BSc. Kristina Schrempf

# SYNTHESIS OF ORGANOTIN REAGENTS SUPPORTED ON A SILICONE BACKBONE FOR STILLE CROSS-COUPLING REACTIONS

**MASTERARBEIT**

zur Erlangung des Grades einer

Diplom Ingenieurin

erreicht an der

Technischen Universität Graz

Univ.-Prof. Dipl.-Chem. Dr.rer.nat. Frank Uhlig

Dipl.-Ing. Dr.techn. Georg Witek

Institut für Anorganische Chemie

**EIDESSTATTLICHE ERKLÄRUNG**

Ich erkläre an Eides statt, dass ich die vorliegende Arbeit selbständig verfasst, andere als die angegebenen Quellen/Hilfsmittel nicht benutzt, und die den benutzten Quellen wörtlich und inhaltlich entnommene Stellen als solche kenntlich gemacht habe.

Graz, am …….. .....……

(Datum) (Unterschrift)

# DANKSAGUNG

Diese Arbeit ist meiner Großmutter **Ridi Zand** gewidmet. Sie hat mich während meiner gesamten Ausbildung tatkräftig mit ihrem unschätzbaren Einsatz für Leib und Seele unterstützt. Meinen Eltern **Gabi** und **Gerhard** danke ich von ganzem Herzen für ihre liebevolle und geduldige Unterstützung während der letzten Jahre.

Ein großes Dankeschön gebührt **Dipl.-Ing**. **Dr.techn. Georg Witek** für sein großes Engagement und die herzliche Motivation während meiner Masterarbeit, Bachelorarbeit und den Projektlabors. Nicht zuletzt bedanke ich mich für die entstandene Freundschaft.

Bedanken möchte ich mich besonders bei **Univ.-Prof. Dipl.-Chem. Dr.rer.nat. Frank Uhlig** für die Betreuung, sowie für die Unterstützung und Hilfe bei meiner Masterarbeit.

Ein großer Dank gilt Andrea Temmel und Michael Lammer, die mich mit Projektlaboren und Bachelorarbeiten unterstützt haben.
Ich danke weiters Rita Ambach, Lisa Schickhofer, Dilek Halici und Sandra Pötz für ihren Einsatz im Labor im Zuge der Projektlaborpraktikas.

Ich bedanke mich vor allem auch bei meinen Kollegen am Institut für Anorganische Chemie, die immer ein offenes Ohr und viele Anregungen für mich parat hatten. Georg Witek, Sandra Wiesenhofer. Johann Pichler und Judith Binder danke ich für die gute Zusammenarbeit im Labor und die nette Atmosphäre im Schreibraum. Kathrin Schittelkopf, Petra Wilfling, Johanna Flock, Roland Fischer, Josef Binder, Amra Suljanovic, Dominik Genser und Birgit Ehmann danke ich für die rege Diskussionsbereitschaft. Bedanken möchte ich mich auch bei Astrid Falk, Barbara Seibt, Monika Filzwieser und Resi Koller für die Unterstützung.

Ein Dank geht auch an Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Hansjörg Weber vom Institut für Organische Chemie für die Unterstützung und Hilfe bezüglich der NMR Messungen.

Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Robert Saf vom Institut für Chemische Technologie von Materialien sei für die EI-TOF-MS Messungen gedankt.

Vor allem möchte ich mich bei meiner langjährigen Mitbewohnerin und Freundin Barbara bedanken, die nie den Glauben an mich verloren hat und mich zu jeder Tages- und Nachtzeit unterstützt hat.

Ich danke vor allem meinem Freund Hans für die Geduld und das große Verständnis während der letzten Monate. Ich danke ihm für die liebevolle Motivation und Unterstützung während meiner Arbeit.

*Phantasie ist wichtiger als Wissen,*
*denn Wissen ist begrenzt*

[Albert Einstein]

# Contents

# Abstract

**Synthesis of Organotin Reagents Supported on a Silicone Backbone for Stille Cross-Coupling Reactions**

The aim of this work is the synthesis of an organotin precursor supported on a silicone or a polydimethylsiloxane (PDMS) backbone in order to perform Stille cross-coupling reactions. Monofunctional PDMS are synthesized via the ring opening polymerization (ROP) of hexamethylcyclotrisiloxane (D3), which is initiated by *tert*-butyllithium (t-BuLi) and terminated by an appropriate chlorosilane. The ROP is quenched in the kinetically controlled regime, hence, monodisperse PDMS with desired chain lengths are produced. Starting from commercially easily available substances, an organotin compound, either allyl-, 3-butenyl- or 11-undecenyldibutylphenylstannane, is synthesized. These tin compounds are reacted with different silanes or the monofunctional PDMS to form the desired Stille cross-coupling reagent via a hydrosilylation reaction. The novel polymeric hybrid material is more easily recyclable and therefore contaminations of tin byproducts are reduced, making this process commercially more attractive.

# Kurzfassung

**Stille Kreuzkupplungsreaktion mit einem Silikon-funktionalisierten Organostannan**

Das Ziel dieser Arbeit ist die Herstellung eines Silikon- bzw. Polydimethylsiloxan- (PDMS) funktionalisierten Organozinn Precusors, der in weiterer Folge als Reagenz fuer die Stille Kreuzkupplung dient. Monofunktionelle PDMS werden ueber die Ringoeffnungspolymerisation (ROP) von Hexamethylcyclotrisiloxan (D3) hergestellt. Initiiert wird diese Polymerisation mit tert-butyllithium (t-BuLi) und nach einer bestimmen Reaktionszeit mit geeigneten Chlorsilanen gestoppt. Die ROP wird im kinetisch kontrollierten Bereich abgebrochen, demzufolge koennen monodisperse PDMS mit gewuenschter Kettenlaenge synthetisiert werden. Ausgehend von kommerziell erhaeltlichen Substanzen wird ein Allyl-, 3-Butenyl- oder 11-undecenyldibutylphenylstannane hergestellt. Ueber eine Hydrosilylierungsreaktion werden anschließend die Organozinnverbindungen mit diversen Silanen bzw. mit einem monofunktionellen PDMS zur Reaktion gebracht. Dieses neuartige Polymerhybrid Material wird in weiterer Folge fuer die Stille Kreuzkupplung eingesetzt. Der synthetisierte Zinn-Precursor ist leichter rezyklierbar und Kontaminationen von Zinnnebenprodukten koennen reduziert werden. Dies macht diesen Gesamtprozess darueber hinaus kommerziell attraktiver.

# 1 Introduction

## 1.1 Introduction

In 1986 John K. Stille[1] developed a novel and innovative methodology for the coupling of organostannanes with functional organic electrophiles. The Stille cross-coupling reaction of organotin compounds is a very useful and versatile method for the catalytic formation of carbon-carbon bonds in organic chemistry. The Stille reaction is one of the two most general and most selective palladium-catalyzed cross coupling reactions, along with the Suzuki reaction of organoboron compounds. Due to the selectivity towards a variety of compatible functional groups, the Stille cross-coupling forms invaluable methods for the formation of a $\sigma$ bond between two $sp^2$ carbon centers.
In the last few years the Stille cross-coupling reaction has been well recognized as an outstanding method for the synthesis of natural products. Moreover, one significant advantage is the facile accessibility and handling of the organo-tin reagents. Unfortunately, the toxicity of these organo-metal compounds reveals its difficulty in chemical processing industry. Figure 1.1 shows the general scheme of the Stille cross-coupling reaction.

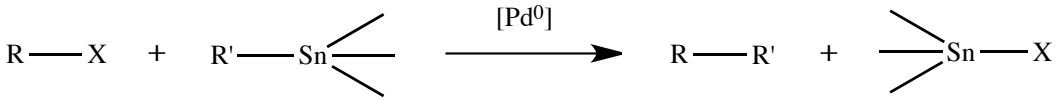


Figure 1.1: The Stille cross-coupling Reaction

One severe disadvantage concerning this powerful C-C coupling reaction is the formation of toxic tin byproducts such as $SnR_3X$. These harmful residues are difficult to separate from the main product.
To solve this problem tin reagents are modified with various functional groups (such as poly-aromatic ring systems or fluorinated alkyl substituents) which reduce the toxicity of these materials.

## 1.2 Definition of the Project

The goal of this work is the synthesis of tin reagents supported on an siloxane backbone in order to perform the Stille cross-coupling reactions. The novel hybrid material should reduce the number of tin byproducts due to a better recyclability and reducing leach out quotes of the tin catalyst, making this process commercially more attractive. Figure 1.2 shows the model reaction of the desired Stille cross-coupling reaction.

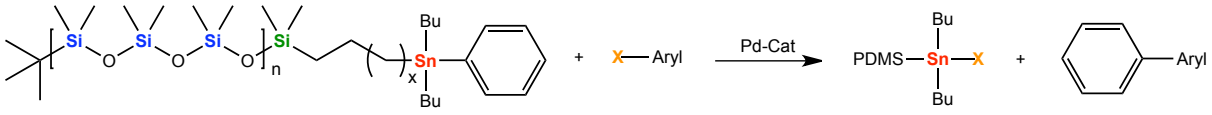


Figure 1.2: Stille cross-coupling reaction with tin reagents supported on a silicon backbone

The guideline of this work is determined as follows:

- Detailed literature review considering C-C bond formation with modified hybrid materials.
- The synthesis of a chemically modified dibutylphenylstannane. The functional groups are either allyl-, 3-butenyl-, or 11-undecenyl moieties (alkyl moieties with a terminal double bond).
- The synthesis of linear, monofunctional oligosiloxanes via the ring opening polymerisation of hexamethylcyclotrisiloxane (D3). This polymerization reaction is initiated with *tert*-butyllithium and stopped with appropriate chlorosilanes to yield PDMS with terminal functional groups.
- The coupling of the organostannane to the silicone support material via the hydrosilylation reaction.
- Performing of the Stille cross-coupling reaction with the novel hybrid material.

# 2 Literature

In the last few decades, palladium catalyzed cross-coupling reactions gained in importance due to their selectivities, the mild reaction conditions as well as the wide range of applications. These reactions are of great interest for chemical and pharmaceutical research and development. In 2010 Richard F. Heck, Ei-ichi Neigshi and Akira Suzuki were awarded with the Nobel prize in Chemistry regarding to their achievement of palladium catalyzed cross-coupling reactions.

In this section the Stille Cross-Coupling reaction[2] and its mechanism is discussed in detail. Furthermore, the synthesis of novel tin reagents for Stille reaction are described. Additionally, the formation of silicon-tin hybrid materials as well as the preparation of monofunctional siloxane substrates is generally presented.

## 2.1 The Stille Cross-Coupling Reaction

### 2.1.1 The Mechanism of the Stille Cross-Coupling reaction [3]

One of the latest discussions about a mechanism of the Stille cross-coupling reaction was published in 2004 by Pablo Espinet and Antonio M. Echavarren. The postulated Pd catalytic cycle is shown in Figure 2.1 which is best described by three different main reactions:

#### The Oxidative Addition

The first step is the oxidative addition of an organic electrophile (halide, sulfonate or a similar compound) to the palladium catalyst. The oxidative addition of a halogenated $sp^3$ hybridized carbon to $Pd^0$ complexes is usually an associative bimolecular process, comparable to an $S_N2$ addition reaction.

#### The Transmetalation

The basic principle of the transmetalation is a ligand substitution on the $Pd^{2+}$ complex.

### The Reductive Elimination

In the reductive elimination the product $R^1$-$R^2$ is formed by the reduction of $Pd^{2+}$ to $Pd^0$. The palladium catalyst then reenters the catalytic cycle.

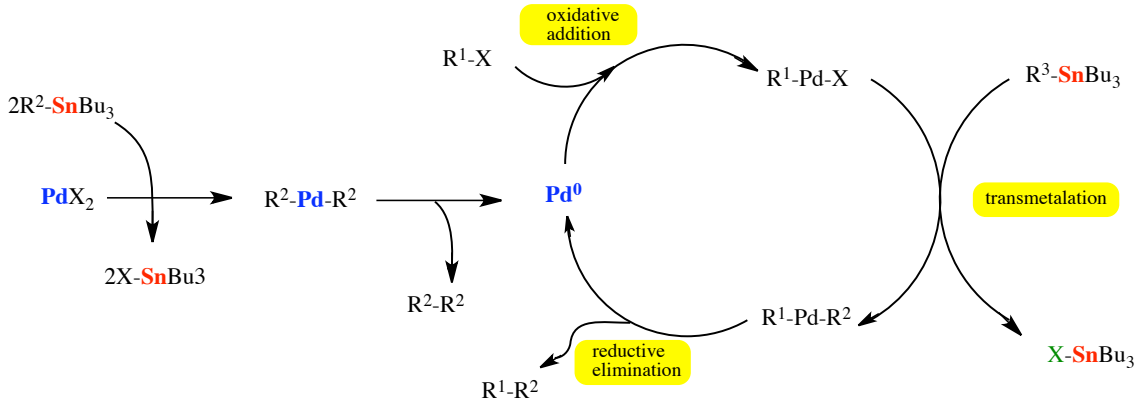


Figure 2.1: A simplified representation of the Stille cross coupling of stannanes with organic electrophiles[3].

## 2.1.2 Novel Stille Cross-Coupling Reagents

The major disadvantage of the Stille cross-coupling reaction is the formation of toxic byorganotin compounds in the product. The effects of three organotin compounds ($Me_3SnCl$, $Me_2SnCl_2$, $Bu_2SnAc_2$) on *Artemia franciscana* [4], a brine shrimp genus, were tested by Hadjispyrou, Kungolos and Anagnastopoulos in 2001. It was found, that there was a strong increase of shrimp mortality at a small concentration increase of stannanes in water. To solve this problem novel tin reagents supported on liquid polymers or solid particles were synthesized. An overview is given in this section.

- **Stille Cross-Coupling Reaction with Tin Reagents Supported on Ionic Liquids [5][6]**

P. D. Pham, J. Vitz et al. describe an approach of using new ionic-liquid-supported tin reagents in order to perform Stille cross-coupling reactions. Tin reagents were used for cross-coupling reactions supported on task-specific ionic liquids (TSILs). In Figure 2.2 a general strategy is shown: various tin reagents are linked to an imidazolium-based ionic liquid (IL) through an alkyl chain spacer.


Figure 2.2: General strategy[5]

First the imidazol compound is substituted with the alkyl spacer and the tin reagent is introduced. The formation of the IL is performed by addition of methyl iodide and $NaBF_4$ in a two step process. Figure 2.3 shows the reaction scheme of this synthetic pathway. From imidazoles (**1**), IL-suppordet tin reagents **4** and **5** were prepared. Product **3** ($R^1$ = Me) was purified by column chromatography, providing 73% yield, whereas product **4** was purified by extraction. Overall yields between 32 and 72% were obtained.

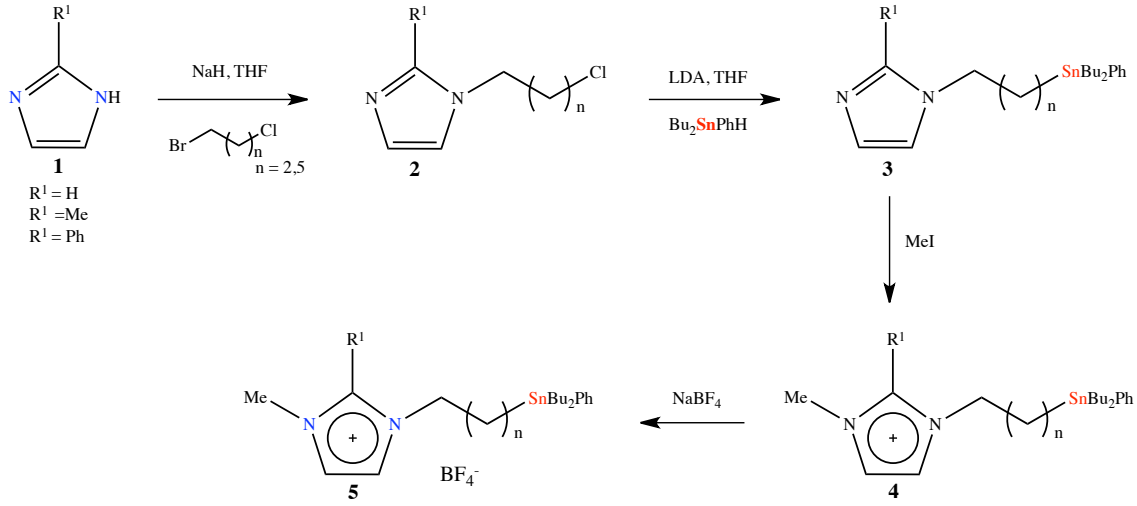


Figure 2.3: Synthesis of IL-supported tin reagents starting from different imidazoles[5].

The IL-supported tin reagents were used for reactions of **4** ($R^1$ = H). Within 6 h in the presence of the catalyst system $Pd_2dba_3$ * $CHCl_3$ high levels of conversion were achieved (see Figure 2.4).

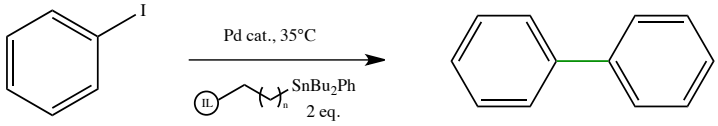


Figure 2.4: Stille reaction with phenyliodide. Conditions: $Pd_2dba_3$ * $CHCl_3$ (5 mole-%); 35°C; 6h; conversion to 100%[5]

Further Stille cross-coupling reactions were carried out, using different aromatics such as aryl iodides, 3-iodopyridine, iodothiophenes, iodonaphthalene and benzoyl chloride. High yields of coupling products were achieved under low-temperature and solvent-free conditions.

Furthermore, recyclation of the tin compound/palladium catalyst system after quantitative reaction was realized. Products and remaining starting materials, as well as side products were extracted with pentane, which is immiscible with the IL. Simple addition of PhLi to a solution of IL-supported -$SnBu_2I$ in THF regenerated the Stille starting material. The tin reagent could be recycled five times without respectable loss of reactivity. Figure 2.5 shows the recyclation process.

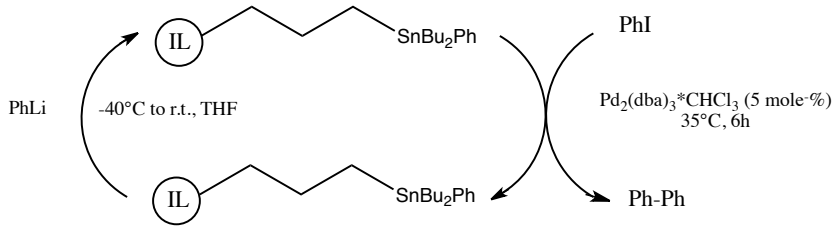


Figure 2.5: Recycling of the tin compounds[5].

- **Stille cross-coupling Reaction with Tin Reagents Supported on Solid Polymers[7]**

J. M. Chrétien et al. reviewed the development of polymer-supported organotin reagents, bearing a vinyl or a 3,3-diethoxyprop-1-en-1-yl substituent, as target compounds .
First of all, the macroporous polymer-supported triorganotin iodide was prepared in a three step process shown in Figure 2.6.

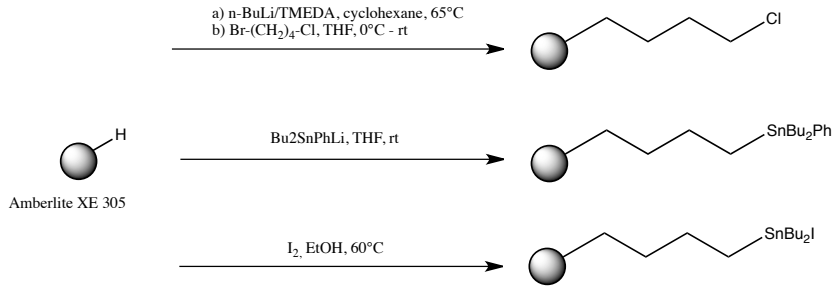


Figure 2.6: Reagents and conditions for the synthesis of polymer-supported triorganotin iodide[7].

Moreover the vinylation of the supported triorganotin iodide was carried out with two equivalents of vinyl-magnesium bromide. Figure 2.7 shows the synthesis of the Stille reagent.

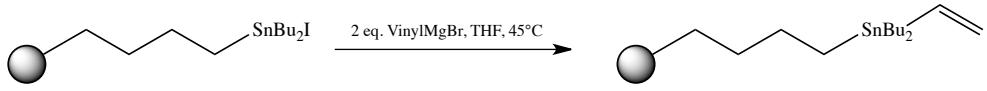


Figure 2.7: Synthesis of the polymer-supported vinyltin reagent[7].

Furthermore the hydrostannation of alkynes as a possible route for the synthesis of polymer-supported functionalized vinyltin reagents was investigated. The synthetic scheme is shown in Figure 2.8.

