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Synthesis and Characterization of Novel Chloroarylsilanes with Sterically Demanding Aryl Substituents and Their Applications

Master Thesis

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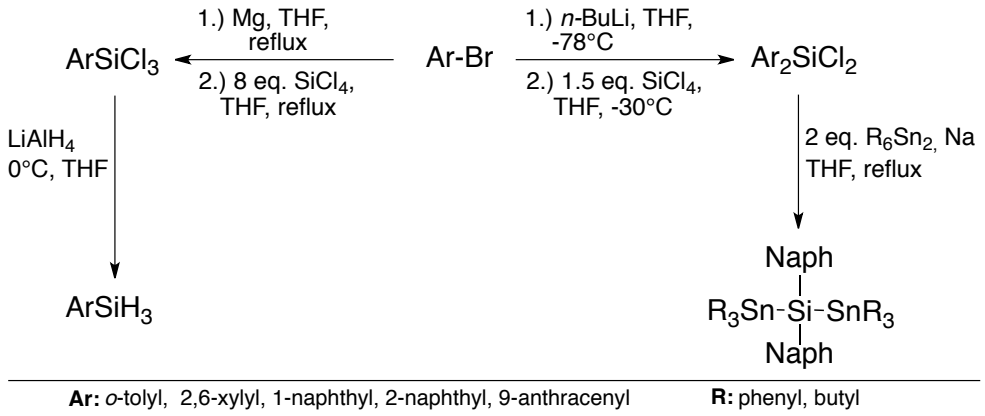
Ever tried. Ever failed. No matter.
Try again. Fail again. Fail better.

Samuel Beckett

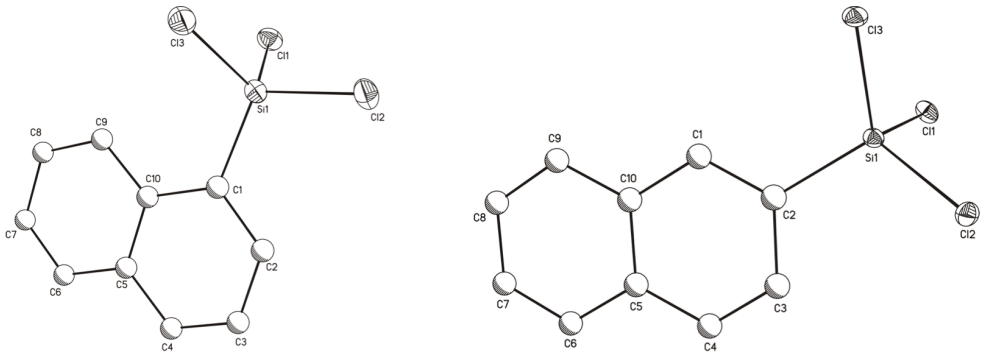
Abstract

This works deals with the synthesis and characterization of novel dichloro- and trichloro- arylsilanes (Ar_2SiCl_2 and $ArSiCl_3$) with sterically demanding aryl substituents. Additionally, these chlorosilanes were used as precursor molecules to generate hydrogen-rich silanes or silyltin sequences (see scheme below).



Whether a dichloro- or trichlorosilane (Ar= *o*-tolyl, 2,6-xylyl, 1-naphthyl, 2-naphthyl, 9-anthracenyl) is formed, strongly depends on the reaction conditions and on the applied organometallic nucleophiles. Due to their higher selectivity, Grignard reagents were used to synthesize trichlorosilanes and organolithium reagents led to the corresponding dichlorosilanes.

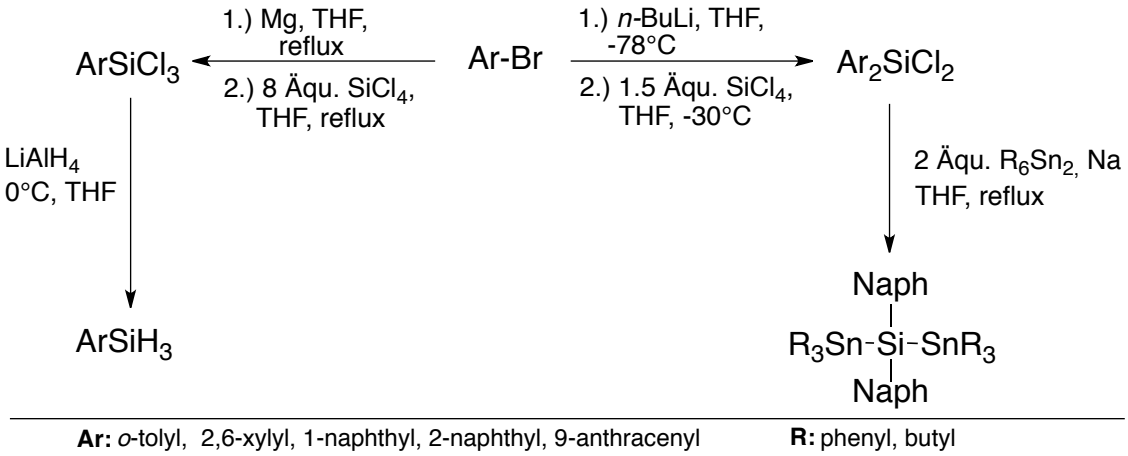
X-Ray data of trichlorosilanes with aromatic residues, are absolutely rare and only a few examples have been reported. So far, crystal structures of polycyclic aromatic trichlorosilanes are not know in literature. We were able to gain the first crystal data of polycyclic aromatic trichlorosilanes (see scheme below).



Furthermore, the functionalized chlorosilanes were used as precursor compounds, in order to synthesize trihydridosilanes and silyltin sequences, exhibiting an alternating arrangement of tin and silicon. Hydrogen-rich silanes were prepared according to literature known procedures using LAH as reducing agent. Silyltin sequences were synthesized subjecting an organodistannane with sodium *via* a Wurtz-type coupling reaction.

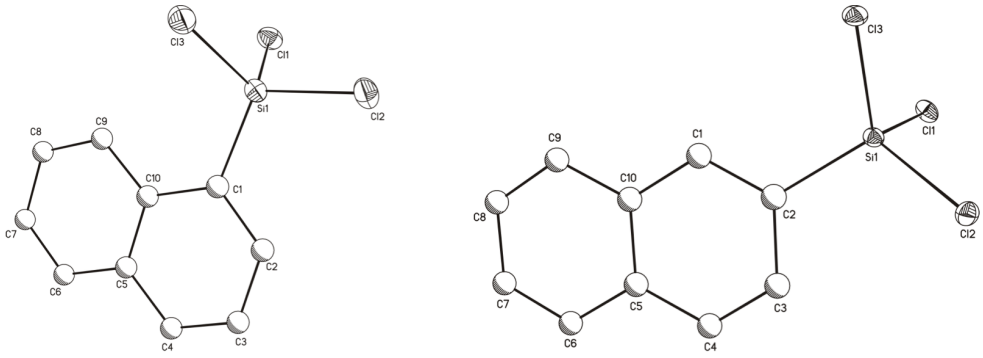
Kurzfassung

Die vorliegende Arbeit beschäftigt sich mit der Synthese und Charakterisierung von neuartigen Aryldichlor- und Aryltrichlorsilanen (Ar_2SiCl_2 und $ArSiCl_3$) mit sterisch anspruchsvollen Arylsubstituenten. Diese Chlorsilane wurden einerseits als Precursor für Aryltrihydriden sowie für die Herstellung von alternierenden Silicium-Zinn-Sequenzen eingesetzt (siehe Reaktionsschema).



Der Grad der Arylsubstitution am Silicium (Ar_2SiCl_2 oder $ArSiCl_3$) wird hauptsächlich durch die Reaktionsbedingungen und den verwendeten organometallischen Nukleophilen beeinflusst. Grignard Reagenzien zeichnen sich durch ihre gute Selektivität aus und wurden bevorzugt für die Synthese von Aryltrichlorsilanen eingesetzt, wohingegen Diaryldichlorsilane mittels Organolithium Reagenzien hergestellt wurden.
Die in der Literatur beschrieben Kristallstrukturdaten beschränken sich auf einige wenige Beispiele für Aryltrichlorsilanen, jedoch sind keine Kristallstrukturen von Trichlorsilanen mit polycyclischen aromatischen Kohlenwasserstoffrest bekannt.

In dieser Arbeit konnten die ersten Kristallstrukturen für Trichlorsilane mit derartigen aromatischen Gruppe erhalten werden (siehe Abbildung).



In weiterer Folge wurden diese Chlorsilane als Precursor für die Synthese von Trihydriden und zur Herstellung von alternierenden Silicium-Zinn-Sequenzen eingesetzt. Die Hydrierung wurde mittels LAH nach einer Literatur bekannten Methode durchgeführt. Silicium-Zinn-Sequenzen wurden *via* Wurtz Kupplungsreaktion mit Organodistannanen und Natrium hergestellt.

Contents

List of Abbreviations

o-	ortho
m-	meta
R	organic residue
X	halide
Ar	aryl
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
DCM	dichloromethane
THF	tetrahydrofuran
av.	average
Ref	reference
n. o.	not observed
eq.	equivalent
ppm	parts per million
NMR	nuclear magnetic resonance spectroscopy
APT	attached proton test
DEPT	distortionless enhancement by polarization transfer
s	singlet
d	doublet
dd	double doublet
t	triplett
DI	direct insertion
EI	electron impact ionization
TOF	time of flight
MS	mass spectroscopy
MALDI	matrix-assisted laser desorption/ionization
GC	gas chromatography
Mp	melting point [℃]

Chapter 1

Introduction

The chemistry of group IV elements is dominated by silicon. Silicon is the second most abundant element in the earth crust and exhibits an essential role in a lot of industrial applications. Elemental silicon is available in all degrees of purity and the production, purification and further chemical processes of raw silicon are well described in literature.[1] In comparison to carbon, the chemical properties of carbon´s heavier homologues, like silicon show higher bond polarities and inversion of the net charge. Due to the large covalent radius of silicon, nucleophilic attack of a donor molecule is easier accomplished in comparison to a carbon center.[2] Organosilicon compounds find broad technical applications and have become indispensable materials in the field of health care, electronic divices to space travel. Recently, organosilicon halides are very common class of functional organosilanes and can be converted easily in various organosilicon derivatives.[3]

Thus, silicon chlorides, especially dichloro- and trichloroorganosilanes, find a wide industrial application as for example in the synthesis of inorganic polymers. Moreover these compounds are frequently used in organic synthesis as protecting groups.[4]

The recent work is focused on novel chloroarylsilanes as very useful functionalized derivatives which can easily be converted into the corresponding trihydrides or silyltin sequences (Figure 1.1).

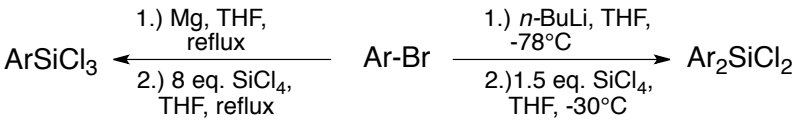


Figure 1.1: General Scheme to Synthesize the Desired Chloroarylsilane Derivatives (Ar= *o*-tolyl, 2,6-xylyl, 1-naphthyl, 2-naphthyl, 9-anthracenyl)

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[1] M. Schmeisser, P. W. Schenk, F. Huber, *Handbuch Der Präparativen Anorganischen Chemie,* Ferdinand Enke Verrlag, **1978**.

[2] U. Klingbiel, N. Auner, *Synthetic Methods of Organometallic and Inorganic Chemistry*, Georg Thieme Verlag, Stuttgart, **1996**.

[3] U. Herzog, *The Chemistry of Organic Silicon Compounds Volume 3*, John Wiley & Sons, Ltd, **2001**.

[4] H. Bock, *Angew. Chem. Int. Ed.* **1989**, *28*, 1627.

1.1 Arylsilanes

Since the late 1880s various studies concerning the preparation of arylsilanes have been reported.[5] Arylsilanes are widely used due to their easy conversion into other functional groups.[6] In general, the synthesis of arylsilanes can be described by reaction of a magnesium or lithium aryl compound serving as nucleophile with a chlorosilane. These silylation reactions are known in literature as Wurtz-Fittig couplings, but also Grignard or organolithium reagents can be applied.

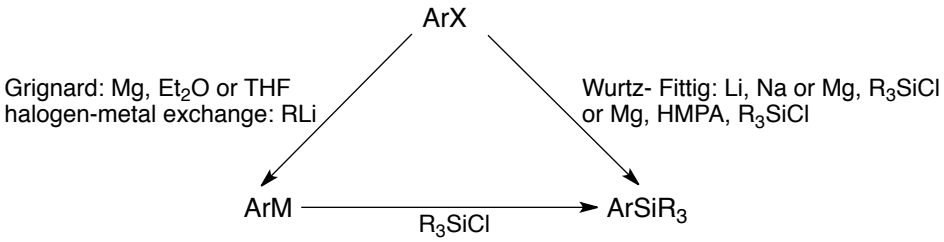

Figure 1.2: Formation of Arylsilanes X= Halides; R= Organic Residue; M= Metal

The Wurtz-Fittig coupling reaction is the oldest known *in-situ* reaction to synthesize arylsilanes.[7] An aryl halide, chlorosilane and a metal are reacted in hexamethylphosphoric triamide (HMPA) at elevated temperature.[8]

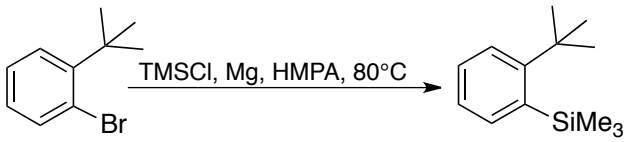

Figure 1.3: Preparation of a Arylsilane *via* Wurtz-Fittig Coupling Reaction

Nowadays, Grignard or organolithium reagents are preferred to synthesize arylsilanes. In 1904 the Grignard method was used the first time to prepare organochlorosilanes. First Grignard reactions were carried out with silicon tetrachloride added to ethyl magnesium iodide as well as the preparation of phenylchlorosilanes from silicon tetrachloride with phenyl magnesium bromide was investigated.[9] Due to their easy preparation, Grignard reagents are also reacted with chlorosilanes under moderate conditions in ether solvents.[10]

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[5] Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications: London, **1960**.
[6] E. Flaming, *Science of Synthesis*, Georg Thieme Verlag, New York, **2002**.
[7] a) A. Wurtz, *Ann. Chim. Phys.* **1855**, *44*, 275. b) B. Tollens, R. Fittig, *Ann. Chem. Pharm.* **1864**, *131*, 303.
[8] a) P. Bourgeois, R. Calas, *J. Organomet. Chem.* **1975**, *84*, 2821. b) F. Effenberger, D. Häbich, *Liebigs Ann. Chem.* **1979**, *842*.
[9] Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications: London, **1960**.
[10] F. Effenberger, D. Häbich, *Liebigs Ann. Chem.* **1979**, *842*.

Aryl substituted silanes show interesting photophysical properties and chemical reactivities. Thus, they potentially can be used in material science, for example as new precursors for sol-gel materials or in organic electroluminescent devices.[11]

1.2 Formation of Carbon Silicon Bonds

1.2.1 Grignard Reagents and Reactions

In 1900, the first synthetic preparation of a Grignard reagent was described by Grignard.[12] Grignard reagents with the composition RMgX are widely used in synthetic chemistry to create σ bonds (e.g. Si-C bonds in organosilanes).[13] However the mechanism is not completely discovered.[14] The reaction progress can be explained by an oxidative addition (Mg^0 to Mg^{II}) going along with the insertion of magnesium into a carbon-halogen bond.[15]

Grignard reagents achieve a polarization change at the carbon-halide bond, due to their negative charge they are acting as an carbanion. Therefore, the carbanion reacts as a nucleophile under the formation of a new σ bond. Diethyl ether and THF are the most commonly used solvents and their behavior based on the Schlenk equilibrium.[16]

In 1904, Kipping and Dilthey published the first experimental procedures to obtain organosilicon compounds, using ethyl- or phenyl-magnesium bromide reacting with tetrachlorosilane.[17]

$$PhMgBr \xrightarrow[ether]{SiCl_4} PhSiCl_3 + Ph_2SiCl_2 + Ph_3SiCl$$

Figure 1.4: Preparation of Chlorophenylsilane Derivatives using a Grignard Reagent

Moreover, the interactions between tetrachlorosilane and the Grignard reagent affects the synthesis of organosilanes. A treatment with less than four equivalents tetrachlorosilane yields in a mixture of the three chlorophenylsilane derivatives (Figure 1.4). According to these findings, Grignard reactions were fundamentally new methods to created Si-C bonds.[18]

[11] S. Yamaguchi, S. Akiyama, K. Tamao, *Organometallics* **1998**, *17*, 4347.
[12] V. Grignard, *Ann. Chem.* **1901**, *24*, 433.
[13] G. E. Coates, K. Wade, *The Main Group Elements*, Methuen: London, **1967**.
[14] H. R. Richey, Ed., *Grignard Reagents: New Developments*, John Wiley & Sons, Ltd, **2000**.
[15] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press Inc., New York, **2001**.
[16] C. Eschenbroich, *Organometallchemie*, B.G. Teubner Verlag/GWV Fachverlage GmbH, Wiesbaden, **2008**.
[17] Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications: London, **1960**.
[18] G. Arkles, *Handbook of Grignard Reagents*, Marcel Dekker, New York, **1996**.

1.2.2 Organolithium Reagents

Over the last decade organolithium reagents have become an important organometallic compound and a powerful synthetic tool in organic and organometallic chemistry.[19]
The nucleophilic carbanion is created by a halogen-metal exchange. This conversion depends on the change of the pK_a value according to the decrease of the basicity. The protonated species of phenyl lithium (benzene pk_a about 43) is less basic (more stable) than the protonated starting organolithium compound (e.g. butane pk_a about 50).[20] Furthermore the lithiated species reacts with an electrophilic compound to generate a new σ bond and lithium halide salt precipitates. Organolithium compounds are well established, commercially available and therefore still attractive in modern synthetic chemistry.[21]
Organolithium reagents have to be stored absolutely free of moisture, because even the contact with air moisture leads to stoichiometric loss of organolithium titre.

