Thomas LAINER, BSc

Partial Chlorinated Hydrosilanes

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Abstract

The primary aim of this thesis was the elaboration of novel and technologically suitable approaches to partially chlorinated higher silicon hydrides. The obtaines results demonstrate that dodecachloroneopentasilane can be partially hydrogenated in an easy to perform procedure with sub-stoichiometric amounts of diisobutylaluminiumhydride to give the trichlorosilyl-silanes $Cl_3SiSi(SiH_3)_3$ (**1**) und $(Cl_3Si)_2Si(SiH_3)_2$ (**2**) as the major products with remarkable selectivity. **1** and **2** could be isolated and characterized spectroscopically. Related transformations involving Si_2Cl_6, Si_3Cl_8 or $HSi(SiCl_3)_3$ also showed the preferential formation of products with intact $SiCl_3$ groups. The partial chlorination of neopentasilan or isotetrasilane, on the contrary, primarily afforded the ClH_2Si-silanes $Si(SiH_2Cl)_4$ (**10**) and $HSi(SiH_2Cl)_3$ (**12**), respectively. The outcome of this work, thus, enables the targeted synthesis of Cl/H-oligosilanes in particular with branched structures with various substitution patterns.

Kurzfassung

Ziel dieser Arbeit war es, neuartige und möglichst auch technologisch gangbare Syntheserouten zu partiell chlorierten H-Silanen $Si_nH_mCl_o$ zu entwickeln. Dabei konnte gezeigt werden, dass sich Dodecachlorneopentasilan mit substöchiometrischen Mengen an Diisobutylalumiumhydrid mit bemerkenswerter Selektivität und einfach durchführbar partiell hydrieren lässt. Hauptprodukte waren die beiden Trichlorsilylsilane $Cl_3SiSi(SiH_3)_3$ (**1**) und $(Cl_3Si)_2Si(SiH_3)_2$ (**2**) die auch isoliert und spektroskopisch charkterisiert werden konnten. Entsprechende Umsetzungen von Si_2Cl_6, Si_3Cl_8 und $HSi(SiCl_3)_3$ mit iBu$_2$AlH zeigten ähnlich Selektivitäten und ergaben ebenfalls bevorzugt Produkte mit intakten $SiCl_3$-Gruppen. Im Gegensatz dazu verlief die Teilchlorierung von Neopentasilan oder Isotetrasilan mit $HCl/AlCl_3$ primär unter Bildung der ClH_2Si-Silane $Si(SiH_2Cl)_4$ (**10**) bzw. $HSi(SiH_2Cl)_3$ (**12**). Somit stehen nun geeignete Methoden zur gezielten Herstellung von Cl/H-Oligosilanen speziell mit verzweigten Strukturen mit verschiedenen Substitutionsmustern zur Verfügung.

1. Introduction and Aim of Work

Chlorosilanes, especially partially hydrogenated chlorosilanes, are ideal precursor compounds for the generation of hyperpure polycrystalline silicon. Because of the dramatic rise of photovoltaic applications, the today production capacity of polysilicon reached the 350 kton/year from the 26 kton/year of the beginning years of this century.[1] The state-of-the-art precursor is trichlorosilane $HSiCl_3$, which has a high volatility.[2] Due to the very limited conversion of $HSiCl_3$ and the huge energy dissipation needed for the reduction to solid silicon, the search for other precursor materials is still ongoing. Based on calculations two mechanisms for the deposition of silicon from $HSiCl_3$ are possible. The disilane mechanism proposed by *Swihart* and *Carr et al*. and the radical mechanism by *Cavallotti et al*.[3] Interestingly, in both mechanisms, the formation of disilanes as reaction intermediates plays a crucial role by enhancing the gas phase reactivity. This is due to their increased reactivity, determined by the relatively low Si−Si bond energy and small barriers for Cl and H intramolecular transfers. Therefore, the use of Cl/H substituted oligosilanes as precursors would have positive effects on the yield of silicon deposition.