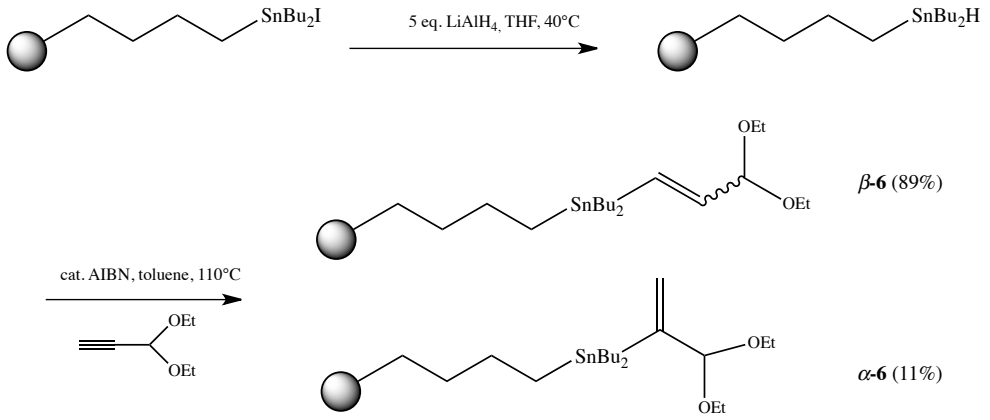


Figure 2.8: Synthesis of the polymer-supported vinyltin reagent[7].

The palladium-catalyzed Stille cross-coupling reaction of polymer supported vinyltin reagents was tested with various aryl iodides and bromides (see Figure 2.9). The ICP-MS analyis showed that very low contamination of organotin residues in the products was achieved. This study demonstrated the efficiency of these polymer-supported vinyltin reagents as non-polluting reagents.

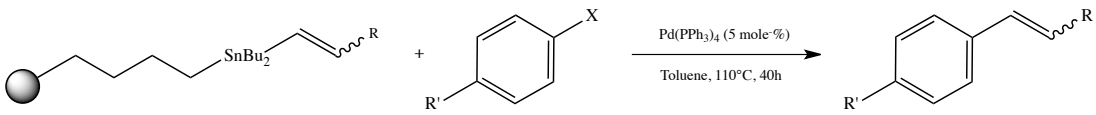


Figure 2.9: Stille cross-coupling reactions of aryl halides with the polymer-supported organotin reagents[7].

# 2.2 Silicon Compounds and Siloxanes

## 2.2.1 Silicone General [8][9][10][11]

Silicones, in particular polydimethylsiloxanes (PDMS), are part of "classical" inorganic polymers besides polyphosphazenes and polysilanes. Due to their high stability towards temperature, oxygen water, UV radiation and weathering in comparison to organic polymers, silicones have a high versatility for a broad range of applications. Figure 2.10 shows the general building block for linear silicones, the Si-O-unit.

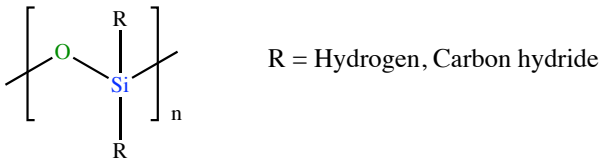


Figure 2.10: General structure of a D- siloxane unit[9].

Table 2.1 shows the typical silicone structure units and several application possibilities of materials bearing these units [10].

Table 2.1: Silicone structural units, symbols and functionality as well as application possibilities.

| SYMBOL | FUNCTIONALITY | APPLICATION |
|---|---|---|
| M | $Si(CH_3)_3O$ monofunctional | chain end in silicone fluids, trimethylsilyl protecting groups |
| D | $Si(CH_3)_2O_2$ difunctional | linear siloxane polymers, silicone fluids, rubber, elastomeres |
| T | $Si(CH_3)O_3$ trifunctional | silicone resins for paints, impregnating agents, masonry protection |
| Q | $SiO_4$ tetrafunctional | silicone resins |

Linear polyorganosiloxanes are synthesized by the reaction of dichlorodiorganosilanes either with water (hydrolysis) or methanol (methanolysis)[8][10][12]. Cyclic oligosiloxanes such as hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) or higher analogues (D5, D6 etc.) are produced as side products in hydrolysis and methanolysis reactions. The industrially most important monomers, D3 and D4 are shown in Figure 2.11

The ring opening polymerization (ROP) of cyclic oligosiloxanes generally yields linear polysiloxanes. This polymerization can be initiated with cationic and anionic catalysts as initiators.

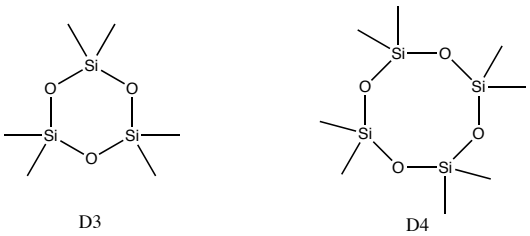


Figure 2.11: Molecular structures of hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4)[8]

Section 2.2.2 describes a typical anionic ring opening polymerization which was discussed in recent literature.

## 2.2.2 Ring Opening Polymerization of Hexamethylcyclotrisiloxane (D3)

Adam M. Hawkridge and Joseph A. Gardella investigated the ring opening polymerization (ROP) of D3 initiated with *sec*- and *n*-butyllithium in order to prevent side reactions such as chain redistribution [13]. The *n*-BuLi initiated species were free of cyclic impurities and showed a narrow molecular weight distributions. The reaction equations are shown in Figure 2.12.

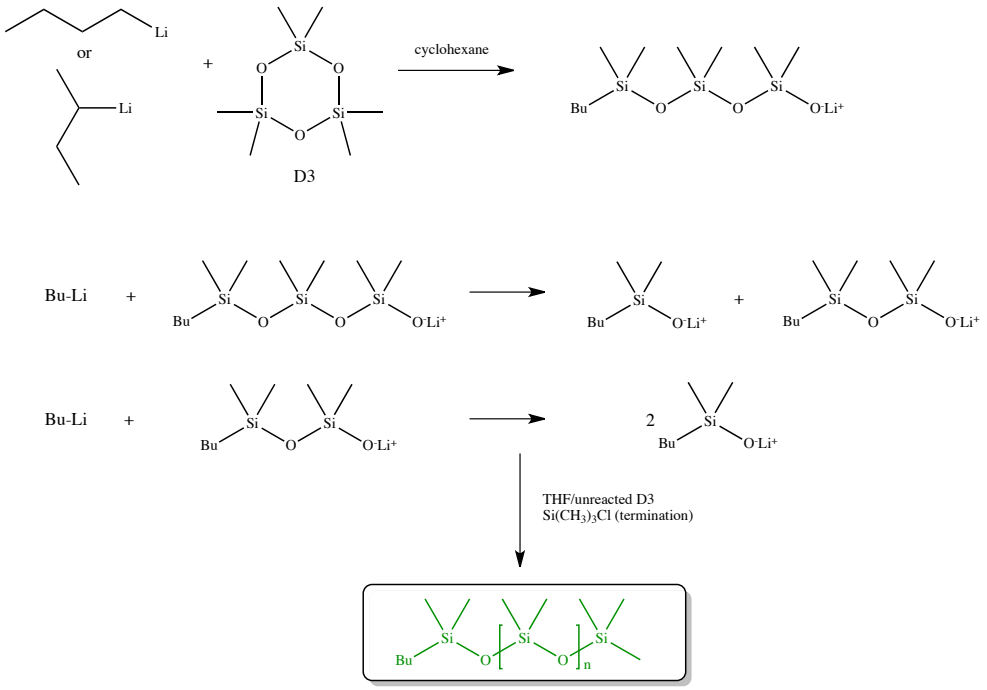


Figure 2.12: ROP of D3, initiated with BuLi in order to produce linear PDMS[13].

In the first step one equivalent of D3 reacts with one equivalent of *n* or *sec*-BuLi to form the silanolate. The silanolate reacts then with other D3 molecules in the anionic ROP, yielding a silanolate polymer. The lithium silanolate reacts with an appropriate chlorosilane in a condensation reaction (elimination of LiCl) to produce the linear PDMS.

Additionally Hammouch et al. synthesized monofunctional PDMS by anionic ROP of D3 in 50 vol% benzene-THF solution [14]. The PDMS chains either beard a hydride or vinyl functional group at the chain end by reaction with the corresponding chlorodimethylsilane (see Figure 2.13). In this investigation, narrow polydispersity ($M_w/M_n$) and the absence of any difunctional species were observed. PDMS in a molecular mass range between 2500 an 40 000 g/mole were prepared

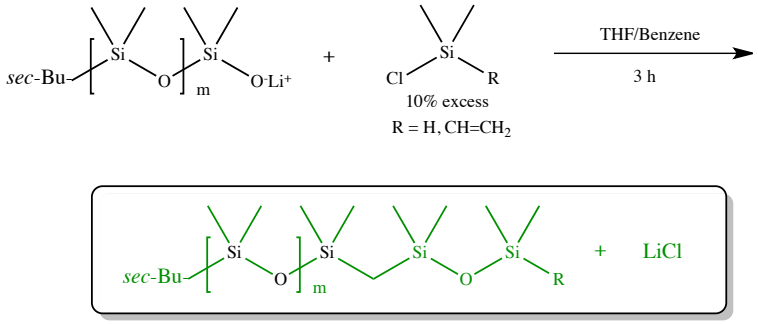


Figure 2.13: ROP of D3 initiated with *sec*-BuLi and terminated with a corresponding chlorosilane for the synthesis of linear, monofunctional PDMS[14].

In the last few years, several investigations concerning uncommon applications of silicones and siloxanes were published. The use of functional polysiloxanes as carriers for transition metal catalysts for enzymes was reported[15]. Moreover, the use of siloxanes as solvents for synthetic chemistry was investigated[16]. Ionic liquids are materials of great interest in synthetic chemistry, therefore the use of polyhedral oligomeric silsesquioxane functionalized ionic liquids was studied[17]. Furthermore the synthesis of polysiloxanes with *tert*-butylamine groups was investigated, in order to study the antimicrobial activity[18].

### 2.2.3 Silicones-Macroinitiator for the Atom Transfer Radical Polymerization of Methacrylates [19]

Matyjaszewski et al. investigated the atom transfer radical polymerization (ATRP) of (meth)-acrylates (MA) from polydimethylsiloxane (PDMS) macroinitiators, in order to produce di- and triblock copolymers. The task of this work was to produce materials composed of silicones with controlled mechanical properties. Figure 2.14 and 2.15 show the general synthetic route for mono- and difunctional ATRP initiators.

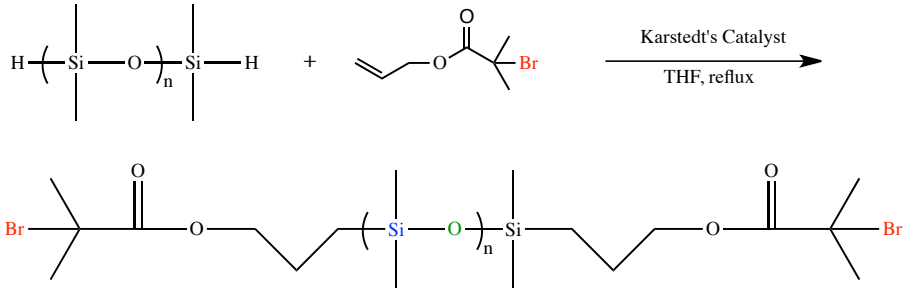


Figure 2.14: Synthesis of the difunctional PDMS macroinitiator through a hydrosilylation reaction of a PDMS and allyl-2-bromo-2-methylpropanoate[19]

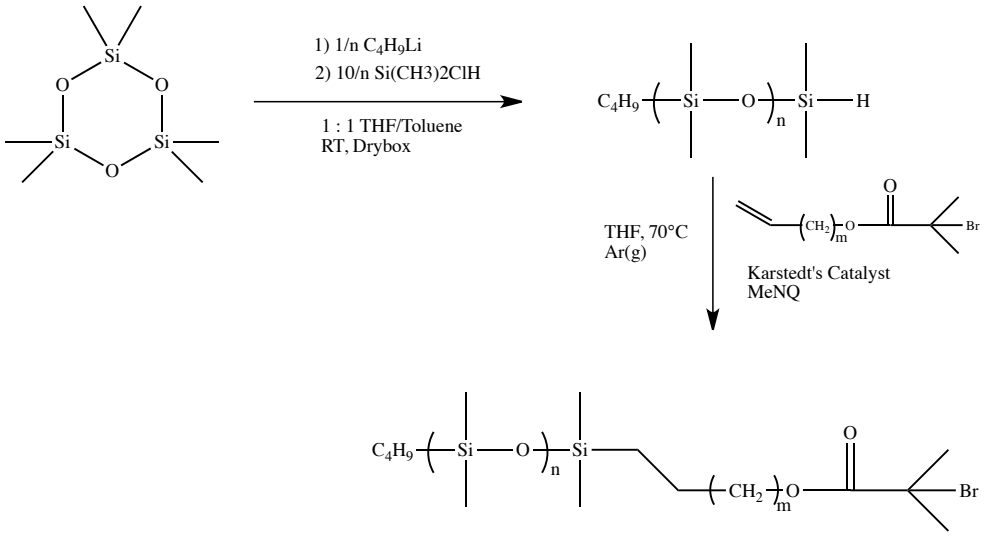


Figure 2.15: Synthesis of the monofunctional PDMS macroinitiator through a hydrosilylation reaction of a PDMS and allyl-2-bromo-2-methylpropanoate[19]

Allyl 2-bromoisobutyrate was synthesized by esterification of allyl alcohol wth 2-bromoisobutyryl bromide. This compound was used in a hydrosilylation reaction with difunctional hydrosilyl-terminal PDMS. 2-bromoisobutyrates are efficient initiators for ATRP of several monomers such as methacrylates and acrylates.

Furthermore, monofunctional 2-bromoisobutyrate terminal inorganic/organic diblock copolymer macroinitiators were synthesized. Living polystyryllithium was used to initiate the anionic ROP of D3 and terminated by chlorodimethylsilane, followed by a hydrosilylation reaction of 3-butenyl-2-bromoisobutyrate. Methyl methacrylate was used as a monomer for the ATRP with a poly(styrene-b-dimethylsiloxane) macroinitiator. Figure 2.16 shows the synthetic route for the inorganic/organic polymeric hybrid material.

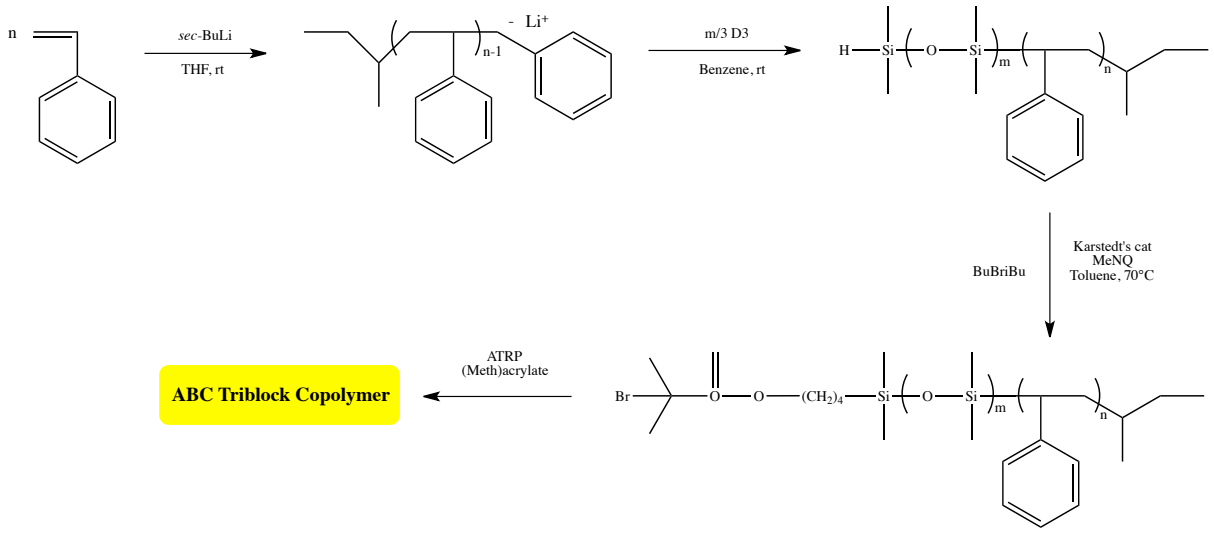


Figure 2.16: Synthesis of inorganic/oganic diblock copolymer[19].

Copolymers with defined chemical and physical properties, particularly with defined chain length and narrow $M_w/M_n$ distributions[20][21] were accessible using the described synthetic pathway. Furthermore, interesting structure-property relationships were obtained from these materials.

## 2.3 Synthesis of Silicon-Tin Hybrid Materials

### 2.3.1 Hydrosilylation Reaction

The hydrosilylation reaction is the addition reaction of Si-H bonds to double or triple bonds. It was first described by Sommer et al. in 1947[22]. The working group of Speier used hexachloroplatinic acid as a high efficient catalyst. In the following subsection a common reaction mechanism of $H_2PtCl_6$ is described. The catalytic reaction represents an important and facile method for the synthesis of a variety of organosilicon compounds [9].

### 2.3.2 The Mechanism of the Hydrosilylation Reaction catalyzed by $H_2PtCl_6$ according to Chalk Harrods [23]

The addition of substituted olefins and silanes relates to anti Markovnikov's rule to build substances with terminal silyl-groups. The reaction is associated to a stereochemical consistent *syn*-addition. The postulated Pt catalytic cycle is shown in Figure 2.17 and can be described by four different main reactions:

#### The Oxidative Addition

The first step is the oxidative addition of a $HSiR_3$ to the platinum catalyst and forms a hydrido(silyl)platinic(II) complex.

#### The Olefin Coordination

One ligand is substituted by olefinic forming a $\pi$- complex.

#### The Olefin Insertion

At this stage of the catalytic cycle the C-Pt $\sigma$ bond is formed. The olefin is inserted in the Pt-H bond and forms an alkyl(silyl)platinic(II) complex.

#### The Reductive Elimination

In the last step of the hydrosilylation reaction cycle the Si-C bond is formed which yields the product. The Pt-catalyst is regenerated by addition of the ligand and reenters the catalytic cycle.

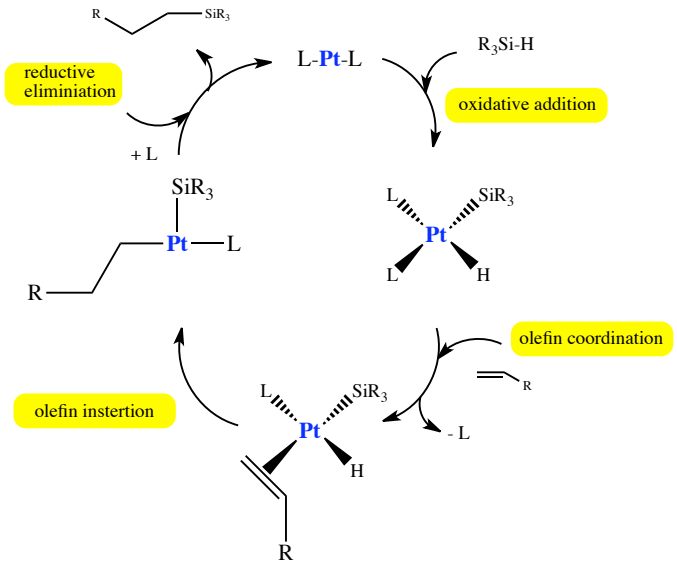


Figure 2.17: Chalk Harrods mechanism for the hydrosilylation reaction[23].

### 2.3.3 Examples of Hydrosilylation Reactions with different substrates

- **Hydrosilylation of Cyclohexene and Allyl Chloride with Trichloro-, Dichloro(methyl)- and Chlorodimethylsilanes in the Presence of Pt(0) Complexes [24]**

Belyakova et al. studied the hydrosilylation reaction of cyclohexene and allyl chloride in the presence of Pt(0) (Karstedt catalyst) complexes with tetramethylvinyldisiloxane and hexavinyldisiloxane. It was reported, that this catalyst is much more active in the hydrosilylation than the Pt(II)-containing Speier catalyst. Different hydrosilylation reactions of cyclohexene were carried out with trichlorosilane, dichloro(methyl)silane and chlorodimethylsilane. The reaction equation is shown in Figure 2.18.

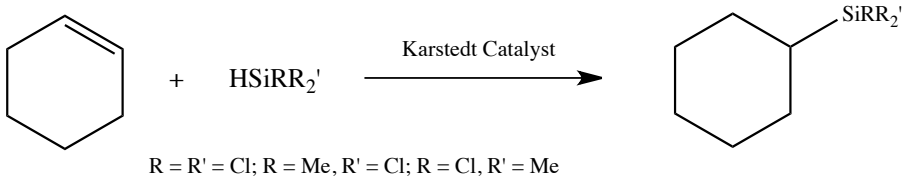


Figure 2.18: Hydrosilylation of cyclohexene with $Cl_3SiH$, $Cl_2SiMeH$ and $ClSiMe_2H$[24]

The hydrosilylation reaction of cyclohexene with trichlorosilane easily proceedes within 1.5 h in the presence of Karstedt's catalyst with a yield of 69.1%. In comparison with the use of Speier's catalyst, the reaction time of the hydrosilylation reaction of trichlorosilane and dichloro(methyl)silane was 72 h and reached 89.0 and 93.2%. Moreover a catalytic amount of allyl glycidyl ether was needed to guarantee the conversion of cyclohexene.