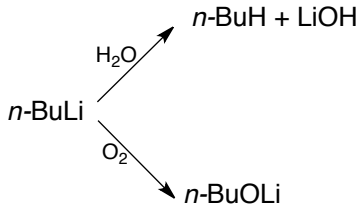


Figure 1.5: Reaction of Organolithium Reagents with Moisture

1954, Sommer *et al.* described one of the first procedures towards *t*-butyltrichlorosilane and dibutylchloro(methyl)silane by using an organolithium reagents, in this case *t*-BuLi.[22]

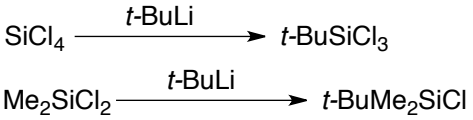


Figure 1.6: Preparation of *t*-Butyltrichlorosilane and Dibutylchloro(methyl)silane

[19] a) B.J. Wakefield, *Organolithium Methods*, Academic Press, London, **1988**. b) Ch. Elschenbroich, A. Salzer, *Organometallics. A Concise Introduction*, VCH, Weinheim, **1992**. c) A.-M. Sapse, P.v.R. Schleyer, *Lithium Chemistry: A Theoretical and Experimental Overview*, Wiley, New York, **1995**.
[20] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press Inc., New York, **2001**.
[21] A. Sekiguchi, V. Y. Lee, N. Masato, *Coord. Chem. Rev.* **2000**, *210*, 11.
[22] L. H. Sommer, L. J. Tyler, *J. Am. Chem. Soc.* **1954**, *76*.

1.3 Dichloro- and Trichloroarylsilanes

All so far in literature known chloroaryl compounds are not completely characterized or only calculated results have been published. Already known silanes are summarized in Table (2.1).[23]

Compound	References
9-phenanthrenyltrichlorosilane	[a]
trichloro(naphthalen-1-yl)silane	[a]
trichloro(naphthalen-2-yl)silane	[a]
trichloro(*o*-tolyl)silane	[b]
trichloro(*m*-tolyl)silane	[c]
trichloro(*p*-tolyl)silane	[d]
trichloro(3,5-dimethylphenyl)silane	[e]
trichloro(2,5-dimethylphenyl)silane	[f]
trichloro(mesityl)silane	[g]
dichloro-diphenylsilane	[h]
dichloro(naphthalen-1-yl)(phenyl)silane	[i]
dichlorodi(*o*-tolyl)silane	[j]
dichlorodi-p-tolylsilane	[k]

Table 1.1: Overview of Synthesized Arylchlorosilanes[23]

In summary, the published results are focused to trichlorophenylsilane derivatives, with aryl compounds substituted in one *ortho*-position.

Among Organosilicon halides, chlorosilanes have attracted by far the greatest attention although they are seldom the final product in a synthetic pathway. For example, tetrachlorosilane is produced on a industrial scale and in most cases used as an intermediate to synthesize other silicon containing compounds. Chlorosilanes are applied in macromoleculare chemistry as precursors for inorganic polymers or as protecting groups in organic synthesis.[24,25]

Since 1968, various procedures to synthesize organohalosilanes have been published.[26] In general, the preparation of dichloro- and trichlorosilanes starts from an organometallic reagent and a subsequent treatment with a stoichiometry amount

[23] **[a]** B. M. Moore, G. R. Yandek, J. M. Mabry, S. M. Ramirezand, T. S. Haddad, *J. Organomet. Chem.* **2011**, *696*, 2676; **[b]** D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 7788; **[c]** A. Khalimon, R. Simionescu, G. I. Nikonov, *J. Am. Chem. Soc* **2011**, *133*, 7033; **[d]** K. Kaeppler, A. Porzel, U. Scheim, K. Ruehlmann, *J. Organomet. Chem.* **1991**, *402*, 155; **[e]** E. A. Chernyshev, N. G. Tolstikova, *J. Gen. Chem. USSR (Engl. Transl.)* **1970**, *40*, 1052; **[f]** A. Motsarev, *J. Gen. Chem. USSR (Engl. Transl.)* **1976**, *46*, 845; **[g]** I. Mitsuo, K. Seiji, K. Makoto, *J. Organomet. Chem.*, **1983**, *248*, 251; **[h]** N. Auner, R. Probst, F. Hahn, E. Herdtweck, *J. Organomet. Chem.* **1993**, *459*, 25. **[i]** K. Kobayashi, T. Kato, S. Masuda, *Chem. Lett.*, **1987**, 101. **[j]** F. T. Ladipo, S. Vallipuram, J. V. Kingston, R. . Huyck, S. Y. Bylikin, S. D. Carr, R. Watts, S. Parkin, *J. Organomet. Chem.* **2004**, *689*, 502. **[k]** R. F. Horvath, T. H. Chan, *J. Org. Chem.* **1987**, *52*, 4489.

[24] S. Pawlenko, Houben-Weyl, **1980**.

[25] U. Herzog, *The Chemistry of Organic Silicon Compounds Volume 3*, John Wiley & Sons, Ltd, **2001**.

[26] C. Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications: London, **1960**

of a chlorosilane. Figure (1.7) summarizes different synthetic routes towards the preparation of organosilicon halides and in Figure (1.8) some synthetic applications of haloorganosilanes are depicted.[27]

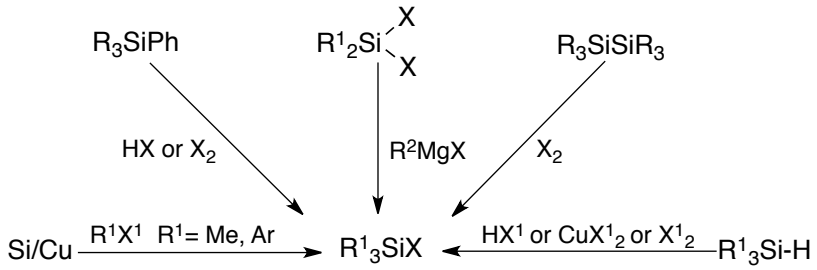


Figure 1.7: General Preparation Routes of Organosilicon Halides

Since the discovery of the „direct process“ in 1940 by Mueller and Rochow, elemental silicon with methyl or aryl halides is used to create chloroorganosilanes. Further pathways include an electrophilic substitution of hydrogen or a silyl group. Additionally, a halogen exchange reaction with a carbon containing chlorosilane is a common used procedure. Moreover, Grignard reagents are used to prepare haloorganosilanes by a halide-exchange reaction.

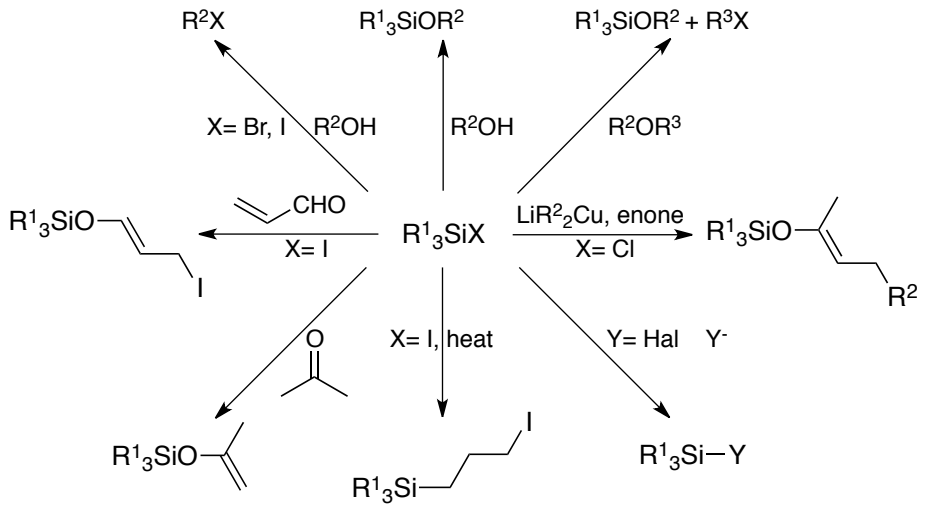


Figure 1.8: Overview of Reaction Routes of Haloorganosilanes

Hydrolysis is basically used for the formation of siloxanes, which serves as precusor compounds for silicone polymers. Other fields of application are to apply chlorosilanes *via* halogen exchange reactions, as well as the formation of a corresponding silylether. Chlorosilanes are also used to create analogue enones or enoates using organocopper compounds for activation.

[27] E. Flaming, *Science of Synthesis*, Georg Thieme Verlag, New York, **2002**.

1.3.1 Dichloroarylsilanes

In 1957, Rosenberg *et al.* reported the first procedure to synthesize dichloro- and trichlororganosilane (R= ethyl or phenyl) in good to moderate yields.[28] Dichlorodiphenylsilanes were prepared by the addition of 2.0 eq. of phenylmagnesium chloride in THF to 0.9 eq. of silicon tetrachloride in heptane. Furthermore, the synthesis of trichlorophenylsilanes was reported using 2.0 eq. of phenylmagnesium chloride and 2.2 eq. of silicon tetrachloride. A mixture of dichlorodiarylsilane (17%) and 47% of the desired product was obtained.

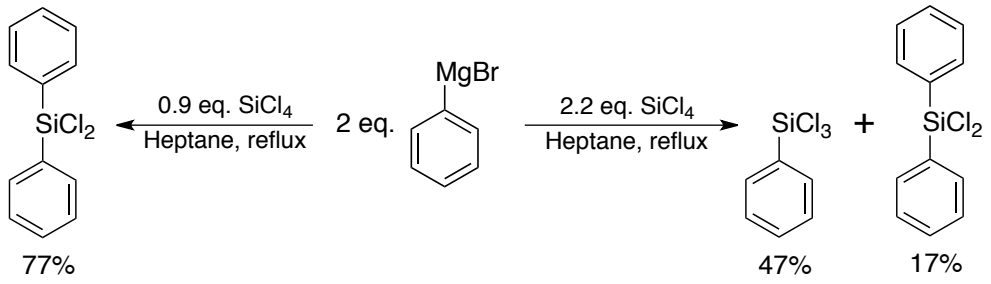


Figure 1.9: Preparation of Chlorophenylsilane Derivatives

In comparison to organolithium compounds, Grignard reagents are more selective and widely used for the synthesis of trichlorosilanes.[29] However, the Grignard method exhibits a major disadvantage concerning the reaction with sterically hindered aryl halides. *"Grignard reagents in general permit a better control of product composition, but they are quite sensitive to the bulk of the organic group."*[30] However, various organosilicon halides with fluoride substituents are published. A possible reason may be the steric properties of fluoride.[31] Therefore, bulky aryl compounds are easier to be obtained by using fluorides substituents. Due to the higher selectivity of Grignard reagents, a better controlled reaction can be achieved.[32] In contrast to organolithium reagents, Grignard reagents with trichlorosilanes give rise to chloroorganosilanes in good to moderate yields.[33]

Figure 1.10: Preparation of Chloroorganosilanes form Tetrachlorosilane and Grignard Reagents

[28] S. D. Rosenberg, J. J. Walburn, H. E. Ramdsen, *J. Org. Chem.* **1957**, *22*, 1606.
[29] C. Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications: London, **1960**
[30] E. Flaming, *Science of Synthesis*, Georg Thieme Verlag, New York, **2002**, p 256.
[31] A. S. Ionkin, W. J. Marshall, *Organometallics* **2003**, *22*.
[32] C. H. Van Dyke, *Organometallic Compounds of the Group IV Elements*, Marcel Dekker, New York, **1972**.
[33] S. Pawlenko, Houben-Weyl, **1980**.

$SiCl_4$	RMgX	$Ratio_{(SiCl_4/\ RMgX)}$	n	Yield [%]
	iPrMgCl	2.0	1	75
	$Me(CH_2)_6MgCl$	2.3	1	54
	PhMgCl	0.5	2	77

Table 1.2: Literature Short Cut of Chloroorganosilanes Using Tetrachlorosilane and Grignard Reagents

Organolithium reagents are another frequently used reaction procedure to synthesize organochlorosilanes. Due to the higher reactivity, organolithium reagents react almost too efficiently with tetrachlorosilanes and are difficult to control.[34] Consequently, organolithium compounds leads to a multiple aryl-substituted chlorosilane.

Another synthetic approach takes advantage of the decomposition of silicon compounds at high temperature to form radicals. This reaction behavior can also be used to create trichlorophenylsilane by reacting chlorobenzene and trichlorosilane in a copyrolysis apparatus at 650 °C (Figure 1.11).[35]

$$HSiCl_3 + PhCl \xrightarrow[\text{radical react.}]{} PhSiCl_3 + HCl$$

Figure 1.11: Preparation of Trichlorosilane using a Trichlorosilaneradical Intermediate

1.3.2 Hydrogen-rich Silanes

Hydrogen-rich silanes have been shown to serve as important substrates for many applications, such as the single-source precursors in CVD processes, as monomeric substrates for σ- bond metathesis and hydrosilylation as well as ligands for transition metal catalyst. Furthermore, hydrogen-rich silanes are used to generate polysilanes *via* dehydrogenative and desilanative coupling.[36] Trichlorosilanes can be reduced to the corresponding trihydride ($RSiH_3$) by hydrogenation with lithium aluminum hydride in ethereal solvents. Sakurai *et al.* reported the reduction of trichlorophenylsilanes to the corresponding trihydrosilane according to a known procedure.[37] Already in 1947, Finholt *et al.* provided a successful hydrogenation of aryltin-chlorides using LAH.[38]

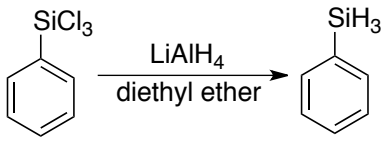


Figure 1.12: Preparation of Phenylsilane with LAH

[34] E. Flaming, *Science of Synthesis*, Georg Thieme Verlag, New York, **2002**.
[35] U. Klingbiel, N. Auner, *Synthetic Methods of Organometallic and Inorganic Chemistry*, Georg Thieme Verlag, Stuttgart, **1996**.
[36] O. Minge, S. Nogai, H. Schmidbauer, *Z. Naturforsch.* **2004**, *59*, 153.
[37] H. Sakurai, S. Masataka, Y. Mikio, H. Akira, *Synthesis* **1984**, *7*, 598.
[38] A. E. Finholt, K. E. Bond, H. Wilzbach, J. Schlesinger, *J. Am. Chem. Soc.* **1947**, *69*, 2692.

Chapter 2

Results and Discussion

The objective of the thesis can be divided in the synthesis and characterization of dichlorodiphenylsilane and trichlorophenylsilane derivatives, respectively. This chapter summarizes all synthesized *ortho*-substituted chlorophenylsilane (Ar_2SiCl_2 and $ArSiCl_3$)(Ar= *o*-tolyl, 1-naphthyl, 2-naphthyl, 2,6-xylyl, 9- anthracenyl) (Table 2.1).

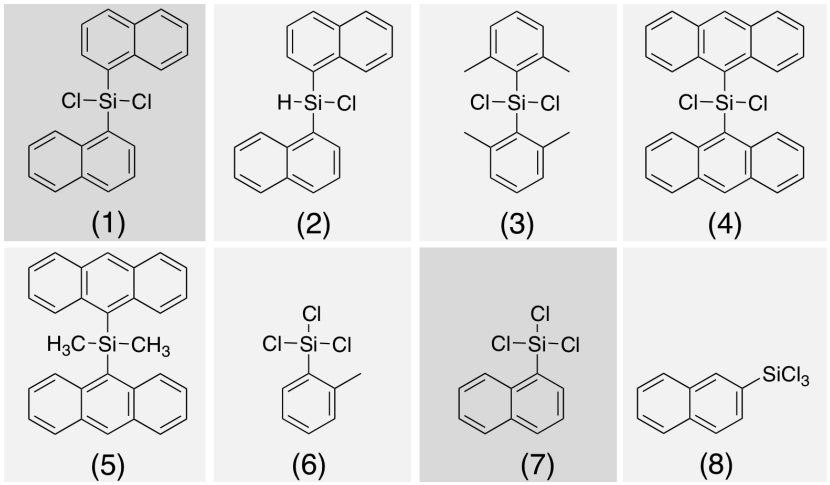


Figure 2.1: Overview of Synthesized Compounds

The synthesis of the arylchlorosilanes were performed in a two step reaction sequence (Figure 2.2).

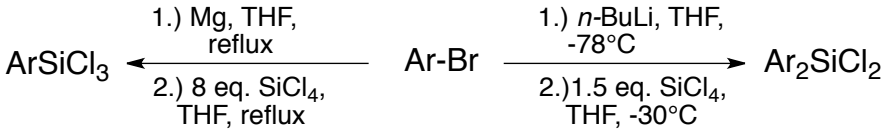


Figure 2.2: General Synthetic Routes for Dichlorodiphenylsilane or Trichlorophenylsilane Derivatives (Ar= *o*-tolyl, 1-naphthyl, 2-naphthyl, 2,6-xylyl, 9- anthracenyl)

The classical synthetic procedure can be separated in the formation of a carbanion at the aryl carbon, forming an organolithium or a Grignard reagents.
Subsequently, the carbanion reacts with a chlorosilane, like tetrachlorosilane to generate the corresponding chloroarylsilane. The prepared dichlorodi(naphthalen-1-yl)silane **(1)** and trichloro(naphthalen-1-yl)silane **(7)** serves as precursors for the synthesis of aryltrihydrides (see chapter 2.3.1) and silyltin sequences (see chapter 2.3.2).
In Table (2.1), all isolated trichloroarylsilane and dichlorodiarylsilane derivatives are listed and marked with $\surd$. According to the literature, synthetic scopes for the preparation of steric hindered trichloroarylsilanes can be limited. More specifically, with regards to the double *ortho*-substituted 9-anthracenyl or 2,6-xylene derivatives, the preparation of trichloroarylsilanes was not successful and marked with an X.

Aryl Residue	**Trichlorosilane**	**Dichlorosilane**
o-Tolyl	$\surd$	$\surd$
1-Naphthyl	$\surd$	$\surd$
2-Naphthyl	$\surd$	$\surd$
1,3-Dimethylbenzyl	X	$\surd$
9-Anthracenyl	X	$\surd$

Table 2.1: Overview of Synthesized Arylchlorosilanes

Two convenient methods for the formation of chloroarylsilane derivatives are on the on hand the reaction of tetrachlorosilane with an organolithium and on the other hand with a Grignard reagent. In general, dichlorodiarylsilanes were synthesized *via* lithiation using *n*-BuLi in THF at -78 °C. The Grignard reagent (ArMgBr) (Ar= *o*-tolyl, 1-naphthyl, 2-naphthyl) was treated with tetrachlorosilanes in THF to obtain the corresponding trichlorosilanes.