The validity of this idea is clearly proved by the comparison of GPC values (growth per cycle in ALD process) for silicon tetrachloride $SiCl_4$, hexachlorodisilane Si_2Cl_6 and octachlorodisilane Si_3Cl_8 in an atomic layer deposition (ALD) process using NH_3 as second precursor under otherwise comparable ALD conditions (Figure 1).[4]

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[1] S. Ravasio, M. Masi, C. Cavallotti, J. Phys. Chem. A 2013, 117, 5221

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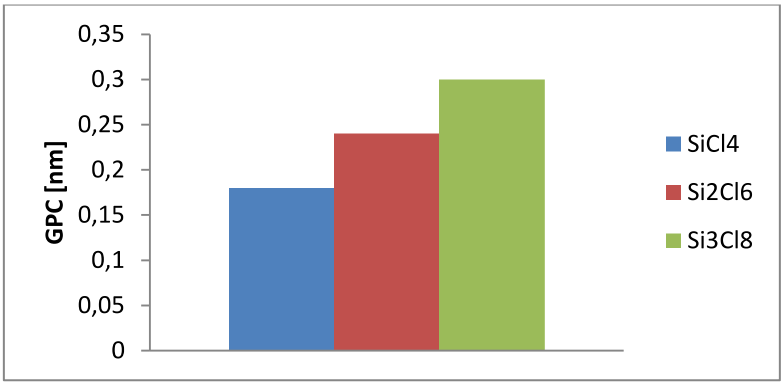

Figure 1 ALD deposition rates of SiN_x layers with different precursors

With an increasing number of Si atoms in the precursor molecules higher deposition rates were observed in the order $SiCl_4$ (0.18 nm) < Si_2Cl_6 (0.24 nm) < Si_3Cl_8 (0.3 nm).

A significant indicator for the quality of SiN_x layers is a high film stability as indicated by a low WER (wet etch rate) value. The deposited films were evaluated by using a diluted 500:1 HF solution at ambient temperature. Low WER values indicate a high film stability. Figure 2 shows a comparison of the WER values of ALD deposited SiN_x layers using Si_2Cl_6 or H_2SiCl_2 (dichlorosilane) and NH_3 as source gases.[5]

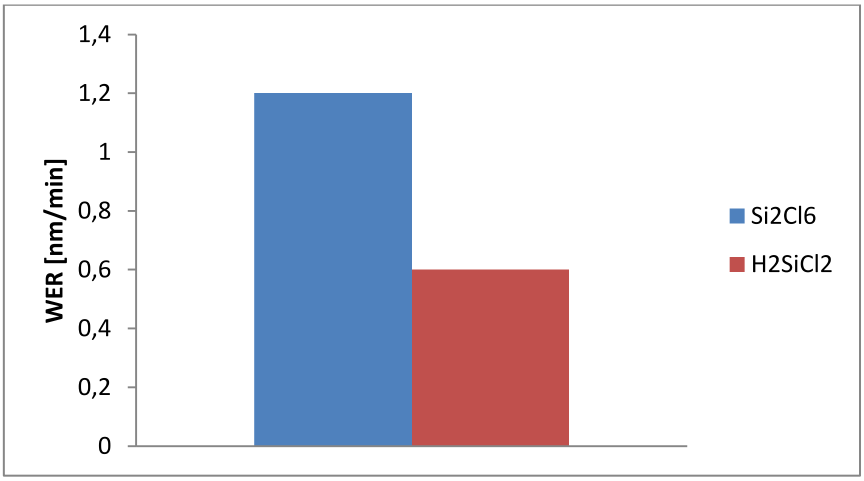

Figure 2. WER values obtained by using a diluted 500:1 HF solution at ambient temperature of ALD processed SiN_x layers with Si_2Cl_6 or H_2SiCl_2 and NH_3 as source gases.

The film obtained from Si_2Cl_6 showed a WER of 1.2 nm/min while the WER value for the film obtained from H_2SiCl_2 was 0.6 nm/min. This comparison indicates, that the application of partially hydrogenated chlorosilane precursors instead of a fully chlorinated silane favours high film stabilities.

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[5] C. H. Han, M. H. Chun, S. K. Rha, *J. Korean Phys. Soc*. 2005, *47*, S598

A recently reported patent from Air Liquide, which claims the use of penta-chlorodisilane HSi_2Cl_5 in several deposition techniques including the fabrication of SiN_x with NH_3 via ALD[6], verifies the above mentioned data. Deposition rates and refraction indices of SiN_x layers deposited via ALD from NH_3 and HSi_2Cl_5, Si_2Cl_6 or Si_3Cl_8 were compared and it was found that HSi_2Cl_5 forms higher quality films at high deposition rates (at low and high temperature) than the simple perchloropolysilanes Si_2Cl_6 and Si_3Cl_8.