- **Functionalization of Poly(methylhydro)siloxanes via Hydrosilylation of Allyl Derivates [25]**

Marciniec et al. tried to find new efficient catalysts for the hydrosilylation reaction of poly-(methylhydro)siloxanes with allyl derivates, in order to synthesize polysiloxane coupling agents containing organofunctional groups in the side chain. Two model poly(methylhydro)siloxane reagents were used for the hydrosilylation reaction of the Si-H bond with allyl derivatives and 1-octene. Figure 2.19 shows the reaction equation of the prepared hydrosilylation reactions.

The functionalization of poly(methylhydro)siloxane (model A) by the olefin was quantitative at optimum conditions. Furthermore it was investigated that the $H_2PtCl_6$ based catalyst was more efficient than the other platinum or ruthenium complexes in the studied hydrosilylation reactions.

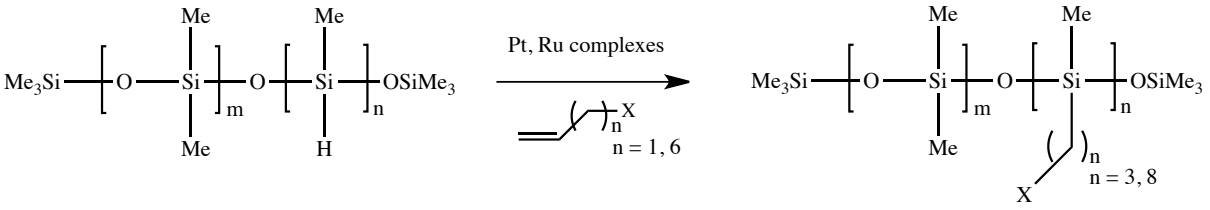


Figure 2.19: Reaction of several poly(methylhydro)siloxanes with allyl derivatives or 1-octene: m = 0, n = 80 (for model A) and m = 21, n = 42 (for model B)[25]

### 2.3.4 Synthesis and Characterization of Silicon-Based Group 14 Dendrimers [26]

Schumann et al. investigated the synthesis of metallodendrimers of the second generation based on the group 14 elements Ge and Sn[27]: $Si\{(CH_2)_2Sn[(CH_2)_4MPh_3]_3]\}_4$. The target of this work was to synthesize of heterometallic dendrimers, which were suggested to improve specific chemical and physical properties of the homometallic dendrimers.
The compound $Si(CH_2CH_2\text{-}GePh_3)_4$ was first synthesized by hydrogermylation of tetravinylsilane with triphenylgermane in the presence of $H_2PtCl_6$ in high purity. Moreover it was investigated, that tetra(but-3-enyl)stannane reacted with triphenylgermane in the presence of 5 mole% AIBN, yielding tetrakis[4-(triphenylgermyl)butyl]stannane.
Tetrakis[2-(trivinylstannyl)ethyl]silane, tetrakis[2-(trivallylstannyl)ethyl]silane and tetrakis silane were generated as starting materials. The products were isolated in yields of 80 to 90%. The reaction scheme is shown in 2.20.

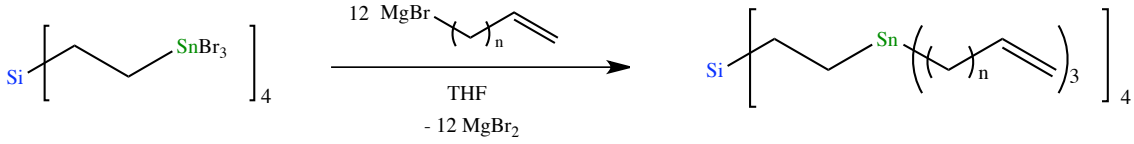


Figure 2.20: Synthesis of several substituted tetrakissilanes by the reaction with the appropriate Grignard reagents[26].

The formation of the second generation dendrimers was realized by the hydrogermilation and hydrostannilation reaction of tetrakis[2-(tributenylstannyl)ethyl]silane with $Ph_3GeH$ and $Ph_3SnH$ forming tetrakis-2-[tris{4-(triphenylgermyl)butyl}stannyl]ethyl}silane and tetrakis-2-[tris{4-(triphenylstannyl)butyl}stannyl]ethyl}silane. The corresponding reaction equation is shown in 2.21.

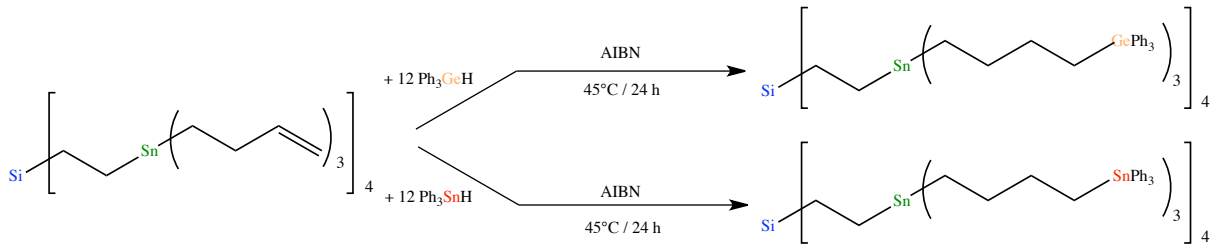


Figure 2.21: Synthesis of the second generation dendrimeres containing Ge and Sn[26].

### 2.3.5 Novel Inorganic Oxide supported Organotin Hydrides for Fine Chemical Catalysis [28]

Fu et al. tried to eliminate or substantially reduce the residual in contamination in organotin hydride products. Attempts were made to support the organotin hydrides onto insoluble materials. The use of typical high surface area inorganic oxides as the organotin hydride carrier was investigated.
First a silane-functionalized tin hydrid complex was synthesized (see Figure 2.22).

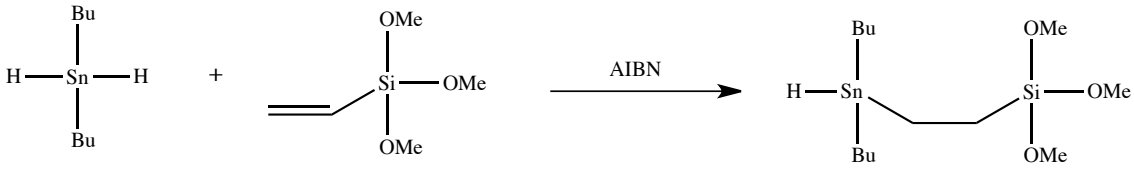


Figure 2.22: Synthesis of a silane-functionalized tin hydride complex[28].

Afterwards the dried oxide powder was reacted with the silane complex as it is shown in Figure 2.23.

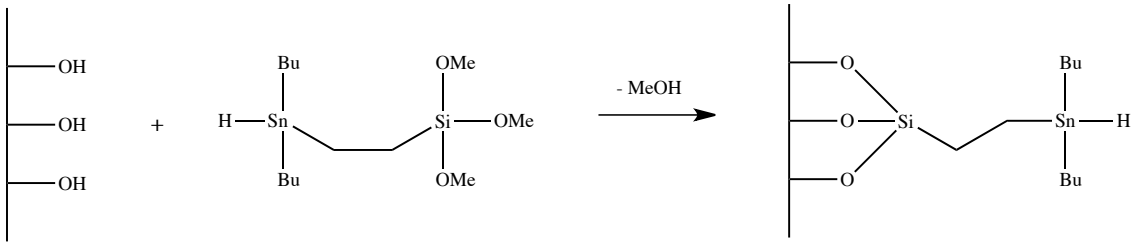


Figure 2.23: Reaction of the silane compound with oxide powder in order to produce a reactive hydride content[28].

The catalytic activity of the reactive hydride content was then checked by reacting with an excess of 1-iodooctane. The use of a small amount of inorganic oxide supported organotin hydride showed high activity for hydrogenation and intramolecular reactions.

# 3 Results and Discussion

## 3.1 General

This section gives an overview of the synthesized products, yields and spectroscopic data. The experimental procedures are described in Section 5. This section is structured in four different subchapters. First, the synthesis of the organostannane compounds is discussed. Secondly, the ROP of D3 is characterized. Afterwards the investigation of the synthesis of the organotin reagent supported on a silicon backbone in order to perform Stille cross-coupling reactions is discussed. The cross coupling coupling reaction is described in the fourth part of this section. Figure 3.1 shows the general synthetic pathway to produce the organotin precursor on a silicon backbone.

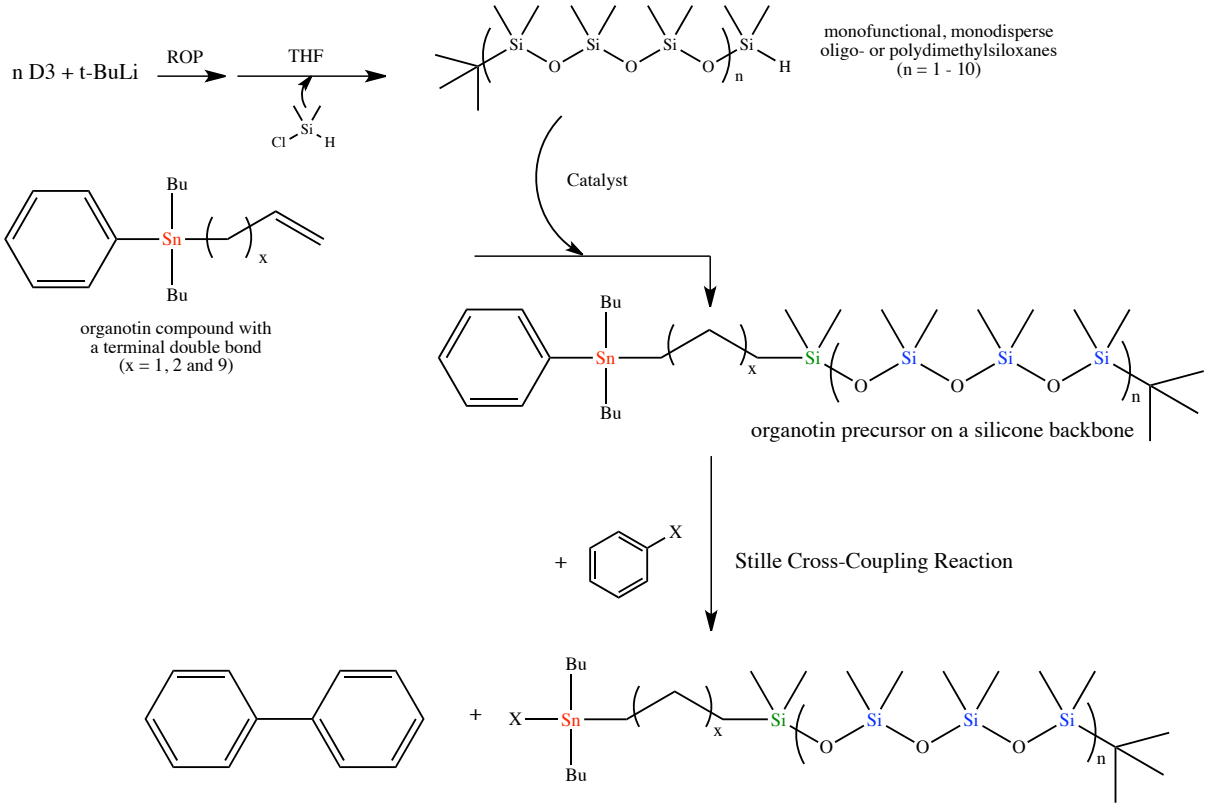


Figure 3.1: General scheme of the synthesis of the novel hybrid tin reagent supported on a siloxane backbone for Stille cross-coupling reaction.

## 3.2 Synthesis and Characterization of the Organotin Materials

Table 3.1 gives an overview of the synthesized organotin reagents.

Table 3.1: Overview of the synthesized organostannanes, their molecular weight and yield.

| REAGENT | MOLECULAR WEIGHT (g/mole) | YIELD % |
|---|---|---|
| $Cl_2SnPh_2$ (3.2.1) | 343.82 | 67% |
| $Bu_2SnPh_2$ (3.2.3) | 387.15 | 76% |
| $Bu_2SnPhCl$ (3.2.3) | 345.5 | 83% |
| Allyl-$SnBu_2Ph$ (3.2.4) | 351.11 | 57% |
| Butenyl-$SnBu_2Ph$ (3.2.5) | 365.14 | 66% |
| Undecenyl-$SnBu_2Ph$ (3.2.6) | 463.33 | 71% (raw product) |

### 3.2.1 Dichlorodiphenylstannane

The redistribution reaction according to Kosheshkov[29] is carried out in the absence of solvents. In general, any organotin compound ($R_nSnX_{4-n}$) can undergo a redistribution of the alkyl and halogen groups. The synthesis occurred satisfactorily. The raw product (brown crystals) was recrystallized twice (precipitated at -30°C) to obtain clear white crystals with an avarage yield of 67%.

### 3.2.2 Dibutyldiphenylstannane

The synthesis of dibutyldiphenylstannane was obtained via two different Grignard reactions:

- *Butylchloride Grignard reaction with dichlorodiphenylstannane*
- *Bromobenzene Grignard reaction with dibutyldichlorostannane*

Both were carried out under inert atmosphere and worked off under aqueous conditions and pure products could be achieved. Generally, the product yield based on the reaction with butylchloride Grignard was lower compared to the bromobenzene Grignard reaction. One major problem concerning the butylchloride Grignard was the precipitation of $MgCl_2$ as it was extracted with water. The yield of $Bu_2SnPh_2$ alternated between 25 and 76%.

### 3.2.3 Dibutylchlorophenylstannane

- *Chlorination of Dibutyldiphenylstannane with Hydrogenchloride in $Et_2O$*

The reaction was carried out at -30°C to guarantee efficient heat dissipation. After the purification the yields alternated between 75 and 83%.

- *Chlorination of Dibutyldiphenylstannane with the Redistribution Reaction according to Kocheshkov*

One severe disadvantage was the very long reaction time (up to 2 days) for quantitative conversion. On the one hand the conversion wasn't completed and on the other hand the residue during the distillation turn to a yellow ochre highly viscous oil and remained in the flask. As a matter of fact the to total yields were between 35 - 69% after purification.

### 3.2.4 Allyldibutylphenylstannane

This reaction was carried out according to literature[30]. The Grignard reaction was carried out at temperatures between -30 and -60°C to give the desired products and to avoid polymerization of the allyl compound. Furthermore, the Grignard reagent was titrated with 0.10 M HCl to determine its exact concentration. Allyl-$SnBu_2Ph$ could be synthesized very pure after distillation with a yield of 57%. The purity was controlled by NMR spectroscopy.

### 3.2.5 Butenyldibutylphenylstannane

This synthesis according to Grignard is also known in literature[31] and lead to good quantitative results. Sometimes $MgCl_2$ precipitated during the aqueous extraction and therefore addition of 5% HCl solution was required. The yield after purification was about 66%. Two according spectras are shown in following figures (Figure 3.2 **A** $^1$H NMR, Figure 3.2 **B** $^{13}$C NMR), the purity is verified by the peak integrals of the $^1$H NMR spectrum, which are in a good correlation to each other. The $^{13}$C NMR and the the $^{119}$Sn NMR spectrum indicate no contaminations.

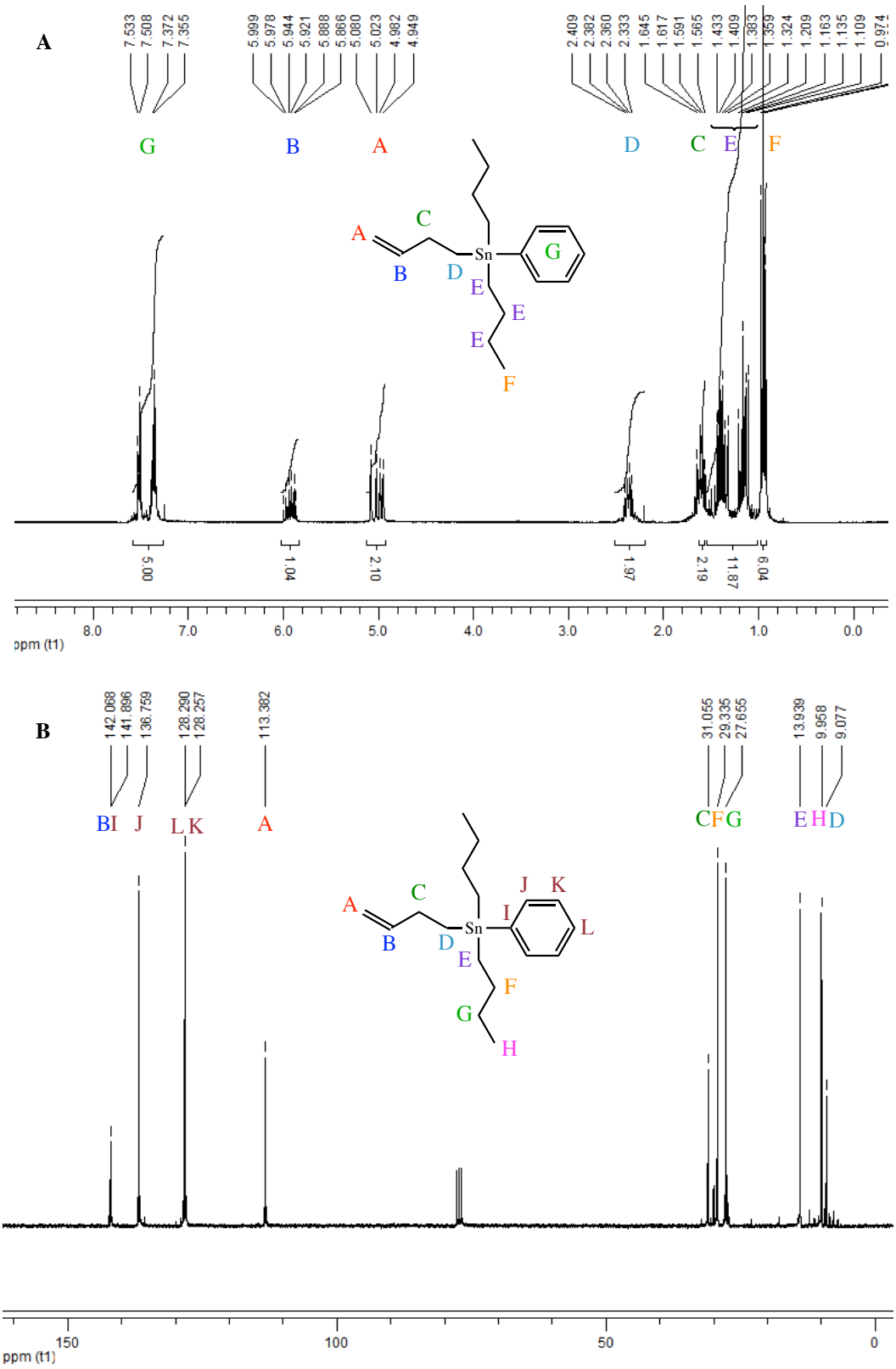


Figure 3.2: **A**: $^{1}$H NMR spectrum of butenyl-$Bu_2SnPh$ with corresponding peak integrals; **B**: $^{13}$C NMR spectrum of allyl-$Bu_2SnPh$.

### 3.2.6 Undecenyldibutylphenylstannane

This synthesis was quantitative; however, the raw product couldn't be purified by distillation due to the high boiling point of the product. The raw product (viscous yellow oil) was characterized by $^{1}H$, $^{13}C$ and $^{119}Sn$ NMR spectroscopy. The corresponding $^{1}H$ and $^{13}C$ NMR spectra are shown in Figure 5.13 **A** and **B**. The integrals of the phenyl group and the double bond of the $^{1}H$ NMR spectrum correlates to each other. This proofs that the formation of the product was quantitative, however, residual amounts of pentane increased the aliphatic peak integral values. According to the $^{13}C$ NMR spectrum, impurities at 65.89 ppm and between 29.7 ppm an 9.56 ppm complicate the interpretation of the spectra, as well as solvent remains. However, the peak at -43.54 ppm corresponds to the desired product. The corresponding $^{119}Sn$ NMR spectrum is shown in Figure 3.4. Two possible impurities were interpreted at 66.8 ppm (halogenated stannane) and -71.29 ppm which corresponds to dibutyldiphenylstannane.