Method (A) (Organolithium Reagents): Starting materials were dissolved in THF and an organolithium reagent was added dropwise at -78 °C. Subsequently, a stoichiometric amount of tetrachlorosilane or trichlorosilane was added dropwise at room temperature and stirred overnight. Work up and purification techniques, of the reaction mixtures are explained in Chapter 2.1.1.
Method (B) (Grignard Reagents): Starting materials were reacted with magnesium turnings in ether solvents and refluxed for 2 h. Subsequently, tetrachlorosilane was added dropwise and refluxed for 2 h. After work up the pure product was obtained *via* distillation or sublimation.
Method (C) (Methylation): Compound **(4)** was dissolved in THF and MeLi was added dropwise at 0 °C. The reaction mixture was stirred for 2 h at room temperature. The pure product **(5)** was obtained after removal of insoluble salts by filtration.

The reaction process was monitored *via* ^{1}H, ^{29}Si and ^{119}Sn NMR using a D_2O capillary as external lock signal. Products were characterized *via* ^{1}H,^{13}C, ^{29}Si,^{119}Sn NMR and GC-MS, unless otherwise stated. The ^{29}Si DEPT NMR pulse sequence was applied to significantly reduce the acquisition time of sterically shielded arylchlorosilanes. The ^{29}Si DEPT pulse sequence is based on a polarization transfer of protons, with a maximum distance of ^{3}J coupling.
In contrast, the sterically hindered compounds **(3)** and **(4)** were characterized *via* direct detection of ^{29}Si NMR with exceptionally long relaxation delay time (d_1= 25 sec), because of a lack of an *ortho* proton. A ^{13}C NMR APT puls sequence was applied to distinguish between Cq and CH groups in the aromatic ring.
DFT- calculations were performed using the Gaussion 03 program. Structures were optimized using the B3LYP DFT method with the G-31F* basis. NMR calculation were performed using the B3LYP method with the IGLO-III basis.

2.1 Synthesis and Characterization of Dichlorodirarylsilanes and Derivatives

In this section the diphenyldichlorosilane derivatives **(1)** to **(5)** are summarized. They were synthesized according to method **(A)** and **(C)**, respectively. Experimental procedures as well as yields of **(1)-(5)** are summed up in Table (2.4).

Compound	Method	Yield [%]
Dichlorodi(naphthalen-1-yl)silane **(1)**	A	60
Dichlorobis(2,6-dimethylphenyl)silane **(3)**	A	5
Dichlorodi(anthracen-9-yl)silane **(4)**	A	35
Chlorodi(naphthalen-1-yl)silane **(2)**	A	10
Di(anthracen-9-yl)dimethylsilane **(5)**	C	82

Table 2.2: Product yields of the **(1)-(5)**

In literature, Yamaguchi *et al.*[1] described the formation of various dichlorodiarylsilane derivatives using organolithium reagents for the carbanion formation (Figure 2.3).

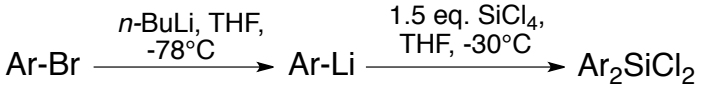


Figure 2.3: General Preparation of Dichlorodirarylsilanes (Ar= *o*-tolyl, 1-naphthyl, 2,6-xylyl, 9-anthracenyl)

Due to the reactivity of organolithium compounds, a selective formation of (Ar_2SiCl_2) (Ar= *o*-tolyl, 1-naphthyl, 2,6-xylyl, 9-anthracenyl) depends on the

[1] S. Yamaguchi, S. Akiyama, K. Tamao, *Organometallics* **1998**, *17*, 4347.

stoichiometric ratio between lithiated aryl compound and added tetrachlorosilane. Treatment of the lithiated 1-naphthyl derivative with trichlorosilane instead of tetrachlorosilane also revealed the same selectivity. Thus, the formation of **(2)** was detected.

2.1.1 Purification and Work Up Procedure of Dichlorodiarylsilanes

Work up procedure of the reaction mixtures (**1**)-(**5**) depends on the different aryl compounds. According to the GC-MS measurements, the reaction mixture of (**1**) and (**2**) contains approximately 10% 1-bromonaphthalene in the reaction mixture. Therefore the previous Grignard formation did not proceed under full conversion. However, the products (**1**) and (**2**) could be separated from the educt by extraction with pentane.
The reaction mixture of (**3**) still contains 2,6-xylene, detected *via* $^{1}H,^{13}C$ NMR and GC-MS. The formation of 2,6-xylene indicates that the substitution with tetrachlorosilane does not proceed selectively. To obtain pure **(3)**, 2,6-xylene (colorless liquid, bp 110°C) was separated *via* distillation.
In comparison to (**3**), crude reaction product of (**4**) also contains the protonated side product, in this case anthracene. Anthracene was detected *via* $^{1}H,^{13}C$ NMR and GC-MS and is a colorless, crystalline solid likely to be sublimed. Therefore the side product was removed *via* sublimation for 2 days at 125°C and 0.015 torr to obtain pure (**4**).

2.1.2 Dichlorodi(naphthalen-1-yl)silane (1)

Dichlorodi(naphthalen-1-yl)silane was prepared by the reaction of the lithiated 1-bromonaphthalene and subsequent treatment with tetrachlorosilane in THF and was isolated as a white, air stable solid (Figure 2.4). This solid was characterized *via* multinuclear NMR spectroscopy ($^{1}H,^{13}C$, ^{29}Si) and GC-MS. In addition, the crystal structure of **(1)** was obtained for the first time.[2]
In 2006, Kondo *et al.* used dichlorodi(naphthalen-1-yl)silane as precursor for the synthesis of the corresponding diol.[3]

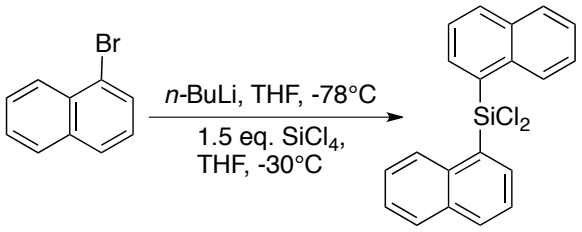


Figure 2.4: Preparation of Dichlorodi(naphthalen-1-yl)silane **(1)**

[2] F. Uhlig, *unpublished results*
[3] S. Kondo, T. Harada, R. Tanaka, M. Unno, *Org. Lett.* **2006**, *8*, 4621.

The identity of **(1)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 352.1). In the ^{29}Si NMR spectra, compound **(1)** shows a shift at 7.5 ppm in $CDCl_3$. The reaction mixture contains residual 1-bromonaphthalene, which was removed by extraction with pentane.

2.1.3 Chlorodi(naphthalen-1-yl)silane (2)

Chlorodi(naphthalen-1-yl)silane was prepared by the reaction of the lithiated 1-bromonaphthalene and subsequent reaction with trichlorosilane in THF and was isolated as white, air stable solid (Figure 2.5).
In literature, neither experimental nor calculated results are reported. As expected, the formation of **(2)** is obtained applying the same reaction conditions as compound **(1)**.

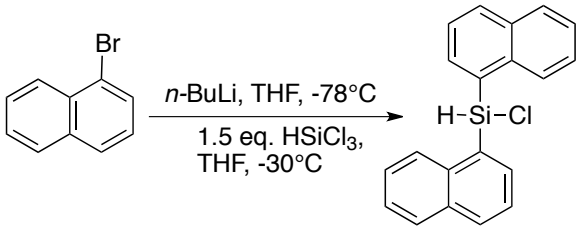


Figure 2.5: Preparation of Chlorodi(naphthalen-1-yl)silane **(2)**

The identity of **(2)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 318.1). In the ^{29}Si NMR spectra, compound **(1)** shows a shift at -7.19 ppm in C_6D_6. The chemical shifts of **(2)** (-7.2 ppm) are located more upfield than **(1)** (7.5 ppm), due to the removal of one chlorine. In the ^{1}H NMR spectra of **(2)**, a shift can be assigned as SiH bond (6.65 ppm, $^{1}J(^{29}Si\text{-}^{1}H)$= n.o.) was observed. The reaction mixture contains residual 1-bromonaphthalene, which was removed by extraction with pentane.

Second part of this section is concentrated on the preparation of two dichlorodiphenylsilane derivatives, dichlorobis(2,6-dimethylphenyl)silane **(3)** and di(anthracen-9-yl)dichlorosilane **(4)**. They can be considered as twofold substituted phenyl derivatives.

2.1.4 Dichlorobis(2,6-dimethylphenyl)silane (3)

Dichlorobis(2,6-dimethylphenyl)silane **(3)** was prepared by the reaction of the lithiated 2-bromo-1,3-dimethylbenzene and subsequent treatment with tetrachlorosilane in THF and was isolated as white, air stable solid (Figure 2.6).

In literature, neither experimental nor calculated results have been reported.

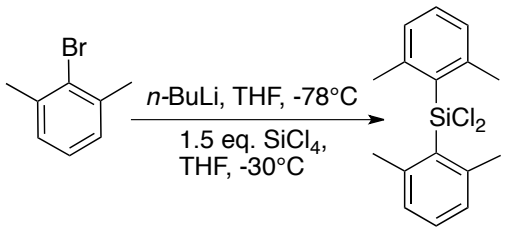


Figure 2.6: Preparation of Dichlorobis(2,6-dimethylphenyl)silane **(3)**

The identity of **(3)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 308.1). In the ^{29}Si NMR spectra, compound **(3)** shows a shift at 2.08 ppm in C_6D_6. In the ^{1}H NMR spectra of **(3)**, a shift assigned as CH_3 groups (6.65 ppm) was observed. The reaction mixture contains 2,6-xylene, which was removed *via* distillation to recieve pure dichlorobis(2,6-dimethylphenyl)silane **(3)**.

2.1.5 Di(anthracen-9-yl)dichlorosilane (4)

Di(anthracen-9-yl)dichlorosilane **(4)** was prepared by the reaction of the lithiated 9-bromoanthracene and subsequent treatment with tetrachlorosilane in THF and was isolated as a yellow, air stable solid (Figure 2.7). Furthermore **(4)** was used to synthesize the corresponding dimethylsilane **(5)**. According to reported procedures, we investigated the formation of di(anthracen-9-yl)dichlorosilane. In 2002, Kondo *et al.*[4] published the preparation of **(4)** by the reaction of 9-anthraceneyl lithium with tetrachlorosilane. However, we are able to provide a selective and efficient work up procedure to gain **(4)** in moderate yields.

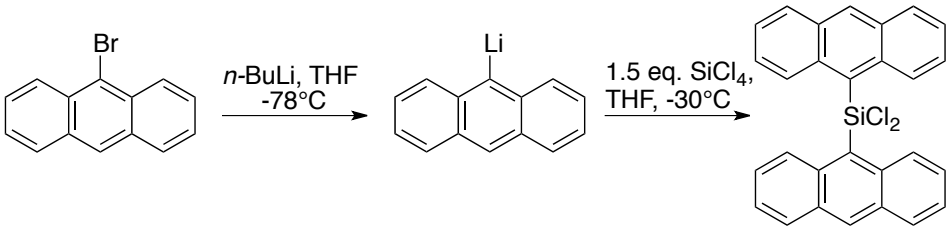


Figure 2.7: Preparation of Di(anthracen-9-yl)dichlorosilane **(4)**

The identity of **(4)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, ^{29}Si) and DI-MS (m/z (relative intensity)= 452.06 [M^+]). In the ^{29}Si NMR spectra, compound **(4)** shows a shift at 2.9 ppm in C_6D_6. The reaction mixture contains anthracene, which was removed *via* sublimation over 2 days at 125°C and 0.015 torr.

[4] S. Yamaguchi, S. Akiyama, K. Tamao, *Organometallics* **1998**, *17*, 4347.

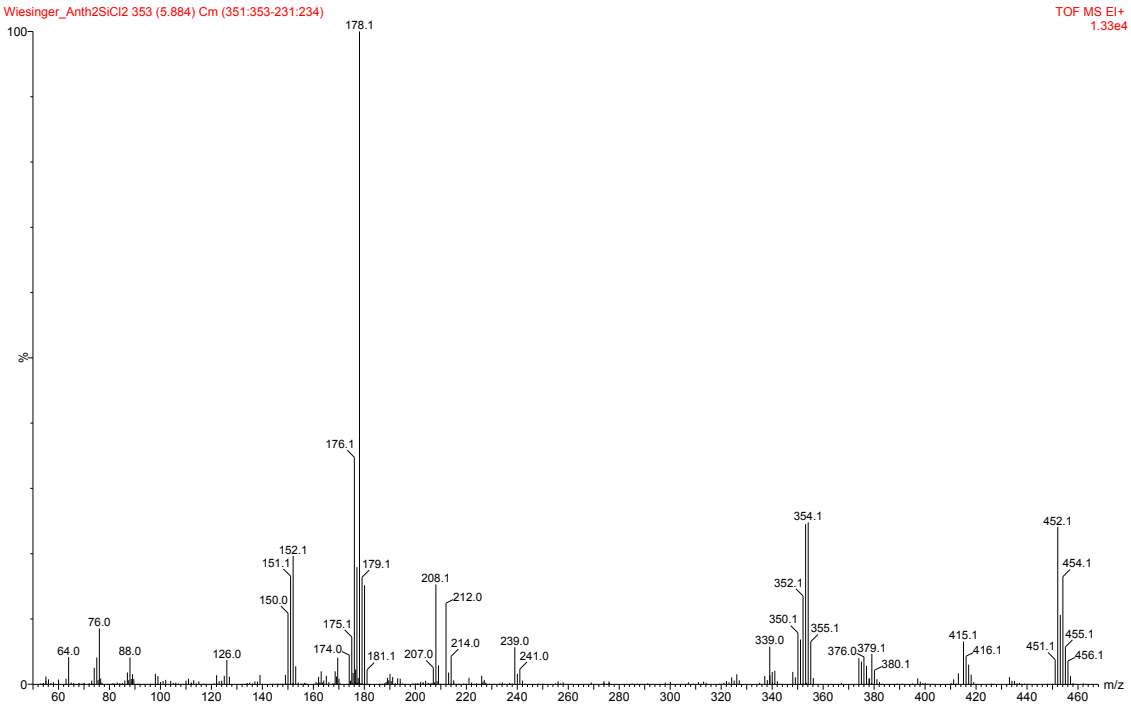


Figure 2.8: M/z Fragmentation of Di(anthracen-9-yl)dichlorosilane **(4)** (DI-EI-TOF)

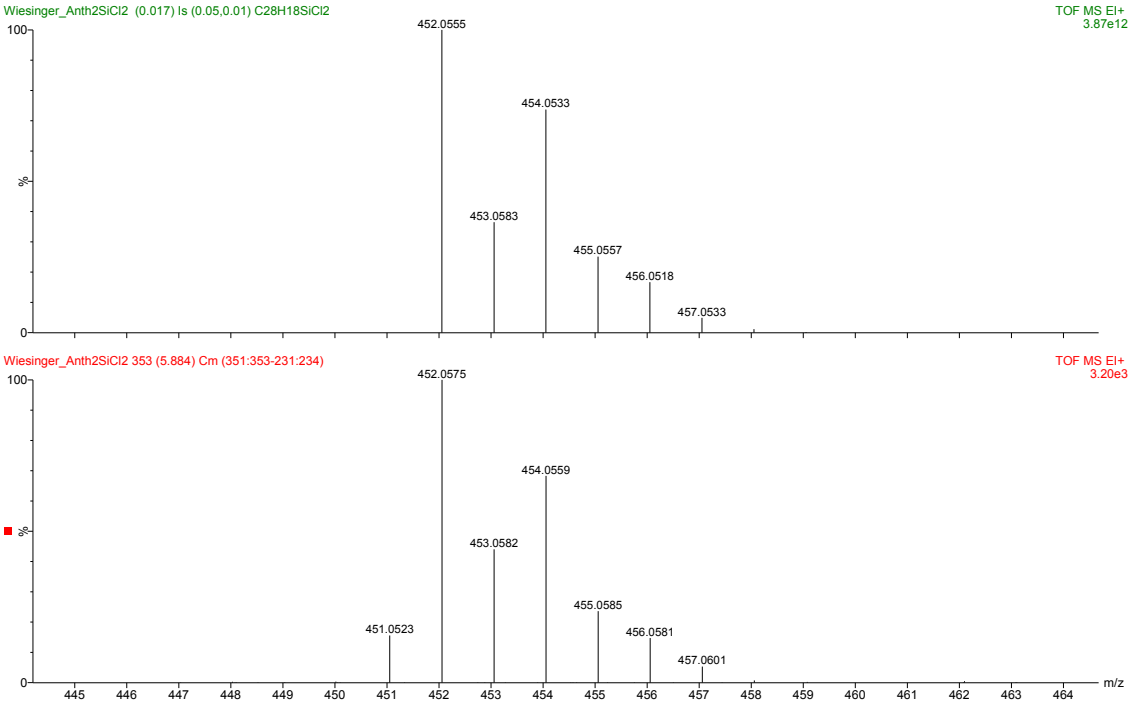


Figure 2.9: Theoretical Isotope Pattern and Experimental Isotope Pattern of M^+

The found isotope pattern of M^+ confirms the formation of di(anthracen-9-yl)dichlorosilane **(4)**.

The characterization *via* multinuclear NMR spectroscopy and GC-MS turned out to be challenging. Due to the lack of an *ortho* proton at the aryl ring, it was not possible to apply a Sidept pulse sequence. Thus, a direct detection of ^{29}Si by overnight measurements with relaxation delays up to 25 sec were necessary.
Because of the molecular weight of di(anthracen-9-yl)dichlorosilane (452.03 g/mol), GC-MS measurements were not possible. To overcome this obstacle, MeLi was used to synthesize compound **(5)** exhibiting a lower molecular weight of (412.2 g/mol).