A further advantage of the application of partially chlorinated hydrosilanes in ALD processes is the reduction of the chlorine content in the precursor molecules. The decomposition of perchlorosilanes during layer fabrication affords large amounts of HCl gas. Due to the corrosive nature of HCl the fabricated metals in the chamber and piping materials are at high risk for the formation of volatile metal impurities. These unwanted metal impurities (parts per billion range) can have severe impact on the quality of the final device. Another problem is the formation of ammonium salts, which are formed by the reaction of HCl with unreacted NH_3. These ammonium salts can cause clogging of the tool exhaust. In both senses the quality of the whole technical process should greatly benefit from the application of precursors with less chlorine content.

In this context the primary goal of this work is the synthesis of partially chlorinated higher hydrosilanes which could be used for deposition processes. Particular emphasis shall be given to target molecules with improved properties and less unfavourable characteristics in the deposition process in comparison to state of the art precursors. To achieve this goal, at least in part completely new preparative approaches had to be developed because of the lack of known and technically viable synthetic methods.

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[6] J. M. Girard, C. Ko, I. Oshchepkov, K. Yanagita, S. Okubo, N. Noda, J. Gatineu, *US2016/0111272A1*

2 Literature Survey

In the following chapters various synthetic approaches to hydrosilanes as described in the technical literature will be summarized. "Gmelins Handbook of Inorganic Chemistry"[7] will be one of the primary supplying source of this literature study, since it provides a synopsis of the state of knowledge till the 1980´s. Furthermore, reviews[8,9] and different studies were used to show the substantial methods of preparation of hydrosilanes and partially chlorinated hydrosilanes.

2.1 Higher Silicon Hydrides

Hydrosilanes are the silicon analogue of hydrocarbons. While all hydrocarbons are chemically basically inert, especially the short chain hydrosilanes are highly reactive species and react with air oxygen under spontaneous combustion[10,11].

These properties can be explained by comparing the different electronegativities. Carbon has an electronegativity of 2.50, silicon 1.74 and hydrogen 2.20. This results in a reversed polarity of the element hydrogen bond to $Si^{\delta+}$-$H^{\delta-}$ in comparison to $C^{\delta-}$-$H^{\delta+}$. Consequently, the silicon-hydrogen bond can be cleaved by nucleophilic attack which does not occur for the carbon-hydrogen bond. Furthermore, silicon can be viewed as coordinatively unsaturated in the tetravalent state which greatly facilitates S_N2 type substitution at silicon centers.

Moreover, the Si-Si bond is weaker than the C-C bond due to the larger covalent radius of 117 pm for silicon in comparison to 77 pm for carbon. Additionally, halogen, nitrogen or oxygen atoms form significantly stronger bonds to silicon and, therefore, Si-halogen or Si-O-bonds are easier to access then the weaker Si-Si, Si-C or Si-H bonds.

These facts prevented the systematic investigation of hydrosilanes for a long time and silicon chemistry was primarily focused on the synthesis and reactivity of the more

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[7] Gmelin Handbook of Inorganic Chemistry, 15(B1), Springer Verlag (1982)

[8] E. Rivard, *Chem. Soc. Rev*. 2016, 45, 989

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stable organosilanes. Higher hydrosilanes were only investigated in theoretical studies. Important exceptions were, on the one hand, studies by *F. Fehér* at the University of Cologne and, on the other hand, the research at this institute.

In recent years the interest in hydrosilanes and their derivatives has risen remarkably mainly due to current developments in the semi-conductor sector which can be summarized with the term of "macroelectronics". In comparison to microelectronics, which has the primary goal of increasing numbers of transistors on a chip while retaining or even decreasing its size, the requirements of macroelecronics are fundamentally different. Electronic circuits with relative low complexity, for instance, should be able to cover large surfaces and also have a reduced price.

2.1.1. Synthesis by the Acidic Hydrolysis of Silicides

Moisson and *Smiles*[12,13] were the first to verify a higher hydrosilane (Si_2H_6) along with monosilane (SiH_4) and higher silanes in the product mixture, which was obtained after the decomposition of magnesium silicide with aqueous HCl (Equation 1).

$$Mg_2Si \xrightarrow{H_3O^+} SiH_4 + Si_2H_6 + Si_3H_9 + Si_4H_{10} \text{ etc.}$$

Equation 1

The product distribution and yield varied in a wide range due to different impact factors such as the quality of the Mg_2Si, the solvent and the choice of the acid[14]. *Stock* carried out further studies of this reaction and was able to isolate and to characterize silanes up to tetrasilane (Si_4H_{10}) and to prove the existence of penta- and hexasilane[15,16,17]. Furthermore, *Johnson* observed that the use of a solution of NH_4Br in liquid ammonia