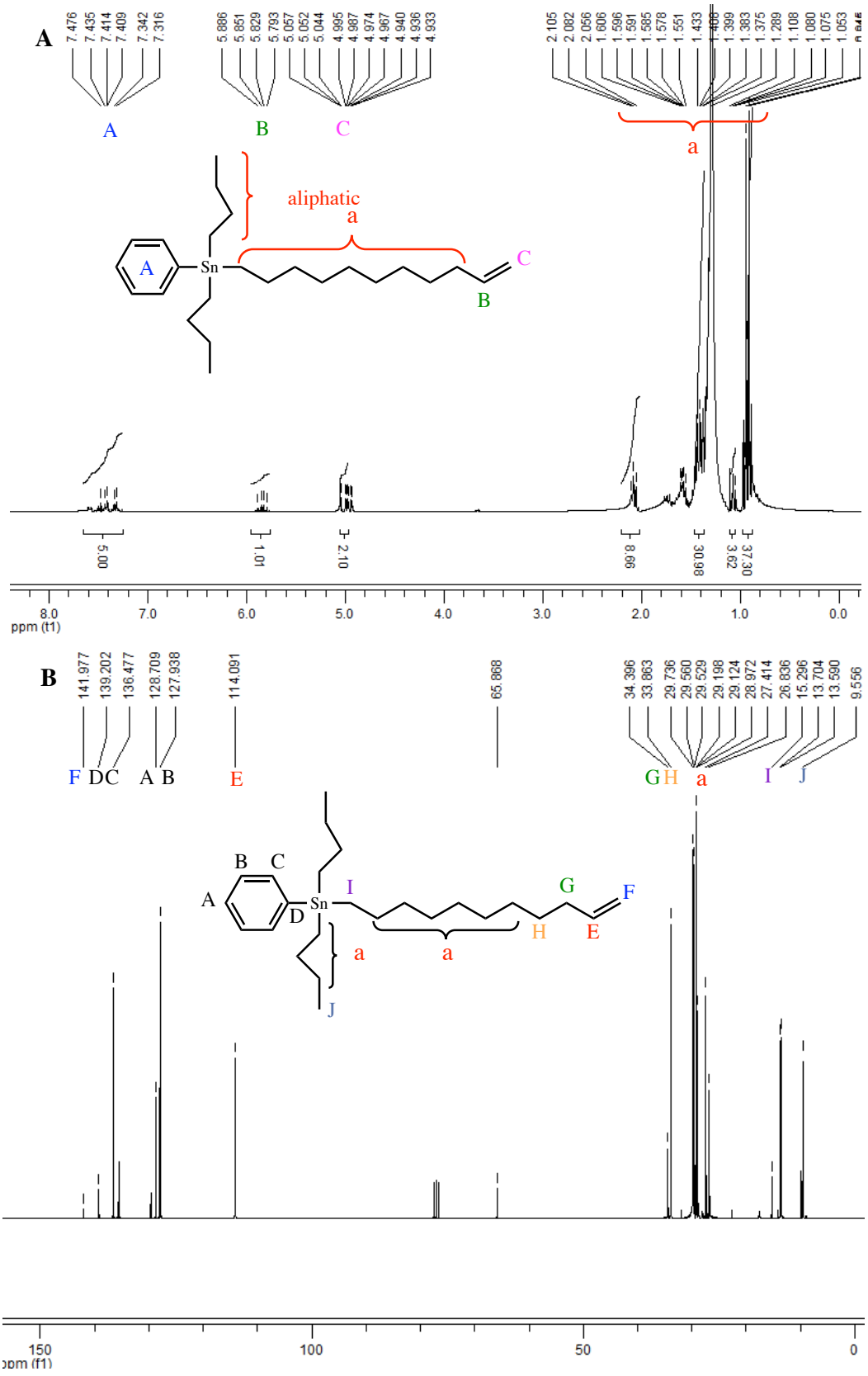


Figure 3.3: A: $^{1}H$ NMR and B: $^{13}C$ NMR spectrum of Undecenyl-$SnBu_2Ph$

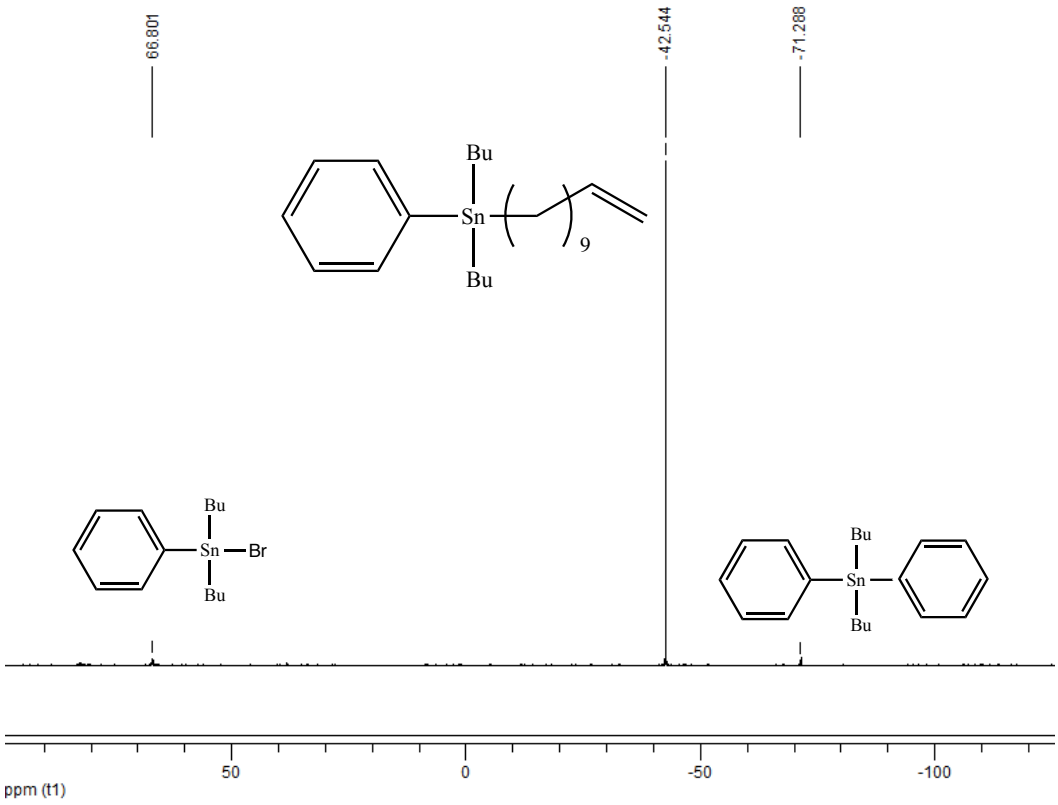


Figure 3.4: $^{119}$Sn NMR NMR spectrum of Undecenyl-Sn$Bu_2$Ph

### 3.2.7 Butenylchloride

The chlorination of 3-buten-1-ol was carried out by a literature procedure[32]. The raw product was extracted with water to remove the excess of thionylchloride. A yield of 59% was achieved.

## 3.3 Ring Opening Polymerization (ROP) of Hexamethylcyclotrisiloxane (D3)

Target in this section was the synthesis of linear, monofunctional polydimethylsiloxanes (PDMS). This compound is starting material for the production of the desired tin hybrid material. The ROP of D3 was systematically investigated by M. Brandstaetter and G. Witek in F. Uhlig's working group[8][9]. The desired compound is shown in Figure 3.5

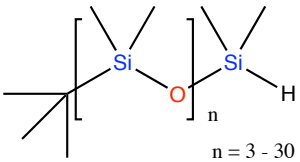


Figure 3.5: Typical molecular structure of a linear, monofunctional PDMS.

In my work, the ROP of D3 was initiated by *tert*-butyllithium (*t*-BuLi). The ROP was stopped by addition of an appropriate chlorosilane in the kinetically controlled regime to produce PMDS with desired chain length and narrow molecular weight distribution (PDI). In the kinetically controlled regime undesirable reactions such as chain redistribution are inhibited. Several ROP reactions of D3 were carried out to produce PDMS with chain length between 3 and 30 Si-O units. An overview of the synthesized PDMS in this work is given Table 3.2, including the reaction conditions and the polymerization degree. The Si-O chain length was determined by $^{1}$H NMR spectroscopy (D3 consumption). The PDI is estimated to be less than 1.2[9][8]. Additionally the purity of the silicone polymers was checked by $^{29}$Siinept NMR spectroscopy. Generally, the $^{29}$Siinept NMR data splits in three different groups of signals: SiH, $SiMe_2R$ and $(Me_2SiO)_n$.

Table 3.2: Overview of the reaction conditions in order to synthesize monofunctional oligo- or polydimethylsiloxanes

| D3 : *tert*-BuLi ratio | Temperature [°C] | Reaction time [min] | Chain lenght |
|---|---|---|---|
| 20 : 1 | 25 | 30 | 29 |
| 20 : 1 | 25 | 15 | 19 |
| 10 : 1 | 25 | 30 | 19 |
| 10 : 1 | 25 | 15 | 15 |
| 10 : 1 | 25 | 10 | 12 |
| 1 : 5 | 25 | 10 | 8 |
| 1 : 1 | 0 | 30 | 3 |

Figures 3.6 and 3.7 show the corresponding spectra of a silicone polymer with a chain length of 3 Si-O units.

Figure 3.6 ($^{1}$H NMR) is split in two parts to distinguish the different peak intensities. The intensities are in a good correlation to each other except the hydride function. This effect is due to the overlap of the background noise and the broad multiplet[8]. Figure 3.7 shows the corresponding $^{29}$Si NMR.

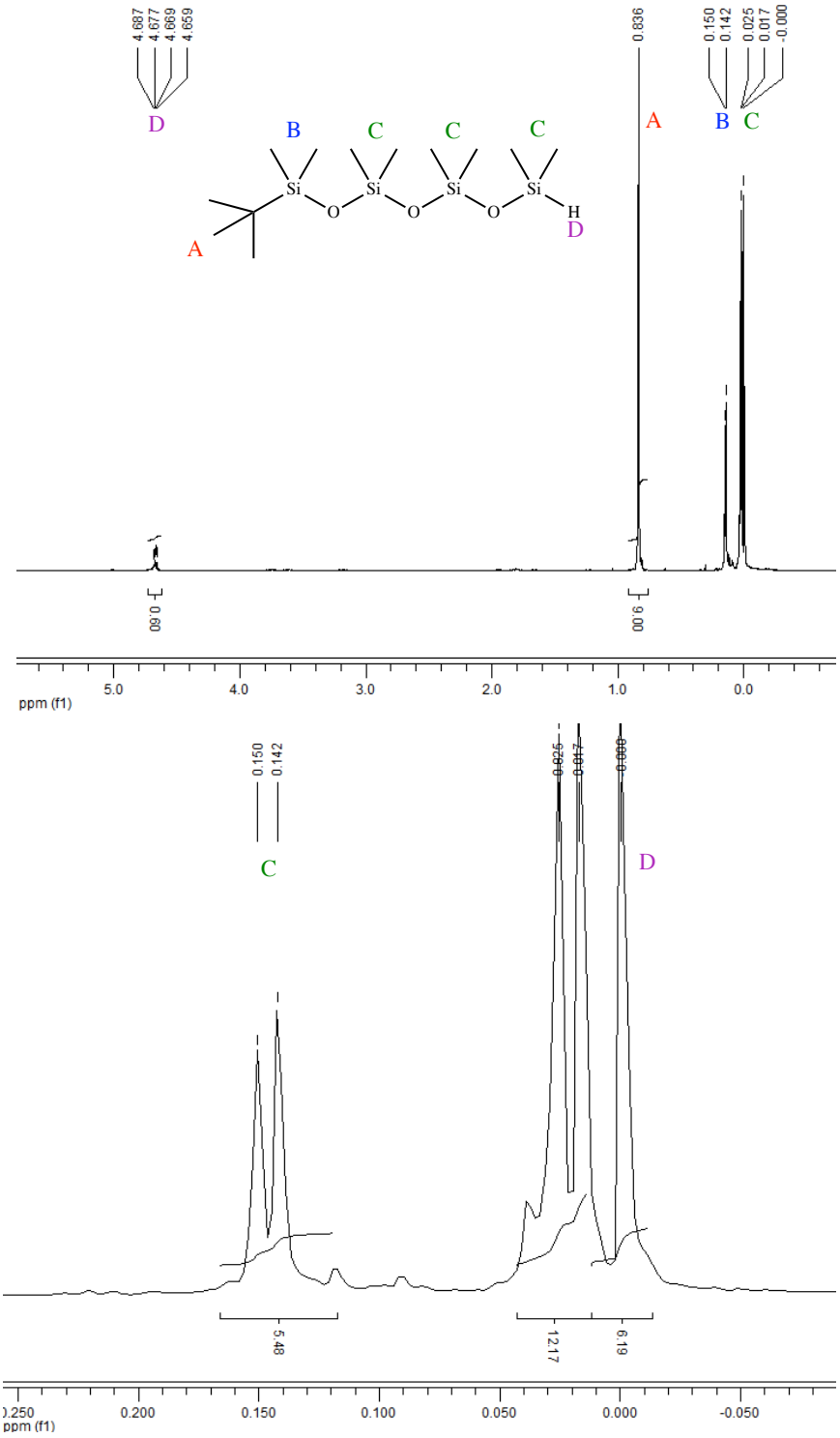


Figure 3.6: Typical $^{1}$H NMR spectrum of a PDMS with 3 Si-O units.

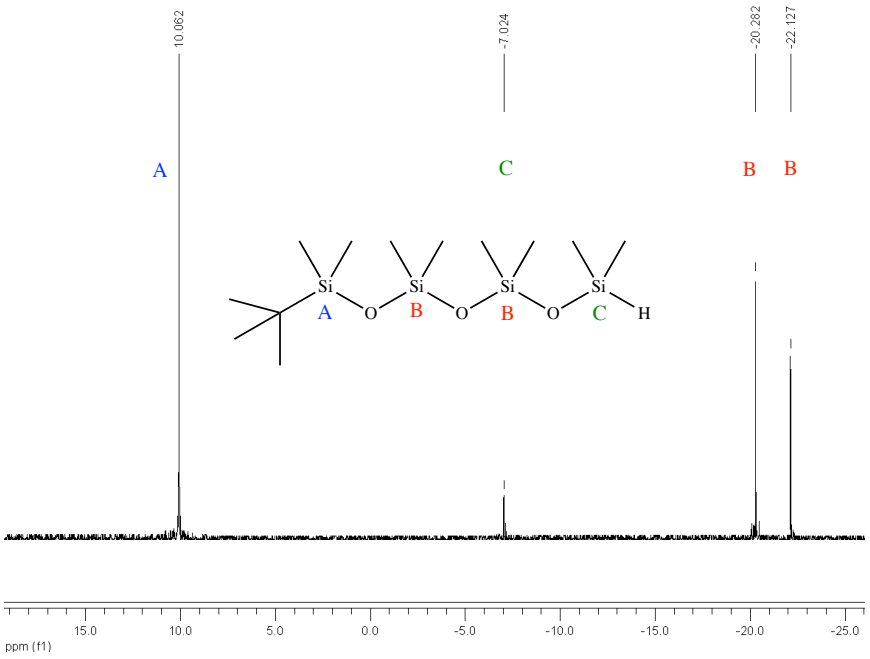


Figure 3.7: Typical $^{29}$Si NMR spectrum of a PDMS with 3 Si-O units.

## 3.4 Synthesis and Characterization of the novel Silicone-Organotin Hybrid Materials

In this section the hydrosilylation reaction is discussed in order to obtain the organotin precursor on a silicon backbone.

### 3.4.1 Hydrosilylation Reactions of different Organic Compounds

Previously some hydrosilylation reactions were carried out without tin compounds to control the conversion of the terminal double bond (see Table 3.3).

Table 3.3: Overview of the previous hydrosilylation reactions to control the conversion of the double bond.

| # | Organic Compound | Silicone Compound | Catalyst | Solvent | Success |
|---|---|---|---|---|---|
| **1** | Cyclohexene | PDMS | Karstedt Catalyst | Toluene | - |
| **2** | Allylchloride | PMDS | Karstedt Catalyst | Toluene | - |
| **3** | Undecenylbromide | Dimethylchlorosilane | Karstedt Catalyst | Toluene | + |

$^{1}$H and $^{13}$C NMR spectroscopy was used to check the reaction progress. Synthesis **1** was prepared by a literature procedure (see Section 2.3). A conversion of 70% to trichloro(cyclohexyl)silane after 1.5 h in the presence of the Karstedt catalyst was reported[24]. Figure 3.8 shows the $^{13}$C NMR spectrum of cyclohexene and PDMS-H after a reaction time of 1 day in the presence of Karstedt's catalyst. No conversion of cyclohexene was achieved. It is assumed that the PDMS with 14 Si-O units is sterically hindered and the catalytic process is inhibited.

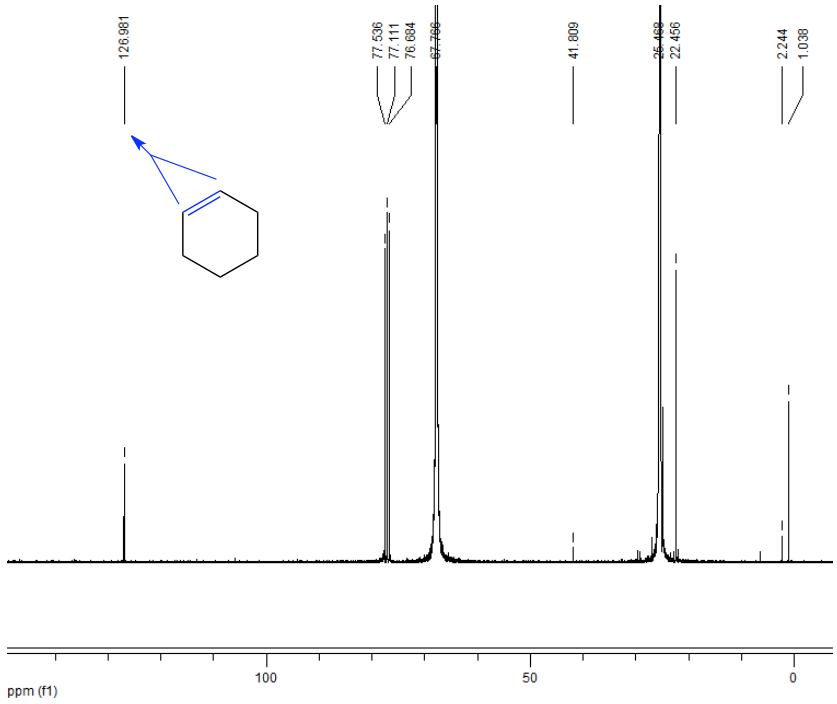


Figure 3.8: $^{13}$C NMR spectrum of the hydrosilylation reaction of cyclohexene with a PMDS chain of 14 Si-O units after 1 day.

Synthesis **2** also was carried out according to literature[24]. The corresponding $^{13}C$ NMR spectrum is shown in Figure 3.9. The hydrosilylation reaction of this compound wasn't efficient too. Conversion of allylchloride double bond occured, however it's assumed that the allylchloride is polymerized due to the high reaction temperatures (110 - 120°C).

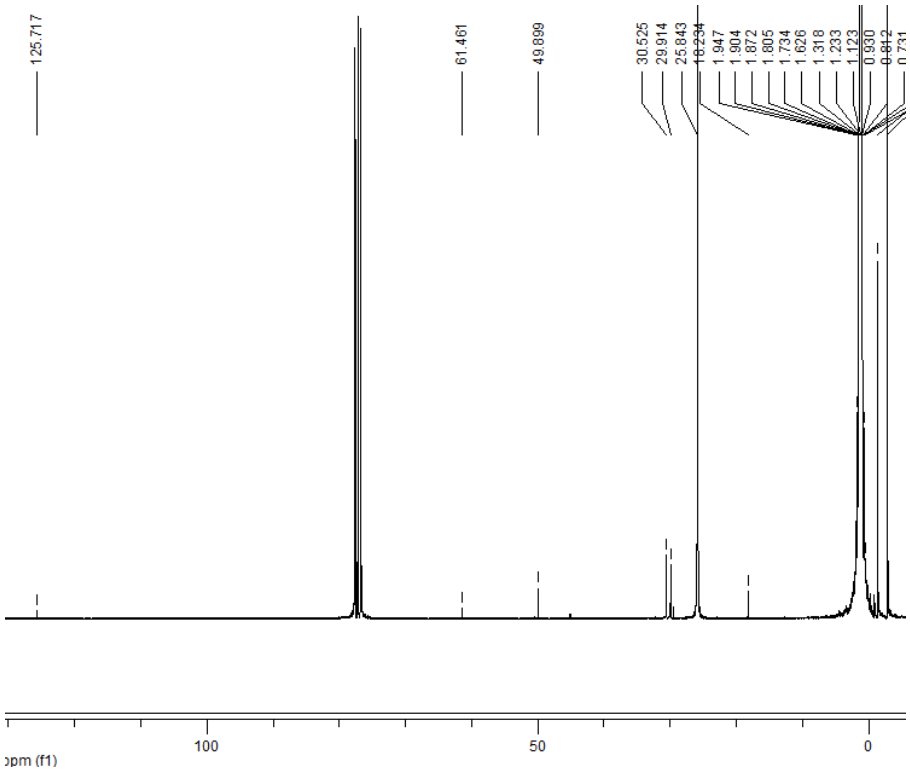


Figure 3.9: $^{13}C$ NMR spectrum of the hydrosilylation reaction of allylchloride with a PMDS chain of 19 Si-O units after 1 day.