2.1.6 Di(anthracen-9-yl)dimethylsilane (5)

Di(anthracen-9-yl)dimethylsilane **(5)** (Figure 2.10) was prepared by the reaction of **(4)** and MeLi in THF and was isolated as an orange solid.

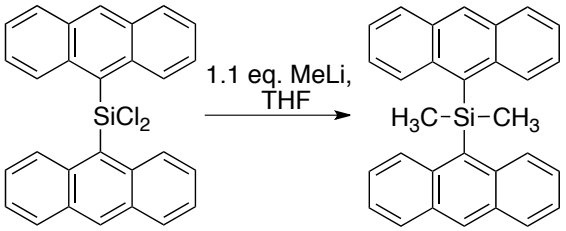


Figure 2.10: Preparation of Di(anthracen-9-yl)dimethylsilane **(5)**

The identity of **(5)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 412.2). In the ^{29}Si NMR spectra compound **(5)** shows a signal at -10.1 ppm in C_6D_6. In the ^{1}H NMR spectra, a shift assigend as CH_3 groups at 1.19 ppm was observed. The residue was taken up in toluene and insoluble LiCl was filtered through celite in order to gain **(5)** in good yields.

Table (2.3) summarize molecular weight and ^{29}Si NMR shifts of dichlorodi-*o*-tolylsilane **A**[5] and **(1)**-**(5)**. The ^{29}Si NMR peaks shifted with respect to the additional substituents at the silicon. The chemical shifts of the **(2)** and **(5)** (-7.2 ppm and -10.1 ppm) are shifted far more upfield than **(1)**, **(3)** and **(5)** (7.5 ppm, 2.1 ppm, 2.9 ppm), due to the electropositive substitents at the silicon.

[5] J. Binder; Master Thesis, TU Graz, 2011

Compound	M_W [g/mol]	^{29}Si NMR [ppm]
Dichlorodi-o-tolylsilane **(A)**	281.3	6.2
Dichlorodi(naphthalen-1-yl)silane **(1)**	353.3	7.5
Dichlorobis(2,6-dimethylphenyl)silane **(3)**	311.3	2.1
Di(anthracen-9-yl)dichlorosilane **(4)**	452.0	2.9
Chlorodi(naphthalen-1-yl)silane **(2)**	318.9	-7.2
Di(anthracen-9-yl)dimethylsilane **(5)**	412.6	-10.1

Table 2.3: Overview of Synthesized Diaryldichlorosilanes

In general, the aryl substitution patterns affects the chemical shift in the ^{29}Si NMR spectra. Concerning to the aryl substituents, anthracenyl or 2,6-xylyl shifted far more upfield (2.1 an 2.9 ppm) than the aryl compounds with only one *ortho* substituent, like 1-naphtalyl (7.5 ppm).

2.2 Synthesis and Characterization of Trichloroarylsilanes

This chapter summarizes various *ortho*-substituted trichlorophenylsilane derivatives ($ArSiCl_3$)(Ar= *o*-tolyl, 1-naphthyl, 2-naphthyl, 2,6-xylyl, 9- anthracenyl).

To this date, a series of different trichloroarylsilanes were published and summarize in Table (2.1).

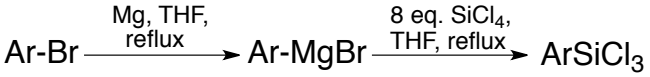


Figure 2.11: General Preparation of Trichloroarylsilanes (Ar= *o*-tolyl, 1-naphthyl, 2-naphthyl, 2,6-xylyl, 9-anthracenyl)

A series of trichlorosilane derivatives **(6)**, **(7)**, **(8)** were synthesized according literature procedures using method **(B)** (Figure 2.11).

Compound	Method	Yield [%]
Trichloro(o-tolyl)silane	B	67
Trichloro(naphthalen-1-yl)silane	B	65
Trichloro(naphthalen-2-yl)silane	B	62

Table 2.4: Product Yields of **(6)-(7)**

Because of the good selectivity of Grignard reagents, the reaction with tetrachlorosilane led to the desired trichloroarylsilanes. Grignard reagents were prepared by reacting magnesium turnings with the corresponding aryl bromide in an etheric solution. The product purity depends on the stoichiometric ratio between tetrachlorosilane and the Grignard reagent.

For example **(7)** was prepared by the reaction of naphtylmagnesium bromide and subsequent treatment with tetrachlorosilane (ratio$_{SiCl4:RMgX}$= 4:1) and shows two ^{29}Si NMR signals at 7.5 ppm and -1.12 ppm. These shifts can be assigned as dichloro- and trichloro(naphthalen-1-yl)silane.
Increasing the stoichiometric ratio of tetrachlorosilane (ratio$_{SiCl4:RMgX}$= 8:1) allows the preparation of trichlorosilanes in moderate yields and the formation of by-products is suppressed.
The synthesis of $ArSiCl_3$ was carried out according to literature procedure.[6,7] Only the ratio between tetrachlorosilane and Grignard reagent was modified to minimize the formation of by-products.

2.2.1 Trichloro(*o*–tolyl)silane (6)

Trichloro(o-tolyl)silane was prepared by an one-pot reaction of *o*-tolylmagnesium bromide and tetrachlorosilane in THF and was isolated as a yellowish oil (Figure 2.12). In 2004, Powell *et al.* have reported the successful preparation of trichloro(*o*-tolyl)silane.

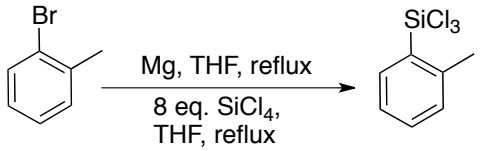


Figure 2.12: Preparation of Trichloro(o-tolyl)silane **(6)**

The identity of **(6)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 223.9). In the ^{29}Sidept NMR spectra compound **(6)** shows a shift at -0.72 ppm in $CDCl_3$. In the ^{1}H NMR spectra of **(6)**, a shift assigned as CH_3 group (2.71 ppm), was observed. The reaction mixture was distillated to obtain pure trichloro(*o*-tolyl)silane as a yellowish oil.

2.2.2 Trichloro(naphthalen-1-yl)silane (7)

Trichloro(naphthalen-1-yl)silane **(7)** was prepared by an one-pot reaction of naphthalen-1-ylmagnesium bromide and tetrachlorosilane in THF and was isolated as a white solid (Figure 2.13). In 2011, the synthesis of the isomeric trichloro(naphthalenyl)silane **(7)** and **(8)** was reported by B. M. Moore *et al*. According to this experimental procedure, we investigated the formation of **(7)**. In addition to spectroscopic results, the crystal structure of **(7)** was obtained by the aforementioned recrystallization technique.

[6] B. M. Moore, G. R. Yandek, J. M. Mabry, S. M. Ramirezand, T. S. Haddad, *J. Organomet. Chem.* **2011**, *696*, 2676.
[7] D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 7788.

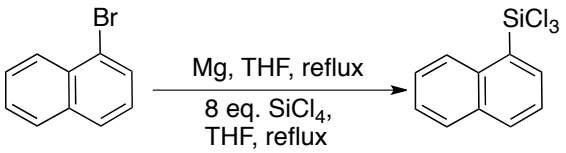


Figure 2.13: Preparation of Trichloro(naphthalen-1-yl)silane **(7)**

The identity of **(7)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 260.0). In the ^{29}Si NMR, spectra compound **(7)** shows a shift at -1.12 ppm in C_6D_6. After distillation, 67% of **(7)** was obtained as a yellowish solid. The mixture was cooled with liquid nitrogen and allowed to warm up at room temperature under *vacuo* in order to observe the formation of white crystals.

According to literature, the presented crystal structure is the first example of polycyclic aromatic trichloroarylsilane. The crystal structure of **(7)** is shown in Figure (2.14).

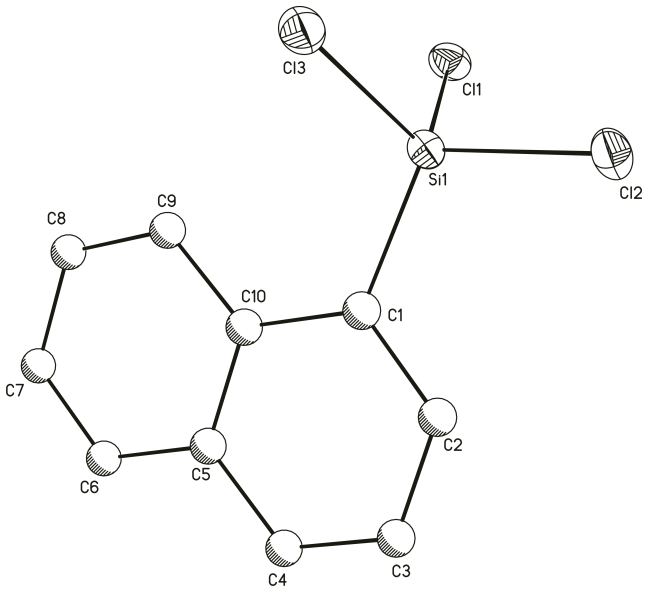


Figure 2.14: Crystal Structure of Trichloro-1-naphthylsilane **(7)**. Hydrogen Atoms Omitted for Clarity.

Trichloro(naphthalen-1-yl)silane **(7)** crystallizes in a monoclinic space group P2(1)/c. Selected bond lengths and angles are given in Table (2.5). The silicon can be found in a distorted tetrahedral environment, coordinated to four different substituents.

Due to the higher steric demand of the naphthyl group the average C-Si-Cl angle (111.9(7)°) is significantly larger than the average Cl-Si-Cl (106.9(4)°) angle.

compound		Trichloro(naphthalen-1-yl)silane **(7)**
space group		P2(1)/c
bond length av.[Å]	Si-C	1.841(2)
	Si-Cl	2.034(8)
angle av. [°]	C-Si-Cl	111.9(7)
	Cl-Si-Cl	106.9(4)

Table 2.5: Selected Bond Lengths [Å] and Angles [°] of Trichloro(naphthalen-1-yl)silane **(7)**

2.2.3 Trichloro(naphthalen-2-yl)silane (8)

Trichloro(naphthalen-2-yl)silane **(8)** was prepared by an one-pot reaction of naphthalen-2-ylmagnesium bromide and tetrachlorosilane in THF and was isolated as a white solid (Figure 2.15).
According to experimental procedure, we investigated the formation of **(8)** and the crystal structure of **(8)** was obtained by the aforementioned technique.[8]

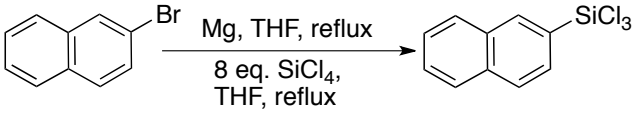


Figure 2.15: Preparation of Trichloro(naphthalen-2-yl)silane **(8)**

The identity of **(8)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 260.0). In the ^{29}Si NMR spectra, compound **(8)** shows a signal at -0.93 ppm in C_6D_6. After distillation, 62% of **(8)** was obtained as white solid. The mixture was cooled with liquid nitrogen and allowed to warm up at room temperature under *vacuo* in order to observe the formation of white crystals.

[8] B. M. Moore, G. R. Yandek, J. M. Mabry, S. M. Ramirezand, T. S. Haddad, *J. Organomet. Chem.* **2011**, *696*, 2676.

In addition to the crystal structure (Figure 2.14), experimental data of the polycyclic aromatic trichlorosilanes **(8)** are unknown so far (Figure 2.16).

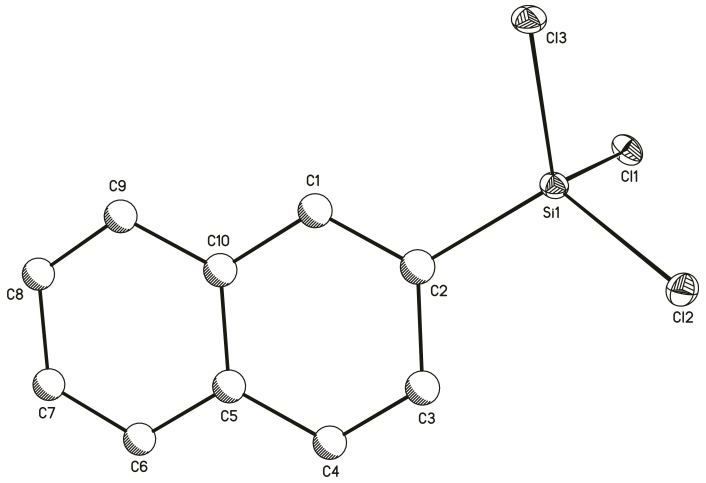


Figure 2.16: Crystal Structure of Trichloro-1-naphthylsilane **(8)**. Hydrogen Atoms Omitted for Clarity.

Trichloro(naphthalen-2-yl)silane **(8)** crystallizes in a monoclinic space group P2(1)/n. Selected bond lengths and angles are given in Table (2.5). The silicon can be found in a distorted tetrahedral environment, coordinated to four different substituents. In comparison to compound **(7)**, Si-C and Si-Cl bond lengths of **(8)** are very similar. Due to the higher steric demand of the naphthyl group the average C-Si-Cl angle (111.7(9)°) is significantly larger than the average Cl-Si-Cl (107.2(4)°) angle.

compound		Trichloro(naphthalen-2-yl)silane
space group		P2(1)/n
bond length av. [Å]	Si-C	1.841(3)
	Si-Cl	2.034(10)
angle av. [°]	C-Si-Cl	111.7(9)
	Cl-Si-Cl	107.2(4)

Table 2.6: Selected Bond Lengths [Å] and Angles [°] of Trichloro(naphthalen-2-yl)silane **(8)**

Table (2.7) summarizes selected bond lengths and angles of the isomeric naphthyltrichlorosilanes **(7)**, **(8)** and literature known compounds (2,6-Dimesitylphenyl)-trichlorosilane ($C_{24}H_{25}Cl_3Si$) and 2,6-bis(2,4,6-Tri-isopropylphenyl)phenyl-trichlorosilane) ($C_{36}H_{49}Cl_3Si$).

compound	space group	bond length av. [Å]	angle av. [°]	Ref
		Si-C/ Si-Cl	C-Si-Cl/ Cl-Si-Cl	
(7)	P2(1)/c	1.841/ 2.034	111.9/106.9	Figure (2.14)
(8)	P2(1)/n	1.838/ 2.042	111.7/107.2	Figure (2.16)
$C_{24}H_{25}Cl_3Si$	P21/c	1.872/ 2.031	110.1/104.9	[9]
$C_{36}H_{49}Cl_3Si$	Pnma	2.007/ 2.016	117.7/103.8	[9]

Table 2.7: Selected Bond Lengths [Å] and Angles [°] of **(7)**, **(8)** and Literature Known Compounds

A slight increase in Si-C_{ipso} bond length due to the increased steric hindrance provoced by the isopropyl groups in 2,6-bis(2,4,6-Tri-isopropylphenyl)phenyl-trichlorosilane) was noticecable. In addition the C-Si-Cl angle widens to 117.72°. The Si-C (1.841 Å) and Si-Cl (2.034 Å) bond distances compared to Si-C (1.872 or 2.007 Å) and Si-Cl (2.031 or 2.016 Å) bond distances for the known crystal structure of a 2,6-Dimesitylphenyl)-trichlorosilane and 2,6-bis(2,4,6-Tri-isopropylphenyl)phenyl-trichlorosilane are in a similar range.[9]

In the following table the isolated trichlorosilanes are listed to their molecular weight, ^{29}Si NMR shifts in $CDCl_3$ and crystal structure. Observed ^{29}Si NMR shifts, compared to $PhSiCl_3$ (^{29}Si NMR: δ -0.8 ppm in $CDCl_3$), lie in the expected range.[10]

Compound	M_W [g/mol]	^{29}Si NMR [ppm]	Crystal Structure
Trichlorophenylsilane **(B)**	211.55	-0.8	liquid
Trichloro(o-tolyl)silane **(6)**	225.57	-0.72	liquid
Trichloro(naphthalen-1-yl)silane **(7)**	261.61	-1.12	$\surd$
Trichloro(naphthalen-2-yl)silane **(8)**	261.61	-0.93	$\surd$

Table 2.8: Overview of Synthesized Trichloroarylsilanes

2.2.4 Attempts Towards Trichloro(anthracen-9-yl)silane and its Derivatives

Various attempts to synthesize the challenging trichloro-9-anthracenylsilane are summarized in this chapter. Consequently, various tries were carried out to gain the desired product by converting 9-bromoanthracene to the corresponding Grignard reagent.

In literature, neither experimental nor calculated results are published for silicon anthracenyl compounds. Various reviews and books have reported the problematic access of hindered trichloroarylsilane.[11] Because of the high steric demand of 9-anthracenyl or 2,6- xylyl the proposed reaction sequence did not succeed in the formation of trichloro(2,6-dimethylphenyl)silane and trichloro(anthracen-9-yl)silane.

The most convenient procedures (Grignard or organolithium reagents) did not turn out

[9] R. S. Simmons, S. T. Haubrich, B. V. Mork, M. Niemeyer, P. P. Power, *Main Group Chem.* **1998**, *2*, 275.

[10] F. Uhlig, H. C. Marsmann, *Silicon Compounds: Silanes and Silicones, Gelest, Inc, 2nd Edition*, Morrisville, **2008**.

[11] E. Flaming, *Science of Synthesis*, Georg Thieme Verlag, New York, **2002**.

to be the reaction pathway of choice. Grignard reagents are assumed to be selective in synthesizing trichlorosilane, but in this case not reactive enough. Whereas organolithium reagents are difficult to control. The substitution of the tetrachlorosilane mostly leads to the dichlorosilane due to increased reactivity.

In summary, 2,6-dimethylbromobenzene and 9-bromoanthracene are sterically very demanding residues and can not be converted to the desired $ArSiCl_3$ using that reaction pathway.

2.2.4.1 Trichloro(2,6-dimethylphenyl)silane

According to previously reported procedures, trichloro(2,6-dimethylphenyl)silane was prepared by the reaction of (2,6-dimethylphenyl)magnesium bromide and tetrachlorosilane in THF (Figure 2.17).

