table 1-6: Comparison of crystallographic data between compound **105** and compounds in Figure 17-6. Bond distances are calculated as mean values.

Compound **105** showed the shortest silicon-metal bond length: probably the alkyne ligand provided less steric hindrance than the lost cyclopentadienyl group, and the silicon atom could closer approach to the titanium atom. The silicon-silicon bond distances of the heterocyclic ring of the titanium complexes were comparable, while in compound **B** they were slightly elongated. The interior angles of these pseudo-square rings were quite different from complex to complex. The most narrowed rhombus was that one of compound **A** with a distance between the metal center and the opposite silicon atom of 3.795 Å. Compound **105** presented an average distortion between the other two complexes. Then, the crystal structure did not make clear the reason why the ^{29}Si NMR signal of Si(2) (Figure 18-6) was so high-field shifted, as no particular ring-strain resulted from angles and distances measurement. Unfortunately, compound **A** was paramagnetic, and no silicon NMR could be acquired and then compared with that one of compound **105**.

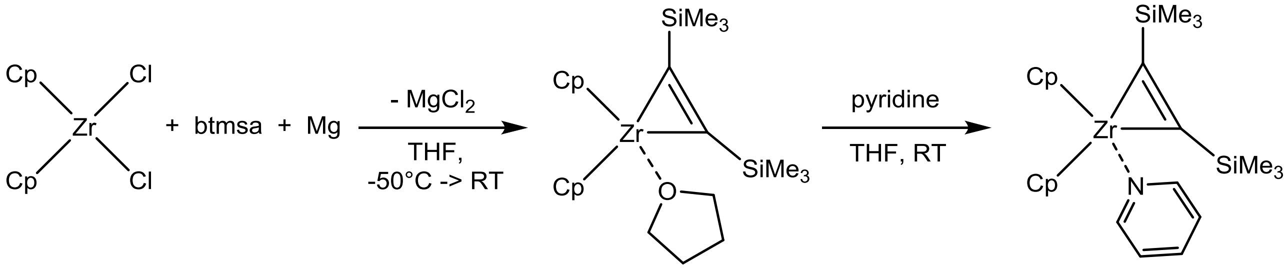
6.3 Reactions between the zirconium Rosenthal reagent and different types of mono and bi-dentate silyl anions

The Rosenthal reagent Cp_2Zr(*btmsa*) was prepared either through the standard procedure (Scheme 11-6),[98] or through the different approach of Tilley and coworkers.[105]

Then a number of reactions were tried to form similar oligosilyl complexes as those one previously reported.

6.3.1 Synthesis of the zirconium Rosenthal reagent

The first synthetic route mentioned above was repeated many times, but it was never really possible in our hands to isolate the zirconocene complex as THF adduct, neither as pyridine adduct.



Scheme 11-6: Synthesis of the zirconium Rosenthal reagents by the standard procedure.

Cleaner reaction were obtained starting the synthesis at low temperature (-60 to -50°C). The ^{29}Si NMR of one of these mixtures is shown in Figure 20-6: a slight excess of *btmsa* (about 5%) was used, and it was visible at -19.5 ppm. The spectrum was quite clean, and the NMR chemical shift of the silicon atoms was consistent with the expected value. However, the cited references[98,105] did not report the data for the ^{29}Si NMR. Nevertheless, the proton NMR spectrum (Figure 21-6) appeared in good agreement with the NMR data reported by Rosenthal[98] (0.10 ppm for the $-SiMe_3$ groups; 5.5 ppm for the cyclopentadienyl groups, in THF_{d8}).

---

[105] J.R. Nitschke, S. Zuercher, T.D. Tilley, *J. Am. Chem. Soc.*, **2000**, *122*, 10345-10352.

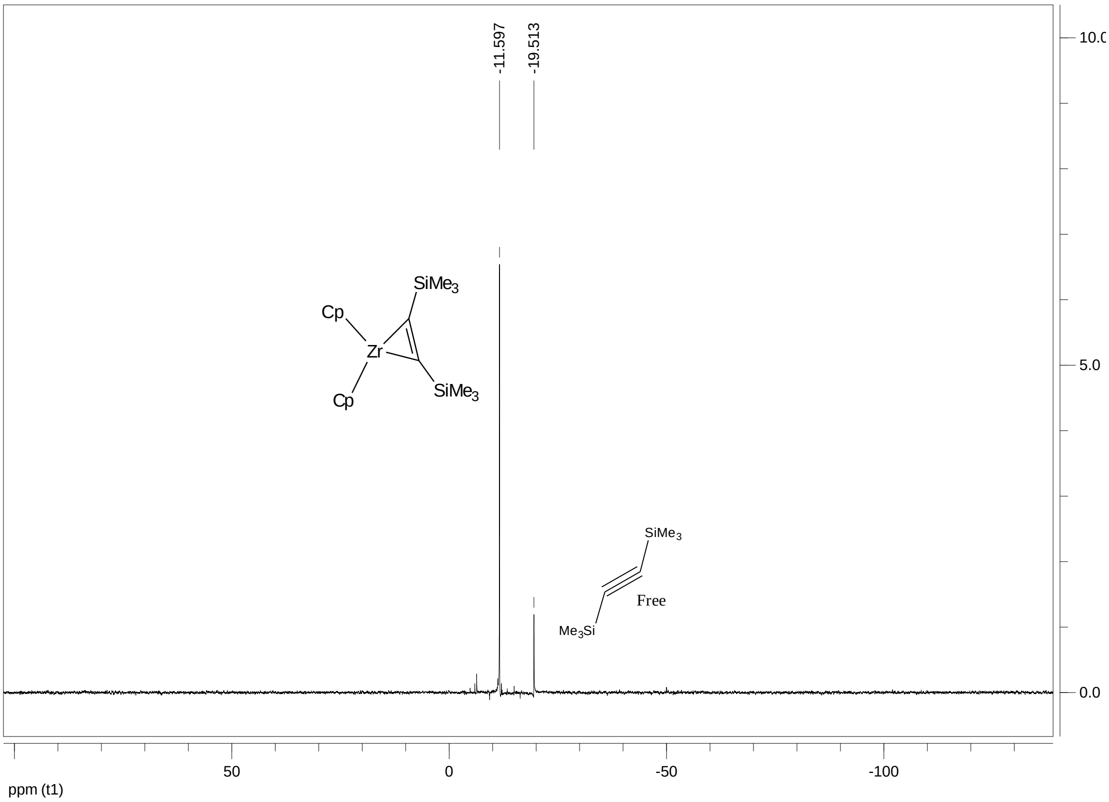


Figure 20-6: ^{29}Si NMR spectrum of the reaction mixture of the zirconium Rosenthal reagent, THF adduct.

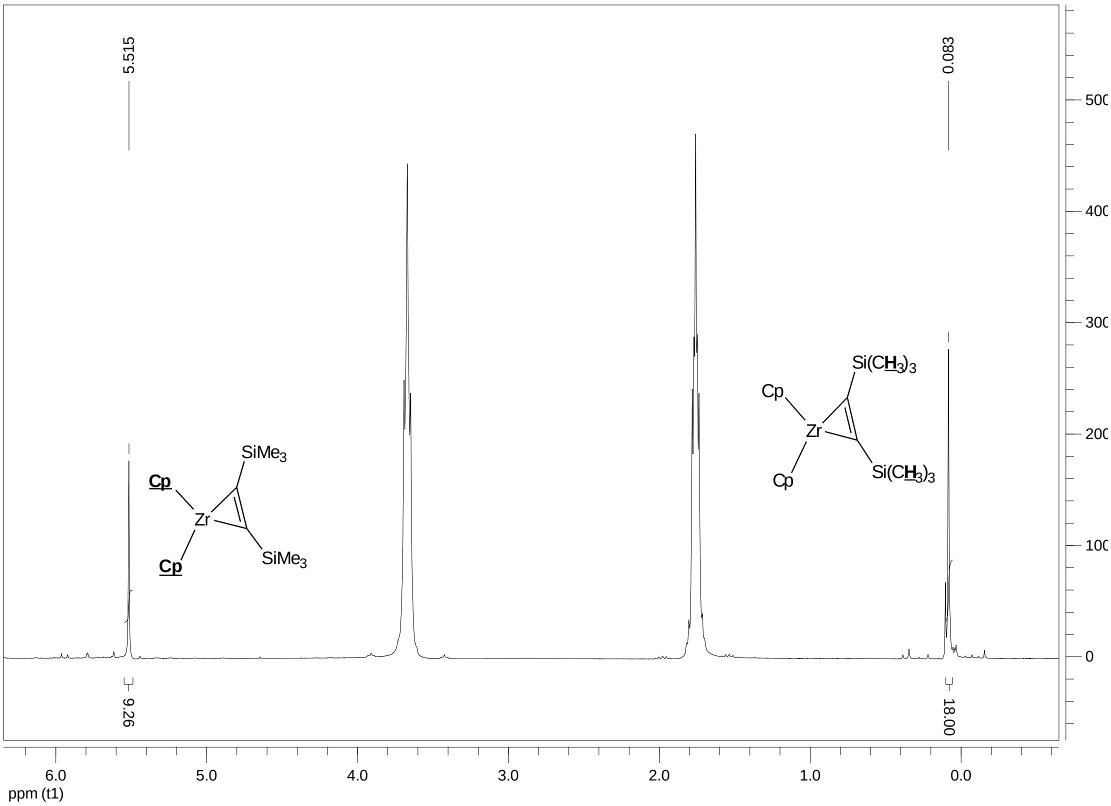


Figure 21-6: ^{1}H NMR spectrum of the reaction mixture of the zirconium Rosenthal reagent, THF adduct.

At that point, every attempt to remove the solvent to obtain a solid product led only to a sticky black mass, formed by the polymerization of the complex. Rosenthal *intentionally* prepared that polymer drying the THF adduct solution under high vacuum. On the other hand, the author said that it was possible to have the monomeric compound just evaporating the solvent.[106] This fact represented a problem, as the pyridine adduct was reported to be prepared from the isolated THF complex, and not directly from the reaction mixture in THF.[107] In fact, after treating the solution of Cp_2Zr(*btmsa*) in THF directly with a slight excess of pyridine, a not clear reaction mixture was obtained. The ^1H NMR spectrum showed two signals in the region of the $-SiMe_3$ groups, instead of one at 0.32 ppm (see reference and experimental part).[105] The singlet of the protons of the Cp groups seemed unchanged compared to the THF adduct, while they should have a slight shift and should be found at 5.4 ppm (Figure 22-6).

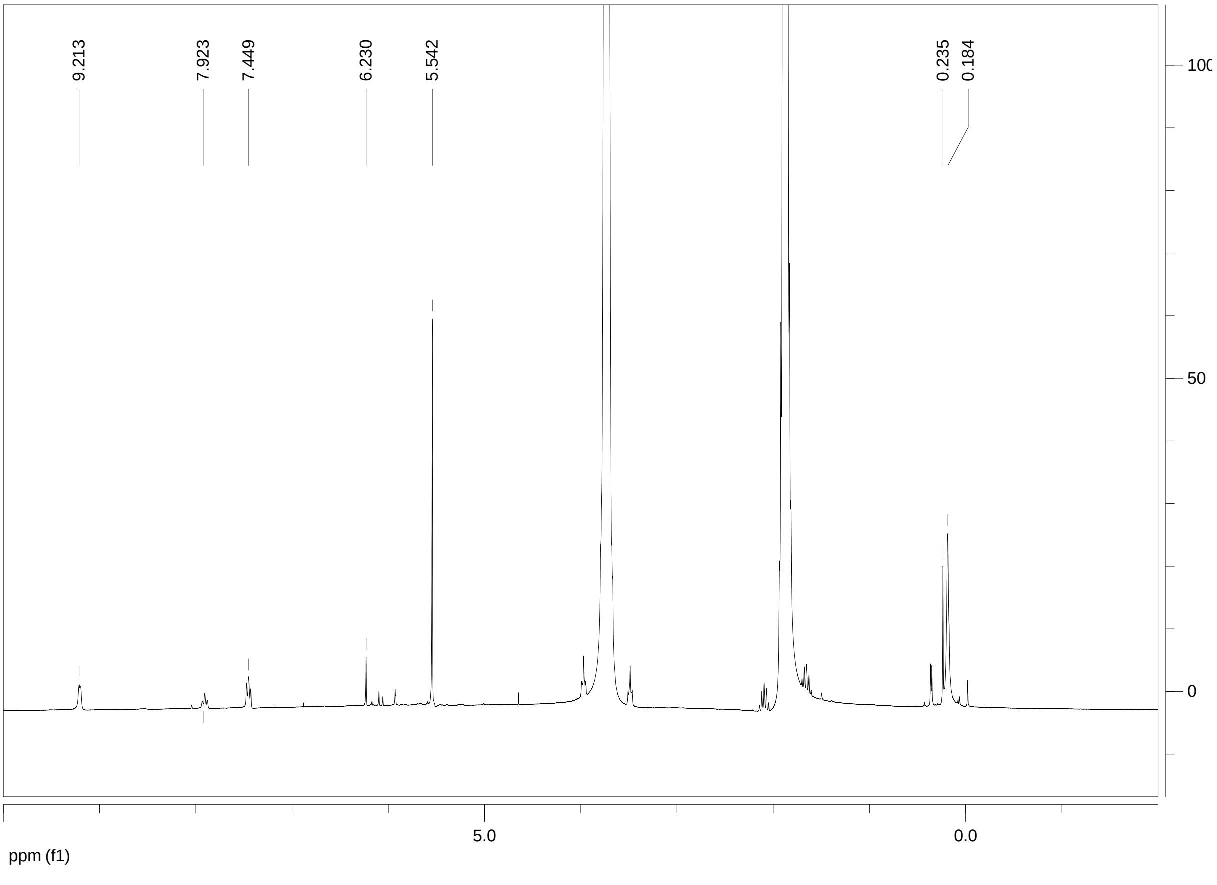


Figure 22-6: ^1H NMR spectrum of the reaction mixture of the zirconium Rosenthal reagent, pyridine adduct.

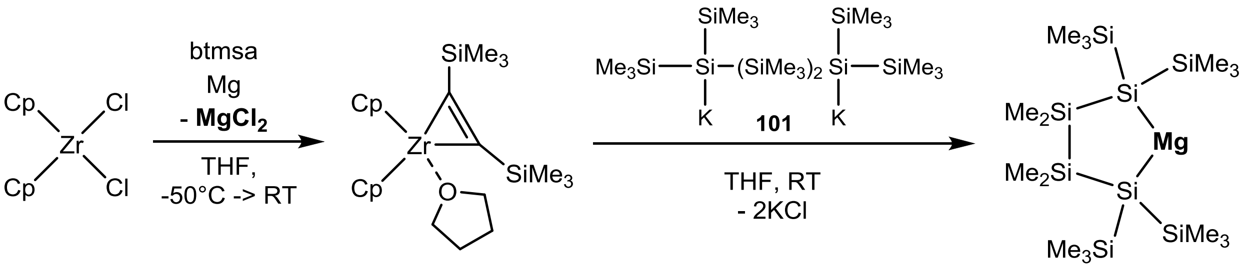
---

[106] U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov, V. B. Shur, *Angew. Chem. Int. Ed. Engl.*, **1993,** *32*, 1193-1195.

[107] U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, *Z. Anorg. Allg. Chem.*, **1995**, *621*, 77-83.

6.3.2 Reaction between the THF adduct of the zirconium Rosenthal reagent with oligosilyl dianions

The Cp_2Zr(*btmsa*)*THF adduct was reacted *in situ* with a THF solution of the 1,4-dipotassium-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane (**101**) (Scheme 12-6), but interestingly the magnesium complex of the silicon dianion was obtained, in a quite clean fashion (Figure 23-6).



Scheme 12-6: *In situ* reaction between the zirconium Rosenthal reagent and disilyl dianion **101**.

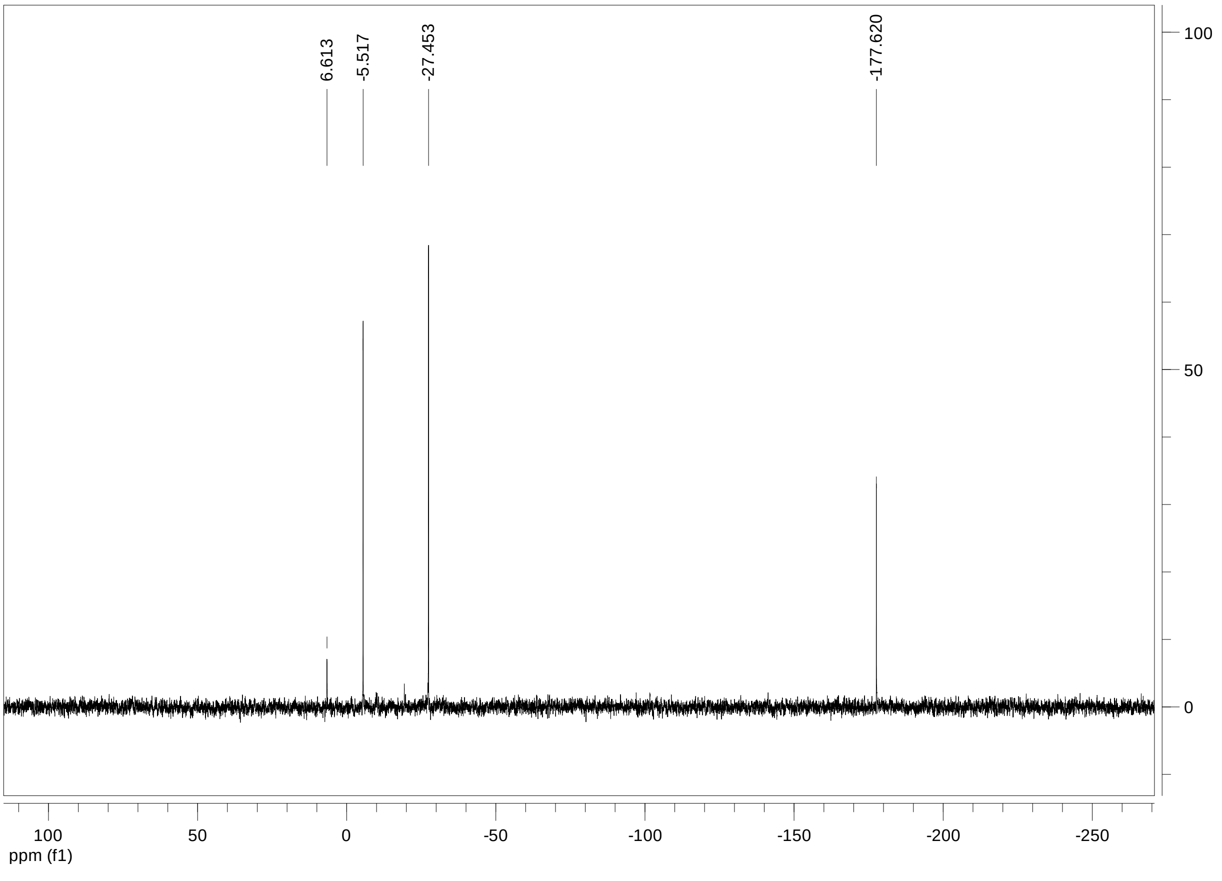
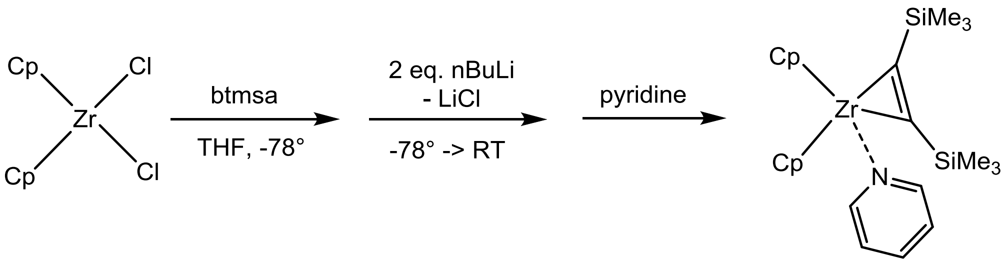


Figure 23-6: ^{29}Si NMR spectrum of the reaction of the zirconium Rosenthal reagent (THF adduct) with disilyl anion **101**.

6.3.3 Synthesis of the zirconium Rosenthal reagent through Tilley reaction

Tilley's procedure to synthesize Rosenthal reagent employed butyl lithium to reduce zirconocene dichloride, in the presence of *btmsa* and in THF as solvent, at very low temperature.[105] After removal of LiCl by filtration, the pyridine adduct was prepared (Scheme 13-6).



Scheme 13-6: Synthesis of Cp_2Zr(*btmsa*)(pyr), Tilley route.

For the ^1H NMR, Tilley reported a chemical shift of 0.32 ppm for the protons of the $SiMe_3$ groups and 5.46 ppm for the protons of the Cp groups (in C_6D_6).[105] The proton spectrum of the product after the work-up, is shown in Figure 22-6. There were some small signals of impurities and by-products, but the main signals appeared as those of the expected product.

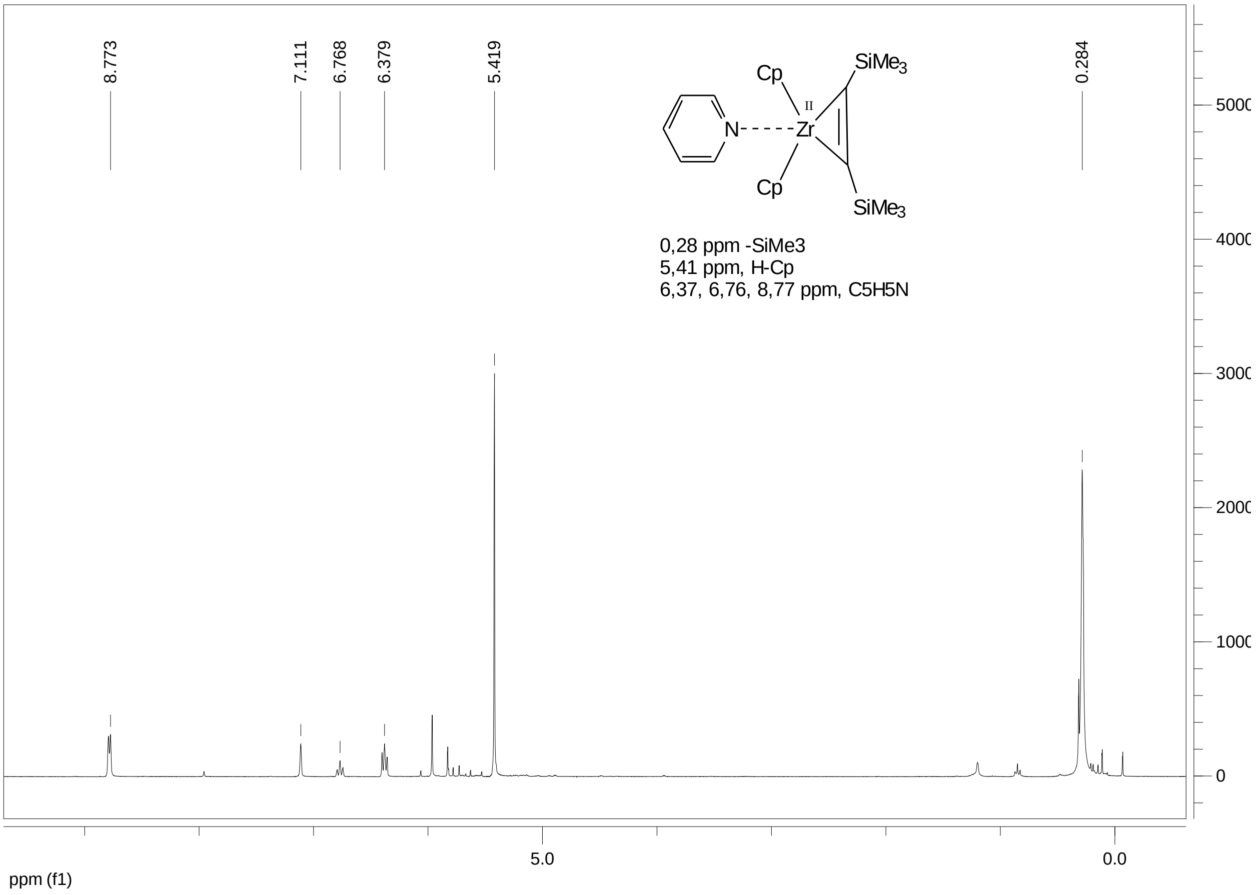
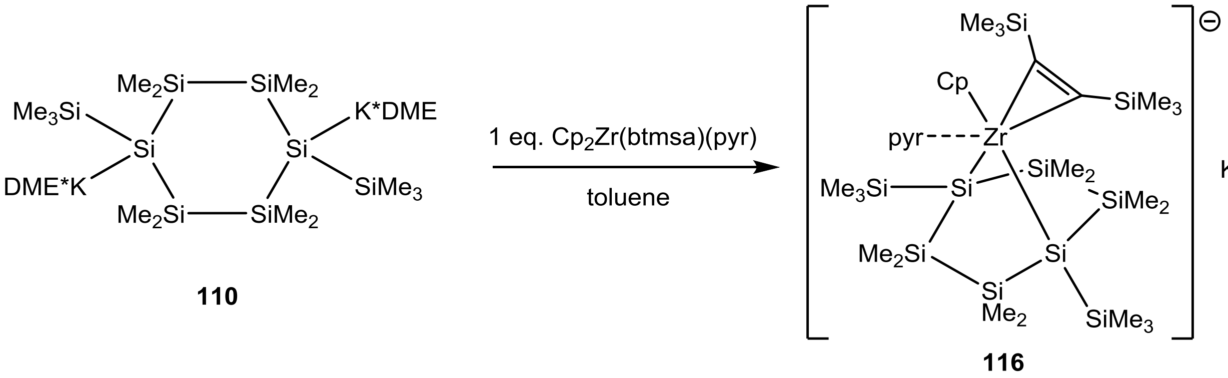


Figure 22-6: ^1H NMR spectra of the worked up complex Cp_2Zr(*btmsa*)(pyr), in C_6D_6.

6.3.4 Reactions between the pyridine adduct of the zirconium Rosenthal reagent and cyclic oligosilyl dianions

The cyclic oligosilyl dianion **110** was prepared in DME, dried and dissolved again in toluene. Then it was reacted with the pyridine adduct of the Rosenthal reagent in toluene (Scheme 14-6).



Scheme 14-6: Reaction of a cyclic oligosilyl dianion **110** with the zirconium Rosenthal reagent.

Surprisingly, the reaction did not proceed as the one for the titanium complex and it seemed that the silyl anion remained unreacted in solution but in the ^{29}Si NMR the signals at ca. -11 ppm for *btmsa* disappeared and a peak at -42 ppm was revealed (Figure 23-6).

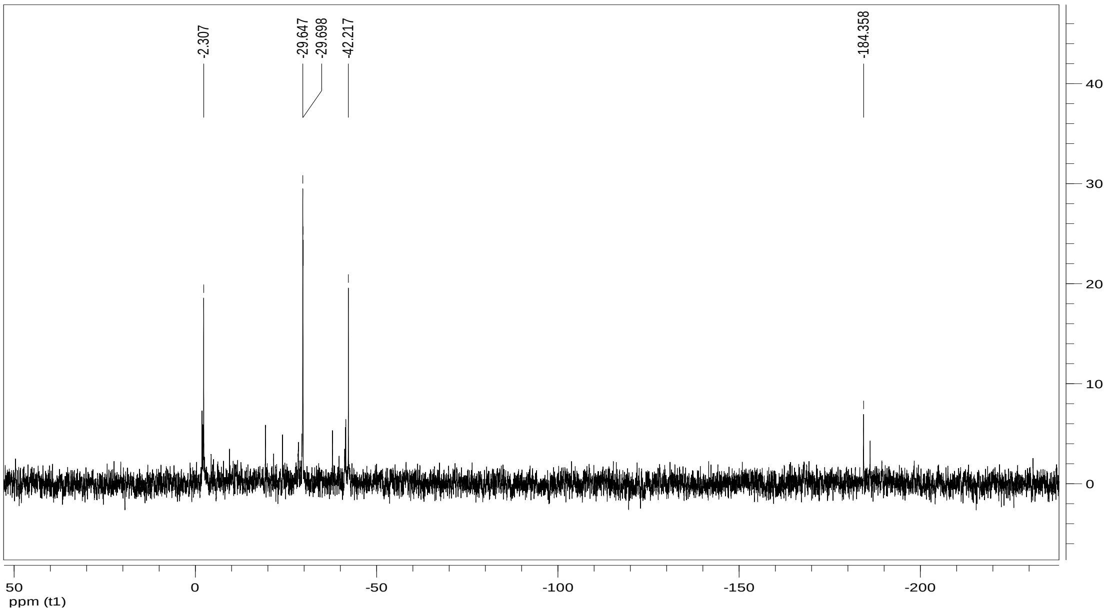
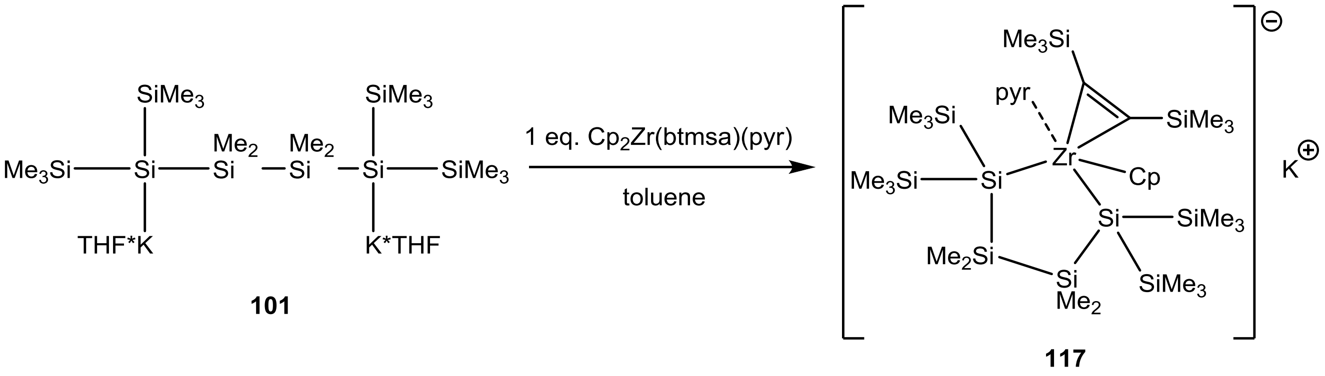


Figure 23-6: ^{29}Si NMR spectrum of the reaction between the zirconium Rosenthal reagent (pyridine adduct) and the cyclic disilyl dianion **110**.

6.3.5 Reactions between the pyridine adduct of the zirconium Rosenthal reagent and linear oligosilyl dianions

The silyl dianion **101** was prepared in THF, dried and dissolved again in toluene. Then it was reacted with the pyridine adduct of the zirconium Rosenthal reagent in toluene (Scheme 15-6).



Scheme 15-6: Reaction of a oligosilyl dianion **101** with the zirconium Rosenthal reagent (pyridine adduct).

The reaction mixture was checked by ^{29}Si NMR (Figure 24-6), but unfortunately the reaction pattern was not as clear as in the case of the titanium complex **102**. The silyl dianion **101** reacted completely, but in this case it seemed that the former neutral compound **100** was again generated (signals at -127.6, -32.9, -9.7 ppm). There were three signals in the range of -110 ppm, which might be reasonably assigned to silicon atoms bonded to a zirconium atom. It might be that some asymmetric structures were formed. In addition, the silyl dianion could coordinate to the metal center only with one silicon atom, and the other one then obtained a -SiMe$_3$ group back through a mechanism supposed in the previous chapters (see Scheme 3-6). For this reason the signals at -130 ppm and -36 ppm could be explained. Some free *btmsa* was present in the mixture (peak at -19 ppm), while for the acetylene coordinated to the zirconium at least two signals from the -SiMe$_3$ groups were detected (-11 ppm). Also the signals given by the -SiMe$_3$ of the silyl heterocycle could be in the typical range for these kind of complexes (ca. -5 ppm). The peak at -13 ppm might be of the *btmsa* as well as to the -SiMe$_2$- groups, which could present a strongly low-field shifted signal as for compound **102**.

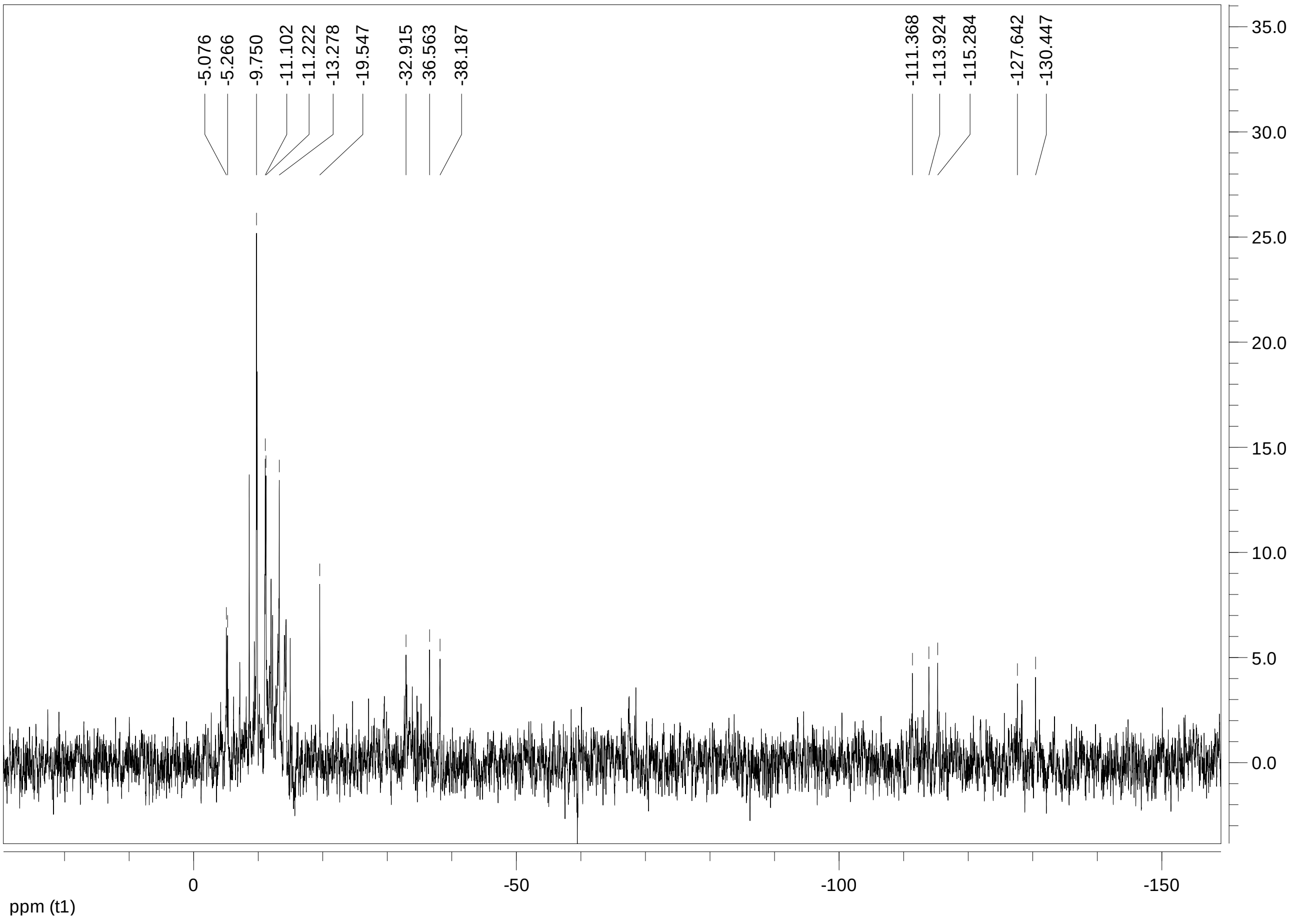


Figure 24-6: ^{29}Si NMR spectrum of the reaction between the zirconium Rosenthal reagent (pyridine adduct) and the linear disilyl dianion **101**.

Slightly differences in the NMR signals might be also due to the displacement of pyridine that could not be argued from the NMR spectra.

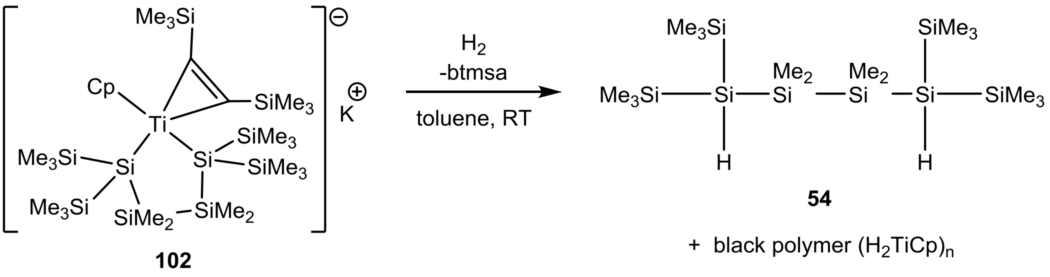
Different attempts to crystallize the expected product were tried, but with no success. It might be useful to underline a critical point. Beside all the useful and fascinating properties of the Rosenthal reagents, one lack is quite remarkable, that is the high difficulty to crystallize these complexes, due to their high solubility even in alkanes. The compounds synthesized and presented in this chapter have for sure some ionic character, but on the other hand the oligosilyl fragments can only increase the solubility of the final compound in nonpolar solvents. Then some solvent is always retained during crystals aggregation and that makes the forming material unstable and deliquescent.

6.4 Further reactions with the Rosenthal reagent - oligosilyl complex

As finally it was found a reliable and reproducible reaction pattern to prepare some oligosilyl derivatives of the titanium Rosenthal reagents (compounds **102** and **105**), a series of subsequent experiments was carried on, to test the reactivity of these news complexes.

6.4.1 Reaction of compound 102 with hydrogen

The titanium oligosilyl complex **102** was prepared as described in last reaction of Scheme 6-6. Then the solution containing the complex was flushed with gaseous H_2 and kept 12 hours under a hydrogen atmosphere (Scheme 16-6).



Scheme 16-6: Reaction of the Rosenthal reagent - oligosilyl complex with hydrogen.

In Figure 25-6 the ^{29}Si NMR of the reaction mixture is shown. It was an extremely clean reaction and revealed the formation of the organosilyldihydride **54**. During the process the ligand *btmsa* was lost (signal at -19 ppm) and an insoluble black polymer precipitated. It was already reported by Steinborn that the Rosenthal reagent could undergo oxidative additions of iodine, methanol, water, methyliodide, and benzenedicarboxylic acids.[108] In these cases the metal center was oxidized to Ti^{III} or Ti^{IV}, depending on the amount of the oxidants, and the acetylene ligand was lost as well. Previously, Brintzinger investigated the $Cp_2Ti^{III}Cl$ complex and the formation of correspondent hydride $[Cp_2TiH_2]^-$, anticipating the hydridic character of the latter compound due to its reactivity towards protonic agents.[109]

---

[108] C. Albrecht, T. Krüger, C. Wagner, T. Rüffer, H. Lang, D. Steinborn, *Z. Anorg. Allg. Chem.*, **2008**, *634*, 2495-2503.
[109] H. H. Brintzinger, J. Am. Chem. Soc., **1967**, *20*, 6871-6877.