The hydrosilylation reaction of undecenylbromide with dimethylchlorosilane succeeded (synthesis **3**) within 18 hours. Figure 3.10 the $^{13}C$ NMR spectrum of the synthesized 11-(dibutyl(phenyl)stannyl)undecyl)dimethyl(chloro)silane is shown. For better presentation, the essential part of the spectrum is characterized.

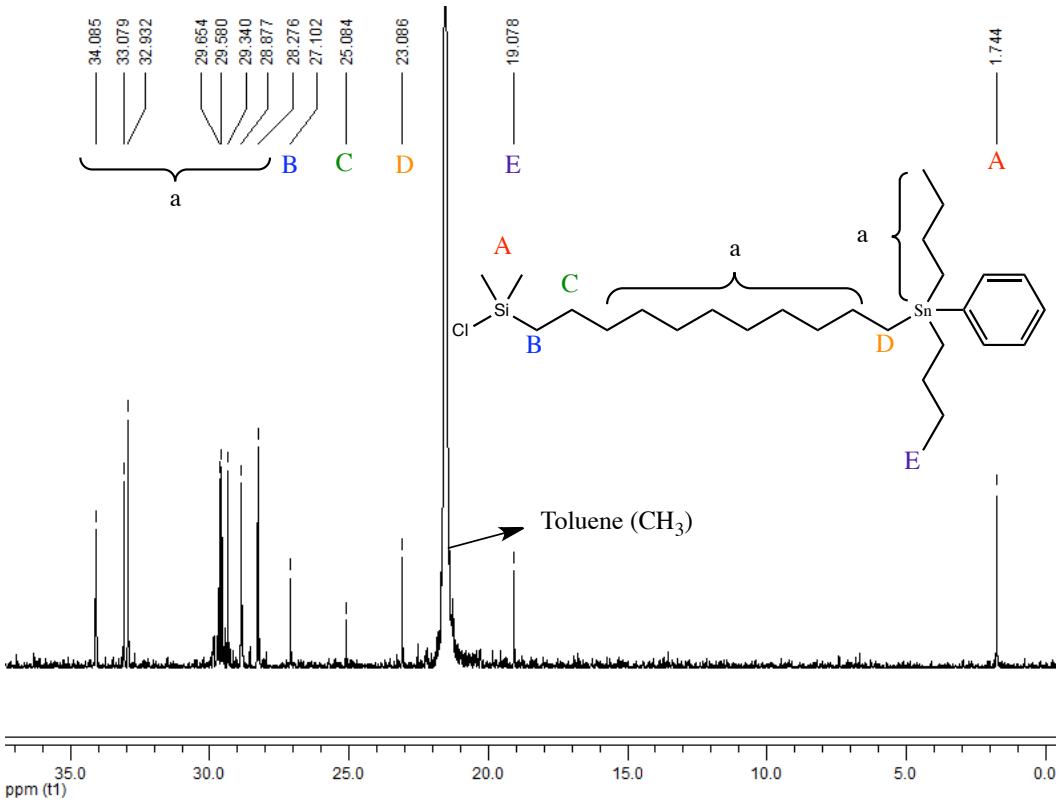


Figure 3.10: $^{13}$C NMR spectrum of the hydrosilylation reaction of undecenylbromide with $Me_2Si(Cl)H$ after 18 h.

### 3.4.2 Hydrosilylation Reactions of the Organotin Compounds

The organotin precursor for Stille cross-coupling reactions was synthesized via a hydrosilylation reaction with poly- or oligodimethylsiloxanes or appropriate chlorosilanes. In Table 3.4 the different hydrosilylation reactions of the allyl substituted tin reagent are listed which were carried out in this work.

Table 3.4: Hydrosilylation reactions of the allyl-$SnBu_2Ph$ compounds and several silicone reagents.

| # | TIN COMPOUND | SILANE COMPOUND | CATALYST | SOLVENT | SUCCESS |
|---|---|---|---|---|---|
| **4** | Allyl-$SnBuPh_2$ | t-Bu-$(Si\text{-}O)_{29}$-SiH | Karstedt Catalyst | Toluene | - |
| **5** | Allyl-$SnBuPh_2$ | t-Bu-$(Si\text{-}O)_{15}$-SiH | Wilkinson Catalyst | THF | - |
| **6** | Allyl-$SnBuPh_2$ | $(CH_3)_2SiClH$ | Karstedt Catalyst | Toluene | - |
| **7** | Allyl-$SnBuPh_2$ | $(EtO_2)_2SiMeH$ | Karstedt Catalyst | Toluene | - |
| **8** | Allyl-$SnBuPh_2$ | $(CH_3)_2SiClH$ | Pd/C and UV | Toluene | - |

Synthesis **4-8** were unsuccessfull. Synthesis **4** was the hydrosilylation reactions of allyl-$SnBu_2$ with a PDMS chain of 29 Si-O units. The reaction time was more than 5 days. Even if more catalyst was added to the reaction solution, no conversion occured. According to the literature[23][25], synthesis **5** (hydrosilylation reaction of allyl-$SnBu_2Ph$ and a PDMS chain of 15 units) was carried out with Wilkinson's catalyst, also here no conversion could be achieved. It's assumed that, as it was discussed before, the PDMS chain negatively influences the catalytic process or even inhibits the Pt or Rh based catalysis. Figure 3.11 shows the corresponding $^1H$ NMR spectrum of synthesis **4** with the essential peak interpretation, that no conversion of the double bond occurred.

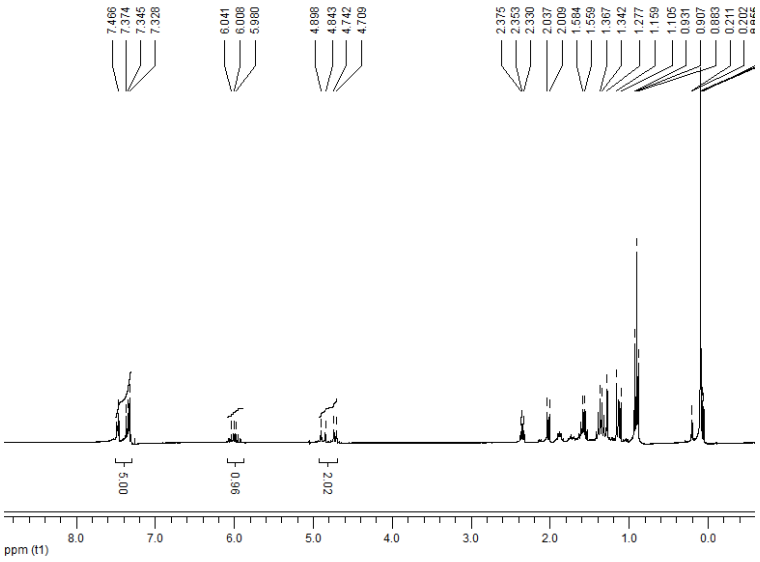


Figure 3.11: $^1H$ NMR spectrum of synthesis **4** and corresponding peak values.

For this reason and based on the primarily maintained conclusions (see Section 3.4.1), subsequent hydrosilylation reactions with of chlorosilanes were carried out. Synthesis **6** seemed to be succesfull at the first view because no double bond was found in the $^{1}H$ and $^{13}C$ NMR spectra. The $^{119}Sn$ spectrum of the reaction solution after 1 day showed a peak at 83.19 ppm, which corresponds to dibutylchlorophenylstannane. Hence, chlorination of the tin compound, similar to a Kocheshkov reaction, occured by the use of chlorosilanes. The corresponding allylsilane formed in this redistribution reaction was not separately characterized. Figure 3.12 shows the suggested reaction equation.

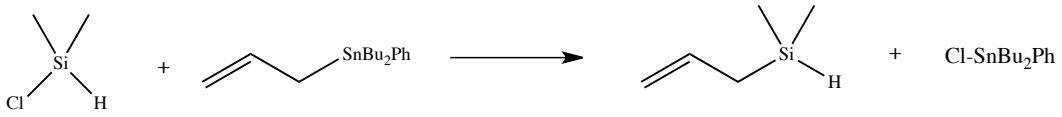


Figure 3.12: Suggested reaction equation of the redistribution reaction of allylstannane with chlorodimethylsilane.

To avoid chlorination of the tin compound, hydrosilylations with diethoxymethylsilane (synthesis **7**) were carried out, however, also here no reaction occurred.

Pd on activated carbon was used as another possible catalyst for the hydrosilylation reaction (synthesis **8**). After 3 days there was no remarkable conversion, but no chlorination of the stannane occurred. For this reason the reaction solution was treated with UV radiation for another 2 days. Also with this method no conversion occurred.

In recent literautre[33] the hydrosilylation reaction of undecenyl substituted stannanes was successfully studied. However, in this case no reaction was observed. From this point of view the allyl substituent tin reagent appears to be not suitable for this type of reaction. To solve this problem other alkenyl substituted tin reagents have to be tested for this reaction.
Table 3.5 shows the reaction of undecenyldibutylphenylstannane with dimethylchlorosilane (synthesis **9**).

Table 3.5: Hydrosilylation reaction of undecenyl-$Bu_2SnPh$ compounds and dimethylchlorosilane.

| # | TIN COMPOUND | SILANE COMPOUND | CATALYST | SOLVENT | SUCCESS |
|---|---|---|---|---|---|
| **9** | Undecenyl-$SnBuPh_2$ | $(CH_3)_2SiClH$ | Karstedt Catalyst | THF | - |

In our case, no conversion of the undecenyldibutylphenylstannen with dimethylchlorosilane occurred. The corresponding reaction equation is shown in Figure 3.13. Neither the desired product nor the unwanted chlorination occurred when using the undecenyl substituted tin compound.

Due to the unsatisfactorily results, further hydrosilylation reactions with butenyldibutylphenylstannane were carried out (see Table 3.6).

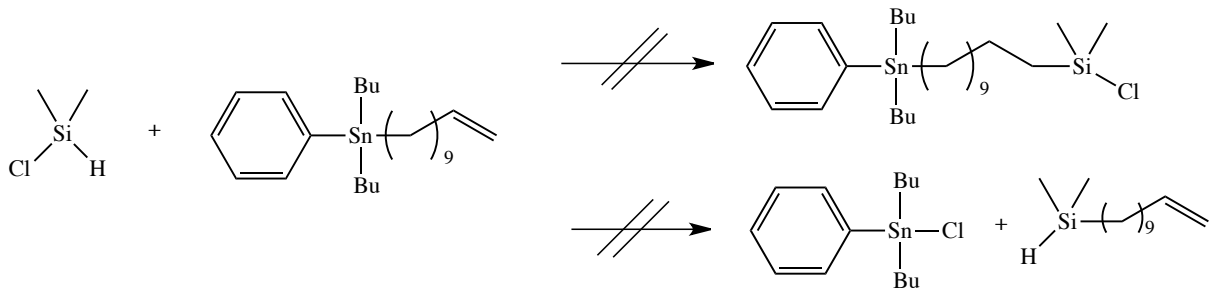


Figure 3.13: Undecenyl-$SnBu_2Ph$ with $Me_2SiClH$ shows no reaction.

Table 3.6: Hydrosilylation reactions of the butenyl-$SnBu_2Ph$ compounds and several silicone reagents.

| # | TIN COMPOUND | SILANE COMPOUND | CATALYST | SOLVENT | SUCCESS |
|---|---|---|---|---|---|
| **10** | Butenyl-$SnBuPh_2$ | t-Bu-[$Si(Me_2)$-O]$_{21}$SiH- | Karstedt Catalyst | Toluene | - |
| **11** | Butenyl-$SnBuPh_2$ | $(CH_3)_2SiClH$ | Karstedt Catalyst | Toluene | +/- |
| **12** | Butenyl-$SnBuPh_2$ | $(EtO_2)_2SiMeH$ | Karstedt Catalyst | i-PrOH | - |
| **13** | Butenyl-$SnBuPh_2$ | $(CH_3)_2SiClH$ | Karstedt Catalyst | - | - |
| **14** | Butenyl-$SnBuPh_2$ | $SiCl_3H$ | Karstedt Catalyst | Toluene | - |
| **15** | Butenyl-$SnBuPh_2$ | $MeSiCl_2H$ | Karstedt Catalyst | Toluene | - |
| **16** | Butenyl-$SnBuPh_2$ | t-Bu-[$Si(Me_2)$-O]$_3$-SiH | Karstedt Catalyst | Toluene | + |

Synthesis **10** was carried out with butenyldibutylphenylstannane and PDMS with a chain lenght of 21 Si-O units. As it was explained before, the polymer influenced the catalytic process.

First positive results were given by the hydrosilylation reaction of butenyldibutylphenylstannane with dimethylchlorosilane (synthesis **11**). The according $^1$H NMR spectrum is shown in Figure 3.15. The peak intensities of the end standing -$CH_3$ groups of butenyldibutylphenylstannane (at 0.82 - 0.88 ppm) were compared with the peaks of the double bond. The values indicates that a conversion occurred. Figure 3.14 shows the corresponding reaction equation.


Figure 3.14: Reaction equation of the hydrosilylation reaction of butenyl-$SnBu_2Ph$ with $Me_2SiClH$.

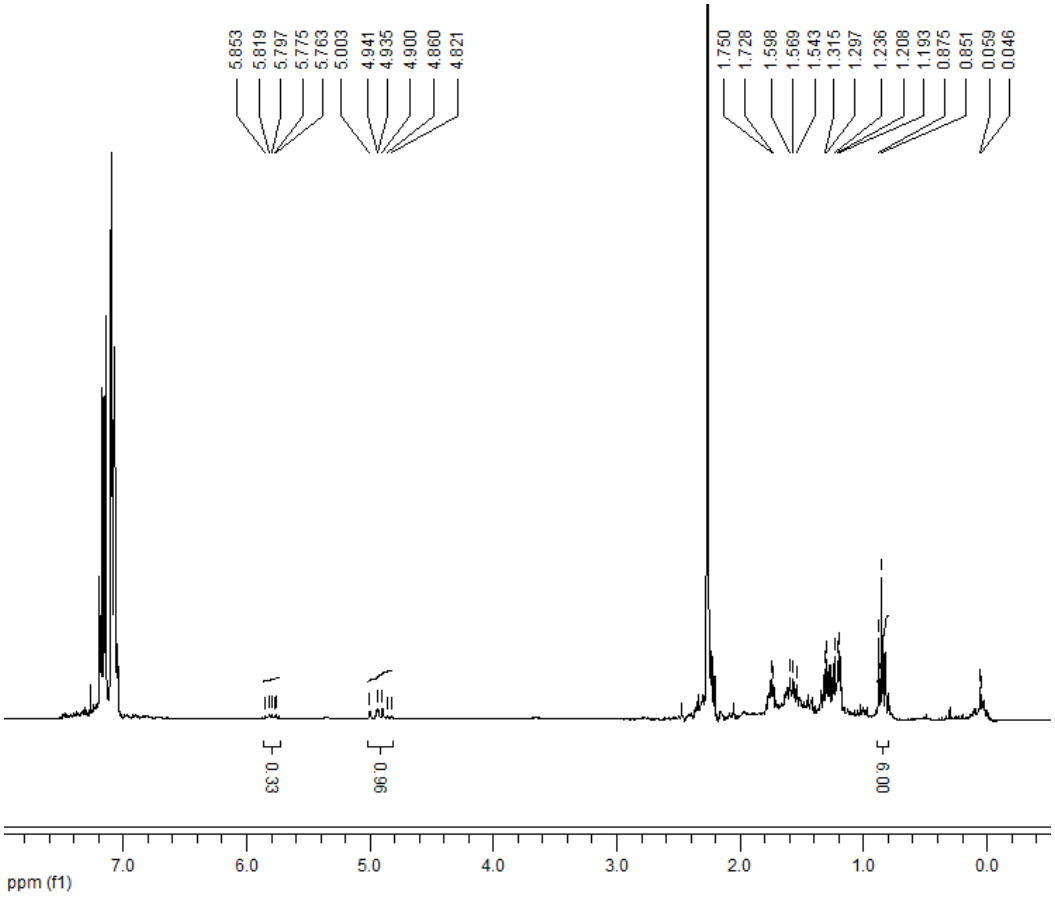


Figure 3.15: $^1H$ NMR spectrum of the hydrosilylation reaction of butenyl-$Bu_2Ph$ with $Me_2ClSiH$ after 2 days.

The reaction conditions of synthesis **12** and **13** were slightly modified. Synthesis **12** was carried out in isopropanole (known as the Speier catalyst). Synthesis **13** was carried out without any solvent. As the chlorosilane was added to the mixture of the organostannane and the catalyst, the reaction mixture turned to a deep brown colour. Both reactions again showed no conversion.

In order to increase the reactivity of the silane compound, synthesis **14** was carried out with trichlorosilane. Trichlorosilane appears to be a strong chlorination reagent as mono- and dihalogenation of the tin compound occurred. In contrast, the reactions with dichloromethylsilane and chlorodimethylsilane showed no remarkable redistribution of the substituents. The $^{119}$Sn NMR spectra of the reaction mixture of synthesis **14** shows a peak at 152.2 ppm, which corresponds to dichlorodibutylstannane. The peak at 87.7 ppm can be identified as chlorodibutylphenylstannane. The corresponding reaction equation is shown in Figure 3.16. The corresponding silane side product formed in this reaction was not separately characterized.

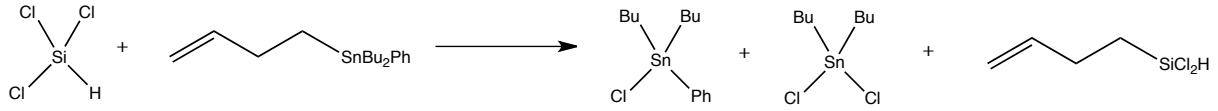


Figure 3.16: Suggested reaction equation of the reaction of butenyl-$SnBu_2Ph$ and $SiCl_3H$.

Due to the fact that trichlorosilane is a strong chlorination agent, synthesis **15** was carried out with dichloromethylsilane. No chlorination as well as no remarkable conversion of the double bond occurred.

Good results were achieved with synthesis **16**. An oligodimethylsiloxane chain with 3 Si-O units was reacted with butenyldibutylphenylstannane. The short chain length of this siloxane compound should reduce the sterically hindrance which was observed when siloxanes with higher molecular mass were used. The corresponding reaction equation is shown in Figure 3.17. The product is subsequently named as compound A.

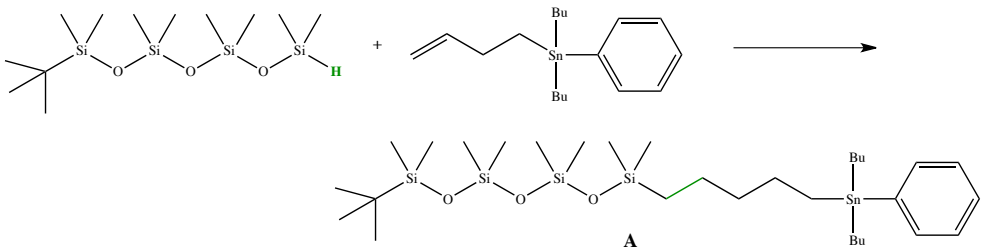


Figure 3.17: Hydrosilylation reaction of butenyl-$Bu_2SnPh$ with PDMS (3 Si-O units).

Figure 3.18 shows the corresponding $^1$H NMR spectrum and the peak integrals. The integrals of the double bond (at 5.9 - 4.9 ppm) and the Si-H bond (at 5.40 ppm) were related to the intensity of the phenyl group (at 7.2 - 7.4 ppm). Therefore the reaction of PDMS-H with butenyl-$SnBu_2Ph$

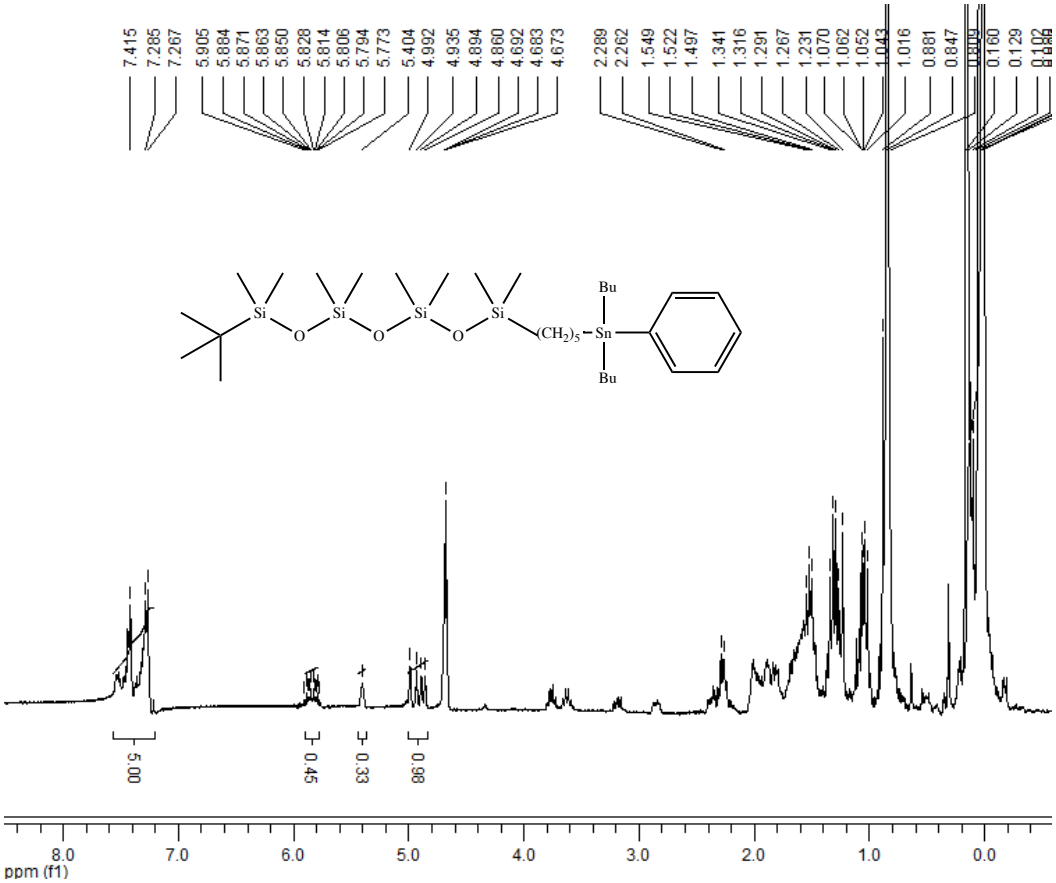


Figure 3.18: $^{1}$H NMR spectrum of the hydrosilylation reaction of butenyl-$Bu_2Ph$ with PDMS (3 Si-O units) to yield compound A after 1 day.

was successfull, a conversion of about 50% was achieved. However, the spectrum also shows some impurities.

