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Polymer precursor synthesis and characterisation of functionalised 1-Naphthylsilanes

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Durch Wissenschaft wird bewiesen,
durch Intuition aber entdeckt.

Henri Poincare (1854 – 1912)

Danksagung

An dieser Stelle will ich die Möglichkeit nutzen, all jenen Danke zu sagen, die für das erfolgreiche Zustandekommen dieser Arbeit einen essentiellen Beitrag lieferten und deren Unterstützung maßgeblich zur Vollendung beigetragen hat.

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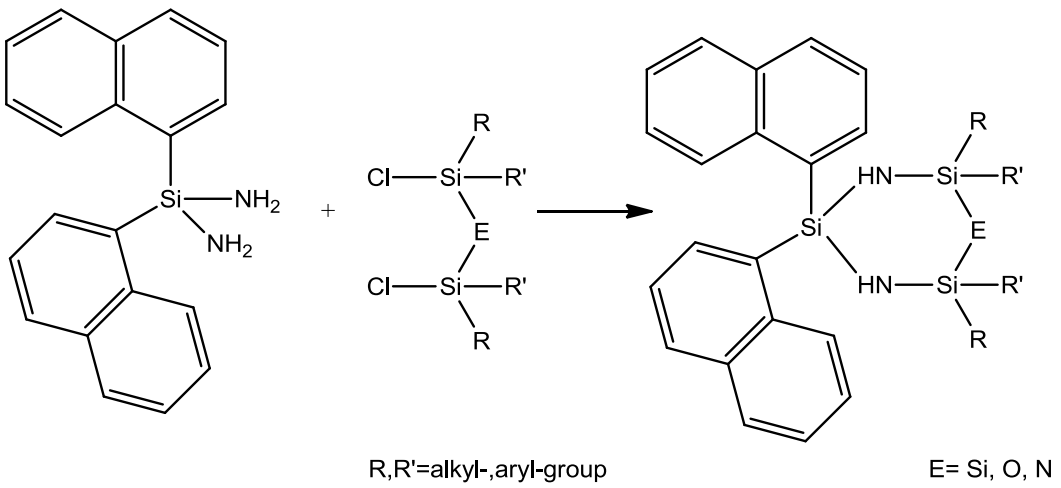
Abstract

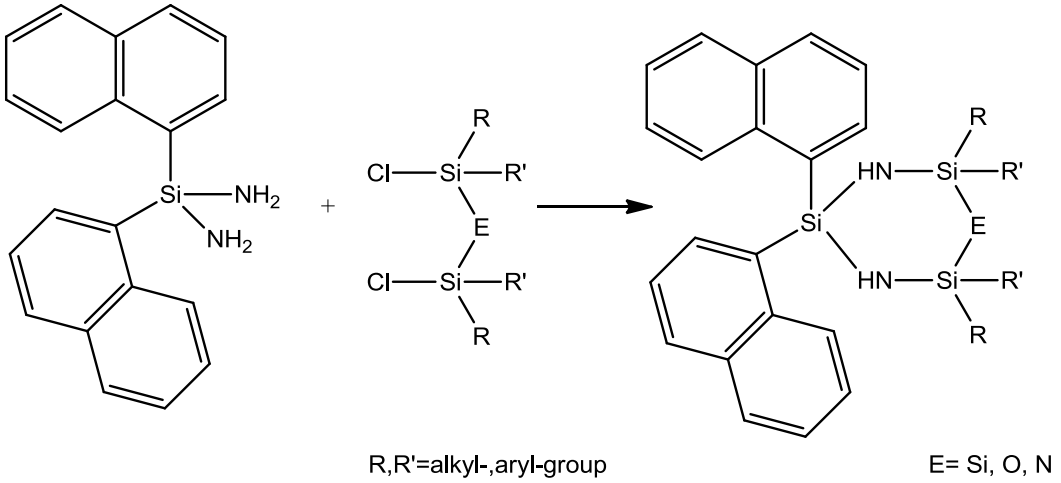
This work deals with the synthesis and characterisation of 1-naphthyl-substituted silicon amines, mostly the di-substituted compound, and initial ring-coupling attempts of the latter with provided α,ω-functionalised chloro-silanes, -siloxanes and -silazanes. Various 1-napthyl-substituted silicon amines were synthesised by standard preparation protocols serving as starting materials for the generation of cyclic systems. (see scheme below).



The cyclisation behaviour of $(1\text{-Naph})_2Si(NH_2)_2$ was investigated. Cyclocondensation of $(1\text{-Naph})_2Si(NH_2)_2$ led to a white solid. Elemental analysis, DI-MS and NMR measurements displayed a six-membered ring of the composition $((1\text{-Naph})_2SiNH)_3$. However, further investigations concerning the crystal structure, which should give the final proof and polymerisation attempts of the cycle have to be carried out.

Kurzzusammenfassung

Die vorliegende Arbeit beschäftigt sich mit der Synthese und Charakterisierung von 1-naphthyl-substituierten Aminosilanen, wobei das Hauptaugenmerk auf dem disubstituierten Aminosilan lag. Letzteres wurde durch Reaktion mit vorhanenden α,ω-funktionalisierten Chlorsilanen, -siloxanen und -silazanen zu Ringen umgesetzt. Die Synthese der 1-naphthyl-substituierten Aminosilane erfolgte nach Standardmethoden. Diese fungierten in weiterer Folge als Ausgangsmaterial für die Herstellung von zyklischen Systemen (siehe Reaktionsschema).



Weiters wurde das Zyklisierungsverhalten von $(1\text{-Naph})_2Si(NH_2)_2$ untersucht. Eine Zyclokondensation von $(1\text{-Naph})_2Si(NH_2)_2$ führte zur Bildung eines weißen Feststoffs. Elementaranalyse, DI-Massenspektrometrie and NMR Messungen weisen auf ein sechsgliedriges Ringsystem, mit der Zusammensetzung $((1\text{-Naph})_2SiNH)_3$, hin. Weitere Untersuchungen bezüglich der Kristallstruktur, die Sicherheit über das Vorliegen des Sechsringes geben soll, sowie Polymerisationsversuche der Verbindung, sollten im Fokus zukünftiger Forschung liegen.

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1 INTRODUCTION

Silicon is a widely used metal. Even in ancient times, silicon compounds were used for the production of glass. Nowadays especially organosilicon compounds have penetrated many different areas and are extensively used. Since 1940, the discovery of cyclosiloxanes, $(R_2SiO)_n$ (n= 3, 4), silicone polymers have played an important role in industry.[1] The use of polysiloxanes in different areas has expanded year by year and still dominates modern society. Oils, greases, rubbers, polishes, coatings and insulating materials are all based on polysiloxanes. Despite their widespread use, silicone polymers have properties that restrict their applicability. They cannot be used at higher temperatures than 300°C, and silicone rubbers lose their elasticity at temperatures below -80°C.[2] Technically speaking, the polymeric silicones in which organosilicon units are linked by Si−O−Si bonds are obtained from monomeric organohalosilanes by hydrolysis or methanolysis followed by polycondensation. Silicone production is thus the largest consumer of monomeric silanes.[3] An interesting alternative to polysiloxanes are polysilazanes where the oxygen linkage of the organosilicon unit is replaced by an N-H group (Figure 1).

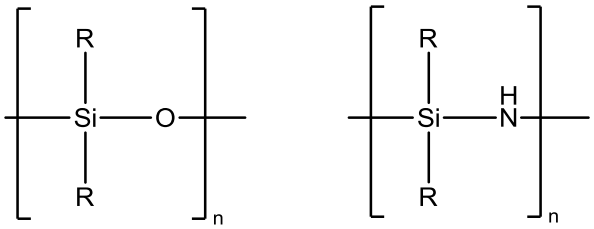


Figure 1: Simplest repeating unit (SRU) of polysiloxane and polysilazanes

Over the years, the interest in such Si-N containing compounds has increased. A significant amount focuses on the synthesis of polymeric Si-N compounds. As the N-H group of the silazane is isoelectronic with the silicon oxygen atom, it seems logical that the silazanes should be studied in an effort to obtain materials with improved properties over those of polysiloxanes.[4] Polysilazanes show many interesting properties, including a high resistance towards extreme environments.[4] Thus, the organosilicon polymers that have been found to be useful precursors for high-performance silicon-

based ceramics are polysilazanes. In order to obtain polysilazanes with controlled architecture, appropriate precursors are required. The focus of this work lies on the synthesis and characterisation of Si-N containing polymer precursors carrying sterically demanding organic substituents, i. e. 1-naphthyl, at silicon. Initially, the controlled synthesis of monomeric diamino(di-1-naphthyl)silane should be achieved. In a further step, literature known synthetic methods should be used to achieve ring coupling between provided α,ω-functionalised- chlorosilanes, siloxanes and silazanes with $Naph_2Si(NH_2)_2$. In the case of cyclic monomers, ring-opening polymerization (ROP) is a powerful tool to have a high level of control of the polymer architectures.[5] Based on this knowledge, polymers with Si-N containing repeating units should be made from the produced ring systems.

2 LITERATURE OVERVIEW

2.1 HISTORY OF SILICON-NITROGEN COMPOUNDS

The study of silicon nitrogen compounds dates back to 1889 when Reynolds reported the preparation of tetraaminosilanes; silicotetraphenylamide, *para*- and *ortho*-silicotetratolylamides, α- and β-silicotetranaphthylamides.[4] In 1960, a comprehensive review about silicon-nitrogen compounds was published by Fessenden and Fessenden.[6] This review already cites 221 references for known silicon-nitrogen compounds. Concurrently, new Si-N containing polymers have been reported.

For example, Henglein et al. obtained polymers of the type $-[Si(CH_3)_2-NH-(CH_2)_x-NH]_n-$ by reacting dimethyldichlorosilane with various diamines.[7]

2.2 SILYLAMINES

2.2.1 Synthesis from halosilanes

The most commonly used method to obtain silylamines is the treatment of a halosilane with ammonia or a protic amine. During the reaction, the released hydrogen halide precipitates as the

ammonium or amine salt, shown in Scheme 1.[8] Without removing the formed salt the reaction is reversible.[6]

$$R_{4-n}SiX_n + 2n\ R'NH_2 \rightleftharpoons R_{4-n}Si(NHR')_n + nR'NH_3X$$

Scheme 1: General reaction of halosilanes with primary amines or ammonia

Due to their reactivity and availability, chlorosilanes are most commonly used.[8] Nevertheless, there are also some reports on the use of fluorosilanes.[9]

2.2.1.1 Synthesis from monohalosilanes

The treatment of a monohalosilane with ammonia usually results in the complete silylation of the ammonia. When silyl chloride is treated with ammonia, trisilylamine (Scheme 2) can be obtained in yields up to 80 %.[6]

$$H_3SiCl + NH_3 \longrightarrow (H_3Si)_3N$$

Scheme 2: Silylchloride treated with ammonia

When primary amines as nitrogen source are used, as illustrated in Scheme 3, there is also a great tendency towards complete silylation.

$$H_3SiCl + CH_3NH_2 \longrightarrow CH_3N(SiH_3)_2$$

Scheme 3: Silylchloride treated with primary amine

As the size of the groups attached to the silicon is increased, the tendency towards complete silylation is decreased. Already the transition from monohalosilane to methyl-chlorosilane leads to the preferred formation of disilazane instead of trisilylamine.[6] Also ethyldimethyl-, diethylmethylchlorosilane and dimethylphenylbromosilane yield the corresponding disilazane upon treatment with ammonia.[6] Only higher triorganochlorosilanes result in silylamines. Triphenylaminosilane can be synthesised by the treatment of triphenylchlorosilane with ammonia (Scheme 4).[10]

$$(C_6H_5)_3SiCl + NH_3 \longrightarrow (C_6H_5)_3SiNH_2 + NH_4Cl$$

Scheme 4: Triphenylchlorosilane treated with ammonia

In 1953, Chugunov et al. reported on the successful synthesis of various 1-naphthylaminosilanes. The reactions performed are shown in Scheme 5 and Scheme 6.[9]

$$(1\text{-}C_{10}H_7)_3SiF + NaNH_2 \longrightarrow (1\text{-}C_{10}H_7)_3SiNH_2 + NaF$$

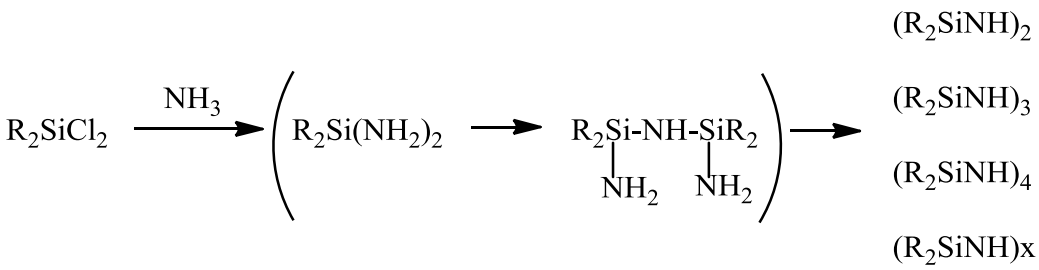
Scheme 5: Synthesis of amino(tri-1-naphthyl)silane

$$2\ (1\text{-}C_{10}H_7)_3SiF + NaNH(C_6H_5) \longrightarrow (1\text{-}C_{10}H_7)_3SiNH(C_6H_5) + NaF + (1\text{-}C_{10}H_7)_3SiF$$

Scheme 6: Synthesis of diamino(di-1-naphthyl)silane

2.2.1.2 Synthesis from dihalosilanes

The reaction of a dihalosilane with ammonia or an amine results in the formation of a silylamine, a cyclosilazane or a polysilazane depending on the organic substituents at the silicon atom, which is shown in Scheme 7.[11]



Scheme 7: Ammonolysis of dichlorosilanes to cyclosilazanes and polysilazanes

It has been observed that by using dihalosilanes with little steric hinderance, the cyclosilazanes and the polysilazanes predominate as the reaction products, while with sterically hindered dihalosilanes, silanediamines can be isolated.[6]

The condensation reactions might be due to silylamine condensation or reaction between silylamines and halosilanes. It is probable that both reactions occur simultaneously.[6]

Thus, the successful synthesis of di(1-naphthyl)-diaminosilane, di(t-butyl)diaminosilane and dimesityl-diaminosilane have been reported (Scheme 8).[9, 12, 13]

$$R_2SiX_2 + NH_3 \longrightarrow R_2Si(NH_2)_2$$

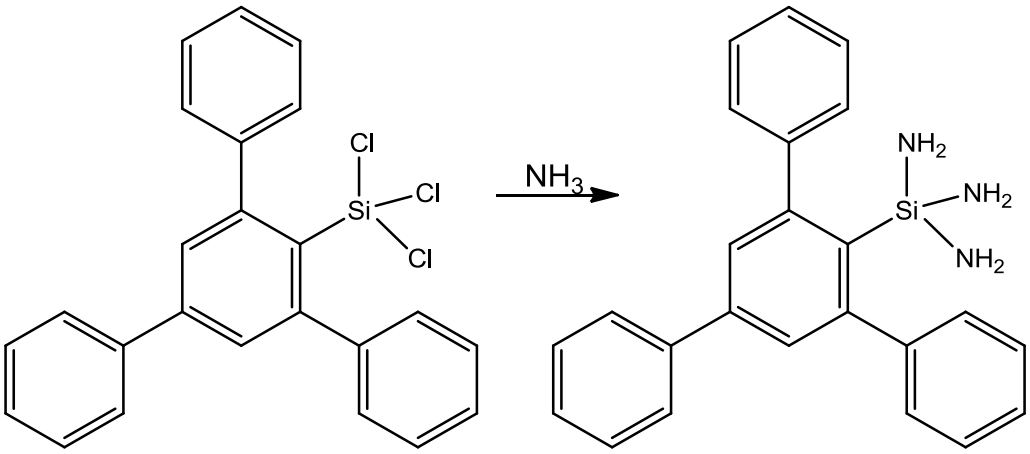
R= 1-naphthyl; ^{t}butyl or 2,4,6-$Me_3C_6H_2$

Scheme 8: Literature known diaminosilanes with bulky substituents

It could be shown that an asymmetrical substitution pattern of organic substituents on the silicon with at least one ^{t}butyl group allows the isolation of stable silanediamines. Based on that knowledge, methyl-, phenyl- and hexadecyl-^{t}butyldichlorosilanes could be converted to stable silanediamines.[13]

2.2.1.3 Synthesis from trihalosilanes

The reaction of a trihalosilane with ammonia results in the formation of polysilazanes. There is only one reported case of a silanetriamine being formed, carrying a bulky organic substituent at the silicon atom, illustrated in Scheme 9.[12] The compound has been characterised by single crystal diffraction analysis.



Scheme 9: Only literature known triaminosilane[12]

Chugunov et al. tried to synthesise 1-naphthyl-triaminosilane from 1-naphthyltrifluorosilane and ammonia, but only obtained uncharacterised polymeric material.[9]

2.3 CYCLOSILAZANES

2.3.1 Nomenclature[6]

Compounds of the type $(NHSiH_2)_nNHSiH_3$ are assigned to the silazanes series. For compounds of the type $(R_2SiNH)_n$ the prefix cyclo is being attached to silazane, the number of silicon atoms involved in the ring systems is included in the name; for example cyclodisilazane, cyclotrisilazane etc.

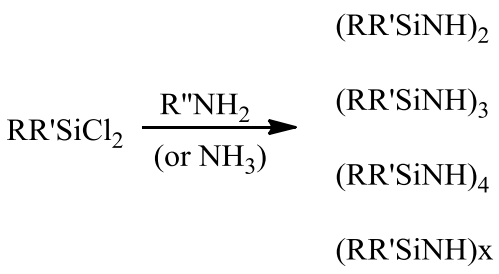
2.3.2 Synthetic Methods[14]

Saturated silicon-nitrogen rings of the type $(R_2SiNR')_n$ are isoelectronic with the corresponding silicon-oxygen rings $(R_2SiO)_n$. Contrary to cyclosiloxanes, however, ring sizes are limited to four-, six- and eight-membered rings for the cyclosilazanes.[14]

The synthesis of ring systems usually occurs *via* the formation of linear intermediates which may either cyclize or undergo chain propagation to form a polymer. In this part, only the generation of cyclic systems will be discussed.[14]

2.3.2.1 Cyclocondensation

Scheme 10 illustrates the most versatile synthetic method to generate rings with alternating silicon and nitrogen atoms.



Scheme 10: Synthetic method to generate cyclosilazanes or polysilazanes

The method involves cyclocondensation of dichlorodiorganosilanes (R_2SiCl_2) with primary amines $R'NH_2$ or ammonia. By using different substituents at the silicon atom or by using dichlorodiorganosilanes of the type $RR'SiCl_2$ ($R \neq R'$) the method can be adapted for the preparation of heterocycles with different substituents.[14] Unsymmetrical systems are made by salt-elimination

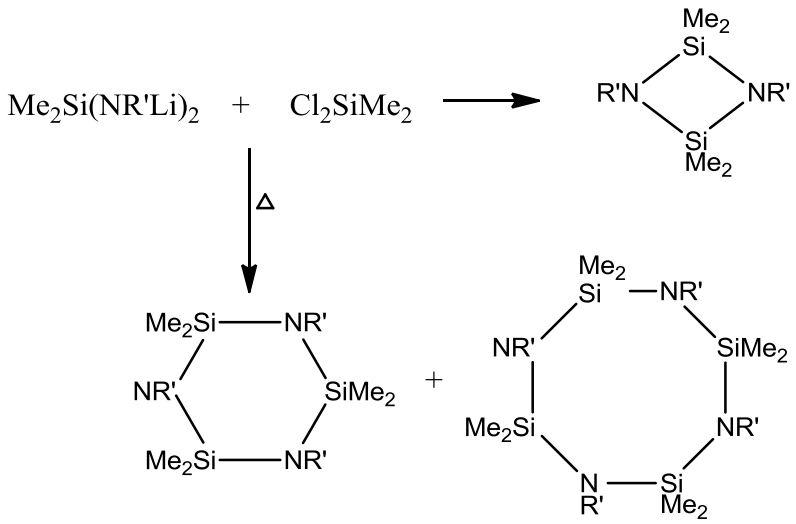
reactions. This approach is also used to incorporate other *p*-block elements into Si-N rings by the reaction of $R_2Si(NLiR'')_2$ with main group element halides.[14]

2.3.2.2 Dehydrogenative coupling

Another method is the dehydrogenative coupling, which includes the loss of H_2 from organoelement dihydrides. This route is promoted thermally, photochemically or by using a catalyst.[15]

2.3.3 Ring size

Low temperatures and short reaction times lead predominately to the kinetically favoured four-membered rings. Otherwise, the thermodynamically preferred products, the six- and eight-membered rings, are formed as exemplified in Scheme 11.[14]



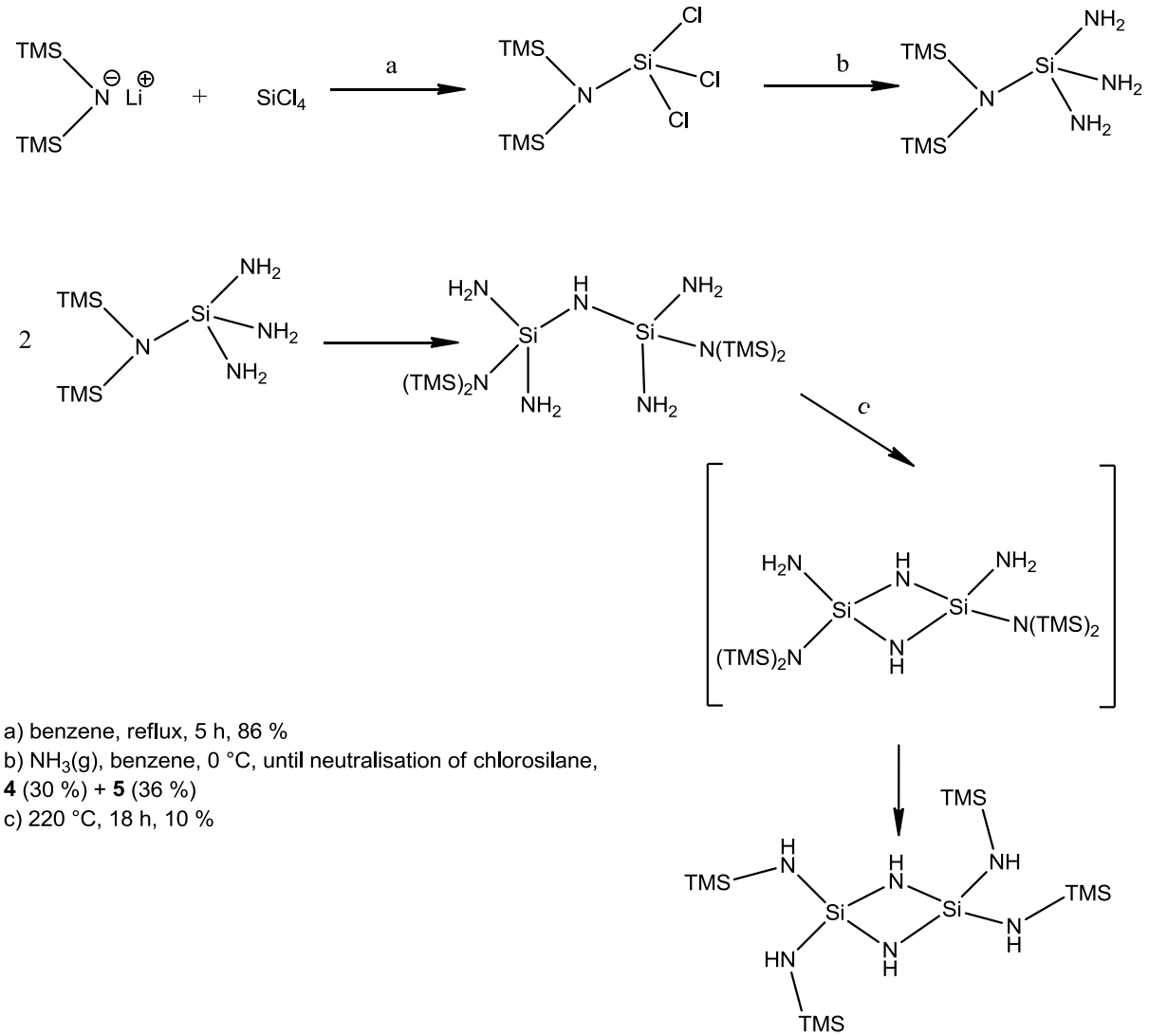
Scheme 11: Kinetically and thermodynamically favoured cyclosilazane products

2.3.4 Cyclodisilazanes

Cyclodisilazanes were first mentioned when NMR spectroscopy and X-ray analysis were in their beginnings.[16] Without those two analytical methods, it was not possible to fully characterise such compounds, as it was not easy to distinguish them from 6- and 8- membered isomers.