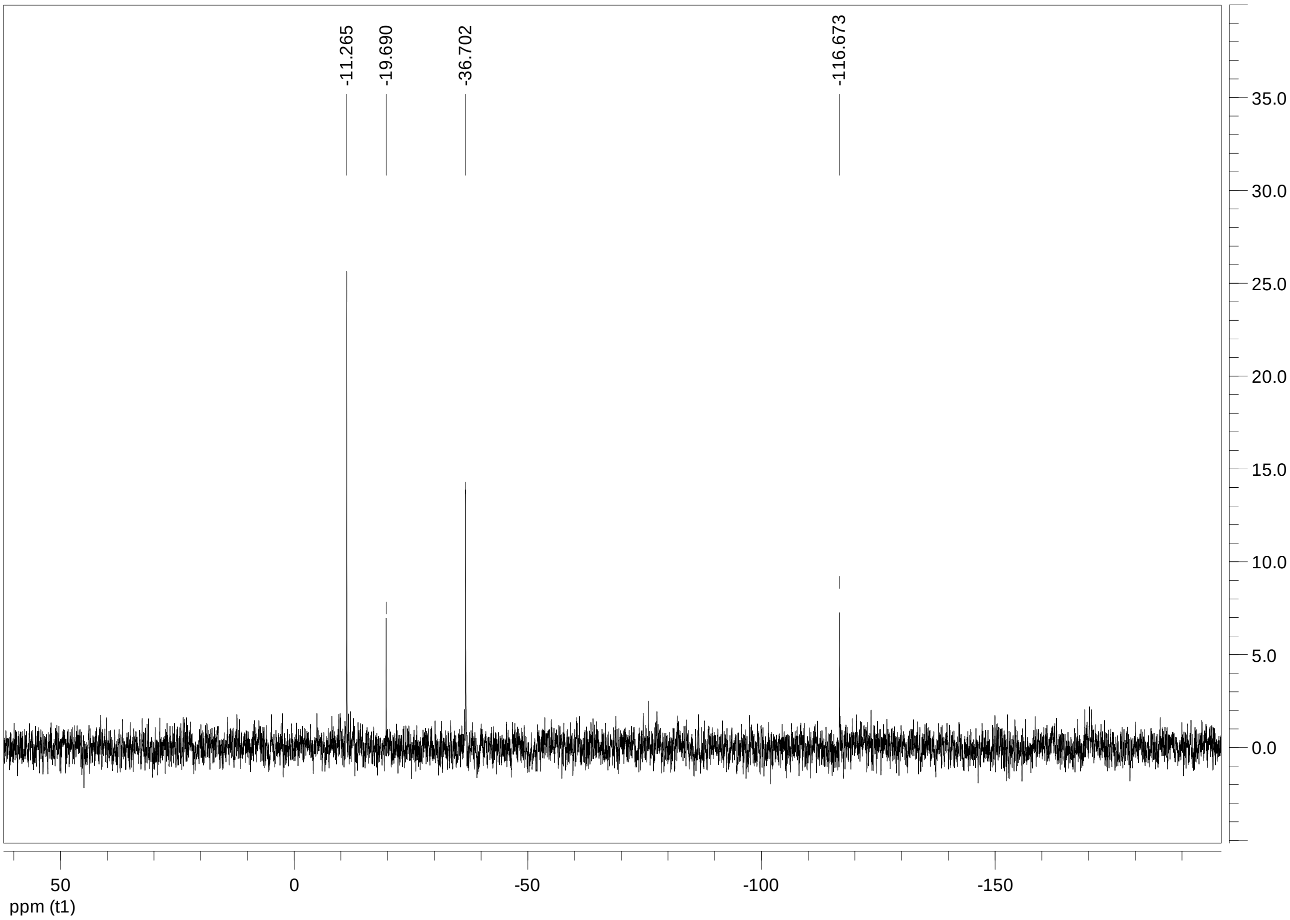
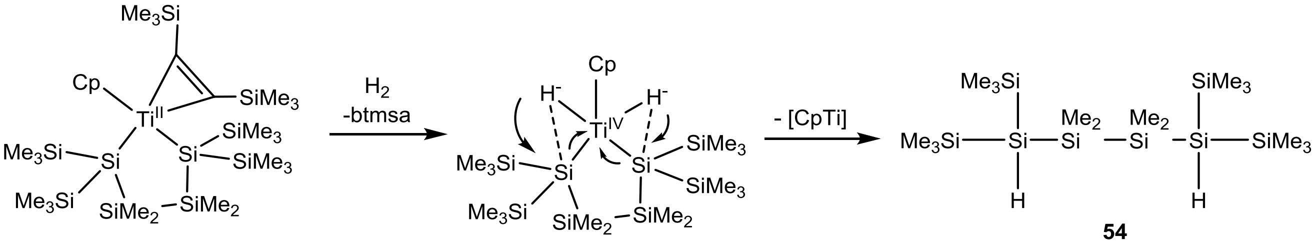


Figure 25-6: ^{29}Si NMR spectrum of the reaction between the oligosilyl - Rosenthal reagent complex **102** and hydrogen gas.

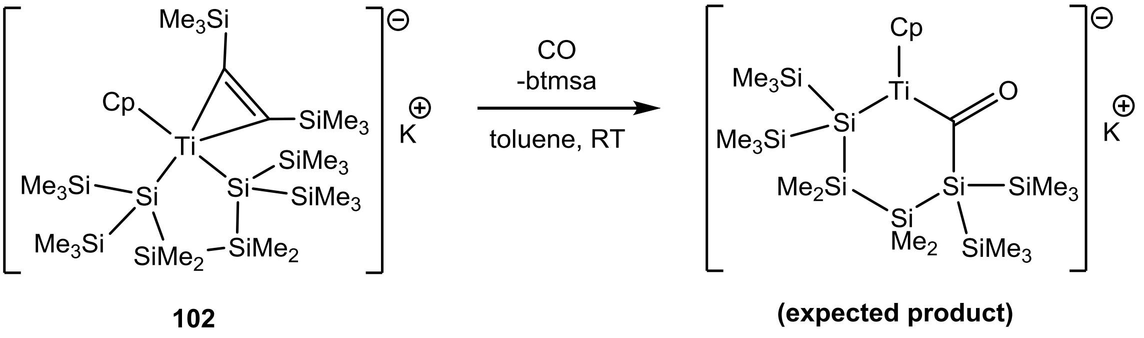
In this experiment, the hydrogen molecule was probably coordinated by the titanium atom with the simultaneous loss of *btmsa*. Then the thus formed hydrides could attack the silicons atoms with consequent elimination of the organosilanes (Scheme 17-6).



Scheme 17-6: Supposed mechanism for the reaction between complex **102** and hydrogen.

6.4.2 Reaction of compound 102 with carbon monoxide

The titanium oligosilyl complex **102** was prepared as described in last reaction of Scheme 6-6. Then the solution containing the complex was flushed with gaseous CO and kept 12 hours under the carbon monoxide atmosphere (Scheme 18-6).



Scheme 18-6: Reaction of Rosenthal reagent - oligosilyl complex with carbon monoxide.

The insertion of one molecule of CO into the Ti-Si bond should generate a six membered ring containing a new Ti-C bond and a new Si-C bond. But afterwards, it was not possible to determine from the ^{29}Si NMR spectrum whether the reaction developed with a further elimination product or if the signals were due to the carbonylated oligosilyl titanium complex. The spectrum (Figure 26-6) was unusually noisy and it presented many signals in different ranges. It was evident at least that the starting material **102** was completely consumed, and that the ligand *btmsa* was lost during the process. The signals around -75 to -80 ppm might be assigned to a $CSiSi_3$ fragment or to the silicon atoms bonded to the metal center. Those peaks at around -30 ppm could be assigned to the $-SiMe_2-$ groups. However, the $-SiMe_3$ groups were detected in the typical range of neutral compounds, and then it raised the suspicion that a further products were present in solution. The signals at ca. -60 ppm were quite uncommon but they might be of the $O=C-SiSi_3$ fragment, in which the presence of oxygen induce a low-field chemical shift of the peaks.

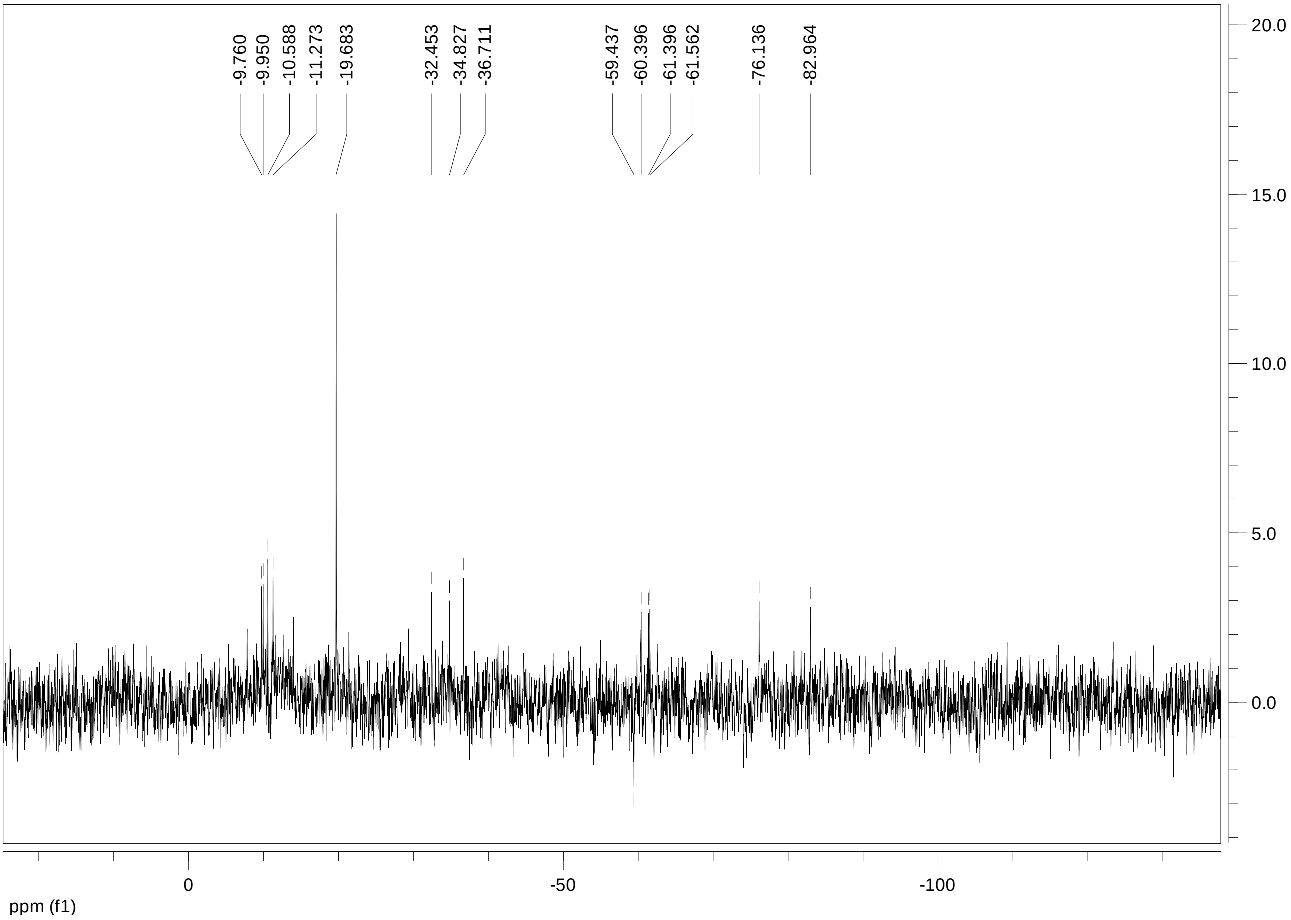
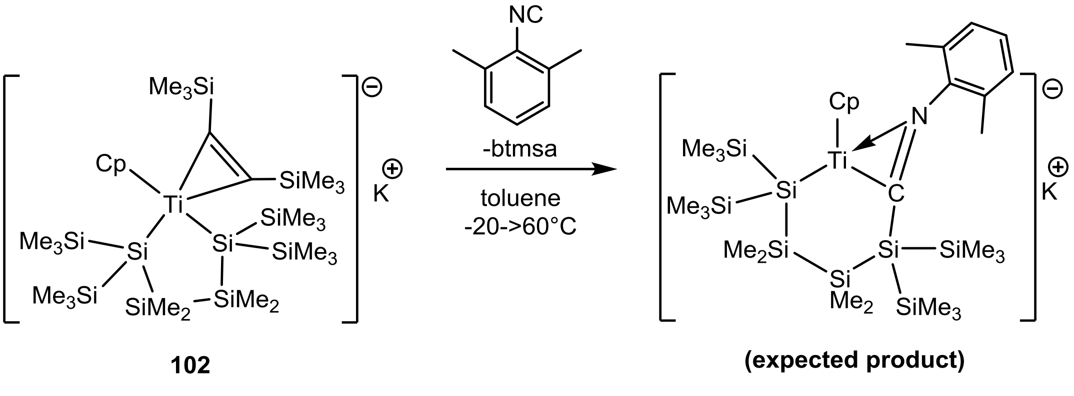


Figure 25-6: ^{29}Si NMR spectrum of the reaction between the oligosilyl - Rosenthal reagent complex **102** and carbon monoxide.

6.4.3 Reaction of compound 102 with 2,6-dimethylphenylisocyanide

The titanium oligosilyl complex **102** was prepared as described in last reaction of Scheme 6-6. Then to the solution containing the complex 1 equivalent of phenylisocyanide was added at ca. -20°C (Scheme 19-6).



Scheme 19-6: Reaction between Rosenthal reagent - oligosilyl complex **102** and 2,6-dimethylphenylisocyanide.

During similar experiments with oligosilyl zirconocene, it was observed the insertion of the cyanide carbon into the Ti-Si bond.[103] In the case of complex **102** the reaction did not proceed until the mixture was heated up at 60°C. In comparison with the oligosilyl Cp_2Zr^{IV} complex, the metallic center of compound **102** was probably fairly rich in electron density and did not need to coordinate to another ligand. It might be also that the acetylene was hardly replaced by the incoming cyanide. In the ^{29}Si NMR spectrum (Figure 26-6) new signals appeared at -114.0, -9.8 and -8.6 ppm. Actually, more peaks were expected, as an asymmetric structure should form. Two different signals should rise up due to the $-SiMe_2-$ groups, that in the supposed product had a slightly but significant different chemical shifts. That was observed in a quite similar compound, Cp_2Zr(**101**)(isocyanide), number 6a in the cited paper.[103] But the signals at -120.6, -18.2, -16.3, -7.3 and -5.0 seemed still to refer to the starting material **102**. Also free *btmsa* was present in the reaction mixture. Probably only a partial ligand exchange between the acetylene and the isocyanide took place (Scheme 20-6).

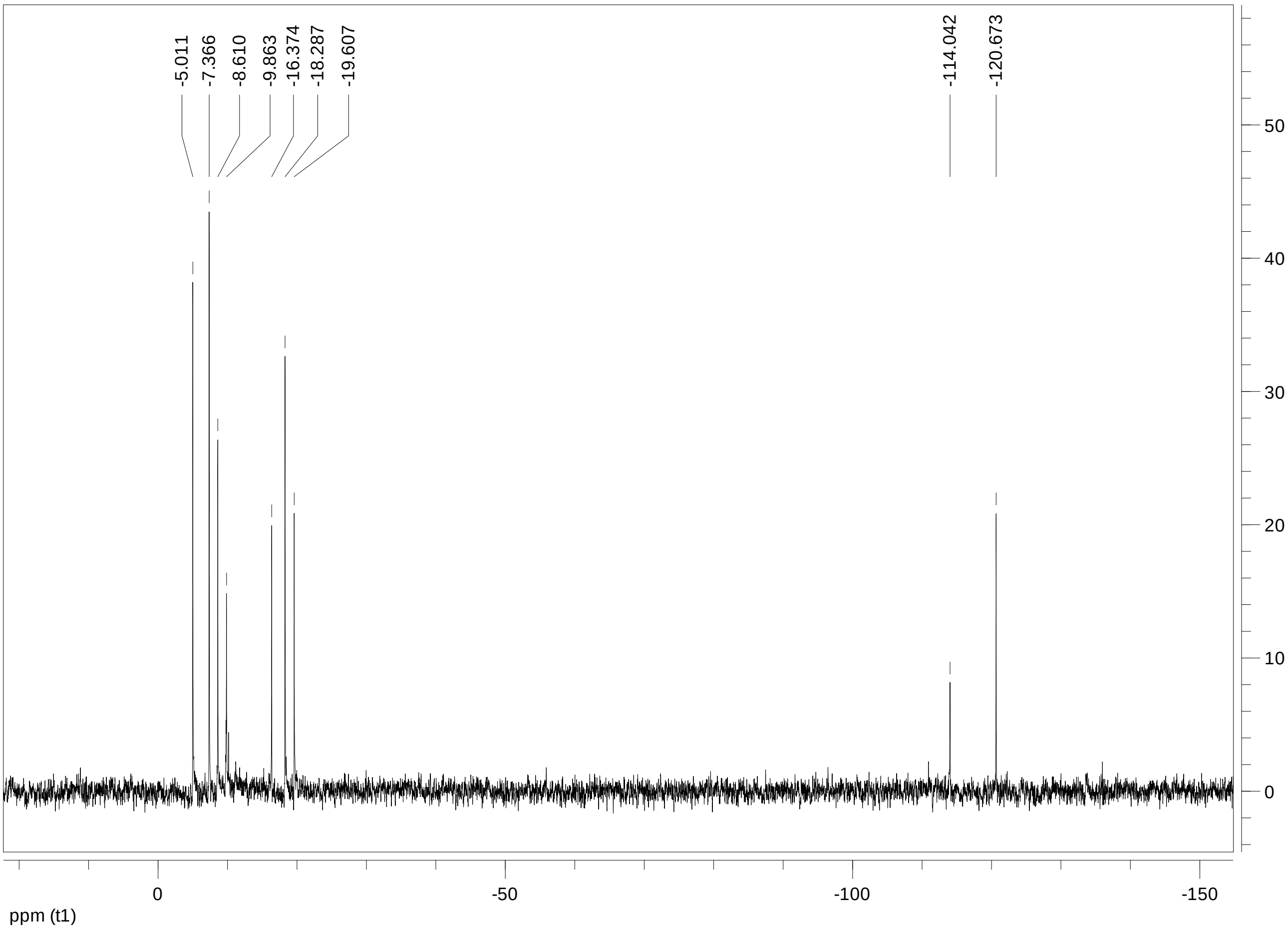
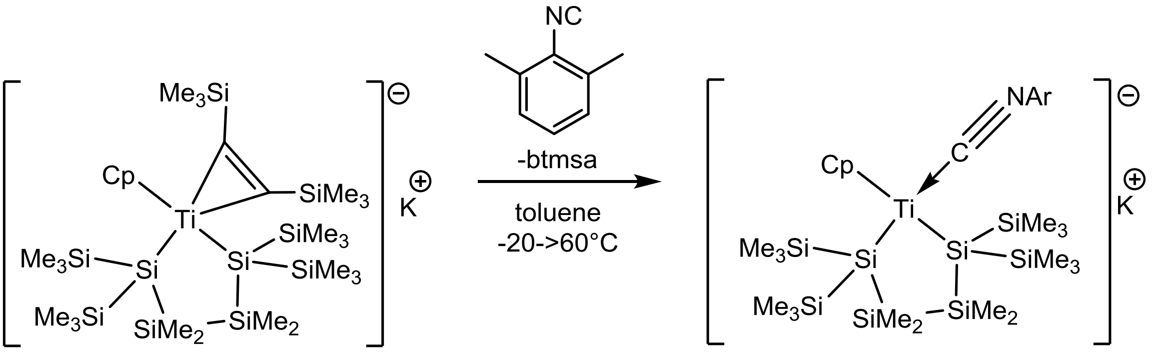


Figure 26-6: ^{29}Si NMR spectrum of the reaction between the oligosilyl - Rosenthal reagent complex **102** and 2,6-dimethylphenylisocyanide.



102

(formed product)

Scheme 20-6: Reaction between Rosenthal reagent - oligosilyl complex **102** and 2,6-dimethylphenylisocyanide (Ar = 2,6-dimethylphenyl).

The process probably did not affect the chemical shift of the remote -$SiMe_2$- groups, that might come together with those ones of reagent **102** at -16 ppm. To support this hypothesis, the integration of the signals of the product and the starting material were compared. These numbers cannot be related with the exact number of each type of silicon atoms in the molecule, but their ratio should remain constant in different spectra acquired under the same conditions. In compound **102** a ratio of 1.0/0.4 was found for (Si_4)/($SiMe_2$). For the same signals in the spectrum of the reaction mixture, a ratio of 1.0/0.8 was found, while all the other integrations were comparable with those ones of the starting material. This means the signal at -16 ppm was not due only to the -$SiMe_2$- groups of compound **102** but also to those ones of the supposed product (Scheme 20-6). The integration data are reported in Table 2-6.

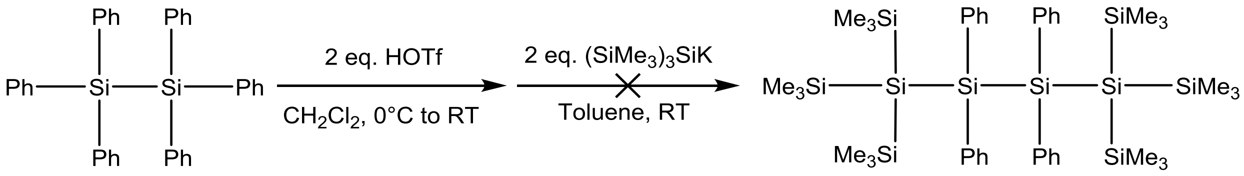
Molecular fragments	Compound **102**/*btmsa* (pure)	Compound **102**/*btmsa* (reaction mixture)	Compound **102**/*CNAr* (reaction mixture)
Si_4	1.00	1.00	0.48
$SiMe_2$	**0.44**	**0.87**	coalescent
$SiMe_3$	2.12, 1.87	1.79, 1.94	1.41, 1.19
btmsa	1.69	1.64	/
free *btmsa*			1.01

Table 2-6: Comparison between the integration values of the ^{29}Si NMR signals of pure compound **102**, compound **102** in the reaction mixture, and the derivative isocyanide complex. Si_4 set to 1.00. Ar = 2,6-dimethylphenyl.

7. New Phenylated and Methylated Organosilylstannanes

7.1 Introduction

During the preparation of the substrates for the synthesis of the silyl cation, different attempts to obtain heavier organosilanes (cyclic or acyclic) were tried. The following variant of compound **70** was thought to be prepared treating hexaphenyldisilane with two equivalent of triflic acid and coupling theresulting ditriflate with 2 equivalents of tris(trimethylsilyl)silyl potassium (Scheme 1-7) :



Scheme 1-7: Synthesis attempt for 2,2,5,5-tetrakis(trimethylsilyl)-3,3,4,4-tetraphenyl-hexamethylhexasilane.

This molecule has four phenyl groups instead of four methyl groups bonded to the silicon atoms that bridge the two hypersilyl groups, with a molecular weight of 859.90 g/mol instead of 611.72 g/mol.

Various attempts to prepare this product were done in the past, starting from 1,2-dibromotetraphenyldisilane.[110] However, because of the steric hindrance of the phenyl and hypersilyl groups, and the relatively small radius of the silicon atom, the reactions never succeed.

To verify if this type of reaction could work with larger atoms than silicon, hexaphenyldistannane was used as starting material and treated with triflic acid. In this case the preparation was successful, and the product was characterized by NMR and X-ray crystallography. Then similar compounds were synthesized. Subsequent characterization by UV/Vis revealed interesting properties of these materials.

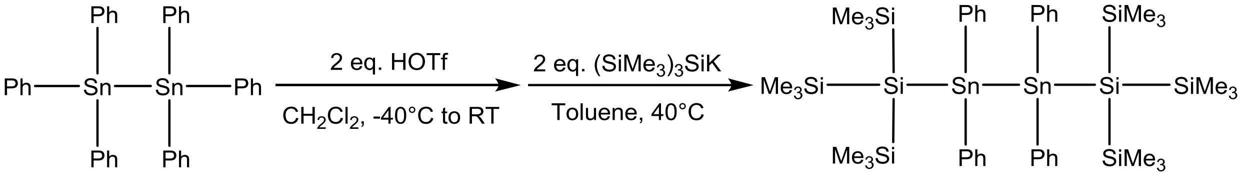
---

[110] Christian Kayser, *Dissertation*, **1997-2001**, Institut für Anorganische Chemie der Technischen Universität Graz.

7.2 Synthesis and characterization

7.2.1 Synthesis of 1,2-bis(hypersilyl)tetraphenyldistannane (80)

Haxaphenyldistannane was treated with triflic acid, through a standard procedure described by W. Uhlig[111] and F. Uhlig.[112] Then the reaction with two equivalents of hypersilyl potassium gave the desired product **80** (Scheme 2-7):



80

Scheme 2-7: Synthesis of 1,2-bis(hypersilyl)tetraphenyldistannane (**80**).

The synthesis of the triflate salt worked either in dichloromethane or in toluene. When the stannyltriflate was prepared in a halogenated solvent, the latter was transferred to another solvent before adding the silyl potassium salt, to avoid side reactions. Particular attention should be paid in the preparation of the hypersilyl anion, as ethereal solvents should not be used in the presence of triflic acid. DME is reported as a stable solvent for triflates preparations, but in our hands it was not possible to obtain compound **80** using DME as solvent. In addition, it is not recommended to employ benzene and crown ether to prepare the hypersilyl anion, as some residue of this co-reagent can affect negatively the work up and the crystallization process. Then, hypersilyl potassium was obtained in THF or in DME, afterwards the solvent was removed, and the salt dissolved again in toluene. In this way the reaction with the ditriflate was accomplished. The ^{29}Si NMR of the final product is here shown (Figure 1-7).

---

[111] W. Uhlig, *J. Organomet. Chem.*, **1991**, *421*, 189-197.

[112] E. Zarl, J. Baumgartner, K. Decker, R. Fischer, B. Seibt, F. Uhlig, *Phosphorus Sulfur*, **2008**, *183*, 1923-1934.

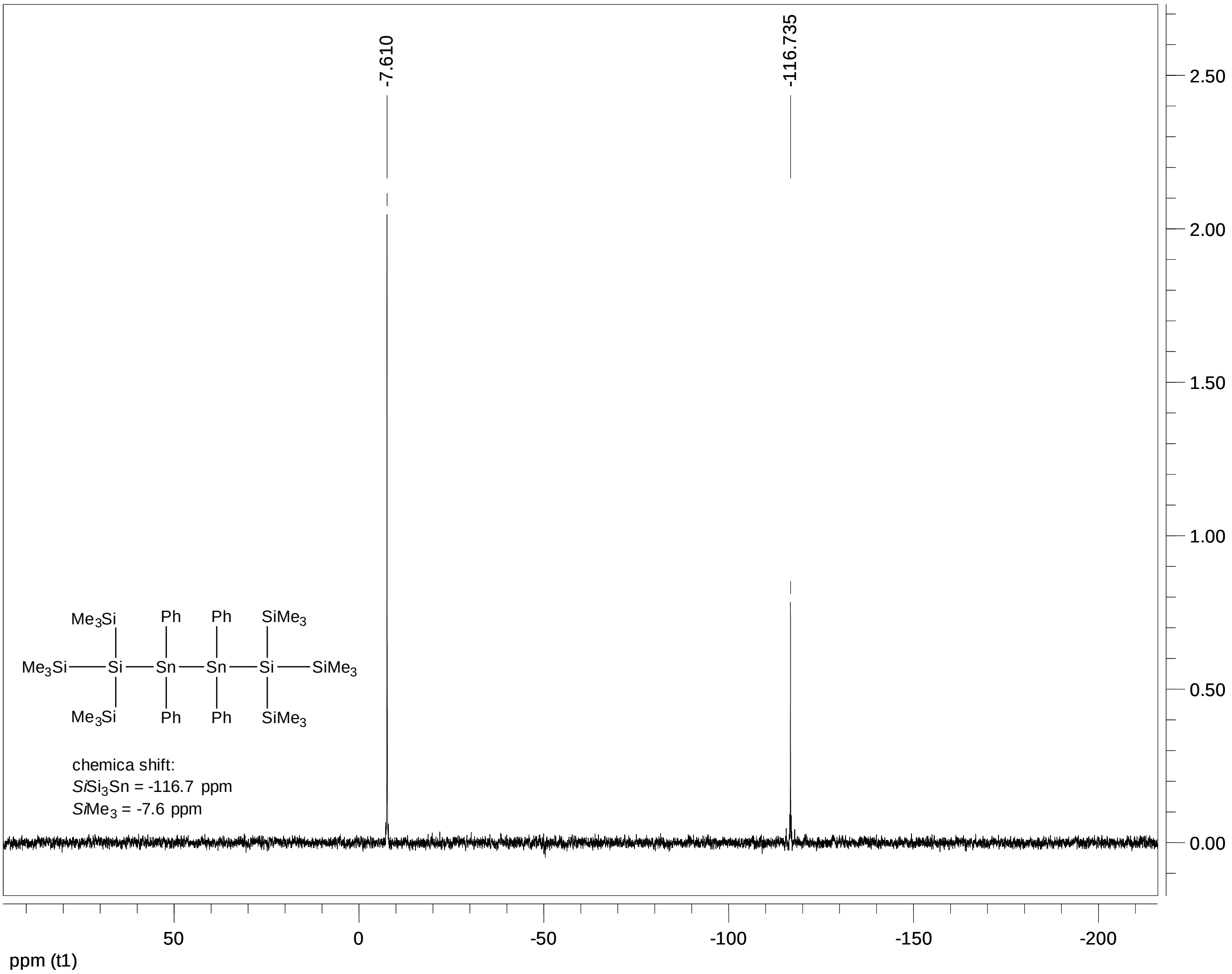
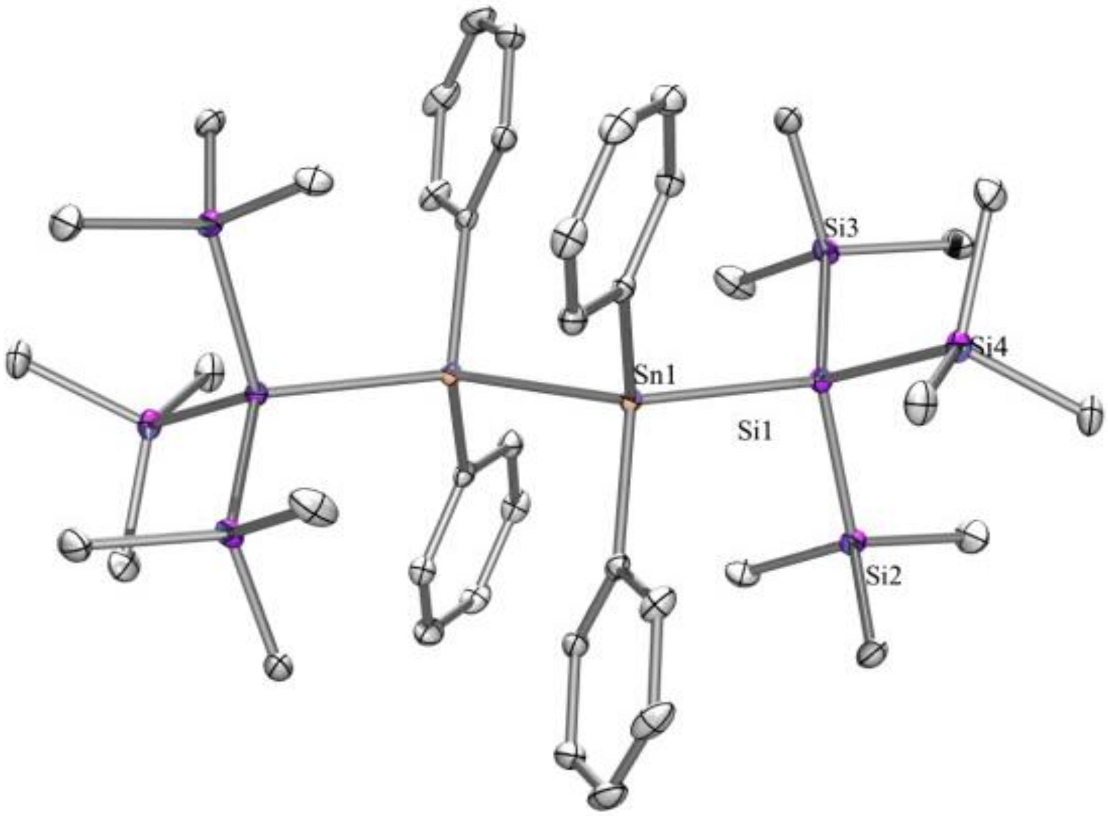


Figure 1-7: ^{29}Si NMR of the worked up product **80**.

The NMR signal of the -$SiMe_3$ groups was in the typical range for this kind of structures which contain tin atoms, while the signal of the quaternary silicon is quite down-field shifted (compared to the chemical shifts of compound **37**). Good crystals for X-ray analysis were obtained by slowly evaporating a benzene solution of the product. Alternatively it was also possible to crystallize it from a mixture of pentane/THF at -20°C. Here the structure is shown (Figure 2-7).



Selected crystallographic data: Crystal system: monoclinic; Space group: P2(1)/n; Goodness-of-fit on F^2: 1.074; Bond lengths [Å]: Sn(1)-Sn(1)# 2.8217 (7); Sn(1)-Si(1) 2.5988(6); Si(1)-Si(4) 2.3602 (8); Sn(1)-C(7) 2.1654 (16); Angles [deg]: Si(1)-Sn(1)-Sn(1)# 119.939 (12); C(1)-Si(1)-Sn(1) 107.28 (4)

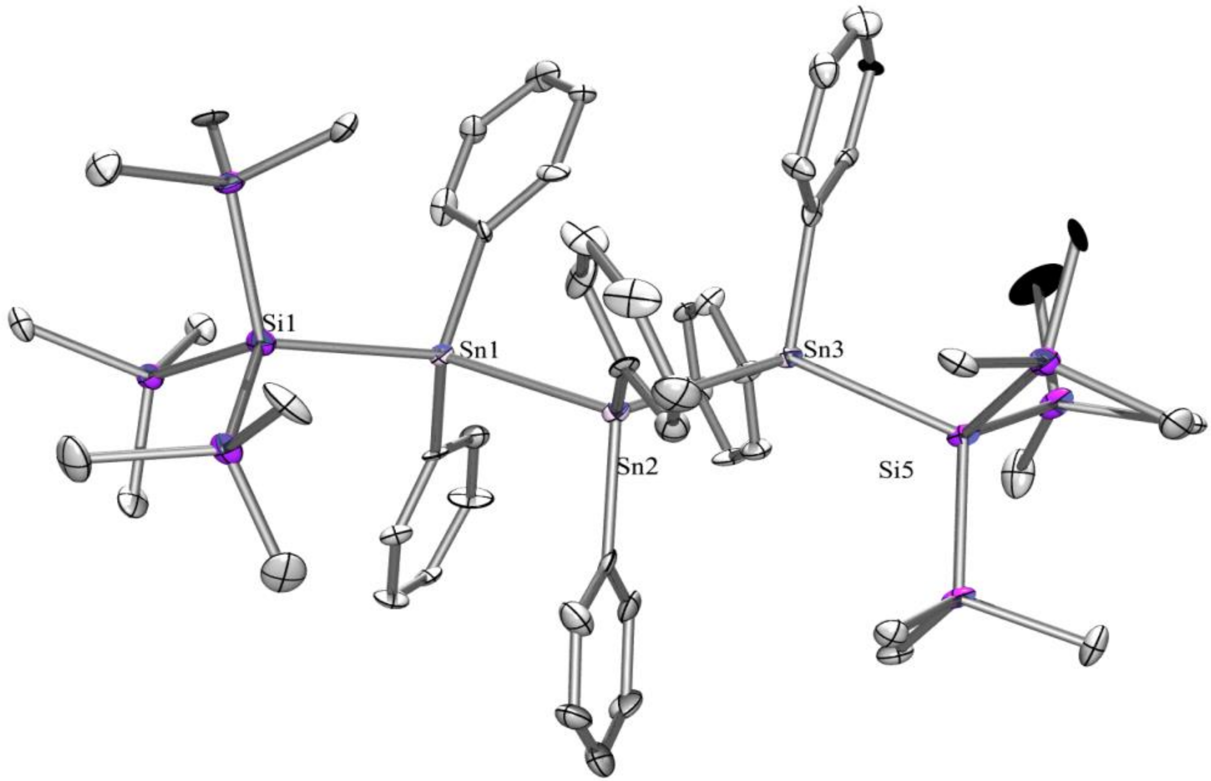
Figure 2-7: Structure of 1,2-bis(hypersilyl)tetraphenyldistannane (**80**).

Silicon-silicon bond lengths were in the usual range of ca. 2.35 Å, and also Sn-Si distances were comparable to measurements previously reported.[113,114] Sn-Sn bond is quite longer than Si-Si bonds in similar compounds as **46** and **70** (by ca. 0.23 Å). With respect to hexaphenyldistannane,[115] the Sn-Sn bond was elongated by ca. 0.05 Å.

---

[113] U. Englich, E. Hengge, U. Hermann, C. Marschner, K. Ruhlandt-Senge, F. Uhlig, *J. Organomet. Chem.*, **2000**, *605*, 22–27.
[114] F. Uhlig, C. Kayser, R. Klassen, U. Hermann, L. Brecker, M. Schuermann, K. Ruhland-Senge, U. Englich, *Z. Naturforsch.* , **1999**, *54b*, 278-287.
[115] D. Dakternieks, F. S. Kuan, A. Duthie, E.R.T. Tiekink, *Main Group Met.Chem.*, **2001**, *24*, 65-66.

It was possible to identify a by-product by mean of a different crystal shape, and the X-ray diffraction analysis revealed that it was 1,3-bis(hypersilyl)hexaphenyltristannane. The crystal structure is here shown (Figure 3-7), but no NMR data could be acquired of the pure compound due to the small amount of material and difficult separation from the main product.



Selected crystallographic data: Crystal system: monoclinic; Space group: P2(1)/n; Goodness-of-fit on F^2: 1.132; Bond lengths [Å]: Sn(1)-Sn(2) 2.8022 (15); Sn(2)-Sn(3) 2.8161 (14); Sn(1)-Si(1) 2.583(4); Sn(3)-Si(5) 2.608(4); Sn(1)-C 2.1565 (av.); Angles [deg]: Sn(1)-Sn(2)-Sn(3) 111.38 (4); Si(1)-Sn(1)-Sn(2) 123.01 (11); Sn(2)-Sn(3)-Si(5) 120.11 (9);

Figure 3-7: Structure of 1,3-bis(hypersilyl)hexaphenyltristannane (**87**).

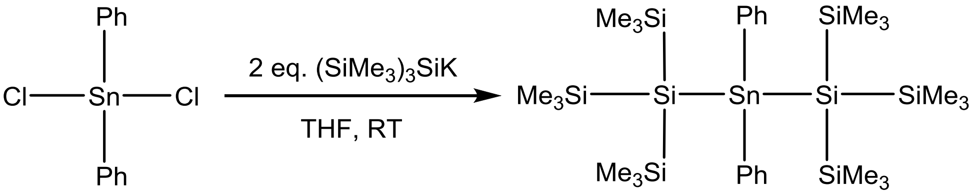
In this molecule Sn-Sn distances were slightly shorter than those of compound **80** by ca. 0.01 Å. The tin-silicon bond lengths were in the same range of distance (2.58-2.60 Å) of **80**, and Si-Si bonds traced the usual measure of ca. 2.35 Å. On the other hand, Si-Sn-Sn angles seemed quite large in respect to similar structures containing this fragment (Fischer et al.[116] reported a Si-Sn-Sn angle of 118.73° for compound $Me_2PhSi(Sn(t\text{-}Bu)_2)_2SiPhMe_2$).

---

[116] R. Fischer, T. Schollmeier, M. Schürmann, F. Uhlig, *Appl. Organometal. Chem.*, **2005**, *19*, 523–529.

7.2.2 Synthesis of 1,1-bis(hypersilyl)diphenylstannane (81)

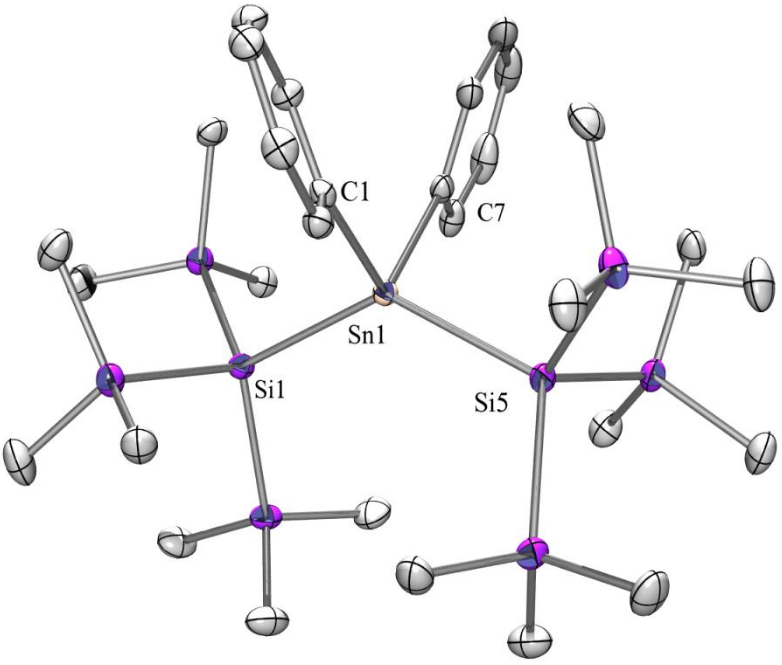
To have some references for the NMR data, this monostannane was prepared reacting dichlorodiphenylstannane with two equivalents of hypersilyl potassium (Scheme 3-7). In this case the reaction worked in THF as solvent.