Figure 3.19 shows the $^{13}C$ NMR spectrum. The peak at 25.84 ppm proofes, that the addition of the Si-H bond to the double bond of butenyl-$SnBu_2$ to form a -$CH_2$- bond was successfull.

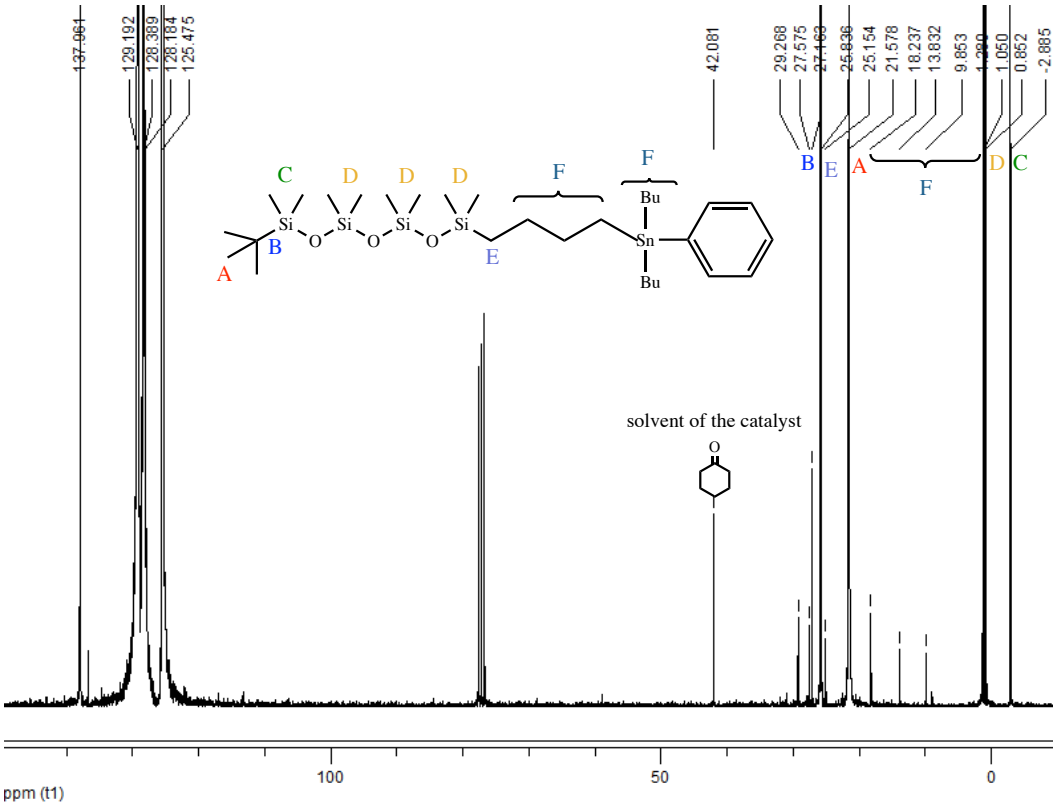


Figure 3.19: $^{13}C$ NMR spectrum of the hydrosilylation reaction of butenyl-$Bu_2Ph$ with PDMS (3 Si-O units) after 1 day.

Figure 3.20 represents the $^{29}$Siinept NMR spectrum. The peak at 10.31 corresponds to the *tert*-butyl-Si- group, furthermore, the smaller peak at 10.30 ppm corresponds to $Si(CH_3)_2$-$CH_2$-. The peaks from -20.07 - -21.87 correspond to the $(Si(CH_3)_2$-O-$)_3$ chain. There was no Si-H peak detected.

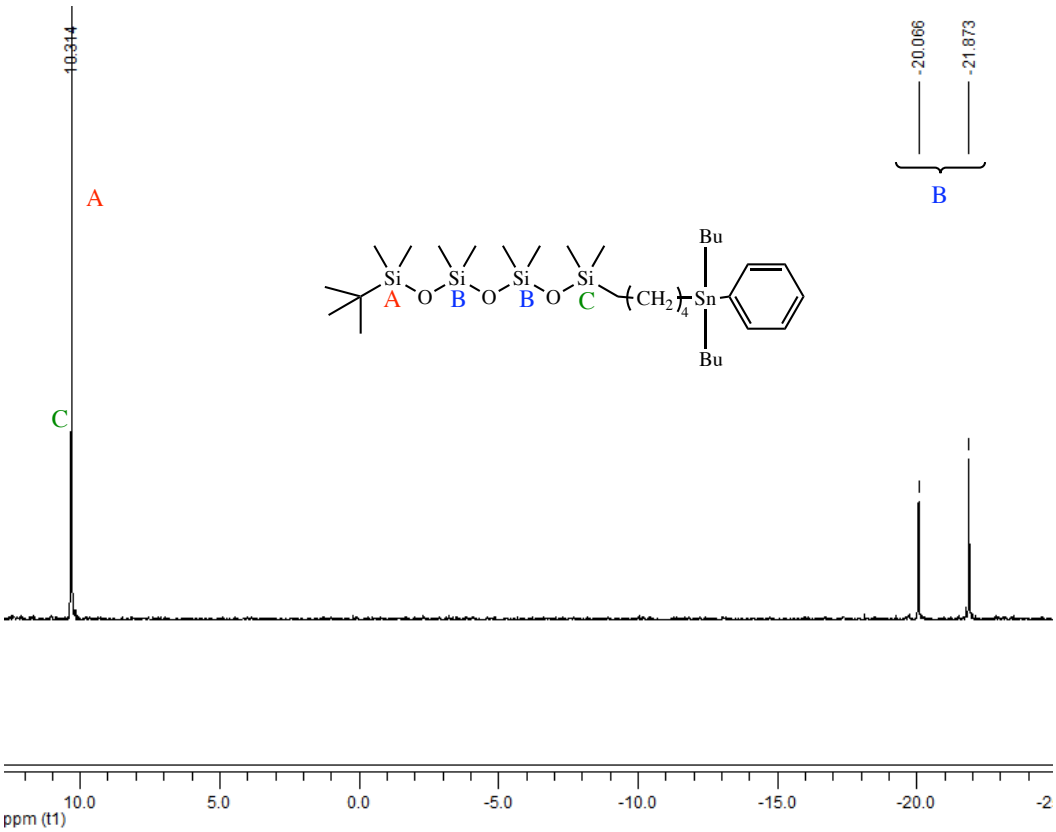


Figure 3.20: $^{29}$Siinept NMR spectrum of the hydrosilylation reaction of butenyl-$SnBu_2Ph$ with PDMS (3 Si-O units) after 1 day.

Figure 3.21 shows the corresponding $^{119}$Sn NMR spectrum. No redistribution reaction (chlorination) occurred, the peak at -41.22 correspond to compound A.

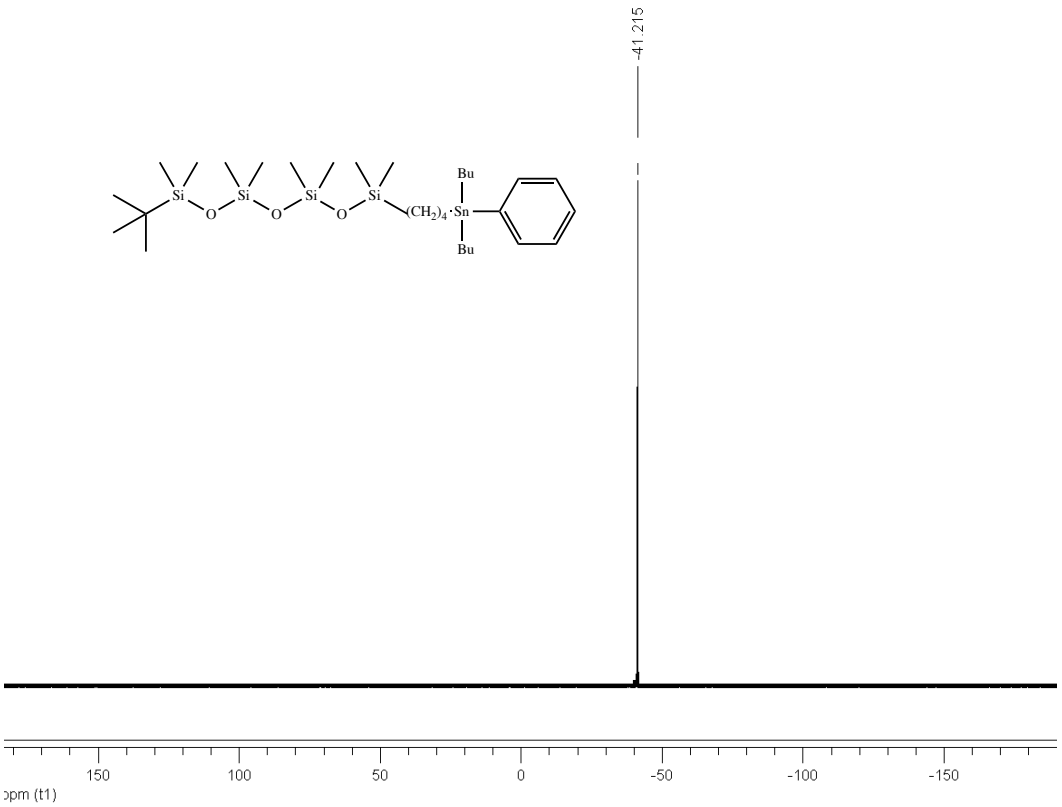


Figure 3.21: $^{119}$Sn NMR spectrum of the hydrosilylation reaction of butenyl-$Bu_2Ph$ with PDMS (3 Si-O units) after 1 day.

The $^{1}$H NMR spectrum shows also residual amounts of the double bond and the Si-H function. Moreover the peak integrals of the PDMS chain in correlation with the phenyl group of the tin compound is in a relation of 40 to 5, suggesting there was much more siloxane compound than tin reagent present. Whereas the $^{13}$C spectrum shows that there is no double bond left, as well as the $^{29}$Siinept spectrum don't dedicate a Si-H signal.

However, ultimate proof for the existence of the product was given by EI-TOF-MS (see Figure 3.22). The mass spectrum proved that the reaction was successful, since the synthesized organometallic hybrid compound was not purified, some side products were shown somehow explaining the inconsistencies in the NMR spectras. The peak at 647.2253 shows the exact mass of the [Si-Butyl]$^{+}$ ion of the desired product.

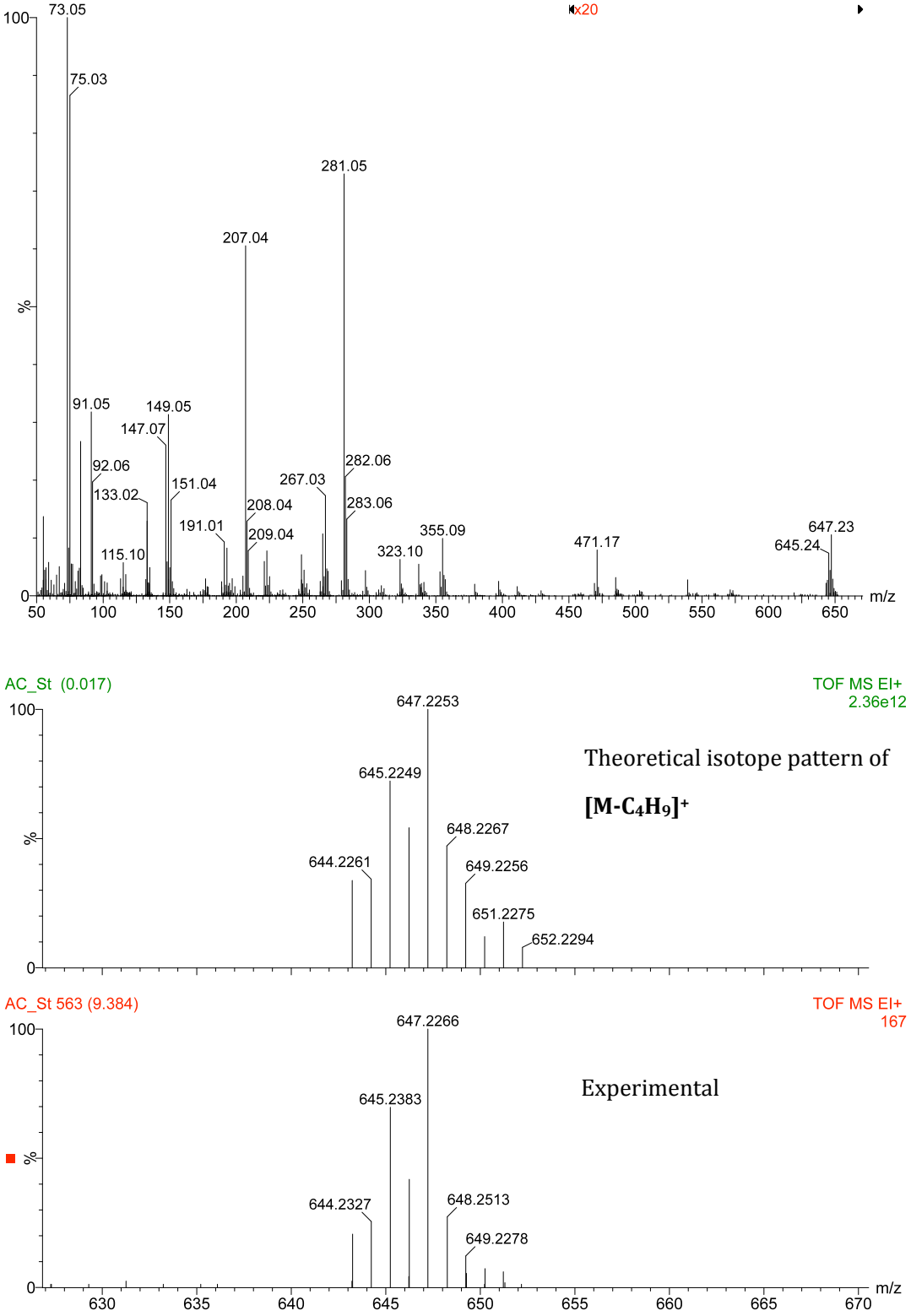


Figure 3.22: EI-TOF-MS of compound A

## 3.5 The Stille Cross Coupling Reaction

A Stille cross-coupling reaction was carried out at ambient temperature (35°C) for 2 days. The reaction equation is shown in Figure 3.23.

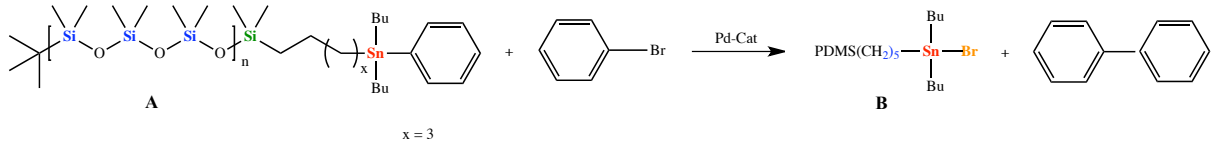


Figure 3.23: Reaction equation of the Stille cross-coupling reaction of compound A with bromobenzene.

The corresponding $^{119}$Sn NMR spectrum is shown in Figure 3.24. The peak at -41.32 corresponds to compound A. The peak at -71.35 corresponds to dibutyldiphenylstannane. The halogenated compound B (PDMS$(CH_2)_5$-Sn$Bu_2$Br should appear around 82 ppm (compareable to dibutylchlorophenylstannane). This proofs that the Stille cross-coupling reaction was successful, but however accompanied by redistribution reactions between the tin species. Further investigations have to be carried out.

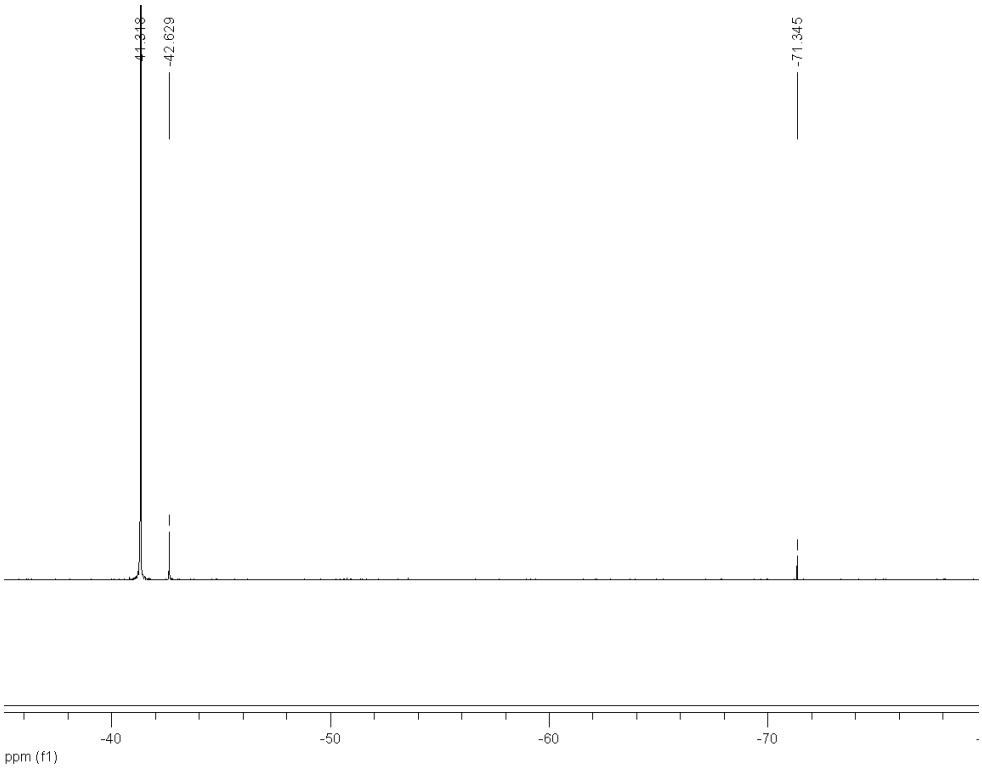


Figure 3.24: $^{119}$Sn NMR spectrum of the Stille cross-coupling reaction of compound A after 2 days.

# 4 Summary

Target of this work was the synthesis of organotin reagents supported on a silicone backbone in order to perform Stille cross-coupling reactions. Starting from commercially easily available substances, dibutyldiphenylstannane ($Bu_2SnPh_2$) was synthesized. Afterwards, the chlorination of this compound was carried to yield dibutylchlorophenylstannen ($Bu_2SnPhCl$). This substance was subsequently functionalized with either allyl-, 3-butenyl- or 11-undecenyl substituent. These tin compounds were reacted with linear mononfunctional polydimethylsiloxanes (PDMS) with different chain lengths, chlorodimethylsiloxane ($Me_2ClSiH$), dichloromethylsilane ($Cl_2MeSiH$), trichlorosilane ($Cl_3SiH$) and diethoxymethylsilane ($(Et_2O)_2MeSiH$) in a hydrosilylation reaction, to obtain a novel organotin hybrid material. The reaction process was controlled via $^{1}H$, $^{13}C$, $^{29}Si$ and $^{119}Sn$ NMR spectroscopy.