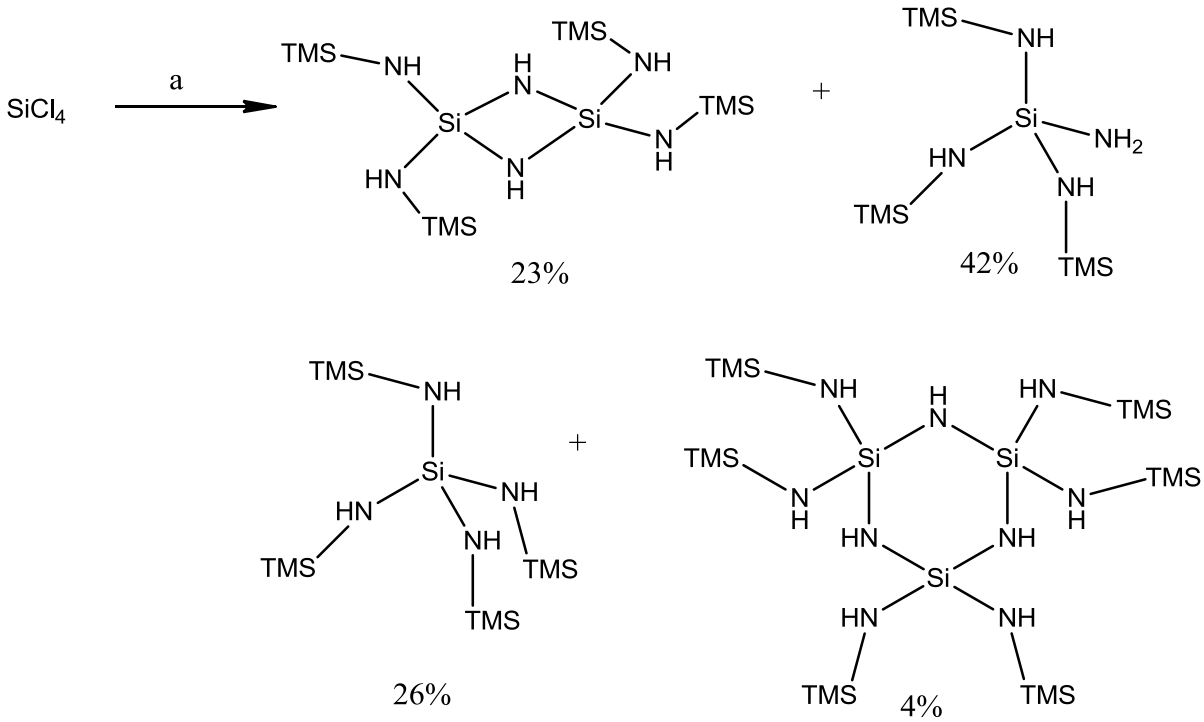
2.3.4.1 *Preparation by ammonolysis of chlorosilanes*[17]

Reaction Scheme 12 summarizes the stepwise synthetic pathway of the ammonolysis of chlorosilanes. At first, lithiated hexamethyldisilazane is reacted with $SiCl_4$, which gives the trichlorosilazane. The latter is treated with ammonia at 0 °C giving the triaminosilazane as well as a disilazane, which is already an *in-situ* generated condensation product. Through thermal promotion, the cyclodisilazane is obtained in very low yields.[18]



Scheme 12: Ammonolysis of chlorosilanes

It was also shown that the cyclodisilazane can also be synthesised in a one-pot reaction of $SiCl_4$ and TMSCl in the presence of liquid ammonia, as shown in Scheme 13. The reaction is not very selective, thus other products were also obtained.

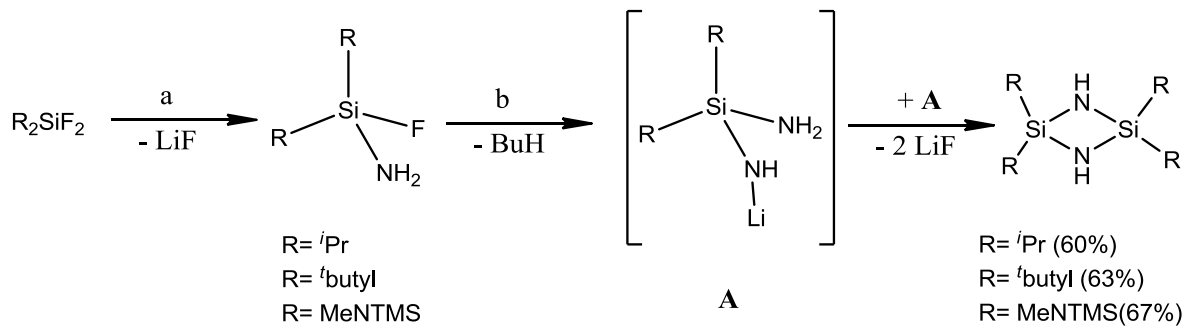


a) TMSCl, NH_3 (l), hexane, -55 °C

Scheme 13: One pot reaction of silicontetrachloride, trimethylsilyl chloride and ammonia

2.3.4.2 Preparation by addition of lithium amides to fluorosilanes

As the formation of 6- and 8-membered rings are favoured, harder nucleophiles such as lithium amides were used.[19,20,21] In this experiment, a dialkyldifluorosilane is reacted with the lithium amide, giving a fluoroaminosilane. In the consecutive step, the fluoroaminosilane is lithiated with ^{n}BuLi. These lithium salts can dimerise upon the release of LiF unless there is no other electrophile in the reaction equilibria. Scheme 14 shows the reaction pathway of different organic substituents used.[22]

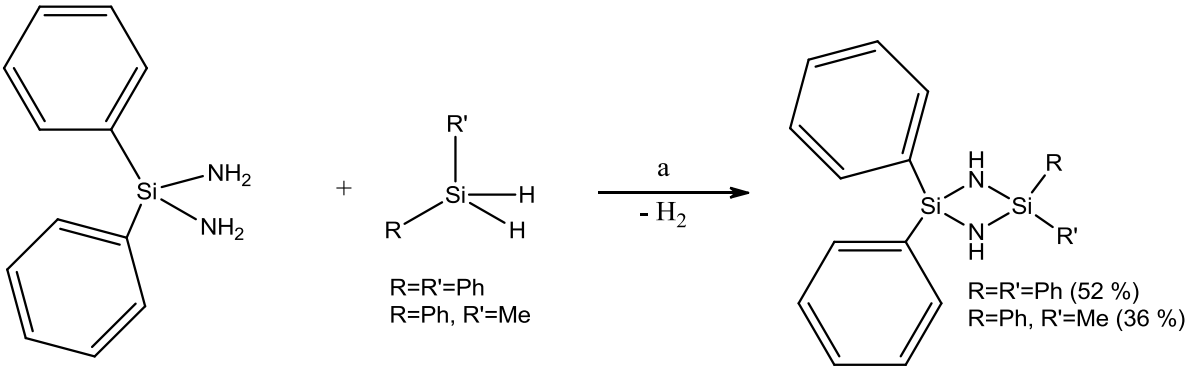


a) $LiNH_2$, hexane, r.t., 2 h, short heating to melt $LiNH_2$
b) ^{n}butylLi, hexane, 0 °C, 2 h, reflux, 1 h

Scheme 14: Addition of lithium amides to fluorosilanes

2.3.4.3 Preparation by dehydrogenative coupling[23]

Silonate base TMSO-K^+ was used as a catalyst for the coupling reaction shown in Scheme 15.



a) $TMSO^-K^+$ (cat.), neat, 20 °C - 170 °C, until hydrogen evolution stops

Scheme 15: Dehydrogenative coupling mechanism with silonate base

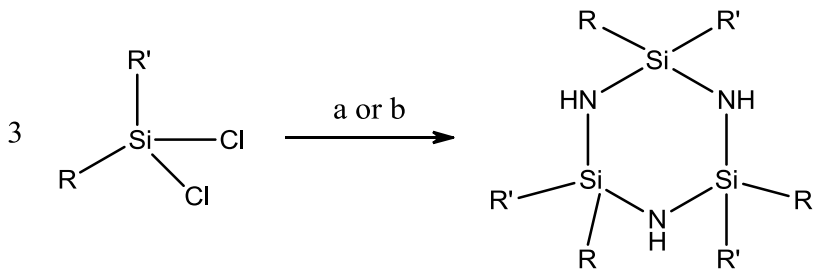
2.3.5 Cyclotrisilazanes

2.3.5.1 Preparation by ammonolysis of chlorosilanes[17]

The first synthetically useful method, which describes the formation of cyclotrisilazanes in detail, was published in 1948. The successful synthesis of hexamethylcyclotrisilazane (HMCTS) from the addition

of dimethylchlorosilane to liquid ammonia was reported.[24] The process also generated the octamethylcyclotetrasilazane (OMCTS), linear silazanes and polymeric silazanes as side products.

Scheme 16 illustrates the most commonly used and cited synthetic pathway to generate cyclotrisilazanes.[17]



a) NH_3 (l), neat, -78 °C - r.t.;
b) NH_3 (g), benzene or toluene or Et_2O, -78 °C or r.t. or reflux

Scheme 16: Synthetic pathway to generate cyclotrisilazanes

A large amount of symmetrically substituted cyclotrisilazane derivatives have been prepared by this method, an overview is given in Table 1.[17]

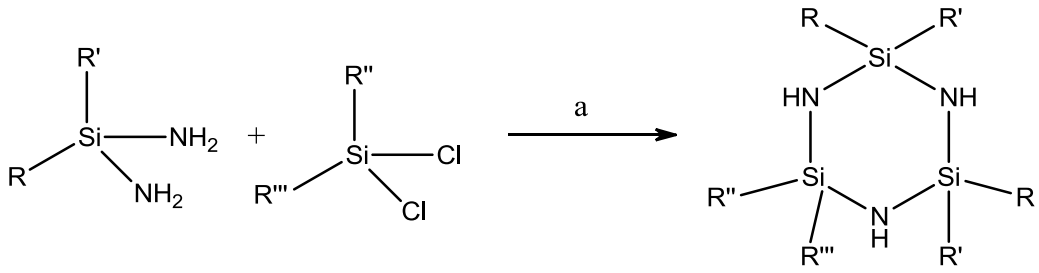
Table 1: Reported cyclotrisilazanes[17] - a summary

R	R'	Method	Melting point	Boiling point
Me	Me	a	-10 °C	188 °C (760 Torr)
Et	Et	a	-41 °C	150 °C (10 Torr)
Me	Et	b	-	91-93 °C (3 Torr)
Me	^{n}butyl	b	-	126-128 °C (1 Torr)
Me	^{n}Hex	b	-	171-173 °C (1 Torr)
Me	^{n}Oct	b	-	185-189 °C (1 Torr)
Me	^{n}Non	b	-	233-234 °C (1 Torr)
Et	^{n}Oct	b	-	224-228 °C (1 Torr)
Ph	Ph	b	213 °C	decomp. at 369 °C
Me	Ph	b	115 -116 °C	218-220 °C (1 Torr)
iPrO	^{i}PrO	b	-	147 °C (4 Torr)
^{n}butylO	^{n}butylO	b	-	245-250 °C (12 Torr)
H	Et	b	-	62 °C (0.5 Torr)
H	^{i}Pr	b	-	87 °C (1 Torr)
nBu	^{n}butyl	b	-	193 °C (2 Torr)
Me	^{i}Pr	b	-	94-96 °C (1 Torr)
Me	^{t}ButylO	b	-	109-110 °C (Torr)
Ph	^{i}Pr	b	-	227-230 °C (1 Torr)
Me	^{i}butyl	b	-	131-132 °C (1Torr
Me	cycHex	b	-	192-195 °C (1 Torr)

Me	$Ph(CH_2)_2$	b	-	263-265 °C (3 Torr)
Me	$(CH_2)_3CN$	b	-	256-260 °C (1.5 Torr)
Et	$Ph(CH_2)_2$	b	-	270-275 °C (2.6 Torr)
Me	$CH_2CH(Me)(Ph)$	b	-	245 °C (1.5 Torr)
Et	$CH_2CH(Me)(Ph)$	b	-	360 °C (2.5 Torr)
Me	$CH_2CH(Me)(CO_2Me)$	b	-	184-187 °C (0.2 Torr)
Et	$CH_2CH(Me)(CO_2Me)$	b	-	252-255 °C (3 Torr)
Me	$CH{=}CH_2$	b	-	100 °C (7 Torr)

2.3.5.2 Preparation by aminolysis of dichlorosilanes

Another approach to make cyclotrisilazanes is the reaction of a diaminosilanes with a dichlorosilane, which is illustrated in Scheme 17. The reaction is carried out in diethylether and in the presence of the auxiliary base Et_3N, which neutralises the HCl, resulting from the reaction.[25]



a) Et_3N, Et_2O - toluene, -70 °C - reflux, 6 h

Scheme 17: Aminolysis of dichlorosilanes

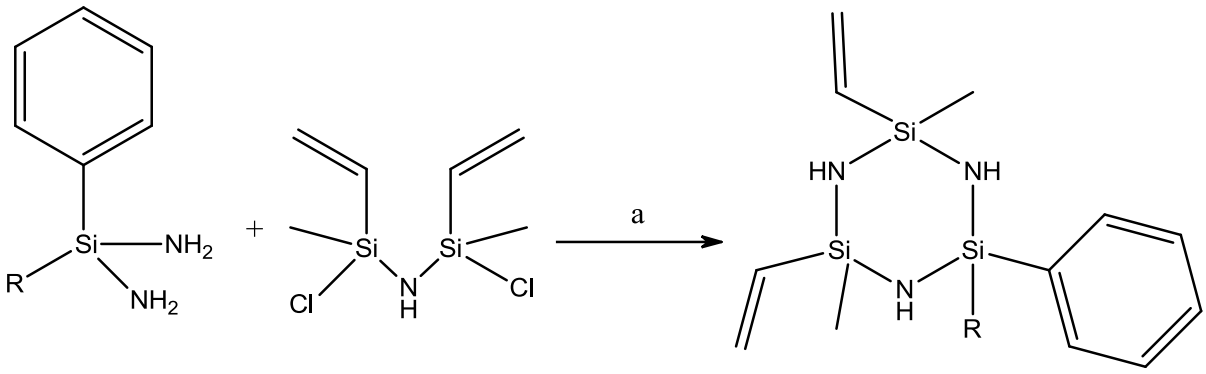
This method is used for the preparation of aryl-substituted compounds, a summary of literature known compounds are listed in Table 2.[17]

Table 2: Reported cyclotrisilazanes with bulky organic substituents[17]

Diaminosilane		**Dichlorosilane**		**Product**					
R	R'	R''	R'''	R	R'	R''	R'''	**Melting point**	**Boiling point**
Ph	Ph	Me	CH=CH2	Ph	Ph	Me	CH=CH2	112 °C	230-238 °C (1 Torr)
Ph	Me	Me	CH=CH2	Ph	Me	Me	CH=CH2	-	175-180 °C (1 Torr)
Ph	Ph	Me	H	Ph	Ph	Me	H	121-123 °C	240-245 °C (2 Torr)
Ph	Me	Me	H	Ph	Me	Me	H	-	168-172 °C (1 Torr)

2.3.5.3 *Preparation by aminolysis of dichlorosilazanes*[17]

By reacting diaminosilazanes with acyclic dichlorosilazanes, cyclotrisilazanes can be obtained.[25] This method also proceeds in the presence of Et_3N base, as exemplified in Scheme 18.



a) Et_3N, Et_2O - toluene, -70 °C - reflux, 6 h

Scheme 18: Aminolysis of dichlorosilazanes

Concerning Scheme 18, phenyl- and methyl substituents were used. The physical data of the known compounds is summarised below. (Table 3)[17]

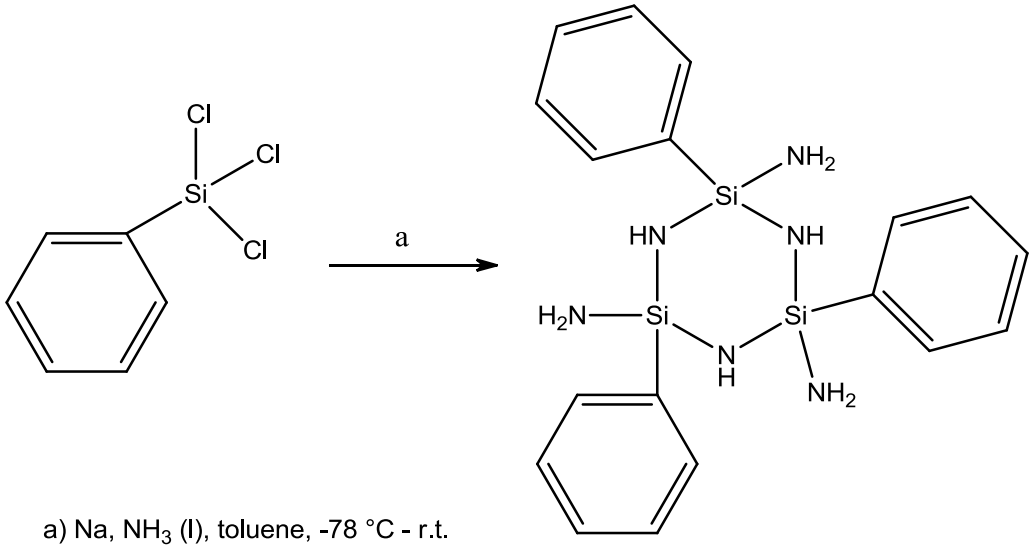
Table 3: Physical data of reported cyclotrisilazanes

R	Melting point	Boiling point
Ph	38-40 °C	170-172 °C (1 Torr)
Me	-	106-110 °C (1 Torr)

There are more synthetic routes reported on the synthesis of cyclotrisilazanes by ammonolysis of chlorosilanes such as the simultaneous ammonolysis of dichlorosilanes with trichlorosilanes and the ammonolysis of tetrachlorosilane, but they will not be closer discussed here, as it is stated that both methods were unsuitable for the preparation of cyclotrisilazanes when it comes to selectivity and yield.[17]

2.3.5.4 *Preparation by substitution of trichlorosilanes with metal amides*

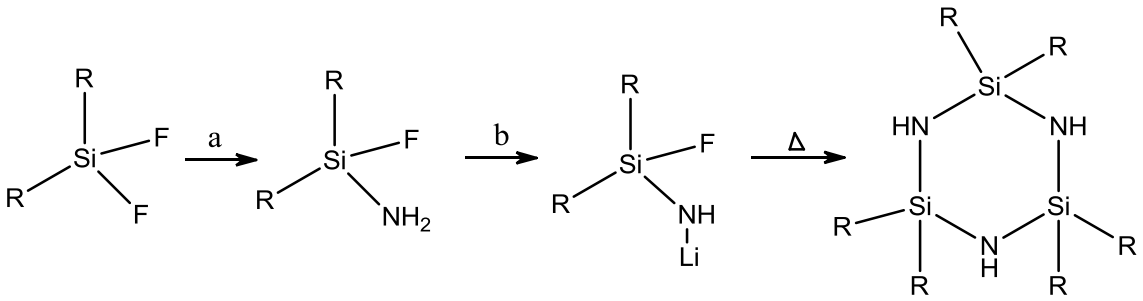
Cyclotrisilazanes can also be synthesised by reacting phenylchlorosilane with metallic sodium in liquid ammonia, which is shown in Scheme 19.[26] It is a nucleophilic substitution of halogens by the NH_2^- anion, which comes from the *in-situ* formed sodium amide.



Scheme 19: Preparation of cyclotrisilazanes via substitution with sodium amide

The reaction mechanism is stated as the most effective synthetic approach to cyclotrisilazanes as far as yield is concerned (yield: 70 %).[17]

Another possibility is the use of lithium amide which is a very reactive nucleophile. Thus, it is used to convert di-^{i}propyldifluorosilane and di-^{t}butyldifluorosilane to the corresponding cyclotrisilazane displayed in Scheme 20.[20,19]

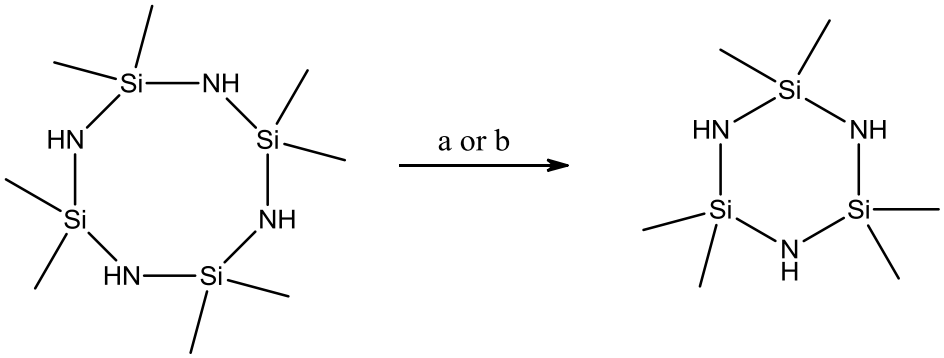


Scheme 20: Preparation of cyclotrisilazanes via substitution with lithium amide

The ^{t}butyl derivative is the bulkiest known cyclotrisilazane that cannot be prepared from di-^{t}butyldiaminosilane by direct ammonolysis.[13] The synthetic method described in Scheme 20 is the only way to access the ^{t}butyl substituted cyclotrisilazane.

2.3.5.5 Preparation by contraction of octamethylcyclotetrasilazane

As demonstrated in Scheme 21, octamethylcyclotetrasilazane (OMCTS) is capable of ring contraction to form the 6-membered ring. This is achieved by the use of acid-catalysts and high temperatures. When $AlCl_3$ or $(NH_4)_2SO_4$ were used while heating, OMCTS was almost quantitatively converted to HMCTS.[27]



a) $AlCl_3$ (3 mol%), 120-170 °C, 1 h, 98 %
b) $(NH_4)_2SO_4$ (3 mol%), 120-170 °C, 1 h, 91 %

Scheme 21: Ring contraction of OMCTS to HMCTS

2.3.6 Cyclotetrasilazanes

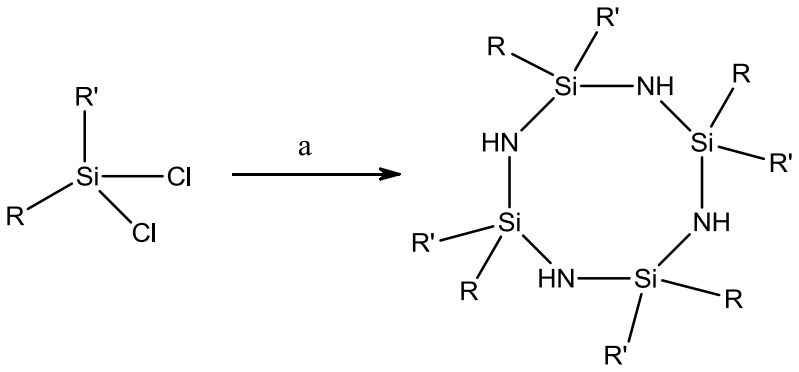
Basically, cyclotetrasilazanes are obtained with the same synthetic methods as cyclotrisilazanes; meaning that they mostly occur as side-products while preparing 6-membered rings.