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[12] H. Moisson, S. Smiles, *Compt. Rend.* 1902, 134, 569
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increases the yield of the silanes, but decreases the amount of the higher hydrosilanes in the product mixture[18,19]. Similar results were obtained later with aqueous HCl in the presence of organic solvents like diethyl ether[20].The application of preparative gas chromatography enabled the isolation and characterization of higher hydrosilanes up to octasilane (Si_8H_{20}) including branched isomers[21]. Later *Fehér et al.* studied the hydrolysis of Mg_2Si with aqueous sulphuric acid or phosphoric acid. This approach was also performed on a semi-technical scale to obtain higher hydrosilanes. Due to this method silanes up to pentadecasilane ($Si_{15}H_{32}$) could be characterized[22,23,24].

Culbertson studied the decomposition of a variety of other metal silicides (i. e: Ca, Al, Na or Li)[25], which showed no further improvement in the formation of higher hydrosilanes. Decomposition of rare-earth silicides such as La_5Si_3, Ce_5Si_3 and Nd_5Si_3 only afforded minor amounts of trisilane (Si_3H_8)[26].

Fluorosilic acid was also used for hydrolysis. This study, however, focused only on the formation of monosilane and disilane and higher hydrosilanes were only mentioned as by-products[27].

The acidic hydrolysis of silicides is the oldest and most studied method for the synthesis of silanes and is the state-of-the-art method to obtain monosilane[28]. This method is also very promising regarding to technical aspects, but has limitations like relatively high impurity levels in the products. Moreover, large quantities of salts like $MgCl_2$ have to be separated and disposed or used further.

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2.1.2 Synthesis by the Impact of Energy on SiH_4

A further possibility to obtain higher silanes is to treat mono-, di- or trisilanes with energy (Equation 2). This procedure intermediately forms silylenes (SiH_2) or silyl-radicals, which subsequently react with Si-H bonds to give new Si-Si bonds. The advantage of these methods is, that there are no further reagents necessary. Thus, the level of impurities can be maintained low. The disadvantage is the concomitant formation of insoluble polymeric silicon subhydrides and amorphous silicon.

$$SiH_4 \xrightarrow{\text{energy}} H_2 + Si_2H_6 + Si_3H_9 + Si_4H_{10} + (SiH_x)_n$$

Equation 2

The easiest way is the application of thermal energy e. g. to pyrolize monosilane to disilane, which was already executed by *Fritz* in 1952[29]. By using disilane instead of monosilane it was possible to obtain trisilane via pyrolysis which further could be pyrolized to tetrasilane[30]. The formation of the highly reactive and unstable silylenes and their subsequent insertion into the Si-H bond was proved by kinetic studies of the pyrolysis of mono-[31], di-[32] and trisilane[33]. The decomposition of monosilane via a radical pathway was also postulatet and proved under experimental condition using a mixture of monosilane and deuterated monosilane (SiD_4)[34].

A further method used was the exposition of SiH_4 to silent electrical discharges in an ozonizer type reactor, which results in the formation of di- and trisilane and smaller fractions of higher hydrosilanes[35,36]. The use of a mixture of mono- and disilane under similar conditions afforded higher branched hydrosilanes up to heptasilane, which could

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be separated via gas chromatography[37]. A similar method was used to obtain ultrapure di- and trisilane[38].

Higher hydrosilanes can also be obtained photochemically. Di- and trisilane were obtained by using mercury as a photosensitizer in the photolysis of SiH_4 with a low pressure mercury lamp[39]. Furthermore, IR irradiation of monosilane with a TEA-CO_2-laser afforded a mixture of higher silanes[40].

2.1.3 Synthesis by the Hydrogenation of Chlorosilanes

On a laboratory scale one of the easiest pathways to obtain hydrosilanes is the hydrogenation of chlorosilanes using soft hydrogenating agents like $LiAlH_4$ or i-Bu_2AlH (Equation 3)[41]. However, the limitations of this method are the insufficient availability of perchlorinated starting materials and side reactions such as Si-Si bond cleavage.