The hydrosilylation reactions, which were carried out with allyl-$SnBu_2Ph$, weren't successful. The reaction with PDMS of different chain length showed no conversion as well as the reaction with $(Et_2O)_2MeSiH$. The reaction with $Me_2ClSiH$ occurred in a chlorination of the tin reagent, similar to the redistribution according to Kocheshkov.
The hydrosilylation reaction with undecenyl-$SnBu_2Ph$ and $Me_2ClSiH$ showed neither conversion nor chlorination of the tin reagent.
The hydrosilylation reaction with butenyl-$SnBu_2Ph$ and PDMS with longer chain lengths was not successful. First positive results were achieved with the reaction of butenyl-$SnBu_2Ph$ and $Me_2ClSiH$. Further succeess was obtained with the reaction of butenyl-$SnBu_2Ph$ and a PDMS chain with 3 Si-O units. This compound was further used in the Stille cross-coupling reaction.

The Stille cross-coupling reaction was carried out with the novel organotin compound on a silicone backbone and bromobenzene. Conversion of the tin reagent was observed, however, the corresponding bromine substituted tin reagent was not found in the reaction solution.

# 5 Experimental

## 5.1 General and Chemicals

All experiments, unless otherwise stated, were carried out under inert atmosphere using Schlenk technique. To obtain dry atmosphere, the nitrogen is directed through a molecular sieve. THF was distilled from purple sodium benzophenone mixture. All other solvents were deoxygenated and dried over a molecular sieve in the solvent drying plant from "innovative technology, inc." Hexamethylcyclotrisiloxane (D3) and THF were stored in the dry box. All chemicals are commercially available substances and were generally used as received, unless otherwise stated.
The starting materials are shown in Table 5.1.

Table 5.1: Starting materials and their purity.

| CHEMICAL | RESOURCE | PURITY |
|---|---|---|
| Tintetrachloride | Sigma Aldrich | Purified by vacuum distillation |
| Magnesium | Sigma Aldrich | Turnings for Grignard Synthesis |
| Butylchloride | Sigma Aldrich | Reagent Plus; 99% |
| Phenylbromide | Merck | For Synthesis; 99% |
| Allylchloride | Sigma Aldrich | 98% |
| 3-Buten-1-ol | Fluka | GC grade 98% |
| Triphenylchlorostannane | Sigma Aldrich | 95% |
| Dibutyldichlorostannane | Fluka | purum 97% |
| Hexamethylcyclotrisiloxane | Sigma Aldrich | dried with $CaH_2$ and distilled |
| *tert*-Butyllithium | Sigma Aldrich | in pentane; Titration according to Gilman [34] |
| Dichloromethylsilane | Sigma Aldrich | 98% |
| Chlorodimethylsilane | Sigma Aldrich | 98% |
| Chlorotrimethylsilane | Sigma Aldrich | purum 98% |
| Diethoxymethylsilane | Sigma Aldrich | 96% |
| Hexachloroplatinic acid | Fischer Chemicals | 99% |
| Palladium plated on activated carbon | Sigma Aldrich | 5 wt% dry base |
| Tris(dibenzylideneacetone)-dipalladium | Sigma Aldrich | - |

## 5.2 Analytics

NMR spectras were recorded on a "Mercury 300'" from Varian. The measurements were carried out at 25°C and the signals are noted in ppm. The $^{29}$Si NMR spectras were measured using the INEPT pulse sequence. The nuclei and their corresponding frequencies can be seen in Table 5.2

Table 5.2: Nuclei and their corresponding frequencies and standards.

| NUCLEUS | FREQUENCY [MHZ] | REFERENCE |
|---|---|---|
| $^{1}$H | 300.22 | $SiMe_4$ |
| $^{13}$C | 75.5 | $SiMe_4$ |
| $^{29}$Si | 59.64 | $SiMe_4$ |
| $^{119}$Sn | 111.92 | $SnMe_4$ |

The EI-MS spectras were recorded with a "GCT Premier" from Waters, the sample was injected via direct insertion.

## 5.3 Synthesis of the Tin Precursor

### 5.3.1 Synthesis of Dichlorodiphenylstannane

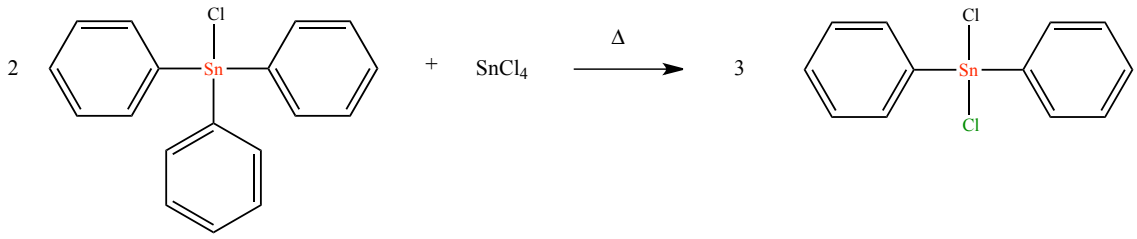


Figure 5.1: Redistribution reaction according to Kocheshkov of $Ph_3SnCl$ and $SnCl_4$ to obtain $Ph_2SnCl_2$

The reaction equation is shown in figure 5.1. 25 g Chlorotriphenylstannane (65 mmole, 2 eq.) was filled in a flask. 3.8 mL tintetrachloride (32 mmole, 1 eq.) was added dropwise. The reaction solution was stirred and heated for 2 hours at 160°C. Afterwards, the brown mixture was recrystallized from petrolether. The product, white crystals, were precipitated at -30°C, filtered and dried.

$^{1}$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.76 - 7.55 (m, 10 H, aromatic)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -27.14

### 5.3.2 Synthesis of Dibutyldiphenylstannane

- *Synthesis via Butylchloride Grignard*

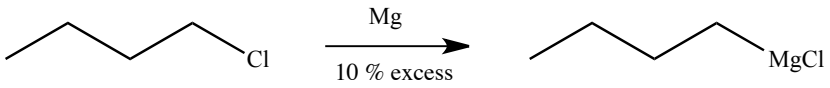


Figure 5.2: First step: Synthesis of BuMgBr

The reaction equation is shown in Figure 5.2. 3.14 g magnesium turnings (129 mmole, 2.2 eq.) and 120 mL $Et_2O$ were filled in a three necked flask an equipped with a dropping funnel and a reflux condenser. The dropping funnel was filled with 12.78 mL butylchloride (123 mmole, 2 eq.) in 50 mL $Et_2O$. The reaction mixture was heated to reflux and the butylchloride solution was added dropwise. The reaction was kept on reflux for 3 hours.

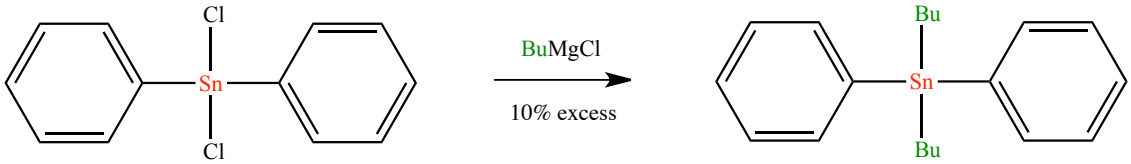


Figure 5.3: Second step: Conversion of BuMgCl with $Cl_2SnPh_2$

The second step of the reaction is shown in Figure 5.3. 21.12 g dichlorodiphenylstannane (61 mmole, 1 eq.) was added in a three necked flask and diluted with 150 mL $Et_2O$ (see Figure 3.3). The Grignard reagent (129 mmole, 2.2 eq.) is added dropwise to the dichlorodiphenylstannane mixture at 0°C. Afterwards the reaction mixture is heated to reflux for 1 hour and stirred overnight at room temperature. The cheerless mixture was filtered and extracted once with a saturated sodiumhydrogencarbonate solution, 3 times with HCl 5% and five times with deionized water. The ethereal phase was dried with sodiumsulfate. The solvent is removed and the yellow oil is vacuum distilled.

$^1$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.6 - 7.3 (m, 10 H, aromatic); 1.8 - 1.4 (m, 12 H, -(C$\mathbf{H_2}$)$_3$-$CH_3$); 1.0 - 0.9 (t, 6 H, -$(CH_2)_3$-C$\mathbf{H_3}$)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -72.3

- *Synthesis via Bromobenzene Grignard*

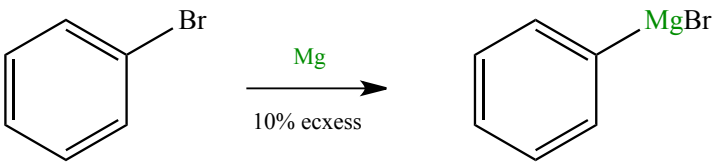


Figure 5.4: First Step: Synthesis of PhMgBr

The formation of the Grignard reagent is shown in Figure 5.4. 5.27 g magnesium turnings (217 mmole, 2.1 eq.) and 120 mL ($Et_2O$) were filled in a three necked flask equipped with a dropping funnel and reflux condenser. 21.8 mL phenylbromide (207 mmole, 2 eq.) and 50 mL $Et_2O$ were filled in the dropping funnel. A 5 mL aliquot of the phenylbromide solution was added to the magnesium mixture and the reaction solution was heated until the reaction starts. At this point the phenylbromide solution was added dropwise to keep the reaction at reflux. Afterwards, the reaction mixture was stirred and heated to reflux for 2 hours.

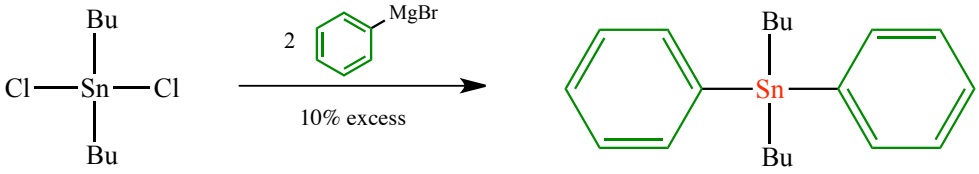


Figure 5.5: Second step: Reaction of PhMgBr and $Ph_2SnCl_2$ to obtain $Ph_2SnBu_2$

30.95 g dibutyldichlorostannane (103 mmole, 1 eq.) diluted with 100 mL $Et_2O$ were added to a three necked flask equipped with a reflux condenser (The reaction equation is shown in Figure 5.5). PhMgBr (217 mmole, 2.2 eq.) was added dropwise to the dibutyldichlorostannane at 0°C. Afterwards the reaction mixture was heated to reflux for 1 hour and stirred overnight at room temperature. The mixture was filtered and extracted once with a saturated sodiumhydrogencarbonate solution, once with 5% HCl and three times with deionized water. The organic phase is dried over sodiumsulfate. The solvent was removed and the slightly yellow oil is vacuum distilled to obtain the product, a colorless oil.

$^1$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.6 - 7.4 (m, 10 H, aromatic); 1.7 - 1.4 (m, 12 H, -(C$\mathbf{H_2}$)$_3$-$CH_3$) ; 0.9 (t, 6 H, -$(CH_2)_3$-C$\mathbf{H_3}$)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -72.71

### 5.3.3 Synthesis of Dibutylchlorophenylstannane

- *Chlorination with Hydrogen Chloride*

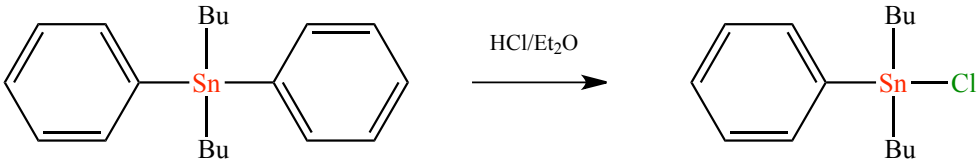


Figure 5.6: Reaction of $Bu_2SnPh_2$ with HCl to obtain $Bu_2SnPhCl$

The reaction equation of the chlorination with HCl is shown in Figure 5.6. 22.88 g dibutyldiphenylstannane (59 mmole, 1 eq.) was filled in a flask and diluted with 150 mL diethylether. An equimolar amount of HCl in $Et_2O$ (18.13 mL, 59 mmole, c = 3,26 M) was added in the dropping funnel and diluted with 20 mL $Et_2O$. This mixture was added dropwise to the dibutyldiphenylstannane at -30°C. The reaction mixture was stirred overnight at room temperature. Afterwards the solvent was removed and the yellow oil was vacuum distilled to obtain the product, a colorless oil.

$^{1}$H NMR (d in ppm, $CDCl_3$, 25C, 300 MHz): 7.5 - 7.4 (m, 5 H, aromatic); 1.7 - 1.4 (m, 12 H, -(C$\mathbf{H_2}$)$_3$-$CH_3$); 0.9 (t, 6 H, -$(CH_2)_3$-C$\mathbf{H_3}$)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 84.1

- *Chlorination via the Redistribution Reaction according to Kocheshkov*

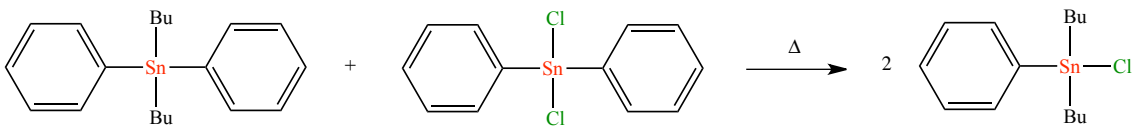


Figure 5.7: Reaction of $Bu_2SnPh_2$ with $Bu_2SnCl_2$ to obtain $Bu_2SnPhCl$

The reaction equation is given in 5.7. 18.88 g dibutyldiphenylstannane (49 mmole, 1 eq.) was mixed with 14, 83 g dibutyldichlorostannane (49 mmole, 1 eq.). The reaction mixture was stirred for one day at 160°C. The colorless product is purified by vacuum distillation.

$^{1}$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.5 - 7.4 (m, 5 H, aromatic); 1.7 - 1.4 (m, 12 H, -(C**H$_2$**)$_3$-CH$_3$); 0.9 (t, 6 H, -(CH$_2$)$_3$-C**H$_3$**)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 84.0

### 5.3.4 Synthesis of Allyldibutylphenylstannane

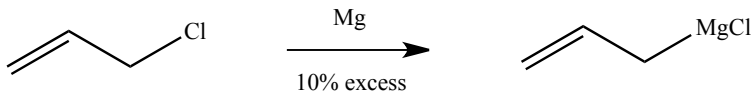


Figure 5.8: First step: Synthesis of $CH_2$=CH-$CH_2$-MgCl

The reaction equation is shown in Figure 5.8. 1.60 g magnesium turnings (65.8 mmole, 1.1 eq.) were filled in a three necked flask, equipped with a dropping funnel and a reflux condenser, and diluted with 60 mL THF. The dropping funnel was filled with 4.85 mL allylchloride (59.8 mmole, 1 eq.) and dissolved with 50 mL THF. The reaction mixture was cooled to -60°C and the allylchloride solution was slowly added. The reaction was stirred overnight at room temperature. Afterward the Grignard reagent was transferred to a separate Schlenk flask. Its concentration was determined by titration with 0.10 M aqueous HCl solution.

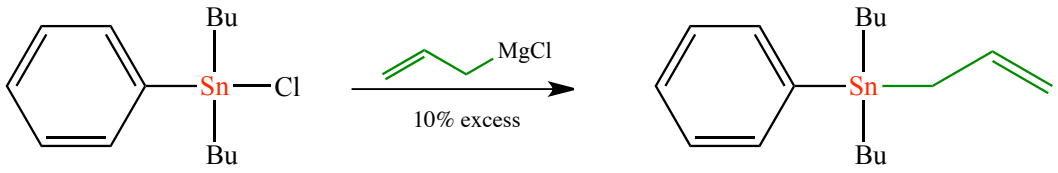


Figure 5.9: Second step: Conversion of $CH_2$=CH-$CH_2$-MgCl with $Bu_2SnPh_2$ to obtain $CH_2$=CH-$CH_2$-$SnBu_2Ph$

The reaction equation of the second step is shown in figure 5.9. 4.0 g dibutylchlorophenylstannane (11.7 mmole, 1 eq.) was added to a three necked flask equipped with a dropping funnel and a reflux condenser. The reactand was diluted with 60 mL THF. 33.2 mL allyl-MgCl (c = 0.434 M, 22.4 mmole, 1 eq.) was added dropwise to the dibutylchlorophenylstannane solution at 0°C. Afterwards the reaction mixture was heated to reflux for 2 hours and stirred overnight at room temperature. The product was filtered and THF was removed. The raw product was dissolved in $Et_2O$ and extracted three times with deionized water. The organic phase was dried

over sodiumsulfate. The solvent was removed and the slightly yellow oil was vacuum distilled to obtain a colorless oil.

$^{1}$H NMR($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.5 - 7.3 (m, 5 H, aromatic); 6.1 - 5.9 (m, 1 H, $CH_2$=C**H**-); 4.9 - 4.7 (m, 2 H, C**H$_2$**=CH-); 2.0 - 1.9 (d, 2 H, Sn-C**H$_2$**-CH=$CH_2$); 1.63 - 1.58 (m, 4 H, -Sn-C**H$_2$**-$CH_2CH_2$-$CH_3$); 1.4 - 1.1 (m, 8 H, -Sn-$CH_2$-(C**H$_2$**)$_2$-$CH_3$); 0.9 - 0.8 (t, 6 H, -$CH_2$-C**H$_3$**)

$^{13}$C NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 141.5 (-Sn-$CH_2$-**C**H=$CH_2$) 141.3 (2 C, aromatic); 137.3 (1 C, aromatic); 128.2 (2 C, aromatic); 128.0 (1 C, aromatic); 110.3 (1 C, -Sn-$CH_2$-CH=**C**$H_2$); 28.9 (2 C, -Sn-$CH_2$-**C**$H_2$-$CH_2$-$CH_3$); 27.3 (2 C, -Sn-$CH_2$-$CH_2$-**C**$H_2$-$CH_3$); 16.8 (-Sn-**C**$H_2$-CH=$CH_2$); 13.7 (2 C,-Sn-**C**$H_2$-$CH_2$-$CH_2$-$CH_3$); 9.7 (2 C, -**C**$H_3$)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -53.9

### 5.3.5 Synthesis of Butenyldibutylphenylstannane

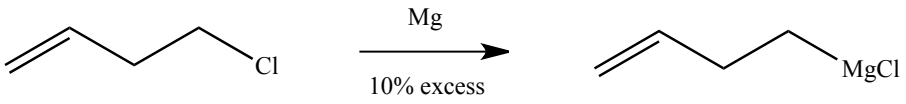


Figure 5.10: First Step: Synthesis of $CH_2$=CH-$CH_2$-$CH_2$-MgCl

The formation of the Grignard reagent is shown in Figure 5.10. 0.81 g magnesium turnings (33.3 mmole, 1.1 eq.) and 80 mL $Et_2O$ were filled in a three necked flask equipped with a dropping funnel and a reflux condenser. The dropping funnel was filled with 2.77 g butenylchloride (30.3 mmole, 1 eq.), dissolved in 50 mL $Et_2O$. The reaction mixture was heated to 35°C and butenylchloride solution was added dropwise to keep the reaction on reflux. The reaction mixture was kept on reflux for 3 hours and stirred overnight at room temperature.