2.3.6.1 Preparation by ammonolysis of chlorosilanes

2.3.6.1.1 Preparation by ammonolysis of dichlorosilanes

Ammonolysis was historically the first reported and still most frequently used method for the synthesis of cyclotetrasilazanes. Haber and Brewer obtained a mixture of the cyclotri- and cyclotetrasilazane when they reacted dimethyldichlorosilane with liquid ammonia, with 42 % and 25 % yield respectively.[24]

Scheme 22 represents the most frequently used route to get cyclotetrasilazanes.



a) NH_3 (l) or NH_3 (g), neat or solvent (benzene, toluene, Et_2O), -78 °C - r.t., or -30 °C - reflux

Scheme 22: Most frequently used method to get cyclotetrasilazanes

An overview of literature known compounds, which were obtained by following this reaction, are listed in Table 4.[17]

Table 4: Literature known cyclotetrasilazanes

R	R'	Melting point	Boiling point
Me	Me	97 °C	134-135 °C (35 Torr)
Et	Et	16 °C	192 °C (8 Torr)
Me	Ph	202-204 °C	-
Bn	Bn	165-165.5 °C	126-128 °C (1 Torr)
^{i}PrO	^{i}PrO	-	191 °C (2 Torr)
Me	Et	-	136-139 °C (3 Torr)
Me	^{n}butyl	-	162-165 °C (11 Torr)
Me	^{n}Hex	-	220-224 °C (1 Torr)
PhO	PhO	129 °C	-
Ph	EtO	-	289-292 °C (1 Torr)
Et	$(CH_2)_3CN$	-	295-300 °C (2 Torr)
H	Me	-	102 °C (0.5 Torr)
H	Et	-	54 °C (1 Torr)
O-$SiMe_2$-$SiMe_2$-O		172 °C	-

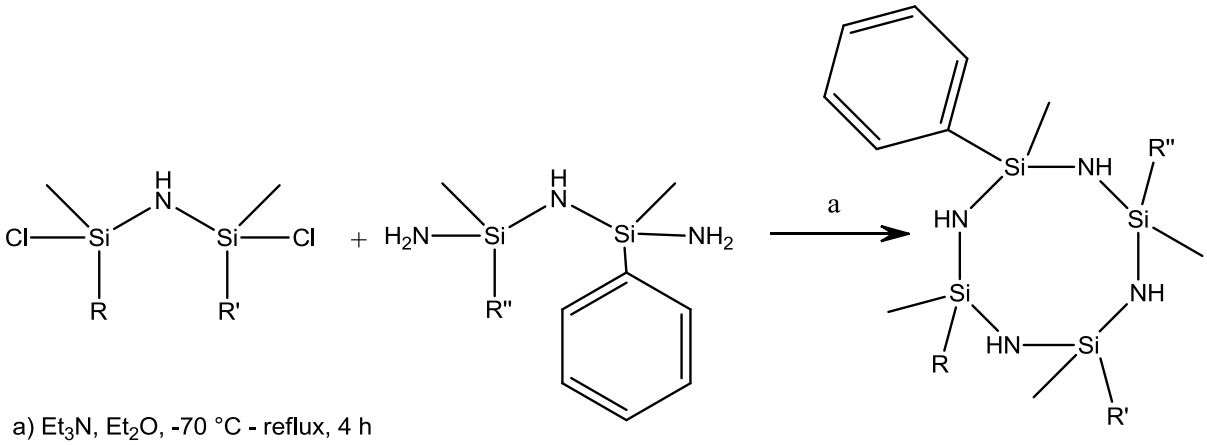
2.3.6.1.2 Preparation by ammonolysis of mixtures of dichlorosilanes

It was observed that by using bulky substituents at the dichlorosilane the formation of cyclotetrasilazane is favoured over the six-membered ring. This was shown by using a nonyltrichlorosilane, instead of ^{i}butyltrichlorosilane.

Methylvinyldichlorosilane was also reacted with ammonia but the 8-membered ring was the minor product. Yields of only 12 % could be achieved.[17]

2.3.6.1.3 Preparation by aminolysis of dichlorodisilazanes

Regarding yields, the preparation of cyclotetrasilazanes by aminolysis of dichlorosilazanes, gives a significant improvement. By reacting 1,3-diaminodisilazanes with 1,3-dichlorodisilazanes, yields of 50 % were reached. The reaction pathway is highlighted below in Scheme 23. The compounds that were prepared by following this method are summarized in Table 5.[17]

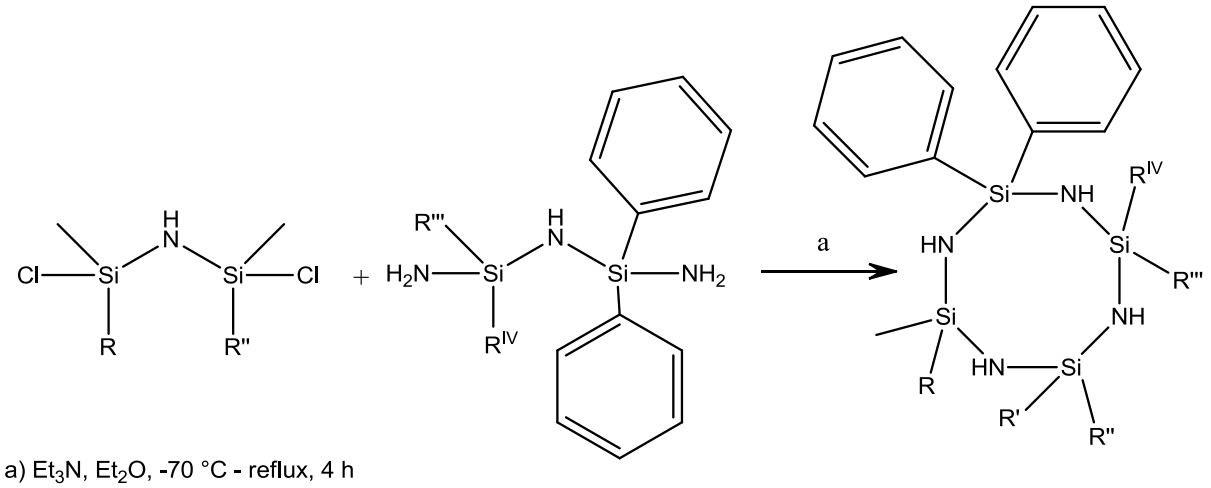


Scheme 23: Preparation of cyclotetrasilazanes by aminolysis of dichlorosilazanes

Table 5: Literature known cyclotetrasilazanes obtained via aminolysis of dichlorosilazanes[17]

R	R'	R''	Melting point	Boiling point
CH=CH2	CH=CH2	Ph	80-81 °C	210-215 °C (1 Torr)
Me	Me	Me	-	101-105 °C (1 Torr)
CH=CH2	CH=CH2	Me	-	148-152 °C (1 Torr)
Me	Me	Ph	94 °C	193-196 °C (1 Torr)
Me	Ph	Me	119-120 °C	194-198 °C (1 Torr)
CH=CH2	Ph	CH=CH2	-	191-198 °C (1Torr)
Ph	Me	Ph	-	228-231 °C (1 Torr)
Ph	Ph	Ph	83-85 °C	256-263 °C (1 Torr)

Scheme 24 shows the same reaction mechanism but with a different substitution pattern at the educts. The obtained compounds are listed in Table 6.[17]



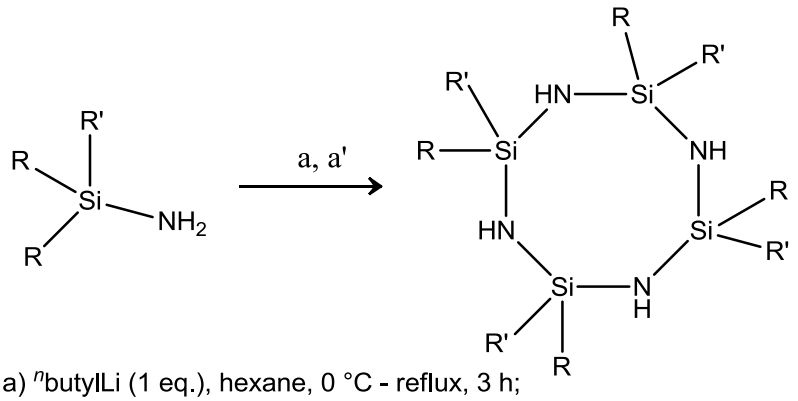
Scheme 24: Aminolysis of dichlorosilazanes with different substitution pattern

Table 6: Literature known cyclotetrasilazane with different substitution pattern[17]

R	R'	R''	R'''	R'^{V}	Melting point	Boiling point
Me	Ph	Ph	Me	Me	165.5-166 °C	-
Me	Me	Me	Me	Me	79.5 °C	179-182 °C (1 Torr)
CH=CH2	CH=CH2	Me	Me	Me	-	196-205 °C (1 Torr)
Me	Me	Me	Ph	Ph	164.5-165 °C	-

2.3.6.2 Preparation by substitution of chlorosilanes with metal amides

The substitution with lithium amide led to the formation of analogous octa-substituted cyclotetrasilazanes, although the yields were low.[28,29] The used synthetic method is shown in Scheme 25.

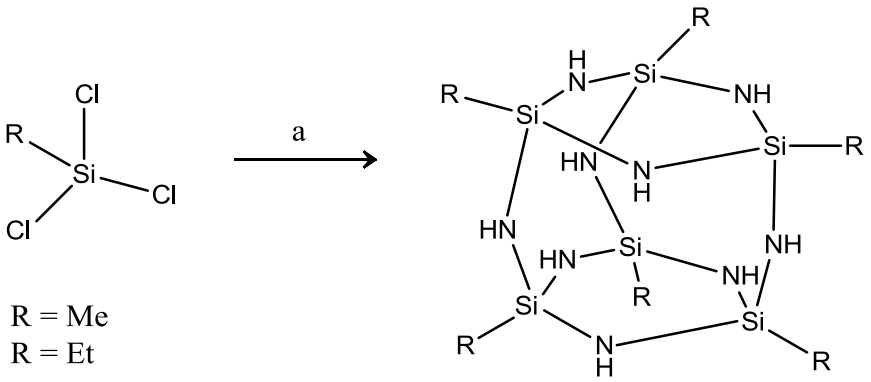


a) ^{n}butylLi (1 eq.), hexane, 0 °C - reflux, 3 h;
a') ^{n}butylLi (2 eq.), Me_2SiCl_2, hexane, 0 °C - reflux, 3 h

R = ^{i}Pr, R' = F	R = ^{i}Pr, R' = ^{i}Pr
R = ^{t}butyl, R' = F	R = ^{t}butyl, R' = ^{t}butyl
R = ^{t}butyl, R' = NH_2	R = ^{t}butyl, R' = Me

Scheme 25: Preparation of cyclotetrasilazanes by substitution of chlorosilanes with metal amides

The substitution with *in-situ* generated, sodium amide at methyl- or ethyltrichlorosilane generated a cage structure shown in Scheme 26.[26,30]



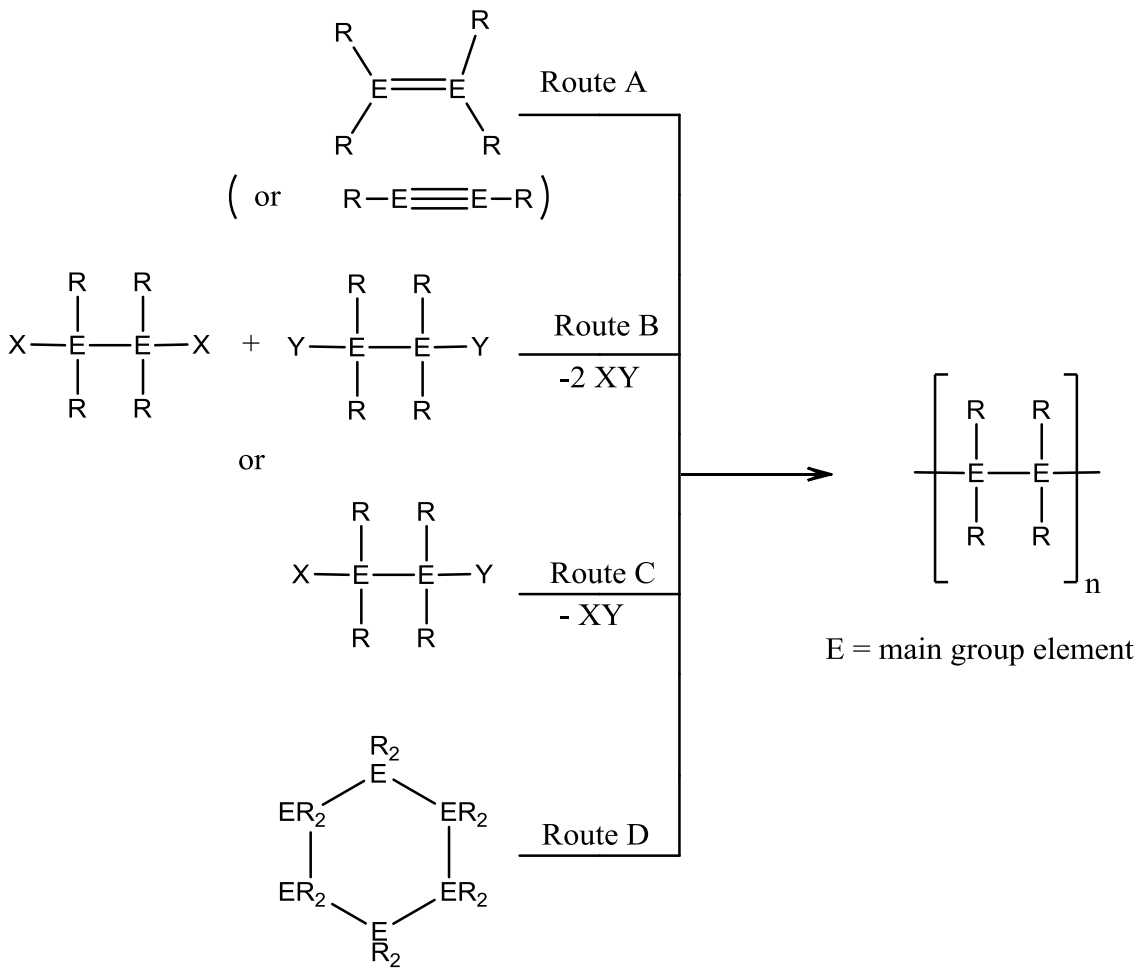
R = Me
R = Et

a) Na, NH_3(l), toluene, -78°C - r.t., 4h

Scheme 26: Synthesis of cage structure

2.3.7 Polysilazanes

Polysilazanes possess a Si-N backbone and have attracted significant attention as polymeric precursors. Scheme 27 highlights the synthetic methods to generate inorganic polymers, which can be applied for polysilazanes as well.[14]



Scheme 27: Synthetic methods to generate inorganic polymers

The preparation of inorganic polymers faces several challenges. Addition polymerisation (Scheme 27, Route A) is very difficult to achieve, as there are barely any stable multiple bonded inorganic precursors.

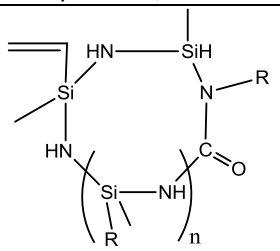
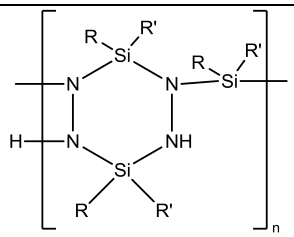
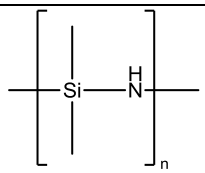
Polycondensation (Scheme 27, Route B) is a commonly used method for the preparation of organic polymers, as it is an easy way to get high molecular weight materials. Crucial about this mechanism is the stoichiometric balance of the educts. Inorganic functional group chemistry is poorly developed and difunctional inorganic monomers (dilithiated species, for example) are often so reactive that they are difficult to prepare and purify. Thus it is not possible to achieve the required reactant stoichiometries and only low molecular weight oligomeric products are generated.

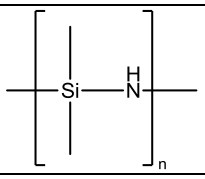
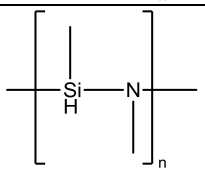
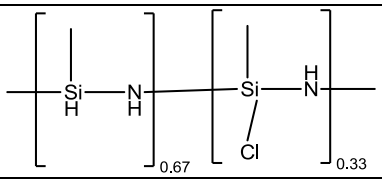
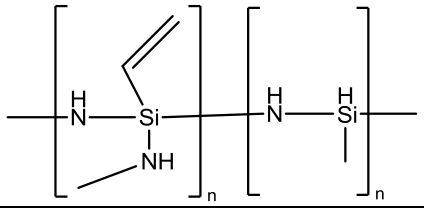
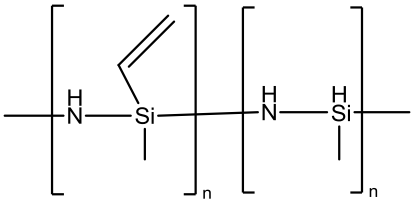
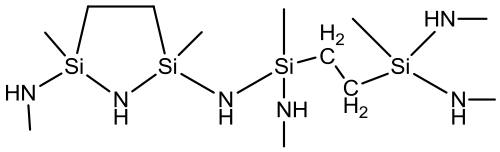
An adaption of polycondensation is shown in Scheme 27, Route C. In this type of reaction only one monomer carrying both necessary functional groups X and Y is being used. Thus the careful control of reaction stoichiometry is circumvented.

However, the most common approach to inorganic polymers to date is ring-opening polymerisation (ROP) (scheme 28, Route D). ROP processes usually occur *via* chain-growth mechanisms that yield high molecular weights and, as inorganic ring chemistry is very well developed, many potential ROP monomers are available.

Table 7[31] lists commercially available oligomeric and polymeric silazanes. Most of them are obtained by ammonolysis of chlorosilanes.

Table 7: Commercially available oligomeric and polymeric silazanes[31]

Supplier	Product name	Composition/ Structure	Properties
Allied Signal Composites Inc.	CERASET™ SZ	 R = H, CH=CH$_2$ n = 1 - 20	Colourless liquid: mp < -78 °C, bp > 150 °C, d= 0.96 g/ml, η(258 °C)= 0.05 Pa s, η(1008 °C)= 15 mPa s
Bayer AG (Germany)	Oligoborosilazane	$[(NMe)_{1.5}Si\text{-}NH\text{-}B(NMe)]n$	M= ~500 g/mol, d= 1.1 g/ml, η(25°)= 0.08 Pa s, η(160°C)= 4 mPa s
Bayer AG (Germany)	Polyvorosilazane	same as oligoborasilazane but thermally cross-linked	M= ~30 000 g/mol, d= 1.2 g/ml, η(160 °C)= 100 Pa s
Elf Attochem (France)	Pyrofine PV	 with R= CH$_3$ and R'= HC=CH$_2$ or CH$_3$	d= 1 g/ml, η(50 °C)= 1 Pa s, η(150 °C)= 0.02 Pa s
Gelest Inc. (USA)	PSN-2M01: poly(1,1-dimethyl-silazane)telomer		d= 1.04 g/ml, η> 0.05 Pa s, M= 500 ± 900 g/mol, Tg= -82 °C

Gelest Inc. (USA)	PSN-2M02: poly(1,1-dimethyl-silazane)cross-linked		η> 1 Pa s
Gelest Inc. (USA)	PSN-2M11: poly(1,2-dimethyl-silazane)		d= 0.99 g/ml, η= 0.5 ± 0.8 Pa s
Höchst AG (Germany)	ET 70	$[CH_3CH_2Si(NH)_{1.5}]n$	M= 1600 g/mol, 70 mol% solution in THF
Höchst AG (Germany)	VB 40		-
Höchst AG (Germany)	VT 50	$[CH_2{=}CH\text{-}Si(NH)_{1.5}]n$	M= 2000 g/mol, 50 mol% solution in THF
Nichimen Inc. (Chisso, Japan)	NCP 100	$[(Me_2Si)_2NH]_x[MeSiHNH]_y[MeSiN]_z$	M= 4000 g/mol, meltable solid
Nichimen Inc. (Chisso)	NCP 200	$[Me_2SiNH]_x[MeSiHNH]_y[MeSiN]_z$ with x=y+z=0.5	M= 1100 g/mol, meltable solid
Tonen Corp. (Japan)	NN 110	$(SiH_2\text{-}NH)n$, pure PHPS (perhydropolysilazane)	Mn= 700 g/mol, 20 wt.%, soluble in xylene
Tonen Corp. (Japan)	NN 310	$(SiH_2\text{-}NH)n$, with $N(SiMe)_2$ groups	Mn= 900 g/mol, 20 wt.%, soluble in xylene
Tonen Corp. (Japan)	NN 710	$(SiHMe\text{-}NH)_x\text{-}(SiH_2\text{-}NH)_y$	Mn= 900 g/mol, 20 wt.%, soluble in xylene
University of Bayreuth, IMA 1 (Germany)	HVNG		M= 620 g/mol, η(20 °C)=29 Pa s
University of Bayreuth, IMA 1 (Germany)	HPS		M= 440 g/mol, η(20 °C)=0.05 Pa s
University of Bayreuth, IMA 1 (Germany)	ABSE		M= 1100 g/mol, solid, mp= 100 °C

2.4 Objective of the Project

The objective of the project can be defined as the synthesis and characterisation of 1-naphthyl substituted silylamines. The prepared silylamines should serve as precursors for the generation of cyclic systems by ring coupling reactions with provided compounds. The synthetic scope is not only based on heterocyclic systems with an alternating Si-N ring, but also rings containing oxygen atoms.

All synthesised educts are mentioned in literature, though they have not been fully characterised yet.

3 Results and Discussion

3.1 Synthesis of educts

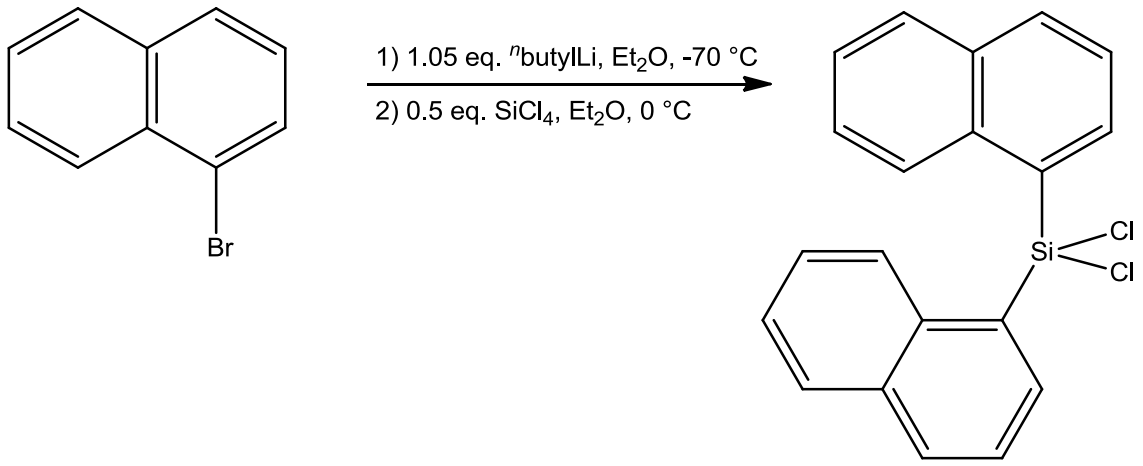
The conversion of 1-napthyl substituted chlorosilanes and 1-napthyl substituted aminosilanes was carried out according to literature procedures.[9] Only the work up and the purification were modified slightly depending on the synthesised derivatives as described below.

3.1.1 Synthesis of chloro(1-naphthyl)silanes

3.1.1.1 Dichloro(di-1-naphthyl)silane (1)

Compound **1** was synthesised *via* a lithiation according to Scheme 28. The resulting yellowish solid was subjected to a ^{29}Si-NMR measurement in C_6D_6. One signal could be found, 7.76 ppm. According to literature[32], the signal can be assigned as dichloro(di-1-naphthyl)silane.

After the work up, the solid was washed with pentane and recrystallized from toluene, which gave white crystals.

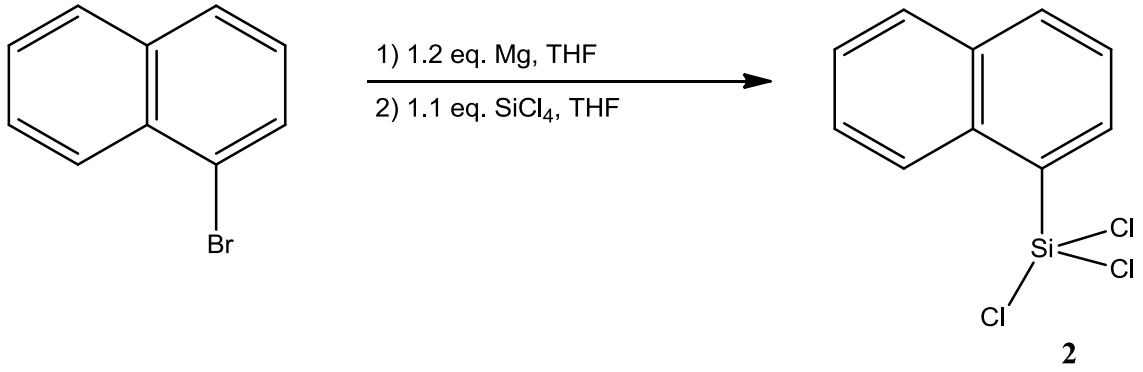


1

*Scheme 28: Preparation of **1***

3.1.1.2 Trichloro(1-naphthyl)silane (2)

Compound **2** was synthesised *via* a Grignard route according to Scheme 29.[33] The reaction afforded a brownish solution which was investigated *via* ^{29}Si-NMR measurement in C_6D_6 revealing two different signals at 7.60 ppm and -0.34 ppm. By comparison with already synthesised napththyl-substituted chlorosilanes, the shift at 7.60 ppm can be assigned to $Naph_2SiCl_2$. The product mixture was purified *via* fractional distillation which led to the isolation of the desired product. A yield of 36 % could be achieved.