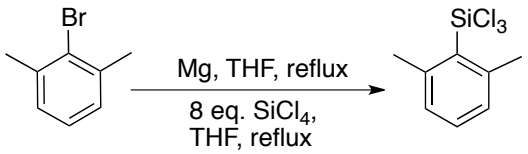


Figure 2.17: Preparation of Trichloro(2,6-dimethylphenyl)silane

C. Zeppek reported the formation of (2,6-dimethylphenyl)magnesium bromide as well as subsequent reaction using the Grignard reagent.[12] Regarding to the working Grignard formation, the reaction progress was prevented during the followed synthetic steps.

2.2.4.2 Trichloro(anthracen-9-yl)silane

In Figure (2.18) various attempts to synthesize the challenging trichloro(anthracen-9-yl)silane are summarized. In literature neither experimental nor calculated results are available.

A and C_1: Grignard Reagents In addition to the previously reported aryltrichlorosilane (Chapter 2.2), trichloro(anthracen-9-yl)silane should also be able to be prepared according to method **(B)**. The formation of the desired intermediate step (Grignard reagent) was disproved by the attempt of trapping it with butyl chloride (1 eq.). The expected 9-butylanthracene was not detected *via* GC-MS. In summary this reaction route is limited due to difficulties in preparing the Grignard reagent.

B and C_2: Organolithium Reagents The formation of the lithiated anthracenyl intermediate was described in Chapter (2.1) and always yields di(anthracen-9-yl)dichlorosilane.

[12] C. Zeppek, Master Thesis, TU Graz, 2012

Precursor compound di(anthracen-9-yl)dichlorosilane was prepared according to Method **(A)**. This intermediate was used to prepare the corresponding dihydride. Furthermore, a three step reaction route was performed to produce the desired compound.

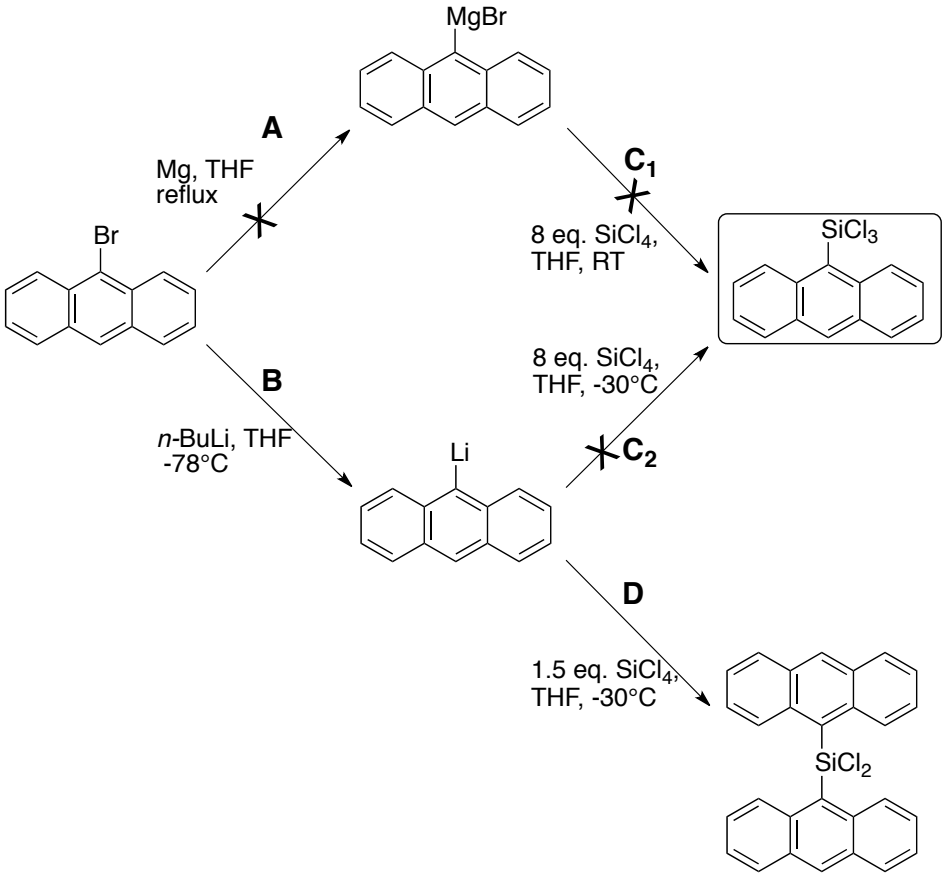


Figure 2.18: Overview of Synthetic Attempts Towards Trichloro(anthracen-9-yl)silane

Figure (2.19) displays another reaction route of di(anthracen-9-yl)dichlorosilane **(4)** towards trichloro(anthracen-9-yl)silane.

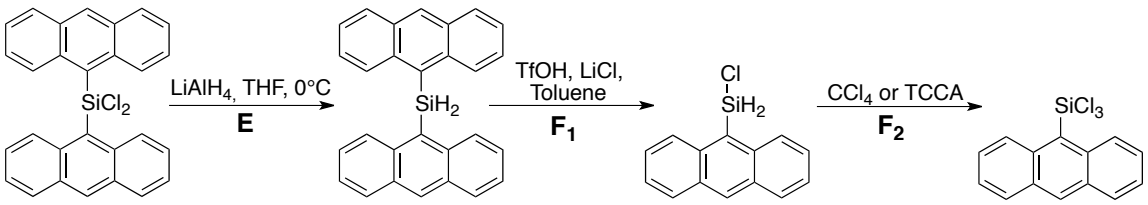


Figure 2.19: Preparation Attempt of Anthracen-9-yltrichlorosilane

E: Hydrogenation of the dichlorosilanes was carried out using LAH in THF.

F_1 and F_2: Trifluoromethanesulfonic acid (TfOH) was used to convert di(anthracen-9-yl)silane by electrophilic substitution of one anthracenyl residue.

Furthermore anthracen-9-ylchlorosilane was obtained by adding lithium chloride. Finally, the chlorination with TCCA or CCl_4 should gain the desired anthracen-9-yltrichlorosilane.

The desired intermediate (anthracen-9-ylchlorosilane) was generated by treating **(4)** with TfOH and lithium chloride. Uhlig *et al.* reported this procedure to functionalize silanes by electrophilic substitution of aryl substituents.[13,14]

The identity of anthracen-9-ylchlorosilane was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and theoretical calculations.
The ^{29}Si NMR spectra shows a signal at -25 ppm in C_6D_6. In comparison to the experimental ^{29}Si shift, theoretical calculations predicted a shift at -28 ppm. In order to gain trichloro(anthracen-9-yl)silane different reagents, like TCCA[15] or CCl_4 were used. Nevertheless, the product compound was not possible to be synthesize.

2.3 Synthesis and Application of Produced Arylchlorosilanes

Organochlorosilanes are the most popular precusor compounds to create functionalized organosilanes.[16] This chapter summarize some possible applications for the generated arylchlorosilanes, **(1)** and **(7)** (Figure 2.20).

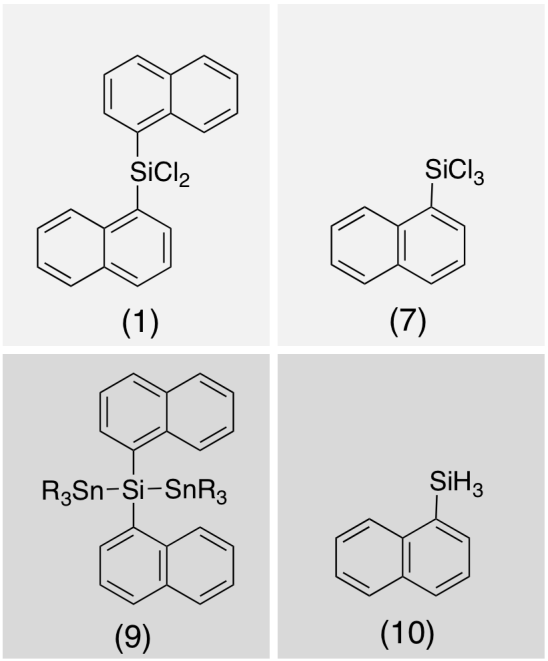


Figure 2.20: Precursors Dichlorodi(naphthalen-1-yl)silane **(1)** and Trichloro(naphthalen-1-yl)silane **(7)** and Their Applications **(9)** and **(10)**

[13] W. Uhlig, *Chem. Ber.* **1992**, *124*, 47.
[14] W. Uhlig,*Chem. Ber.* **1996**, *129*, 733.
[15] S. Varaprath, D. H. Stutts, *J. Organomet. Chem.* **2007**, *692*, 1892.
[16] U. Herzog, *The Chemistry of Organic Silicon Compounds Volume 3*, John Wiley & Sons, Ltd, **2001**.

Starting form **(1)**, a silyltin sequence was prepared by the reaction of hexaphenylstannane with sodium in THF. Naphthalen-1-ylsilane **(10)** was prepared by the reaction of **(7)** with lithium aluminum hydride.

Silyltin Sequence: Starting materials (e.g. hexaphenyldistanne) were dissolved in THF and treated with 2 equivalents of sodium. The reaction mixture was refluxed overnight and was added *via* a cannula to **(1)** in THF at 0 °C. The solvent was evaporated under reduced pressure and dichloromethane was added to remove insoluble salts. The product solution was concentrated under reduced pressure to obtain a white solid.

Naphthalen-1-ylsilane (10): (7) was reduced to the corresponding hydrogen-rich silanes by stirring with lithium aluminum hydride in THF at 0 °C for 3 h. The excess of LAH was quenched with degassed H_2SO_4. Furthermore the solution was dried over $CaCl_2$ and the phases were separated to obtain a brownish oil in moderate yields.

2.3.1 Silyltin Compounds (9) and (9a)

The chemistry of silyltin compounds has been established and summarized in a review by R. Fischer and F. Uhlig. Compounds exhibiting Si-Sn bond are interesting for novel polymeric materials, catalytic systems and scientific research.[17] The reaction scheme follows a Wurtz-type reductive coupling reaction mediated by sodium, lithium or magensium.

In 1986, Adams *et al.* reported a synthetic procedure to create a silyltin sequence, based on the reaction of Ph_3SnLi with Ph_2SiCl_2 in THF.[18]

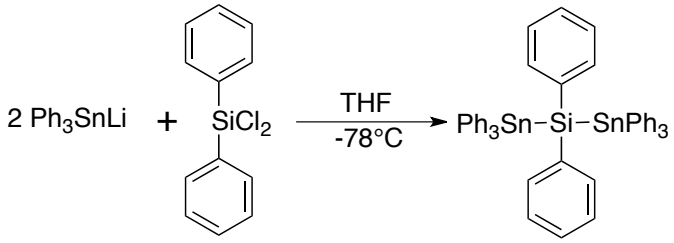


Figure 2.21: Preparation of $(Ph_3Sn)_2SiPh_2$

Recently, Wurtz-type reductive coupling reactions have been used to obtain silyltin compounds. Therefore alkali metals like Na, Li or Mg were used to create an anionic stannane species, for example R_3Sn-Na. In order to gain alternating silyltin sequences, the anionic intermediate was reacted with **(1)**.

[17] R. Fischer, F. Uhlig, *Coord. Chem. Rev.* **2005**, *249*, 2075.
[18] S. Adams, M. Draeger, *J. Organomet. Chem.* **1987**, *323*, 11.

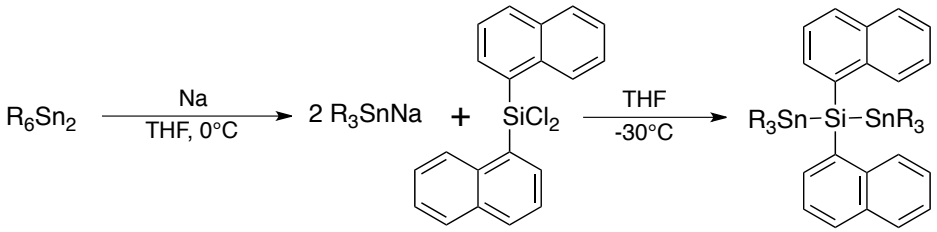


Figure 2.22: Preparation of a Silyltin Seqeunces (R= phenyl, butyl)

(9) was prepared by the reaction of hexaphenyldistannane and 2 equivalents of sodium in THF. The corresponding anionic species was obtained by refluxing the reaction mixture overnight. The reaction progress was monitored *via* ^{119}Sn NMR. Then R_3SnNa was added to **(1)** in THF at -30 ℃ and **(9)** was isolated as a white amorphous solid.

2.3.1.1 2,2-Di(naphthalen-1-yl)-1,1,1,3,3,3-hexaphenyldistannasilane (9)

The identity of **(9)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C,^{119}Sn and ^{29}Si) and DI-MS (m/z (relative intensity)= 982.1276 [M^+]). In the ^{29}Si NMR spectra compound **(9)** shows a signal at -27 ppm in $CDCl_3$. The ^{119}Sn NMR spectra shows a shift at -162 ppm (Figure 5.4) and coupling constants (^1J(^{119}Sn-^{29}Si)= 518 Hz); (^2J(^{119}Sn-^{117}Sn)= 658 Hz); (^1J(^{119}Sn-^{13}C)= 413 Hz). Both shifts are in the expected range compared to $(Ph_3Sn)_2SiPh_2$ (Table 2.9).
Furthermore, recrystallization attempts were performed in various solvents, like acetone, toluene and THF lead to an amorphous solid in 17% yield.

Additionally, the product was identified *via* high resolution mass spectroscopy leading to following spectra (Figures 2.23 & 2.24).

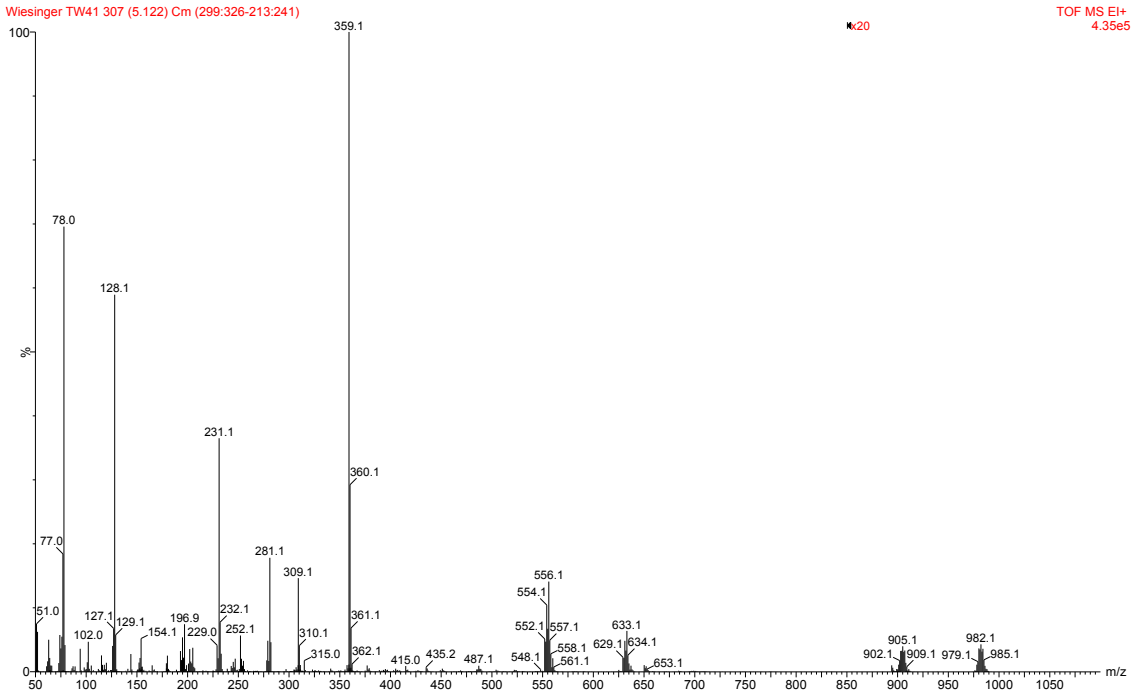


Figure 2.23: M/z Fragmentation of **(9)** (DI-EI-TOF)

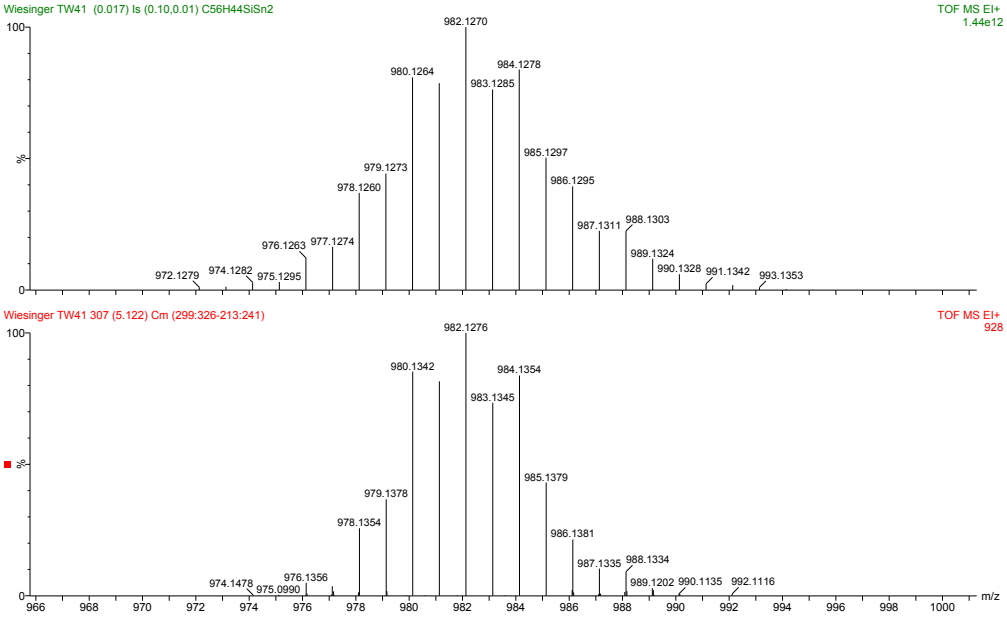


Figure 2.24: Theoretical Isotope Pattern and Experimental Isotope Pattern of M^+

The detected isotope pattern of M^+ confirms the formation of 2,2-di(naphthalen-1-yl)-1,1,1,3,3,3-hexaphenyldistannasilane **(9)**.