81

Scheme 3-7: Synthesis of 1,1-bis(hypersilyl)diphenylstannane (**81**).

In the ^{29}Si NMR the chemical shifts for the $-SiMe_3$ groups and the quaternary silicon atoms were consistent with those of distannane **80**. Product **81** was crystallized from dichloromethane and its structure is here shown (Figure 4-7).



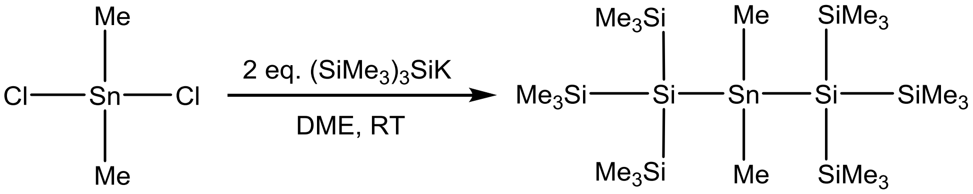
Selected crystallographic data:
Crystal system: monoclinic;
Space group: P2(1)/c;
Goodness-of-fit on F^2: 1.009
Bond lengths [Å]:
Sn(1)-Si(1)2.6071 (7)
Sn(1)-Si(5)2.6099 (8)
Sn(1)-Si(5) 2.608(4) Sn(1)-C(7) 2.1603 (19)
Angles [deg]:
Si(1)-Sn(1)-Si(5) 132.507 (17)
Si(5)-Sn(1)-C(7) 101.85 (6)
Si(2)-Si(1)-Sn(1) 110.02 (2)

Figure 4-7: Structure of bis(hypersilyl)diphenylstannane (**81**).

Silicon-tin bonds Si(1)-Sn(1) were slightly longer than those of the previous compounds **80** and **87** (Sn(1)-Si(1), same notation for both product), but always around the value of ca. 2.60 Å. Also Si-Si bonds and Sn-C bonds were nearly equal to those of products **80** and **87**. A very broad angle was measured for the Si-Sn-Si fragment, with a value of 132.5°. In this case, the phenyl groups were able to rotate and to arrange themselves almost perpendicularly to the Si-Sn-Si plane, so that the hypersilyl groups could minimize steric interactions.

7.2.3 Synthesis of 1,1-bis(hypersilyl)dimethylstannane (82)

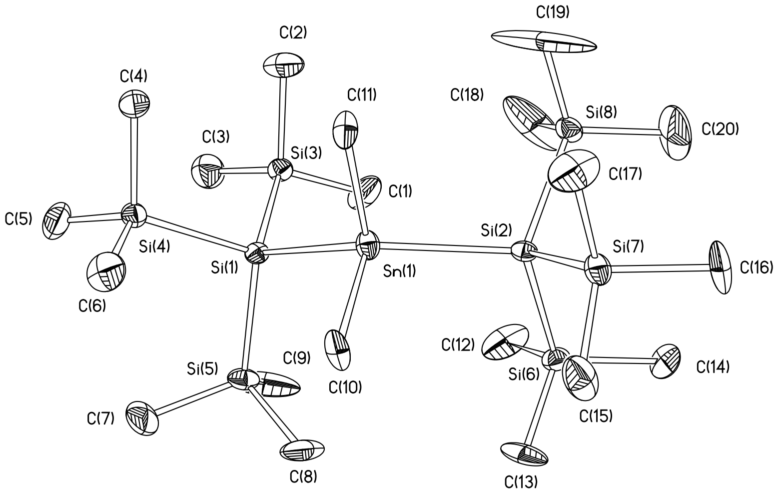
Compound **82**[117] was prepared as NMR reference and for subsequent UV studies and comparisons (Scheme 4-7).



82

Scheme 4-7: Synthesis of 1,1-bis(hypersilyl)dimethylstannane (**82**).

Product **82** was previously crystallized by H. Wagner.[118] The structure and main crystallographic data are here shown for following discussion (Figure 5-7).



Selected crystallographic data:
Crystal system: monoclinic;
Space group: P2(1)/c;
Goodness-of-fit on F^2: 1.009
Bond lengths [Å]:
Sn(1)-Si(1)2.611 (3)
Sn(1)-Si(5)2.351 (4)
Sn(1)-C(n) 2.2035 (av.)
Angles [deg]:
Si(1)-Sn(1)-Si(2) 128.29 (3)
Si(1)-Sn(1)-C(10) 104.7 (3)
Si(5)-Sn(1)-Si(1) 110.90 (13)

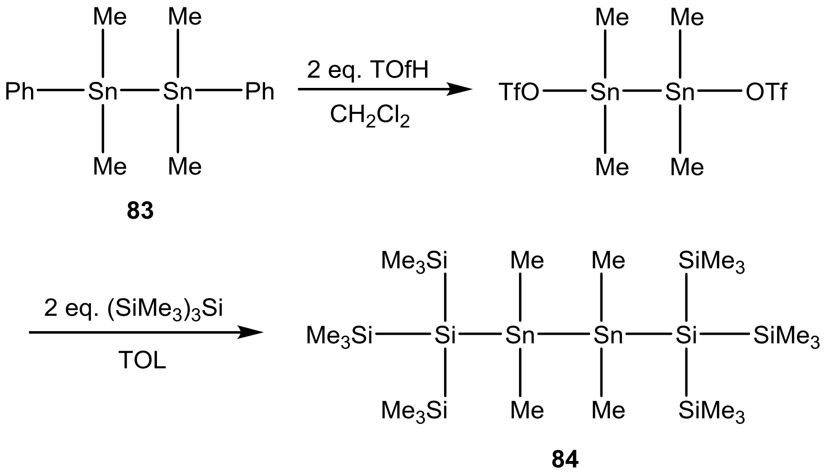
Figure 5-7: Structure of bis(hypersilyl)diphenylstannane (**82**).

---

[117] S. P. Mallela and al., *Inorg.Chem.*, **1990**, *29*, 3525-3528.
[118] H. Wagner, *unpublished results*

7.2.4 Synthesis of 1,2-bis(hypersilyl)tetramethyldistannane (84)

This compound was prepared reacting two equivalent of tris(trimethylsilyl)silyl potassium with one equivalent of the ditriflate derived from $(PhMe_2Sn)_2$ (**83**) (Scheme 5-7).



83

84

Scheme 5-7: Synthesis of 1,2-bis(hypersilyl)tetramethyldistannane (**84**).

The ^{29}Si NMR is shown in Figure 6-7. Due to the $-SnPh_2-$ units the signal of the quaternary silicon atoms were quite high-field shifted (ca. -129 ppm against -116 ppm for products **80** and **81**, see Table 1-7 for a summary of chemical shifts of all these compounds). Probably in the case of methyl groups the higher electronegativity of carbon in respect to tin was balanced by the typical inductive effect of these substituents. As a consequence, the chemical shift of the adjacent silicon remained around its common value of ca. -130 ppm. On the other hand, phenyl groups might drain electron density from the tin atom through 2*p*/4*d* orbital interaction and as a result the next silicon was deshielded and its NMR signal appeared at lower field.

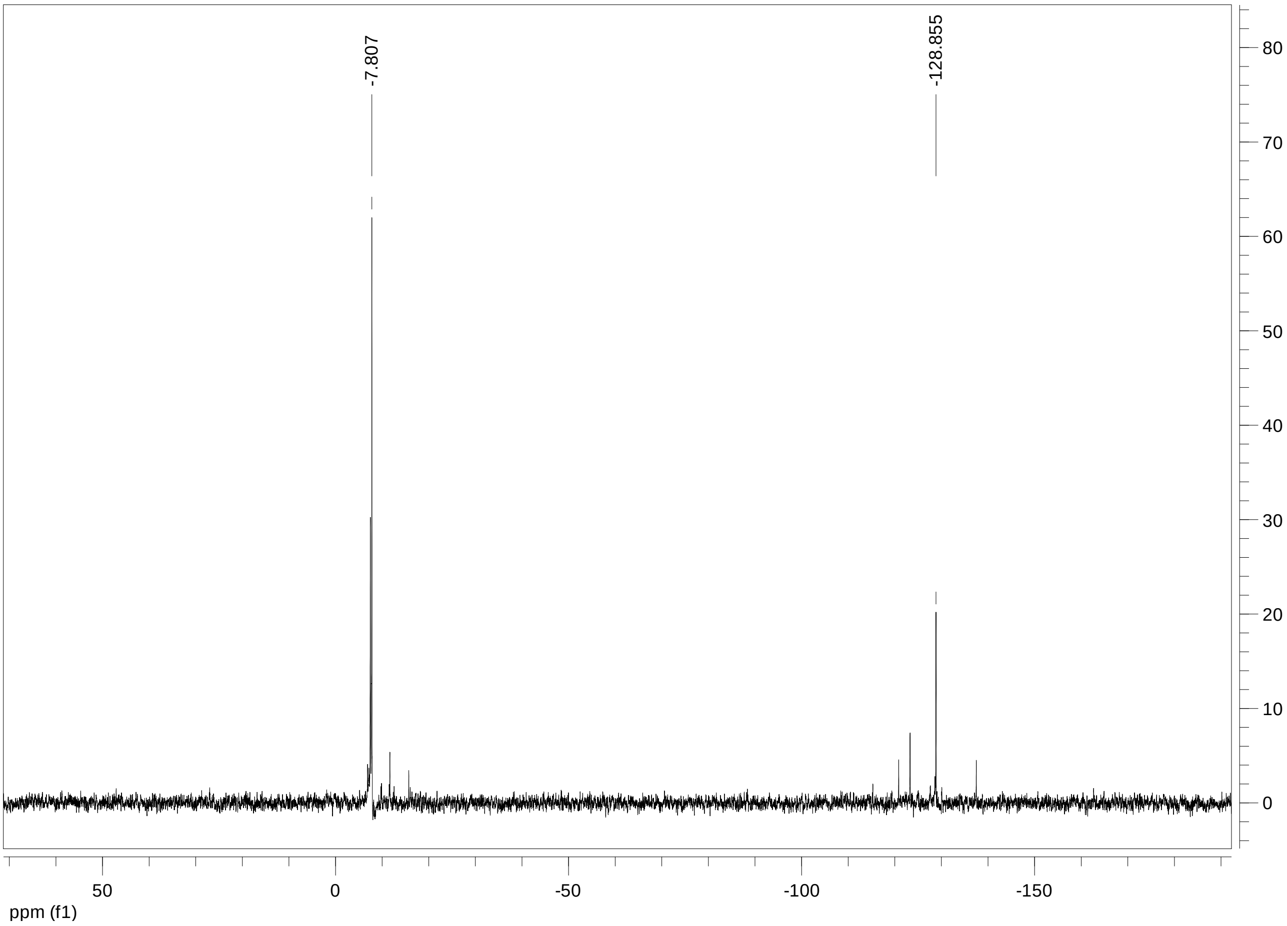
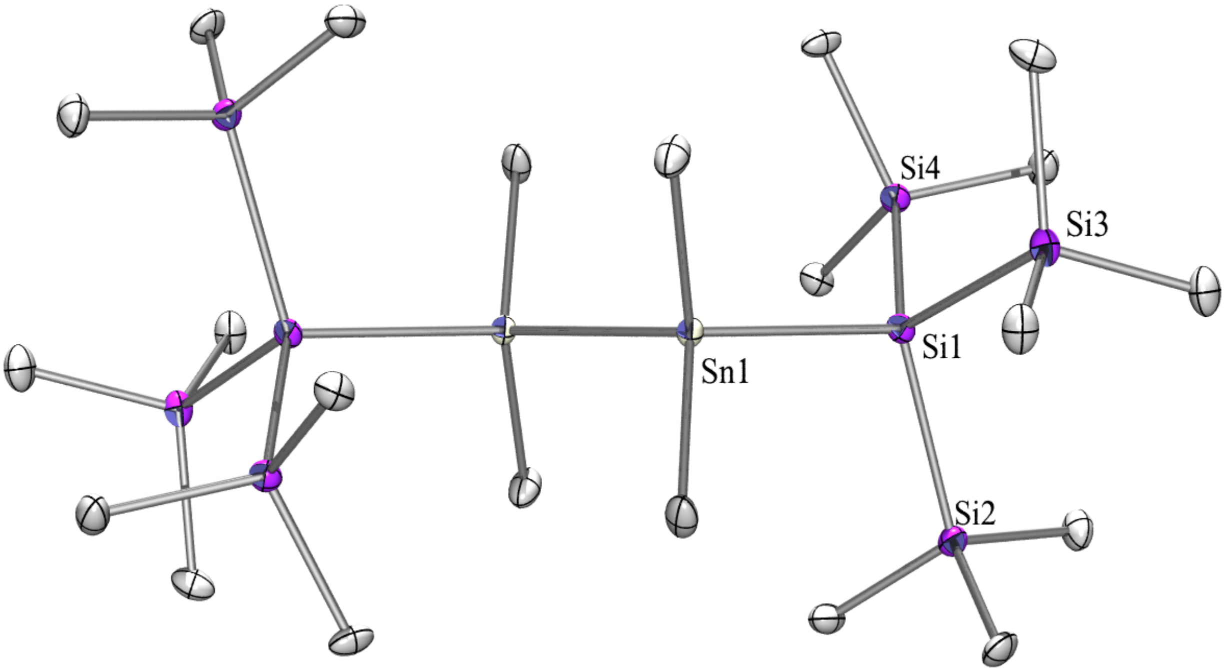


Figure 6-7: ^{29}Si NMR of the worked up product **84**.

This phenomenon was generally evident also in the ^{119}Sn NMR spectra. Phenylated -$SnPh_2$- and -$(SnPh_2)_2$- groups showed low-field shifted NMR signals for tin, in comparison with methylated -$SnMe_2$- and -$(SnMe_2)_2$- units (see Table 1-7 for detailed NMR data).

Suitable crystals for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution of the product (Figure 7-7).



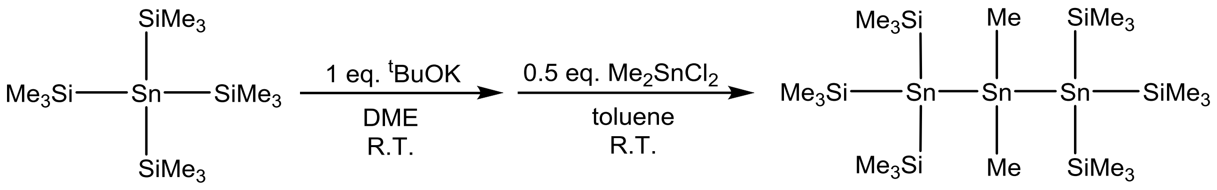
Selected crystallographic data: Crystal system: triclinic; Space group: P-1; Goodness-of-fit on F^2: 1.088; Bond lengths [Å]: Sn(1)-Sn(1)# 2.7950 (13); Sn(1)-Si(1) 2.579(3); Sn(1)-C 2.1755 (av.); Si(1)-Si(4) 2.344 (3). Angles [deg]: Si(1)-Sn(1)-Sn(1)# 116.47 (6); Sn(1)-Si(1)-Si(2) 109.20 (10); C(10)-Sn(1)-Si(1) 108.30 (3).

Figure 7-7: Structure of product **84**.

Tin-tin bond length was shorter than that of compound **80** by ca. 0.025 Å and also the Sn-Si distance was lowered by ca. 0.020 Å. Compound **84** showed an angle between Si-Sn-Sn atoms 3° less wide than the phenylated product **80**.

7.2.5 Synthesis of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-dimethyltristannane (85)

To have a higher number of tin atoms into the backbone of the molecule, compound **85** was synthesized starting from tetrakis(trimethylsilyl)stannane and dimethyldichlorostannane (Scheme 6-7).



85

Scheme 6-7: Synthesis of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-dimethyltristannane (**85**).

One main signal was detected in the ^{29}Si NMR at ca. -7 ppm (Figure 8-7). Slow evaporation of a solution in dichloromethane led thin colorless plates suitable for X-ray analysis (Figure 9-7).

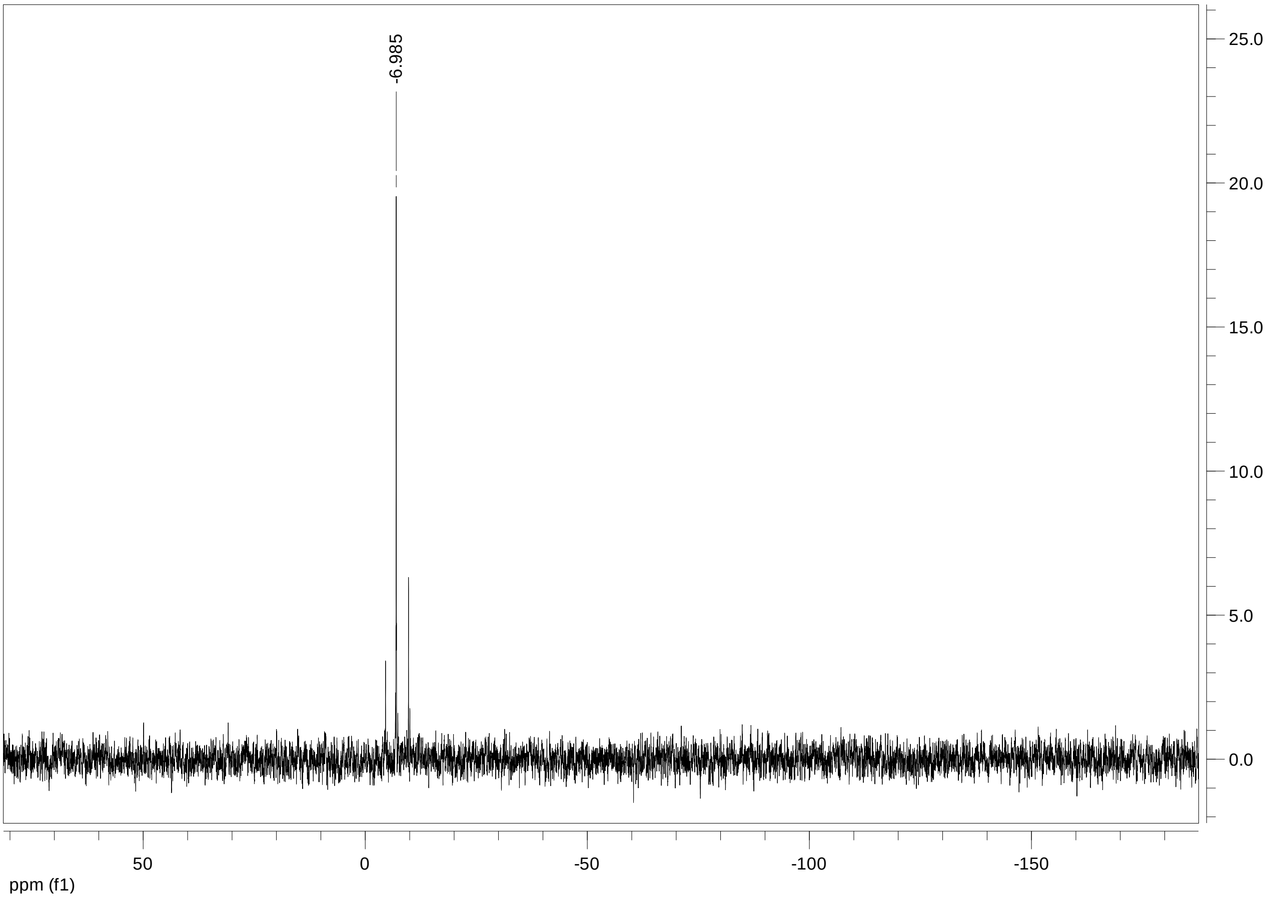
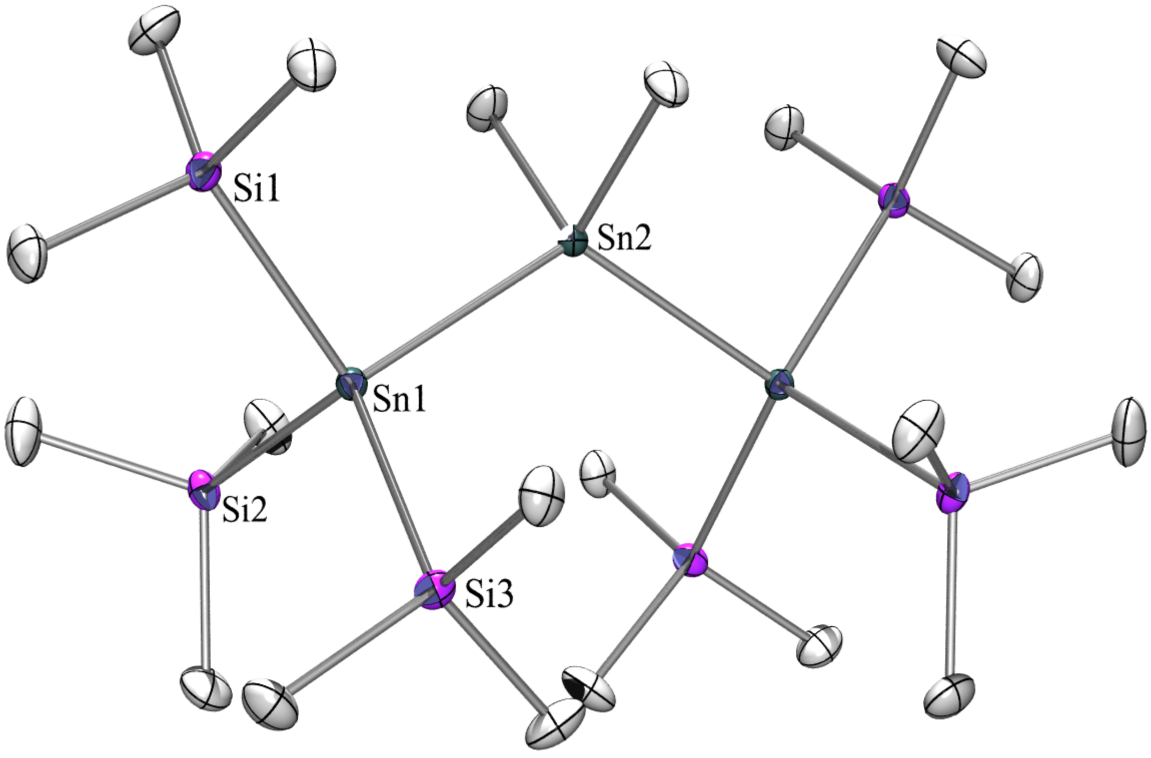


Figure 8-7: ^{29}Si NMR of the reaction mixture before workup of compound **85**.



Selected crystallographic data: Crystal system: monoclinic; Space group: C2/c; Goodness-of-fit on F^2: 1.063; Bond lengths [Å]: Sn(1)-Sn(2)2.7871 (6); Sn(2)-Sn(1)# 2.7871(6); Sn(1)-Si(1) 2.5728 (8); Sn(2)-C(10) 2.179 (3). Angles [deg]: Sn(1)-Sn(2)-Sn(1)# 122.946 (18); Si(1)-Sn(1)-Sn(2) 105.02 (2); Si(2)-Sn(1)-Sn(2) 110.40 (3); Si(1)-Sn(1)-Si(2) 107.86 (3)

Figure 9-7: Crystal structure of product **85**.

In this molecule tin-tin bond lengths were the shortest ones observed, with a difference of ca. 0.04 Å from compound **80**, ca. 0.02 Å from compound **87** and ca. 0.01 Å from compound **84**. The Sn-Sn-Sn angle was quite narrowed in respect to that one measured in compound **82** (ca. 5° greater) and that one measured in compound **81** (ca. 9° greater).

For an easier comparison between all these molecules, their respective starting materials and other similar compounds, the silicon and tin NMR data are collected in the following Table 1-7:

Stannane	**^{29}Si NMR, -*Si*Me$_3$ (ppm)**	**^{29}Si NMR, Si$_n$*Si*Sn$_{4-n}$ (ppm)**	**^{119}Sn NMR (ppm)**
$SnCl_2Ph_2$[112]	---	---	-26.4
$SnPh_4$[119]	---	---	-127.0
Sn_2Ph_6[112]	---	---	-143.6
$HypSnPh_3$	-8.0	-131.6	-114.4
Hyp($SnPh_2$)Hyp	-7.6	-116.8	-174.3
Hyp(Sn_2Ph_4)Hyp	-7.6	-116.7	-113.8
TMS(Sn_2Ph_4)TMS[9] (*****)	-4.1	---	-227.1
Hyp($SnMe_2$)Hyp	-7.7	-123.7	-175.7
Hyp(Sn_2Me_4)Hyp	-7.8	-128.8	-206.0
$TMS_3Sn(SnMe_2)SnTMS_3$	-7.0	---	-276.5(Sn_q); -156.7($SnMe_2$)
$(SiMePh_2)_2$	---	-23.4	---
Hyp$(SiMePh)_2$Hyp	-9.4	-124	---

Table 1-7: Hyp = -Si$(SiMe_3)_3$. TMS = -$SiMe_3$. (*****)This compound was prepared as reported,[116] but our assignment of the chemical shifts was different from that one reported by the authors.

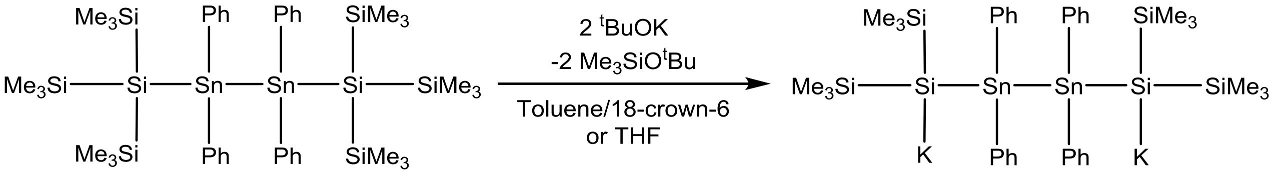
---

[119] Flock M., Pichler J., Torvisco A., Uhlig F., Zeppek C., *J. Organomet. Chem.*, **2013**, *740*, 41-49.

7.3 Reactions of phenylated and methylated organosilylstannanes

7.3.1 Synthesis of tetraphenyldistannane-1,2-bis(hypersilyl) dipotassium (88)

Substrate **80** was treated with two equivalents of potassium *tert*-butoxide, to check the reactivity of the -SiMe$_3$ groups (Scheme 7-7):



80 **88**

Scheme 7-7: Attempt to synthesize a disilanyldipotassium salt from compound **80**.

A first attempt was carried on using toluene as solvent, adding 18-crown-6 to favor subsequent crystallization of product **88**. However, the reaction was not clean and only a weak signal was observed in the ^{29}Si NMR for the silyl anion in its typical range between -170 to -200 ppm. The main signal for the quaternary silicon atom was found at ca. -140 ppm, only 24 ppm high-field shifted in respect to compound **80** (in the case of hypersilyl potassium the signal for *Si*-K is usually shifted of ca. -60 ppm).

The experiment was repeated with THF as solvent, and a clearer silicon spectrum was obtained (Figure 10-7). In the ^{29}Si NMR spectrum, one signal for the -SiMe$_3$ groups was observed, nearly unchanged in respect to the starting material. Again, the quaternary silicon was shifted by ca. 25 ppm towards high-field.

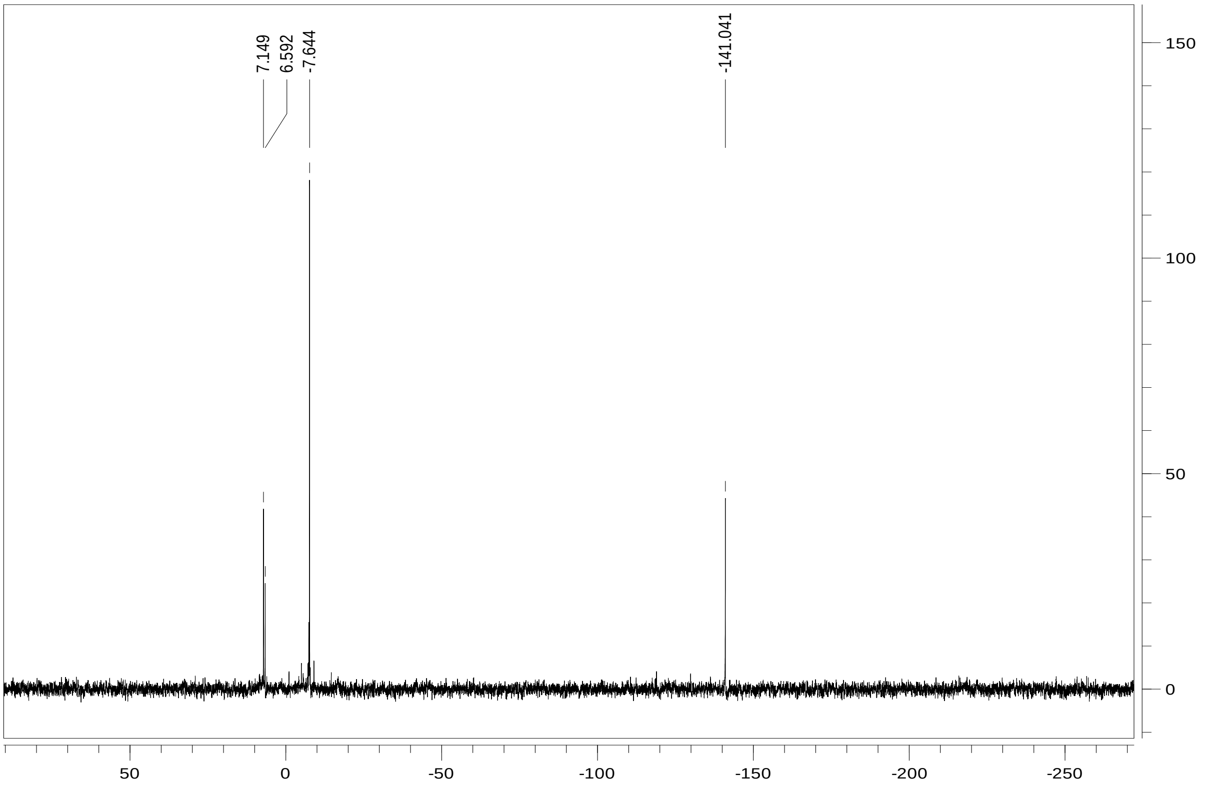


Figure 10-7: ^{29}Si NMR of the reaction mixture of compound **80** treated with ^{t}BuOK (in THF). Peak at 6.6 ppm of Me_3SiO*t*-Bu, peak at 7.1 ppm of $Me_3SiOSiMe_3$.

Despite the quite clean ^{29}Si NMR spectrum, the ^{119}Sn NMR analysis revealed two main signals (Figure 11-7).

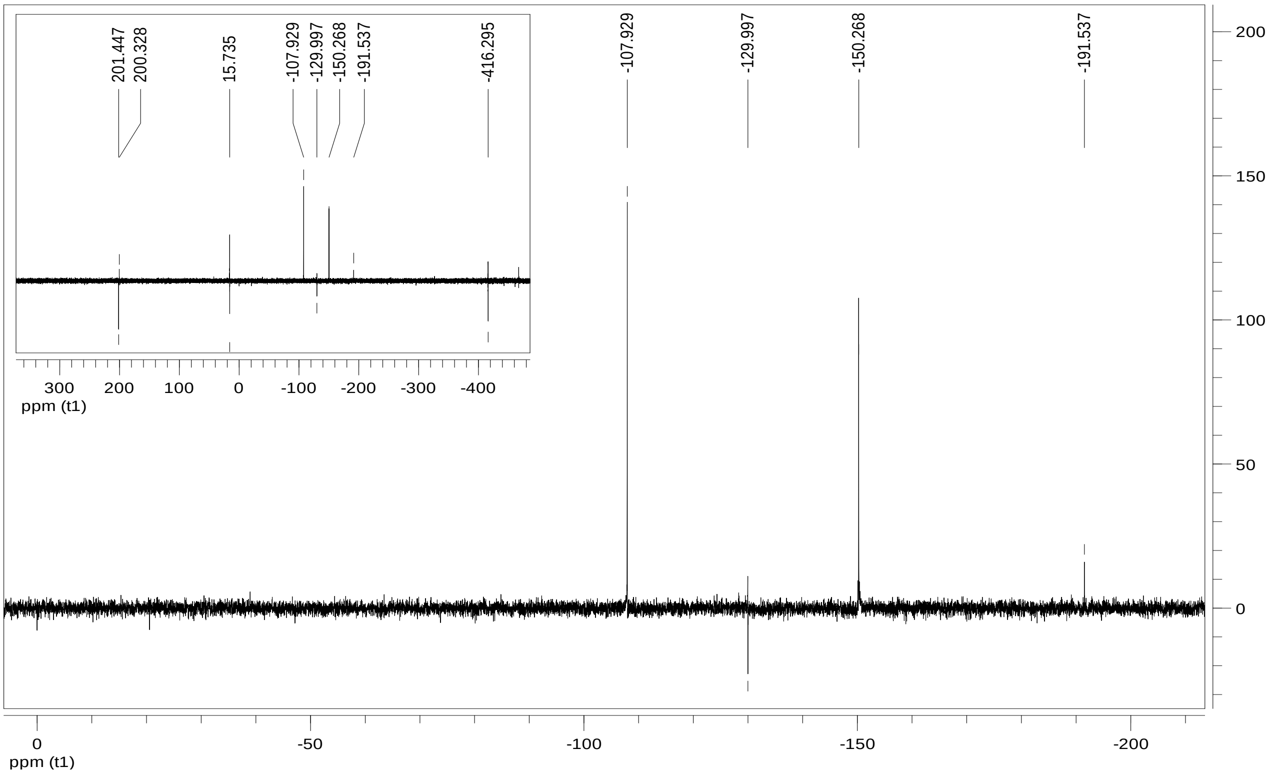


Figure 11-7: ^{119}Sn NMR of the reaction mixture containing the presumed product **88**.The region of interest is enlarged, but the full spectrum showed many signals and artifacts and it was not possible to phase it entirely.

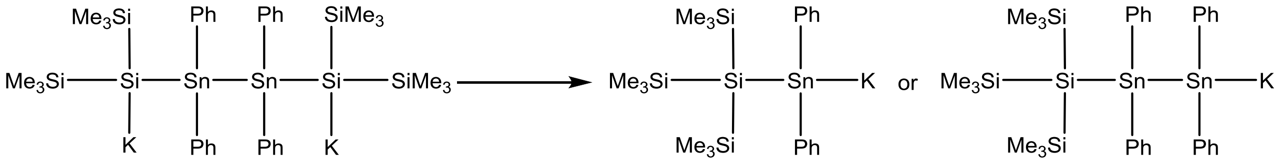
Because the tin-tin bond is not extremely strong, it might be happened that *t*-BuOK or the forming silyl anion attacked the -Ph_2Sn-$SnPh_2$- central unit. Then, a cation exchange could take place with the formation of a -Ph_2SnK fragment. Indeed, tin-alkaline metal salts are more stable than silicon ones, as it was already observed by Mori et al. in a simple experiment where $Bu_3SnSiMe_3$ was treated with CsF (Scheme 8-7).[120]

$$\mathrm{Bu_3Sn{-}SiMe_3} \xrightarrow[\text{DME or THF}]{\text{CsF}} \mathrm{Bu_3Sn{-}Cs} + \mathrm{SiMe_3{-}F}$$

Scheme 8-7: Preferential reaction path for the formation of a stannyl anion.

Then the signals in the ^{119}Sn might be explained as follow:

1. by the presence of side products as Ph_3SnK ($\delta(^{119}Sn) = -108.4$),[121]
2. by the formation of new substances from the self-reaction of compound **88**,
3. by the attack of potassium *tert*-butoxide at the tin-tin bond (Scheme 9-7).



88

Scheme 9-7: Preferential reaction path for the formation of a stannyl anion.

Nevertheless, from the ^{29}Si NMR it was evident that the first reaction step was the formation of the silyl ether due to the abstraction of a -$SiMe_3$ group by *t*-BuOK. In the case of the reaction in toluene/18-crown-6, the by-product $Me_3SiOSiMe_3$ was not forming in such a large amount. In addition, from the ^1H NMR only one set of multiplets was detected in the aromatic region, as if only one type of phenyl group were present in the product. Finally, only one main signal appeared for the methyl groups in the ^1H NMR (Figure 12-7).

To discover what would be the product of reaction in Scheme 7-7 and 9-7, it would be necessary to undergo a derivatization reaction and then analyzed the obtained neutral products.

---

[120] H. Sato, N. Isono, K. Okamura, T. Date, M. Mori, *Tetrahedron Lett*., **1994**, *35*, 2035-2038.

[121] U. Edlund, T. Lejon, P. Pyykko, T. K. Venkatachalam, E. Buncel, *J. Am. Chem. Soc*., **1987**, *109*, 5982-5985.

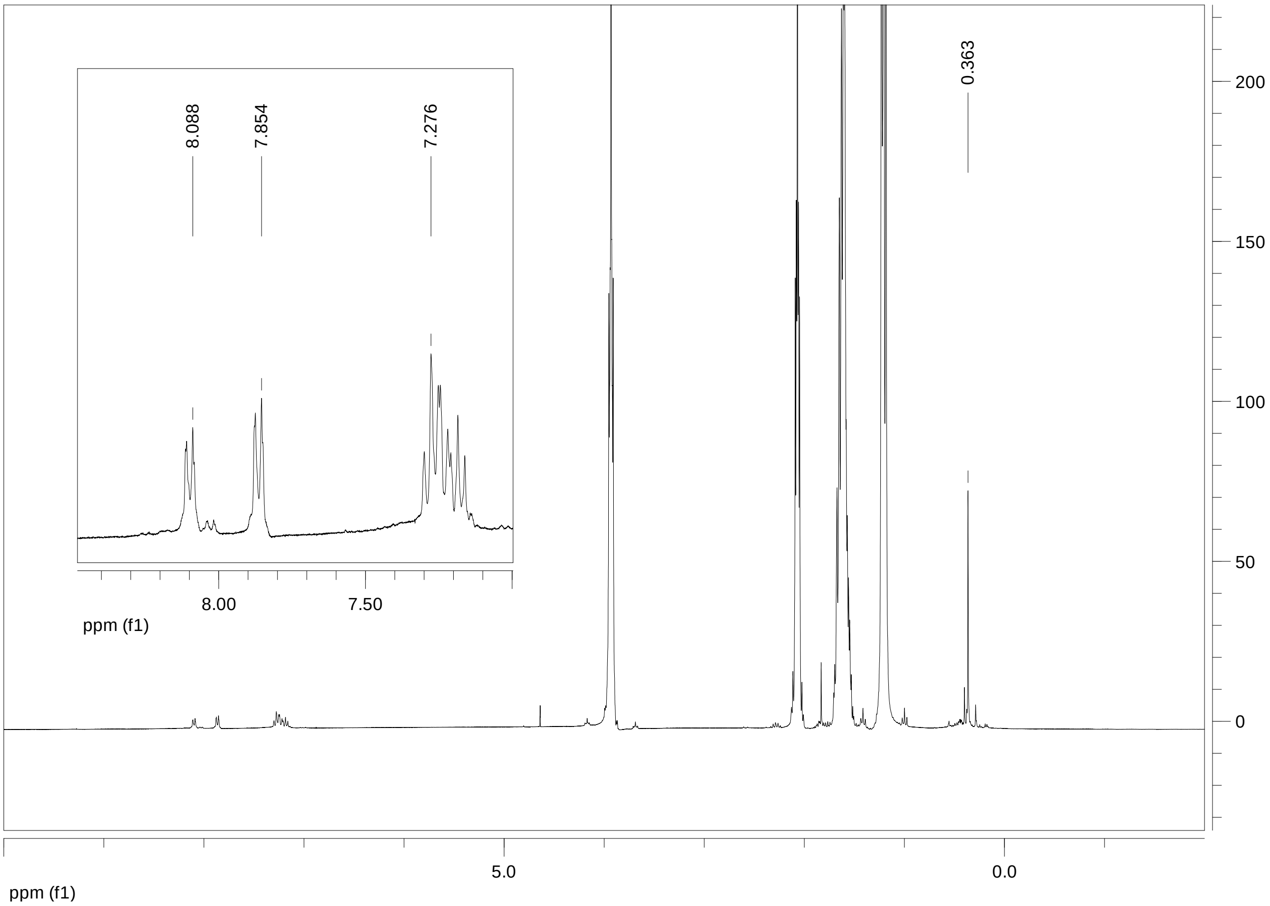
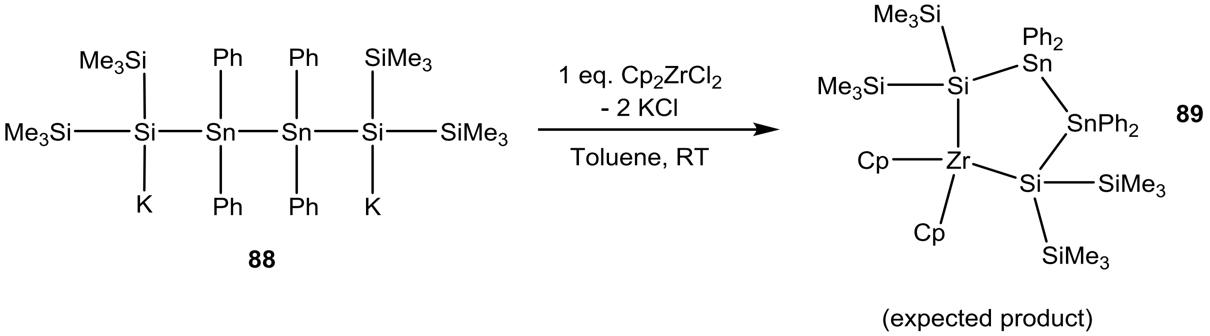


Figure 12-7: ^{1}H NMR of the product **88** in a THF/pentane mixture, during crystallization attempt.