$$Si_nCl_m \xrightarrow{\text{i-}Bu_2AlH\text{ or }LiAlH_4} Si_nH_m$$

Equation 3

The first reaction of this kind was performed by *Schlesinger* in 1947 who hydrogenated Si_2Cl_6 with $LiAlH_4$ to obtain disilane Si_2H_6[42]. In the same manner Si_3Cl_8 was hydrogenated to Si_3H_8[43]. Because of the limited availability of n-Si_4Cl_{10}, 1,4-dibromotetrasilane was used as an educt to prepare n-tetrasilane by the hydrogenation with $LiAlH_4$[44]. In all cases, however, proper precautions have to be taken to avoid

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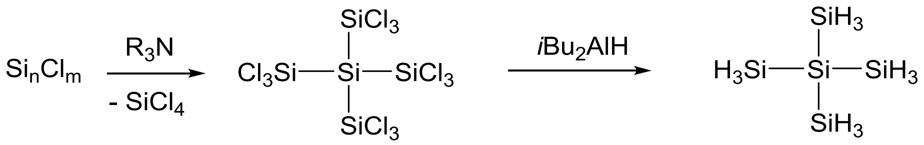
[37] T. D. Andrews, C. S. G. Phillips. *J. Chem. Soc. A*, 1966, 1, 46
[38] M. Akhtar, *Synth. React. Inorg. Metal-Org. Chem*. 1986, 16, 729
[39] H. Niki, G. J. Mains, *J. Phys. Chem*. 1964, 68, 304
[40] P. A. Longeway, F. W. Lampe, J. Am. Chem. Soc. 1981, 103, 6813
[41] Ref [1] gives a representative overview of the fundamental research
[42] A. E. Finhold, A. C. Bond, Jr. K. E. Wilzbach, H. I. Schlesinger, *J. Am. Chem. Soc*. 1947, 68, 2692
[43] P. P. Gaspar, C. A. Levy, G. M. Adair, *Inorg. Chem*. 1970, 9, 1272
[44] A. Haaland, K. Rypdal, H. Stüger, H. V. Volden, *Acta Chem. Scand*. 1994, 48, 46

extensive Si-Si bond scission reactions during the hydrogenation process, leading to disilane and monosilane as side products.

Höfler used $LiAlH_4$ for the hydrogenation of dodecachloroneopentasilane (Si_5Cl_{12}), which is easily accessible via the catalytic rearrangement of Si_2Cl_6 or Si_3Cl_8[45]. However, only low yields of neopentasilane ($Si(SiH_3)_4$) were obtained again due to extensive Si-Si bond cleavage[46]. An improved protocol for the high yield synthesis of neopentasilane using $i\text{-}Bu_2AlH$ (DIBAlH) as a hydrogenation reagent was claimed in a recent patent (Equation 4)[47].



$$Si_nCl_m \xrightarrow[-\ SiCl_4]{R_3N} Si(SiCl_3)_4 \xrightarrow{iBu_2AlH} Si(SiH_3)_4$$

Equation 4

Hengge et al. were the first to synthesize the cyclic silanes cyclopentasilane (Si_5H_{10})[48,49] and cyclohexasilane (Si_6H_{12})[50]. The yields were significantly higher as observed for acyclic substrates because Si-Si bond cleavage reactions were not observed at all. The merit of this synthesis approach, however, is strongly impeded by the problematic synthesis of the starting materials.

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[45] G. Urry, *J. Inorg. Nucl. Chem*. 1964, 26, 409

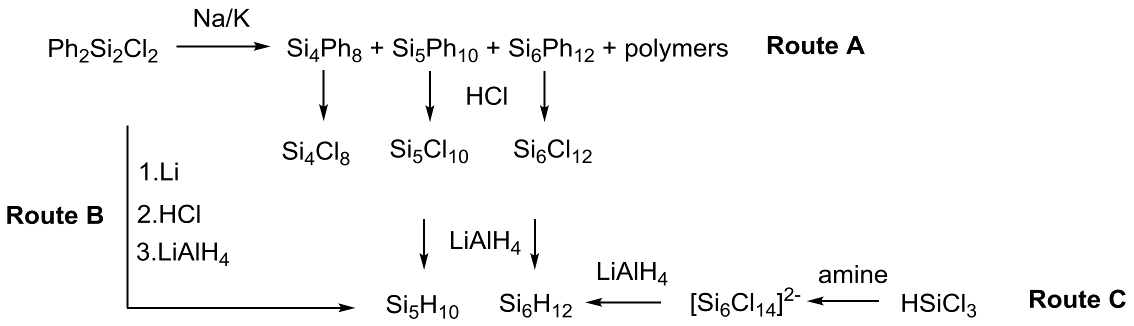
[46] F. Höfler, R. Jannach, *Inorg. Nucl. Chem. Letters* 1973, 9, 723