*Scheme 29: Preparation of **2***

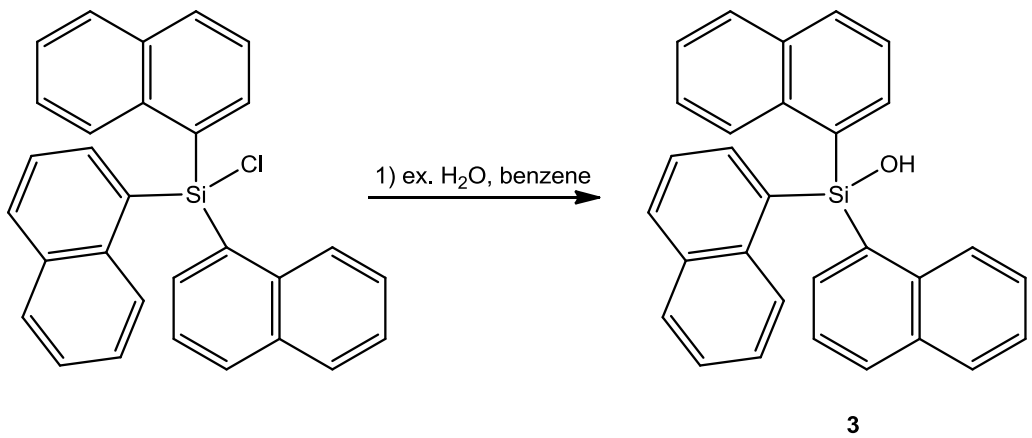
The reported product ^{29}Si-NMR shift is at -0.50 ppm ($CDCl_3$)[33], which fits quite well to the found product peak at -0.34 ppm (C_6D_6).

3.1.2 Synthesis of (1-naphthyl)silanols

3.1.2.1 Tri(1-naphthyl)silanol (3)

Compound **3** was synthesised as displayed in Scheme 30.[34] The reaction gave a white solid, which was investigated *via* ^{29}Si-NMR measurement in C_6D_6, giving two different shifts at -3.97 ppm and -21.8 ppm.

As the ^{29}Si-NMR shift of the educt, 1-Naph$_3$SiCl, is known, the major peak at -3.97 ppm could be assigned to residual educt. Obviously the sterically demanding substituents slow down the hydrolysis of the chlorosilane, as the chloride is shielded by the aryl-groups. The mixture was not subjected to further purification procedures.



*Scheme 30: Preparation of **3***

So far, the ^{29}Si-NMR shift for **3** was not published. The reported silicon shifts for tri-phenylsilanol and tri-9-anthracenylsilanol were compared with the obtained silicon shift and summarised in Table 8. Taking into account that the silicon NMR of compound **3** was measured in an apolar solvent, the obtained shift seems to be reasonable.

Table 8: ^{29}Si-NMR shifts of tri-arylsilanols

compound	δ^{29}Si [ppm]
Ph_3SiOH[35]	-12.0 ($CDCl_3$)
1-$Naph_3SiOH$	-21.8 (C_6D_6)
9-$Anth_3SiOH$[36]	-17.4 (C_4D_8O)

3.1.2.2 Di(1-naphthyl)silanediol (4)

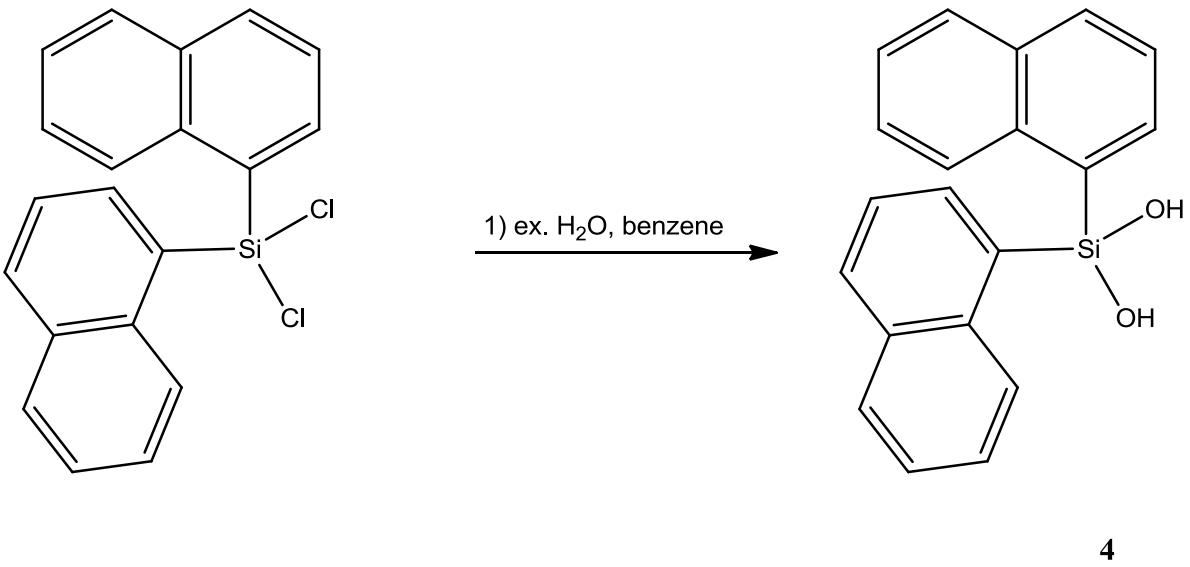
Compound **4** was synthesised by hydrolysis as depicted in Scheme 31.[37] The reaction gave a white solid. The ^{29}Si-NMR measurement conducted in C_6D_6 gave two signals, the major peak at -26.8 ppm and the minor peak at 7.55 ppm. The minor peak at 7.55 ppm could be assigned to residual starting material. Apparently, the reaction time of 24h is too short to achieve complete hydrolysis. Due to the bulky aryl-substituents, the nucleophilic attack of the hydroxide-anion might be hindered and thus the reaction proceeds slower. The same behaviour was observed with $Naph_3SiOH$, where the silanol peak is still the minor NMR-peak after 24h reaction time. The recorded ^{29}Si-NMR shift for compound **4** fits quite well to shifts collected in our working group and the published value of -25.2 ppm ($CDCl_3$).[38]

Furthermore the ^{29}Si-NMR shifts of compound **3** and **4** were compared with the ^{29}Si-NMR shifts of phenyl substituted silanols. The shift trend which is displayed in Table 9 fits quite well with the obtained shifts. With increasing the number of hydroxyl substituents the silicon atom is shielded from the external magnetic field resulting in a significant upfield shift.

Table 9: Comparison of ^{29}Si-NMR shifts of aryl substituted silanols

compound	δ^{29}Si [ppm]	compound	δ^{29}Si [ppm][39]

3	$Naph_3SiOH$	-21.8	Ph_3SiOH	-14.0
4	$Naph_2Si(OH)_2$	-26.8	$Ph_2Si(OH)_2$	-29.73
-	-		$PhSi(OH)_3$	-49.3



*Scheme 31: Preparation of **4***

The IR spectrum of **4** (Figure 2) clearly shows the significant asymmetric and symmetric –OH stretching vibrations at 3561 cm^{-1} and 3351 cm^{-1}, respectively.

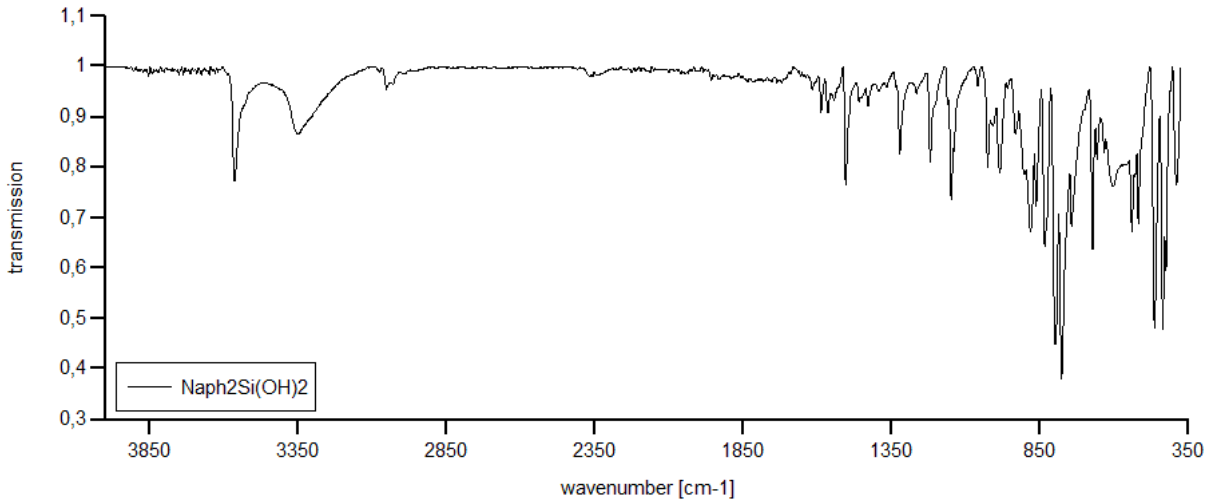


*Figure 2: IR spectrum of **4***

Further assignments of the significant vibrations are summarised in Table 10.

*Table 10: IR assignments of **4***

wavenumber [cm-1]	**assignments**	
3561	Si-OH	asym.str.vib.

3351	Si-OH	sym.str.vib.
3051	C-H	asym.str.vib.
3032	C-H	str.vib.
1540	C=C	asym.str.
1503	C=C	sym.str.
1322	C-C	asym.str.
1220	C-C	sym.str.
1149	C-H	bend
1021	C-C	str.vib.
985	CH	wagging
931	CH	wagging
882	O-H	def.vib.
860	CH	wagging
831		ring def
799	CH	wagging
774	CC	torsion
742	CH	out-of-plane C-H vib.
669	CH	wagging
652	CH	wagging
600	Si-O	str.vib.
539	CC	torsion
515	CCC	bend
463	CCC	bend
432		ring def.
422		ring def.
385	CC	torsion

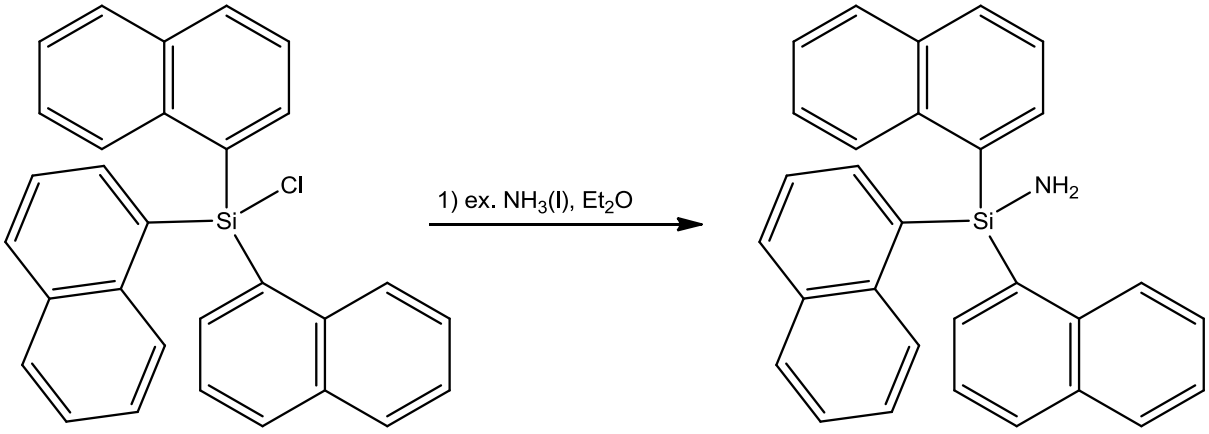
Schafer et al. stated similar values for the most significant IR vibrations of compound **4**; 3420, 3017, 1576, 1495, 1024 and 684 cm^{-1}.[40]

3.1.3 Synthesis of amino(1-naphthyl)silanes

3.1.3.1 Amino(tri-1-naphthyl)silane (5)

Compound **5** was obtained *via* ammonolysis of the corresponding chlorosilane, shown in Scheme 32. A white amorphous solid was obtained. For further purification the solid was recrystallized from toluene, which gave colourless crystals (Figure 3). Confirmation on the structure of the product synthesised was given by single crystal X-ray analysis, revealing that it is the triaryl derivative amino(tri-1-naphthyl)silane.

So far, only Chugunov reported about the synthesis of amino(tri-1-naphthyl)silane in the year 1953 without structural proof.[9] The compound was prepared *via* treatment of the corresponding fluorosilanes with freshly prepared sodamide. The stated melting point at 204 – 206 °C fits quite well with the obtained melting point at 207- 208 °C.



5

*Scheme 32: Preparation of **5***

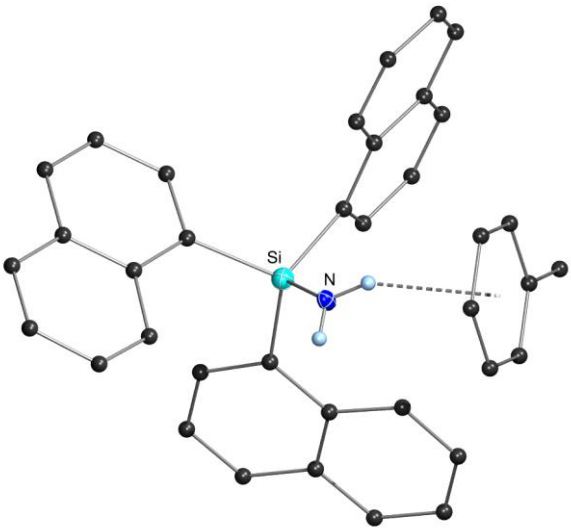


*Figure 3: Crystal structure of **5**.Non carbon atoms displayed as 30% ellipsoids. Most hydrogen atoms removed for clarity.*

Table 11 summarizes selected bond lengths and angles of **5**.

*Table 11: Selected bond lengths and bond angles of **5***

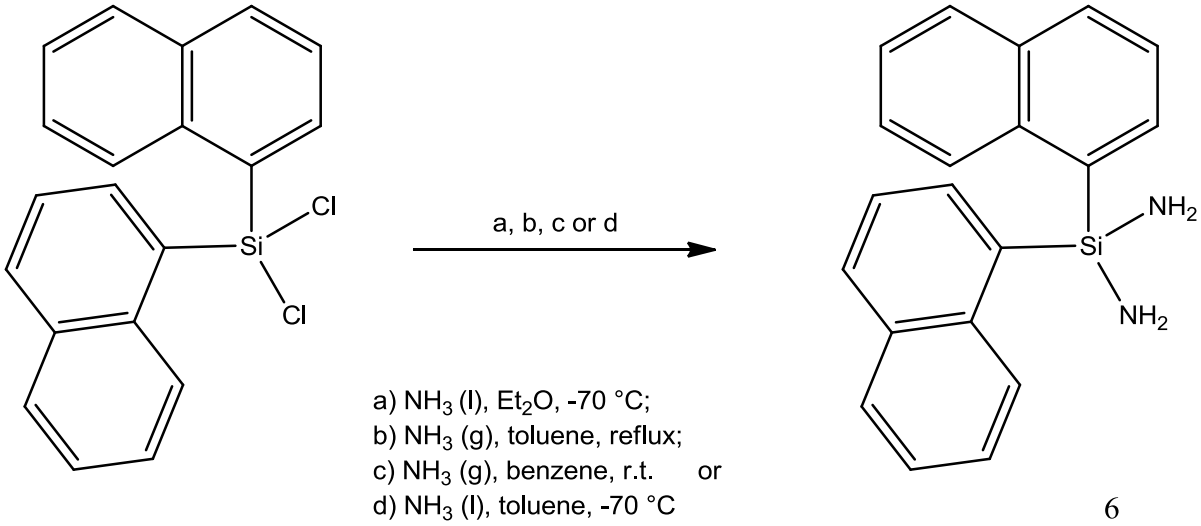
	space group	bond length av. [Å]		bond angle av. [°]	
compound		Si-C	Si-N	C-Si-C	C-Si-N
$Naph_3SiNH_2$	P-1	1.887(3)	1.717(2)	108.4(3)	110.5(3)

Amino(tri-1-naphthyl)silane **5**, crystallizes in the triclinic space group P-1, whereas the silicon can be found in a distorted tetrahedral environment as displayed in Figure 3. The silicon is coordinated to three naphthyl-ligands with an average bond length of 1.887(3) Å and to the amine group with a bond length of 1.717(2) Å. The average C-Si-C angle (108.4(3)°), as well as the C-Si-N angle are bigger than the ideal tetrahedral one provoked by the steric demand of the naphthyl-substituents. The values for bond lengths and angles lie in the expected area as compared to other tri-naphthyl silicon species (1.877(2)).[41,42] In addition, a weak N-H···π interaction (2.62 Å) is seen between an amino hydrogen interacting with a molecule of toluene which cocrystallizes with the amino(tri-1-naphthyl)silane **5**. This type of weak intermolecular interaction is also observed in hydroxy(tri-1-naphthyl)silane (2.58 Å).[41]

3.1.3.2 Diamino(di-1-naphthyl)silane (6)

Compound **1** was treated with an excess of liquid or gaseous ammonia, which gave **6**, according to Scheme 33. The synthesis of **6** gave a white slightly yellow powder, when following approach a,b and c. When approach d was used, a colourless oil was obtained after work up. The reported synthesis of compound **6** differs a little from our procedure. Chugunov treated an ethereal solution of di(1-naphthyl)difluorosilane with dry ammonia. After the work up, the crude product was recrystallized from pyridine.[9] ^{29}Si-NMR measurements of the crude product in C_6D_6 displayed three different shifts; -21.5 ppm, -29.8 ppm and -44.2 ppm. Except when route c was applied, only one ^{29}Si-NMR shift at -21.5 ppm (C_6D_6) could be found. Route d only gave ^{29}Si-shifts at -29.8 ppm and -44.2 ppm.

The product mixture was washed in pentane and recrystallized from toluene. The crystals were investigated by single crystal X-ray analysis, which confirmed the structure of diamino(di-1-naphthyl)silane **6** (Figure 4).



*Scheme 33: Preparation of **6***

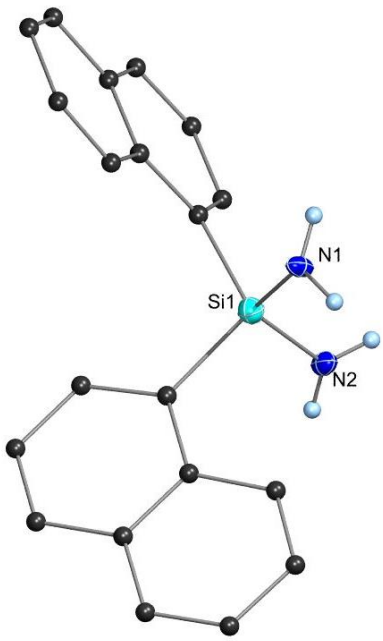


*Figure 4: Crystal structure of **6**. Non carbon atoms displayed as 30% ellipsoids. Most hydrogen atoms removed for clarity.*

Table 12 summarizes selected bond lengths and angles of **6**. ^{29}Si-NMR measurements of **6** gave one signal at -21.5 ppm (C_6D_6). To date, no crystal structure of **6** has been reported. Chugunov synthesised the compound without any structural proof.[9]

*Table 12: Selected bond lengths and bond angles of **6***

	space group	bond length av. [Å]		bond angle av. [°]	
compound		Si-C	Si-N	C-Si-C	C-Si-N
$Naph_2Si(NH_2)_2$	$Pca2_1$	1.883(2)	1.707(2)	110.8(1)	108.5 (4)

Diamino(di-1-naphthyl)silane **6** crystallizes in the orthorhombic space group $Pca2_1$. The silicon can be found in a distorted tetrahedral environment. It is bonded to two amine groups and two 1-naphthyl substituents (Figure 4). Due to the high steric demand of the 1-naphthyl substituent the C-Si-C angle (110.8(1)°) is bigger than the average C-Si-N (108.5(4)°) angle. The values for bond lengths and angles compare to those found for the aforementioned amino(tri-1-naphthyl)silane **5**.

Further comparison of the obtained ^{29}Si-NMR shift with literature known compounds are shown in Table 13.

Table 13: Comparison of ^{29}Si-NMR shifts

compound	δ^{29}Si [ppm]	compound	δ^{29}Si [ppm][43]
		$Me_2Si(NMe_2)_2$	-1.07
6 $Naph_2Si(NH_2)_2$	-21.5	$MePhSi(NMe_2)_2$	-9.06
		$Ph_2Si(NMe_2)_2$	-17.04

Taking into account that the transition from $-NH_2$ to $-NMe_2$ is relatively small and does not significantly influence the silicon atom, the ^{29}Si-NMR shifts are comparable. Obviously the di-aryl substitution pattern of silicon leads to a significant upfield shift due to shielding of the silicon from the external magnetic field when compared to the di-alkyl substitution pattern. Therefore the transition from di-phenyl substitution to the di(1-naphthyl) substitution pattern should result in a slight upfield shift, as the 1-naphthyl groups are larger. The assumption matches quite well with the obtained shift of **6** at -21.5 ppm.

Moreover, the ^{1}H-NMR of **6** gives a broad singlet at 0.97 ppm, with an integral of four protons. Ruhlandt-Senge et al. prepared $Mes_2Si(NH_2)_2$ giving a broad singlet at 0.831 ppm[12], with an integral of four protons in the ^{1}H-NMR spectrum, which fits quite well with the obtained shift.

In the IR spectrum (Figure 5) of **6**, the $-NH_2$ and -NH-stretching vibrations can be clearly seen at 3470 cm^{-1}, 3450 cm^{-1} and 3373 cm^{-1}, which is marked with number 1. Furthermore, the $-NH_2$ deformation vibration at 1540 cm^{-1}, and N-Si-N stretching vibrations at 885 cm^{-1} and 848 cm^{-1} can be seen in the marked region 2 and 3 in Figure 5, respectively. Ruhlandt-Senge et al. also give the IR vibrations of

the prepared $Mes_2Si(NH_2)_2$ *v* N-H = 3495, 3455, 3449, 3430, 3370, 3350 cm^{-1}, the range of the reported and obtained N-H vibrations fit quite well.

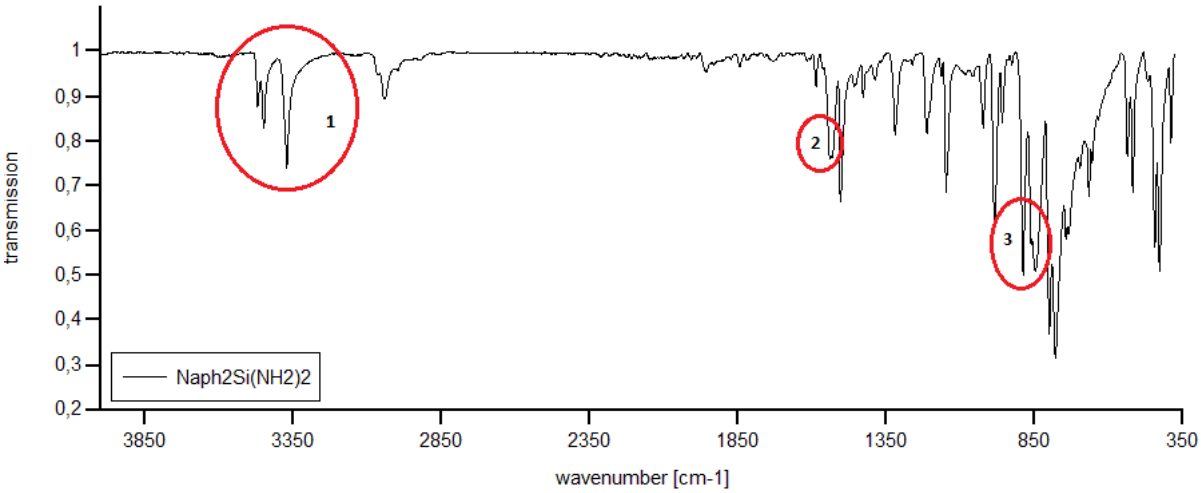


*Figure 5: IR spectrum of **6***

Further assignments are listed in Table 14.

*Table 14: IR assignments of **6***

wavenumber [cm-1]	assignments	
3470	NH_2	asym.str.vib.
3450	NH_2	sym.str.vib
3373	NH	single band
3064	C-H	asym.str.vib.
3041	C-H	str.vib.
1540	NH_2	defor.vib.
1526	C=C	asym.str.
1501	C=C	sym.str.
1321	C-C	asym.str.
1215	C-C	sym.str.
1147	C-H	bend
1019	C-C	str.vib.
982	CH	wagging
975	CH	wagging
885	N-Si-N	asym.str.vib
848	N-Si-N	sym.str.vib.
797	CC	torsion
777	CC	torsion
740	CH	out-of-plane C-H vib.
731	CH	wagging
665	CH	wagging
654	CH	wagging
537	CC	torsion
517	CCC	bend

462	CCC	bend
440		ring def.
425		ring def.
384	CC	torsion

A C, H, N- elemental analysis of the obtained crystals of **6** was carried out. Although the single crystal X-ray analysis gave the structural proof of **6**, the results of the elemental analysis did not give the expected values, as it can be derived from Table 15.