The volume of the THF solution was reduced, pentane was added and the mixture was stored at -67°C. After three month, no crystal precipitated. Then the solution was checked by NMR (it was preserved) and completely dried. The residue was dissolved in toluene and stored again at -67°C.

7.3.2 Reaction between tetraphenyldistannane-1,2-bis(hypersilyl) dipotassium (88) and zirconocene dichloride

The supposed compound **88**, prepared in toluene and with18-crown-ether, was reacted with Cp_2ZrCl_2, in toluene at room temperature (Scheme 10-7). The ^{29}Si NMR spectrum of the reaction mixture is then shown (Figure 13-7).



Scheme 10-7: Derivatization reaction of dianion **88** with zirconocene dichloride.

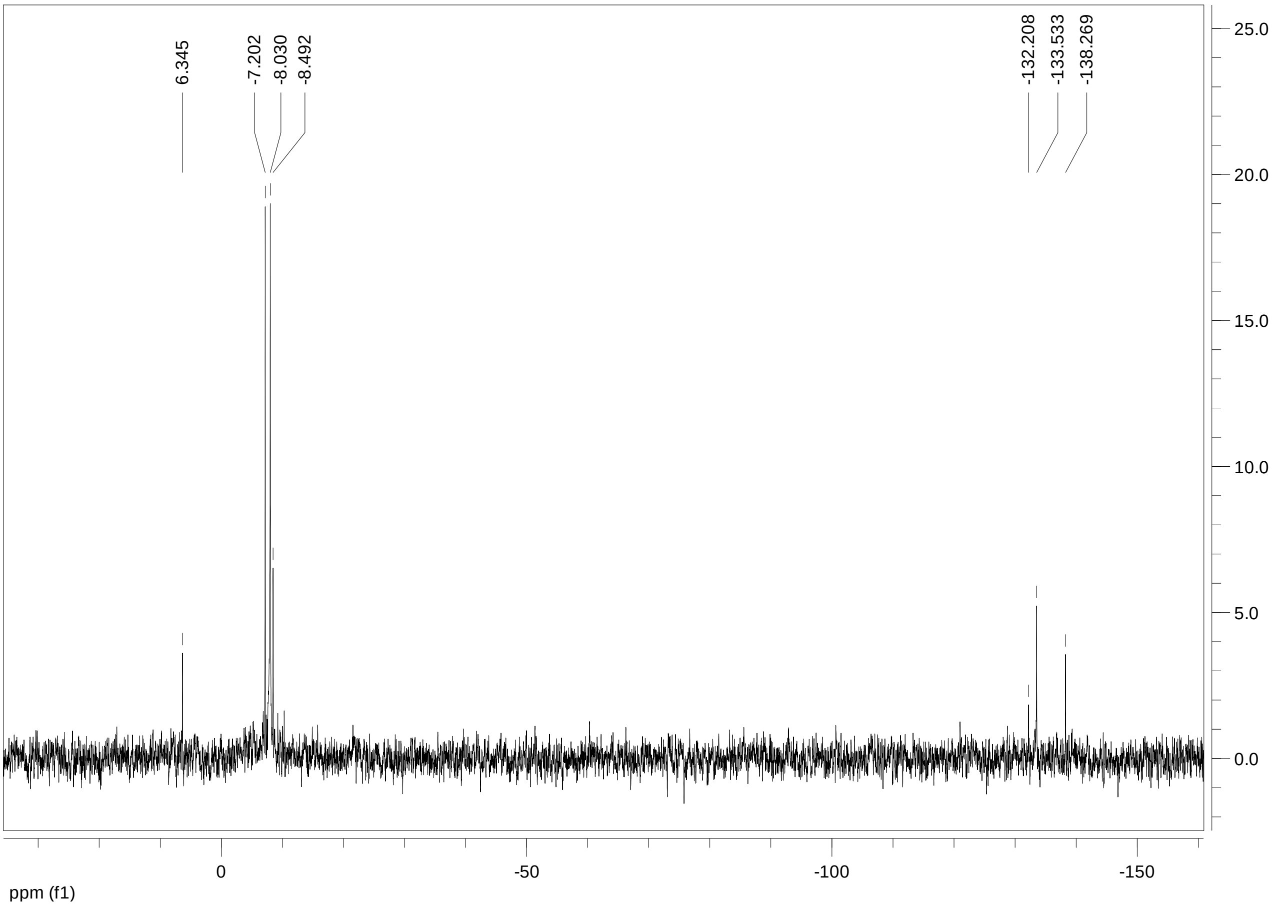


Figure 13-7: ^{29}Si NMR of the reaction mixture of compound **88** treated with zirconocene dichloride.

The starting material reacted completely, but the chemical shift of the silicon that should be bonded to zirconium and tin, left some doubts about the course of the reaction.

In similar compounds,[104] the signal of the silicon bonded to the zirconium atom presented the NMR signal down-field shifted of ca. 60 ppm, in respect to the corresponding oligosilane. Here the starting material had already a chemical shift of -116 ppm. The observed value (-133 ppm) seemed not consistent with literature[104] and the previous experiments.

Also the -$SiMe_3$ groups should give a signal at ca. -2 ppm, but in this case nearly the same value of the substrate was detected. In addition, the close peaks at -7.2 and -8.0 ppm could suggest some asymmetry in the molecule, but this was not observed in the case of the oligosilanyl zirconium heterocycle. For clarity, in Table 2-7 the measured chemical shifts and those ones of the cited reference[104] were reported.

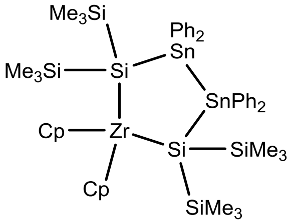
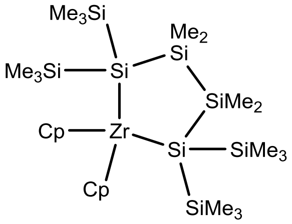
Zirconocene complex	**^{29}Si NMR, -*Si*Me$_3$ (ppm)**	**^{29}Si NMR, -*Si*Me$_2$- (ppm)**	**^{29}Si NMR, -*Si*Zr (ppm)**
	-7.2 , -8.0	---	-133.5 , (-138.3)
	-2.4	-29.2	-65.2

Table 2-7: ^{29}Si NMR chemical shifts of the presumed compound **89** and the oligosilanyl zirconium complex referenced.[104]

In the ^{119}Sn NMR the chemical shifts at -107 ppm and -150 ppm measured for compound **88** were disappeared, but no new clear peak was emerging and many artifacts gave high uncertainty for solving the spectrum (Figure 14-7).

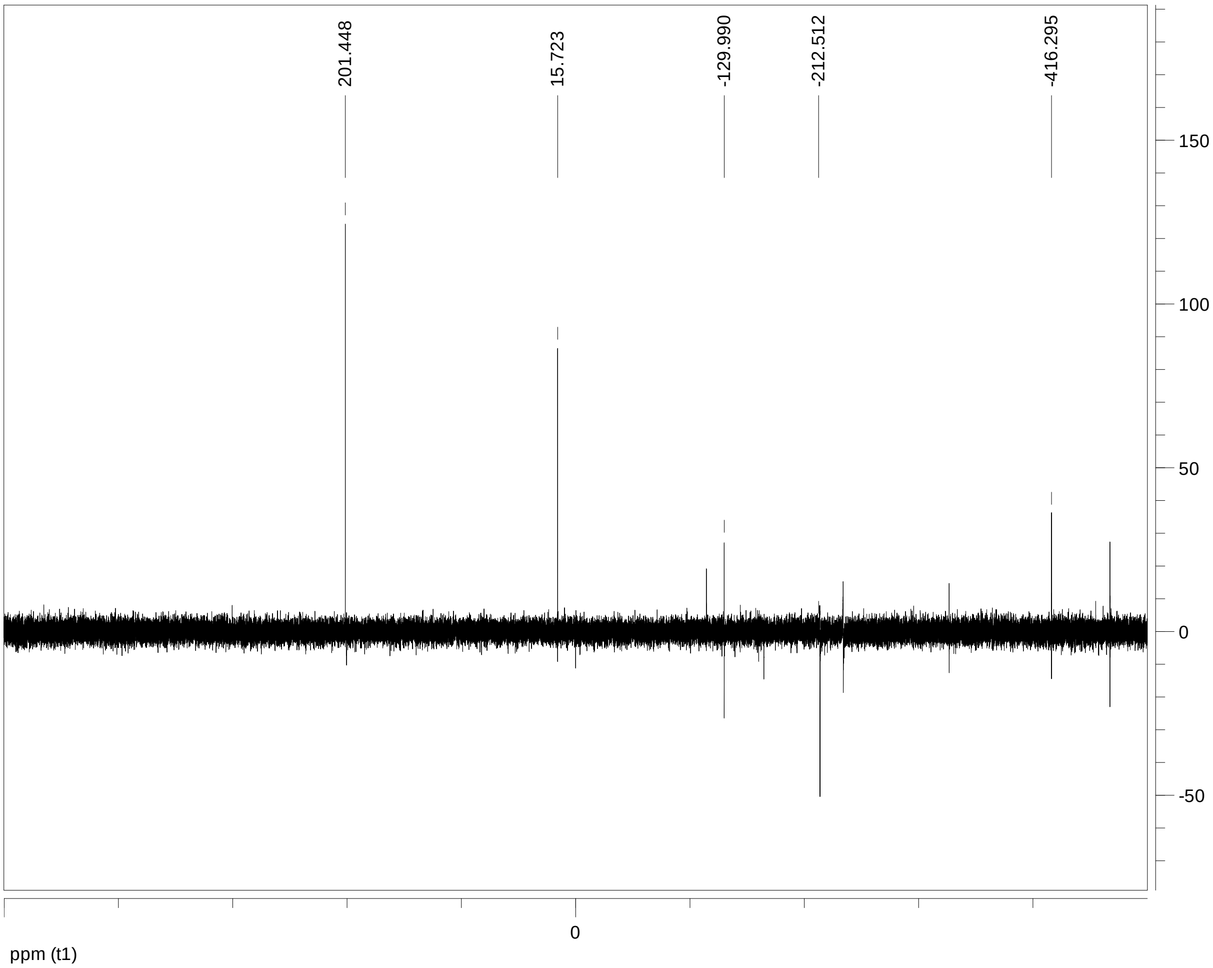
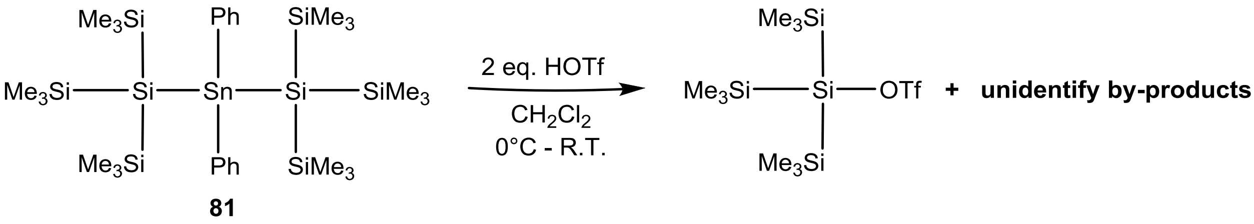


Figure 14-7: ^{119}Sn NMR of the reaction mixture of compound **88** treated with zirconocene dichloride.

7.3.3 Reaction of bis(hypersilyl)diphenylstannane (81) with triflic acid

To verify the possibility of introducing functional groups to the tin atom, compound **81** was treated with two equivalents of triflic acid. The expectation was to remove the phenyl groups, forming the ditriflate and then try the coupling with nucleophilic substrates (Scheme 11-7).



Scheme 11-7: Reaction of bis(hypersilyl)dimethylstannane (**81**) with triflic acid.

However, the formation of hypersilyltriflate was the preferred reaction path, with a quite clean conversion (Figure 15-7). It was not possible to determine the fate of the tin atom by ^{119}Sn NMR.

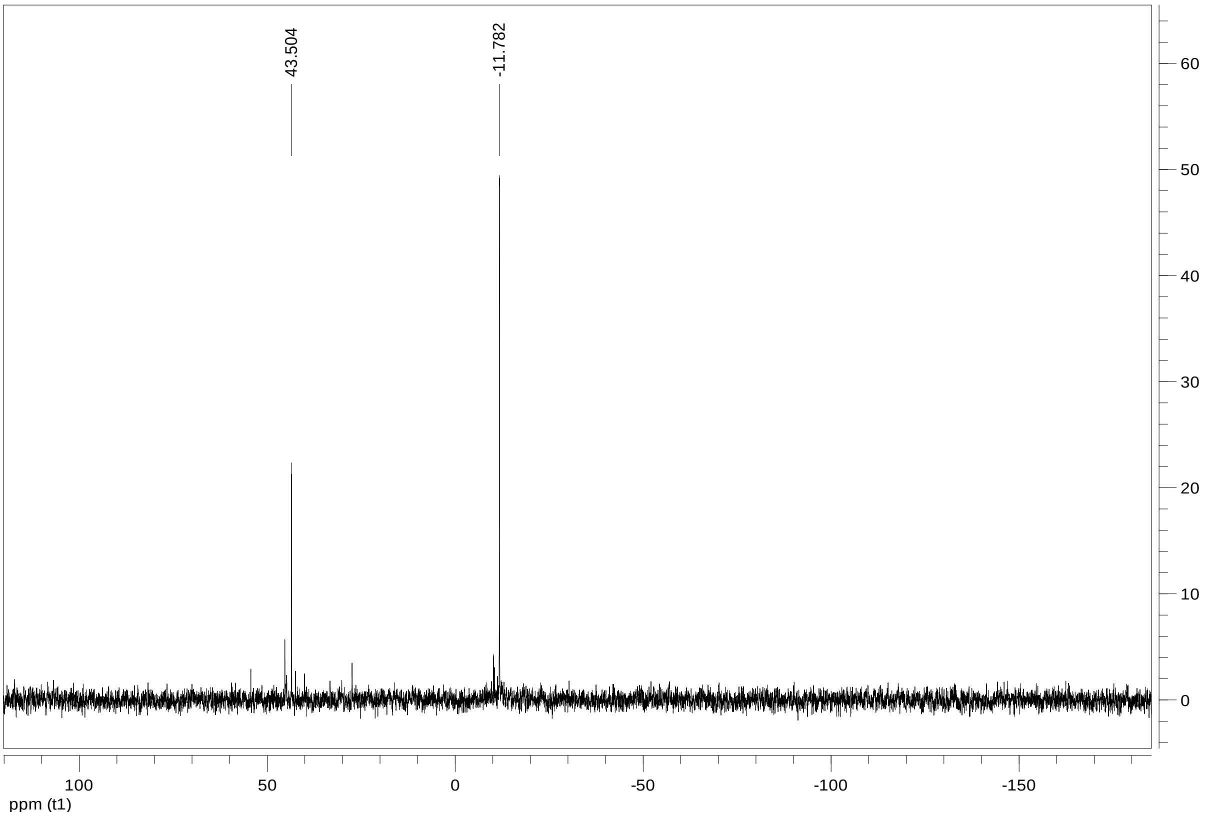
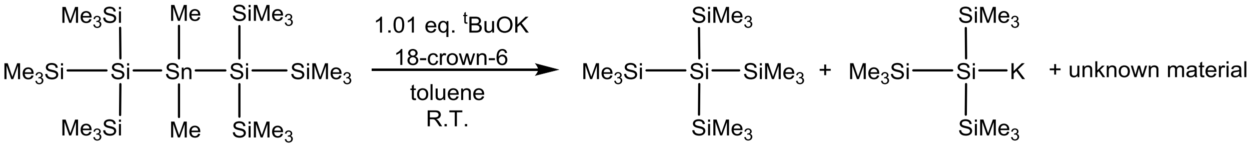


Figure 15-7: ^{29}Si NMR of the reaction between compound **81** and triflic acid: $(SiMe_3)_3SiOTf$ was the only product revealed by silicon NMR.

7.3.4 Attempt to react bis(hypersilyl)dimethylstannane (82) with potassium *tert*-butoxide

Compound **82** was treated with one equivalent of *t*-BuOK in toluene as solvent and in the presence of 18-crown-6 (Scheme 12-7).



82

Scheme 12-7: Reaction of bis(hypersilyl)dimethylstannane (**82**) with potassium *tert*-butoxide.

After 12 hours of reaction, the ^{29}Si NMR revealed a complex mixture, in which different products can be identified (Figure 16-7). It seemed that potassium *tert*-butoxide cleanly abstract a -SiMe$_3$ group (signal at 6.3 ppm for the silyl ether *t*-BuOSiMe$_3$). But then a rearrangement/decomposition occurred with the formation of tetrakis(trimethylsilyl)silane (**1**) (peaks at -136.1 ppm and -10.3 ppm) and the hypersilyl anion (-193.5 ppm, -4.5 ppm). It might be that the unusual signals at -170 ppm and -148 ppm correspond to the quaternary silicon atoms of the desired product. The asymmetry of the molecule should therefore determines the numbers of peaks in the –SiMe$_3$ region (-8 to -2 ppm). To solution pentane was added and stored at ca. -67°C, but no crystal or precipitate could be recovered.

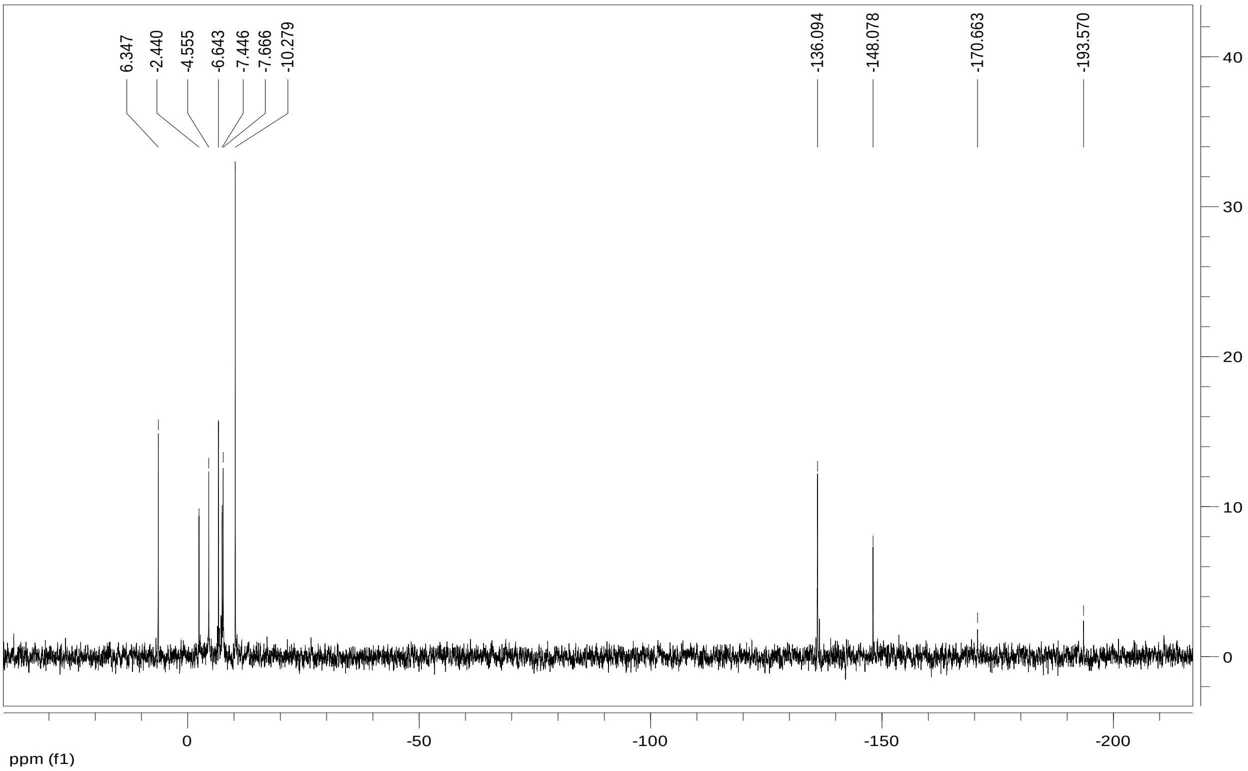


Figure 16-7: ^{29}Si NMR of the reaction mixture of compound **82** treated with ^{t}BuOK.

7.4 UV studies of hypersilylated organosilylstannane

Most of the compounds synthesized and presented before in this chapter were characterized by UV spectroscopy. These analyses revealed bands of absorption between 250 and 310 nm, due to the delocalization of the sigma bond electrons. This phenomenon is well known and documented for similar structures based on silicon and/or germanium atoms,[122,123] but here it was found that the presence of chained silicon/tin atoms could enhance the bathocromic effect usually observed for organosilanes or organogermanes.

In the next figures, the most interesting spectra will be shown, together with significant bond lengths.

---

[122] A. Wallner, H. Wagner, J. Baumgartner, C. Marschner, H. W. Rohm, M. Köckerling, C. Krempner, *Organometallics*, **2008**, *27*, 5221–5229.

[123] J. Hlina, R. Zitz, F. Stella, H. Wagner, J. Baumgartner, C. Marschner, *Inorg. Chim. Acta.*, **2014**, *422,* 120-133.

7.4.1 UV measurements for bis(hypersilyl)dimethylstannane (82)

The UV spectrum was acquired in a diluted solution of compound **82** in pentane. A band of absorption was registered and its maximum was detected at ca. 260 nm (Figure 17-7).

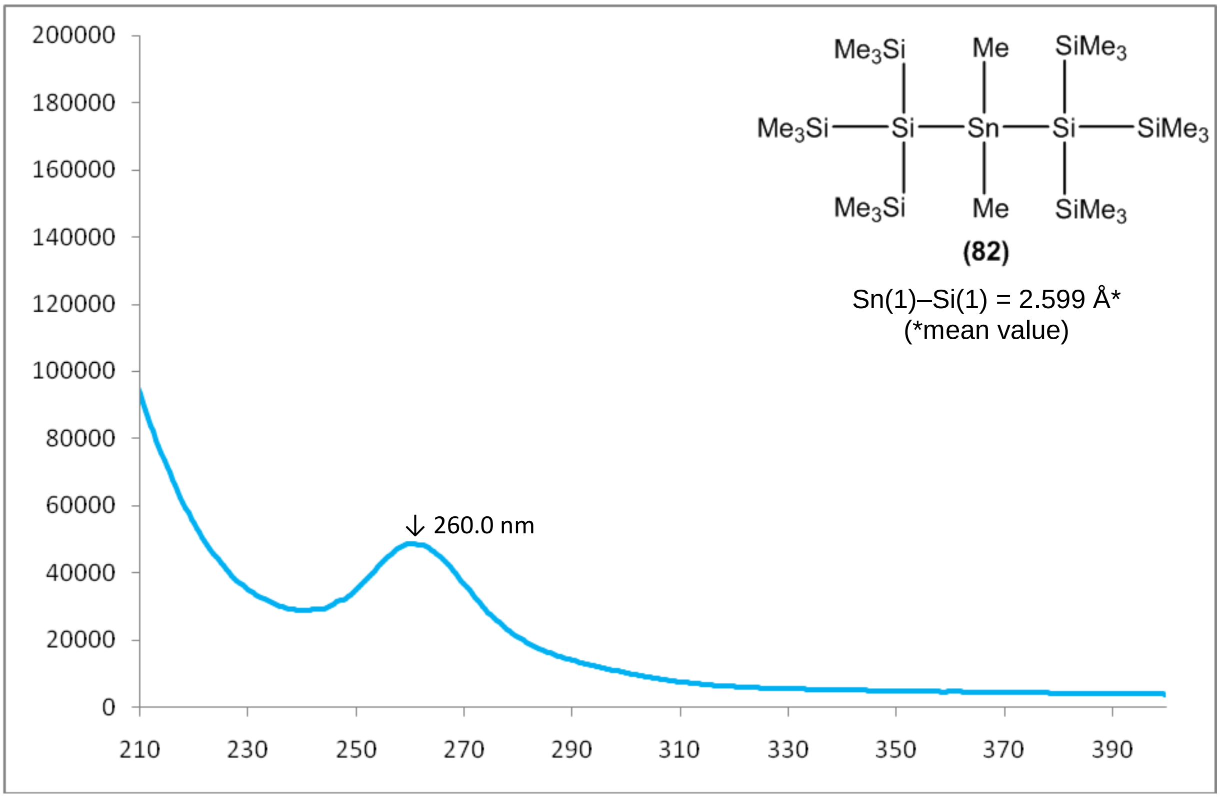


Figure 17-7: UV spectrum of compound **82**; ε = $1.033 \cdot 10^{-5}$ $Mol^{-1}cm^{-1}$; Λ_{max} = 285.5 nm.

The correspondent compound having only silicon atoms in the backbone (bis(hypersilyl)dimethylsilane), showed a bathochromic shift of 245 nm.[122] For compound **82** a red-shift of ca. 15 nm was observed.

7.4.2 UV measurements for 1,1,1,3,3,3-hexakis(trimethylsilyl)dimethyltristannane (85)

The UV spectrum was acquired of a diluted solution of compound **85** in pentane. A band of absorption was registered and its maximum was detected at ca. 285 nm (Figure 18-7)

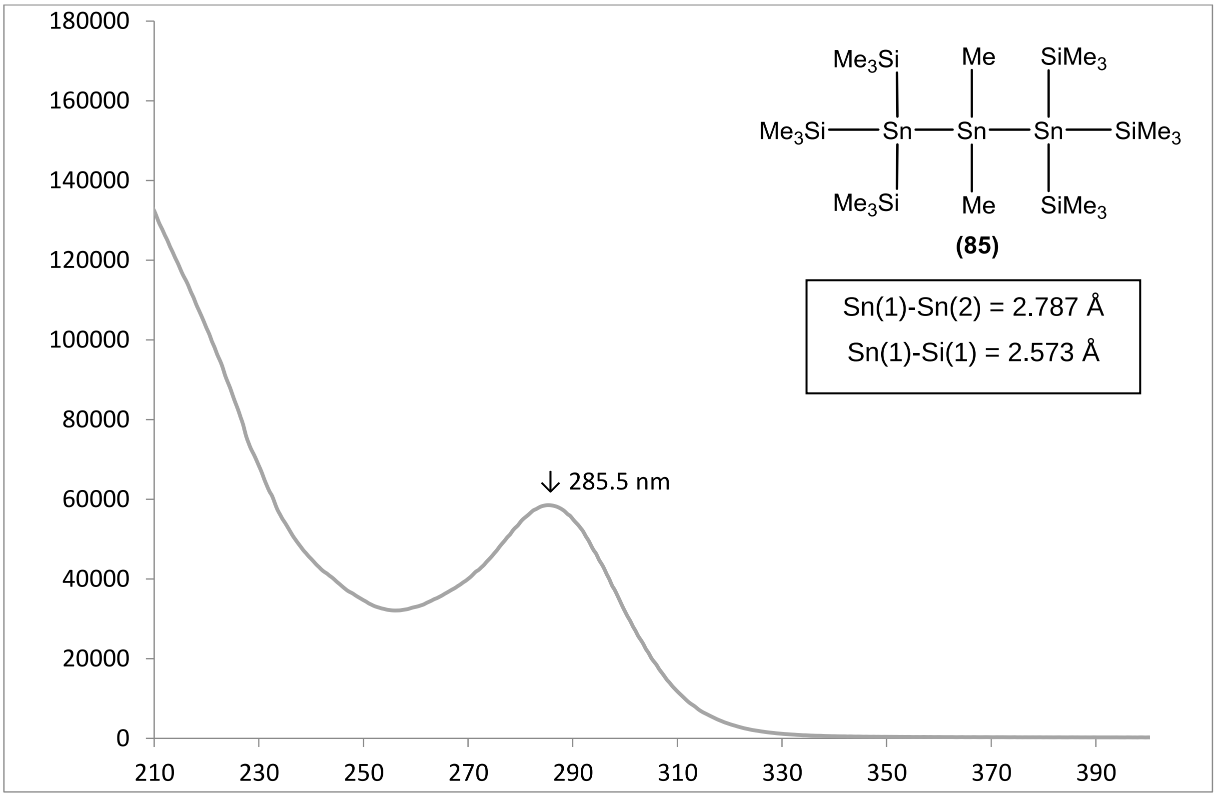


Figure 18-7: UV spectrum of compound **85**; ε = $1.001 \cdot 10^{-5}$ $Mol^{-1}cm^{-1}$;λ_{max} = 285.5 nm.

In this case, the presence of three tin atoms in the backbone chain caused a red shift of 15 nm in comparison to compound **82** and a red shift of 30 nm with respect to bis(hypersilyl)dimethylsilane.[122]

7.4.3 UV measurements for 1,2-bis(hypersilyl)tetramethyldistannane (84)

The UV spectrum was acquired of a diluted solution of compound **84** in pentane. A band of absorption was registered and its maximum was detected at ca. 279 nm (Figure 19-7).

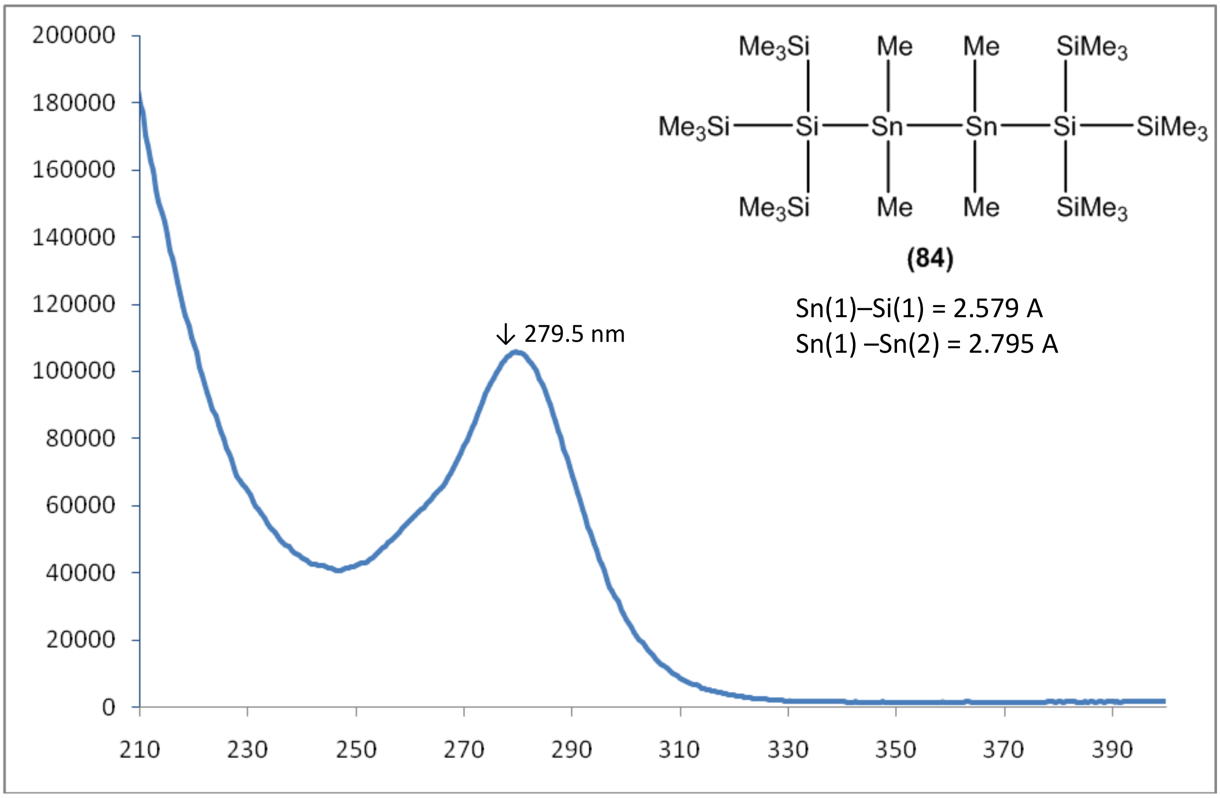


Figure 19-7: UV spectrum of compound **84**; ε = $2.774 \cdot 10^{-6}$ $\mathrm{Mol^{-1}cm^{-1}}$; λ_{max} = 279.5 nm

In respect to the organosilanes **70**, compound **84** revealed a red-shift of the absorption band by ca. 25 nm. However, despite the longer main tin/silicon chain, compound **84** showed a slightly blue-shift in comparison to the tristannane **85** by ca. 6 nm.

7.4.4 UV measurements for 1,1,1,3,3,3-hexakis(trimethylsilyl)dipjenylstannane (81)

The UV spectrum was acquired of a diluted solution of compound **81** in pentane. A small group of bands of absorption was registered, and its maximum was detected at ca. 279 nm (Figure 20-7).

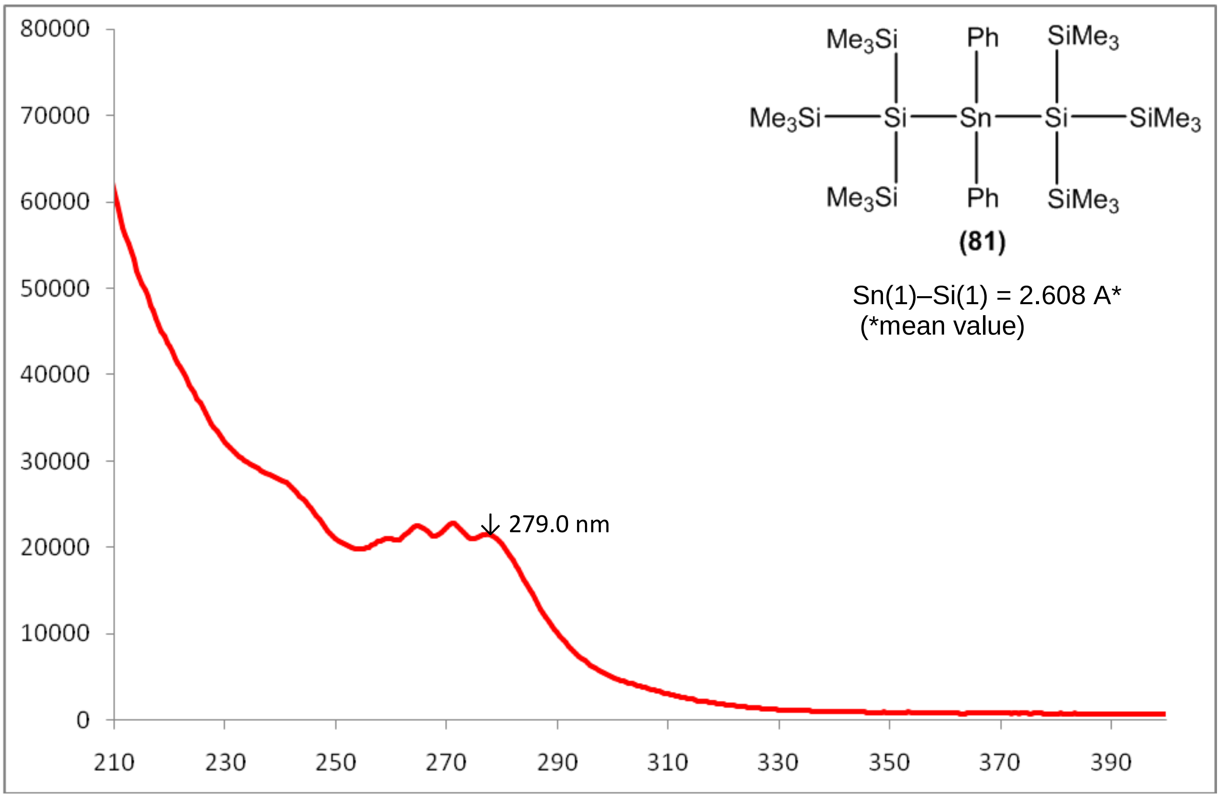
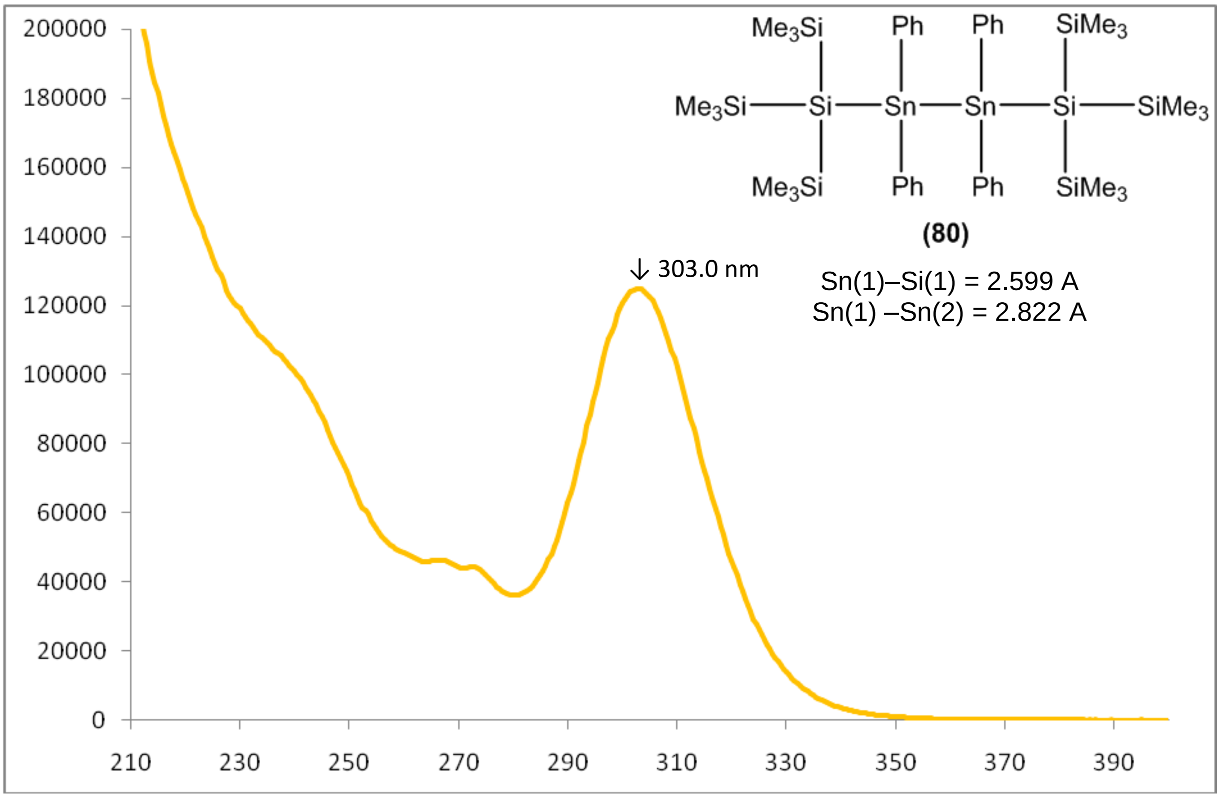


Figure 20-7: UV spectrum of compound **81**; $\varepsilon = 1.075 \cdot 10^{-5}$ $Mol^{-1}cm^{-1}$; $ʎ_{max}$ = 279.0 nm.

In this case, the phenyl groups gave a strong bathochromic effect and the band of absorption was shifted by ca. 20 nm towards the red light in comparison to the permethylated compound **82**.

7.4.5 UV measurements for 1,2-bis(hypersilyl)tetraphenyldistannane (80)

The UV spectrum was acquired of a diluted solution of compound **80** in pentane. Strong bands of absorption were registered, and the maximum was detected at 303 nm (Figure 21-7).



Sn(1)–Si(1) = 2.599 A
Sn(1) –Sn(2) = 2.822 A

Figure 21-7: UV spectrum of compound **80**; $\varepsilon = 7.933 \cdot 10^{-6}$ $\mathrm{Mol^{-1}cm^{-1}}$; $\lambda_{max} = 303.0$ nm.