10.4 g dibutylchlorophenylstannane (30.3 mmole, 1 eq.) and 80 mL $Et_2O$ werde filled in a three necked flask equipped with a dropping funnel and a reflux condenser. The Grignard reagent solution (82.5 mmole, 1.1 eq.) was added dropwise to the dibutylchlorophenylstannane at 0°C. Afterwards, the reaction mixture was heated to reflux for 1 hour and stirred overnight at room temperature. The mixture was extracted three times with deionized water. The organic phase was dried over sodiumsulfate and the solvent was removed. The slightly yellow oil was vacuum distilled to obtain the product, a colorless oil. (See figure 5.11 for the corresponding

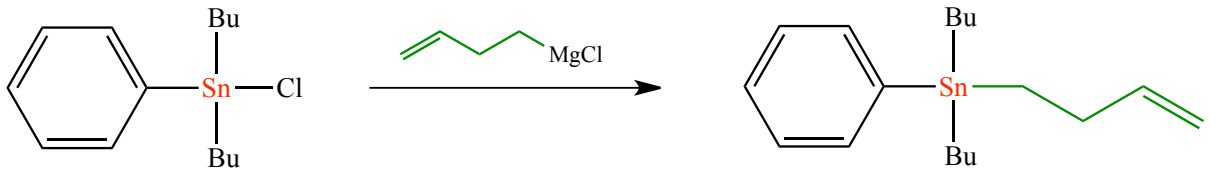


Figure 5.11: Second Step: Conversion of $CH_2$=CH-$CH_2$-$CH_2$-MgCl with $Bu_2SnPhCl$ to obtain $CH_2$=CH-$CH_2$-$CH_2$-$SnBu_2Ph$

reaction)

$^1$H NMR($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.5 - 7.3 (m, 5 H, aromatic); 5.9 - 5.8 (m, 1 H, -Sn-$CH_2$-$CH_2$-C**H**=$CH_2$); 5.0 - 4.9 (m, 2 H, -Sn-$CH_2$-$CH_2$-CH=C**H$_2$**); 2.4 - 2.3 (m, 2 H, -Sn-C**H$_2$**-$CH_2$-CH=$CH_2$); 1.78 - 1.70 (m, 2 H, -Sn-$CH_2$-C**H$_2$**-CH=$CH_2$); 1.6 - 1.5 (m, 4 H, -Sn-C**H$_2$**-$CH_2$-$CH_2$-$CH_3$); 1.4 - 1.1 (m, 8 H, -Sn-$CH_2$-(C**H$_2$**)$_2$-$CH_3$); 0.9 - 0.8 (t, 6 H, -$CH_2$-C**H$_3$**)

$^{13}$C NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 141.2 (-Sn-$CH_2$-$CH_2$-**C**H=$CH_2$) 141.0 (2 C, aromatic); 136.5 (1 C, aromatic); 128.0 (2 C, aromatic); 127.9 (1 C, aromatic); 113.13 (1 C, -Sn-$CH_2$-$CH_2$-CH=**C**$H_2$); 30.8 ( -Sn-**C**$H_2$-$CH_2$-CH=$CH_2$); 29.1 (2 C, -Sn-$CH_2$-**C**$H_2$-$CH_2$-$CH_3$); 27.4 (2 C, -Sn-$CH_2$-$CH_2$-**C**$H_2$-$CH_3$); 17.7 (-Sn-$CH_2$-**C**$H_2$-CH=$CH_2$); 13.7 (2 C,-Sn-**C**$H_2$-$CH_2$-$CH_2$-$CH_3$); 9.7 (2 C, -**C**$H_3$) 8.79 (-Sn-$CH_2$-**C**$H_2$-CH=$CH_2$)

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -41.2

### 5.3.6 Synthesis of Undecenyldibutylphenylstannane

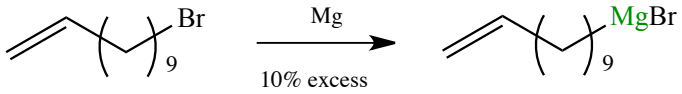


Figure 5.12: First Step: Synthesis of undecenylmagnesiumchloride

The formation of the Grignard reagent is shown in Figure 5.12. 0.26 g magnesium turnings (10.5 mmole, 1.1 eq.) and 50 mL $Et_2O$ were filled in a three necked flask, equipped with a dropping funnel and a reflux condenser. Afterwards, the dropping funnel was filled with 2.23 g undecenylbromide (9.5 mmole, 1 eq.) dissolved in 40 mL $Et_2O$. The reaction mixture was heated to reflux and the undecenylbromide solution was added dropwise to keep the reaction on reflux. The mixture was kept on reflux for 3 hours and stirred overnight at room temperature.

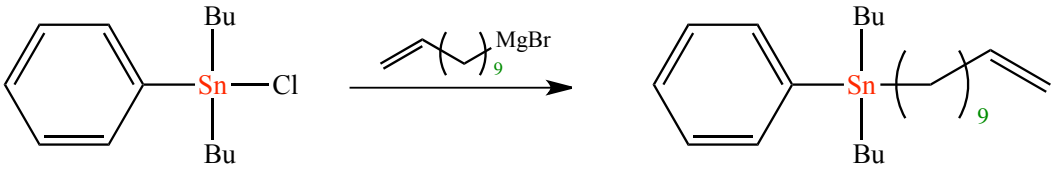


Figure 5.13: Second Step: Reaction of undecenylmagnesiumbromide with dibutylchlorophenylstannane

The corresponding reaction equation is shown in Figure 5.13. 3.0 g dibutylchlorophenylstannane (8.6 mmole, 1 eq.) was added to a three necked flask and diluted with 50 mL $Et_2O$. The Grignard reagent mixture (9.5 mmole, 1.1 eq.) was added dropwise to the dibutylchlorophenylstannane solution at 0°C. Afterwards, the reaction mixture was heated to reflux for 1 hour. The mixture was extracted three times with deionized water. The organic phase was dried over sodiumsulfate and the solvent was removed. The raw product, a yellow oil, was not distilled as the boiling point of the substance is too high.

$^{1}$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 7.5 - 7.3 (m, 5 H, aromatic); 5.82 - 5.79 (m, 1H, -Sn-$CH_2$-$CH_2$-$(CH_2)_6$-$CH_2$-C**H**=$CH_2$); 5.1 - 4.9 (m, 2H, -Sn-$CH_2$-$CH_2$-$(CH_2)_6$-$CH_2$-CH=C**H$_2$**); 2.08 - 2.03 (m, 2H, -Sn-$CH_2$-$CH_2$-$(CH_2)_6$-C**H$_2$**-CH=$CH_2$); 1.5 - 1.3 (m, 10 H, m, 1H, -Sn-$CH_2$-$CH_2$-(C**H$_2$**)$_6$-$CH_2$-CH=$CH_2$; 1.15 - 1.1 (m, 1H, -Sn-C**H$_2$**-$CH_2$-$(CH_2)_6$-$CH_2$-CH=$CH_2$); 1.0 - 0.9 (m, 2H, -Sn-$CH_2$-$CH_2$-(C**H$_2$**)$_6$-$CH_2$-CH=$CH_2$)

$^{13}$C NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 142.0 (-Sn-$CH_2$-$CH_2$-$(CH_2)_6$-$CH_2$-**C**H=$CH_2$); 136.5 (1 C, aromatic); 128.0 (2 C, aromatic); 127.9 (2 C, aromatic); 114.1 (-Sn-$CH_2$-$CH_2$-$(CH_2)_6$-$CH_2$-CH=**C**$H_2$); 33.9 (-Sn-$CH_2$-$CH_2$-$(CH_2)_6$-**C**$H_2$-CH=$CH_2$); 34.4 - 29.3 (6 C, -Sn-$CH_2$-$CH_2$-(**C**$H_2$)$_6$-$CH_2$-CH=$CH_2$); 26.8 (-Sn-$CH_2$-**C**$H_2$-$(CH_2)_6$-$CH_2$-CH=$CH_2$); 25.8 (-Sn-**C**$H_2$-$CH_2$-$(CH_2)_6$-$CH_2$-CH=$CH_2$);

$^{119}$Sn NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -42.6

## 5.3.7 Synthesis of Butenylchloride

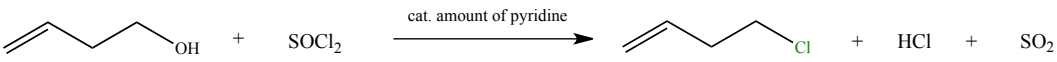


Figure 5.14: Reaction of 3-buten-1-ol with thionylchloride

The corresponding reaction equation is shown in Figure 5.14. 9.64 mL 3-buten-1-ol (111 mmole, 1 eq.) was cooled to 0°C and a catalytic amount of pyridine was added. $SOCl_2$ was

slowly added and the reaction commenced instantaneously . The reaction mixture was heated to reflux for 1 hour. The product was dissolved in $Et_2O$ and extracted 3 times with deionized water The organic phase was dried over sodiumsulfate and the solvent was removed. The product was isolated by distillation at ambient pressure.

$^1$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 5.89 - 5.75 (m, 1H, $H_2C$=C**H**-); 5.17 - 5.11 (t, 2H, **$H_2$**C=CH-); 3.58 - 3.53 (t, 2H, -$CH_2$-C**$H_2$**-Cl); 2.53 - 2.50 (m, 2H, -C**$H_2$**-$CH_2$-Cl)

$^{13}$C NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 134.3 ($CH_2$=**C**H-); 117.6 (**C**$H_2$=CH-); 43.80 (-$CH_2$-**C**$H_2$-Cl); 36.82 (-**C**$H_2$-$CH_2$-Cl)

## 5.4 Synthesis of monofunctional Polydimethylsiloxanes (PDMS) by the Ring Opening Polymerization (ROP) of Hexamethylcyclotrisiloxane (D3)

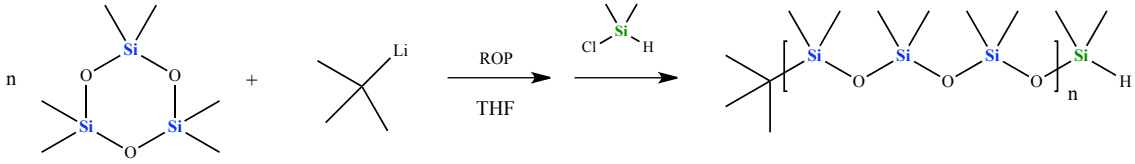


Figure 5.15: ROP of D3 to obtain the monofunctional PDMS with a specific chain length.

Figure 5.15 shows the formation of linear monofunctional PDMS. 2.50 g D3 (11,24 mmole, 1 eq.) was filled in a Schlenk flask, equipped with a reflux condenser, and dissolved with 10 mL THF. The reaction mixture was cooled to 0°C and the ROP was initiated by addition of 7.02 mL *tert*-BuLi solution (11.24 mmole, 1 eq.). After 30 minutes the polymerization was stopped by addition of 2.01 mL chlorodimethylsilane (22.48 mmole, 2 eq.) at 0°C. All volatile components (solvent, unreacted D3 and excess of chlorosilane) were removed and the polymer was separated from LiCl by decantation.

$^1$H NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): 4.69 - 4.66 (m, 1H, -Si-**H**); 0.84 (s, 9H, $C_4$**H$_9$**-Si); 0.15 - 0.14 (d, 6H, -O-Si-(C**H$_3$**)$_2$-H); 0.02 - 0.017 (2s, 12H, -O-Si-(C**H$_3$**)$_2$-$O_2$-); 0.00 (s, 6H, $C_4H_9$-(SiC**H$_3$**)$_2$-O-)

$^{29}$Siinept NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -20.23 - -22.12 (2s, O-(**Si**$(CH_3)_2$-O)$_2$); -7.0 (s, **Si**-H); 10.06 (s, $C_4H_9$-**Si**)

## 5.5 Synthesis of Stille Cross-Coupling Hybrid Materials by Hydrosilylation Reaction

Due to the broad range of experiments carried out in this investigation only a general method is described in this section. All experimental details are summerized in section 3 (results and discussion). A general scheme of the hydrosilylation reaction for the formation of the Stille cross-coupling hybrid material is given in Figure 5.16.

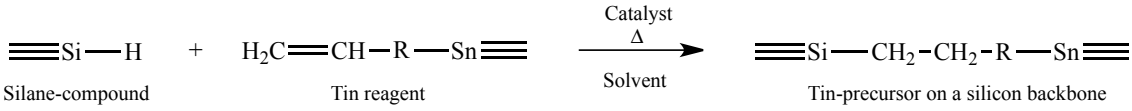


Figure 5.16: General reaction equation of a typical hydrosilylation reaction to obtain the desired Stille cross-coupling reagent.

The tin reagents (allyl-, butenyl-, undecenyldibutylphenylstannane) were reacted with various silane compounds. $Cl_3SiH$, $Cl_2SiMeH$, $Me_2SiClH$, $(Et_2O)SiMeH$ and monofunctional PDMS were used as starting materials in order to obtain a versatile hybrid material for subsequent Stille cross-coupling reaction. The reactions were catalyzed either by $H_2PtCl_6$, Pd plated on activated carbon or $(PPh_3)_3RhCl$ (Wilkinson catalyst). The composition of the catalyst systems is shown in Table 5.3 In general, toluene was used as the solvent; however, the reactions were also investigated using isopropylalcohole, THF or no solvent.

Table 5.3: List of the used catalysts in order to perform hydrosilylation reactions

| CATALYST 1 | CATALYST 2 | CATALYST 3 | CATALYST 4 |
|---|---|---|---|
| 0.10 g $H_2PtCl_6$ in 10 mL cyclohexanone | 0.10 g $H_2PtCl_6$ in 10 mL isopropanol | tip of a spatula Pd/C without any solvent | 0.10 g $(PPh_3)_3RhCl$ in 10 mL THF |

- *General Procedure*

The silane compound (1.1 eq.) and the tin reagent (1 eq.) were put in a Schlenk flask equipped with a reflux condenser. The solvent and a small amount of the catalyst were added and the mixture was heated to approximately 80°C for at least 1 day. The progress of the reactions was checked by $^1H$ and $^{13}C$ NMR spectroscopy. When the reaction was completed, the solvent was removed and the Stille precursor was isolated and characterized with NMR spectroscopy and MALDI-TOF-MS.

The synthesis of 1-(tert-butyl)-5-(4-(dibutyl(phenyl)stannyl)butoxy)-hexamethyltrisiloxane was satisfactorily and is subsequently constituted as Compound A (see Figure 5.17).

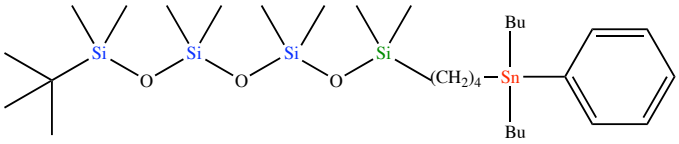


Figure 5.17: Molecular structure of the synthesized organotin hybrid material on a silicone backbone.

$^{29}$Siinept NMR ($\delta$ in ppm, $CDCl_3$, 25°C, 300 MHz): -20.23 - -22.12 (2s, O-(**Si**$(CH_3)_2$-O)$_2$); 10.06 (s, $C_4H_9$-**Si**)
All other measured NMR spectras are discussed in section 3.4.

## 5.6 The Stille Cross-Coupling Reaction

### 5.6.1 Activation of the Pd(dba)$_2$ Catalyst


Figure 5.18: Activation of the Pd(dba)$_2$ catalyst with $PPh_3$ in toluene.

200 mg Pd(dba)$_2$ (0.35 mmole, a eq.) and 320 mg $PPh_3$ (1.22 mmole, b eq.) were filled in a dry flask. 15 mL dry THF was added and the catalyst solution was stirred overnight.

### 5.6.2 The Stille Cross-Coupling Reaction of Component A and Bromobenzene

The reaction equation is shown in Figure 5.19. 2.87 g (4.0 mmole, 1 eq.) of component A was filled in a Schlenk flask equipped with a reflux condenser. 0.42 mL bromobenzene (4.0 mmole, 1 eq.) was added and the reaction mixture was heated to 35°C. Afterwards 1.0 mL of the catalyst solution was added. The progress of the reaction was controlled by $^{119}$Sn NMR spectroscopy.

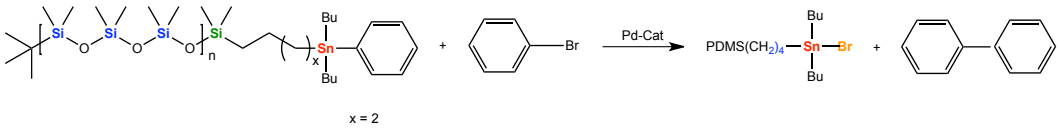


Figure 5.19: Stille cross-coupling reaction of the novel hybrid material and bromobenzene.

# List of Figures

# List of Tables

# Bibliography


[1] J. K. Stille. Palladium-katalysierte kupplungsreaktionen organischer elektrophile mit organozinnverbindungen. *Angewandte Chemie*, 98(6):504–519, 1986.

[2] Thomas Laue and Andreas Plagens. *Namen- und Schlagwort-Reaktionen der Organischen Chemie*. Vieweg + Teubner, 2006.

[3] Pablo Espinet and Antonio M. Echavarren. The mechanisms of the stille reaction. *Angewandte Chemie*, 43:4704–4734, 2004.

[4] Hadjispyrou; et al. Toxicity, bioaccumulation and interactive effects of organotin, cadmium, and chromium on artemia franciscana. *Ecotoxicology and Environmental Safty*, 49, 2001.

[5] Jürgen Vitz et al. Stille cross-coupling reactions with tin reagents supported on ionic liquids. *Eur. J. Org. Chem.*, pages 3249–3257, 2009.

[6] Jürgen Vitz et al. Ionic liquid supported tin reagents for stille cross-coupling reactions. *Green Chemistry*, 9:431–433, 2006.

[7] Jean-Mathieu Chrétien; Aurélie Mallinger et al. Evaluation of polymer-supported vinyltin reagents in the stille cross-coupling reaction. *Tetrahedron Letters*, 48:1781–1785, 2007.

[8] Georg Witek. *SCALE-UP OF THE PRODUCTION OF MONOFUNCTIONAL POLYSILOXANES*. PhD thesis, TU Graz, 2010.

[9] Margot Brandstätter. *Funktionelle Silikone und Siloxane*. PhD thesis, TU Graz, 2010.

[10] Hans-Heinrich Moretto, Manfred Schulze, and et al. *Silicones*, volume 7. Ullmann's Encyclopedia of Industrial Chemistry, 2005.

[11] Margot Brandstätter. *Monofunktionelle Oligosiloxane*. TU Graz, diplomarbeit edition, 2006.

[12] Robert Drake et al. Recent advances in the chemistry of siloxane polymers and copolymers. *The Chemistry of Organic Silicon Compounds*, 2:2217–2244, 1998.

[13] Adam M. Hawkridge and Joseph Gardella. Evaluation of matrix-assisted laser desorption ionization mass spectrometry for studying the sec-butyllithium and n-butyllithium initiated ring-opening polymerization of hexamethylcyclotrisiloxane (d3). *American Society for Mass Spectroscopy*, 14:95–101, 2003.

[14] S. Ouland Hammouch et al. Synthesis and characterization of monofunctional polydimethylsiloxanes with a narrow molecular weight distribution. *Polymer*, 36(2):421–426, 1995.

[15] Marek Cypryk et al. Siloxane polymers as supports for transition metals and enzymes. Books of Abstracts; Silicone Days, 2009.

[16] P.D. Lickiss; V. Colquhoun et al. The use of siloxanes as solvents for synthetic chemistry. Books of Abstracts; Silicone Days, 2009.

[17] Matjaz Kozelj and Boris Orel. Polyhedral oligomeric silsesquioxane ionic liquids. Silicone Days; Books of Abstracts, 2009.

[18] U. Mizerska et al. Synthesis and antimicrobial activity of polysiloxanes with t-butylamine groups. Books of Abstracts; Silicone Days, 2009.

[19] Peter J. Miller and Krzsysztof Matyjaszewski. Atom transfer radical polymeriazation of (meth)acrylates from poly(dimethylsiloxane) macroinitiatros. *Macromolecules*, 32(26):8760–8767, 1999.

[20] Hosei Shinoda and Krzsysztof Matyjaszewski. Structural control of poly(methylmethacrylate)-g-poly(dimethylsiloxane) copolymers using controlled radical polymerization. *Macromolecules*, 36:4772–4778, 2003.

[21] Hosei Shinoda; Krzystof Matyjaszewski et al. Improving the structural control of graft copolymers by combining atrp with the macromonomer method. *Macromolecules*, 34:3186–3194, 2001.

[22] L. Sommer; E. Petrusza; et al. *Journal of the American Chemical Society*, 69:188, 1947.

[23] Dirk Steinborn. *Grundlagen der metallorganischen Komplexkatalyse*. Teubner Studienbücher Chemei, 2007.

[24] Z.V. Belyakova; E. A. Chernyshew et al. Hydrosilylation of cyclohexene and allyl chloride with trichloro-, dichloro(methyl)- and chlorodimethylsilanes in the presence of pt(0) complexes. *Russian Journal of General Chemistry*, 76(6):967–972, 2006.

[25] Bogdan Maciniec; Jacek Gulinski et al. Functionalization of poly(methylhydro)siloxanes via hydrosilylaion of allyl derivates. *Applied Organometallic Chemistry*, 11:843–849, 1997.

[26] Herbert Schumann and Yilmaz Aksu. Synthesis and characterization of silicon-based group 14 dendrimers. *Organometallics*, 26:397–402, 2007.

[27] Herbert Schumann et al. Si(ch2ch2snh3)4 - unique organotin hydride featuring 12 snh units in a dendritic molecule. *Journal of Organometallic Chemistry*, 609:189–195, 2000.

[28] Qi Jia Fu et al. Novel inorganic oxide supported organotin hydrides for fine chemical catalysis. *Green Chemistry*, 3:71–73, 2001.

[29] Ivan A. Portnyagin; Valery V. Lunin et al. Reverse kocheshkov reaction - redistribution reaction between rsn(och2ch2nme)2cl (r = alk, ar) and phsncl3. *Journal of Organometallic Chemistry*, 693(26):3847–3850, 2008.

[30] Willis T. Schwartz; Howard W. Post. The preparation and properties of a series of olefinic tin compounds. *Journal of Organometallic Chemistry*, 2:357–360, 1964.

[31] Yilmaz Aksu; Sevil Aksu; Herbert Schumann. Synthesis and characterization of a,w-bis[tri-(w-triphenylstannyl)butylstannyl]alkanes as starting materials for oganotin dendrimers. *Applied Organometallic Chemistry*, 21:521–530, 2007.

[32] John D. Roberts; Robert H. Mazur. Small-ring compounds. iv. interconversion reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives. *Journal of American Chemical Society*, 73:2509–2520, 1951.

[33] Thierry Toupance et al. Recent developments in the field of functional tin oxide based hybrid materials. ICCOC GTL Graz; oral presentation, 2010.

[34] H. Gilman; et al. *Journal of American Chemical Society*, 66:1515–1516, 1944.