*Table 15: Measured, calculated and reported C, H, N, Si values of **6***

6	%N	%C	%H	%Si
calculated	8.95	76.39	8.93	8.93
measured	5.48	76.81	5.46	-
reported[9]	8.6	-	-	8.6

Specifically the deviation of the measured nitrogen content from the calculated value showed that elemental analysis might not be the method of choice to determine the composition.

Nevertheless, the nitrogen content could be determined *via* the Kjeldahl method. For that, 97.2 mg of **6** (0.031 mol) were dissolved in THF and completely hydrolysed with a saturated boric acid, to convert the diamine to NH_4^+. In the next step, the ammonium ion could be back-titrated with a 0.1 M HCl. The precise equation is shown below.

$$NH_4^+{}_{(aq.)} + B(OH)_4^- + HCl_{(aq.)} \longrightarrow NH_4Cl_{(aq.)} + B(OH)_{3(aq.)} + H_2O$$

For the back-titration, an indicator mixture of methyl blue/methyl red was used. A volume of 6.10 mL 0.1 M HCl was needed until the equivalence point was reached and the indicator changed from green to grey. As there are two amine groups present there are two moles of H^+ needed for neutralisation. Calculating back, a molar ratio of n[HCl] : n[$Naph_2Si(NH_2)_2$] = 2:1 could be determined.

Table 15 also shows the reported values for silicon and nitrogen content. The authors do not give any details on the technique they used, nevertheless these values fit well with the calculated ones.

Assumptions were made that the two other ^{29}Si-NMR signals obtained during the synthesis of **6** might be hydrolysis products. By comparing the ^{29}Si-NMR shifts with the corresponding di-1-naphthylsilanediol ($Naph_2Si(OH)_2$ = -26.8 ppm), no decisive relation could be withdrawn from the data.

Based on the knowledge that the perphenylated- cyclotrisiloxane and cyclotetrasiloxane shift in the same region, -33.8 ppm[44] and -46.0 ppm[44] respectively, further analytics have been conducted.

IR spectra of $Naph_2Si(OH)_2$ **(4)** and the side-product mixture were recorded and compared. Figure 6 shows the overlay of the IR spectrum of **4** and the unknown mixture. Based on the IR spectra it can be stated, that the side products cannot be hydrolysis products, as there are amino functionality vibrations visible at 3471 cm^{-1} and 3386 cm^{-1} (see highlighted region in Figure 6).

Moreover, in the overlay it becomes quite obvious, that the silanol functionality vibrations appear at other wavenumbers (3561 cm^{-1}, 3351 cm^{-1}) than the unidentified by-products.

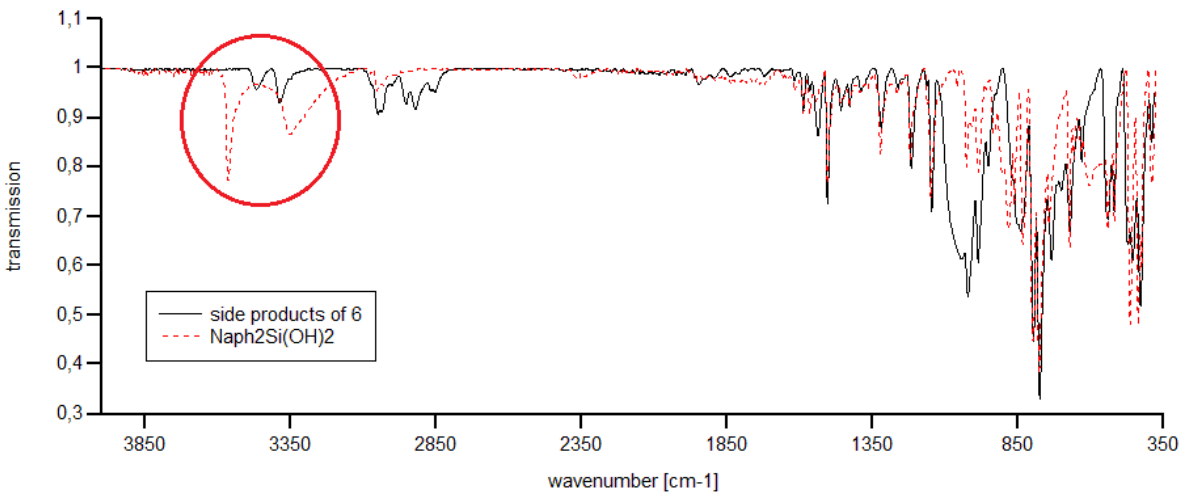


*Figure 6: Overlay of IR spectrum of **4** and side-products of **6***

Finally, it was observed that the side-products always appeared after the work-up. Due to this finding, a further ammonolysis with **1** was carried out. After filtering off the salt, a ^{29}Si-NMR with a D_2O-capillary was measured. The spectrum showed only a single peak, which was the desired product **6** (Figure 7: before work up).

Then the reaction solution was divided into two different flasks; designated **Batch I** and **Batch II**. **Batch I** was kept at 24°C, while **Batch II** was heated to 90°C with a H_2O bath while removing the solvent under reduced pressure. In both flasks a white solid was obtained. ^{29}Si-NMR measurements in C_6D_6 were recorded for both crude products.

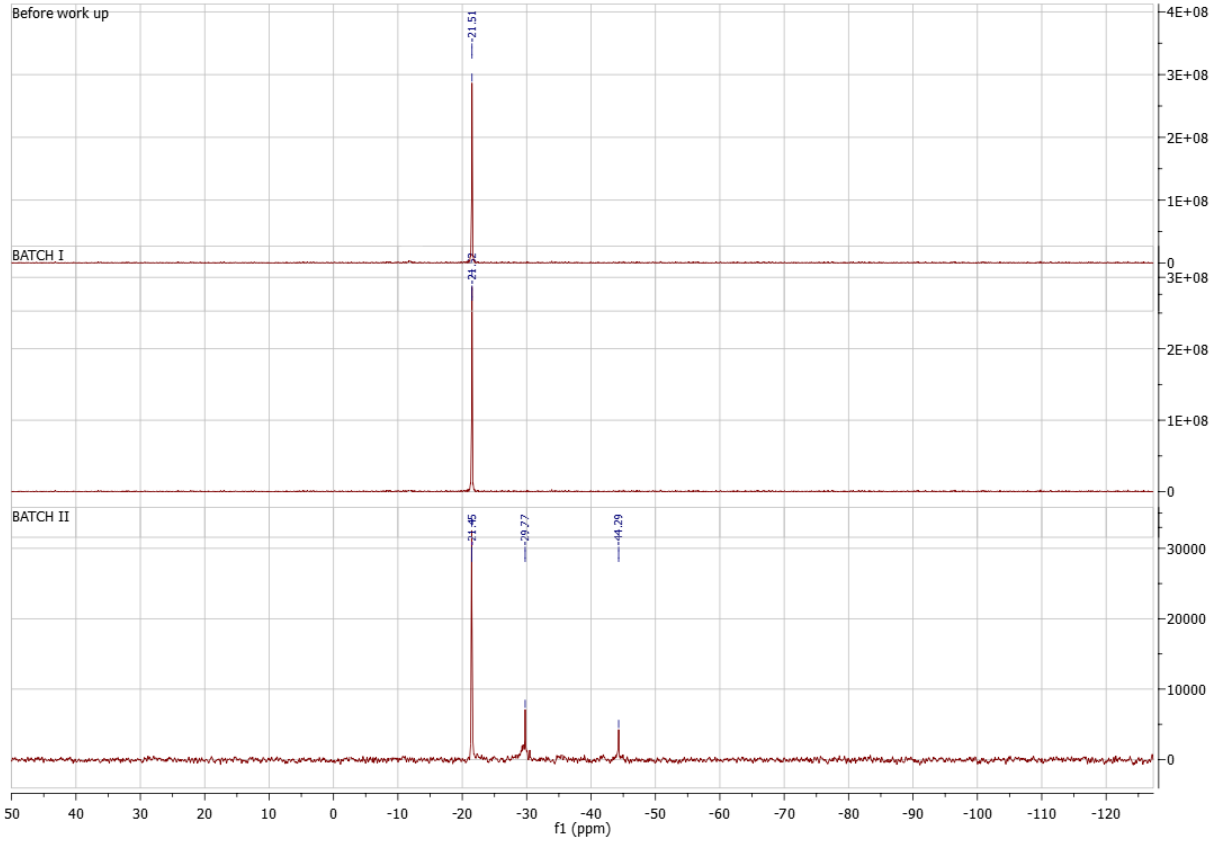


Figure 7: ^{29}Si-NMR of $Naph_2Si(NH_2)_2$ before and after work up; BATCH I and BATCH II

Surprisingly, the spectrum of **Batch I** still showed a single peak (-21.5 ppm; Figure 7, spectrum in the centre) which can be assigned to compound **6**, whereas the spectrum of **Batch II** (Figure 7; spectrum at the bottom) shows three peaks, the major peak at -21.5 ppm (**6**) and two minor peaks at -29.9 ppm and -44.2 ppm. At this point it was quite obvious that the side-products obtained while synthesising **6** resulted from the work up.

Applying heat under reduced pressure most probably leads to the internal formation of condensation products of **6**.

To date, no final structure of the side-product(s) could be found but it is believed that they might resemble the structures illustrated in Figure 8.

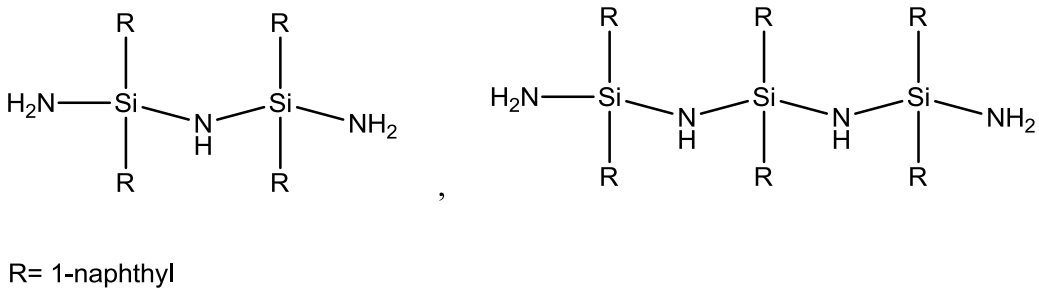
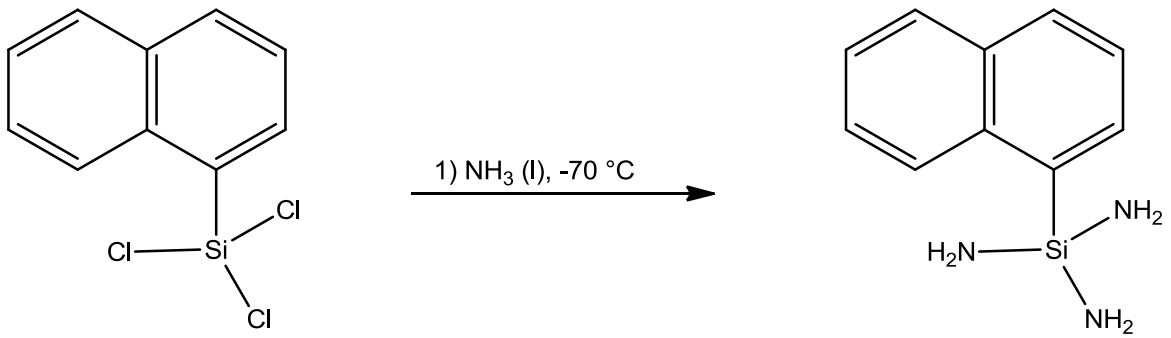


Figure 8: Possible structures of side-products

3.1.3.3 Triamino(1-naphthyl)silane (7)

Based on Chugunov's work, where they attempted to prepare the compound by treating trifluoro(1-naphthyl)silane with gaseous ammonia[9], compound **7** was obtained by reacting **3** with liquid ammonia, illustrated in Scheme 34. After 1.5h ^{29}Si-NMR measurements in C_6D_6 showed the formation of **7**. The overnight ^{29}Si-NMR measurement showed several peaks which indicates that **7** is labile and forms condensation products upon NH_3 cleavage. The NMR shifts obtained for the mono-, di- and tri- substituted silylamine were compared to the series of N-methyl substituted silylamines. The trend of the ^{29}Si-NMR shift should be the same for the prepared silylamine series, as the same substitution pattern and the change from $–NH_2$ to $–NMe_2$ should not significantly affect the group trend. The literature known values and the obtained values for **5-7** are listed in Table 16.



7

*Scheme 34: Preparation of **7***

Table 16: Comparison of ^{29}Si-NMR shifts

compound	δ^{29}Si [ppm]	compound	δ^{29}Si [ppm][44]
5 $Naph_3SiNH_2$	-11.9	Me_3SiNMe_2	5.90
6 $Naph_2Si(NH_2)_2$	-21.5	$Me_2Si(NMe_2)_2$	-1.70
7 $NaphSi(NH_2)_3$	-30.4	$MeSi(NMe_2)_3$	-17.5

Apparently, the ^{29}Si-NMR shift series of $Naph_{4-n}Si(NH_2)_n$ fit quite well to the found ^{29}Si-NMR values of the $Me_{4-n}Si(NMe_2)_n$ group. Increasing the number of amino functionalities on the silicon atom results in a significant upfield shift. If the number of electron donating groups ($-NH_2$ and $-NR_2$) increases, the electron density at the silicon rises. Thus, the silicon atom is shielded from the external magnetic field and therefore a significant upfield shift occurs.

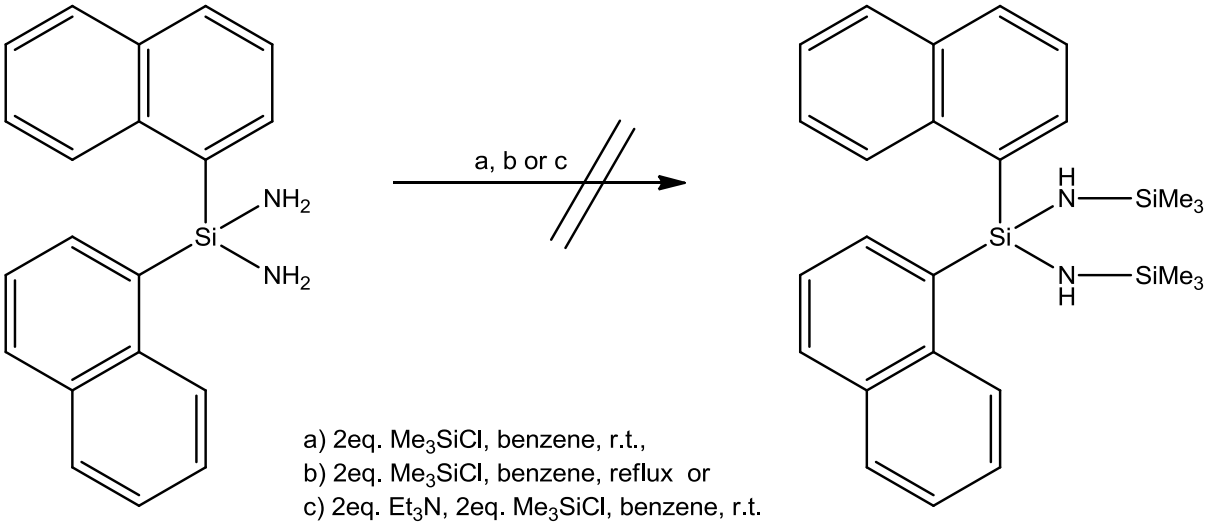
Though, the NMR measurements gave reasonable results, no crystals could be isolated, which would enable X-ray analysis to give the final structural proof of **7**.

3.1.3.4 1,1-di-(1-naphthyl)-N,N'-bis(trimethylsilyl)silanediamine

The reaction shown in Scheme 35 was run at different conditions (route a-c), nevertheless it did not give the desired product 1,1-di-(1-naphthyl)-N,N'-bis(trimethylsilyl)silanediamine. The ^{29}Si-DEPT measurements of the reaction mixtures, conducted with a D_2O-capillary, showed 3 different peaks; 29.9 ppm, 2.97 ppm and -21.50 ppm. As the reaction proceeded the peaks of the educts (29.9 ppm and -21.50 ppm) decreased leaving one single peak at 2.97 ppm. This shift was compared with literature known silicon shifts. At this point the reported shift range of hexamethyldisilazane (HMDS; 1.7 ppm – 3.6 ppm[44]) matched quite well to the obtained one.

Based on that knowledge, a ^{29}Si-DEPT of purchased HMDS was measured, giving a peak at 2.35 ppm. In order to see if the formed product is hexamethyldisilazane, neat HMDS was added to the reaction mixture. From the ^{29}Si-DEPT spectrum, where a D_2O-capillary was used as external lock, it could be seen, that the peak at 2.97 ppm had increased in its intensity. Due to this findings, it can be stated that the reaction highlighted in Scheme 35 does not give the product illustrated, but results in the formation of 1,1,1,3,3,3-hexamethyldisilazane. Furthermore it could be proven that the amine base,

Et_3N, already forms an ammonium salt upon the reaction with Me_3SiCl, giving one peak in the ^{29}Si-NMR at 6.89 ppm, measured with a D_2O-capillary. Literature reports were found where similar salt formations were observed.[45,46,47]



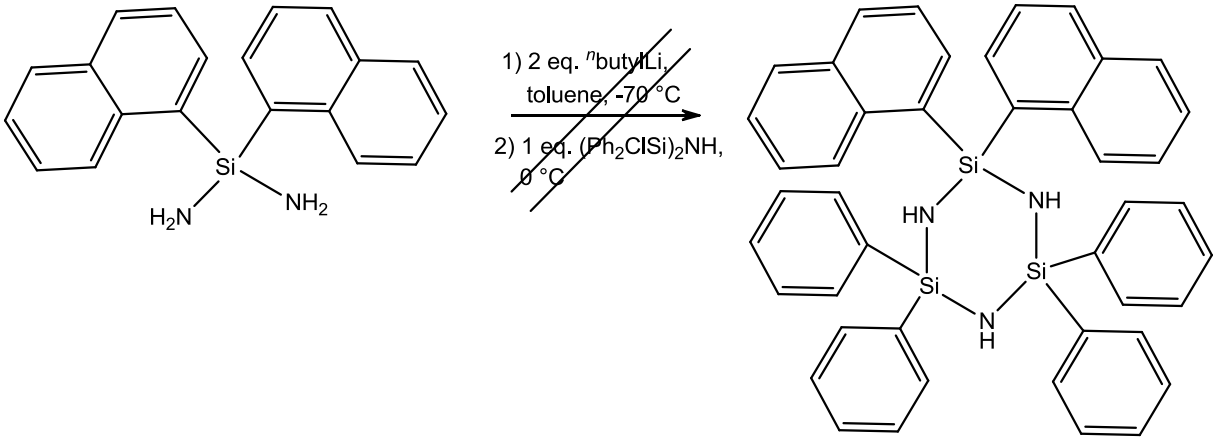
Scheme 35: Synthesis attempts of 1,1-di-(1-naphthyl)-N,N'-bis(trimethylsilyl)silanediamine

3.2 SYNTHESIS OF CYCLIC SYSTEMS

3.2.1 1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane

a) *Via* ^{n}butylLi

The attempt to prepare 1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane gave a white yellowish oil, which was insoluble in all commonly used organic solvents. The reaction is shown in Scheme 36.



Scheme 36: Synthesis attempts of 1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane

Before the work up a ^{29}Si-NMR was measured of the reaction mixture. The spectrum is shown in Figure 9.

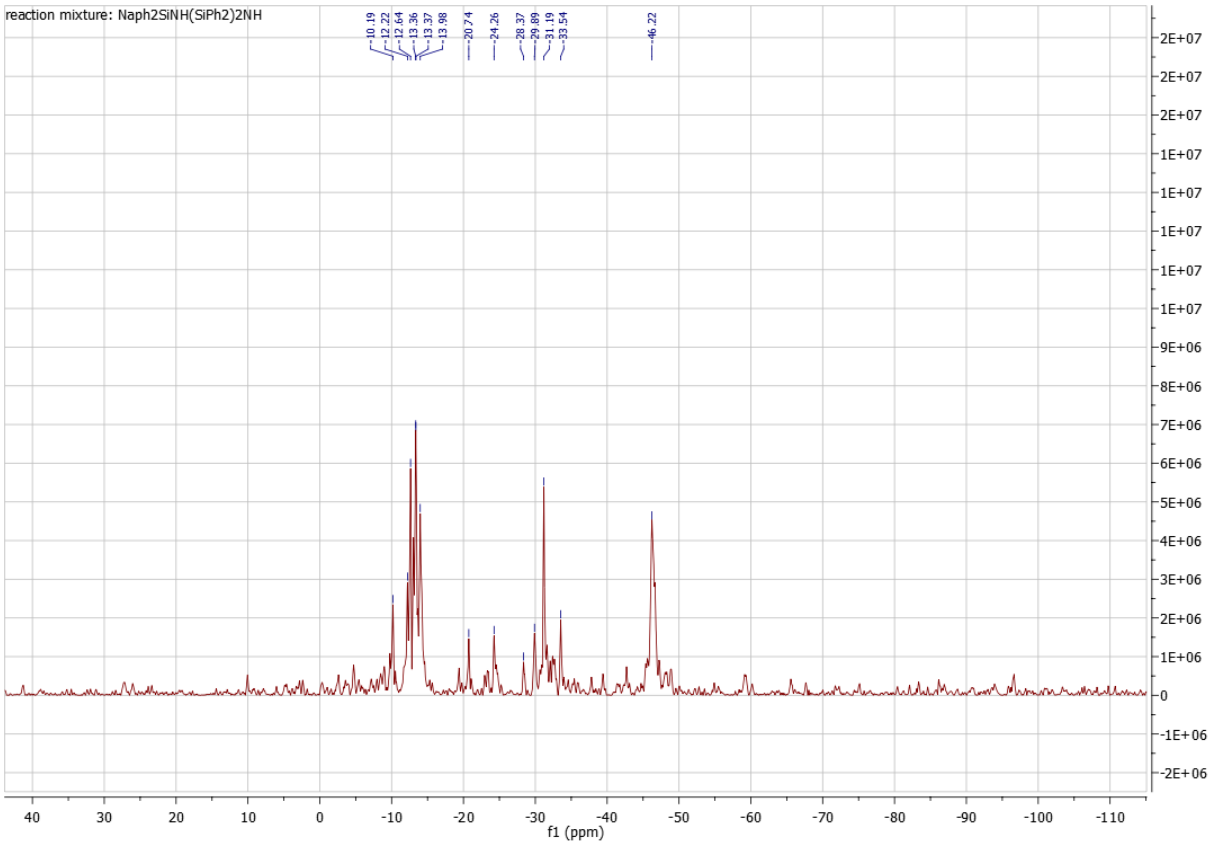


Figure 9: ^{29}Si-NMR of attempted $Naph_2Si(NH)_2(SiPh_2)_2NH$ synthesis

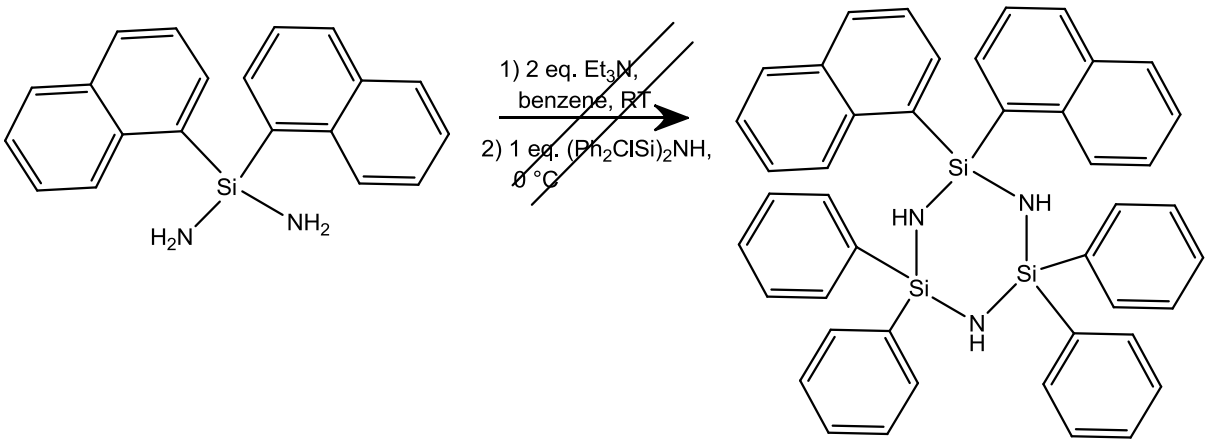
For the desired product two different silicon shifts were expected. As it can be seen in Figure 9 the reaction gave several unidentified peaks. Though, the educt peaks of $Naph_2Si(NH_2)_2$ at -21.5 ppm and

$ClPh_2SiNHSiPh_2Cl$ at -8.00 ppm disappeared. In order to get more information on which compounds formed during the reaction, it was tried to recrystallize the oil from benzene. Due to the insufficient solubility no crystals, which would enable a single crystal X-Ray analysis, could be obtained.