For product **80** the joined effect of the phenyl groups and the tin atoms in the structure gave a bathochromic effect of ca. 20 nm in comparison to permethylated compound **84** and of ca. 45 nm in respect to organosilanes **70**.

7.4.6 Conclusions

The superposition of all these spectra is then shown in Figure 22-7:

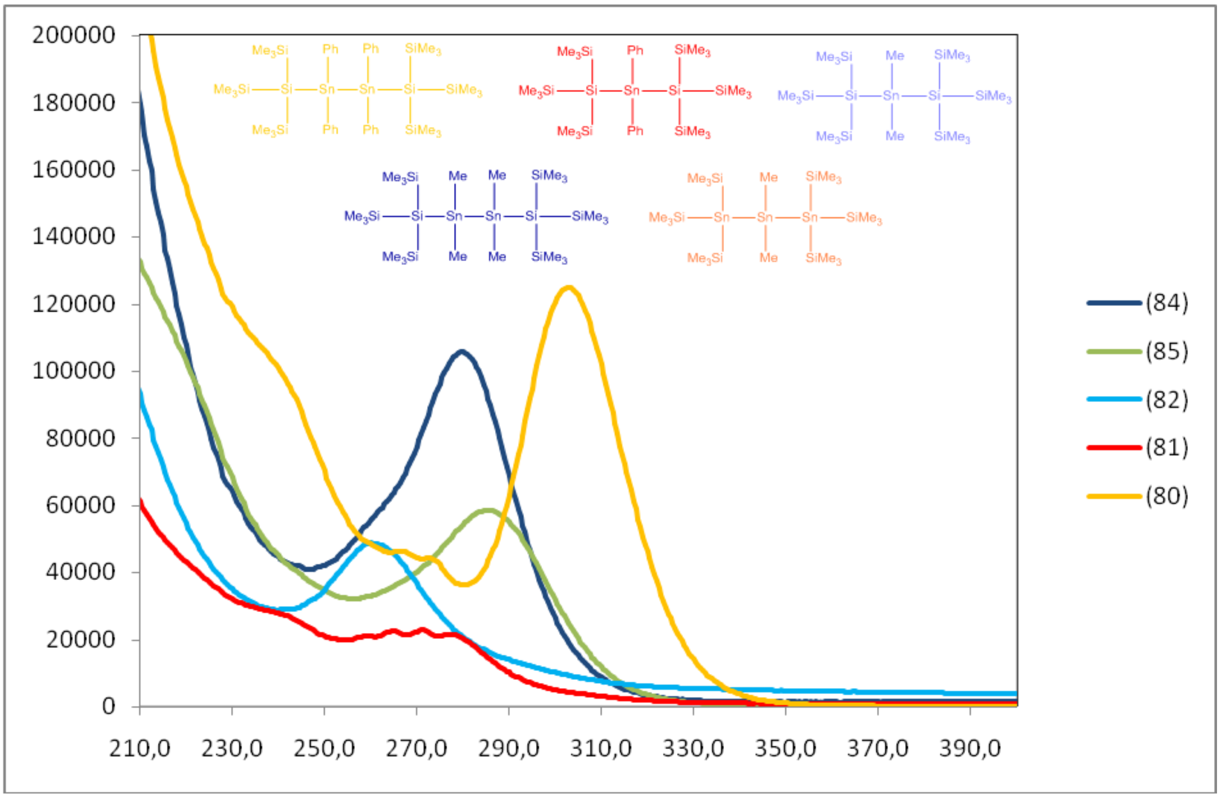


Figure 21-7: Superposition of the UV spectra from phenylated and methylated organosilylstannanes.

Increasing the number of tin atoms in the main chain of the molecules led to a red-shift of the absorption bands. In fact:

82, $(SiMe_3)_3Si$-(**Sn**Me_2)-$Si(SiMe_3)_3$ absorbs at 260 nm;

84, $(SiMe_3)_3Si$ -(**Sn**Me_2)$_{\mathbf{2}}$**-**$Si(SiMe_3)_3$ absorbs at 279.5 nm;

85, $(SiMe_3)_3$**Sn**-(**Sn**Me_2)-**Sn**$(SiMe_3)_3$ absorbs at 285.5 nm.

In the last case, even if the main chain was shorter in respect to compound **84**, the sigma delocalization is more efficient with three tin atoms than with only two.

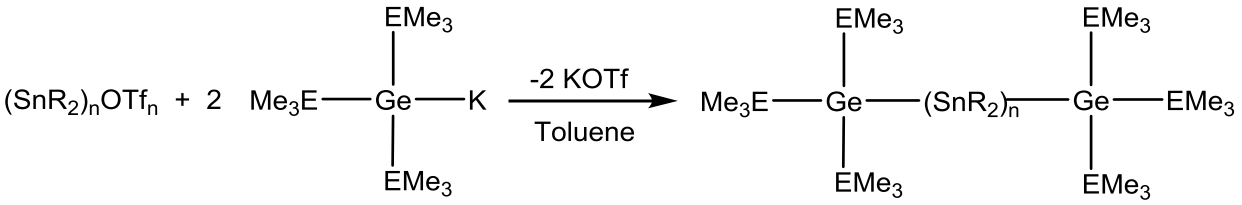
A red-shift was observed also when the methyl groups bonded to the tin atoms were replaced by phenyl groups:

81, $(SiMe_3)_3Si$-(Sn**Ph**$_2$)-$Si(SiMe_3)_3$ absorbs at 279.0 nm (while **82** at 260.0 nm)

80, $(SiMe_3)_3Sn$-(Sn**Ph**$_2$)$_{\mathbf{2}}$-$Sn(SiMe_3)_3$ absorbs at 303.0 nm (while **84** at 279.5 nm)

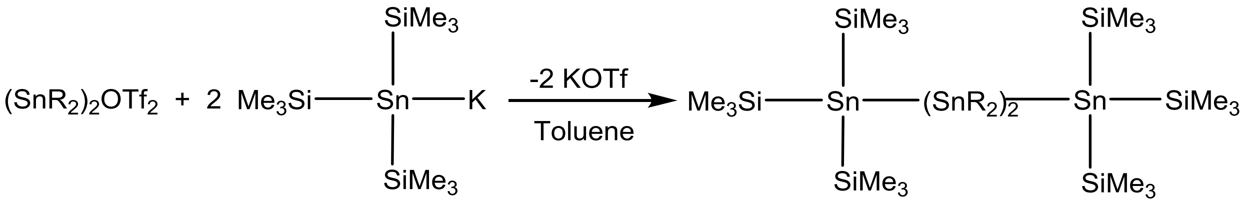
7.4.7 Further developments

The number of compounds synthesized was limited, but it can be implemented by introducing new functional groups and by improving the reaction conditions. Mono- and distannane triflates could be reacted with tris(trimethylsilyl)germyl potassium or with tris(trimethylgermyl)germyl potassium, in the same way as the previous experiments (Scheme 13-7).



Scheme13-7: General way of synthesis for compounds containing long Sn/Ge/Si chains.
R = Me or Ph ; E = Si or Ge.

In some preliminary attempts, it was tried to introduce more tin atom into the back bone of the molecules by reacting tris(trimethylsilyl)stannyl potassium with distanny ditriflate (Scheme 14-7).



Scheme 14-7: Synthesis of 1,1,1,4,4,4-hexakis(trimethylsilyl)tetraorganotetrastannane. R = Me or Ph.

Even if the desired product seemed to be formed, the ^{1}H, ^{29}Si, and ^{119}Sn NMR spectra were not clean and they showed the presence of at least one by-product. Subsequent isolation of crystalline precipitate from different reaction mixtures revealed the formation of hexakis(trimethylsilyl)distannane and the coordination polymer $[Cl_2Sn(Ph)_2O]_n$. Unfortunately, tin-tin bonds were probably forming but they were not as strong as silicon-silicon bond or even silicon-tin bond, to survive the presence of a strong base as the hypersilylstannyl anion. Also the synthesis of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-diphenyltristannane did not succeeded.

Experimental Part

General Experimental

All manipulations involving air and/or moisture sensitive compounds were performed under nitrogen atmosphere employing standard Schlenk techniques or were carried out in nitrogen filled glove boxes Unilab 150-Inovative Technologies Inc.

A column solvent purification system by Inovative Technologies was used for solvents.

Kugelrohr-distillations were carried out using a Büchi <R> / Heating Bath B-490.

If not otherwise stated, chemical substances used were purchased from chemical suppliers. Potassium *tert*-butoxide was purchased exclusively from MERCK.

Chemical substances used as starting materials were prepared according to the literature procedures.

The mixture from the reaction of a silicon anion and a chlorosilane was usually worked up by adding ca. 10 mL of H_2SO_4 2M and ethyl ether or *n*-pentane, moving the suspension into a funnel, separating the organic phase and drying it on anhydrous Na_2SO_4.

Analytical Methods

NMR Spectroscopy

NMR spectra were recorded on a Varian INOVA 300 (^{1}H 300.0 MHz, ^{19}F 300.0 MHz, ^{13}C 75.4 MHz, ^{29}Si 59.6 MHz, ^{11}B 96.2 MHz, ^{31}P 121.4 MHz, ^{119}Sn 111.8 MHz) spectrometer. Samples were dissolved in benzene-d6 or in the case of reaction mixtures, run in a not deuterated solvent, using a capillary filled with D_2O for deuterium lock. Shifts are reported in ppm downfield from TMS (tetramethylsilane) and are referenced to solvent residual signals. To compensate for the low isotopic abundance of ^{29}Si, the INEPT2 pulse sequence was applied.[124,125]

Gaschromatography / Mass Spectroscopy

GC/MS analyses were carried out on a HP 7890A (GC) / 5975C (MS) a DB-1HT capillary column; 15 m x 0.251 mm; 0.1µ. Assignment of peaks was either accomplished by comparison to data from a database or, for the mass spectra not included in the library, identification by standard techniques for their interpretation.

X-ray Structure Analysis

Data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer (wavelength 0.71073 Å). The data were reduced to F2 0 and corrected for absorption effects with SAINT4 and SADABS5, respectively. The structures were solved by direct methods and refined by full-matrix least squares method (SHELXL97).[126,127,128]

Elemental Analysis

Elemental analyses were carried on a Vario EL by HERAEUS Elementar.

Melting Points

Melting point determination was carried out on a Stuart Scientific Schmelzpunkt SMP10 instrument.

---

[124] G. A. Morris, R. Freeman, *J. Am. Chem. Soc.*, **1979**, *101*, 760–762.

[125] B. J. Helmer, R. West, *Organometallics*, **1982**, *1*, 877–879.

[126] SAINTPLUS: *Software Reference Manual*, Version 6.45; BrukerAXS: Madison, WI, **1997−2003**.

[127] G. M. Sheldrick, SADABS. Version 2.10; Bruker AXS, Madison, WI, **2003**.

[128] G.M. Sheldrick, *Acta Crystall. A-Crys*, **2008**, *64*, 112–122.

Experimental data

Chapter 1 and 2

Synthesis of tetrakis(trimethylsilyl)silane (1)
Above a sea-sand large box, 700 mL of THF are put in a three necks flask provided with a dripper funnel and a cooling hose; the system is set under nitrogen. Stirring the solvent, 19.5 g of wires Lithium are chopped into the flask as small pieces of about 2 cm of length. The funnel is loaded with 135 mL of trimethylchlorosilane and the reagent is slowly dropped into the mixture (ca. 30 minutes). Then the funnel is loaded with 30 mL of tetrachlorosilane and the reagent is added drop by drop to the mixture. After about 20 minutes the solution became coffee-brown colored and the temperature slightly increases, but never reaching the boiling point. After ca. 72 h. there are still some thin Lithium wires floating on the liquid surface. A mixture of 500 mL of H_2SO_4 2M and the same amount of ice is prepared in a beaker (2 liters volume). Through a teflon tube (Ø 4 mm) capped at one end with a qualitative paper filter, the liquid phase is transferred into the beaker. The solid phase in the flask is washed one time with THF and the solvent is transferred again into the beaker. About 100 mL of Ethyl ether are added in the beaker to promote phase separation. The organic phase is moved into a separating funnel; some Et_2O and some brine are added and then water is separated. The water phase left in the beaker is extracted two times with Ethyl ether; all the organic phases are joined and put under Na_2SO_4 for 30 minutes. Then the solution is moved by little portions in a single neck flask (1 liter volume) and the solvent is completely removed under vacuum. A pale yellow solid is obtained. The product is recrystallized from warm acetone overnight: a white crystalline solid precipitates. It is filtered with a G3 gooch filter and washed two times with acetone. Then the solid is moved in single neck flask and dried under vacuum.
1st recrystallization tetrakis(trimethylsilyl)silane : 22.76 g (≈ 27% of the theoretical yield of 83.42 g)
Acetone contains some product still, so other recrystallizations are performed:
2nd recrystallization tetrakis(trimethylsilyl)silane : 5.05 g
3rd recrystallization tetrakis(trimethylsilyl)silane : 19.28 g
4th recrystallization tetrakis(trimethylsilyl)silane : 6.27 g
5th recrystallization tetrakis(trimethylsilyl)silane : 5.36 g
Total amount of product : 58.72 g (70% of the theoretical yield)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.23 (s, 36H)
^{13}C: 2.49
^{29}Si: -136.13; -10.18

Synthesis of 1,1,1-tris(trimethylsilyl)triisopropyldisilane (2)

In a single neck flask with stopcock 3002 mg of tetrakis(trimethylsilyl)silane (**1**) (9.36 mmol) and 1102 mg of potassium *tert*-butoxide (9.82 mmol, 1.05 eq) are dissolved with ca. 20 mL of anhydrous THF. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the complete conversion of the substrate is checked by ^{29}Si NMR. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1859 mg (9.64 mmol, 1.03 eq.) of triisopropyllchlorosilane are dissolved with ca. 20 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 9 h and then the mixture isis stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR and the spectrum revealed that the conversion of the anion is complete.

After usual work up and solvent elimination a pale yellow solid is obtained (3529 mg, 93% of the Th. Y.). Three crystallizations from acetone led to 3053 mg of large and transparent crystals (80% of the Th. Y.).

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.31 (s, 27H); 1.15 (d, 18H); 1.25 (sept, 3H);
^{13}C: 3.97; 14.58; 20.12;
^{29}Si: -136.43; -10.10; 13.6.

Synthesis of 1,1,1-tris(trimethylsilyl)tributyldisilane (4)

In a single neck flask with stopcock 1902 mg of tetrakis(trimethylsilyl)silane (**1**) (5.93 mmol) and 698 mg of potassium *tert*-butoxide (6.22 mmol, 1.05 eq) are dissolved with ca. 20 mL of anhydrous DME. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si: there is still a small portion of starting material, so the reaction is continued for another 4 hours. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1407 mg (5.99 mmol, 1,01 eq.) of tributylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 2 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. The peak of the Silicon bonded to the butyl groups is upside-down. After usual work up and solvent elimination a pale yellow oil is obtained (2.38 g , 90% of the Th. Y.). It is tried a crystallization from acetone but the product has probably no crystal form. To eliminate any possible chlorinated and polar by-products, the oil is dissolved in n-Pentane and filtered on a silica gel bed prepared in a pasteur pipette. A transparent and clear oil is obtained.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.30 (s, 27H); 0.80-1.00 (m, 15H); 1.25-1.55 (m, 12H);
^{13}C: 3.13; 13.56; 15.89; 27.03; 27.50
^{29}Si: -2.07; -10.12; -137.56.

Melting point: Not applicable

Elemental analysis ($C_{18}H_{48}Si_5$, 447.08): Calculated: C 56.42; H 12.17
Found: C 55.95; H 11.87

Synthesis of 1,1,1-dimethylthexyl-tris(trimethylsilyl)disilane (6) – method I

In a single neck flask with stopcock 1130 mg of tetrakis(trimethylsilyl)silane (**1**) (3.52 mmol) and 415 mg of potassium *tert*-butoxide (3.70 mmol, 1.05 eq) are dissolved with ca. 40 mL of DME. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si and ^{1}H NMR. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 635 mg (3.56 mmol, 1.01 eq.) of dimethylthexylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture isis stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a pale yellow oil is obtained. It is tried a crystallization from acetone but the product has probably no crystal form. To eliminate any possible chlorinated and polar by-products, the oil is dissolved in n-Pentane and filtered on a silica gel bed prepared in a pasteur pipette. A transparent and clear oil is obtained (1184 mg, 86% of the Th. Y.). Some residual by-products are still present: they should be tetrakis(trimethylsilyl)silane (signal at -136 ppm) and tris(trimethylsilyl)silane (signal at -116 ppm).

Synthesis of 1,1,1-tris(trimethylsilyl)dimethylthexyldisilane (6) – method II

In a single neck flask with stopcock 2000 mg of tetrakis(trimethylsilyl)silane (**1**) (6.23 mmol), 706 mg of potassium *tert*-butoxide (6.30 mmol, 1.01 eq) and 1664 mg of 18-Crown-6 (6.30 mmol, 1.01 eq.) are dissolved with ca. 40 mL of Benzene. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si: it is complete but there is an unknown peak at 6.94 ppm. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1114 mg (6.23 mmol, 1.0 eq.) of dimethylthexylchlorosilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred over the week-end. After usual work up and solvent elimination, a pale yellow oil is obtained (2192 mg, 90% of the Theoretical Yield).

As in the previous procedure, there is the formation of a little amount of tris(trimethylsilyl)silane (^{29}Si signals at -116.1 ppm and -11.4 ppm); to remove the hypersilylsilane, a distillation under vacuum is tried (b.p. $(TMS)_3SiH$ 73°C/5mmHg). Also in this case the product is filtered on a thin pad of silica gel: a clear and transparent oil is obtained (1555 mg, 70.1% of the Th. Y.).

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.23 (s, 3H); 0.26 (s, 3H); 0.29 (s, 3H);
0.83-0.85 (d, 6H); 0.91 (s, 6H); 1.72(sept, 1H);
^{13}**C**: 1.47; 2.51; 3.50; 18.68; 22.03; 34.29
^{29}**Si**: -134.75; -9.87; 8.68

Synthesis of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (3) – method I

In a single neck flask with stopcock 1.94 g of 2,2-bis(trimethylsilyl)octamethyltetrasilane (5.11 mmol), 0.60 g of potassium *tert*-butoxide (5.36 mmol, 1.05 eq) and 1.41 g of 18-crown-6 (5.36 mmol, 1.05 eq.) are solubilize with ca. 20 mL of benzene. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After 12 hours the reaction mixture is checked by ^{29}Si NMR and ^{1}H NMR: the conversion is complete. The solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 2.07 g (10.73 mmol, 1.05 eq.) of triisopropylchlorosilane are dissolved with ca. 20 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. The next morning the ^{29}Si NMR reveals that the product has formed but there is also about 10% of some impurity (peak at -136.3 ppm). After the usual workup the solvent is evaporated and a white sticky semisolid product is obtained (1.32 g). Recrystallization from different kind of solvents (cold ether, acetone/pentane) is tried, but without any clear improvement of the purity of the product. Also a sublimation process is performed, to remove possible traces of tetrakis(trimethylsilyl)silane, but without any great result. There is still about 8% of residual silane, probably tetrakis(trimethylsilyl)silane (**1**) or 2,2-bis(trimethylsilyl)octamethyltetrasilane.
Theoretical Yield: 5.11 mmol x 463.16 mg/mmol = 2.37 g; gained: 1.32 g (55 %)

Synthesis of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (3) – method II

In a single neck flask with stopcock 582 mg of 1,1,1-tris(trimethylsilyl)triisopropyldisilane (**2**) (1.44 mmol), 169 mg of potassium *tert*-butoxide (1.51 mmol, 1.05 eq) and 399 mg of 18-crown-6 (1.51 mmol, 1.05 eq.) are solubilize with ca. 10 mL of benzene. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the complete conversion of the substrate is checked by ^{29}Si and ^{1}H NMR. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 252 mg (1.51 mmol, 1.05 eq.) of pentamethyl chlorodisilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete and the spectrum seems very clear, without by-products. After the usual workup the solvent is evaporated and a white sticky semisolid product is obtained (576 mg, 86% Th. Y.). Recrystallization is performed from cold acetone, and it gives a white solid of small and slightly sticky crystals.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.14 (s, 6H); 0.30 (s, 18H); 0.34 (s, 9H);
1.13-1.16 (d, $^{3}J_{HH}$ = 6.7 Hz, 18H); 1.19-1.33(sept, 3H);
^{13}C: -0.60; 0.11; 4.31; 14.81; 22.27;
^{29}Si: -129.79; -37.89; -12.75; -9.68; 13.46.

Melting point: 151°C

Elemental analysis ($C_{20}H_{54}Si_6$, 463.16): Calculated: C 51.86; H 11.75.
Found: C 51.42; H 11.49.

Synthesis of 1,1,1-tributyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (5)

In a single neck flask with stopcock 1104 mg of 1,1,1-tris(trimethylsilyl)tributyldisilane (**4**) (2.47 mmol) and 291 mg of potassium *tert*-butoxide (2.59 mmol, 1.05 eq) are dissolved with ca. 20 mL of DME. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si: the conversion is complete. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 420 mg (2.52 mmol, 1.02 eq.) of pentamethyldichlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. After usual workup and evaporation of the solvent a clear oil was obtained (1118 mg, 90% of the Th.Y.).

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.20 (s, 9H); 0.33 (s, 18H); 0.36 (s, 6H);
0.85-1.00 (mp, 12H); 1.25-1.30(mp, 15H)
^{13}**C**: -0.86 (Si(CH$_3$)$_3$Si(CH$_2$)$_2$, 5C); 3.52; 13.57; 16.17; 27.05; 27.64
^{29}**Si**: -132.83; -39.59; -14.54; -9.75; -2.41

Melting point: Not applicable

Elemental analysis ($C_{20}H_{54}Si_6$, 463.16): Calculated: C 51.86; H 11.75.
Found: C 52.91; H 11.39

Synthesis of 1,1,1-dimethylthexyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (7)

In a single neck flask with stopcock 1071 mg of 1,1,1-tris(trimethylsilyl)dimethylthexylsilylsilane (**6**) (2.74 mmol), 760 mg of 18-crown-6 (2.88 mmol, 1.05 eq.) and 323 mg of potassium *tert*-butoxide (2.88 mmol, 1.05 eq) are dissolved with ca. 20 mL of Benzene. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si and ^{1}H NMR: the conversion is complete, but there are small peak of some by-products probably due to the not perfect purity of the chlorothexyldimethylsilane use in the previous reaction. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 466 mg (2.79 mmol, 1.02 eq.) of pentamethyldichlorosilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. After usual workup and evaporation of the solvent, a clear oil was obtained (1086 mg, 88% of the Th.Y.)

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.18 (s, 6H); 0.32 (s, 18H); 0.36 (s, 6H);
0.83 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H); 0.92 (s, 6H); 1.65-1.85 (mp, 1H)
^{13}**C**: -0.66; -0.25; 1.68; 3.92; 18.66; 22.42; 34.28; 70.72
^{29}**Si**: -129.99; -38.77; -14.00; -9.45; 9.09

Melting point: Not applicable

Elemental analysis ($C_{19}H_{52}Si_6$, 449.13): Calculated: C 50.81; H 11.67.
Found: C 51.14; H 11.05

Chapter 3

Rearrangement 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (3) – in dichloromethane

In a 25 mL Schlenk flask equipped with a bar stir, 122 mg (0.263 mmol) of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane and 12 mg (0.013 mmol, 0.05 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of CH_2Cl_2, at room tempereature. The amount of catalyst had been increased till 0,4 eq. (96 mg, 0.105 mmol), as shown in Table I:

Equivalents of TTPFPB	*Days of reaction*	*Approximate conversion*
0.05	3	0%
0.10	4 (3+1)	0%
0.20	6 (4+2)	0%
0.40	9 (6+3)	0%

Table I: Conversion in respect to the amount of catalyst

No rearrangement occurred under these conditions.

Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropyldisilane (2) – in dichloromethane

In a 25 mL Schlenk flask equipped with a bar stir, 201 mg (0.496 mmol) of 1,1,1-tris(trimethylsilyl)triisopropyldisilane and 23 mg (0.025 mmol, 0.05 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of CH_2Cl_2. After one day, no reaction was observed. The temperature iswas increased to 40°C and kept at this value for 1 hour. After other two days of stirring, no rearrangement occurred.

Rearrangement 1,1,1-tributyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (5) – in dichloromethane

In a 25 mL Schlenk flask equipped with a bar stir, 183 mg (0.362 mmol) of 1,1,1-tributyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane and 33 mg (0.036 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of CH_2Cl_2, at room tempereature. The amount of catalyst had been increased till 0.2 eq. (66 mg, 0.072 mmol), as shown in Table II:

Equivalents of TTPFPB	*Days of reaction*	*Approximate conversion*
0,10	2	0%
0,20	10 (2+8)	0%

Table II: Conversion in respect to the amount of catalyst.

No rearrangement occurred under these conditions.

Synthesis of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane (14)

In a single neck flask with stopcock 1050 mg of 1,1,1-tris(trimethylsilyl)triisopropyldisilane (**2**) (2.59 mmol) and 294 mg of potassium *tert*-butoxide (2.62 mmol, 1.01 eq) are dissolved with ca. 20 mL of anhydrous DME. The solution turns red after few minutes. The system is set under nitrogen and stirred overnight at room temperature. The next morning the conversion of the substrate is checked by ^{29}Si and it was complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 252 mg (2.67 mmol, 1.03 eq.) of dimethylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 6 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless waxy solid is obtained (787 mg, 78% of the Th. Y.). It is tried a crystallization from acetone, that led to colorless small crystals (475 mg, 47% of the Th. Y.).

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.31 (s, 18H); 0.35-0.37 (d, $^3J_{HH}$ = 3.4 Hz, 6H);
1.12-1.15 (d, $^3J_{HH}$ = 6.1 Hz, 18H); 1.15-1.30 (sept, 3H);
4.30-4.45 (sept, 1H)
^{13}C: -1.27; 13.58; 14.28; 20.03
^{29}Si: -139.71 (SiSi$_4$); -30.65 (Me$_2$$Si$H); -9.64 (Me$_3$$Si$Si);
14.47 (i-Pr$_3$$Si$Si)
Melting point: 187°C (with sublimation)
Elemental analysis ($C_{17}H_{46}Si_5$, 390.97): Calculated: C 52.22; H 11.86.
Found: C 50.86; 11.70.

Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane (14) – in dichloromethane

In a 25 mL Schlenk flask equipped with a bar stir, 150 mg (0.384 mmol) of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane and 35 mg (0.038 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of CH_2Cl_2. After three days, the starting material was completely consumed. Two main products were observed in the reaction mixture:

1,1,1-tris(trimethylsilyl)triisopropyldisilane (**2**), ^{29}Si NMR Data (δ in ppm, CH_2Cl_2 with D_2O capillary): -136.25 (SiSi$_4$); -10.08 (Me$_3$$Si$Si); 13.46 ($i$-Pr$_3$$Si$Si)

1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyl-3-chlorotrisilane (**9**), ^{29}Si NMR Data (δ in ppm, CH_2Cl_2 with D_2O capillary): -129.40 (SiSi$_4$); -9.93 (Me$_3$$Si$Si); 14.18 ($i$-Pr$_3$$Si$Si); 34.08 (Me$_2$$Si$Cl).

Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3-dimethyltrisilane (14) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 102 mg (0.261 mmol) of **14** and 24 mg (0.026 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane, and heated up at 80°C with a metal mantel. At the beginning the catalyst is in suspension, then slowly the powder goes into solution and the solvent takes a pale yellow color. After four hours some new peaks are detected by ^{29}Si NMR. After four days of stirring the reaction mixture is cooled down and filtered on a thin pad of Silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete) and the solvent slowly evaporated. A dense colorless oil is obtained (45 mg, 44% of the Th. Y.). There are three main products, but only for two of these it was possible a correct interpretation of the ^{29}Si NMR spectra:

1) 1,1,1-tris(dimethylisopropylsilyl)trimethyldisilan (**15**)
^{29}Si NMR Data (δ in ppm, C_6D_6): -136.79 (*Si*Si$_4$); -9.58 (Me$_3$*Si*Si); -1.46 (*i*-PrMe$_2$*Si*Si)
2) 1,1-bis(diisopropylmethylsilyl)-1-dimethylisopropylsilyltrimethyldisilane (**15**^{I})
^{29}Si NMR Data (δ in ppm, C_6D_6): -136.16 (*Si*Si$_4$); -9.72 (Me$_3$*Si*Si); -1.72 (*i*-PrMe$_2$*Si*Si);
6.01 (*i*-Pr$_2$Me*Si*Si)
3): unknown (maybe tetrakis(trimethylsilyl)silane (**1**))
^{29}Si NMR Data (δ in ppm, C_6D_6): -135.88 (*Si*Si$_4$); -9.84 (Me$_3$*Si*Si)

Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropyldisilane (2) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 166 mg (0.410 mmol) of 1,1,1-tris(trimethylsilyl)triisopropydisilane and 38 mg (0.041 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. At the beginning the catalyst is in suspension, then slowly the powder goes into solution and the solvent takes a pale yellow color. After five days, the reaction mixture is cooled down and filtered on a thin pad of Silica gel (0.06-0.20 mm mesh), through a Pasteur pippete. A glassy colorless mass is isolated (111 mg, 67% of the Th. Y.), **15**^{I}. Different attempts to crystalize the material was tried (from acetone, CH_2Cl_2, ethyl acetate), but with no success.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.43 (s, 18H); 0.51 (s, 9H); 1.18-1.25 (d, b, 18H);
1.25-1.34 (m, 3H)
^{13}C: -0.8 (Si(*i*-Pr)$_2$(*C*H$_3$)); 3.7 (Si(*C*H$_3$)$_3$);
15.3 (*C*H(CH$_3$)$_2$); 18.7 (CH(*C*H$_3$)$_2$)
^{29}Si: -136.80 (*Si*Si$_4$); -9.49 (Me$_3$*Si*Si); -1.22 (*i*-Pr$_2$Me*Si*Si)
Melting point: 211-212°C
Elemental analysis ($C_{18}H_{48}Si_5$, 405.01): Calculated: C 53.38, H 11.95.
Found: C 52.68, H 11.70.

Rearrangement 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (3) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 1067 mg (2.303 mmol) of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane and 21 mg (0.023 mmol, 0.01 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. The amount of catalyst was increased until 0.07 eq. (126 mg, 0.137 mmol), as shown in Table III:

Equivalents of TTPFPB	*Days of reaction*	*Approximate conversion*
0.01	1	0%
0.03	4 (1+3)	0%
0.05	7 (4+3)	50%
0.07	10 (7+3)	100%

Table III: Conversion in respect to the amount of catalyst

At the beginning of the reaction the catalyst is in suspension, then slowly the powder goes into solution and the solvent takes a pale yellow color. After ten days, the reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil with thin needle crystals inside is isolated (623 mg, 58% of the Th. Y.). This oil is a mixture that contains one main product and two by-products in a small amount.

1,1,1-diisopropylmethyl-2,2-dimethyl-3,3-bis(trimethylsilyl)dimethylisopropyltetrasilane (**11**)

^{29}Si NMR Data (δ in ppm, C_6D_6): -130.69 (*Si*Si_4); -37.77 (Si*Si*Me_2Si) -9.21 (Me_3*Si*Si);
-8.63 (*i*-Pr_2Me*Si*SiMe_2Si); -1.27 (*i*-PrMe_2*Si*Si)

Rearrangement of 1,1,1-tris(trimethylsilyl)tributyldisilane (4) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 237 mg (0.53 mmol) of **4** and 49 mg (0.053 mmol, 0.1 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. The amount of catalyst had been increased till 0.20 eq. (98 mg, 0.106 mmol), as shown in Table IV:

Equivalents of TTPFPB	*Days of reaction*	*Approximate conversion*
0.10	3	0%
0.20	5 (3+2)	100%

Table IV: Conversion in respect to the amount of catalyst

After five days, the reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (181 mg, 76% of the Th. Y.).

Main product: 1,1,1-tris(dimethylbutylsilyl)trimethyldisilane (**16**)

Secondary product: 2-(dibutylmethylsilyl)-2-(dimethylbutylsilyl)hexamethyltrisilane (**16^{I}**)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.42 (Si(CH_3)$_2$Bu, s, 18H); 0.44 (Si(CH_3)$_3$, s, 9H);
0.79 - 0.94, 1.11 (Si(CH$_3$)$_2$CH_2CH_2CH_2CH_3, m, 27H);
^{29}Si: -136.8 (*Si*Si$_4$); -9.9 (Me$_3$*Si*Si); -7.8 (BuMe$_2$*Si*Si)

Melting point: not applicable

Synthesis of 1,1,1,4,4,4-hexaisopropyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane (17)

In a single neck flask with stopcock 867 mg of hexakis(trimethylsilyl)silane (1.75 mmol) and 403 mg of potassium *tert*-butoxide (3.59 mmol, 2.05 eq) are dissolved with ca. 20 mL of anhydrous benzene, in the presence of 18-crown-6 (948 mg, 2.05 eq.). The solution turns gold-red after few minutes. The system is set under nitrogen and stirred over weekend at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that there was still some substrate as potassium mono anion. So other 100 mg of *t*-BuOK were added. Then, after one day the anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 692 mg (3.59 mmol, 2.05 eq.) of triisopropylchlorosilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 6 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless crystalline solid is obtained (251 mg , 21% of the Th. Y.). Some small crystals are recovered for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.31 (s, 36H); 1.10-1.20 (d, 24H); 1.20-1.38 (m, 6H);
^{13}C: 3.96 (Si(*C*H$_3$)$_3$); 14.58 (Si*C*HMe$_2$); 20.12 (SiCH(*C*H$_3$)$_2$)
^{29}Si: -136.33 (*Si*Si$_4$); -10.10 (Me$_3$*Si*Si); +13.72 (*i*-Pr$_3$*Si*Si)

Rearrangement of 1,1,1,4,4,4-hexa(triisopropyl)-2,2,3,3-tetra(trimethylsilyl) tetrasilane (17) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 156 mg (0.235 mmol) of **17** and 22 mg (0.023 mmol, 0.1 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. The amount of catalyst had been increased till 0.20 eq. (44 mg, 0.046 mmol), as shown in Table V:

Equivalents of TTPFPB	*Days of reaction*	*Approximate conversion*
0.10	10	0%
0.20	13 (10+3)	100%

Table V: Conversion in respect to the amount of catalyst

After thirteen days, the reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless semisolid material is obtained (42 mg, 26% of the Th. Y.). This is a mixture of at least three different rearrangement products that were not possible to identify. More, any suitable crystal for X-ray analysis was obtained.

Synthesis of 1,1,1-tris(trimethylsilyl)triisopropylgermylsilane (18)

In a single neck flask with stopcock 938 mg of tetrakis(trimethylsilyl)silane (**1**) (2.92 mmol) and 344 mg of potassium *tert*-butoxide (3.07 mmol, 1.05 eq) are dissolved with ca. 20 mL of anhydrous THF. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 839 mg (2.98 mmol, 1.02 eq.) of triisopropylchlorogermane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorogermane solution in ca. 6 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless crystalline solid is obtained (1201 mg, 91.5% of the Th. Y.). Some small crystals are recovered for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.30 (s, 27H); 1.23 (d, $^3J_{HH}$ = 7.39 Hz, 18H);
1.53 (sept, 3H);
^{13}C: 3.8 (Si(CH$_3$)$_3$); 17.8 (SiCHMe$_2$); 21.4 (SiCH(CH$_3$)$_2$)
^{29}Si: -115.75 (Ge*Si*Si$_3$); -9.21 (Me$_3$*Si*Si)
Melting point: 266-268°C
Elemental analysis ($C_{18}H_{48}GeSi_4$, 449.55): Calculated: C, 48.09; H, 10.76.
Found: C, 46.02; H, 10.26

Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropylgermylsilane (18)

In a 25 mL Schlenk flask equipped with a bar stir, 843 mg (1.87 mmol) of **18** and 80 mg (0.087 mmol, 0.05 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After three days of stirring the starting material was completely consumed (checked by ^{29}Si NMR). The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless semisolid material is obtained (42 mg, 26.9% of the Th. Y.); any suitable crystal for X-ray analysis was obtained. NMR analysis suggests the formation of tris(dimethylisopropylsilyl)trimethylsilylgermane (**19**).

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.26 (Si(CH_3)$_2$*i*-Pr, s, 18H); 0.31 (Si(CH_3)$_3$, s, 9H);
(CH(CH_3)$_2$, 1.03 (d, b, 18H); 1.20 (CH(CH$_3$)$_2$, sept, b, 3H)
^{13}C: -0.4 (Si(CH$_3$)$_2$*i*-Pr); 4.1 (Si(CH$_3$)$_2$); 15.9 (SiCHMe$_2$);
18.6 (SiCH(CH$_3$)$_2$)
^{29}Si: -5.31 (Me$_2$*i*-Pr*Si*Si); -4.53 (Me$_3$*Si*Si)
Melting point: 251°C
Elemental analysis ($C_{18}H_{48}GeSi_4$, 449.55): Calculated: C, 48.09; H, 10.76.
Found: C, 46.84; H, 9.54.

Rearrangement of 1,1,1-dimethylthexyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (7) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 358 mg (0.797 mmol) of 1,1,1-dimethylthexyl-2,2-bis(trimethylsilyl) pentamethyl tetrasilane and 73 mg (0.080 mmol, 0.1 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are dissolved with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After six days of stirring the starting material was completely consumed (checked by ^{29}Si NMR). The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (153 mg, 42.7% of the Th. Y.); this oil is a mixture and the main product is 1,1,1-tris(trimethylsilyl)pentamethyltrisilane.

NMR-Data (δ in ppm, C_6D_6): **^{29}Si**: -132.50 (*Si*Si$_4$); -39.97 (Si*Si*Me$_2$Si) -9.87 (Me$_3$*Si*Si$_4$);
-15.13 (Me$_2$Si*Si*Me$_3$)

Synthesis of 1,1,1-tris(trimethylsilyl)diisopropyloctyldisilane (20)

In a single neck flask with stopcock 1126 mg of tetrakis(trimethylsilyl)silane (**1**) (3.51 mmol) and 402 mg of potassium *tert*-butoxide (3.58 mmol, 1.02 eq) are dissolved with ca. 20 mL of anhydrous THF. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 969 mg (3.69 mmol, 1.05 eq.) of diisopropyloctylchlorosilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 6 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless oil is obtained (1473 mg , 88% of the Th. Y.).

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.32 (Si(C*H*$_3$)$_3$, s, 27H);
1.50-0.80 (*i*-Pr+octyl groups, m, 31H)
^{13}C: 14.6 (Si(*C*H(CH$_3$)$_2$)$_2$C$_8$H$_{15}$); 19.8,19.9 (Si(CH(*C*H$_3$)$_2$)$_2$C$_8$H$_{15}$);
13.9, 14.0, 22.7, 25.5, 29.3, 29.4, 31.9, 34.5
(Si(CH(CH$_3$)$_2$)$_2$*C*$_8$H$_{15}$)
^{29}Si: -137.5 (*Si*Si$_4$); -10.1 (Me$_3$*Si*Si); 9.1 (*i*-Pr$_2$C$_8$H$_{17}$*Si*Si)

Melting point: not applicable

Elemental analysis ($C_{23}H_{58}Si_5$, 475.14): Calculated: C, 58.14; H, 12.30.
Found: C 59.57; H 12.06.

Synthesis of 1,1,1-diisopropyloctyl-3,3,3-diisopropyloctyl-2,2-bis(trimethylsilyl)trisilane (21)

In a single neck flask with stopcock 1355 mg of 1,1,1-diisopropyloctyl-2,2,2-tris(trimethylsilyl) disilane (2.85 mmol) and 336 mg of potassium *tert*-butoxide (2.99 mmol, 1.05 eq) are dissolved with ca. 20 mL of anhydrous DME. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 824 mg (3.14 mmol, 1.10 eq.) of diisopropyloctylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 2 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless and dense oil is obtained (1733 mg , 96.0% of the Th. Y., crude product). The oil is purified by finger distillation under vacuum (ca. 1 mbar) at 150°C (final yield = 770 mg, 43.0% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.42 (Si(C*H*$_3$)$_3$, s, 18H);1,50-0,80 (*i*-Pr+octyl groups, m, 62H);
^{13}C: 15.6 (Si(*C*H(CH$_3$)$_2$)$_2$C$_8$H$_{15}$); 20.3, 20.5 (Si(CH(*C*H$_3$)$_2$)$_2$C$_8$H$_{15}$);
13.7, 14.0, 22.7, 26.1, 29.3, 29.4, 32.0, 34.6
(Si(CH(CH$_3$)$_2$)$_2$*C*$_8$H$_{15}$)
^{29}Si: -133.7 (*Si*Si$_4$); -9.9 (Me$_3$*Si*Si); 8.4 (*i*-Pr$_2$C$_8$H$_{17}$*Si*Si)

Melting point: not applicable

Elemental analysis ($C_{34}H_{80}Si_5$, 629.44): Calculated: C, 64.88; H, 12.81.
Found: C 63.86; H, 12.18.