2.3.1.2 2,2-Di(naphthalen-1-yl)-1,1,1,3,3,3-hexabutyldistannasilane (9a)

The desired product was prepared by the reaction of hexaphenyldistannane, 2 equivalents of sodium and a catalytic amount of naphthalene in THF. The corresponding anion was obtained by refluxing the reaction mixture overnight. Reaction progress was monitored *via* ^{119}Sn NMR. Subsequently, **(1)** was added dropwise to the anionic intermediate in THF at -30 °C.

The identity of **(9a)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C,^{119}Sn and ^{29}Si). In the ^{29}Si NMR spectra compound **(9a)** shows a signal at -16.5 ppm in $CDCl_3$. In the ^{119}Sn NMR spectra, a main shift at -82 ppm (distannane) was observed. Another ^{119}Sn shift at - 107.8 ppm was detected and assigned as the desired product. In summary, detected ^{119}Sn and ^{29}Si shifts were not found in the expected range and primarily hexabutyldistannane was generated. However an exact identification of the desired product was not possible.

In Table (2.9) and (2.10) observed NMR data were compared to literature.[19]

	$(Ph_3Sn)_2SiPh_2$		**(9a) $(Bu_3Sn)_2SiNaph_2$**		**(9) $(Ph_3Sn)_2SiNaph_2$**	
	(Ph_3Sn)	Ph_2Si	(Bu_3Sn)	$Naph_2Si$	(Ph_3Sn)	$Naph_2Si$
δ ^{119}Sn (ppm)	-167		-107		-162	
^{2}J(^{119}Sn-^{117}Sn) (Hz)	724				658	
δ Si (ppm)		-26		-16		-27
^{1}J(^{29}Si-^{119}Sn) (Hz)		515		n.o.		n.o.

Table 2.9: ^{29}Si and ^{119}Sn NMR data of $(Ph_3Sn)_2SiPh_2$, $(Bu_3Sn)_2SiNaph_2$ and **(10)**; δ in ppm; *J* in Hz

	$(Ph_3Sn)_2SiPh_2$		**(9) $(Ph_3Sn)_2SiNaph_2$**	
	(Ph_3Sn)	Ph_2Si	(Ph_3Sn)	$Naph_2Si$
δ C_{ipso}	139	133	140	137
^{1}J	413	22.3	414	
^{2}J	10			
^{3}J	6			
δ C_{ortho}	137	136	138	[a]
^{2}J	37		36	
^{3}J		17		
δ C_{meta}	128	128	128	[a]
^{3}J	46		45	
δ C_{para}	128	133	128	[a]

Table 2.10: ^{13}C NMR data of $(Ph_3Sn)_2SiPh_2$ and **(10)**; δ in ppm; ^{n}J(^{119}Sn-^{13}C) in Hz

[a] In the ^{13}C NMR spectra, naphthyl and phenyl substituents were possible to be recorded and C_q´s were identified *via* an APT pulse sequence.

[19] S. Adams, M. Draeger, *J. Organomet. Chem.* **1987**, *323*, 11.

In addition to the reaction of dichlorodibutylstannane treated with sodium, a new synthetic procedure was been selected to prepare the desired silyltin sequence. Therefore tributylstannane was treated with LDA in THF in order to abstract the proton and create a R_3SnLi intermediate (Figure 2.25). The corresponding anionic species was obtained by refluxing the reaction mixture overnight. Reaction progress was monitored *via* ^{119}Sn NMR. Subsequently, the anionic intermediate was added to **(1)** in THF at 0℃ to obtain the desired product.

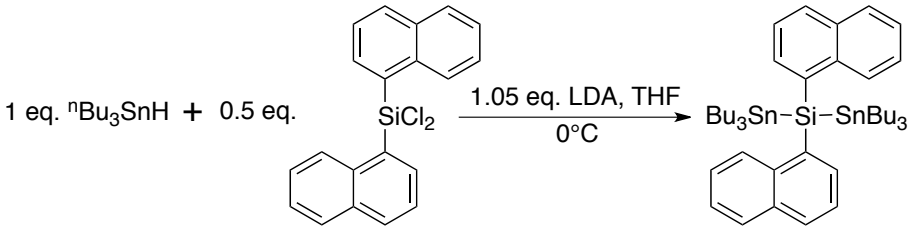


Figure 2.25: Preparation of a Six Membered Silyltin Cycle (Organic Moieties= *n*-butyl, naphtyl)

The identity of the desired product was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C,^{119}Sn and ^{29}Si). ^{119}Sn NMR measurements in $CDCl_3$ showed a main shift at -85.6 ppm, which could be identified as hexabutyldistannane (Figure 5.5). Hexabutyldistannane (177 Da) was also identified *via* high resolution mass spectroscopy.

It can be concluded that this reaction pathway only leads to the formation of a Sn-Sn bond (hexabutyldistannane).

2.3.2 Naphthalen-1-ylsilane (10)

Naphthalen-1-ylsilane was prepared by the reaction of **(1)** and 1.67 equivalents of lithium aluminum hydride in THF and was isolated as a yellow oil (Figure 2.26).
Recently, in 2012 Tran *et al.* reported the synthetic procedure for the hydrogenation of trichloro(naphthalen-1-yl)silane.[20]

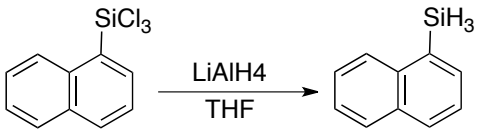


Figure 2.26: Preparation of Naphthalen-1-ylsilane

The identity of **(10)** was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C, and ^{29}Si) and GC-MS (m/z= 158.1). In the ^{29}Si NMR spectra compound **(10)** shows a signal at -62.8 ppm and a coupling constant ($^{1}J(^{1}H\text{-}^{29}Si)$= 200 Hz) in C_6D_6. In

[20] N. T. Tran, S. O. Wilson, A. K. Franz, *Org. Lett.* **2012**, *14*, 186.

the ^{1}H NMR spectra, a shift assigned as SiH function (4.4 ppm) was observed. **(10)** was obtained as a brownish oil in moderate yields (60%).

In addition to these published results, we decided to focus on the preparation of silyltin cycles or chains.

2.3.3 Synthesis of Novel Tin Modified Silanes

Furthermore, various attempts towards the synthesis of a sillytin cyclic derivatives containing the precursor compound **(1)** were carried out in THF. In 2003, Bleckmann *et al.* described the formation of novel tin modified silanes.[21]

The desired product was prepared by the reaction of dichlorodibutylstannane with magnesium turnings in THF and refluxed for 6 days. Reaction progress was monitored *via* ^{119}Sn NMR and after 6 days a shift at 76.5 ppm was observed. Subsequently, **(1)** was added dropwise to the generated intermediate in THF at 0 °C.

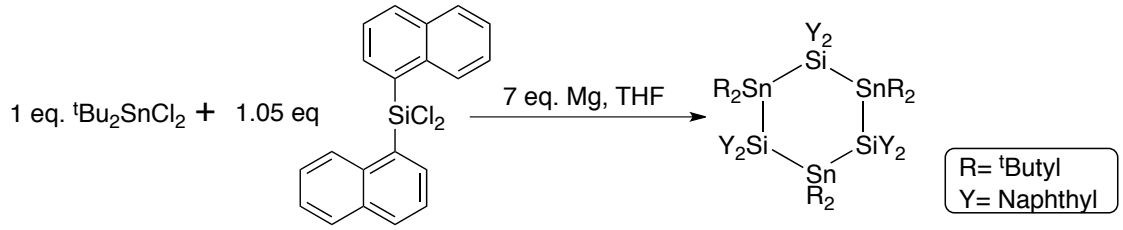


Figure 2.27: Preparation of a Six Membered Silyltin Cycle

The identity of the target silyltin cycle was confirmed on the basis of multinuclear NMR spectroscopy (^{1}H,^{13}C,^{119}Sn and ^{29}Si). The ^{119}Sn NMR spectra shows shifts at 180 ppm, 75 ppm and -6 ppm in $CDCl_3$). According to published results of Lechner *et al.*, the reaction mixture has been identified as 1,1,2,2,3,3,4-hepta-^{t}butyl-4-chloromagensiotetrastannacyclobutane. [22]

[21] P. Bleckmann, T. Brüggemann, S. Maslennikov, T. Schollmeier, M. Schürmann, I. Spirina, M. Tsarev, F. Uhlig, *J. Organomet. Chem.* **2003**, *686*, 332.

[22] M.-L. Lechner, K. Früpaß, J. Sykora, R. Fischer, J. H. Albering, F. Uhlig, *J. Organomet. Chem.* **2009**, *694*, 4209.

2.3.4 Synthesis of a Six- Membered Silicon Cycle

In previous work the synthesis of a six membered silicon cycle, with phenyl moieties was carried out.[23] In comparison to the reaction of dichlorodiphenylsilane treated with lithium, precursor **(1)** was reacted with magnesium turnings and activated with iodide to obtain the desired product.

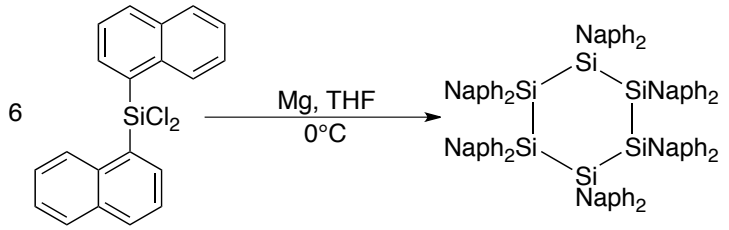


Figure 2.28: Preparation of a Six- Membered Silicon Cycle (Y= naphthyl)

^{29}Si NMR measurements in $CDCl_3$ show two shifts at -38 ppm and -40 ppm in a ratio (1:4). In comparison to unpuplished NMR data from Stueger *et al.*, these signals were assigned as the corresponding five respectively six membered silicon ring. In the ^{13}C and ^{1}H NMR ($CDCl_3$) shifts were observed to naphthyl residues. However a detailed description and interpretation of the spectra were not possible. Educt conversion was complete due to missing chloride fragments in the mass spectra. In the range between 1629/1347/1065/783 and 1379/1097/815/53, fragments with 282 Da ($Naph_2Si$) were observed. MALDI-TOF measurements revealed the formation of an polysiliane oligomere (Figure 2.30), probably with the chemical composition of $Naph_{10}Si_4$ (1379 Da) (Figure 2.31).

In 2003 Bratton *et al.* have reported the coupling of dichlorodiorganosilane mediated by sodium to generate polysilanes.[24]

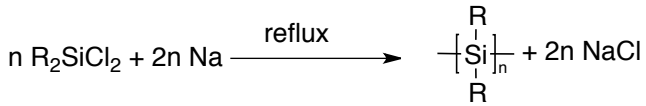


Figure 2.29: Preparation of Polysilane *via* Wurtz-Type Reductive Coupling Reaction

Furthermore recrystallization attempts were performed in acetone, toluene, THF and in a toluene/pentane solution (1:1) lead to a amorphous solid.

[23] H. Stueger, unpublished results
[24] D. Bratton, S. Holder, R. G. Jones, W. K. C. Wong, *J. Organomet. Chem.* **2003**, *685*, 60.

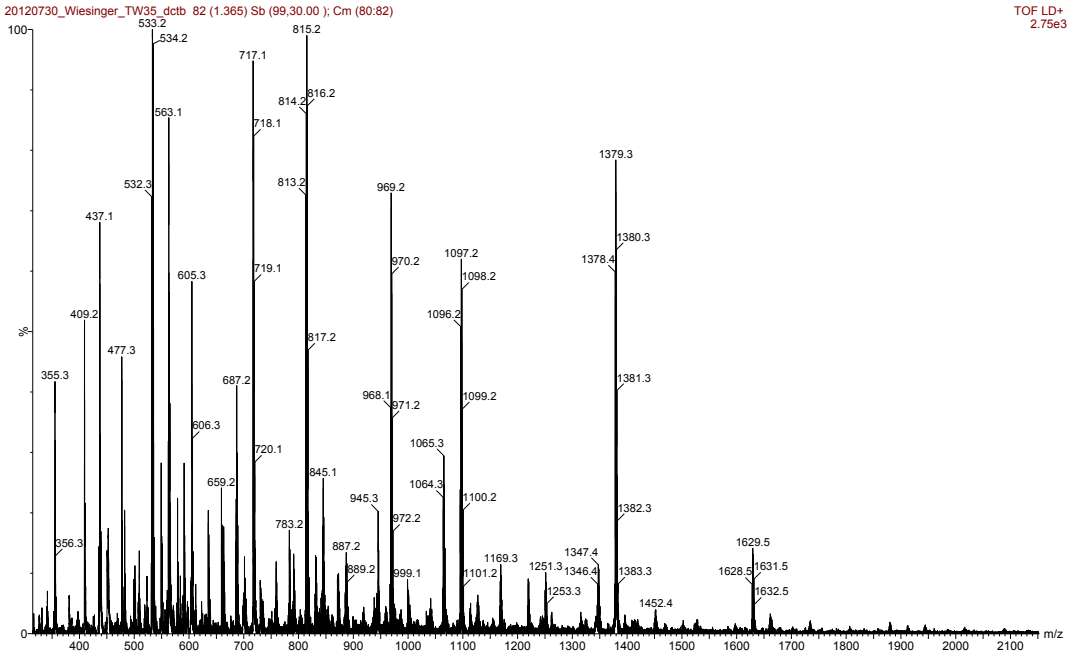


Figure 2.30: MALDI-TOF Spectra of a Six-Membered Silicon Cylce

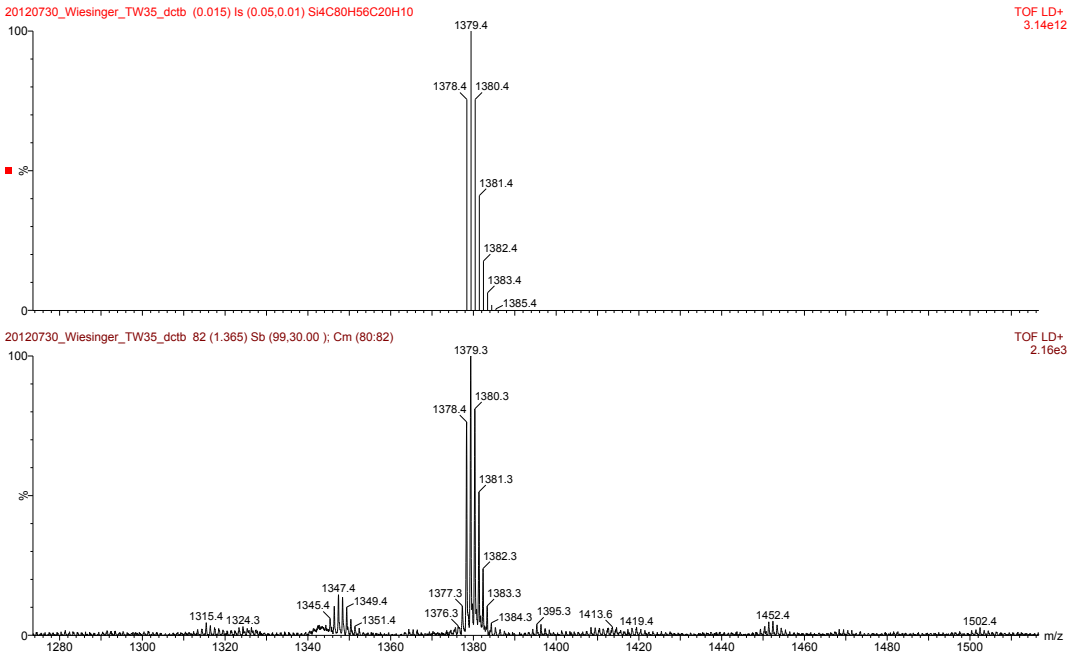


Figure 2.31: Theoretical Isotope Pattern and Experimental Isotope Pattern of $M[Naph_{10}Si_4]^+$

2.4 Conclusion and Outlook

During this work novel dichloro- and trichloroarylsilanes (Ar_2SiCl_2 and $ArSiCl_3$) were successfully synthesized. The formation of dichlorodiarylsilanes was performed according to method **(A)** with different work up procedures. In this case, organolithium reagents were used, due to their higher reactivity. Considering to the higher reactivity, organolithium compoumds are not easy to control and mostly multiple-substituted arylchlorosilane, like Ar_3SiCl, are generated. With dichlorodiarylsilanes, substituted on one ortho position good yields could be achieved. However, for products with bulky aryl substituents, like dichlorobis(2,6-dimethylphenyl)silane **(3)** and di(anthracen-9-yl)dichlorosilane **(4)** only low yields were obtained.
The reaction procedure using method **(B)** yielded in trichlorosilanes and depends on the ratio between Grignard reagent and tetrachlorosilane. Due to the higher selectivity of Grignard reagents, the formation of the desired product was limited by bulky aryl compounds. Thus, the formation of hindered trichloroarylsilane, like trichloro(anthracen-9-yl)silane was not successful. In contrast to published results of trichloro(naphth-1-yl)silane and trichloro(naphth-2-yl)silane, we were able to provide a recrystallization procedure to obtain the first crystal structures of polycyclic aromatic trichlorosilanes.
Wurtz-type coupling experiments of dichlorodi(naphthalen-1-yl)silane **(1)** and magnesium turnings were carried out to generate silyltin cycles or sequences, with an alternating tin silicon arrangement. In order to obtain an alternating silyltin sequence, various distannane educts were tested and showed different reaction behaviors. Alkylstannane always led to thermodynamically stable compounds, like the corresponding distannane or a 4-membered tin cycle.[25] In contrast, the formation of an silyltin sequence with **(1)** and hexaphenyldistannane was successful in although low yields (17%) due to the less sterically hindered phenyl substituent.

In order to obtain a six-membered silicon ring, reaction conditions have to be optimized. Due to sterical properties of naphthyl moiety a reductive coupling reaction leads to a silicon based oligomer.
Based on the formation of a silicon oligomer further investigations focusing on the coupling behaviors, as well as on the properties can be declared as future goals.

[25] M.-L. Lechner, K. Früpaß, J. Sykora, R. Fischer, J. H. Albering, F. Uhlig, *J. Organomet. Chem.* **2009**, *694*, 4209.