[47] J. P. Cannady, X. Zhou 2008 WO/2008/051328

[48] E. Hengge, G. Bauer, *Angew. Chem*. 1973, 85, 304

[49] E. Hengge, G. Bauer, *Monatsh. Chem*. 1975, 106, 503

[50] E. Hengge, D. Kovar, *Angew. Chem*. 1977, 89, 417



Equation 5

A more convenient way to obtain Si_6H_{12} was published recently by *Boudjouk et al.*, who used trichlorsilane and amino bases to obtain $Si_6Cl_{14}^{2-}$, which could be hydrogenated with $LiAlH_4$ to obtain Si_6H_{12}[51]. Furthermore the inverse sandwich structure $[Si_6Cl_{12}*2Cl]^{2-}$ can also be obtained from the reaction of Si_2Cl_6 and $[nBu_4N]Cl$ in CH_2Cl_2[52].

2.1.4 Further Synthetic Methods

In a Japanese patent from 1962 the direct synthesis of silanes from the elements silicon and hydrogen in the presence of catalytic amounts of H_2S or various sulphides was described[53]. The product distribution could be controlled by the hydrogen pressure, so that either conversion to mono-, di-, tetra- or pentasilane was achieved. Unfortunately, no further studies on this topic appeared in the literature. One of the reasons is certainly the contamination of the products with sulphur-containing impurities.

Furthermore, *Timms et al* described the reaction of SiO with 10% aqueous HF to a silane mixture Si_nH_{2n+2} with yields ranging from 9 to 24%[54]. The treatment of polymeric $(SiF_2)_n$ with HF lead to similar results[55].

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[51] a) S. B. Choi, B. K. Kim, P. Boudjouk, D. G. Grier, *J. Am. Chem. Soc*. 2001, 123, 8117. b) A. Elangovan, K. Anderson, P. R. Boudjouk, D. L. Schulz (NSDU Res. Foundation), US 20120294791.

[52] J. Tillmann, L. Meyer, J. I. Schweizer, M. Bolte, H.-W. Lerner, M. Wagner, M. C. Holthausen, *Chem. Eur. J.* 2014, 20, 9234.

[53] K. Tachiki, Y. Yamashita (Showa), JP 36021507 (1961)

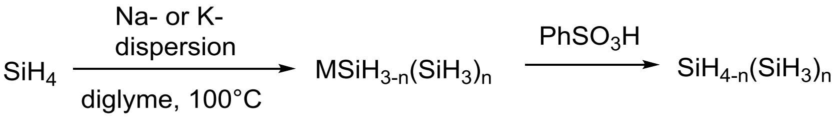
[54] P. L. Timms, C. S. G. Phillips, *Inorg. Chem. 3*, 1964, 606

[55] P. L. Timms R. A. Kent, T. C. Ehlert, J. L. Margrave*, J. Am. Chem. Soc*. 1965, 87, 2824

Catalytic dehydrogenative coupling was also used to obtain higher hydrosilanes by the oligomerisation of SiH_4[56,57].

Eventually reactions of SiH_4 with sodium or potassium can be used as building blocks to obtain sodium silanides $NaSi_nH_{2n+1}$ (n =1–4) or potassium silanides KSi_nH_{2n+1} (n = 1-4) [58,59,60].

Sundermeyer et. al. used a specifically engineered reactor to produce a highly reactive dispersion of Na and K, while a continuous SiH_4 supply enabled production yields of MSi_4H_9 up to 20 %[61] The synthesized silyl anions can be protonated with $PhSO_3H$ to higher hydrosilanes. The obtained silanes $SiH_{4-n}(SiH_3)_n$ (n =1-3) were then separated and characterized by gas chromatography[62].



$$SiH_4 \xrightarrow[\text{diglyme, 100°C}]{\text{Na- or K-dispersion}} MSiH_{3-n}(SiH_3)_n \xrightarrow{PhSO_3H} SiH_{4-n}(SiH_3)_n$$

Equation 6

Recently, our working group presented an alternative approach for the synthesis of alkali-metal silanides $MSi(SiH_3)$[63]. Further experiments showed that these silanides react with certain elemental chlorides ECl_x under transmetallation. Thus, the reaction of Si_4H_9Li with equivalent amounts of 1,2 dibromoethane, $SiCl_4$ or $GeCl_4$ gave the previously unknown oligomeric hydrosilanes $(SiH_3)_3SiSi(SiH_3)_3$ and $(SiH_3)SiSi(SiH_3)_2Si(SiH_3)_3$ in isolable amounts as shown in Equation 7[64].