To get a detailed understanding on the reaction it would be better to measure a ^{29}Si-NMR already after the lithiation step of the diamine or to crystallize the lithiated compound with TMEDA to ensure the dilithiated species. The consecutive ring formation upon LiCl elimination only occurs with the dilithiated compound. The high number of unidentified silicon shifts might originate from an incomplete lithiation step.

b) *Via* Et_3N

1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane was also tried to be prepared with the auxiliary base Et_3N. Kavala et al. also used Et_3N for similar ring coupling reactions.[17] The synthetic pathway is shown in Scheme 37.



Scheme 37: Synthesis attempt 2 of 1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane

Similar coupling reactions are reported in literature where the reactions were kept at reflux for several hours, the reaction mixture was also heated to reflux for 2 h.[17] After the formed solid was filtered off a ^{29}Si-NMR was measured. The obtained spectrum is shown in Figure 10.

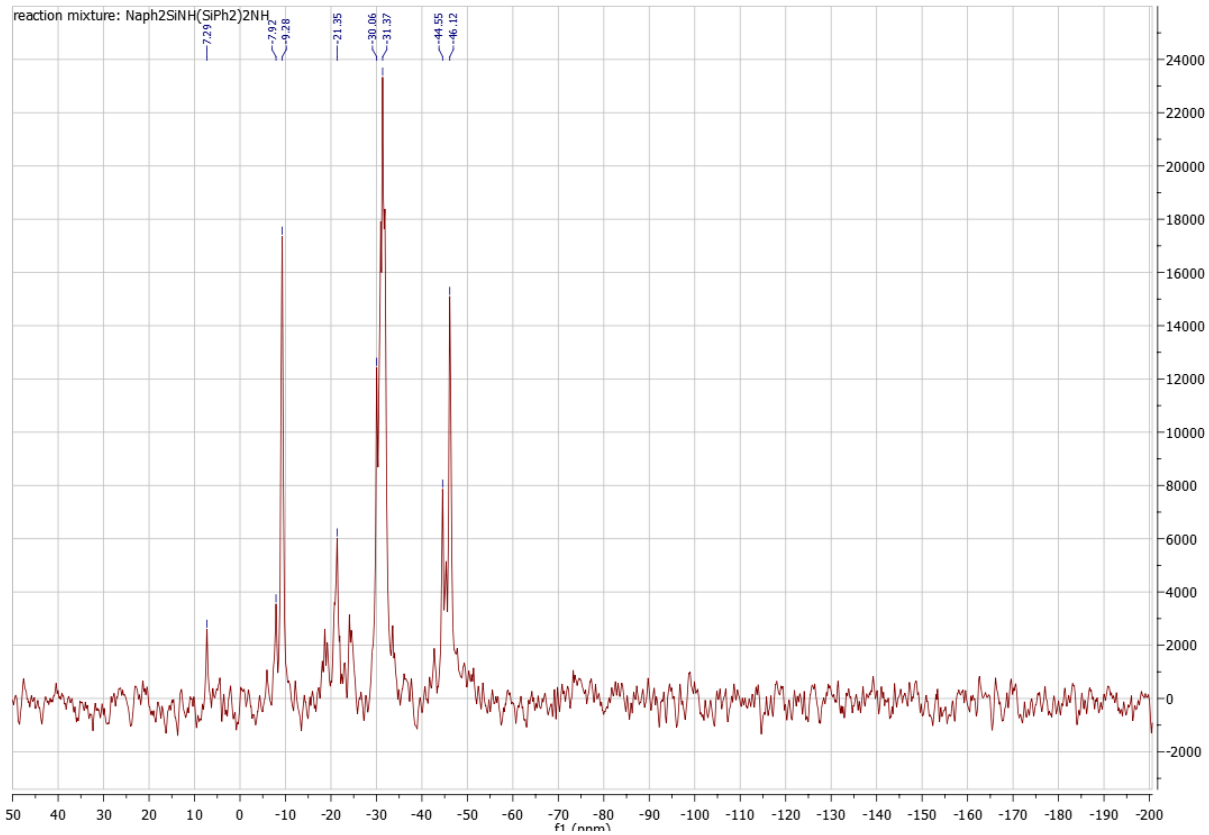


Figure 10: ^{29}Si-NMR of attempted $Naph_2Si(NH)_2(SiPh_2)_2NH$

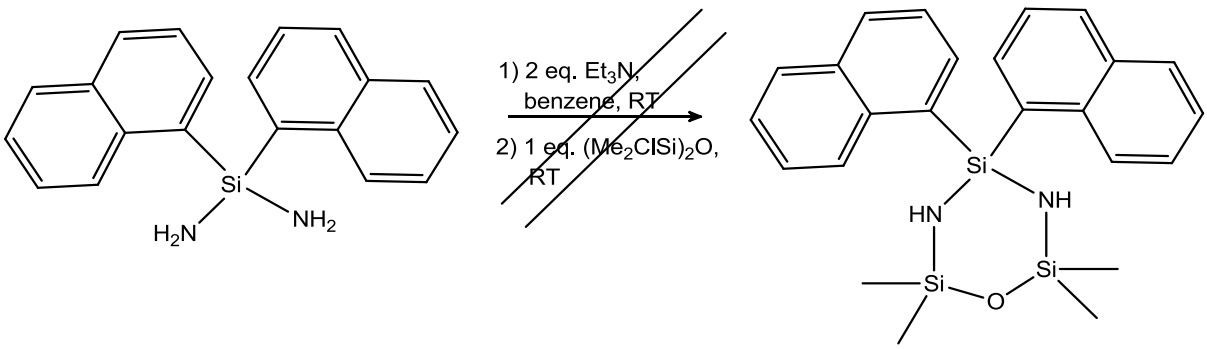
Though, the product should give two different silicon shifts in the ^{29}Si-NMR spectrum several more were found. Interestingly, the two different synthesis attempts of one and the same product did not give the same peaks. Table 17 lists the most significant silicon shifts of both attempts. From those values no peak could be assigned. Obviously the reaction with the auxiliary base Et_3N gives less silicon species when compared to the preparation attempt with ^{n}butylLi. Initially, it was assumed that the amine base does not react with the educts. But later findings showed that the amine base reacts with the silicon chloride species (Me_3SiCl) to form a salt. Thus the reaction stops at the point of the ammonium salt formation, which is described in section 3.1.3.4. It might be possible that the amine base also reacts with the $ClPh_2SiNHSiPh_2Cl$ upon salt formation and thus further ring coupling is prohibited. Whether the amine base reacts with the silicon chloride educt or not the reaction between those two could be monitored via ^{29}Si-NMR measurements. Maybe one of the peaks found in Figure 10 can be assigned to the formed ammonium salt.

Table 17: Comparison of ^{29}Si-NMR shifts of reaction mixture of attempt a) and b)

a) ^{n}butylLi	b) Et_3N
δ^{29}Si [ppm]	
	7.29
-10.19	-7.92
-12.22	-9.28
-12.46	
-13.36	
-13.37	
-13.98	
-20.74	-21.35
-24.26	
-28.37	
-29.89	-30.06
-31.19	-31.37
-33.54	-44.55
-46.22	-46.12

3.2.2 2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-1-oxa-3,5-diaza-2,4,6-trisilacyclohexane

The synthesis attempt shown in Scheme 38 resulted in a clear yellowish product mixture.[17] After removing the salt which was formed during the reaction a ^{29}Si-NMR with a D_2O-capillary was measured.



Scheme 38: Synthesis attempt of 2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-1-oxa-3,5-diaza-2,4,6-trisilacyclohexane

Figure 11 shows the measured ^{29}Si-NMR spectra of the product mixture. As it was not clear if the peak at +7.22 ppm is remaining educt $(Me_2SiCl)_2O$ (-6.88 ppm), the reaction was kept at reflux for 2 h.

After refluxing a second ^{29}Si-NMR measurement was conducted giving the spectrum shown at the bottom of Figure 11.

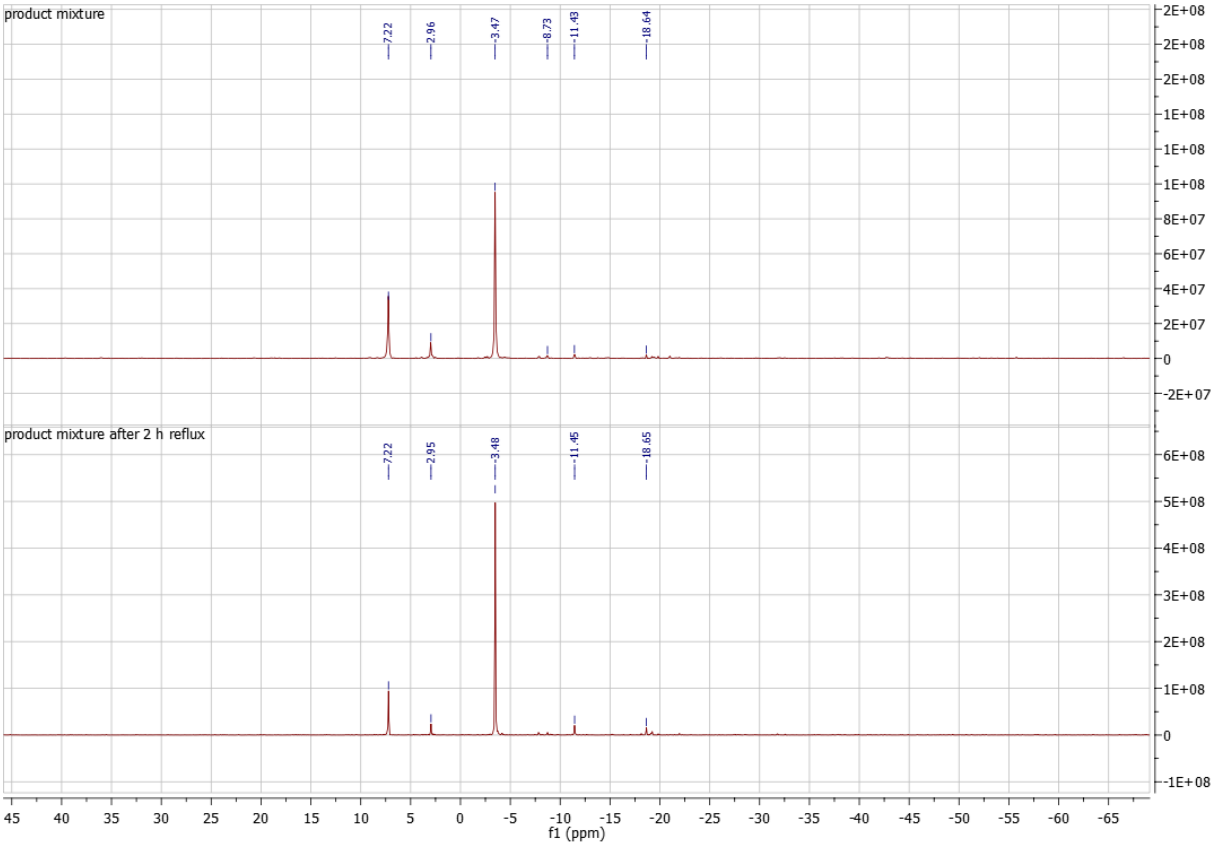


Figure 11: ^{29}Si-NMR of product mixture before and after refluxing

For the desired product two different ^{29}Si-NMR shifts were expected. Apparently, there are two major peaks in both spectra at 7.22 ppm and -3.48 ppm (Figure 11), which were increasing in their intensity after refluxing for 2 h. The two major peaks found were compared with ^{29}Si-NMR shifts of similar compounds shown in Figure 12.[48] Starting from the ^{29}Si shifts of the educts, -6.88 ppm for $(Me_2SiCl)_2O$ and -21.5 ppm for $Naph_2Si(NH_2)_2$, two negative product shifts were expected. Though, the obtained shift at -3.48 ppm seems to be reasonable the shift at 7.22 ppm does not fit quite well with the literature values of similar rings (Figure 12). Furthermore the pernaphthylated cyclotrisilazane shifts at -20.8 ppm, which leads to the assumption that **Si(1)** (Figure 12 framed product) should be more upfield shifted than **Si(2)** because of the more sterically demanding substituents. Unfortunately, Kupce et al. do not give a silicon shift for the phenyl substituted silicon

of 2,2,6,6-tetramethyl-4,4-di(1-phenyl)-1-oxa-3,5-diaza-2,4,6-trisilacyclohexane, which would be the most similar silicon shift to **Si(1)** of the attempted product.[48]

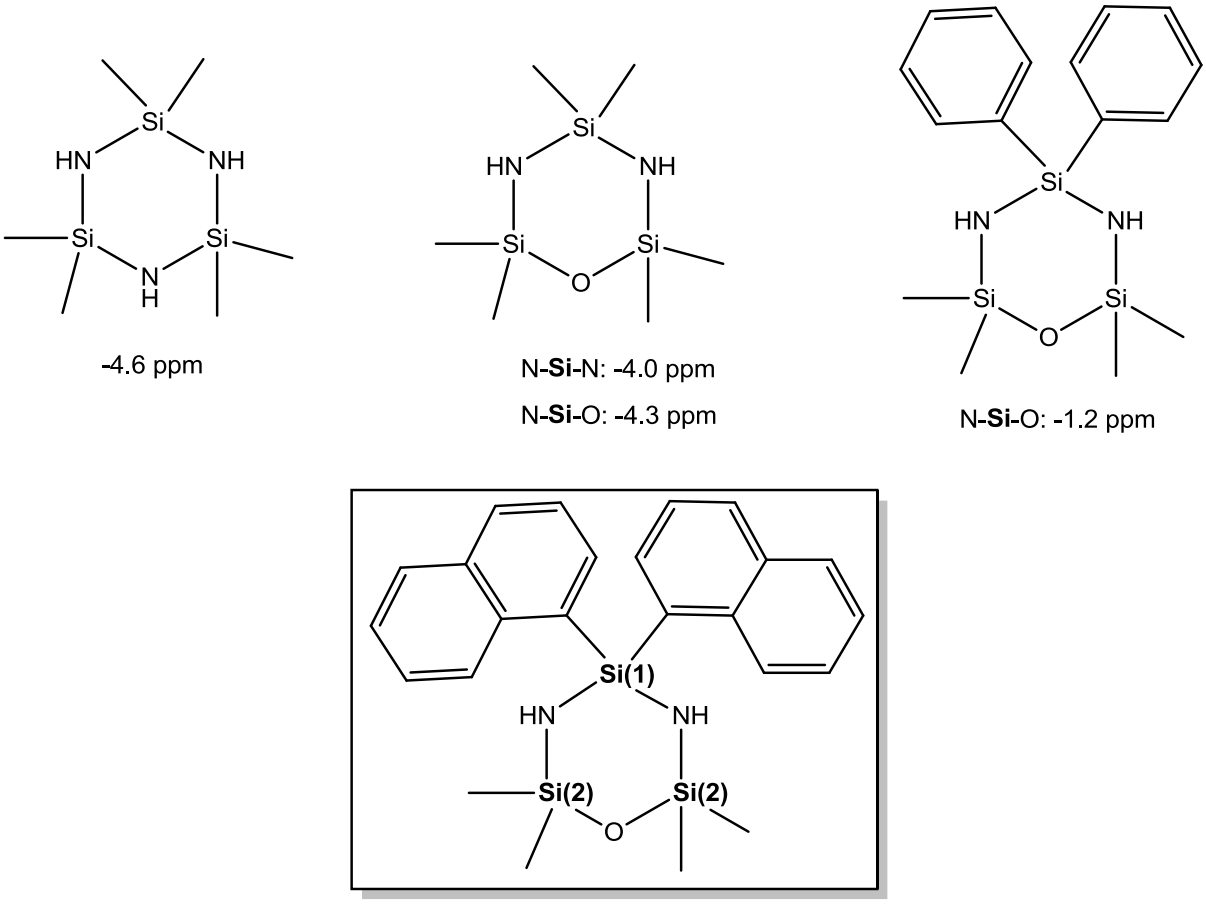
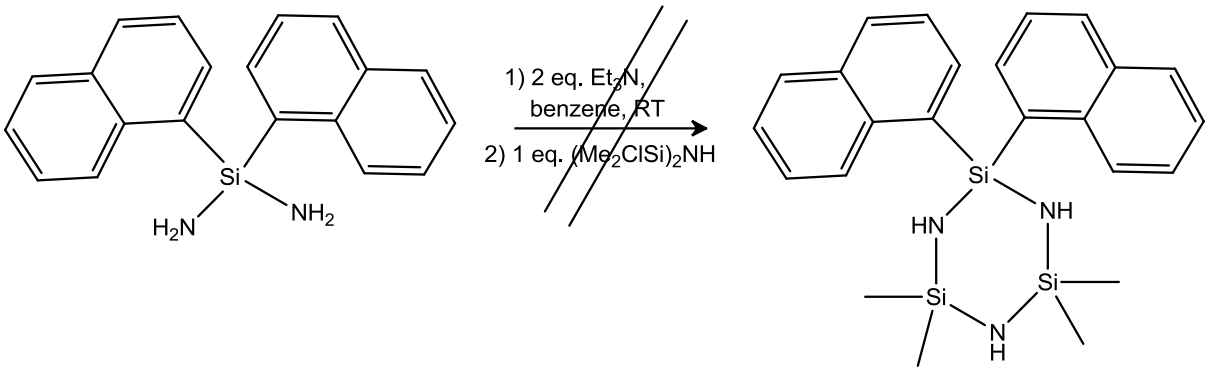


Figure 12: ^{29}Si-NMR shifts of literature known compounds and the desired product (framed)

Based on earlier findings, the unwanted ammonium salt formation between Et_3N and chlorosilane educts occurs. When Et_3N was reacted with Me_3SiCl, an ammonium salt formed which could be detected *via* ^{29}Si-NMR measurements, giving a peak at 6.89 ppm. The obtained shift at 7.22 ppm could be an ammonium salt originating from the unwanted reaction between the amine base and $(Me_2SiCl)_2O$. Further investigations have to be carried out.

3.2.3 2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-trisilazane

In order to quickly screen whether the ring coupling reaction between the diamine and $(Me_2ClSi)_2NH$ works out or not, the reaction shown in Scheme 39 was run on a 0.54 mmol scale in a screwable NMR-tube.



Scheme 39: Synthesis attempt of 2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-trisilazane

After 24 h reaction time a ^{29}Si-NMR was measured revealing two peaks at -5.11 ppm and -21.7 ppm which could be assigned to the two educts $(Me_2ClSi)_2NH$ and $Naph_2Si(NH_2)_2$, respectively.

As there are a several literature reports on the preparation of cyclosilazanes where they refluxed the reaction mixtures for hours[17, 19], this might be the key for all cyclisation attempts.

Obviously the coupling reaction of $(Me_2ClSi)_2NH$ and $Naph_2Si(NH_2)_2$ has to be repeated on a larger scale and more necessarily keeping the reaction at elevated temperatures for some hours to see if the desired product forms.

3.2.4 2,2,4,4,6,6-hexa-(1-naphthyl)cyclotrisilazane (8)

It was attempted to realize the formation of a 1-naphthyl substituted cyclosilazane. The reaction progress was monitored *via* ^{29}Si-NMR measurements with a D_2O-capillary. After refluxing a toluene solution of **6** for about 80h a second peak at -20.83 ppm appeared in the NMR spectrum besides the peak for **6**. After 96h reaction time, the ^{29}Si-NMR shift of the starting material **6** had disappeared, leaving one product peak at -20.83 ppm. When washing the oily product with pentane an amorphous white powder was obtained. Attempts were made to recrystallize the crude product from THF, toluene and ethylacetate. So far, no crystals could be isolated.

Subsequently, the product was subjected to high resolution mass spectroscopy leading to the following spectra (Figure 13). The compound was inserted *via* direct insertion (DI).

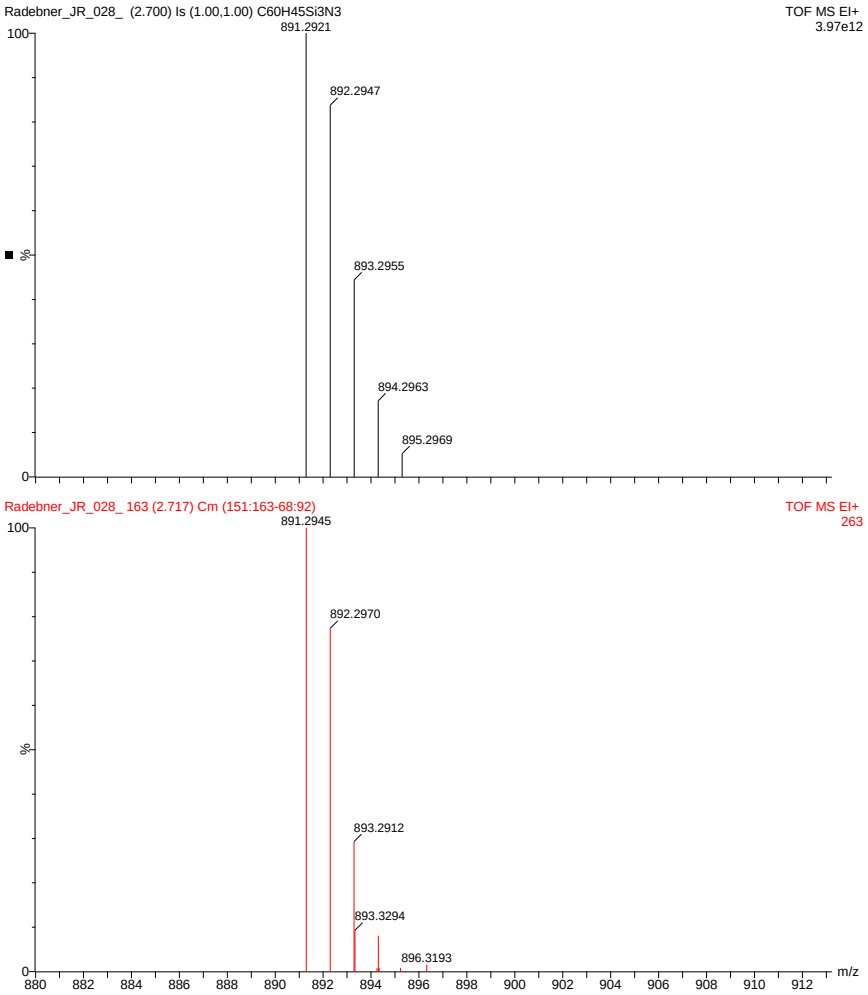
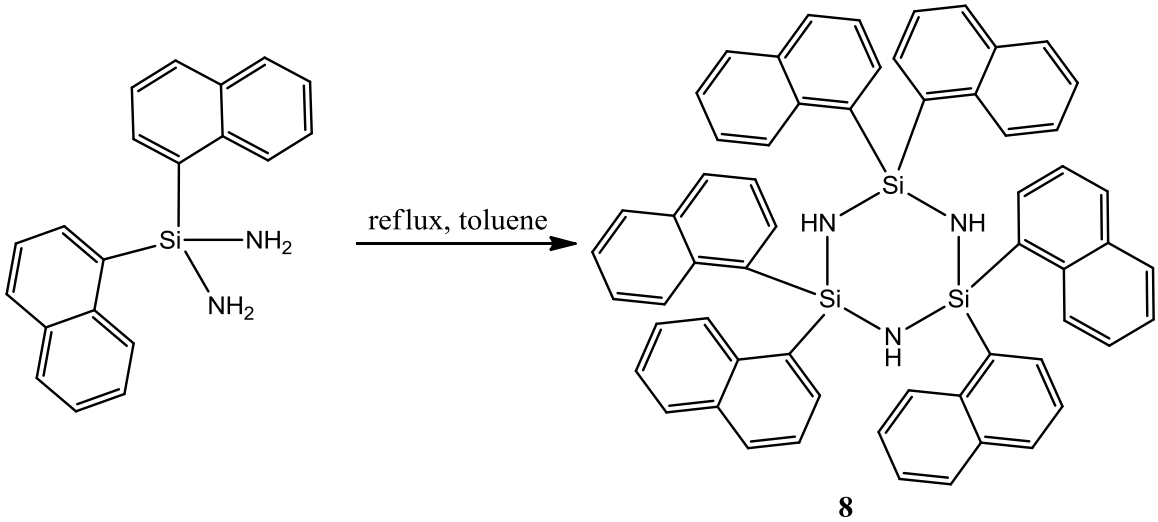


*Figure 13: Molecule peak isotope pattern of **8***

The found isotope pattern of M+ indicates the formation of 2,2,4,4,6,6-hexa-(1-naphthyl)cyclotrisilazane **8.** Obviously, the reaction proceeds as depicted in Scheme 40.