Chapter 3

Experimental Section

3.1 General and Used Chemicals

All reactions, unless otherwise stated were carried out under inert nitrogen atmosphere. Organic solvents for synthesis were purchased at VWR and Lactan. Tetrachlorosilane and Trichlorosilane were obtained from ABCR and destilled before use. All dried and deoxygenated solvents were obtained from a solvent drying plant (Innovative Technology, inc). All chemicals from commercial source were utilized without further purification. All other starting materials were synthesized according to literature known procedures. THF was distilled over CaH_2 under nitrogen atmosphere. Degassed H_2SO_4 (10%) was diluted with deionized water.

Compound	Provider
1-bromo-2-methyl-benzene	Sigma Aldrich
2-bromo-1,3-dimethylbenzene	Alfa Aeser
9-bromoanthracene	Sigma Aldrich
1-bromonaphthalene	Sigma Aldrich
2-bromonaphthalene	Sigma Aldrich
magnesium turnings	Sigma Aldrich
sodium	Sigma Aldrich
lithium, ribbon	Sigma Aldrich
lithium aluminium hydride pellets	Sigma Aldrich
n-BuLi 1.6 M in hexane	Sigma Aldrich
n-BuLi 2.5 M in hexane	Sigma Aldrich
t-BuLi 1.6 M in pentane	Sigma Aldrich
MeLi 1.6 M in diethylether	Sigma Aldrich
silicon tetrachloride	ABCR
silicon trichloride	ABCR
hexabutyldistannane	Sigma Aldrich

Table 3.1: Used Chemicals and Commercial Sources

3.2 Analytics

3.2.1 NMR- Spectroycopy

^{1}H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25℃ not otherwise mentioned.

nucleus	frequency [MHz]
^{1}H	300.22
^{13}C	75.5
^{29}Si	59.65
^{119}Sn	111.92

Table 3.2: Frequencies of Observed Nuclei (300 MHz Spectrometer)

Chemical shifts are given in parts per million (ppm) relative to TMS (δ = 0 ppm) regarding ^{1}H, ^{13}C, ^{29}Si and relative to $SnMe_4$ in the case of ^{119}Sn. Coupling constants *(J)* are reported in Hertz (Hz). The spectra were processed and analyzed in MestReNova 5.2.5. As solvents C_6D_6 or $CDCl_3$ are used if not otherwise mentioned.

3.2.2 Elemental Analysis

All elemental analysis were performed with an Elementar Vario EL using sulfanilic acid as standard.

3.2.3 Melting Point Measurements

For these measurements a Stuart Scientific SMP 10 (up to 300℃) was used.

3.2.4 X-Ray Analysis

XRD data collection was performed on a Bruker Apex II diffractometer with use of Mo Kα radiation (λ=0.71073 $\mathring{A}$) and a CDD area detector. Empirical absorption corrections were applied using SADABS[1,2] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[3] The space group assignments and structural solutions were evaluated using PLATON.[4]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles.

[1] R. H. Blessing, *Acta Crystallogr. A*, **1995**, *51*, 33.
[2] G. M. Sheldrick, *SADABS, Version 2.10, Siemens Area Detector Correction*, Universitaet Goettingen, Germany, **2003**.
[3] G. M. Sheldrick, *SHELXTL, Version 6.1, Bruker AXS, Inc., Madison, WI,* **2002**.
[4] G. M. Sheldrick, *SHELXS97 and SHELXL97, Universität Göttingen*, Germany, **2002**.

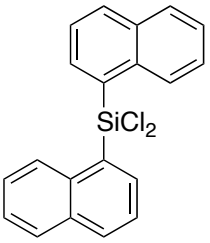
3.2.5 MS-Measurements

GC-MS measurements were performed on a Aligent Technologies GC system (column: HP-5MS) with mass selective detector Typ Agilent 5975C using EI at 70 eV.

Electron impact (EI, 70 eV) mass spectras were recorded on a Waters GCT Premier equipped with a direct insertion (DI).

3.3 Synthesis of Dichlorodiarylsilanes

3.3.1 Dichlorodi(naphthalen-1-yl)silane (1)



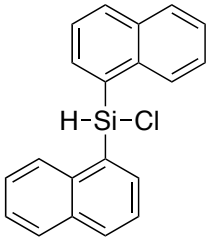
dichlorodi(naphthalen-1-yl)silane

353.32 [g/mol]

A solution of 66 ml *n*-butyllithium (2.5 M in hexane, 1.1 eq., 170 mmol) was added dropwise to a mixture of 21 ml 1-bromonaphthalene (1 eq., 150 mmol) and 200 ml diethyl ether at -78 °C. The mixture was allowed to warm gradually to room temperature and 8.61 ml tetrachlorosilane (0.5 eq., 75 mmol) were added dropwise. The solution was stirred overnight at room temperature and the solvent was evaporated under reduced pressure to give a brownish solid. The residue was taken up in toluene and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 12.08 g (60%) of a white solid were obtained by extraction with pentane.

^{1}H NMR (300.22 MHz, $CDCl_3$): δ 8.35 (d, 2H), 8.2 (d, 2H), 8.0 (d, 2H),7.9 (d, 2H), 7.577-7.540 (dd, 4H), 7.510- 7.463 (dd, 2H).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 136.1 (s, 2), 135.4 (C_{ipso}), 133.6 (C_q), 133.0 (CH), 129.6 (C_q), 129.1 (CH), 127.9 (CH), 126.8 (CH), 126.2 (CH), and 125.0 (CH).
^{29}Si NMR (59.64 MHz, $CDCl_3$): δ 7.5.
GC-MS: t_R = 23.853; m/z = 352.1.
MP (°C): 138-139.
Anal. Calcd for $C_{20}H_{14}Cl_2Si$: C, 67.99; H, 3.99. Found: C, 68.25; H, 4.05.

3.3.2 Chlorodi(naphthalen-1-yl)silane (2)



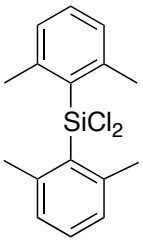
dichlorodi(naphthalen-1-yl)silane

318.87 [g/mol]

A solution of 12.6 ml *n*-butyllithium (2.5 M in hexane, 1.1eq., 23 mmol) was added dropwise to a mixture of 3 ml 1-bromonaphthalene (1 eq., 21 mmol) and 40 ml diethyl ether at -78 °C. The mixture was allowed to warm gradually to 0 °C and 4.33 ml trichlorosilane (2 eq., 42 mmol) were added dropwise. The solution was stirred overnight at room temperature and the solvent was evaporated under reduced pressure to give a white solid. The residue was taken up in dichloromethane and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 0.8 g (10%) of a white solid were obtained by extraction with pentane.

^{1}H NMR (300.22 MHz, dBenzene): δ 8.32 (d, 2H), 8.29 (d, 2H), 7.91 (d, 2H), 7.48 (d, 2H), 7.26 (dd, 2H), 7.16 (dd, 4H), 6.65 (s, SiH)
^{13}C NMR (75.5 MHz, dBenzene): δ 136.9 (C_{ipso}), 136.1 (CH), 133.4 (C_q), 132.0 (CH), 129.6 (C_q), 129.0 (CH), 127.3 (CH), 126.7 (CH), 126.1 (CH) and 125.3 (CH).
^{29}Si NMR (59.64 MHz, dBenzene): δ -7.2.
GC-MS: t_R = 23.640; m/z = 318.1.
MP (°C): 114-116.
Anal. Calcd for $C_{20}H_{15}ClSi$: C, 75.00; H, 4.70. Found: C, 78.55; H, 5.45.

3.3.3 Dichlorobis(2,6-dimethylphenyl)silane (3)



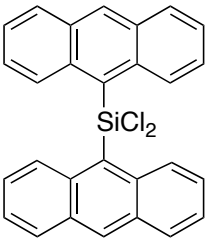
dichlorobis(2,6-dimethylphenyl)silane

309.31 [g/mol]

A solution of 85 ml *t*-butyllithium (1.6 in pentane, 1.5eq., 139 mmol) was added dropwise to a mixture of 11.93 ml 2-bromo-1,3-dimethylbenzene (1.5 eq., 134 mmol) and 250 ml diethyl ether at -78 °C. The mixture was allowed to warm gradually to 0°C and 8.4 ml tetrachlorosilane (0.75 eq., 75 mmol) were added dropwise. The solution was stirred overnight at room temperature and the solvent was evaporated under reduced pressure to give a brownish solid. The residue was taken up in toluene and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 0.4 g (5%) of a white solid were obtained by extraction with pentane and vacuum distillation.

^{1}H NMR (300.22 MHz, dBenzene): δ 6.92 (t, 2H), 6.71 (d, 4H), 2.37 (s, 12H).
^{13}C NMR (75.5 MHz, dBenzene): δ 143.4 (C_{ortho}), 133.9 (C_{ipso}),131.1 (C_{para}), 129.7 (C_{meta}), 24.51(CH_3).
^{29}Si NMR (59.64 MHz, dBenzene): δ 2.08 (s).
GC-MS: t_R = 19.190 ; m/z = 308.1.

3.3.4 Di(anthracen-9-yl)dichlorosilane (4)



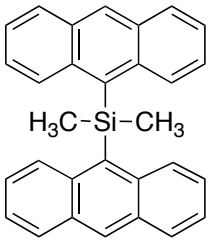
di(anthracen-9-yl)dichlorosilane

453.43 [g/mol]

A solution of 10.9 ml *n*-butyllithium (2.5 M in hexane, 1.5 eq., 17.5 mmol) was added dropwise to a mixture of 3 g 9-bromoanthracene (2 eq., 12 mmol) and 180 ml THF at -78 °C. The mixture was allowed to warm gradually to-50°C and 0.65 ml tetrachlorosilane (0.5 eq., 5.8 mmol) were added dropwise. The solution was stirred overnight at room temperature and the solvent was evaporated under reduced pressure to give a white solid. The residue was taken up in toluene and undissolved salts were filtered through celite. The filtrate was concentrated under reduced pressure and 1.86 g (35%) of a yellow solid were obtained by sublimation over 2 days.

^{1}H NMR (300.22 MHz, dBenzene): δ 8.71 (s, 2H), 8.66 (d, 4H) 8.02 (d, 4H), 7.42- 7.37 (dd, 4H), 7.24- 7.21 (dd, 4H).
^{13}C NMR (75.5 MHz, dBenzene): δ 136.5 (C_q), 134.0 (C_q), 131.8 (CH), 129.7 (C_{ipso}), 128.1 (CH), 126.7 (CH), 125.3 (CH), 119.7 (CH).
^{29}Si NMR (59.64 MHz, dBenzene): δ 2.9.
MS (EI): m/e (relative intensity)= 452.03 [M^+].
MP(°C)= 161-162.

3.3.5 Di(anthracen-9-yl)dimethylsilane (5)



di(anthracen-9-yl)dimethylsilane

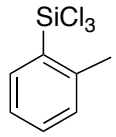
412.60 [g/mol]

A solution of 1.7 ml MeLi in hexane (1.6 M in hexane, 2.5 eq., 2.7 mmol) was added dropwise to a mixture of 0.5 g di(anthracen-9-yl)dichlorosilane (1 eq., 1.1 mmol) and 10 ml THF at 0 °C. The solution was stirred 2 h at room temperature and the solvent was evaporated under reduced pressure to give a yellow/orange solid. The residue was taken up in toluene and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure to give 0.38 g (82%) of an orange solid.

^{1}H NMR (300.22 MHz, dBenzene): δ 8.70 (d, 4H), 8.22 (s, 2H) 8.02 (d, 4H), 7.76 (d, 4H), 7.11- 7.06 (dd, 4H), 7.01- 6.96 (dd, 4H) 1.19 (s, 6H).
^{13}C NMR (75.5 MHz, dBenzene): δ 137.6 (C_q), 136.8 (C_q) 132.1 (C_q), 130.1 (CH), 130.0 (CH), 128.3 (CH), 125.7 (CH), 124.9 (CH).
^{29}Si NMR (59.64 MHz, dBenzene): δ -10.1.
GC-MS: t_R = 34.182; m/z = 412.2.
MP(°C)= 86-87.

3.4 Synthesis of Aryl-Trichlorosilanes

3.4.1 Trichloro(o-tolyl)silane (6)



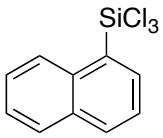
trichloro(*o*-tolyl)silane

225.57 [g/mol]

A flask furnished with a dropping funnel and a reflux condenser was charged with 0.78 g (1.1 eq., 32 mmol) magnesium turnings in 40 ml THF as well as the dropping funnel was filled with a solution of 3.5 ml 1-bromo-2-methyl-benzene (1 eq., 29 mmol, 5 g) in 40 ml THF. After the Grignard reaction was started with dibromoethane, the ethereal solution was added dropwise and the reaction mixture was refluxed for 2 h. A second flask furnished with a reflux condenser was charged with 27 ml tetrachlorosilane (8 eq., 230 mmol, 40.04 g) in 40ml THF. The Grignard solution was added dropwise and the mixture refluxed for 2 h to obtain a brownish solution. The solvent was evaporated under reduced pressure to give a white solid. The residue was taken up in toluene and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 4.23 g (67%) of a yellowish oil were obtained by vacuum distillation.

^{1}H NMR (300.22 MHz, $CDCl_3$): δ 7.92 (d, J = 7.34 Hz, 1H), 7.52 (d, 1H), 7.135 (dd, 2H), 2.71(s, 3H)
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.71 (Cq), 135.10 (CH), 133.06 (CH), 131.18 (CH), 129.40 (Cq), 125.52 (CH), 22.61 (s, CH3) .
^{29}Si NMR (59.64 MHz, $CDCl_3$): δ -0.7.
GC-MS: t_R = 11.208; m/z = 223.9 ($MW_{(theo)}$= 225.57)
Anal. Calcd for $C_7H_7Cl_3Si$: C, 36.04; H, 3.04. Found: C, 37.27; H, 3.13.

3.4.2 Trichloro(naphthalen-1-yl)silane (7)



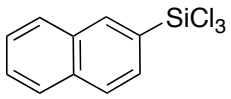
trichloro(naphthalen-1-yl)silane

261.61 [g/mol]

A flask furnished with a reflux condenser was charged with 53 ml tetrachlorosilane (8 eq., 462 mmol, 75.8 g) in 120ml THF. 145 ml of a 1-bromonaphthalene Grignard solution in THF (0.402 M, 1eq., 58 mmol) were added dropwise and the mixture refluxed for 2 h to obtain brownish solution. The solvent was evaporated under reduced pressure to give a brownish solid. The residue was taken up in toluene and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 10.4 g (67%) of a yellowish oil were obtained by vacuum distillation.

^{1}H NMR (300.22 MHz, $CDCl_3$): δ 8.388 (d, 1H), 8.172 (d, 1H), 8.086 (d, 1H), 7.946 (d, 1H), 7.689- 7.632 (dd, 2H), 7.591- 7.534 (dd, 2H).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 134.9 (CH), 133.7 (Cq), 133.5 (s, CH), 133.0 (Cq), 128.8 (CH), 126.9 (CH), 126.8 (Cq), 126.3 (CH) 125.9 (CH), 123.9 (CH).
^{29}Si NMR (59.64 MHz, $CDCl_3$): δ -1.1.
GC-MS: t_R = 15.689; m/z = 260.0.
MP (°C): 48-50.
Anal. Calcd for $C_{10}H_7Cl_3Si$: C, 45.91; H, 2.70. Found: C, 49.19; H, 2.56.

3.4.3 Trichloro(naphthalen-2-yl)silane (8)



trichloro(naphthalen-2-yl)silane

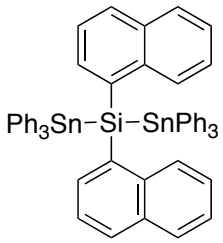
261.61 [g/mol]

A flask furnished with a dropping funnel and a reflux condenser was charged with 0.76 g (1.1 eq., 31 mmol) magnesium turnings in 40 ml THF as well as the dropping funnel was filled with a solution of 5.81 g 2-bromonaphthalene (1 eq., 29 mmol) in 40 ml THF. After the Grignard reaction was started with dibromoethane, the ethereal solution was added dropwise and the reaction mixture was refluxed for 2 h. A second flask furnished with a reflux condenser was charged with 10 ml tetrachlorosilane (8 eq., 232 mmol, 14.83 g) in 20ml THF. Then 20ml of the Grignard solution were added dropwise and the mixture refluxed for 2 hours to obtain a brownish solution. The residue was taken up in dichloromethane and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 0.6 g (62%) of a yellowish oil were obtained by vacuum distillation.

^{1}H NMR (300.22 MHz, $CDCl_3$): δ 8.28 (d, 1H), 7.90 (d, 1H), 7.83 (d, 1H), 7.73 (d, 1H), 7.70 (d, 1H), 7.53- 7.52 (dd, 1H), 7.51- 7.50 (dd, 1H).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.5 (CH), 135.1 (Cq), 132.3 (Cq), 128.9 (Cq), 128.5 (CH), 128.4 (CH) 127.9 (CH), 127.4 (CH), 127.0 (CH), 125.8 (CH).
^{29}Si NMR (59.64 MHz, $CDCl_3$): δ -0.9.
GC-MS: t_R = 15.563; m/z = 260.0.
MP (°C): 42-44.
Anal. Calcd for $C_{10}H_7Cl_3Si$: C, 45.91; H, 2.70. Found: C, 48.01; H, 3.05.

3.5 Synthesis and Applications of the Arylchlorosilanes

3.5.1 2,2-Di(naphthalen-1-yl)-1,1,1,3,3,3-hexaphenyldistannasilane (9)



2,2-di(naphthalen-1-yl)-1,1,1,3,3,3-hexaphenyldistannasilane

982.45 [g/mol]

A flask furnished with a reflux condenser was charged with 0.25 g (2 eq., 11 mmol) sodium, 3.96g (1 eq., 5.6 mmol) 1,1,1,2,2,2-hexaphenyldistannane in 25 ml THF and was refluxed overnight to give a dark green solution. The solution was added to a mixture of 2.06 g **(1)** (1 eq., 5.6 mmol) in 40 ml THF at 0°C. The reaction mixture was stirred for 3 h and allowed to warm up to room temperature. The solvent was removed under reduced pressure. The residue was taken up in dichloromethane and insoluble salt was filtered through celite. The filtrate was concentrated under reduced pressure and 0.92 g (17%) of a white solid were obtained.