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[56] Y. Okumura, K. Takatsuna, J. Yagihashi (Tonen Sikiyukagaku KK) 1990, JP 0218451

[57] N. Brausch, A. Ebbers, G. Stochniol, M. Trocha, Y. Önal, J. Sauer, B. Stützel, D. Wolf, H. Stüger 2010 WO/2010/003729 A1

[58] M. A. Ring, L. P. Freeman, A. P. *Fox. Inorg. Chem.* 1964, 3, 1200

[59] F. Fehér, R. Freund, *Inorg. Nucl. Chem. Letters* 1974, 10, 561

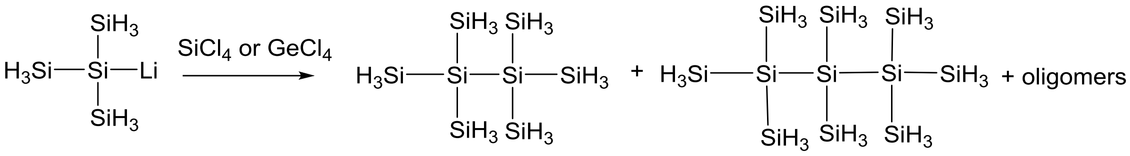
[60] F. Fehér, M. Krancher, *Z. Naturforsch. B* 1985, 40, 1010

[61] T. Lobreyer, J. Oeler, W. Sundermeyer, H. Oberhammer, *Chem Ber*. 1993, 126, 665

[62] T. Lobreyer, W. Sundermeyer, H. Oberhammer, *Chem. Ber*. 1994, 127, 2111

[63] H. Stueger, T. Mitterfellner, R. Fischer, C. Walkner, M. Patz, S. Wieber. *Chem. Eur. J*. 2012, 18, 7662

[64] M. Haas, V. Christopoulos, J. Radebner, M. Holthausen, T. Lainer, L. Schuh, H. Fitzek, G. Kothleitner, A. Torvisco, R. Fischer, O. Wunnicke, H. Stueger, *Angew. Chem. Int. Ed*. 2017, *56*, 14071



Equation 7

2.2 Higher Halohydrosilanes

The chemical properties of halohydrosilanes also differ considerably from those of their carbon analogues. They easily react with water forming Si–O–Si linkages and hydrogen halides, HX. Additionally they are often spontaneously inflammable in contact with air. Halogen/hydrogen exchange reactions are very common, which is not the case for haloalkanes[65].

Nowadays there exist three basic synthetic approaches to partially halogenated hydrooligosilanes:

- partial halogenation of higher silicon hydrides
- selective halogenation of heteroatom-H-silanes
- partial hydrogenation of higher halosilanes

The primary task of these reactions is the introduction of halogen substituents into the target molecule under preservation of the Si-Si-H skeleton. Mainly due to the high chemical reactivity of Si-Si-, Si-H- and Si-halogen bonds the number of higher halohydrosilanes described in the literature is rather limited. The following chapters present an overview of previously published synthetic methods.

2.2.1 Partial Halogenation of Si-H bonds

The standard method for the synthesis of partially halogenated higher silicon hydrides is the exchange of one or more hydrogen atoms of an appropriate higher silane by halogen. The general problem of this pathway is frequently the formation of mixtures of several halogenated species, which are hardly or even impossible to separate.

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[65] J. Baumgartner, C. Grogger, Comprehensive Inorganic Chemistry II, 2013, 1, 51-82

2.2.1.1 With Elemental Halides

The reaction of di-, tri- and tetrasilane with elementary iodine leads to the formation of mono- and numerous polyhalogenated products (Equation 8). Some of these species could be isolated via gas chromatography by *Fehér et al.*[66].

$$Si_nH_m + I_2 \longrightarrow Si_nH_{m-x}I_x + HI$$

Equation 8

The same method could also be accomplished with Br_2 and Cl_2 at low temperature in highly diluted systems. Bromination[67] and iodination[68,69] of di- and trisilane could also be realized in the absence of a solvent at low temperature. For every reaction of higher silanes with elementary halides Si-Si bond cleavage represents a major problem[70].