Rearrangement of 1,1,1-diisopropyloctyl-3,3,3-diisopropyloctyl-2,2-bis(trimethylsilyl) trisilane (21) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 770 mg (1.22 mmol) of **21** and 56 mg (0.06 mmol, 0.05 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 24 hours of stirring, the starting material was completely consumed (checked by ^{29}Si NMR). The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (420 mg, 55% of the Th. Y.); this oil is a mixture containing two main products:

a) 1,1-bis(diisopropylmethylsilyl)-1,1-bis(dimethyloctylsilyl)silane (**23**)
b) 1,1-bis(isopropyldimethylsilyl)-1,1-bis(isopropylmethyloctylsilyl)silane (**22**).

NMR-Data (δ in ppm, C_6D_6): **^{1}H (a+b)**: 0.36-0.39 (Si(C*H*$_3$)$_3$, m, 18H);
1.50-0.90 (*i*-Pr+octyl groups, m, 62H);
^{13}C: 34.09, 33.76, 31.96, 29.32, 25.45, 24.12, 23.43, 22.69, 19.98, 19.75, 19.51, 19.22, 18.97, 17.60, 17.40, 16.60, 15.59, 15.45, 15.17, 15.08, 13.95, 13.61, 1.26, -0.2, -2.74, -3.25
^{29}Si: a) -133.9 (*Si*Si$_4$); -7.9 (Me$_2$Octyl*Si*Si); 5.6 (*i*-Pr$_2$Me*Si*Si)
b) -134.5 (*Si*Si$_4$); -1.8 (Me$_2$*i*-Pr*Si*Si);
-0.1 (*i*-PrMeOctyl*Si*Si)

Melting point: not applicable

Elemental analysis ($C_{34}H_{80}Si_5$, 629.43): Calculated: C, 64.88; H, 12.8
Found: C 64.57; H, 12.63

Synthesis of 1,1,1-triisopropyl-3,3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (24)

In a single neck flask with stopcock 919 mg of **2** (2.27 mmol) and 267 mg of potassium *tert*-butoxide (2.38 mmol, 1.05 eq) are dissolved with ca. 20 mL of anhydrous DME. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 587 mg (2.50 mmol, 1.10 eq.) of tributylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 4 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination colorless oil is obtained. The oil is purified by finger distillation under vacuum (ca. 1 mbar) at 100°C. Final yield = 980 mg, 81% of the Th. Y.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.39 (Si(C*H*$_3$)$_3$, s, 18H); 1.21 (CH(C*H*$_3$)$_2$, d, 18H);
0.8-1.6 (H butyl groups and C*H*(CH$_3$)$_2$, m, 30H)
^{13}C: 4.6 (Si(*C*H$_3$)$_3$); 20.3 (CH(*C*H$_3$)$_2$); 27.1 (*C*H(CH$_3$)$_2$)
13.6^a , 14.9^b , 16.7^c , 27.8^d (SiC^{a}H$_2$C^{b}H$_2$C^{c}H$_2$C^{d}H$_3$)
^{29}Si: -134.7 (*Si*Si$_4$); -10.0 (Me$_3$*Si*Si); -3.3 (Bu$_3$*Si*Si); 13.8 (*i*-Pr$_3$*Si*Si)

Melting point: not applicable

Elemental analysis ($C_{27}H_{66}Si_5$, 531.25): Calculated: C, 61.04; H, 12.52.
Found: C, 59.71; H 11.90.

Rearrangement of 1,1,1-triisopropyl-3,3-tributyl-2,2-bis(trimethylsilyl)trisilane (24) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 145 mg (0.19 mmol) of **24** and 17 mg (0.02 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspened with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 48 hours of stirring, the starting material was completely consumed (checked by ^{29}Si NMR). The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (121 mg, 83% of the Th. Y.); this oil is a mixture containing two main products:

a) 1,1,1-tris(dimethylbutylsilyl)triisopropylsilylsilane (**26**)
b) 1,1-dimethyl-1-butyl-2-dibutylmethylsilyl-2-trimethylsilyltriisopropyltrisilane (**25**)

NMR-Data (δ in ppm, $\mathrm{C_6D_6}$): ^{1}**H (a+b)**: 0.32 ($\mathrm{Si(C}H_3)_3$, m, 6H);
0.80-1.40 (isopropyl+butyl groups, m, 60H);
^{29}**Si**: a) -135.4 ($Si\mathrm{Si_4}$); -8.6 ($\mathrm{Me_2Butyl}Si\mathrm{Si}$); 13.6 ($i$-$\mathrm{Pr_3}Si\mathrm{Si}$)
b) 134.9 ($Si\mathrm{Si_4}$); -10.1 ($Si\mathrm{Me_3Si}$); -8.0 ($\mathrm{Me_2Butyl}Si\mathrm{Si}$);
-6.1 ($\mathrm{MeButyl_2}Si\mathrm{Si}$); 13.6 ($i$-$\mathrm{Pr_3}Si\mathrm{Si}$)

Melting point: not applicable

Elemental analysis ($\mathrm{C_{27}H_{66}Si_5}$, 531.24): Calculated: C, 61.04; H, 12.52
Found: C, 60.51; H 11.15

Synthesis of 1,1,1-tris(trimethylsilyl)dimethyl-(2-norbornyl)disilane (27)

In a single neck flask with stopcock 2000 mg of tetrakis(trimethylsilyl)silane (**1**) (6.23 mmol), 721 mg of potassium *tert*-butoxide (6.42 mmol, 1.03 eq) are dissolved with ca. 40 mL of DME at 60°C. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred 1 hour. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1294 mg (6.85 mmol, 1.1 eq.) of dimethylcycloheptylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. After usual work up and solvent elimination, a white solid is obtained (1285 mg, 51% of the Theoretical Yield). It was possible to crystalize this compound from acetone at room temperature. Big colorless needles suitable for X-ray analysis are collected.

NMR-Data (δ in ppm, $\mathrm{C_6D_6}$): ^{1}**H**: 0.16 ($\mathrm{C_7H_{11}SiC}H_3\mathrm{Me}$, s, 3H);0.21 ($\mathrm{C_7H_{11}SiMeC}H_3$, s, 3H);
0.26 ($\mathrm{Si(C}H_3)_3$, s, 27H); 1.13 – 2.31 ($\mathrm{C_7}H_{11}\mathrm{Si}$, m, 11H)
^{13}**C**: -0.5, -0.3 ($\mathrm{Si(}C\mathrm{H_3)_2C_7H_{11}}$); 2.9 ($\mathrm{Si(Si(}C\mathrm{H_3)_3)_3}$);
28.8, 30.5, 33.5, 34.2, 37.1, 37.7, 38.8 ($\mathrm{Si(CH_3)_2}C_7\mathrm{H_{11}}$)
^{29}**Si**: -136.3 ($Si\mathrm{Si_4}$); -10.82 ($Si\mathrm{Me_3}$); -5.6 ($\mathrm{SiMe_2C_7H_{11}}$)

Melting point: 55-60°C

Elemental analysis ($\mathrm{C_{18}H_{44}Si_5}$, 400.97): Calculated: C, 53.92; H, 11.06.
Found: C, 54.61; H, 10.75.

Synthesis of 1,1,1-dimethylnorbornyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (28)

In a single neck flask with stopcock 344 mg of **27** (1.16 mmol) and 137 mg of potassium *tert*-butoxide (1.22 mmol, 1.05 eq) are dissolved with ca. 10 mL of anhydrous THF. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 214 mg (1.28 mmol, 1.10 eq.) of pentamethylchloro disilane are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 4 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination, a colorless oil is obtained. Final yield = 257 mg, 48.0% of the Th. Y.

NMR-Data (δ in ppm, C$_6$D$_6$): ^{1}**H**: 0.17 (Si(CH$_3$)$_2$Si(C*H*$_3$)$_3$, s, 9H); 0.20, 0.25 (Si(C*H*$_3$)$_2$C$_7$H$_{11}$,
2s, 6H); 0.30 (Si(Si(C*H*$_3$)$_3$)$_2$, s, 18H);0.33 (SiSi(C*H*$_3$)$_2$Si(CH$_3$)$_3$,
s, 6H); 0.8-2.4 (*H* 2-norbornyl group, m, 11H)
^{13}**C**: -1.1 (SiSi(*C*H$_3$)$_2$Si(CH$_3$)$_3$); -0.94 (SiSi(CH$_3$)$_2$Si(*C*H$_3$)$_3$);
-0.10, 0.02 (Si(*C*H$_3$)$_2$C$_7$H$_{11}$); 3.3 (Si(Si(*C*H$_3$)$_3$)$_2$);
28.8, 30.3, 33.7, 34.2, 37.1, 37.8, 38.9 (Si(CH$_3$)$_2$*C*$_7$H$_{11}$);
^{29}**Si**: -132.0 (*Si*Si$_4$); -39.7 (Me$_2$*Si*SiMe$_3$); -14.7 (Me$_2$Si*Si*Me$_3$);
-9.8 (Me$_3$*Si*Si); -5.3 (Me$_2$(C$_7$H$_{11}$)*Si*Si)

Melting point: not applicable

Elemental analysis (C$_{20}$H$_{50}$Si$_6$, 459.12): Calculated: C, 52.32; H, 10.98.
Found: C, 50.63; H, 10.83.

Rearrangement of 1,1,1-dimethyl(2-norbornyl)-2,2-bis(trimethylsilyl)pentamethyl tetrasilane (28) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 218 mg (0.47 mmol) of **28** and 44 mg (0.05 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 4 days of stirring, the starting material conversion is about 50% (checked by ^{29}Si NMR). Other 0.1 eq. of catalyst are added, but after three days more, no improvement in the conversion is observed. The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (101 mg, 46.0% of the Th. Y.); this oil is a mixture containing two main products:

a) 1,1,1-dimethyl(2-norbornyl)-2,2-bis(trimethylsilyl)pentamethyltetrasilane (**28**)
b) 1,1,1,3,3-pentamethyl-2,2-bis(trimentylsilyl)-4,4,4-dimethyl(2-norbornyl)tetrasilane (**29**)

NMR-Data (δ in ppm, C_6D_6): **^{1}H (a+b)**: 0.20-0.50 ($\mathrm{Si(C\mathit{H}_3)_3}$, $\mathrm{Si(C\mathit{H}_3)_2}$,
$\mathrm{Si(C\mathit{H}_3)_2(C_7H_{11})}$, m, 39H);
1.0-3.00 (2-norbornyl groups, m, 22H);
^{29}Si: **a**) -131.7 ($\mathrm{\mathit{Si}Si_4}$); -39.7 ($\mathrm{Me_2\mathit{Si}SiMe_3}$);
-14.6 ($\mathrm{Me_2Si\mathit{Si}Me_3}$); -9.6 ($\mathrm{Me_3\mathit{Si}Si}$);
-5.2 ($\mathrm{Me_2(C_7H_{11})\mathit{Si}Si}$)
b) -131.0 ($\mathrm{\mathit{Si}Si_4}$); -38.6 ($\mathrm{Me_2\mathit{Si}SiMe_3}$);
-12.5 ($\mathrm{Me_2(C_7H_{11})\mathit{Si}Si}$); -9.6 ($\mathrm{Me_3\mathit{Si}Si}$)

Melting point: not applicable
Elemental analysis ($C_{20}H_{50}Si_6$, 459.12): Calculated: C, 52.32; H, 10.98.
Found: C, 53.06; H, 10.40.

Synthesis of 1,1,1-tris(trimethylsilyl)dimethylcyclohexyldisilane (30)

In a single neck flask with stopcock 1506 mg of tetrakis(trimethylsilyl)silane (**1**) (4.69 mmol), 553 mg of potassium *tert*-butoxide (4.93 mmol, 1.05 eq) are dissolved with ca. 20 mL of DME at 60°C. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred 5 hours. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. The anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 912 mg (5.16 mmol, 1.1 eq.) of dimethylcyclohexylchlorosilane are dissolved with ca. 10 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 4 h and then the mixture is stirred overnight. After usual work up and solvent elimination, a colorless oil is obtained (1708 mg, 94% of the Theoretical Yield). After some days, this compound solidifies as a glassy mass.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.19 ($\mathrm{Si(C\mathit{H}_3)_2C_6H_{11}}$, s, 6H); 0.26 ($\mathrm{Si(CH_3)_3}$, s, 27H);
0.7-1.9 ($\mathrm{SiMe_2C_6H_{11}}$, m, 11H)
^{13}C: -1.3 ($\mathrm{Si(\mathit{C}H_3)_2C_6H_{11}}$); 2.9 ($\mathrm{Si(\mathit{C}H_3)_3}$);
26.8 ($\mathrm{SiCH(CH_2)_2(CH_2)_2\mathit{C}H_2}$); 27.6 ($\mathrm{Si\mathit{C}H(CH_2)_2(CH_2)_2CH_2}$);
28.2 ($\mathrm{SiCH(\mathit{C}H_2)_2(CH_2)_2CH_2}$); 28.6 ($\mathrm{SiCH(CH_2)_2(\mathit{C}H_2)_2CH_2}$)
^{29}Si: -137.2 ($\mathrm{\mathit{Si}Si_4}$); -10.0 ($\mathrm{\mathit{Si}Me_3}$); -4.2 ($\mathrm{\mathit{Si}Me_2C_6H_{11}}$)

Melting point: 40-45°C
Elemental analysis ($C_{17}H_{44}Si_5$, 388.96): Calculated: C, 52.49; H, 11.40.
Found: C, 55.22; H, 11.15

Synthesis of 1,1,1-dimethylcyclohexyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (31)

In a single neck flask with stopcock 738 mg of **30** (3.79 mmol) and 434 mg of potassium *tert*-butoxide (3.87 mmol, 1.02 eq) are dissolved with ca. 15 mL of anhydrous THF. The solution turns yellow after few minutes. The system is set under nitrogen and stirred overnight at room temperature. After this time ^{29}Si NMR spectrum of the reaction mixture revealed that the conversion into the potassium monoanion is complete. Then, the anion solution is moved into a dropping funnel using a syringe. The funnel is connected to a flask with stopcock in which 695 mg (4.17 mmol, 1.10 eq.) of pentamethylchloro disilane are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. Then the reaction mixture is checked by ^{29}Si NMR: the conversion of the anion is complete. After usual work up and solvent elimination a colorless oil is obtained. The product is purified by finger distillation under vacuum (ca. 1 mbar) at 100°C. Final yield = 939 mg, 55% of the Th. Y.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.17 ($SiMe_2Si(C\mathit{H}_3)_3$, s, 9H); 0.21 ($SiMe_3Si(C\mathit{H}_3)_2$, s, 6H);
0.29 [$((CH_3)_3Si)_3Si$, s 18H]; 0.32 (cyclohexyl-$Si(C\mathit{H}_3)_2$, s, 6H);
1.0-2.0 (H cyclohexyl group, m, 11H)
^{13}C: -1.1 ($SiSi(\mathit{C}H_3)_2Si(CH_3)_3$); -0.99 ($Si(\mathit{C}H_3)_2C_6H_{11}$);
-0.94 ($SiSi(CH_3)_2Si(\mathit{C}H_3)_3$); 3.4 ($Si(Si(\mathit{C}H_3)_3)_2$);
26.8 ($SiCH(CH_2)_2(CH_2)_2\mathit{C}H_2$); 27.3 ($Si\mathit{C}H(CH_2)_2(CH_2)_2CH_2$);
28.2 ($SiCH(\mathit{C}H_2)_2(CH_2)_2CH_2$); 28.6 ($SiCH(CH_2)_2(\mathit{C}H_2)_2CH_2$)
^{29}Si: -133.1 ($\mathit{Si}Si_4$); -39.5 ($Me_2\mathit{Si}SiMe_3$); -14.7 ($Me_2Si\mathit{Si}Me_3$);
-9.6 ($Me_3\mathit{Si}Si$); -4.2 ($Me_2(C_6H_{11})\mathit{Si}Si$)

Melting point: not applicable

Elemental analysis ($C_{19}H_50Si_6$, 447.11): Calculated: C, 51.04; H, 11.27.
Found: C, 50.63; H, 10.83.

Rearrangement of 1,1,1-dimethylcyclohexyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (31) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 260 mg (0.58 mmol) of **31** and 54 mg (0.06 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 3 days of stirring, the starting material conversion is about 50% (checked by ^{29}Si NMR). Some drops of chlorbenzene are added, but after one day more, no improvement in the conversion is observed. The reaction mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (142 mg, 55% of the Th. Y.); this oil is a mixture containing two main products:

a) 1,1,1-dimethylcyclohexyl-2,2-bis(trimethylsilyl)pentamethyltetrasilane (**31**)
b) 1,1,1,3,3-pentamethyl-2,2-bis(trimthylsilyl)-4,4,4-dimethylcyclohexyltetrasilane (**32**)

NMR-Data (δ in ppm, C_6D_6): **^{1}H (a+b)**: 0.20-0.50 ($Si(C\mathit{H}_3)_3$, $Si(C\mathit{H}_3)_2$, $Si(C\mathit{H}_3)_2(C_6H_{11})$, m, 39H); 1.3-2.0 (cyclohexyl groups, m, 22H);
^{29}Si: a) -132.8 ($\mathit{Si}Si_4$);-39.4 ($Me_2\mathit{Si}SiMe_3$);-14.6 ($Me_2Si\mathit{Si}Me_3$);
-9.4 ($Me_3\mathit{Si}Si$); -4.0 ($Me_2(C_6H_{11})\mathit{Si}Si$)
b) -130.8 ($\mathit{Si}Si_4$); -38,5 ($Me_2\mathit{Si}SiMe_3$);
-12.2 ($Me_2(C_6H_{11})\mathit{Si}Si$); -9.6 ($Me_3\mathit{Si}Si$)

Synthesis of 1,1,1-dimethyl(2-norbornyl)-2,2-bis(trimethylsilyl)-3,3,3-triisopropyltrisilane (33)

In a single neck flask with stopcock 639 mg of **2** (1.58 mmol), 186 mg of potassium *tert*-butoxide (1.66 mmol, 1.05 eq) are dissolved with ca. 10 mL of DME at 60°C. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred 1 hour. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 328 mg (1.74 mmol, 1.1 eq.) of dimethylcycloheptylchlorosilane are dissolved with ca. 5 mL of DME. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred overnight. After usual work up and solvent elimination, a colorless oil is obtained (529 mg, 69% of the Theoretical Yield). It was possible to crystalize this compound from acetone at room temperature. Colorless plates suitable for X-ray analysis are collected.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.25 and 0.31 ($C_7H_{11}Si(C\mathit{H}_3)_2$, s, 3H+3H);
0.33 and 0.34 ($Si(C\mathit{H}_3)_3$, s, 9H+9H);
1.18 ($SiCH(C\mathit{H}_3)_2$, d, $^2J_{HH}$ = 6.9 Hz, 18H);
1.28 ($SiC\mathit{H}(CH_3)_2$, sept, 3H); 1.50–2.50 ($C_7\mathit{H}_{11}Si$, m, 11H)
^{13}C: 0.9 and 1.2 ($Si(\mathit{C}H_3)_2C_7H_{11}$); 4.31 and 4.35 ($Si(\mathit{C}H_3)_3$);
14.8 ($Si\mathit{C}H(CH_3)_2$); 20.2 ($SiCH(\mathit{C}H_3)_2$); 28.9, 29.8, 33.9,
34.0, 37.0, 38.0, 39.1 ($Si(CH_3)_2\mathit{C}_7H_{11}$);
^{29}Si: -134.2 ($\mathit{Si}Si_4$); -10.1 ($\mathit{Si}Me_3$); -4.9 ($\mathit{Si}Me_2C_7H_{11}$);
13.5 (*Sii*-Pr$_3$)

Melting point: 110°C
Elemental analysis ($C_{24}H_{56}Si_5$, 485.14): Calculated: C, 59.42; H, 11.64.
Found: C, 58.58; H, 11.67.

Rearrangement of 1-(2-norbornyl)-1,1-dimethyl-2,2-bis(trimethylsilyl)-3,3,3-triisopropyl trisilane (33) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 77 mg (0.57 mmol) **33** and 53 mg (0.06 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 4 days of stirring, no conversion is observed (by ^{29}Si NMR). 53 mg (0.1 eq.) of TTPFPB are added, and after three days more, another equivalent of catalyst is suspended into the reaction mixture. Finally, after ten days of reaction, the conversion is complete. The mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A colorless oil is obtained (130 mg, 47% of the Th. Y.); attempts to crystalize this product from acetone or dichloromethane fail. The main product seems to be 1,1,1-tris(isopropyldimethyl)dimethylcycloheptyldisilane (**34**).

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.20-0.40 ($C_7H_{11}Si(CH_3)_2$ and $Si(CH_3)_3$, m, broad);
1.0-1.2 ($SiCH(CH_3)_2$, m, broad);
1.50 to 2.50 ($C_7H_{11}Si$, m, broad)
^{29}**Si**: -137.2, -136.4, -135.5 ($SiSi_4$); -10.1, -10.0, -9.9 ($SiMe_3$);
-5.2,-5.5 ($SiMe_2C_7H_{11}$); -1.6, -1.7 ($SiMe_2i$-Pr); 5.7 ($SiMei$-Pr_2)

Synthesis of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3,3-triisopropyltrisilane (35)

In a single neck flask with stopcock 764 mg of **2** (1.89 mmol), 222 mg of potassium *tert*-butoxide (1.98 mmol, 1.05 eq) and 523 mg of 18-crown-6 (1.98 mmol, 1.05 eq.) are dissolved with ca. 10 mL of benzene at room temperature. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred overnight. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 400 mg (1.98 mmol, 1.05 eq.) of triisopropylchlorosilane are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 48 h and then the mixture is stirred over the weekend. After usual work up and solvent elimination, a semisolid wax is obtained (884 mg, 95% of the Theoretical Yield). It was possible to crystalize this compound from acetone at room temperature.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.42 ($Si(CH_3)_3$, s, 18H);
1.23 ($Si(CH(CH_2)_3$, d, $^3J_{HH}$=7.33, 36H);
1.43 ($Si(CH(CH_2)_3$, sept, 6H)
^{29}**Si**: -129.6 ($SiSi_4$); -9.7 ($SiMe_3$); 14.9 (Sii-Pr_3)

Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3,3-triisopropyltrisilane (35) – in cyclohexane

In a 25 mL Schlenk flask equipped with a bar stir, 312 mg (0.64 mmol) of **35** and 88 mg (0.10 mmol, 0.15 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 2 days of stirring, no conversion is observed (by ^{29}Si NMR). 88 mg (0.15 eq.) of TTPFPB are added, and after two days more, the conversion is complete. The mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A pale yellow oil is obtained (103 mg, 33% of the Th. Y.), containing at least three different products.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.0-0.50 (unknown, m); 0.8-1.4 (unknown, m)
^{29}**Si**: -140.1, -140.0, -137.2 ($SiSi_4$); -9.9, -9.7 ($SiMe_3$);
-1.6, -1.2 ($SiMe_2i$-Pr); 4.9 (main signal, unknown)

GS/MS: 287.1, 245.2, 217.2, 175.1, 133.0, 119.0, 73.0

Rearrangement of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)-3,3,3-triisopropyltrisilane (35) – in cyclohexane in the presence of Et_3SiH

In a 25 mL Schlenk flask equipped with a bar stir, 248 mg (0.51 mmol) of **35**, 10 mg (0.01 mmol, 0.02 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) and one drop of triethylsilane are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal block mantel. After 24 hours of stirring, no conversion is observed (by ^{29}Si NMR). 10 mg (0.02 eq.) of TTPFPB and another drop of Et_3SiH are added. After 24 hours, new peaks are detected in the ^{29}Si NMR, but some starting material is still present in solution. The addition of 10 mg of catalyst complete the conversion of the substrate within other 24 hours. The mixture is cooled down and filtered on a thin pad of silica gel (0,06-0,20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). A transparent and colorless oil is obtained.

NMR-Data (δ in ppm, cyclohexane/D_2O capillary): **^{29}Si**: -130, -80, -30, -2, 5.

Synthesis of 1,1,1-tris(trimethylsilyl)triphenylstannylsilane (37)

In a single neck flask with stopcock 844 mg of tetrakis(trimethylsilyl)silane (**1**) (2.63 mmol) and 310 mg of potassium *tert*-butoxide (2.76 mmol, 1.05 eq) are dissolved with ca. 10 mL of THF at room temperature. The solution turns yellow after few minutes. The system is kept under nitrogen and the mixture stirred overnight. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1115 mg (2.89 mmol, 1.1 eq.) of triphenylchlorostannane are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the stannane solution in ca. 6 h and then the mixture is stirred overnight. After usual work up and solvent elimination, a colorless solid is obtained (1462 mg, 93% of the Theoretical Yield). It was possible to recrystallize this compound from a mixture of pentane/acetone at room temperature.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.20 ($Si(CH_3)_3$, s, 27H); 7.00 – 7.80 ($Sn(C_6H_5)_3$, m, 15H)
^{13}C: 2.9, ($Si(CH_3)_3$); 128.2 (2 peaks collapsed), 137.4, 140.9 ($Sn(C_6H_5)_3$)
^{29}Si: -131.6 ($SiSi_3Sn$); -8.1 ($SiMe_3$)
^{119}Sn: -114.4

Melting point: 120°C

Elemental analysis ($C_{27}H_{42}Si_4Sn$, 597.68): Calculated: C, 54.26; H, 7.08.
Found: C, 53.63; H, 6.84

Synthesis of 1,1,1-tris(trimethylsilyl)trimethylstannylsilane (38)

In a single neck flask with stopcock 533 mg of tetrakis(trimethylsilyl)silane (**1**) (1.66 mmol) and 196 mg of potassium *tert*-butoxide (1.74 mmol, 1.05 eq) are dissolved with ca. 10 mL of THF at room temperature. The solution turns yellow after few minutes. The system is kept under nitrogen and the mixture stirred overnight. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 1.74 mL of a 1M solution of trimethylchlorostannane (1.74 mmol, 1.05 eq.) are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the stannane solution in ca. 6 h and then the mixture is stirred overnight. After usual work up and solvent elimination, a colorless solid is obtained (627 mg, 91% of the Theoretical Yield). It was possible to recrystallize this compound from acetone at -20°C.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.22 (Si(CH_3)$_3$, s, 27H); 0.21 (Sn(CH_3)$_3$, s, 9H)
^{29}**Si**: -138.1 (*Si*Si$_3$Sn); -8.1 (*Si*Me$_3$)
^{119}**Sn**: -70.1

Synthesis of 1,1,1-tris(trimethylgermyl)trimethylstannylgermane (39)

In a single neck flask with stopcock 351 mg of tetrakis(trimethylgermyl)germane (0.65 mmol), 76 mg of potassium *tert*-butoxide (0.68 mmol, 1.05 eq) and 179 mg of 18-crown-6 (0.68 mmol, 1.05 eq.) are dissolved with ca. 10 mL of toluene at room temperature. The solution turns red after few minutes. The system is kept under nitrogen and the mixture is stirred overnight. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 0.68 mL of a 1M solution of trimethylchlorostannane (0.68 mmol, 1.05 eq.) are dissolved with ca. 5 mL of toluene. The anion is slowly dropped into the stannane solution in ca. 2 h and then the mixture is stirred ovenight. After usual work up and solvent elimination, a colorless solid is obtained (301 mg, 79% of the Theoretical Yield). It was possible to crystalize this compound from acetone at -20°C.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.30 (Sn(CH_3)$_3$, s, 9H); 0.39 (Si(CH_3)$_3$, s, 27H)
^{13}**C**: -7.5 (Sn(*C*H$_3$)$_3$); 2.8 (Ge(*C*H$_3$)$_3$)
^{119}**Sn**: -55.2

Melting point: 210°C with sublimation and then decomposition

Elemental analysis ($C_{12}H_{36}Ge_4Sn$, 589.65): Calculated: C, 24.44; H, 6.15.
Found: C, 27.52; H, 6.38

Rearrangement of 1,1,1-tris(trimethylsilyl)triisopropylstannylgermane

In a 25 mL Schlenk flask equipped with a bar stir, 236 mg (0.44 mmol) of 1,1,1-tris(trimethylsilyl)triisopropylstannylgermane and 40 mg (0.04 mmol, 0.10 eq.) of trityltetra(pentafluorophenyl) borate (TTPFPB) are suspended with ca. 5 mL of cyclohexane and heated up at 80°C with a metal mantel. After 2 days of stirring, no conversion is observed (by ^{29}Si NMR). 40 mg (0.10 eq.) of TTPFPB are added. After one week, the starting material is still the main product. Then after ten days more, the conversion is completed. The flask shows a quite large amount of a black precipitate. The mixture is cooled down and filtered on a thin pad of silica gel (0.06-0.20 mm mesh; ca. 3 cm of silica gel in a Pasteur pippete). No product is obtained, as nothing remains after the evaporation of the solvent.

NMR-Data (δ in ppm, C_6H_{12}/D_2O capillary, before the work-up): ^{29}**Si**: -19.7; -0.02; 6.8

Synthesis of undecamethyl*tert*-butylsilylcyclohexasilane (49)

In a single neck flask with stopcock 1630 mg of dodecamethylcyclohexasilane (3.63 mmol) and 611 mg of potassium *tert*-butoxide (5.44 mmol, 1.5 eq) are dissolved with ca. 15 mL of diglyme at room temperature. The solution turns red after few minutes. The system is kept under nitrogen and the mixture is stirred for one week. The anion solution is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 602 mg of chlorodimethyl*tert*-butylsilane (4.0 mmol, 1.1 eq.) are dissolved with ca. 5 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 6 h and then the mixture is stirred for 12 hours. After usual work up and solvent elimination, a colorless glassy solid is obtained (464 mg, 29% of the Th. Y.).

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.15 ($Si(CH_3)_2t$-Bu, s, 6H); 0.16 ($Si_2{}^1Si(CH_3)$, s, 3H);
0.18 ($^4Si(CH_3)_2$, s, 3H); 0.19 ($^{2,6}Si(CH_3)_2$, s, 6H);
0.21 ($^{2,6}Si(CH_3)_2$, s, 6H); 0.25 ($^4Si(CH_3)_2$, s, 3H);
0.28 ($^{3,5}Si(CH_3)_2$, s, 6H); 0.32 ($^{3,5}Si(CH_3)_2$, s, 6H);
0.97 ($C(CH_3)_3$, s, 9H)
^{13}**C**: -9.2 ($Si(CH_3)_2t$-Bu); -7.0 ($Si_2{}^1Si(CH_3)$);-6.8 ($^4Si(CH_3)_2$);
-4.9, -4.5 ($^{2,6}Si(CH_3)_2$); -3.1, -2.8 ($^{3,5}Si(CH_3)_2$);
14.0 ($(CH_3)_3C$); 27.6 ($(CH_3)_3C$)
^{29}**Si**: -81.9 ($SiMeSi_2$);-42.7,-40.4,-38.2 ($SiMe_2$); 2.9 ($SiMe_2t$-Bu)

Melting point: 204°C

Synthesis of 1,4-bis(triisopropylsilyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (65)

In a glass vial 48 mg of 1,2-dichlorotetramethyldisilane (0.25 mmol) are dissolved with ca. 2 mL of THF at RT. 1,4-bis(trimethylsilyl)-1,4-bis(triisopropylsilyl)-2,2,3,3-tetramethyl-1,4-silyl dipotassium (prepared from 0.26 mmol of 1,1,4,4-tetrakis(trimethylsilyl)-1,4-bis(triisopropylsilyl)tetramethyltetrasilane and 2.1 equivalent of *t*-BuOK in DME) is slowly dropped into the chlorosilane solution. The mixture is stirred for 24 hours. After usual work up and solvent elimination, a colorless powder is obtained (80 mg, 39% of the Th. Y.). Crystals suitable for X-ray analysis were obtained recrystallizing the product from Et_2O. It was possible to separate manually the cis-conformer and the trans-conformer crystals.

cis-1,4-bis(triisopropylsilyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.40 ($Si(CH_3)_3$, s, 18H);0.47, 0.48 ($Si(CH_3)_2$, s, 12H+12H);
1.20 ($Si(CH(CH_3)_2)_3$, d, 36H, $^3J_{HH}$ =7.2 Hz);
1.35 ($Si(CH(CH_3)_2)_3$, sept, 6H);
^{13}**C**: 0.9, 1.2 ($Si(CH_3)_2$); 5.4 ($Si(CH_3)_3$);
14.6 ($Si(CH(CH_3)_2)_3$); 20.6 ($Si(CH(CH_3)_2)_3$)
^{29}**Si**: -128.9 ($SiSi_4$); -37.0 ($Si(CH_3)_2$); -8.7 ($Si(CH_3)_3$);
22.8 ($Si(CH(CH_3)_2)_3$)

Melting point: 229-231°C

trans-1,4-bis(triisopropylsilyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.40 ($\mathrm{Si(C}H_3)_3$, s, 18H);0.46, 0.53 ($\mathrm{Si(C}H_3)_2$, s, 12H+12H);
1.21 ($\mathrm{Si(CH(C}H_3)_2)_3$, d, 36H, $^3J_{HH}$ =7.2 Hz);
1.40 ($\mathrm{Si(C}H\mathrm{(CH_3)_2)_3}$, sept, 6H);
^{13}C: 0.8, 1.6 ($\mathrm{Si(}C\mathrm{H_3)_2}$); 5.5 ($\mathrm{Si(}C\mathrm{H_3)_3}$); 14.8 ($\mathrm{Si(}C\mathrm{H(CH_3)_2)_3}$);
20.5 ($\mathrm{Si(CH(}C\mathrm{H_3)_2)_3}$)
^{29}Si: -127.8 ($Si\mathrm{Si_4}$); -35.3 ($Si\mathrm{(CH_3)_2}$); -9.3 ($Si\mathrm{(C}H_3)_3$);
17.2 ($Si\mathrm{(CH(CH_3)_2)_3}$)

Melting point: 240-242°C

Elemental analysis ($C_{32}H_{84}Si_{10}$, 749.86): Calculated C, 51.25; H, 11.29
Found: C, 48.66, H, 10.91

Synthesis of tris(dimethylisopropylsilyl)silyl potassium (113) *(S291)*

In a glass vial 120 mg **15** (0.296 mmol), 34 mg of potassium *tert*-butoxide (0.302 mmol, 1.02 eq) and 80 mg of 18-crown-6 (0.302 mmol, 1.02 eq.) are dissolved with ca. 2 mL of toluene at room temperature. The solution turns immediately dark red. After 12 hours of stirring the ^{29}Si NMR reveals a complete and selective conversion of the reagent into the silyl anion. The solution is moved to the freezer at -67°C. After several days, only a amorphous red mass precipitates. The product is solubilize again at room temperature and few drops of pentane are added to the solution. Storing again at low temperature this mixture did not produce any crystals. The reaction is repeated under the same conditions using benzene as solvent. The result is the same and then the solvent is slowly evaporated from the vial. Only a glassy red mass is obtained that does not contain suitable crystals for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.34 ($\mathrm{Si(C}H_3)_2i\text{-Pr}$, s, 18H);
1.20 ($\mathrm{Si(CH(C}H_3)_2\mathrm{)Me_2}$, d, 18H, $^3J_{HH}$ =6.9 Hz)
^{29}Si: -204.5 (SiK); 4.7 ($Si\mathrm{Me_2}i\text{-Pr}$)

Melting point: Not applicable

Elemental analysis ($C_{15}H_{39}KSi_4$, 370.92): Not applicable

Synthesis of 1,1,1-tris(dimethylisopropylsilyl)triphenyldisilane (114)

In a glass vial 125 mg **15** (0.309 mmol), 36 mg of potassium *tert*-butoxide (0.318 mmol, 1.03 eq) and 84 mg of 18-crown-6 (0.318 mmol, 1.03 eq.) are dissolved with ca. 2 mL of toluene at room temperature. The solution turns immediately dark red. After 12 hours of stirring the ^{29}Si NMR reveals a complete and selective conversion of the reagent into the silyl anion. The reaction mixture is then slowly dropped with a syringe into a THF solution of Ph_3SiCl (1.1 eq., 100 mg, 0.340 mmol). The solution is stirred 12 hours and worked up in the usual manner. Crystallization from a mixture of pentane/acetone gives only the by-product $Ph_3SiOSiPh_3$, while the main product precipitates as a glassy colorless mass.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.18 (Si(C*H*$_3$)$_2$*i*-Pr, s, 18H);0.88 (Si(C*H*(CH$_3$)$_2$)Me$_2$, sept, b, 3H); 1.02 (Si(CH(C*H*$_3$)$_2$)Me$_2$, d, 18H, $^3J_{HH}$ =5.9 Hz); 7.0-7.7 (Si(C$_6$H$_5$)$_3$, m, b, 15H)
^{29}Si: -128.3 (*Si*Si$_4$); -11.4 (*Si*Ph$_3$); -3.0 (*Si*Me$_2$*i*-Pr)

Melting point: Not applicable

Synthesis of 1,1,1,4,4,4-hexakis(dimethylisopropylsilyl)tetramethyltetrasilane (115)

In a glass vial 94 mg **15** (0.232 mmol), 27 mg of potassium *tert*-butoxide (0.239 mmol, 1.03 eq) and 63 mg of 18-crown-6 (0.232 mmol, 1.03 eq.) are dissolved with ca. 2 mL of benzene at room temperature. The solution turns immediately dark red. After 12 hours of stirring the ^{29}Si NMR reveals a complete and selective conversion of the reagent into the silyl anion. The reaction mixture is then slowly dropped with a syringe into a THF solution of (SiMe$_2$Cl)$_2$ (0.5 eq., 22 mg, 0.116 mmol). The solution is stirred 12 hours and worked up in the usual manner. Crystallization from a mixture of pentane/acetone or from dichloromethane gives a dense colorless oil.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.12 (Si(C*H*$_3$)$_2$, s, 12H); 0.26 (Si(C*H*$_3$)$_2$*i*-Pr, s, 36H); 1.04 (Si(C*H*(CH$_3$)$_2$)Me$_2$, sept, b, 6H); 1.04 (Si(CH(C*H*$_3$)$_2$)Me$_2$, d, b, 18H)
^{29}Si: -131.8 (*Si*Si$_4$); -36.0 (*Si*Me$_2$); -1.2 (*Si*Me$_2$*i*-Pr)

Melting point: Not applicable

Chapter 4

Synthesis of 1,1,1-triisopropyl-2,2-bis(trimethylsilyl)disilyl triflate (45)

In a single neck flask with stopcock 435 mg of 1,1,1-triisopropyl-2,2-bis(trimethysilyl)disilane (**44**) (1.31 mmol) are dissolved with ca. 10 mL of dichloromethane at room temperature. 196 mg of triflic acid (1.31 mmol, 1.0 equivalent) are slowly added to the stirring solution at room temperature. The system is kept under nitrogen and the mixture is stirred overnight. The mixture is checked by NMR and then stored at -20°C. Transparent colorless plate crystalized within one month.