*Scheme 40: Preparation of **8***

An IR spectrum of compound **8** was recorded (Figure 14). In the marked regions typical vibrations can be seen; the N-H stretching at 3458 cm^{-1} and 3369 cm^{-1} (region 1), the deformation vibration of N-H at 1140 cm^{-1} (region 2) and the Si-NH-Si stretching vibrations at 904 cm^{-1} and 876 cm^{-1} (region 3).

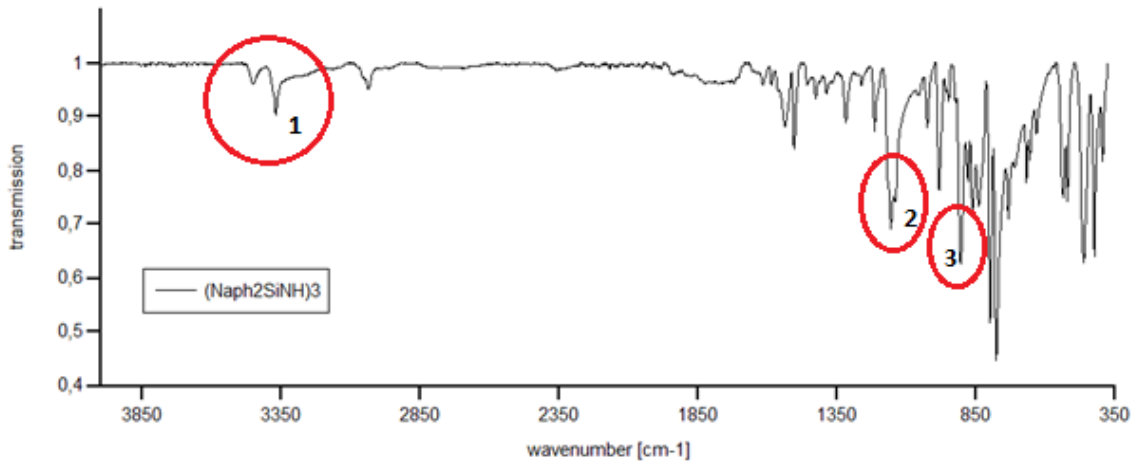


*Figure 14: IR spectrum of **8***

Further assignments are listed in Table 18.

*Table 18: IR assignments of **8***

wavenumber [cm^{-1}]	assignments	
3458	NH	str.vib.
3369	NH	str.vib.
3057	C-H	asym.str.vib.
3036	C-H	str.vib.
1534	C=C	asym.str.
1503	C=C	sym.str.
1315	C-C	asym.str.

1213	C-C	sym.str.
1156	C-H	bend
1140	N-H	def. vib.
1024	C-C	str.vib.
981	CH	wagging
947	CH	wagging
904	Si-NH-Si	asym. str.vib.
876	Si-NH-Si	sym.str.vib.
860	CH	wagging
839		ring def
801	CC	torsion
799	CC	torsion
776	CH	out-of-plane C-H vib.
732	CH	wagging
710	CH	wagging
668	CH	wagging
655	CH	wagging
631	CC	torsion
535	CC	torsion
520	CCC	bend
460	CCC	bend
422		ring def.
392	CC	torsion

The melting point was also determined. While heating the capillary containing **8**, a pH indicator stripe was wetted with water and placed on top of the capillary to monitor the release of NH_3.

The starting temperature was set to 150 °C and a heating rate of 1° C/min was selected until 173 °C were reached, then the heating rate was decreased to 0.5° C/min.

At 190 °C the compound started to melt and releasing NH_3. Gas bubbles were rising through the melting substance. The substance was heated to the maximum temperature of the melting point apparatus (296 °C), no decomposition could be observed but constant release of basic gases (NH_3).

In order to get more detailed information on the decomposition of **8**, a thermal gravimetric analysis (TGA) has to be performed. If the cyclotrisilazane is a suitable precursor for ROP will be tested.

3.3 CONCLUSION AND OUTLOOK

During this work, 1-napthyl substituted silylamines were successfully synthesised and characterised by commonly used methods. Single crystal X-ray analysis and NMR measurements were conducted.

So far neither the crystal structures, nor the NMR data of the prepared 1-naphthyl aminosilanes have been reported in literature. The preparation of silylamines was realized *via* ammonolysis of the respective chlorosilane. Due to the fact that the Si-N bond is isoelectronic with the Si-O bond, the distinction of them was crucial. Therefore, corresponding 1-naphthyl substituted silanols were prepared in order to compare the analytical data of silanols and silylamines.

The latter also served as starting materials for the preparation of cyclic systems with α,ω-functionalised- chlorosilanes. Unfortunately, no attempt of any coupling reaction, which was carried out, led to an isolable ring system. Nevertheless, the successful synthesis of 2,2,4,4,6,6-hexa-1-naphthyl-cyclotrisilazane can be reported. Different characterisation methods were run with the novel compound. No crystals for X-ray analysis could be obtained yet, which would enable the final structural proof. Based on these findings further investigations on the cyclotrisilazane and polymerisation attempts *via* ROP as well as improvements of the cyclisation attempts with α,ω-functionalised- chlorosilanes will be carried out.

4 EXPERIMENTAL SECTION

4.1 MATERIALS AND METHODS

All reactions, unless otherwise stated were carried out under inert conditions using Schlenk technique and nitrogen as inert gas. In order to ensure dry atmosphere, the used nitrogen passed a drying tower filled with P_4O_{10} to remove residual moisture. 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, unless otherwise mentioned.

4.2 CHARACTERISATION

4.2.1 NMR-Spectroscopy

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25°C.

Table 19: Frequencies of observed nuclei (300 MHz spectrometer)

nucleus	frequency [MHz]
^{1}H	300.22
^{13}C	75.5
^{29}Si	59.64

Chemical shifts are given in parts per million (ppm) relative to TMS (δ = 0 ppm). Coupling constants (*J*) are reported in Hertz (Hz). The spectra were processed and analysed in MestReNova 6.0.2. C_6D_6 or D_2O-capillary were used as internal or external lock, respectively.

4.2.2 Elemental Analysis

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

4.2.3 Single Crystal X-ray Diffraction Analysis

XRD data collection was performed on a Bruker Apex II diffractometer with use of Mo Kα radiation (λ=0.71073 Å) and a CDD area detector. Empirical absorption corrections were applied using

SADABS.[49,50] 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.[51, 52] The space group assignments and structural solutions were evaluated using PLATON.[53,54] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to N for all compounds were located in a difference map. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Intermolecular interactions for presented and published compounds were determined by the calculation of centroids and planes feature of the programs Mercury and Diamond.[55,56] Table 26 contains crystallographic data and details of measurements and refinement for compounds **5** and **6**.

4.2.4 ATR Measurements

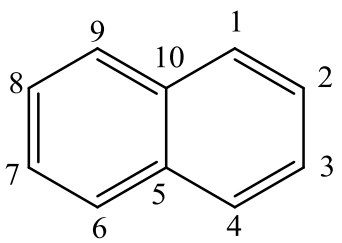
For ATR measurements a Bruker Alpha-P was used.

4.2.5 MS-Measurements

Compounds were ionized *via* electron impact (70 eV) ionization. Mass spectra were recorded on a Waters GCT Premier equipped with direct insertion (DI).

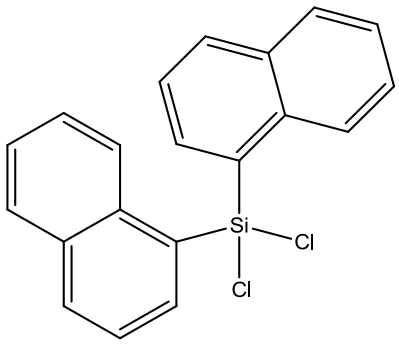
4.3 SYNTHESIS

For all naphthyl moieties the NMR assignment for carbon and hydrogen atoms is according to the IUPAC numbering (Scheme 41).



Scheme 41: IUPAC numbering of naphthyl moiety

Dichloro(di-1-naphthyl)silane (1)



A three necked flask was charged with 20.51 g 1-naphthyl bromide (1 eq., 0.099 mol) in 100 mL Et_2O and cooled to -70 °C with a N_2/EtOH cooling bath. 41.6 mL ^{n}*b*utylLi (1.05 eq., 0.104 mol, 6.66 g) was slowly added with a syringe. After complete addition of ^{n}*b*utylLi the reaction mixture was stirred for 40 min at -70 °C. A second flask was charged with 5.69 mL $SiCl_4$ (0.5 eq., 0.050 mol, 8.41 g) in 120 mL Et_2O under ice cooling. The reaction mixture of flask one was added *via* cannula and stirred overnight. The solvent was evaporated to give a yellowish powder which was suspended in dichloromethane (DCM) and filtered through celite. Again the solvent was removed under reduced pressure. The raw product was washed with pentane and recrystallized from toluene to give 27.3 g (yield 78 %) white crystals.

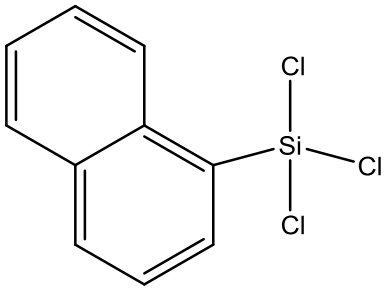
^{1}H-NMR (300.22 MHz, C_6D_6): δ 6.99-7.08 (m, 6H, H-3, H-8,H-9), 7.45-7.57 (dd, 4H, H-4, H-7, J_{H-H}= 8.0 Hz), 8.08-8.10 (d, 2H, H-2), 8.47-8.50 (d, 2H, H-10). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 136.10, 135.57, 133.67, 132.97, 129.66, 129.08, 127.89, 126.89, 126.10, 124.87. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:7.76 GC-MS: t_R= 23.968; m/z= 352.2. IR:

*Table 20: IR assignments of **1***

wavenumber [cm^{-1}]	assignments	
3054	C-H	asym.str.vib.
3031	C-H	str.vib.
1540	C=C	asym.str.
1503	C=C	sym.str.
1321	C-C	asym.str.
1215	C-C	sym.str.
1151	C-H	bend
1024	C-C	str.vib.
986	CH	wagging
948	CH	wagging

860	CH	wagging
831		ring def
801	CC	ring def
792	CC	torsion
767	CH	torsion
731	CH	out-of-plane C-H vib.
675	CH	wagging
665	CH	wagging
625	Si-Cl	str.vib.
551	Si-Cl	asym.str.vib.
536	Si-Cl	sym.str.vib.
511	CCC	bend
500	Si-Cl	str.vib.
445		ring def.
414		ring def.
392	CC	torsion

Trichloro-1-naphthylsilane (2)

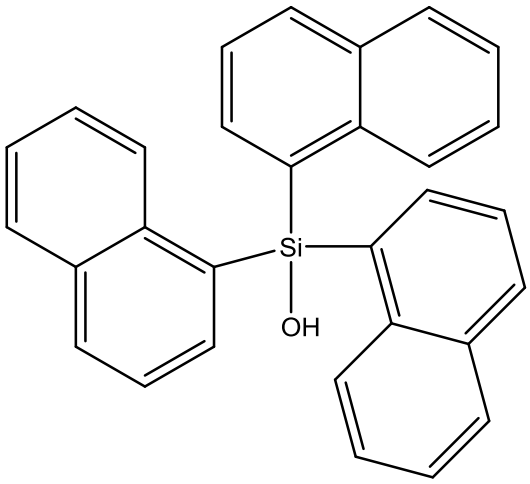


A flask equipped with a dropping funnel and a reflux condenser was charged with 1.68 g (1.2 eq. 0.0691 mol) magnesium turnings in 15 mL THF and the dropping funnel was filled with a solution of 8.07 mL 1-naphthyl bromide (1 eq., 0.0577 mol, 11.95 g) in 70 mL THF. The Grignard reaction started after addition of 5 mL of the 1-naphthyl bromide solution and applying heat with the heatgun. The 1-naphthyl bromide solution was added dropwise so that gentle reflux continued. After completion of the addition, the reaction mixture was refluxed for 1.5 h. A second flask furnished with a mechanical stirrer and a reflux condenser was charged with 7.29 mL $SiCl_4$ (1.1 eq., 0.0635 mol, 10.79 g) in 80 mL THF. After cooling the Grignard reagent to room temperature, the reaction mixture was added *via* cannula to the THF solution of $SiCl_4$ and stirred overnight. The mixture was evaporated to dryness,

extracted with pentane and filtered to remove the salt. The pentane-soluble trichloro-1-naphthylsilane was distilled at 120 °C under vacuum to provide 5.33 g pure product. (yield: 36 %)

^{1}H-NMR (300.22 MHz, C_6D_6): δ 6.88-6.93(m, 1H), 7.09-7.19 (m, 2H), 7.36-7.45 (dd, 2H), 7.83-7.85 (d, 1H), 8.35-8.38 (d, 1H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 135.32, 134.29, 133.89, 133.43, 129.18, 127.31, 126.90, 126.29, 125.99, 124.30. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-0.38 ppm. GC-MS: t_R= 15.440; m/z= 260.0.

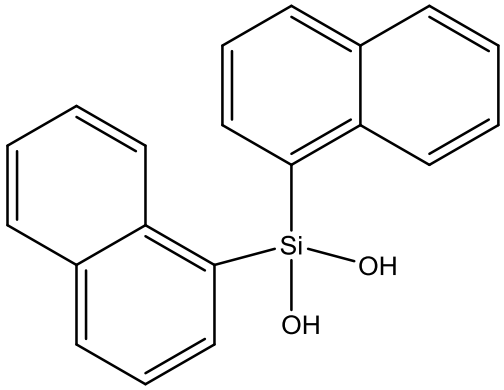
Hydroxy(tri-1-naphthyl)silane (3)



In a flask, 0.93 g (1 eq., 0.0021 mol) chloro(tri-1-naphthyl)silane were dissolved in 20 mL benzene. 20 mL of deionized H_2O (531 eq., 1.11 mol, 20 g) were added with a syringe. The reaction mixture was vigorously stirred overnight. The crude product was transferred to a separating funnel and separated from the aqueous phase. The organic phase was dried with Na_2SO_4. The salt was filtered off and the solvent was removed under reduced pressure giving a white product.

^{1}H-NMR (300.22 MHz, C_6D_6): δ 6.89-6.94(m, 3H), 7.01-7.06 (m, 6H), 7.53-7.62 (dd, 6H), 7.82-7.84 (d, 3H), 8.60-8.63 (d, 3H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 135.41, 134.22, 134.01, 131.1, 129.0, 128.7, 128.48, 126.29, 125.16, 125.08. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-21.81 ppm

Dihydroxy(di-1-naphthyl)silane (4)



After dissolving 1.60 g dichloro(di-1-naphthyl)silane (1 eq., 0.0045 mol) in 30 mL benzene, 30 mL deionized H_2O were added to the solution and vigorously stirred overnight. The crude product was separated from the aqueous phase with a separating funnel. The organic phase was dried with Na_2SO_4. The salt was filtered of and the solvent was removed under reduced pressure giving a white product.

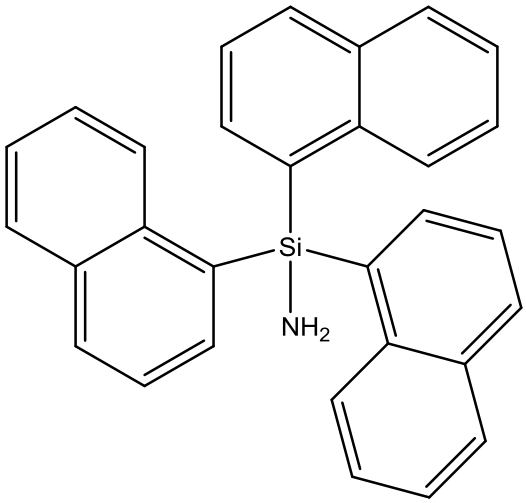
^{1}H-NMR (300.22 MHz, C_6D_6): δ 6.99-7.08(m, 4H), 7.14-7.19 (m, 4H), 7.55-7.64 (dd, 2H), 7.99-8.02 (d, 2H), 8.47-8.50 (d, 2H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 135.60, 133.29, 131.1, 129.0, 128.7, 128.5, 126.3, 125.6, 125.1, 124.30. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-26.81 ppm. IR:

*Table 21: IR assignments of **4***

wavenumber [cm-1]	assignments	
3561	Si-OH	asym.str.vib.
3351	Si-OH	sym.str.vib.
3051	C-H	asym.str.vib.
3032	C-H	str.vib.
1540	C=C	asym.str.
1503	C=C	sym.str.
1322	C-C	asym.str.
1220	C-C	sym.str.
1149	C-H	bend
1021	C-C	str.vib.
985	CH	wagging
931	CH	wagging
882	O-H	def.vib.
860	CH	wagging
831		ring def
799	CH	wagging
774	CC	torsion
742	CH	out-of-plane C-H vib.

669	CH	wagging
652	CH	wagging
600	Si-O	str.vib.
539	CC	torsion
515	CCC	bend
463	CCC	bend
432		ring def.
422		ring def.
385	CC	torsion

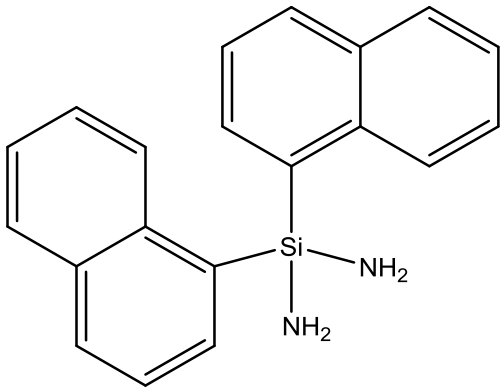
Amino(tri-1-naphthyl)silane (5)



3.02 g Chloro(tri-1-naphthyl)silane (1 eq., 0.0068 mol) were dissolved in 320 mL Et_2O. A second flask equipped with a dropping funnel was cooled to -70 °C with a N_2/EtOH cooling bath. Dry ammonia was condensed into this flask for 20 min. The chloro(tri-1-naphthyl)silane solution was added fast *via* the dropping funnel to the liquid ammonia. The reaction mixture was stirred overnight without removing the cooling bath. The reaction mixture was filtered. The solvent was evaporated and the crude product recrystallized from toluene.

^{1}H-NMR (300.22 MHz, C_6D_6): δ 6.99-7.18(m, 9H), 7.59-7.64 (m, 6H), 7.77-7.79 (d, 3H), 8.37-8.40 (d, 3H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 137.54, 136.92, 135.31, 133.86, 130.55, 129.45, 128.96, 125.70, 125.34, 125.22. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-11.86 ppm. mp: 207 - 208°C

Diamino(di-1-naphthyl)silane (6)



Approach 1 with liquid ammonia:

This reaction was carried out in toluene as well as in ether. First, 2.4 g dichloro(di-1-naphthyl)silane (1 eq., 0.0068 mol) were dissolved in the solvent; either 200 ml ether or 35 ml when toluene were used. In a second flask, which was cooled to -70 °C *via* N_2/EtOH cooling bath, ammonia was condensed for 20 min. The educt solution was quickly added with a syringe at -70 °C. Without removing the cooling bath, the reaction mixture was stirred overnight.

The formed salt was filtered off with a cannula. The solvent was removed under reduced pressure giving a white powder. (yield: >70 %)

The crude product was washed in pentane and recrystallized from toluene at -20 °C, giving clear colourless crystals.

Approach 2 with gaseous ammonia:

This reaction was carried out in ether, benzene or toluene. 5.80 g dichloro(di-1-naphthyl)silane (1 eq., 0.016 mol) were dissolved in the respective solvent. While stirring at room temperature, gaseous ammonia was bubbled through the solution for 15-20 min. The reaction mixture was stirred overnight. For the work up and cleaning of the product, the same procedure as mentioned in approach 1, was used.

Approach 3 with gaseous ammonia and reflux

In a flask, equipped with a condenser, 1.00 g dichloro(di-1-naphthyl)silane (1 eq., 0.0028 mol) were dissolved in 80 mL toluene. The solution was kept at reflux while ammonia was bubbled through the solution. After 30 min the addition of ammonia was stopped and the reflux continued for half an hour. After cooling to room temperature gaseous ammonia was again bubbled through the solution for 20 min. The reaction mixture was stirred for 2 hours. The salt was filtered off and the solvent evaporated to give a white powder as product.

Approach 4 with $NaNH_2$

0.53 g $NaNH_2$ (2 eq., 0.0136 mol) were dissolved in 50 mL ether. In a second flask, 2.4 g dichloro(di-1-naphthyl)silane (1 eq., 0.0068 mol) were dissolved in 120 mL ether. This solution was added to the $NaNH_2$ at 0 °C. The reaction mixture was stirred overnight. The work up procedure as described in approach 1 was used.

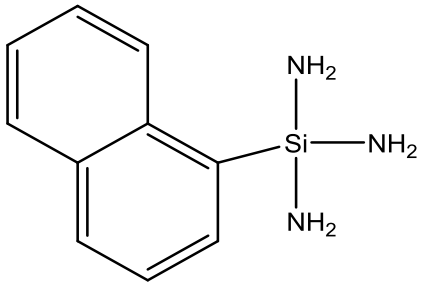
^{1}H-NMR (300.22 MHz, C_6D_6): δ 0.97 (s, 4H(N-H)), 7.15-7.27 (m, 6H), 7.60-7.67 (m, 4H), 7.95-7.98 (d, 2H) 8.42-8.45 (d, 2H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 137.25, 137.17, 135.20, 133.77, 130.13, 129.23, 128.80, 125.64, 125.24, 125.08. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-21.53 ppm**.** mp: 150 -152°C. IR:

*Table 22: IR assignments of **6***

wavenumber [cm-1]	assignments	
3470	NH_2	asym.str.vib.
3450	NH_2	sym.str.vib
3373	NH	single band
3064	C-H	asym.str.vib.
3041	C-H	str.vib.
1540	NH_2	defor.vib.
1526	C=C	asym.str.
1501	C=C	sym.str.
1321	C-C	asym.str.
1215	C-C	sym.str.
1147	C-H	bend
1019	C-C	str.vib.
982	CH	wagging
975	CH	wagging
885	N-Si-N	asym.str.vib

848	N-Si-N	sym.str.vib.
797	CC	torsion
777	CC	torsion
740	CH	out-of-plane C-H vib.
731	CH	wagging
665	CH	wagging
654	CH	wagging
537	CC	torsion
517	CCC	bend
462	CCC	bend
440		ring def.
425		ring def.
384	CC	torsion

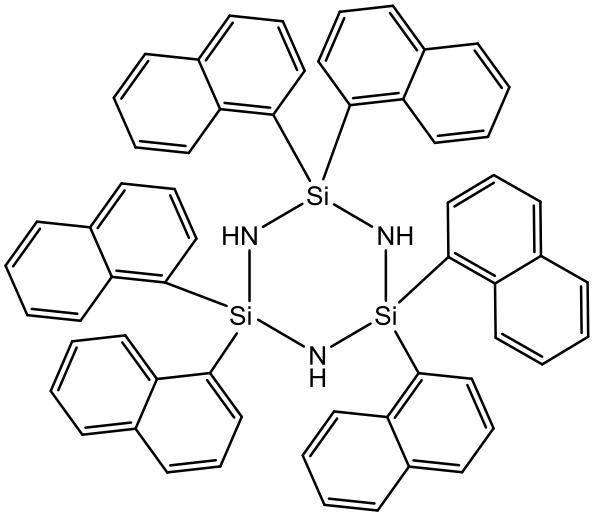
Triamino(1-naphthyl)silane (7)



Dry ammonia was condensed into a flask for 20 min. 0.8 mL trichloro(1-naphthyl)silane (0.00423 mol, 1.10 g) were added neat to the liquid NH_3. The cooling bath was removed and the ammonia evaporated. The solid residue was dissolved in benzene and the salt was filtered off. The solvent was reduced to half of its original volume and the flask stored in the fridge.

^{29}Si-NMR (D_2O-capillary): δ:-30.4 ppm

2,2,4,4,6,6-hexa-(1-naphthyl)-cyclotrisilazane (8)



In a flask equipped with a condenser, 0.500 g diamino(di-1-naphthyl)silane crystals (0.0016 mol) were dissolved in 35 mL toluene and refluxed for 102 h. A colourless oil was obtained after evaporation of the solvent. The oil was washed in pentane and recrystallized from toluene.