^{13}C NMR (75.5 MHz, dbenzene): δ 140.4 (^{1}J($^{13}C_{ipso}$-^{119}Sn)= 415 Hz), (^{1}J($^{13}C_{ipso}$-^{117}Sn)= 396 Hz), 138.0 (^{2}J($^{13}C_{ortho}$-$^{119/117}$Sn)= 37 Hz), 137.5 ($C_{q,Naph}$), 133.9 ($C_{q,Naph}$),133.4 ($C_{q,Naph}$), 131.2 (CH_{Naph}), 130.4 (CH_{Naph}), 129.1 (CH_{Naph}), 129.0 (CH_{Naph}),128.8 (^{2}J($^{13}C_{meta}$-$^{119/117}$Sn)= 46 Hz), 128.7 (^{2}J($^{13}C_{para}$-$^{119/117}$Sn)= n.o.), 126.3 (CH_{Naph}), 126.2 (CH_{Naph}), 125.8 (CH_{Naph}).

^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ -162 ppm (^{1}J(^{119}Sn-^{29}Si)= 518 Hz); (^{2}J(^{119}Sn-^{117}Sn)= 658 Hz); (^{1}J(^{119}Sn-^{13}C)= 413 Hz).

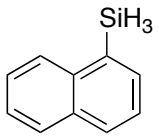
^{29}Si NMR (59.64 MHz, $CDCl_3$): δ -27 ppm.

MS (EI): m/e (relative intensity)= 982.1276 [M^+], [M^+]$_{theo.}$ = 982.1270.

MP (°C): 180-181.

Anal. Calcd for $C_{56}H_{44}SiSn_2$: C, 68.46; H, 4.51. Found: C, 68.66.19; H, 4.55.

3.5.2 Naphthalen-1-ylsilane (10)



naphthalen-1-ylsilane

158.27 [g/mol]

A flask furnished with reflux condenser and a dropping funnel was charged with 3.86 g LAH pellets (1.67 eq., 102 mmol) and 100 ml diethyl ether. The suspension was stirred at room temperature until all of the LAH was dissolved. A solution of 15.82 g **(1)** (1 eq, 60.8 mmol) in 100 ml diethyl ether and 25 ml THF was added slowly via the dropping funnel under cooling to 0°C. The reaction mixture was stirred for 3 h and allowed to warm up to room temperature. Subsequently, degassed H_2SO_4 (conc. 10%) was added. Then the phases were separated *via* a cannula, the aqueous layer was washed twice with ether and dried over $CaCl_2$. Furthermore the phases were separated, solvent was evaporated under reduced pressure to afford 5.77 g (60%) of a brownish oil.

^{1}H NMR (300.22 MHz, dbenzene): δ 7.86 (d, 1H), 7.54 (m, 3H), 7.18 (dd, 2H), 7.08 (dd, 1H) 4.44 (s, $^{1}J(^{1}H\text{-}^{29}Si)$= 200.708 Hz, 3H).
^{13}C NMR (75.5 MHz, dbenzene): δ 137.9 (Cq) 137.1 (CH), 133.5 (Cq), 131.2 (CH), 129.1 (CH), 128.1 (CH) 127.3 (Cq), 126.7 (CH), 126.1 (CH), 125.5 (CH).
^{29}Si NMR (59.64 MHz, dbenzene): δ -62,819 (s).
GC-MS: t_R = 11.797; m/z = 158.1.

Chapter 4

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Chapter 5

Appendix

5.1 NMR Spectra

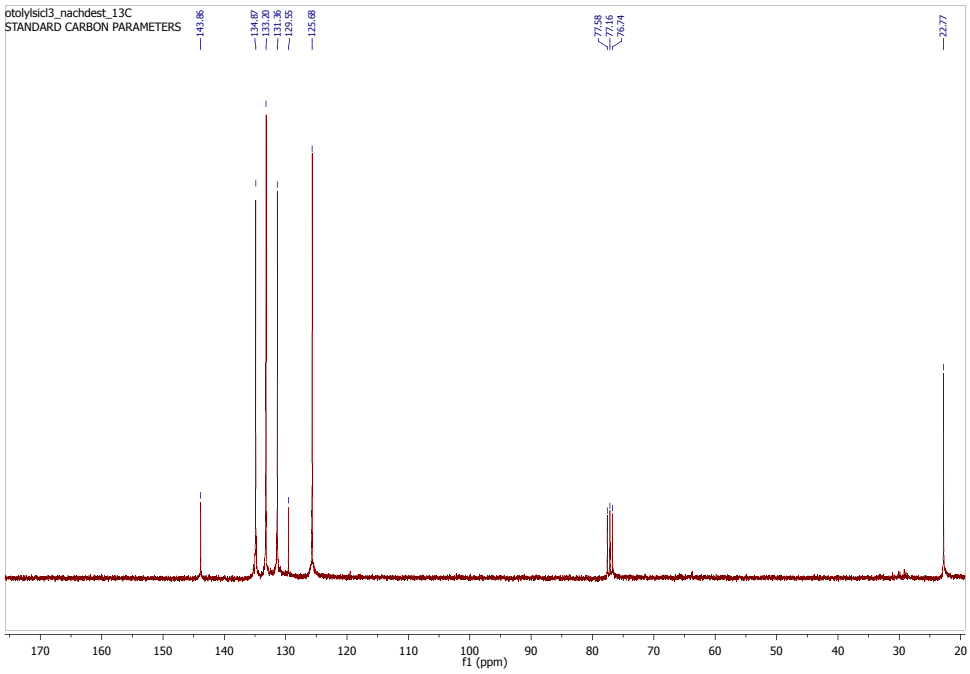

Figure 5.1: ^{13}C NMR of pure Trichloro(o-tolyl)silane after Distillation

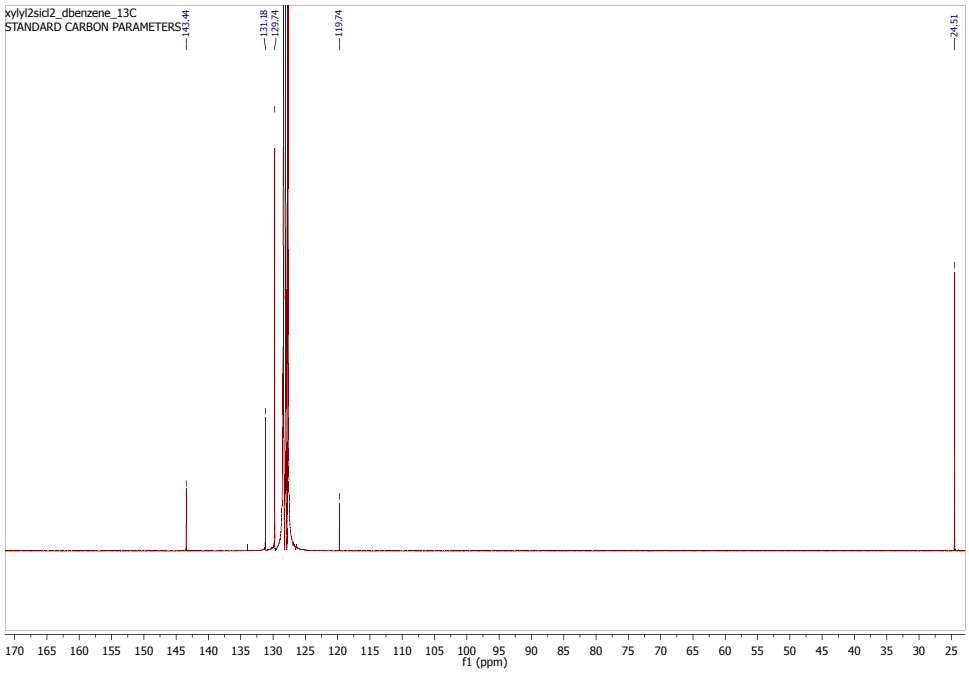

Figure 5.2: ^{13}C NMR of pure Dichlorobis(2,6-dimethylphenyl)silane after Extraction with Pentane

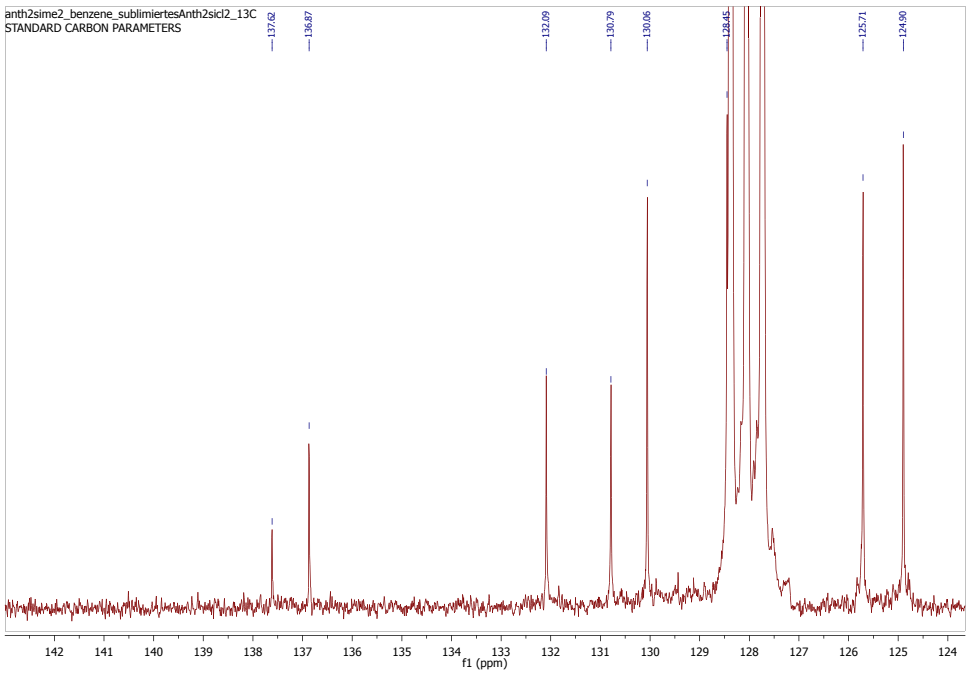

Figure 5.3: ^{13}C NMR of pure Di(anthracen-9-yl)dichlorosilane after Sublimation

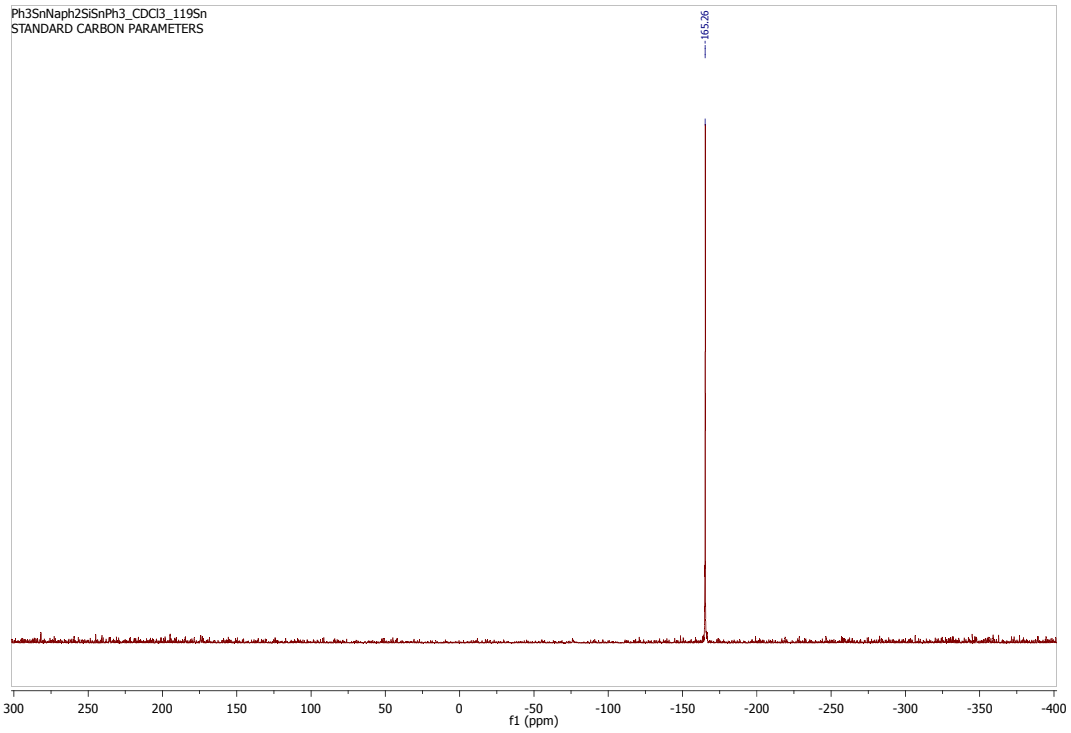

Figure 5.4: ^{119}Sn NMR of a Six- Membered Silyltin Cylce (Educt= Ph_6Sn_2; **1**; sodium; THF)

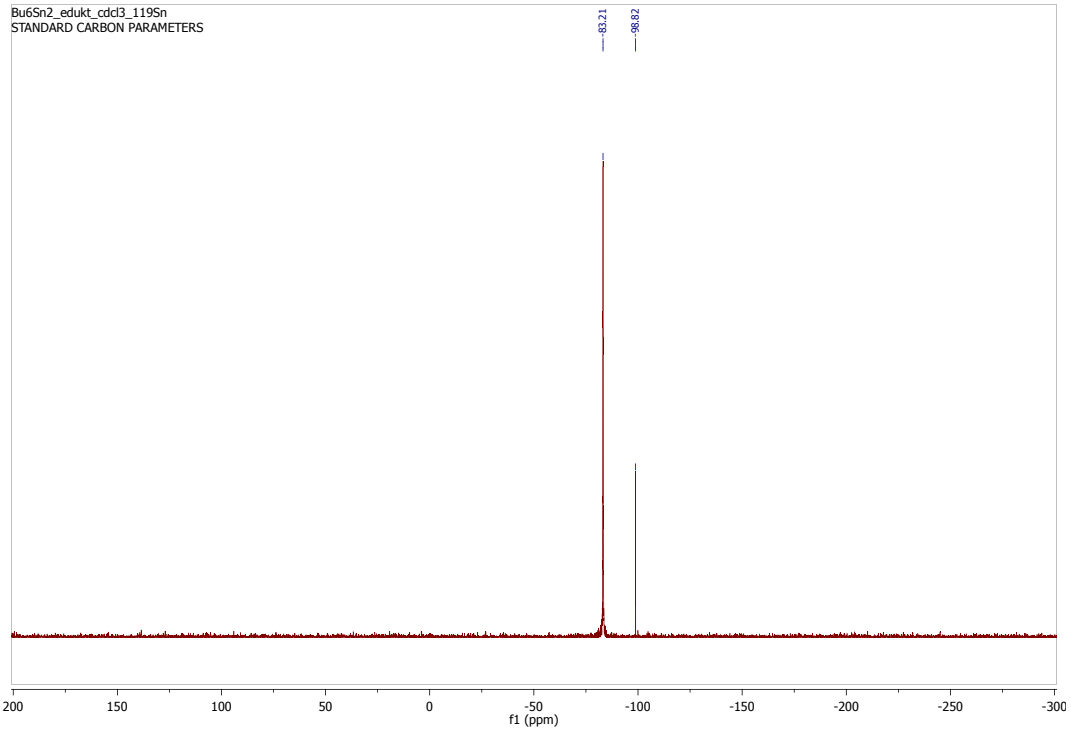

Figure 5.5: ^{119}Sn NMR of a Six- Membered Silyltin Cylce (Educt= Bu_3SnH; **1**; LDA; THF)

5.2 Crystal Structure Analysis Data

5.2.1 X-Ray Data of Trichloro-1-naphthylsilane

Empirical formula	$C_{10}H_7Cl_3Si$
Formula weight	261.60
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.9473(4) Å α= 90°.
	b = 9.0965(4) Å β = 93.312(2)°.
	c = 12.3302(6) Å γ = 90°.
Volume	1113.84(9) $Å^3$
Z	4
Density (calculated)	1.560 Mg/m^3
Absorption coefficient	0.885 mm^{-1}
F(000)	528
Crystal size 0.20 x 0.15 x 0.14 mm^3	
Theta range for data collection	2.05 to 27.10°.
Index ranges	-12<=h<=12, -11<=k<=11, -15<=l<=15
Reflections collected	31043
Independent reflections	2452 [R(int) = 0.1197]
Completeness to theta = 27.10°	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.3962
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2452 / 0 / 127
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0993
R indices (all data)	R1 = 0.0462, wR2 = 0.1066
Largest diff. peak and hole	0.495 and -0.331 $e.Å^{-3}$

Table 5.1: Crystallographic Data for Trichloro-1-naphthylsilane

5.2.2 X-Ray Data of Trichloro-2-naphthylsilane

Empirical formula	$C_{15}H_{11}Cl_3Si$
Formula weight	325.68
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 13.5797(8) Å α= 90°.
	b = 6.0837(4) Å β= 91.442(2)°.
	c = 17.6511(10) Å γ = 90°.
Volume	1457.78(15) $Å^3$
Z	4
Density (calculated)	1.484 Mg/m^3
Absorption coefficient	0.692 mm^{-1}
F(000)	664
Crystal size	0.10 x 0.05 x 0.03 mm^3
Theta range for data collection	1.87 to 27.10°.
Index ranges	-17<=h<=17, -7<=k<=7, -22<=l<=22
Reflections collected	34827
Independent reflections	3198 [R(int) = 0.0785]
Completeness to theta = 27.10°	99.5 %
Absorption correction	vSemi-empirical from equivalents
Max. and min. transmission	0.74 and 0.65
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3198 / 0 / 172
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0782
R indices (all data)	R1 = 0.0797, wR2 = 0.0907
Largest diff. peak and hole	0.449 and -0.446 $e.Å^{-3}$

Table 5.2: Crystallographic Data Trichloro-2-naphthylsilane

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Deutsche Fassung:

Beschluss der Curricula-Kommission für Bachelor-, Master- und Diplomstudien vom 10.11.2008

Genehmigung des Senates am 1.12.2008

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