NMR-Data (δ in ppm, CH_2Cl_2/D_2O capillary): **^{29}Si**: -11.1(*Si*Me$_3$), 21.3 (*Si*(*i*-Pr)$_3$), 48.7(*Si*OTf)

Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-2,3-dimethyl-2,3-diphenyltetrasilane (46)

1,2-dimethyltetraphenyldisilane (775 mg, 1.9 mmol) is dissolved in ca. 10 mL of dichloromethane at room temperature. Triflic acid (2.05 equivalents, 604 mg) is slowly dropped into the stirring solution. After 12 hours the reaction is completed (one clear signal in the ^{29}Si NMR spectrum at 17.7 ppm). The solvent is evaporated and the remaining white solid is suspended in ca. 10 mL of toluene. Into this stirring slurry, a solution of tris(trimethylsilyl)silyl potassium (prepared from the reaction of 1192 mg, 3.7 mmol, 1.9 equivalents, of **1** and 3.9 mmol of *t*-BuOK in toluene/18-crown-6 (3.9 mmol)) is slowly dropped within 24 hours. The reaction continues for other 24 hours and then it is worked up with acidic water and a mixture 1:1 of THF/Et$_2$O. The organic liquid phases is collected and the solvent is evaporated. A colorless glassy solid is obtained (1427 mg, 98% of the Th. Y.). The semisolid material contains some residual 18-crown-6, tetrakis(trimethylsilyl)silane (**1**) and the by-product tris(trimethylsilyl)silane formed during the work up. Suitable crystals for X-ray analysis are precipitated from a solution of the product in acetone stored at -20°C.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.30 ($\mathrm{Si(C}H_3)_3$, s, 54H); 0.39 ($\mathrm{Si(C}H_3)_2$, s, 6H);
6.70 ($\mathrm{Si(C_5H_6)_2}$, m, 10H)
^{13}**C** (in $CDCl_3$)**:** -0.6 ($\mathrm{Si(}C\mathrm{H_3)_2Ph_2}$); 3.1 ($\mathrm{(Si(}C\mathrm{H_3)_3)}$;
127.9, 128.2, 135.7, 138.8 ($\mathrm{Si(CH_3)_2(}C_6\mathrm{H_5)_2}$);
^{29}**Si**: -124.2 (Si_q); -30.3 (*Si*MePh); -9.5 ($Si\mathrm{(CH_3)_3}$)

Melting point: 271°C

Elemental analysis ($C_{32}H_{70}Si_{10}$, 735.76): Calculated: C, 52.24; H, 9.59.
Found: C 49.73, H 9.36

Synthesis of 1,4-dipotassium-1,4-bis(trimethylsilyl)-2,3-dimethyl-2,3-diphenyltetrasilane (47)

Compound **46** (0.38 mmol, 283 mg) is treated with 2.05 equivalents of *t*-BuOK (88 mg) in benzene in the presence of 18-crown-6 (2.05 eq., 208 mg). After 12 hours of stirring at room temperature, the reaction mixture is checked by ^{1}H and ^{29}Si NMR: the conversion of the starting material is complete. The solvent is evaporated and the semisolid red residue is dissolved in the minimum amount of toluene and stored at -67°C. After two weeks plate crystals precipitates, suitable for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: -0.03 ($\mathrm{Si(C}H_3)_3$, s, 36H);0.33 (*t*-BuOSi(CH_3)$_3$, s, 2x9H);
1.01(($\mathrm{C}H_3)_3\mathrm{COSiMe_3}$, s, 2x9H); 1.11 ($\mathrm{Si(C}H_3\mathrm{)Ph}$, s, 6H);
6.70 ($\mathrm{Si(C_5}H_6\mathrm{)Me}$, b, 10H)
^{29}**Si**: -180.5 (*Si*K); -22.7 (*Si*MePh); -5.0 ($Si\mathrm{(CH_3)_3}$)

Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-2,3-diphenyl-2,3,5,5-tetramethylcyclopentasilane (48)

The silyl potassium anion (**47**) formed with the previous reaction (0.38 mmol, 283 mg) is slowly dropped in a toluene solution containing 0.35 mmol (45 mg) of dichlorodimethylsilane. After 12 hours of stirring at room temperature, the reaction mixture is worked up and the solvent is evaporated. A colorless solid is obtained (213 mg, 85% of the Th. Y.). Recrystallization from acetone at room temperature gives crystalline plates suitable for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.14 ($Si(CH_3)_3$, s, 18H); 0.36 ($Si(CH_3)_3$, s, 18H);
0.64 ($Si(CH_3)_2$, s, 6H); 0.81 ($Si(CH_3)Ph$, s, 6H);
7.00-7.70 ($Si(C_5H_6)Me$, mp, 10H)
^{13}**C**: -1.1 ($Si(CH_3)_2$); 3.5, 4.1 ($Si(CH_3)_3$); 4.2 ($Si(CH_3)Ph$);
127.8, 128.3, 135.4, 138.7 ($Si(C_5H_6)Me$)
^{29}**Si**: -127.6 (Si_q); -23.4, -20.7 (*Si*MePh);
-8.1, -6.6 ($Si(CH_3)_3$)

Melting point: 195°C
Elemental analysis: $C_{28}H_{58}Si_9$ (647.54): Calc.: C, 51.94; H, 9.03.
Found: C, 49.97; H, 8.66

Chapter 5

Reaction between $[Et_3Si^+][B(C_6F_5)_4^-]$ and tetrakis(trimethylsilyl)silane (1)

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 11 mg of triethylsilane (0.095 mmol) and 86 mg of trityl salt (1 equivalent) are dissolved in ca. 0.3 mL of chlorobenzene at ca. -50°C. The mixture is stirred overnight while the temperature slowly comes back to ambient. The solvent is then dried and the pale yellow solid is washed with few drops of pentane, 2-3 times. The residual solid is dissolved in chlorobenzene, cooled down at ca. -50°C and then slowly dropped into a chlorobenze solution of tetrakis(trimethylsilyl) silane (1 equivalent, 30 mg, in 0.6 mL of solvent), that is cooled down at the same temperature. After five hours of reaction the clear solution is checked by NMR, but no signal in the ^{29}Si NMR could be found, while the proton spectrum shows broad signals.

NMR-Data (δ in ppm, PhCl/D_2O cap.): ^{1}**H**: -0.38, -0.11, 0.35, 0.56 (broad, unknown);
4.64 (s, H_2 ?), 5.06 (s, Ph_3CH)
^{19}**F**: -128.1, -142.8, -160.2 ($B(C_6F_5)_3$);
-132.3, -162.9, -166.7 ($[B(C_6F_5)_4^-]$)

Reaction between tris(trimethylsilyl)silane (52) and TTPFPB in the presence of benzo-15-crown-5 ether

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 40 mg of **52** (0.16 mmol), 44 mg of crown ether (1 equivalent) and 150 mg of trityl salt (1 equivalent) are quickly dissolved in ca. 2 mL of chlorobenzene, mixed, and stored in the freezer at -67°C overnight. The solution is clear and has an intense violet color. After NMR measurements, half volume of the solution is layered with pentane in a NMR tube at room temperature, and the other half mixed with some drops of pentane and stored at -67°C. In both of the containers a solid precipitate formed.

NMR-Data (δ in ppm, PhCl/D_2O cap.): ^{29}**Si**: -89.4, -88.6, -86.3, -15.5, -13.2, -11.6, 11.2, 26.3, 108.5

Reaction between 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) and TTPFPB in the presence of TMEDA

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 40 mg of **51** (0.13 mmol), 15 mg TMEDA (1 equivalent) and 119 mg of trityl salt (1 equivalent) are dissolved in ca. 2 mL of chlorobenzene at ca. -50°C. After overnight stirring, the solvent is dried and the residue washed 2-3 times with few drops of pentane. The residue was not completely soluble in chlorobenzene neither in dichloromethane. The ^{29}Si NMR of the halogenated solvents shows only a baseline. The chlorobenzene solution is added with few drops of pentane and stored at -67°C. The pentane fraction is checked by ^{29}Si NMR and shows a quite pure and large amount of the starting material (see NMR data below)

NMR-Data (δ in ppm, pentane/D_2O cap.): ^{29}**Si**: -137.2 (*Si*Si_4), -33.4 ($SiMe_2H$), -9.9 ($SiMe_3$)

Reaction between 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) and TTPFPB in C_6D_6

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 30 mg of **51** (0.09 mmol), and 90 mg of trityl salt (1 equivalent) are dissolved in ca. 1 mL of deuterated benzene at R.T. After overnight stirring, the solution is divided in two phases, the upper one yellow, the lower one dark-red. The solvent is dried and the residue washed 2-3 times with few drops of pentane. The residue is dissolved in toluene and stored at -67°C.

The volume of the solution is reduced time by time, to promote crystals precipitation. But this was not observed. The pentane fraction is checked by ^{29}Si NMR and shows a quite pure and large amount of tetrakis(trimethylsilyl) silane (see NMR data below).

NMR-Data (δ in ppm, pentane/D_2O cap.): ^{29}**Si**: -136.2 (*Si*Si_4), -10.3 ($SiMe_3$)

Synthesis of 1,1,1-tris(trimethylsilyl)diphenylsilylgermane (53)

In a single neck flask with stopcock 948 mg of 1-tris(trimethylsilyl)germyl-1,1,1-triphenyl silane (1.72 mmol) are dissolved with ca. 10 mL of toluene at 0°C. Then 271 mg of triflic acid (1.80 mmol, 1.05 eq.) are slowly dropped into the reaction mixture with stirring. The system is kept under nitrogen and the mixture is stirred overnight. Then 76 mg of $LiAlH_4$ (Et_2O solution, 2.06 mmol, 1.2 eq.) are slowly dropped into the solution, cooled down again at 0°C with an ice bath. The white suspension is stirred overnight. After usual work up a colorless solid is collected (645 mg, 79% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.23 ($Si(CH_3)_3$, s, 27H); 5.49 ($SiPh_2H$, s, 1H);
7.09 – 7.90 ($Si(C_6H_5)_2H$, m, 10H)
^{29}Si: -20.8 ($SiPh_2H$); -4.4 ($SiMe_3$)
^{13}C: 2.9 ($Si(CH_3)_3$; 127.3, 127.6, 127.8, 135.7 ($Si(C_6H_5)_2H$)

Melting point: 65°C

Elemental analysis ($C_{21}H_{38}GeSi_4$, 476.13): Calc.: C, 53.04; H, 8.06.
Found: C, 54.79; H, 7.72.

Reaction between 1-tris(trimethylsilyl)germyl-1,1-diphenylsilane (53) and TTPFPB in C_6D_6

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 59 mg of oligosilane (0.12 mmol) are dissolved in ca. 1 mL of deuterated benzene and then set at -50°C with a metal block mantel. 114 mg of trityl salt (1 equivalent) are suspended in ca. 1 mL of C_6D_6 and slowly dropped above the solidified reaction mixture. Then the system is let go back to room temperature. After overnight stirring, the solution is divided in two phases, the upper one yellow, the lower one dark-red. The solvent is dried and the residue washed 2-3 times with few drops of pentane (collected separately). After evaporating completely the volatile, a kind of yellow sponge is formed. Part of this residue is dissolved in toluene, layered with heptane and stored at -67°C. The remaining solid is dissolved with few drops of chlorobenzene, added with some drops of toluene and stored at -67°C.

The volumes of both the solutions are reduced time by time, to promote crystals precipitation. But this was not observed. The pentane fraction is checked by ^{29}Si NMR, but nothing is detected. The ^{1}H NMR shows just a small amount of triphenylmethane.

NMR-Data (δ in ppm, pentane/D_2O cap.): **^{1}H**: 5.21 (Ph_3CH, s, 1H)

Reaction between 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) and TTPFPB in 1,2-dichloroethane

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 193 mg of **51** (0.63 mmol), and 290 mg of trityl salt (0.5 equivalent) are dissolved in ca. 0.7 mL of 1,2-dichloroethane at R.T. . After an intense bubbling a red clear solution is formed. ^{29}Si NMR reveals the clean formation of three products: (*1*) tetrakis(trimethylsilyl) silane; (*2*) 1,1,1-tris(trimethylsilyl)-2,2-dimethyl chlorodisilane and (*3*) 1,1,4,4-tetramethyl-2,2,3,3-tetra(trimethylsilyl)-dichlorotetrasilane (see NMR data below).

NMR-Data (δ in ppm, 1,2-C_2H_4/D_2O cap.): **^{1}H**: (*1*) -0.098 ($\mathrm{Si(C}\mathit{H}_3)_3$)
(*2*) -0.055 ($\mathrm{Si(C}\mathit{H}_3)_3$); 0.29 ($\mathrm{Si(C}\mathit{H}_3)_2\mathrm{Cl}$)
(*3*) -0.011 ($\mathrm{Si(C}\mathit{H}_3)_3$); 0.34 ($\mathrm{Si(C}\mathit{H}_3)_2\mathrm{Cl}$)
^{29}Si: (*1*) -136.1 ($\mathit{Si}\mathrm{Si}_4$), -10.3 ($\mathrm{SiMe_3}$)
(*2*) -129.7 ($\mathit{Si}\mathrm{Si}_4$), -10.3 ($\mathrm{SiMe_3}$),
33.0 ($\mathrm{SiClMe_2}$)
(*3*) -124.0 ($\mathit{Si}\mathrm{Si}_4$), -10.3 ($\mathrm{SiMe_3}$),
31.1 ($\mathrm{SiClMe_2}$)

Reaction between 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) and TTPFPB in 1,2-dichlorobenzene

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 158 mg of **51** (0.51 mmol), and 237 mg of trityl salt (0.5 equivalent) are dissolved in ca. 0.7 mL of 1,2-dichlorobenzene at R.T. . After stirring 30 minutes, the clear red solution is checked with ^{29}Si NMR, but no signal appears in the spectrum. ^{19}F NMR reveals decomposition of the borate counter anion. ^{1}H and ^{13}C NMR shows the presence of triphenylmethane and only a broad signal in the oligosilane usual regions. The solution is layered with about the double volume of pentane. During few days the two phases mix up and at the bottom of the vial a kind of crystals appear. Microscope analysis reveals they are microcrystalline agglomerates. It is not possible anyway to manipulate them without disruption.

Reaction between 1,1,1-tris(trimethylsilyl)-2,2-dimethyldisilane (51) and TTPFPB in trimethylchlosilane

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 99 mg of **51** (0.32 mmol), and 298 mg of trityl salt (1 equivalent) are dissolved in ca. 0.7 mL of trimethylchlorislane at R.T. . After stirring 30 minutes, a red solution with some pale yellow solid ins suspension is formed. ^{29}Si NMR reveals just the solvent signal and no presence of any type of silyl cation. Layering pentane (a two times the reaction mixture volume) does not lead to any crystalline precipitate.

Synthesis of 1,1,1,44,4-hexakis(trimethylsilyl)octamethylhexasilane (55)

In a 20 mL glass vial, 1184 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (1.94mmol) and 2.1 equivalents of *t*-BuOK (4.07 mmol, 456 mg) are dissolved with ca. 10 mL of DME, at RT. After 12 hours of stirring, the red solution is checked by ^{29}Si NMR to verify complete conversion of the starting material into disilanyl potassium (**101**). Then the solution is slowly dropped in a second 20 mL glass vial containing 4.0 equivalents of $\mathrm{ClSiMe_2H}$ (27.76mmol, 734 mg). The white suspension is stirred 12 hours and the product worked up in the usual manner. A white powder is obtained (800 mg, 71% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.32 (Si(C*H*$_3$)$_2$H, d, $^2J_{HH}$ = 4.4 Hz, 12H);
0.29 (Si(C*H*$_3$)$_3$, s, 36H); 0.49 (Si(*C*H$_3$)$_2$, s, 12H);
4.35 (Si(CH$_3$)$_2$*H*, sept, $^2J_{HH}$ = 4.4 Hz, 12H)
^{29}Si: -131.2 (*Si*Si$_4$); -32.5 (*Si*Me$_2$H); -29.9 (*Si*Me$_2$);
-9.2 (SiMe$_3$)
^{13}C: -1.71 (Si(*C*H$_3$)$_2$H); 3.08 (Si(*C*H$_3$)$_3$); 0.60 (Si(*C*H$_3$)$_2$)

Melting point: 165°C
Elemental analysis: $C_{20}H_{62}Si_{10}$ (583.57): Calc.: C, 41.16; H, 10.71
Found: 37.41; H, 9.78

Synthesis of 1,1,3,3-hexakis(trimethylsilyl)-1,1,2,2,3,3-hexamethylpentasilane (57)

In a 20 mL glass vial, 400 mg of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-dimethyltrisilane (0.72 mmol) and 2.1 equivalents of *t*-BuOK (1.52 mmol, 170 mg) are dissolved with ca. 5 mL of DME, at RT. After 12 hours of stirring, the red solution is checked by ^{29}Si NMR to verify complete conversion of the starting material into disilanyl potassium (**104**). Then the solution is slowly dropped in a second 20 mL glass vial containing 4.0 equivalents of ClSiMe$_2$H (2.88 mmol, 275 mg). The white suspension is stirred 12 hours and the product worked up in the usual manner. A white waxy solid is obtained (253 mg, 66% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.31 (Si(C*H*$_3$)$_3$, s, 36H); 0.34 (Si(C*H*$_3$)$_2$H, d*b*, 12H);
0.50 (Si(*C*H$_3$)$_2$, s, 6H);4.39 (Si(CH$_3$)$_2$*H*,sept, $^2J_{HH}$ = 4.4 Hz, 12H)
^{29}Si: -125.5 (*Si*Si$_4$); -31.9 (*Si*Me$_2$H); -26.7 (*Si*Me$_2$);
-8.9 (SiMe$_3$)
^{13}C: -1.8 (Si(*C*H$_3$)$_2$H); 3.4 (Si(*C*H$_3$)$_3$); 3.6 (Si(*C*H$_3$)$_2$)

Melting point: 81-85°C
Elemental analysis ($C_{18}H_{26}Si_9$, 525.41): Calculated: C, 41.15; H, 10.74
Found: C, 40.12; H, 9.80

Synthesis of 1,1,1,3,3,3-hexakis(trimethylsilyl)methyltrisilane (59)

In a 20 mL glass vial, 1022 mg of **1** (3.18 mmol) and 1.05 equivalents of *t*-BuOK (3.34 mmol, 375 mg) are dissolved with ca. 5 mL of DME, at RT. After 12 hours of stirring, the red solution is checked by ^{29}Si NMR, to verify complete conversion of the starting material in the silanyl potassium. Then the solution is slowly dropped in a second 20 mL glass vial containing 0.52 equivalents of SiCl$_2$MeH (1.67 mmol, 192 mg). The white suspension is stirred 12 hours and the product worked up in the usual manner. A white waxy solid is obtained (893 mg, 87% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_5Cl): **^{1}H**: 0.24 (Si(C*H*$_3$)$_3$, s, 54H); 0.44 (Si(C*H*$_3$)H, d,
$^2J_{HH}$ = 5.1 Hz, 3H); 4.05 (Si(CH$_3$)*H*, q, $^2J_{HH}$ = 5.1 Hz, 1H)
^{13}C: -0.8 (Si(*C*H$_3$) H); 3.1 (Si(*C*H$_3$)$_3$)
^{29}Si: -124.8(*Si*Si$_4$); -65.6 (*Si*MeH); -9.3 (*Si*Me$_3$)

Reaction between 2,2,5,5-tetra(trimethylsilyl)-3,3,4,4-tetramethyl-1,1,6,6-tetramethyl hexasilane (55) and TTPFPB in C_6D_5Cl - Low temperature experiment

Inside the glovebox, in a 25 mL Schlenk flask equipped with Teflon cap and a stir bar, 135 mg of **55** (0.23 mmol) are dissolved in 0.5 mL of deuterated chlorobenzene. Then the flask is moved outside the glovebox and connected to the Schlenk line. The solution is cooled down to ca. -40°C with an ethanol/liquid nitrogen bath (the solvent solidifies). In the meanwhile 213 mg of TTPFPB (1 equivalent) are dissolved in 0.5 mL of C_6D_5Cl in a glass vial and the solution is cooled down in the freezer (-67°C) till almost the freezing point. Then the mixture is quickly taken with a syringe, transferred outside the glovebox, and slowly dropped into the Schlenk flask of the oligosilane solution, under a nitrogen flow. At ca. -35°C the system starts to be completely liquid. The solution is stirred ca. 30 minutes. In another ethanol bath set at -30°C a big Schlenk flask filled with hexane is cooled down with a NMR tube inside. In this tube 0.6 mL of the reaction mixture are quickly moved with a cooled syringe under a nitrogen flow. The tube is then closed and moved in a smaller ethanol bath and moved to the pre-cooled NMR instrument (-30°C). After NMR analysis no crystallization is tried because no signal shows up in the ^{29}NMR spectrum, after standing 4 hours at room temperature.

NMR-Data (δ in ppm, C_6D_5Cl, -30°C) **^{1}H**: 0.046, 0.10, 0.21, 0.43 ($Si(CH_3)_3$ and $Si(CH_3)_2$, s, 60H); 1.99 ($Me_2Si\text{-}H^+\text{-}SiMe_2$, s, 1H); 5.31 ($Ph_3CH$, s, 1H); 6.90-7.10 ($(C_6H_5)_3CH$, mp, 15H)

^{29}Si: -122.83 ($SiSi_4$); -40.1 ($SiMe_2$); -7.4 ($SiMe_3$); 85.9 ($Me_2Si\text{-}H^+\text{-}SiMe_2$)

Reaction between bis(hypersilyl)methylsilane (59) and TTPFPB in deuterated chlorobenzene – Low temperature experiment

Inside the glovebox, in a 25 mL Schlenk flask equipped with Teflon cap and a stir bar, 111 mg of **59** (0.21 mmol) are dissolved in 0.5 mL of deuterated chlorobenzene. Then the flask is moved outside the glovebox and connected to the Schlenk line. The solution is cooled down to ca. -40°C with an ethanol/liquid nitrogen bath (the solvent solidifies). In the meanwhile 95 mg of TTPFPB (0.5 equivalent) are dissolved in 0.5 mL of C_6D_5Cl in a glass vial and the solution is cooled down in the freezer (-67°C) till almost the freezing point. Then the mixture is quickly taken with a syringe, transferred outside the glovebox, and slowly dropped into the Schlenk flask of the oligosilane solution, under a nitrogen flow. At ca. -30°C the system starts to be completely liquid. The solution is stirred ca. 30 minutes. In another ethanol bath set at -30°C a big Schlenk flask filled with hexane is cooled down with a NMR tube inside. In this tube 0.6 mL of the reaction mixture are quickly moved with a cooled syringe under a nitrogen flow. The tube is then closed and moved in a smaller ethanol bath and moved to the pre-cooled NMR instrument (-30°C). ^{29}NMR spectrum reveals only the presence of the starting material. Increasing slowly the temperature, does not lead to any conversion. After standing overnight at room temperature, the solution contains just the starting material.

Reaction between bis(hypersilyl)methylsilane (59) and TTPFPB in chlorobenzene
Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 128 mg of **59** (0.24 mmol) and 219 mg of trityl salt (1 equivalent) are dissolved in ca. 1.0 mL of chlorobenzene at RT. After 2 hours of stirring, convertion of the starting material is observed. The solution is heated up to 80°C and stirred overnight. The ^{29}Si NMR reveals that the substrate is reacted completely, but tetrakis(trimethylsilyl) silane is also formed (-136.4 ppm, -10.5 ppm). Two groups of signal are visible in the ^{19}F NMR. The solution is layered with pentane (ca. two times its volume). Some semitransparent solid precipitates but microscope analysis reveals that a kind of microcrystalline agglomerate is formed, that is not suitable for X-ray measurement.

NMR-Data (δ in ppm, chlorobeneze/D_2O cap.): **^{1}H**: -0.38, -0.14, 0.19, 3.4, 4.6, 5.0
^{29}Si: -136.4 (*Si*Si$_4$), -10.5 (*Si*Me$_3$);
-133.4 (*Si*Si$_4$), -7.7 (*Si*Me$_3$);
46.7 (Hyp$_2$MeSi$^+$?)
-0.8, 76.2 (unknown)

Reaction between bis(hypersilyl)methylsilane (59) and TTPFPB in triethylsilane
Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 102 mg of **59** (0.19 mmol) are dissolved in 0.7 mL Et_3SiH at RT. To the clear solution 175 mg (1 equivalent) of trityl salt are added. A violent bubbling is observed. After 24 hours of stirring, the ^{29}Si NMR shows signals from the solvent, tetraethyl silane and triethylmethylsilane. A number of peaks are present in the ^{19}F NMR.

NMR-Data (δ in ppm, triethylsilane/D_2O cap.): **^{29}Si**: 0.23 (Et$_3$*Si*H), 6.8 (Et$_3$*Si*Me),
7.9 (Et$_4$*Si*)
^{19}F: -126.8, -148.0, -159.7 (B(C$_6$*F*$_5$)$_3$)
-132.1, -161.5, -168.2 (B(C$_6$*F*$_5$)$_4^-$)
-132.8, -151.4, -156, -163 (unknown)

Reaction between bis(hypersilyl)methylsilane (59) and TTPFPB in pentane/toluene

Inside the glove-box, in a 20 mL glass vial equipped with plastic/silver paper cap, 103 mg of **59** (0.19 mmol) and 88 mg of trityl salt (0.5 equivalent) are suspende in ca. 0.7 mL of pentane at RT. After 4 hours of stirring, no color change is observed. Ca. 0.5 mL of toluene are added and the mixture is stirred over the weekend. A thin layer of a red oil deposits at the bottom of the vial, but in solution there is still pure starting material. Ca. 1 mL of chlorobenzene is added and the solution (clear and red) is stirred overnight. No change in the NMR spectrum is observed, so one drop of triethyl silane is added. After 12 hours of stirring, the ^{29}Si NMR shows that there is no more substrate in solution, but very small signals could be detected, even after overnight measurement. Two groups of signals are found in the ^{19}F NMR (decomposition of the catalyst towards $B(C_6F_5)_3$). The solution is dried and redissolved in chlorobenzene. The silicon NMR is acquired again, and it shows two quite big signals in the region of ca. +70 ppm (see NMR data below). Layering pentane leads to a kind of fishbone precipitate. When the two phases are completely mixed, the vial is stored at -67°C. After some days the precipitate seems to get a crystalline form, but it should be checked under the microscope.

NMR-Data (δ in ppm, chlorobeneze/D_2O cap.): **^{29}Si**: -136.3 (*Si*Si_4), -133.4 (*Si*Si_4),
-10.5 ($SiMe_3$); 67.5 (Hyp_2MeSi^+?),
76.1 (unkwon)

Reaction between pentaphenyldisilane (60) and TTPFPB

Inside the glove-box, in a 20 mL glass vial, equipped with plastic/silver paper cap, 30 mg of pentaphenyldisilane (0.068 mmol) and 63 mg of trityl salt (1 equivalent) are dissolved in ca. 1 mL of chlorobenzene at room temperature and stirred overnight. An orange suspension is formed. No NMR signal could be detected in the ^{29}Si NMR and just the solvent in the ^{1}H NMR. The solvent is dried under vacuum and the residue washed 2-3 times with pentane. The residue is stirred ca. 10 mL of toluene and the solution is stored at -67°C. The remaining solid is dissolved in ca. 5 mL of chlorobenzene, added with some drops of pentane and stored at -67°C. In both cases, no crystalline precipitate was observed.

Synthesis of trityltetra(pentafluorophenyl) borate – TTPFPB

In a 1 liter dried two necks flask (one with stopcock) 11,899 g (48,82 mmol, 1,11 eq. in respect to the amount of *n*-BuLi) of BrC_6F_5 are dissolved in ca. 250 mL of pentane. The system is cooled down with an ethanol/liquid nitrogen bath at -80°C and a hexane solution of *n*-BuLi (27,1 mL, 1,6M, 43,368 mmol) is added drop wise in ca. 2 hours and a half. After 1 hour 10,8 mL of BCl_3 (1M solution, 10,842 mmol, 1 eq.) are added in ca. 20 minutes. The temperature of the bath is increased till -50°C and kept at this value for 1 hour. The system is let to come back at room temperature and the mixture is stirred overnight. The solvent is taken away via cannula and the white solid is washed 2 times with 100 mL of dried pentane. The liquid is completely evaporated and the solid suspended again in pentane. 3,02 g (10,842 mmol, 1 eq.) of Ph_3CCl are added to the solution: an orange solid is immediately forming and the mixture turns orange. The mixture is stirred overnight. The solvent is then evaporated and the solid residue is suspended in CH_2Cl_2: the LiCl formed during the reaction is filtered on a glass filter (G3). The liquid phase is concentrated till ca. 50 mL of volume and then a double amount of Heptane is added. No precipitate is forming, just a dark sticky oil. The solvent is dried again, dissolved in ca. 50 mL of CH_2Cl_2 and moved into a bigger flask (3 liters) and then about 1 liter of pentane is added. After stirring overnight, some yellow crystals are forming. The suspension is stirred for a week, then the solid is decanted and the solvent is removed via cannula. The precipitate is washed 2 times with ca. 500 mL of pentane and then dried under vacuum. A thin yellow-orange powder is collected (2.34 g, ca. 20% of the Th. Y.)

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 6.82 (d, 6H, $^{3}J_{HH}$=7.4 Hz); 7.16 (t, 3H); 7.53 (t, 6H)
^{19}**F**: -166.84 (t, 8F, m-C_6F_5); -163.05 (t, 4F, p-C_6F_5); -132.61 (d, 8F, o-C_6F_5);
^{11}**B**: -16.82

Chapter 6

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 404 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.66 mmol) and 152 mg of *t*-BuOK (1.35 mmol, 2.05 eq.) are dissolved in ca. 4 mLL of THF. The reaction continues at room temperature under stirring over the weekend. The dianion formation is checked by ^{29}Si NMR. Then it is dropped through a syringe into a Rosenthal reagent solution (4 mL in THF, 230 mg of $TiCp_2$(*btmsa*), 0.66 mmol, 1 eq.) over a period of 5 minutes. The solution is stirred for 1 hour. Then ca. 4 mL of pentane are added and after stirring for 5 minutes, the mixture is let standing overnight. Next morning the solution is centrifuged, the upper liquid phase collected and the solvent evaporated. A black solid mass was obtained. It is tried a crystallization by lairing pentane on a concentrate solution in benzene; by cool down at -60°C a concentrated solution in toluene; by slowly evaporating solvent from a solution of the product in CH_2Cl_2. No one of these methods affords to suitable crystals for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.45 (s, 18H); 0.60 (s, 18H); 1.41 , 3.40 (m, THF);
5.85 (s, 5H, KCp); 6.41 (s, 5H, CpTi)
^{29}Si: -115.6 (Ti*Si*Si_3); -36.5 (Si*Si*Me_2Si);
-17.5, -15.3, -11.2, -7.2, -4.9 (Me_3*Si*)

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 529 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.865 mmol) and 194 mg of *t*-BuOK (1.73 mmol, 2.0 eq.) are dissolved in ca. 4 mL of THF, in the presence of 18-crown-6 (1.73 mmol, 457 mg). The reaction continues over the weekend and the dianion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (301 mg, 0.865 mmol) is dissolved in ca. 4 mL of THF and the dianion is slowly dropped in through a syringe. After 3 days the suspension is added with some pentane and then centrifuged. The upper solution is collected and dried under vacuum. Black brilliant flakes are obtained. The ^{29}Si NMR of this material shows a mixture of at least three products, with a very complicated situation in the Me_3Si region. The solid has no crystalline structure (it melts into the oil during the preparation of the X-ray sample.

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetra(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclotetrasilane (102)

In a 20 mL glass vial 110 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.180 mmol) and 40 mg of *t*-BuOK (0.36 mmol, 2.0 eq.) are dissolved in ca. 1 mL of DME. The reaction continues over the weekend and the dianion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (63 mg, 0.180 mmol) is dissolved in ca. 2 mL of THF and the dianion is slowly dropped in through a syringe. After 3 days the suspension is added with some pentane and then centrifuged. The upper solution is collected and dried under vacuum. A black mass is obtained. As in the previous synthesis, the ^{29}Si NMR of this material shows a mixture of at least three products, with a very complicated situation in the Me_3Si region.

Synthesis of CpTi(*btmsa*)-1,1,1-tris(trimethylsilyl)silane) (106)

In a 20 mL glass vial 522 mg of tetrakis(trimethylsilyl)silane (1.63 mmol), 184 mg of *t*-BuOK (1.64 mmol, 1.01eq.) and 433 mg of 18-crown-6 (1.64 mmol, 1.01 eq.) are dissolved in ca. 4 mL of THF. The reaction continues overnight and the anion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (568 mg, 1.63 mmol.) is dissolved in ca. 4 mL of THF and the anion is slowly dropped into the Rosenthal reagent solution through a syringe. After 1 day the suspension is added with some pentane and then centrifuged. The upper solution is collected and dried under vacuum. A sponge-gummy black solid is obtained. This mass is treated 3 times with few milliliters of pentane; the solvent is then collected and dried under vacuum. ^{29}Si NMR shows that this is material is pure tetrakis(trimethylsilyl)silane.

Synthesis of CpTi(*btmsa*)-bis(1,1,1-tris(trimethylsilyl)silyl) potassium (108)

In a 20 mL glass vial 1027 mg of tetrakis(trimethylsilyl)silane (3.20 mmol), 363 mg of *t*-BuOK (3.23 mmol, 1.01eq.) and 853 mg of 18-crown-6 (3.23 mmol, 1.01 eq.) are dissolved in ca. 4 mL of THF. The reaction continues over the weekend and the anion formation is checked by ^{29}Si NMR. Then 0.5 eq. of Cp_2Ti(*btmsa*) (557 mg, 1.60 mmol.) is dissolved in ca. 4 mL of THF and the anion is slowly dropped into the Rosenthal reagent solution through a syringe. After 1 day the suspension is added with some pentane and then centrifuged. The upper solution is collected and dried under vacuum. A sponge-gummy black solid is obtained. This mass is treated 5 times with few milliliters of pentane; the solvent is then collected and dried under vacuum. ^{29}Si NMR shows that this is material is pure tetrakis(trimethylsilyl)silane.

Synthesis of CpTi(*btmsa*)-bis(1,1,1-tris(trimethylsilyl)silyl) potassium (108)

In a 20 mL glass vial 517 mg of tetrakis(trimethylsilyl)silane (1.61 mmol) and 185 mg of *t*-BuOK (1.64 mmol, 1.02eq.) are dissolved in ca. 4 mL of DME. The reaction continues for 4 hours at 60°C and the anion formation is checked by ^{29}Si NMR. Then 0.5 eq. of Cp_2Ti(*btmsa*) (280 mg, 0.805 mmol.) is dissolved in ca. 4 mL of DME and the anion is slowly dropped into the Rosenthal reagent solution through a syringe. After 3 days the ^{29}Si NMR shows that the main product in the reaction mixture is tetrakis(trimethylsilyl)silane.

Reaction between Cp$_2$Ti(*btmsa*) and 1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyl-cyclotetrasilyl magnesium (103)

In a 20 mL glass vial 448 mg of tetrakis(trimethylsilyl)silane (0.732 mmol) and 169 mg of *t*-BuOK (1.50 mmol, 2.05 eq.) are dissolved in ca. 4 mLmL of THF. The reaction continues for about. 30 hours and the dianion formation is checked by ^{29}Si NMR. Then 1.01 eq. of $MgBr_2$•Et_2O (0.739 mmol, 191 mg) are added to the solution, that immediately turns yellow. After 1 hour the ^{29}Si NMR spectrum shows the formation of the Magnesium complex. 1 eq. of Cp_2Ti(*btmsa*) (255 mg, 0.732 mmol.) are dissolved in ca. 4 mL of THF and the dianion is slowly dropped into the Rosenthal reagent solution through a syringe. After 3 days (2 days running at 80°C) the ^{29}Si NMR shows that the dianion has not reacted.

Reaction between Cp$_2$Ti(*btmsa*) and (tris(trimethylsilyl)silyl) magnesium bromide (107)

In a 20 mL glass vial 459 mg of tetrakis(trimethylsilyl)silane (1.43 mmol) and 164 mg of *t*-BuOK (1.46 mmol, 1,02 eq.) are dissolved in ca. 4 mLmL of THF. The reaction continues for about. 30 hours and the anion formation is checked by ^{29}Si NMR. Then 1.0 eq. of $MgBr_2$•Et_2O (1.43 mmol, 369 mg) are added to the solution, that immediately turns yellow. After 1 hour the ^{29}Si NMR spectrum shows the formation of the magnesium complex. 0.5 eq. of Cp_2Ti(*btmsa*) (247 mg, 0.715 mmol) are dissolved in ca. 4 mL of THF and the anion is slowly dropped into the Rosenthal reagent solution through a syringe. After 3 days (2 days running at 80°C) the ^{29}Si NMR shows that the anion is still present in the reaction mixture.

Reaction between Cp_2Ti(*btmsa*) and bis(tris(trimethylsilyl)silyl) magnesium (108)

In a 20 mL glass vial 335 mg of tetrakis(trimethylsilyl)silane (1.04 mmol) and 120 mg of *t*-BuOK (1.06 mmol, 1.02 eq.) are dissolved in ca. 4 mL of THF. The reaction continues for about. 1 hour at 80°C and the anion formation is checked by ^{29}Si NMR. Then 0.5 eq. of $MgBr_2 \bullet Et_2O$ (0.52 mmol, 155 mg) are added to the solution, that immediately turns yellow. After 1 hour the ^{29}Si NMR spectrum shows the formation of the Magnesium complex. 0.5 eq. of Cp_2Ti(*btmsa*) (182 mg, 0.52 mmol.) are dissolved in ca. 4 mLL of DME and the anion is slowly dropped into the Rosenthal reagent solution through a syringe. After 1 day the ^{29}Si NMR shows that the anion is still present in the reaction mixture.

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 477 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.74 mmol) and 170 mg of *t*-BuOK (1.52 mmol, 2.05 eq.) are dissolved in ca. 4 mL of THF. The reaction continues over the weekend and the dianion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (301 mg) is dissolved in ca. 4 mL of THF and put in a metal mantel stored overnight at -60°C. The dianion is slowly dropped in the Rosenthal reagent solution through a syringe. The reaction continues over the weekend. After this time the anion is completely consumed, but the ^{29}Si NMR of the reaction mixture is not clear. The usual work up led to a black mass from which was not possible to isolate any crystal for X-ray analysis.

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 375 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.61 mmol) and 145 mg of *t*-BuOK (1.29 mmol, 2.10 eq.) are dissolved in ca. 4 mL of 2,4-dioxane. The reaction continues over the weekend and the dianion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (214 mg) is dissolved in ca. 4 mL of dioxane and the dianion is slowly dropped in the Rosenthal reagent solution through a syringe. After 2 hours the anion is completely consumed. The reaction mixture is layered with ca. 8 mL of pentane, but after the two solvent phases vanished, no precipitate was observed. Slow evaporation of the solvent led only a semisolid red residue.

NMR-Data (δ in ppm, 1,4-dioxane/D_2O cap.): **^{29}Si**: -113.7 (Ti*Si*Si_3); -116.0 (Ti*Si*Si_3); -36.3 (Si*Si*Me_2Si); -19.0 (*Si*Me_3, free *btmsa*); -14.4 (*Si*Me_3, bonded *btmsa*); -10.6, -9.4, -8.1, -5.0 (Me_3*Si*)

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 216 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.35 mmol) and 81 mg of *t*-BuOK (0.72 mmol, 2.05 eq.) are dissolved in ca. 4 mL of benzene in the presence of 18-crown-6 (191 mg, 0.72 mmol). The reaction continues for 6 hours at 60°C and the dianion formation is checked by ^{29}Si NMR. Then 1 eq. of Cp_2Ti(*btmsa*) (123 mg) is dissolved in ca. 4 mL of benzene and the dianion is slowly dropped in the Rosenthal reagent solution through a syringe. After 48 hours the anion is completely consumed. The solvent is dried and then two attempts of extracting the product are tried: a first extraction with pentane at R.T. and consequent evaporation of the solvent lead to no product. A second extraction with heptane at 80°C lead to no product too.

NMR-Data (δ in ppm, benzene/D_2O cap.): **^{29}Si**: -121.1 (Ti*Si*Si_3); -18.2 (*Si*Me_3, *btmsa*);
-16.4 (Si*Si*Me_2Si); -7.3, -5.0 (Me_3*Si*);
-131.1, -9.8: tetrakis(trimethylsilyl)silane

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 205 mg of 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.33 mmol) and 79 mg of *t*-BuOK (0.70 mmol, 2.10 eq.) are dissolved in ca. 4 mL of THF. The reaction continues overnight at 60°C and the dianion formation is checked by ^{29}Si NMR. The solvent is evaporated, the remaining oily washed with benzene and dried again. This procedure is repeated three times. Then 1 eq. of Cp_2Ti(*btmsa*) (123 mg) is dissolved in ca. 4 mL of benzene and the dianion (in benzene) is slowly dropped in the Rosenthal reagent solution through a syringe. After 24 hours the anion is completely consumed. Some pentane is added and the mixture is stirred for half a hour. Then the black oil forming is decanted and the liquid solution is removed with a syringe, dried and solubilize in 2-3 mL of benzene in a 5 mL vial. This vial is moved into a 20 mL vial containing ca. 3 mL of pentane (double vial precipitation). No crystals occurred after the solvent mixed together, neither after a slow evaporation of the formed solution.

NMR-Data (δ in ppm, benzene/D_2O cap.): **^{29}Si**: -116.1 (Ti*Si*Si_3); -17.7 (Si*Si*Me_2Si);
-15.6 (*Si*Me_3, *btmsa*); -7.4 , -5.0 (Me_3*Si*)

Synthesis of CpTi(*btmsa*)-1,4- bis(trimethylsilyl)bipentacyclo(octamethyl)heptasilane

In a 20 mL glass vial 245 mg of 1,1,4,4-tetra(trimethylsilyl)-2,2,3,3,5,5,6,6-octamethyl cyclohexasilane (0.42 mmol) and 104 mg of *t*-BuOK (0.93 mmol, 2.2 eq.) are dissolved in ca. 4 mL of THF. The reaction continues at room temperature for 18 hours to give **110**. A white precipitate has formed. Then 1 eq. of Cp_2Ti(*btmsa*) (147 mg) is dissolved in ca. 4 mLmL of benzene and the solution of **110** is slowly dropped in with syringe. After 24 hours the anion seems completely consumed. The ^{29}Si NMR reveals two signals in the region of -100 to -112 ppm (sfor the silicon bonded to titanium atom) and many peaks for the $–SiMe_3$ groups. 1-2 mL of pentane are added to the reaction mixture and the forming solid is decanted. The clear red solution is moved with a syringe into another vial, it is dried and dissolved in the minimum amount of THF. Then a double vial crystallization is tried, using cyclohexane as antisolvent. After some days the solvent have mixed up, but only a dark red powder is formed.