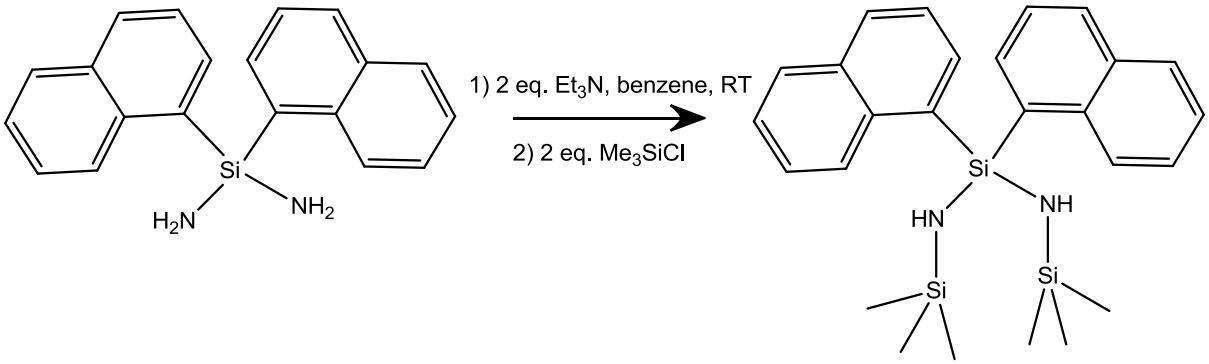
^{1}H-NMR (300.22 MHz, C_6D_6): δ 1.15 (s, 3H(N-H)), 7.14-7.17 (m, 12H), 7.58-7.64 (m, 18H), 7.93-7.96 (d, 6H) 8.43-8.46 (d, 6H). ^{13}C-NMR (75.5 MHz, C_6D_6): δ 136.42, 135.53, 133.37, 131.51, 130.91, 130.66, 128.92, 126.16, 125.41, 124.95. ^{29}Si-NMR (59.64 MHz, C_6D_6): δ:-20.69 ppm. Melting range: 190°C - 296°C (steady release of NH_3 monitored with pH-indicator stripe). IR:

*Table 23: IR assignments of **8***

wavenumber [cm^{-1}]	assignments	
3458	NH	str.vib.
3369	NH	str.vib.
3057	C-H	asym.str.vib.
3036	C-H	str.vib.
1534	C=C	asym.str.
1503	C=C	sym.str.
1315	C-C	asym.str.
1213	C-C	sym.str.
1156	C-H	bend
1140	N-H	def. vib.
1024	C-C	str.vib.
981	CH	wagging
947	CH	wagging
904	Si-NH-Si	asym. str.vib.
876	Si-NH-Si	sym.str.vib.
860	CH	wagging

839		ring def
801	CC	torsion
799	CC	torsion
776	CH	out-of-plane C-H vib.
732	CH	wagging
710	CH	wagging
668	CH	wagging
655	CH	wagging
631	CC	torsion
535	CC	torsion
520	CCC	bend
460	CCC	bend
422		ring def.
392	CC	torsion

1,1,1,3,3,3-hexamethyl-2,2-di(-1-naphthyl)trisilazane

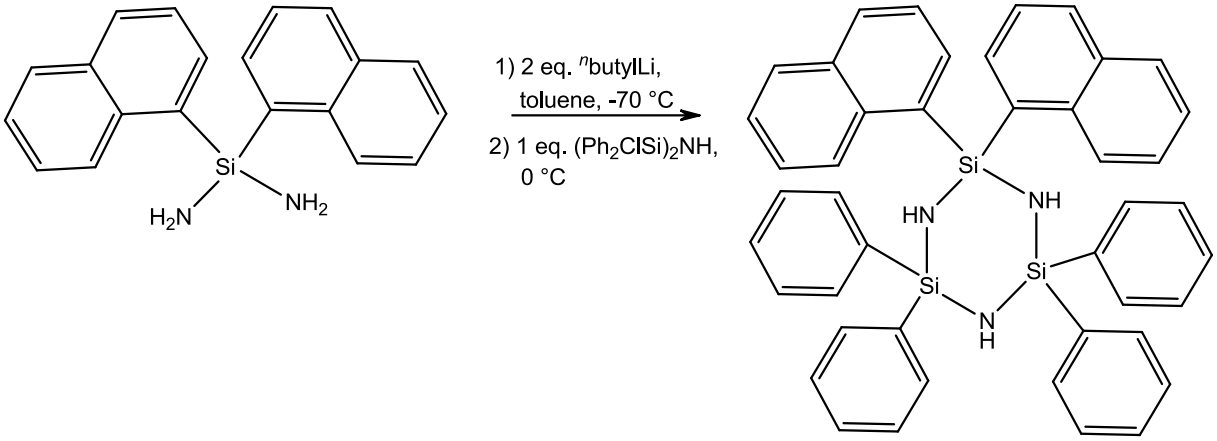


0.100 g Diamino(di-1-naphthyl)silane (1 eq., $3*10^{-4}$ mol) were dissolved in 0.9 mL benzene. 0.088 mL of dry triethylamine (2 eq., $6.4*10^{-4}$ mol, 0.064 g) (Karl Fischer Titration: 100 ppm H_2O) were added with a syringe. After 5 min, 0.082 mL chloro-trimethylsilane (2 eq., $6.4*10^{-4}$ mol, 0.069 g) were added. The reaction mixture was stirred for 72 h. The salt was filtered off and the solvent removed under reduced pressure to give a white solid.

^{29}Si-NMR (59.64 MHz, D_2O-capillary): δ: -2.97 ppm

1,1,3,3-tetraphenyl-2,2-di-(1-naphthyl)-cyclotrisilazane

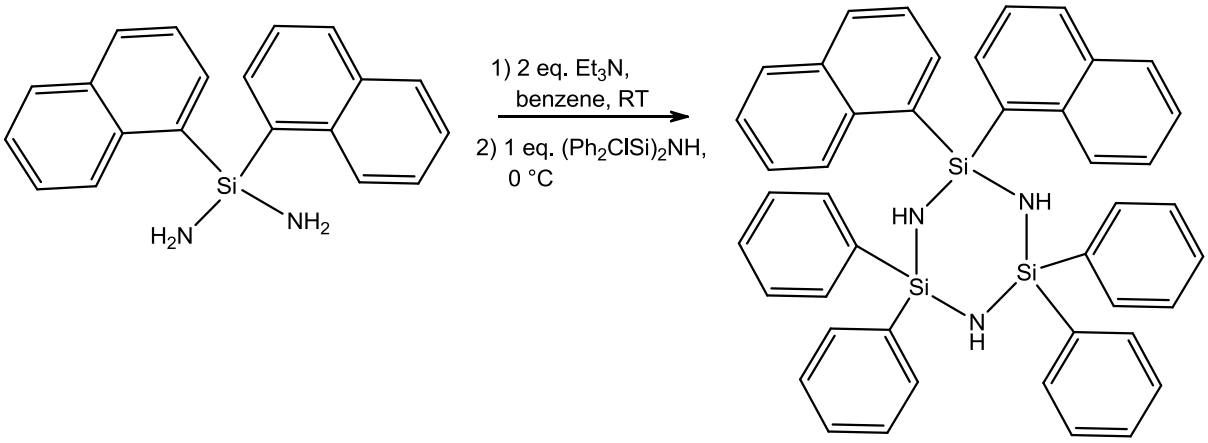
a) Via **^{n}butylLi**



2.6 g diamino(di-1-naphthyl)silane (1 eq., 0.0083 mol) and 3.71 g dichloro-tetraphenyldisilazane (1 eq., 0.0083 mol) were dissolved in 78 mL and 120 mL toluene respectively. The diamine-solution was cooled to -70 °C while adding 6.61 mL ^{n}butylLi (2 eq., 0.0165 mol, 1.06 g) *via* a syringe. The mixture was stirred at -70 °C for one hour before it was added to the dichloro-tetraphenyldisilazane solution *via* a cannula at 0 °C. The mixture was stirred for one hour at 0 °C. The salt was filtered off and the solvent evaporated to obtain a white yellowish oil.

^{29}Si-NMR (59.64 MHz, D_2O-capillary): δ: -10.19, -12.22, -12.64, -13.36, -13.37, -13.98, -20.74, -24.26, -28.37, -29.89, -31.19, -33.54, -46.22 ppm

***b) Via* Et$_3$N**

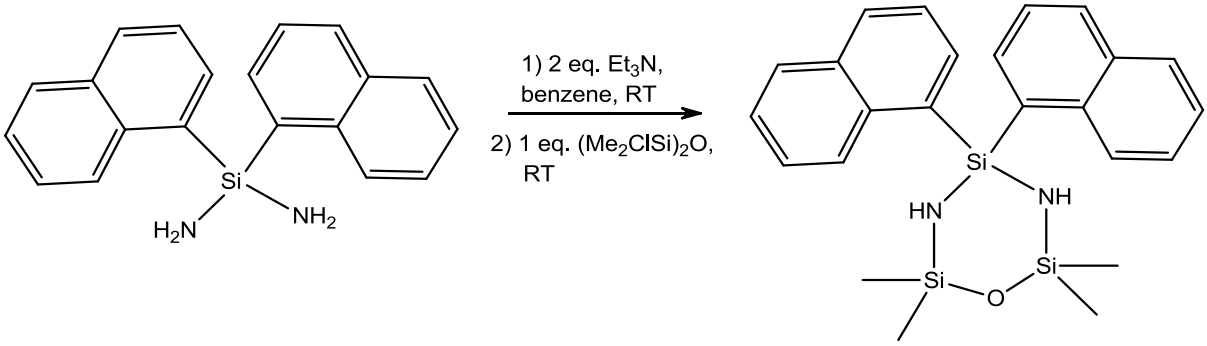


2.0 g Diamino(di-1-naphthyl)silane (1 eq., 0.0064 mol) and 2.23 g dichloro-tetraphenyl-disilazane (1 eq., 0.0063 mol) were dissolved in 70 mL and 20 mL benzene respectively. 1.76 mL of Et_3N (2 eq., 0.013 mol, 1.29 g) were added to the amine solution. Afterwards, the mixture was cooled to 0 °C

while adding the dichloro-tetraphenyl-disilazane solution *via* a cannula. The mixture was stirred overnight. The salt was filtered off and the solvent evaporated to obtain a white yellowish powder.

^{29}Si-NMR (59.64 MHz, D_2O-capillary): δ: 7.29, -7.92, -9.28, -21.35, -30.06, -31.37, -44.55, -46.12 ppm

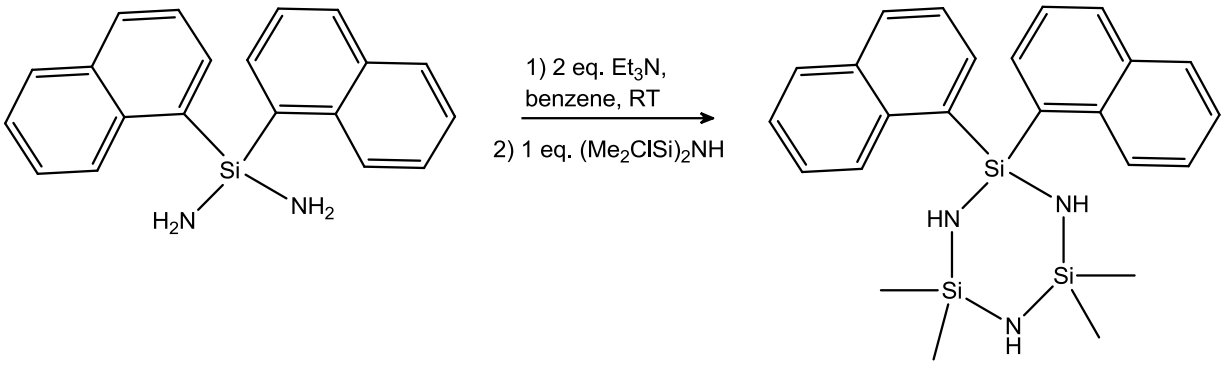
2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-1-oxa-3,5-diaza-2,4,6-trisilacyclohexane



1.0 g Diamino(di-1-naphthyl)silane (1 eq., 0.0032 mol) were dissolved in 50 mL benzene. 0.88 mL of Et_3N (2 eq., 0.006 mol, 0.64 g) were added to the amine solution. Afterwards 1.04 mL tetramethyl-disiloxane (1 eq., 0.0032 mol, 0.65 g) were added at r.t. The mixture was stirred overnight. After refluxing the reaction mixture for 2 hours, the salt was filtered off to obtain a white yellowish product mixture.

^{29}Si-NMR (59.64 MHz, D_2O-capillary): δ: 7.22, 2.95, -3.48, -11.45, -18.65 ppm. GC-MS: t_R= 10.870; m/z= 483.0, t_R= 9.544; m/z= 301.0, t_R= 8.060 m/z= 227.0, t_R= 6.390; m/z= 261.0.

2,2,6,6-tetramethyl-4,4-di(1-naphthyl)-trisilazane



0.170 g Diamino(di-1-naphthyl)silane (1 eq., 0.00054 mol) were dissolved in 1 mL benzene in a screwable NMR-tube. 0.15 mL of Et_3N (2 eq., 0.0011 mol, 0.11 g) were added to the amine solution. Afterwards 0.11 mL tetramethyl-disilazane (1 eq., 0.00054 mol, 0.11 g) were added at room temperature. The reaction mixture was kept at r.t. overnight.

^{29}Si-NMR (59.64 MHz, D_2O-capillary): δ: -5.11, -21.7 ppm

5 REFERENCES

1. L. Rösch, P. John, R. Reitmeier, Ullmann's Encyclopedia of Industrial Chemistry. *Organic Silicon Compounds* [Online] John Wiley and Sons: **2005**.
2. C.R. Krüger, E.G. Rochow, *Journal of Polymer Science Part A* **1964,** *2*, 3179-3189.
3. W. Simmler, *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 32*, John Wiley and Sons, **2000**.
4. J. D. Byrd, J. E. Curry *Technical Memorandum X-53197* **1965**.
5. M. Bouquey, C. Brochon, S. Bruzaud, A-F. Mingotaud , M. Schappacher, A. Soum, *Journal of Organometallic Chemistry* **1996,** *521*, 21-27.
6. R. Fessenden, J. S. Fessenden, *Chemical Reviews* **1960,** *61*, 361.
7. F. A. Henglein , K. Lienhard *Makromolekulare Chemie* **1959,** *32*, 218.
8. Tansjö, L., *Acta Chemica Scandinavica* **1964,** *18*, 456-464.
9. Chugunov, V. S., *The Journal of General Chemistry of the USSR* **1953,** *23*, 811-813.
10. C.A. Kraus , R. Rose *Journal of American Chemical Society* **1925,** *47*, 2739.
11. Fink, W., *Chemische Berichte* **1963,** *96*, 1071-1079.
12. K. Ruhlandt-Senge, R.A. Bartlett, M.M. Olmstead, P.P. Power *Angewandte Chemie* **1993,** *105*, 459.
13. L. H. Sommer, L. J. Tyler *Journal of the American Chemical Society* **1954,** *76*, 1030-1033.
14. T. Chivers, I. Manners, *Inorganic Rings and Polymers of the p-Block Elements - From Fundamentals to Applications*. The Royal Society of Chemistry: **2009**.
15. T.J. Clark, K. Lee, I. Manners, *Chemistry - A European Journal* **2006,** *12*.
16. A. Stock , K. Somieski *Chemische Berichte* **1921,** *54*, 1921.
17. M. Kavala , A. Hawkins , P. Szolcsányi *Journal of Organometallic Chemistry* **2013,** *732*, 58-91.
18. K. A. Andrianov, G. V. Kotrelev, V. V. Kazakova, I. E Rogov, *Russian Chemical Bulletin* **1975,** *24*.
19. U. Klingebiel , N. Vater *Chemische Berichte* **1983,** *116*, 3277-3528.
20. U. Klingebiel, N. Vater, *Angewandte Chemie* **1982,** *94*.
21. U. Kliebisch, U. Klingebiel, N. Vater *Chemische Berichte* **1985,** *118*, 4561.
22. U. Klingebiel, N. Vater *Angewandte Chemie Supplement* **1982**, 1865.
23. K. A. Andrianov , Zh. S. Systsova, V. M. Kopylov, T. K. Augustinenen *Chemistry of Heterocyclic Compounds* **1972**, 679.
24. S. D. Brewer , Ch. P. Haber *Journal of American Chemical Society* **1948,** *70*, 3888.
25. A. A. Zhdanov, K. A. Andrianov, T. V. Astapova , B. D. Lavrukhin *Russian Chemical Bulletin* **1978**, 1858.
26. C. Ackerhans, B. Räke, R. Krätzner, P. Müller, H. W. Roesky, I. Usón, *European Journal of Inorganic Chemistry* **2000**, 827.
27. T. Shinohara, A.Yokoo, M. Kudo, M. Iwabuchi , K. Matsumura, U.S. Patent 5466847A, **1995**.
28. K. A. Andrianov, A. A. Zhdanov, B. A Astapov, B. D. Lavrukhin, T. V. Strelkova, T. V. Astapova *Russian Chemical Bulletin* **1979,** *28*, 338.
29. T. Kottke , U. Klingebiel , M. Noltemeyer , U. Piper , S. Waler, D. Stalke *Chemische Berichte* **1991,** *124*, 1941.
30. B. Räke , H. W. Roesky, I. Usón, P. Müller, *Angewandte Chemie International Edition* **1998,** *37*, 1432.
31. E. Kroke , Li Ya-Li , C. Konetschny , E. Lecomte , C. Fasel , R. Riedel *Materials Science and Engineering* **2000,** *26*, 97-199.
32. M. F. Shostakoskii, Kh. I. Kondrat'ev, *Russian Chemical Bulletin* **1957,** *36*.
33. B. M. Moore , S. M. Ramirez , G. R. Yandek , T. S. Haddad , J. M. Mabry, *Polymer Reprints* **2011,** *52*, 438.
34. H. Gilman, C. G. Brannen, *Journal of American Chemical Society* **1951,** *73*, 4640-4644.

35. A. Lyčkaa, D. Šnobla, K. Handlířb, J. Holečekb, M. Nádvorníkb *Collection of Czechoslovak Chemical Communications* **1981,** *46*, 1383-1388.
36. S. Yamaguchi, S. Akiyama, K. Tamao, *Organometallics* **1998,** *17*, 4347-4352.
37. V. Chandrasekhar, R. Boomishankar, S. Nagendran, *Chemical Reviews* **2004,** *104*, 5847-5910.
38. Tran N. T., Wilson S. O., Franz A. K., *Organic Letters* **2012,** *14*, 186-189.
39. B. P. S. Chauhana, A. Sarkara, M. Chauhanb, A. Rokab, *Applied Organometallic Chemistry* **2009,** *23*, 385-390.
40. A. G. Schafer, J. M. Wieting, A. E. Mattson, *Organic Letters* **2011,** *13*, 5228–5231.
41. S. A. Bourne, L. R. Nassimbeni *Journal of Organic Chemistry* **1992,** *57*, 2438-2442.
42. M. Mantina, A. C. Chamberlin, R. Valero , C. J. Cramer ,D. G. Truhlar *Journal of Physical Chemistry A* **2009,** *113*, 5806-5812.
43. R. H. Cragg, R. R. Lane, *Journal of Organometallic Chemistry* **1985,** *294*, 7-22.
44. F. Uhlig, H. Marsmann *29Si NMR Some practical aspects*. 2nd ed.; Gelest Inc.: **2008**; p 208-222.
45. Qikun Zhang, Yiling Bei, Song Qian *Shandong Shifan Daxue Xuebao, Ziran Kexueban* **2009,** *24*, 70-73.
46. Ji Dae Yun, Lee Byeong Se, Lee Jae Hak, Kim Seon Mi, Jung Un Jeong, KR 2012067258 A, **2012**.
47. D. V. Partyka, R. H. Holm, *Inorganic Chemistry* **2004,** *43*, 8609-8616.
48. E. Kupce, E. Liepins, E. Lukevics, *Journal of the Chemical Society, Dalton Transactions* **1987**, 1593-1596.
49. Bruker, *Bruker AXS Inc.* **2012,** *Madison, Wisconsin, USA*.
50. Blessing, R., *Acta Crystallographica Section A* **1995,** *51*, 33-38.
51. Sheldrick, G., *Acta Crystallographica Section A* **1990,** *46*, 467-473.
52. Sheldrick, G., *Acta Crystallographica Section A* **2008,** *64*, 112-122.
53. Spek, A. L., *Journal of Applied Crystallography* **2003,** *36*, 7-13.
54. Spek, A. L., *Acta Crystallographica Section D* **2009,** *65*, 148-155.
55. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *Journal of Applied Crystallography* **2008,** *41*, 466-470.
56. H. Putz, K. Brandenburg, *3.2i ed., Crystal Impact: Bonn, Germany*.

6 APPENDIX

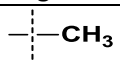
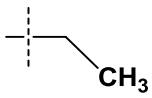
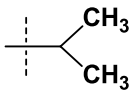
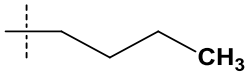
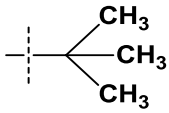
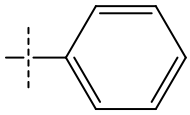
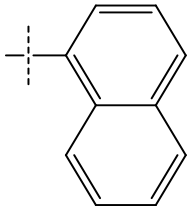
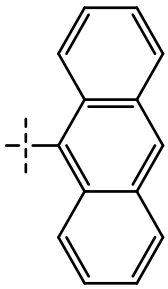
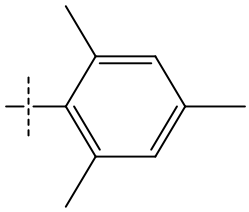
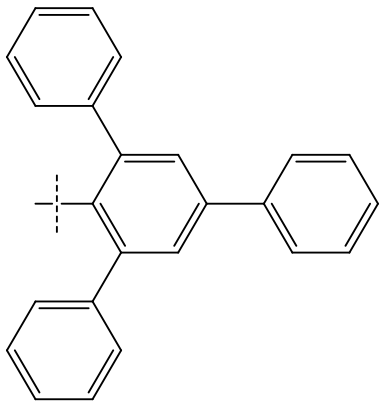
6.1 ABBREVIATIONS

Table 24: Table of Abbreviations

asym.	asymmetrical
av.	average
aq.	aqueous
ATR	attenuated total reflectance
bp	boiling point
DCM	dichloromethane
DI	direct insertion
eq.	equivalent
GC-MS	gas chromatography mass spectroscopy
h	hour
HCl	hydrochloric acid
IR	infrared
M	molar
mp	melting point
MS	mass spectroscopy
R	organic residue
THF	tetrahydrofuran
TMS	tetramethylsilane
r.t.	room temperature
SRU	simplest repeating unit
str.	stretching
sym.	symmetrical
vib.	vibration
X	halide

6.2 CHEMICAL SHORT NAMES

Table 25: Chemical short names

abbreviation	fragment name	fragment structure
Me	methyl	
Et	ethyl	
^{i}Pr	*iso*-propyl	
^{n}butyl	*n*-butyl	
^{t}butyl	*tert*-butyl	
Ph	Phenyl	
1-Naph	1-naphthyl	
9-Anth	9-anthracenyl	
Mes	Mesityl	
Triph	2,4,6-triphenyl benzene	

6.3 Crystal Structure Analysis Data

*Table 26: Crystallographic data and details of measurements for compounds **5** and **6***

Mo Kα (λ=0.71073Å). $R_1 = \Sigma/ |F_o|- |F_c|/|\Sigma|F_d$; $wR2 = [\Sigma_w(F_o^2-F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$

Compound	**1-Naph$_3$SiNH$_2$ 5**	**1-Naph$_2$Si(NH$_2$)$_2$ 6**
Formula	$C_{30}H_{23}NSi{\cdot}C_7H_8$	$C_{20}H_{18}N_2Si$
Fw (g mol^{-1})	517.72	314.45
a (Å)	9.2883 (4)	21.0446 (10)
b (Å)	12.4156 (6)	9.3205 (4)
c (Å)	13.3966 (7)	8.2986 (4)
α (°)	116.185 (1)	90
β (°)	91.568 (2)	90
γ (°)	93.319 (1)	90
V (Å^3)	1381.61 (12)	1627.74 (13)
Z	2	4
Crystal size (mm)	0.10 × 0.09 × 0.08	0.20 × 0.19 × 0.15
Crystal habit	Colorless block	Colorless block
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	*Pca*2$_1$
d_{calc} (mg/m^3)	1.244	1.283
μ (mm^{-1})	0.11	0.14
T (K)	100(2)	100(2)
2*ϑ* range (°)	2.7–30.9	2.9–27.2
F(000)	548	664
R_{int}	0.044	0.035
independent reflns	8576	3611
No. of params	361	224
R1, wR2 (all data)	R1 = 0.0500 wR2 = 0.1077	R1 = 0.0270 wR2 = 0.0677
R1, wR2 (>2*σ*)	R1 = 0.0393 wR2 = 0.0992	R1 = 0.0254 wR2 = 0.0665

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