Synthesis of CpTi(*btmsa*)-1,4-bis(trimethylsilyl)bipentacyclo(octamethyl)heptasilane

In a 20 mL glass vial 214 mg of 1,1,4,4-tetra(trimethylsilyl)-2,2,3,3,5,5,6,6-octamethyl cyclohexasilane (0,37 mmol) and 91 mg of *t*-BuOK (0,81 mmol, 2,2 eq.) are dissolved in ca. 4 mL of benzene in the presence of 18-crown-6 (214 mg, 0,81 mmol). The reaction continues overnight at 60°C and the dianion formation is checked by ^{29}Si NMR (no starting material in solution). A white precipitate has formed. Then 1 eq. of Cp_2Ti(*btmsa*) (123 mg) is dissolved in ca. 4 mL of benzene and it is slowly dropped in dianion solution through a syringe. After 24 hours the anion is completely consumed. Some milliliters of pentane are added and the mixture is stirred for half a hour. Then the black oil forming is decanted and the liquid solution is removed with a syringe and dried. A small fraction of the red solid formed is dissolved in ca. 0,5 mL of benzene, moved in a NMR tube and layered with ca. 2 mL of pentane. The remaining material is dissolved in a 50/50 toluene/pentane solution and stored in the fridge at -67°C.

No crystals appeared at low temperature; the vial has moved outside the fridge and the solvent is allowed to slowly evaporate. Brilliant particles have precipitated, and some of them are submitted to X-ray analysis: the poor quality of the crystals lead to a structure not well resolved, even if the expected product could be identified.

From the NMR tube it was possible to collect small transparent and colorless crystals, that were suitable for X-ray analysis but it was found they were the by-product salt KCp.

NMR-Data (δ in ppm, benzene/D_2O cap.): **^{29}Si**: -101.8 (Ti*Si*Si_3);
-27.7, -23.4 (Si*Si*Me_2Si);
-19.6 (*Si*Me_3, free *btmsa*?);
-17.6 (*Si*Me_3, *btmsa*); -5.6 (Me_3*Si*)

Synthesis of CpTi(*btmsa*)-1,1,2,2-tetra(trimethylsilyl)-tricyclodigermane (112)

In a 20 mL glass vial 168 mg of 1,1,1,2,2,2-hexakis(trimethylsilyl)-digermane (0.29 mmol) and 68 mg of *t*-BuOK (0.60 mmol, 2.1 eq.) are dissolved in ca. 4 mL of benzene in the presence of 18-crown-6 (159 mg, 0.60 mmol). The reaction continues for 3 hours at room temperature. Then 1 eq. of Cp_2Ti(*btmsa*) (100 mg) is dissolved in ca. 4 mL of benzene and it is slowly dropped in dianion solution through a syringe. The mixture is stirred overnight; then 5 mL of pentane are added and the mixture is centrifuged for 5 hours. The liquid phase is collected and dried under vacuum. The dark red semisolid residue is washed with small portions of pentane and dried again. A red powder is obtained: few milligrams are dissolved in C_6D_6 in a NMR tube and layered with pentane. The remaining solid is dissolved in the minimum amount of toluene and stored in the fridge at -67°C. No crystals were collected from both of the system employed to precipitate the product.

NMR-Data (δ in ppm, C_6D_6.): **^{1}H**: 0.53 (Si(C*H*$_3$)$_3$, s, 18H, *btmsa*);
0.83 (GeSi(C*H*$_3$)$_3$, s, 18H); 0.92 (GeSi(C*H*$_3$)$_3$, s, 18H);
3.17 (-C*H*$_2$-, s, 24H, crown ether); 6.16 (C$_5$*H*$_5$K, s);
6.63 (TiC$_5$*H*$_5$, s, 5H);
^{13}C: 2.3 (Si(*C*H$_3$)$_3$, *btmsa*); 7.4, 7.6 (GeSi(*C*H$_3$)$_3$);
69.0 (-*C*H$_2$-, crown ether); 104.3 (*C*$_5$H$_5$K); 107.0 (Ti*C*$_5$H$_5$);
276.7 (*C*≡*C*, *btmsa*); 305.2 (*C*≡*C*, *btmsa*);
^{29}Si: -21.1 (*Si*Me$_3$, *btmsa*); -4.3 , -0.6 (Me$_3$*Si*)

Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-1,4-bis(2-norbornyl)-hexamethylhexasilane (75)

In a single neck flask with stopcock 1285 mg of **27** (3.20 mmol) and 377 mg of potassium *tert*-butoxide (3.36 mmol, 1.05 eq) are dissolved with ca. 40 mL of THF at room temperature. The solution turns yellow after few minutes. The system is set under nitrogen and is stirred 12 hours. The anion complete formation is checked by ^{29}Si NMR. The reaction mixture is moved into a dropping funnel using a syringe. The funnel is put on a flask with stopcock in which 300 mg (1.6 mmol, 0.5 eq.) of tetramethyldichlodisilane are dissolved with ca. 10 mL of THF. The anion is slowly dropped into the chlorosilane solution in ca. 8 h and then the mixture is stirred for 12 hours. After usual work up and solvent evaporation, a white solid is obtained (1010 mg, 82% of the Th. Yield). The product was not completely pure (by NMR), but after a finger distillation and recrystallization from acetone at room temperature, it was possible to obtain colorless sea urchin needles, suitable for X-ray analysis.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.24, 0.31 (Si(C$_7$H$_{11}$)(C*H*$_3$)$_2$, s, 6H+6H);
0.33, 0.34 (Si(*C*H$_3$)$_3$, s, 36H);
0.57 (Si(C*H*$_3$)$_2$Si(C*H*$_3$)$_2$, s, 12H);
0.90-2.5 (Si(C$_7$*H*$_{11}$)(CH$_3$)$_2$, s, 22H)
^{13}C: 0.4, 0.6 (Si(C$_7$H$_{11}$)(*C*H$_3$)$_2$); 1.8 (Si(*C*H$_3$)$_2$Si(*C*H$_3$)$_2$);
3.8 (Si(*C*H$_3$)$_3$);
28.8, 32.3, 33.8, 34.1, 37.1, 39.9, 38.9 (Si(*C*$_7$H$_{11}$)(CH$_3$)$_2$)
^{29}Si: -127.4 (*Si*Si$_4$); -29.1 (*Si*Me$_2$*Si*Me$_2$); -9.7, -9.6 (*Si*Me$_3$);
-5.2 (*Si*Me$_2$C$_7$H$_{11}$)

Melting point: 125°C

Elemental analysis: $C_{34}H_{82}Si_{10}$ (771.88): Calc.: C, 52.91; H, 10.71
Found: C 52.41; H 10.59

Reaction between Cp_2Ti(*btmsa*) and 1,4-dipotassio-1,4-bis(trimethylsilyl)-1,4-bis(dimethyl(2-norbornyl)silyl)tetramethyltetrasilane (76)

In a 20 mL glass vial 386 mg of 1,1,4,4-tetrakis(trimethylsilyl)-1,4-bis(2-norbornyl)-hexamethylhexasilane (**75**) (0.59 mmol) and 138 mg of *t*-BuOK (1.24 mmol, 2.2 eq.) are dissolved in ca. 4 mL of toluene in the presence of 18-crown-6 (326 mg, 1.24 mmol). The reaction continues for 12 hours at room temperature. The anion formation is not complete, so ca. 50 mg of *t*-BuOK are added and the vial is heated up to 80°C. After 8 hours, 1 eq. of Cp_2Ti(*btmsa*) (205 mg) is dissolved in ca. 4 mL of toluene and the dianion solution is slowly dropped in through a syringe. The mixture is stirred overnight; then the ^{29}Si NMR spectrum is acquired but it is not clear. The solvent is removed under vacuum and the semisolid dark red residue is extract with pentane. The clear red solution is allowed to slowly evaporate, but it contains only few drops of a reddish oil. The residue of the extraction is dissolved in the minimum quantity of toluene and stored in the fridge at -67°C.

Synthesis of CpTi(*btmsa*)-1,1,3,3-tetrakis(trimethylsilyl)-2,2-(dimethyl)tricyclosilane (105)

In a 20 mL glass vial 349 mg of 1,1,1,3,3,3-tetrakis(trimethylsilyl)-2,2-trimethyltrisilane (0.63 mmol) and 148 mg of *t*-BuOK (1.32 mmol, 2.1 eq.) are dissolved in ca. 4 mL of toluene in the presence of 18-crown-6 (350 mg, 1.32 mmol). The reaction continues for 24 hours at room temperature. Then 1 eq. of Cp_2Ti(*btmsa*) (219 mg) is dissolved in ca. 4 mL of toluene and the dianion solution is slowly dropped into the Rosenthal reagent solution through a syringe. The mixture is stirred ca. 6 hours; then the ^{29}Si NMR spectrum is acquired but it is not extremely clean (only main peaks are then reported). The solvent is dried completely and the residue is dissolved in the minimum amount of toluene and stored in the fridge at -67°C.

NMR-Data (δ in ppm, tol./D_2O cap.): **^{29}Si**: -123.1 (*Si*Si_4); -59.6 (*Si*Me_2); -18.4 (*btmsa*);
-6.0, -4.5 (*Si*Me_3)

Synthesis of CpTi(*btmsa*)-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-(tetramethyl)pentacyclo tetrasilane (102)

In a 20 mL glass vial 362 mg of 1,1,1,4,4,4-hexa(trimethylsilyl)-2,2,3,3-tetramethyl tetrasilane (0.59 mmol) and 140 mg of *t*-BuOK (1.24 mmol, 2.10 eq.) are dissolved in ca. 4 mL of DME. The reaction continues overnight at room temperature and the dianion formation is checked by ^{29}Si NMR. The DME is evaporated and the remaining yellow oil is dissolved in toluene. Then 1 eq. of Cp_2Ti(*btmsa*) (206 mg) is dissolved in ca. 4 mL of toluene and the dianion solution is slowly dropped in the Rosenthal reagent solution through a syringe. After 12 hours the anion is completely consumed. The reaction mixture is stored directly into the fridge at -67°C. After 3 days a big solid semi-crystalline mass has formed in the vial. It was not possible to take out some crystals because the quickly melt up at room temperature. So the solvent is (still) allowed to slowly evaporate at room temperature.

NMR-Data (δ in ppm, tol./D_2O cap.): ^{1}**H**: 0.33 (SiSi(CH_3)$_3$, s, 18H);
0.43 (SiSi(CH_3)$_3$, s, 18H); 0.63, 0.64 (Si(CH_3)$_2$Si(CH_3)$_2$, s, 12H);
0.68 (CSi(CH_3)$_3$, s, 18H); 2.91 (-CH_2-, s, 24H, crown ether); 5.9 (C_5H_5K, s, 5H);
6.4 (C_5H_5Ti, s, 5H)
^{29}**Si**: -119.1 (Ti*Si*Si_3); -18.1 (*Si*Me_3, *btmsa*); -16.1 (*Si*Me_2*Si*Me_2); -7.4 , -5.0 (Me_3*Si*)

Synthesis of CpTi(*btmsa*)-1,1,3,3-tetrakis(trimethylsilyl)-2,2-(dimethyl)tricyclosilane (105)

In a 20 mL glass vial 359 mg of 1,1,1,3,3,3-tetrakis(trimethylsilyl)-2,2-dimethyltrisilane (0.63 mmol) and 148 mg of *t*-BuOK (1.32 mmol, 2.1 eq.) are dissolved in ca. 4 mL of DME. The reaction continues for 24 hours at room temperature to form **104**. After the reaction is complete, the ethereal solvent is completely dried and the oily residue is kept under vacuum for three hours. Then 1 eq. of Cp_2Ti(*btmsa*) (226 mg) is dissolved in ca. 4 mL of benzene and the dianion solution is slowly dropped into the Rosenthal reagent solution through a syringe. The mixture is stirred ca. 6 hours; ^{29}Si NMR spectrum is clean and reveal that **104** is completely consumed, and the complex has formed without by-products. The solvent is dried completely and the residue is dissolved in the minimum amount of toluene, added with pentane and stored at -67°C. After four weeks, small red crystals shaped as needles finally formed and they were suitable to obtain a crystal structure from X-ray analysis.

NMR-Data (δ in ppm, tol./D_2O cap.): ^{1}**H**: 0.37 (CSi(CH_3)$_3$, s, 18H, *btmsa*);
0.50, 0.68 (SiSi(CH_3)$_3$, s, 18H+18H);
0.53 (Si_2Si(CH_3)$_2$);
5.92 (C_5H_5K, s, 5H); 6.39 (TiC_5H_5, s, 5H);
^{29}**Si**: -121.0(*Si*Si_4); -61.0 (*Si*Me_2); -18.0 (*btmsa*);
-6.8, -4.5 (*Si*(CH_3)$_3$)

Synthesis of zirconium Rosenthal reagent (Cp_2Zr^{II}*btmsa*-THF adduct) – Rosenthal route

In a 20 mL glass vial 1444 mg of zirconocene dichloride (4.94 mmol), 883 mg of bis(trimethylsilyl) acetylene (5.19 mmol, 1.05 eq.) and 126 mg of magnesium turnings (5.19 mmol, 1.05 eq.) are dissolved in ca. 10 mL of THF at ca. -50°C. After one hour of stirring, the solution turns dark red. The reaction continues overnight at room temperature. At this point, the NMR data are in good agreement with the expected value. The volume of the mixture is reduced till some precipitate appears and then an equal amount of pentane is added. The solution is filtered and the solvent is removed under vacuum. A big solid black mass is formed. The ^{29}Si NMR reveals at least 6 signals between -5 ppm and -20 ppm, while in the proton spectrum a number of signals in the range of 5-7 ppm (Cp protons chemical shifts) are detected.

Synthesis of zirconium Rosenthal reagent (Cp_2Zr^{II}*btmsa*-pyridine adduct) – Rosenthal route

In a 20 mL glass vial 260 mg of zirconocene dichloride (0.89 mmol), 151 mg of bis(trimethylsilyl) acetylene (0.89 mmol, 1.0 eq.) and 22 mg of magnesium turnings (0.91 mmol, 1.02 eq) are dissolved in ca. 10 mL of THF at ca. -50°C. After one hour of stirring, the solution turns dark red. In this case, the reaction continues for 4 days at room temperature to go to completion. At this point, the NMR data are in good agreement with the expected value. Then, 77 mg (1.0 eq.) of pyridine are added to the reaction mixture. The solution is stirred overnight and after this time the ^{29}Si NMR is acquired: as in the previous description, more than 6 signals between -5 ppm and -20 ppm are present, while in the proton spectrum a number of signals in the range of 5-7 ppm (Cp protons chemical shifts) are detected.

Synthesis of zirconium Rosenthal reagent (Cp_2Zr^{II}*btmsa*-pyridine adduct) – Tilley route

In a single neck flask with stopcock 2670 mg of zirconocene dichloride (9.31 mmol) and 1556 mg of bis(trimethylsilyl)acetylene (1.0 eq) are dissolved with ca. 50 mL of THF and then cooled down to -80°C. *n*-Butyl lithium (2 eq., 11.4 mL of a 1.6 M solution in hexane) is slowly added to the stirring reaction mixture via syringe. The reaction continues for at -80°C for one hour and then the cooling system is removed. Stirring goes on overnight at room temperature. Before adding pyridine, the mixture is checked by ^{1}H and ^{13}C NMR. Pyridine is then slowly added and the reaction continues for other two hours at room temperature. The solvent is reduced to half of its original volume and 100 mL of dry pentane are added. The upper solution is moved via cannula in another flask and cooled down to -80°C. A red-wine solid precipitates. The solvent is removed and collected for a second crystallization process, while the precipitated solid is dried under vacuum.

First fraction (Th. Y. = 4299 mg): 2251 mg (52% of Th. Y.)

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.28, 0.29, 0.32 ($Si(CH_3)_3$, s, 18H);
5.97 ($Cp\text{-}H_5$, s, 58H);
6.5, 6.9, 8.0, 8.6 (pyridine, m, 5H)
^{13}C: 1.6, 2.1, 3.3 ($Si(CH_3)_3$); 110.7 ($Cp\text{-}C_5$);
122.9, 135.4, 148.0, 154.2 (pyridine);
254 (C≡C, *btmsa*)
^{29}Si: -14.4, -16.0 (*Si*Me_3, *btmsa*)

Chapter 7

Synthesis of 1,2-bis(hypersilyl)tetraphenyldistannane (80)

In a single neck flask with stopcock 2000 mg of hexaphenyldistannane (2.8 mmol) are suspended in 20 mL of CH_2Cl_2 at room temperature. 858 mg of triflic acid (5.7 mmol, 2 equivalent) are slowly dropped into the stirring mixture. The system is kept under nitrogen and stirred overnight. The clear solution is checked by ^{119}Sn NMR (chemical shift 98 ppm, correct). The solvent is dried and the residual solid suspended in 20 mL of toluene. 5.7 mmol of hypersilyl potassium (prepared from 1832 mg (2 equivalent) of tetrakis(trimethylsilyl)silane (**1**) and 6.0 mmol (1.05 equivalent) of *t*-BuOK in THF, then dried, washed 3-4 times with benzene and dissolved again in toluene) are slowly dropped into the triflate solution. The system is gently warmed with a water bath at 40°C. The reaction solution turns yellow, then orange and finally brown. The dropping lasts about 10 hours and then the mixture is stirred overnight. Then a 1:1 pentane/THF solution is added (ca. 10 mL) and the mixture is treated with ca. 10 mL of a 2M H_2SO_4 water solution. After phases separation and solvent evaporation, the residual pale yellow solid is recrystallized from pentane/THF at -20°C (good crystals were also obtained from slow evaporation of benzene) and 400 mg of substance are obtained as first crystallization fraction (13% of the Th. Yield). Other 219 mg are obtained from a second crystallization fraction (total y. 20% of the Th. Yield). Better yields were obtained under slightly different reaction conditions, but in this case the purest product was obtained.

NMR-Data (δ in ppm, C_6D_6): **^{1}H**: 0.05 ($Si(C\mathit{H}_3)_3$, s, 54H);7.20-8.00 ($Sn(C_6\mathit{H}_5)_2$,mp, 20H)
^{13}C: 2.9 ($Si(\mathit{C}H_3)_3$), 128.2, 128.4, 137.3, 138.7($Sn(\mathit{C}_6H_5)_2$)
^{29}Si: -116.7 ($Sn\mathit{Si}Si_3$), -7.6 ($\mathit{Si}Me_3$)
^{119}Sn: -113.8

Melting point: 227-228°C

Elemental analysis: $C_{42}H_{74}Si_8Sn_2$ (1041.15): Calc.: C, 48.45; H, 7.16.
Found: C, 24.99; H, 3.11

Synthesis of 1,1-bis(hypersilyl)diphenylstannane (81)

In a single neck flask with stopcock 446 mg of dichlorodiphenylstannane (1.3 mmol, 0.95 equivalent) are dissolved in 10 mL of THF at room temperature. 2.4 mmol of hypersilyl potassium (prepared from 757 mg (2.4 mmol, 1 equivalent) of tetrakis(trimethylsilyl)silane (**1**) and 2.5 mmol (1.05 equivalent) of *t*-BuOK in DME) are slowly dropped into the solution in ca. two hours. The white suspension is then stirred overnight. After usual work up a semitrasparent pale yellow oil is obtained (613 mg, 61% of the Th. Yield). Colorless crystals are precipitated by slow evaporation from a solution of pentane/acetone, at room temperature.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.20 ($Si(CH_3)_3$,s,54H); 7.00-7.90 ($Sn(C_6H_5)_2$,mp,20H)
^{13}**C**: 3.5 ($Si(\mathit{C}H_3)_3$), 127.7, 127.9, 138.4, 142.7($Sn(\mathit{C}_6H_5)_2$)
^{29}**Si**: -116.8 ($Sn\mathit{Si}Si_3$), -7.6 ($\mathit{Si}Me_3$)
^{119}**Sn**: -174

Melting point: at 110°C there is a transition phase (the colorless material becomes transparent but it seems still solid), then at 145°C the product becomes liquid

Elemental analysis: $C_{30}H_{64}Si_8Sn$ (768.23): Calc.: C, 46.90; H, 8.40.
Found: C, 44.65; H, 8.33

Synthesis of 1,1-bis(hypersilyl)dimethylstannane (82)

In a single neck flask with stopcock 262 mg of dichlorodimethylstannane (1.2 mmol, 0.51 equivalent) are dissolved in 5 mL of THF at room temperature. 2.3 mmol of hypersilyl potassium (prepared from 750 mg (2.3 mmol, 1 equivalent) of tetrakis(trimethylsilyl)silane (**1**) and 2.4 mmol (1.05 equivalent) of *t*-BuOK in DME) are slowly dropped into the solution in ca. six hours. The white suspension is then stirred 12 hours. After usual work up, a semitransparent pale yellow oil is obtained (668 mg, 86% of the Th. Yield). Colorless crystals are obtained by slow evaporation of a pentane/acetone 1:1 solution, at room temperature.

NMR-Data (δ in ppm, C_6D_6): ^{1}**H**: 0.30 ($Si(C\mathit{H}_3)_3$, s, 54H); 0.55 ($Sn(CH_3)_2$, s, 6H)
^{29}**Si**: -123.7 ($Sn\mathit{Si}Si_3$), -7.7 ($\mathit{Si}Me_3$)
^{119}**Sn**: -176

Synthesis of dimethyldiphenylstannane

A solution of PhMgBr in Et_2O is prepared by mixing 19.2 mmol (466 mg) of magnesium with 1 equivalent (2986 mg) of bromobenzene and stirring the reagents for ca. 6 hours, till the metal is mostly consumed and the Grignard solution assumes a dark gray color. The Grignard solution is then transferred via cannula into a THF solution containing 0.5 equivalents of dimethyldichlorostannane (2057 mg), set at 0°C with an ice bath. The mixture slowly returns to room temperature and it is stirred for 12 hours. After this time it is treated with 10 mL of a NH_4Cl solution in water. The organic phase is separated, reduced in volume and then passed through a pad of silica gel (ca. 5x1 cm, in a 10 mL plastic syringe). After evaporation of the solvent, a clear and colorless oil is obtained (1829 mg, 64% of the Th.Y.)

NMR-Data (δ in ppm, neat/D_2O cap.): ^{1}**H**: -0.37 ($Sn(C\mathit{H}_3)_2$, s, 6H);
6.30-6.70 ($Sn(C_6\mathit{H}_5)_2$, m, 10H)
^{119}**Sn**: -61

Synthesis of chlorodimethylphenylstannane

Dimethyldiphenylstannane (1829 mg, 5.3 mmol) is dissolved in Et_2O, cooled down at 0°C with an ice bath and then treated with 1.2 equivalents of HCl (1 Mol/l solution in ethyl ether). The mixture slowly returns at room temperature and then it is stirred for 12 hours. The reaction solution is treated with 10 mL of a NH_4Cl/water solution and the organic layer is separated through a funnel, collected in a flask and then the solvent is removed by evaporation. A clear and colorless oil is obtained (851 mg, 61% of the Th. Y.). The product is used without further purification.

NMR-Data (δ in ppm, neat/D_2O cap.): **^{1}H**: -0.16 ($Sn(CH_3)_2$, s, 6H);
6.40-6.70 ($Sn(C_6H_5)$, m, 5H)
^{13}C: -2.1 ($Sn(CH_3)_2$);
126.3, 128.0, 129.2, 134.6 ($Sn(C_6H_5)$)
^{119}Sn: 91

Synthesis of 1,2-diphenyltetramethyldistannane (83)

Chlorodimethylphenylstannane (851 mg, 3.3 mmol) is dissolved in THF and added with 1 equivalent of metallic sodium (75 mg). The suspension is stirred at room temperature for 48 hours. After this time, the alkaline metal has disappeared and a white suspension has formed. After usual work up with a NH_4Cl/water solution, extraction with Et_2O and evaporation of the solvent, a clear, dense and colorless oil is obtained (578 mg, 48% of the Th. Y.)

NMR-Data (δ in ppm, THF/D_2O cap.): **^{1}H**: 0.44 ($Sn(CH_3)_2$, s, 12H);
7.00-7.50 ($Sn(C_6H_5)$, m, 10H)
^{119}Sn: -118

Synthesis of 1,2-bis(hypersilyl)tetramethyldistannane (84)

In a single neck flask with stopcock 578 mg of **83** (1.3 mmol) are dissolved in 10 mL of CH_2Cl_2 at -40°C. 384 mg of triflic acid (2.6 mmol, 2 equivalent) are slowly dropped into the stirring mixture. The reaction mixture slowly returns at room temperature and is stirred for 12 hours. The clear solution is checked by ^{119}Sn NMR (chemical shift 107 ppm). The solvent is dried and the residual solid suspended in 10 mL of toluene. 2.6 mmol (2 equivalent) of hypersilyl potassium (prepared from 821 mg of tetrakis(trimethylsilyl)silane (**1**) and 6.0 mmol (1.05 equivalent) of *t*-BuOK in DME, dried, washed 3-4 times with benzene and dissolved again in toluene) are slowly dropped into the triflate solution at R.T. The reaction solution turns yellow and then dark orange. The dropping lasts about 6 hours and then the mixture is stirred for 12 hours. Then a 1:1 pentane/THF solution is added (ca. 10 mL) and the mixture is treated with ca. 10 mL of a 1M H_2SO_4 water solution. After separation of the liquid phases and solvent evaporation, a semisolid material is obtained (483 mg, 48% of the Th. Y.). The product is recrystallized by slow evaporation of a dichloromethane solution.

NMR-Data (δ in ppm, $CDCl_3$): **^{1}H**: 0.05 ($Si(CH_3)_3$, s, 54H); 7.20-8.00 ($Sn_2(CH_3)_4$, s,12H)
^{13}C: 2.9 ($Si(CH_3)_3$), 128.2 ($Sn_2(CH_3)_4$)
^{29}Si: -128.9 ($SnSiSi_3$), -7.8 ($SiMe_3$)
^{119}Sn: -206
Melting point: 225°C with decomposition
Elemental analysis: $C_{22}H_{66}Si_8Sn_2$ (792.87): Calc.: C, 33.33; H, 8.39
Found: C, 30.06; H, 7.01

Synthesis of 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-dimethyltristannane (85)
Tetrakis(trimethylsilyl)stannane (397 mg, 0.97 mmol) is reacted with 1.03 equivalent of *t*-BuOK (112 mg, 0.99 mmol) in DME at room temperature. The red solution is stirred for 12 hours. The reaction mixture is then dried and the residue dissolved in toluene. This solution is slowly dropped in a THF solution of dichlorodimethylstannane (0.5 equivalents, 106 mg). After 12 hours of stirring the suspension is treated with a NH_4Cl solution in water and extracted with a mixture of 1:1 THF/Et_2O. The organic phases are collected and the solvent is evaporated. A yellow solid is obtained (272 mg, 66% of the Th. Y.). Colorless crystals are obtained from slow evaporation of a dichloromethane solution of the product.

NMR-Data (δ in ppm, $CDCl_3$): **^{1}H**: 0.05 ($Si(CH_3)_3$, s, 54H); 7.20-8.00 ($Sn(CH_3)_2$, s, 6H)
^{13}C: 2.9 ($Si(CH_3)_3$), ($Sn(CH_3)_2$)
^{29}Si: -7.0 ($SiMe_3$)
^{119}Sn: -276 ($Sn(Si(CH_3)_3)$), -156 ($SnMe_2$)
Melting point: 135°C
Elemental analysis: $C_{20}H_{60}Si_6Sn_3$ (825.34): Calc.: C 29.11; H 7.33
Found: C 30.02; H 7.21

9. Crystallographic Tables
of
New Compounds

9.1 Structure parameters of new compounds synthesized in this work.

	18	**27**	**33**
Empirical formula	$C_{18}H_{48}GeSi_4$	$C_{20}H_{60}Si_8$	$C_{24}H_{56}Si_5$
Formula weight	449.51	525.40	485.14
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	hexagonal, R3	monoclinic, P2(1)/c	monoclinic, P2(1)/c
a [Å]	14.513(2)	14.992(3)	19.296(4)
b [Å]	14.513(2)	9.2896(19)	9.3678(19)
c [Å]	10.772(2)	18.990(4)	18.715(4)
α [°]	90	90	90
β [°]	90	100.66	114.64
γ [°]	120	90	90
Volume [Å^3]	1965.0(6)	2598.9(9)	3074.7(11)
Z, Calculated density [gcm^{-3}]	3, 1.140	4, 1.343	4, 1.048
Absorption coefficient [mm^{-1}]	1.352	0.423	0.242
F(000)	732	1168	1080
Crystal size [mm]	0.32 x 0.22 x 0.20	0.46 x 0.35 x 0.20	0.42 x 0.25 x 0.15
Theta range for data collection [°]	2.49 to 26.29	1.38 to 26.37	2.18 to 26.35
Limiting indices	-18<=h<=17 -18<=k<=18 -13<=l<=13	-18<=h<=18 -11<=k<=11 -23<=l<=23	-24<=h<=23 -11<=k<=11 -23<=l<=23
Reflections collected / unique	5024 / 1763	19548 / 5291	23776 / 6262
Completeness to theta [%]	100.0	99.8	99.8 %
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.7552 and 0.6715	0.9202 and 0.8293	0.9646 and 0.9052
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1763 / 1 / 78	5291 / 10 / 256	6262 / 0 / 282
Goodness-of-fit on F^2	1.054	1.172	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0234, wR2 = 0.0575	R1 = 0.0661, wR2 = 0.1590	R1 = 0.0700, wR2 = 0.1728
R indices (all data)	R1 = 0.0240, wR2 = 0.0578	R1 = 0.0757, wR2 = 0.1649	R1 = 0.0734, wR2 = 0.1757
Largest diff. peak and hole [e$^-$A^{-3}]	0.431 and -0.193	0.865 and -0.542	2.227 and -1.396

Table 9-1: Structures parameters for compounds **18**, **27** and **33.**

	45	**46**	**47**
Empirical formula	$C_{16}H_{39}F_3O_3SSi_4$	$C_{32}H_{70}Si_{10}$	$C_{50}H_{100}K_2O_{12}Si_8$
Formula weight	480.89	735.78	1196.22
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, P2(1)/n	monoclinic, P2(1)/n	monoclinic, Cc
a [Å]	9.0436(18)	12.147(2)	15.024(3)
b [Å]	30.943(6)	9.4628(19)	20.707(4)
c [Å]	9.781(2)	22.116(4)	22.101(4)
α [°]	90	90	90
β [°]	108.79	100.22	92.50
γ [°]	90	90	90
Volume [$Å^3$]	2591.2(9)	2501.8(9)	6869(2)
Z, Calculated density [gcm^{-3}]	4, 1.233	2, 0.977	4, 1.157
Absorption coefficient [mm^{-1}]	0.345	0.281	0.327
F(000)	1032	804	2584
Crystal size [mm]	0.28 x 0.22 x 0.22	0.38 x 0.22 x 0.12	0.48 x 0.36 x 0.28
Theta range for data collection [°]	2.30 to 26.33	1.79 to 26.35	1.68 to 26.37
Limiting indices	-11<=h<=11, -38<=k<=38, -12<=l<=11	-15<=h<=14 -11<=k<=11, -27<=l<=27	-17<=h<=18, -25<=k<=25, -20<=l<=27
Reflections collected / unique	20481 / 5271	15247 / 4995	19475 / 10423
Completeness to theta [%]	99.9	97.8	94.8
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.9280 and 0.9097	0.9671 and 0.9008	0.9141 and 0.8590
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5271 / 0 / 256	4995 / 0 / 200	10423 / 2 / 663
Goodness-of-fit on F^2	1.115	1.269	1.147
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0849	R1 = 0.0636, wR2 = 0.1328	R1 = 0.0652, wR2 = 0.1567
R indices (all data)	R1 = 0.0347, wR2 = 0.0855	R1 = 0.0723, wR2 = 0.1367	R1 = 0.0674, wR2 = 0.1585
Largest diff. peak and hole [e^-A^{-3}]	0.445 and -0.258	0.621 and -0.330	2.436 and -0.419

Table 9-2: Structures parameters for compounds **45**, **46** and **47.**

	48	**65-*trans***	**65-*cis***
Empirical formula	$C_{28}H_{58}Si_9$	$C_{32}H_{84}Si_{10}$	$C_{32}H_{84}Si_{10}$
Formula weight	647.55	749.89	749.89
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, P2(1)/c	monoclinic, C2/c	monoclinic, C2/c
a [Å]	13.371(3)	36.810(7)	16.054(3)
b [Å]	20.559(4)	9.1954(18)	10.615(2)
c [Å]	14.604(3)	31.596(6)	27.564(5)
α [°]	90	90	90
β [°]	91.24	117.88	99.26
γ [°]	90	90	90
Volume [$Å^3$]	4013.5(14)	9453(3)	4636.1(15)
Z, Calculated density [gcm^{-3}]	4, 1.072	8, 1.054	4, 1.074
Absorption coefficient [mm^{-1}]	0.314	0.298	0.304
F(000)	1408	3328	1664
Crystal size [mm]	0.38 x 0.27 x 0.18	0.30 x 0.30 x 0.26	0.34 x 0.26 x 0.12
Theta range for data collection [°]	1.71 to 26.38	1.25 to 26.37	1.50 to 25.00
Limiting indices	-16<=h<=16, -25<=k<=25, -18<=l<=18	-45<=h<=45 -11<=k<=11 -39<=l<=39	-19<=h<=18, -12<=k<=12, -32<=l<=32
Reflections collected / unique	28438 / 8149	36797 / 9665	13825 / 4066
Completeness to theta [%]	99.1	99.8	99.3
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.9457 and 0.8901	0.9266 and 0.9159	0.9645 and 0.9038
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8149 / 0 / 350	9665 / 0 / 405	4066 / 0 / 203
Goodness-of-fit on F^2	1.025	1.089	1.298
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1225	R1 = 0.0351, wR2 = 0.0830	R1 = 0.0954, wR2 = 0.1836
R indices (all data)	R1 = 0.0562, wR2 = 0.1274	R1 = 0.0396, wR2 = 0.0851	R1 = 0.1124, wR2 = 0.1904
Largest diff. peak and hole [e^-A^{-3}]	0.570 and -0.347	0.468 and -0.208	0.821 and -0.486

Table 9-3: Structures parameters for compounds **48**, **65-*trans*** and **65-*cis***.

	75	**80**	**81**
Empirical formula	$C_{34}H_{82}Si_{10}$	$C_{48}H_{80}Si_8Sn_2$	$C_{30}H_{64}Si_8Sn$
Formula weight	771.90	1119.22	768.22
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, P-1	monoclinic, P2(1)/n	monoclinic, P2(1)/c
a [Å]	9.6033(19)	13.099(3)	10.605(2)
b [Å]	15.262(3)	16.486(3)	18.310(4)
c [Å]	18.530(4)	13.735(3)	22.826(5)
α [°]	106.80	90	90
β [°]	102.56	98.99	91.74
γ [°]	106.32	90	90
Volume [Å^3]	2359.5(8)	2929.6(10)	4430.3 (15)
Z, Calculated density [gcm^{-3}]	2, 1.086	2, 1.269	4, 1.152
Absorption coefficient [mm^{-1}]	0.300	1.045	0.810
F(000)	852	1160	1624
Crystal size [mm]	0.40 x 0.24 x 0.10	0.26 x 0.22 x 0.18	0.44 x 0.25 x 0.19
Theta range for data collection [°]	1.21 to 26.37	1.94 to 26.37	1.43 to 26.37
Limiting indices	-12<=h<=12, -19<=k<=19, -23<=l<=23	-16<=h<=16, -20<=k<=20, -17<=l<=17	-13<=h<=12, -22<=k<=22 -27<=l<=28
Reflections collected / unique	16509 / 8754	23090 / 5950	28319 / 8939
Completeness to theta [%]	90.9	99.2	98.6
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.9706 and 0.8893	0.8343 and 0.7729	0.8613 and 0.7169
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8754 / 0 / 417	5950 / 0 / 271	8939 / 0 / 370
Goodness-of-fit on F^2	1.144	1.074	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0801, wR2 = 0.2215	R1 = 0.0208, wR2 = 0.0526	R1 = 0.0289, wR2 = 0.0685
R indices (all data)	R1 = 0.1105, wR2 = 0.2576	R1 = 0.0222, wR2 = 0.0535	R1 = 0.0360, wR2 = 0.0706
Largest diff. peak and hole [e^-A^{-3}]	1.536 and -1.247	0.411 and -0.557	0.733 and -0.264

Table 9-4: Structures parameters for compounds **75**, **80** and **81.**

	84	**85**	**87**
Empirical formula	$C_{22}H_{54}Si_8Sn_2$	$C_{20}H_{54}Si_6Sn_3$	$C_{54}H_{84}Si_8Sn_3$
Formula weight	780.75	819.24	1314.00
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, P-1	monoclinic, C2/c	monoclinic, P2(1)/n
a [Å]	9.0702(18)	17.304(4)	16.707(3)
b [Å]	9.1599(18)	9.3904(19)	25.803(5)
c [Å]	14.035	24.871(5)	17.153(3)
α [°]	92.14	90	90
β [°]	103.36	105.54	112.76
γ [°]	113.61	90	90
Volume [Å^3]	1028.4(4)	3893.6(14)	6819(2)
Z, Calculated density [gcm^{-3}]	1, 1.261	4, 1.398	4, 1.280
Absorption coefficient [mm^{-1}]	1.457	2.101	1.260
F(000)	398	1632	2680
Crystal size [mm]	0.48 x 0.34 x 0.12	0.44 x 0.41 x 0.10	0.32 x 0.28 x 0.28
Theta range for data collection [°]	1.51 to 26.33	1.70 to 26.36	1.44 to 25.00
Limiting indices	-11<=h<=11, -11<=k<=11, -17<=l<=17	-21<=h<=21, -11<=k<=11, -30<=l<=30	-19<=h<=19, -30<=k<=30, -20<=l<=20
Reflections collected / unique	7977 / 4064	15120 / 3956	37389 / 11449
Completeness to theta [%]	96.7	99.4	95.4
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.8445 and 0.5414	0.8174 and 0.4583	0.7192 and 0.6885
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4064 / 0 / 154	3956 / 0 / 141	11449 / 24 / 604
Goodness-of-fit on F^2	1.088	1.063	1.132
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1677	R1 = 0.0223, wR2 = 0.0580	R1 = 0.1056, wR2 = 0.2392
R indices (all data)	R1 = 0.0605, wR2 = 0.1681	R1 = 0.0234, wR2 = 0.0587	R1 = 0.1477, wR2 = 0.2797
Largest diff. peak and hole [e$^-$A^{-3}]	3.751 and -1.390	0.849 and -0.855	2.969 and -2.478

Table 9-5: Structures parameters for compounds **84**, **85** and **87.**

	105		
Empirical formula	$C_{83}H_{195}K_3O_{12}Si_{18}Ti_2$		
Formula weight	2104.11		
Temperature [K]	100(2)		
Wavelength [Å]	0.71073		
Crystal system, space group	monoclinic, C2/c		
a [Å]	12.187(5)		
b [Å]	23.235(11)		
c [Å]	44.919(18)		
α [°]	90		
β [°]	95.052		
γ [°]	90		
Volume [$Å^3$]	12670(9)		
Z, Calculated density [gcm^{-3}]	4, 1.103		
Absorption coefficient [mm^{-1}]	0.439		
F(000)	4568		
Crystal size [mm]	0.33 x 0.28 x 0.17		
Theta range for data collection [°]	1.82 to 26.37		
Limiting indices	-13<=h<=14, -28<=k<=28, -56<=l<=55		
Reflections collected / unique	38278 / 12765		
Completeness to theta [%]	98.4		
Absorption correction	SADABS		
Max. and min. transmission	0.9291 and 0.8686		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	12765 / 6 / 563		
Goodness-of-fit on F^2	0.800		
Final R indices [I>2sigma(I)]	R1 = 0.0852, wR2 = 0.1626		
R indices (all data)	R1 = 0.1720, wR2 = 0.1807		
Largest diff. peak and hole [e^-A^{-3}]	0.760 and -0.666		

Table 9-6: Structures parameters for compound **105.**