2.2.1.2 With Boron Trihalides

Disilane reacts with boron trichloride to diborane and a mixture of mono-, di- and trichlorodisilane (Equation 9)[71]. The reaction of disilane with boron tribromide leads to a mixture of mono-, di-, tri- and tetrabromodisilane[72].

$$Si_2H_6 + n/3\ BX_3 \longrightarrow Si_2H_{6-n}X_n + n/6\ B_2H_6\ (X = Cl,Br)$$

Equation 9

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[66] F. Fehér, P. Plichta, R. Guillery, *Chem. Ber.* 1970, 103, 3028
[67] T. C. Geisler, C. G. Cooper, A. D. Norman, *Inorg. Chem*. 1972, 11, 1710
[68] F. Fehér, B. Mosert, A. G. Wronka, G. Betzen, *Monatsh. Chem*. 1972, 103, 959
[69] F. Fehér, A. G. Wronka, B. Mosert, *Monatsh. Chem*. 1973, 104, 360
[70] F. Fehér, P. Plichta, R. Guillery, *Inorg. Chem*. 1971, 10, 606
[71] C. H. Van Dyke, A. G. MacDiarmind, *J. Inorg. Nucl. Chem*. 1963, 25, 1503
[72] J. E. Drake, J. Simpsons. *Inorg. Nucl. Chem. Letters* 1966, 2, 219

Furthermore, the reactions of trisilane with boron trichloride and boron tribromide were found to produce mixtures of the corresponding monohalides with higher halogenated trisilanes[73,74].

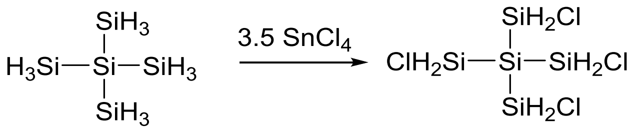
2.2.1.3 With Metal Chlorides

The reaction of Si_2H_6 with one equivalent of $SnCl_4$ lead to the formation of mono- and 1,2-dichlorodisilane (Equation 10). Under similar conditions $SnCl_4$ and Si_3H_8 afforded 1- and 2-chlorotrisilane along with 1,3-dichlorotrisilane. Treatment of n- or iso-tetrasilane and n-pentasilane[75] with 1 eq. of $SnCl_4$ mainly gave the mono or dichlorinated species. In all cases neither disubstitution at a single silicon atom nor Si-Si bond cleavage were detected[76].

$$Si_2H_6 + n\ SnX_4 \longrightarrow Si_2H_{6\text{-}n}X_n + n\ SnX_2 + n\ HX\ (X = Cl,Br)$$

Equation 10

Recently, our working group reported the preparation and isolation of the previously unknown tetrakis(chlorosilyl)silane from $Si(SiH_3)_4$ and $SnCl_4$ (Equation 11).[77].



$$Si(SiH_3)_4 \xrightarrow{3.5\ SnCl_4} Si(SiH_2Cl)_4$$

Equation 11

The reaction equation for the chlorination of Si_2H_6 with silver chloride is depicted in Equation 12. In a gas-solid-phase process $ClSi_2H_5$ and higher chlorinated products were

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[73] J. E. Drake, N. Goddard *Inorg. Nucl. Chem. Letters* 1968, 4, 385
[74] J. E. Drake, N. Goddard, N. P. C. Westwood *J. Chem. Soc. (A*), 1971, 3305
[75] F. Fehér, F. Ocklenburg, *Z. Anorg. Allg. Chem*. 1984, 515, 36
[76] J. E. Bentham, S. Cradock, E. A. V. Ebsworth, *Inorg. Nucl. Chem. Letters* 1971, 7, 1077
[77] H. Stueger, T. Mitterfellner, R. Fischer, C. Walkner, M. Patz, S. Wieber, *Inorg. Chem*. 2012, 51, 6173

formed[78,79,80]. The reaction of gaseous trisilane with AgCl under high temperature conditions additionally afforded 2-chlorotrisilane[81].

$$Si_2H_6 + n\ AgCl \longrightarrow Si_2H_{6-n}Cl_n + Ag + n/2\ H_2\ (n = 1 - 3)$$

Equation 12

In a analogous manner Si_6H_{12} reacted with AgCl in CH_2Cl_2 solution to give a mixture of 70 % $ClSi_6H_{11}$ with 12 % of $Cl_2Si_6H_{10}$ and unreacted educt [82]. $HgCl_2$ reacts similarly which was shown in a few experiments with di-, tri-, tetra-, penta- and iso-tetrasilane and cyclohexasilane (Equation 13)[82].

$$Si_2H_6 + n\ HgCl_2 \longrightarrow Si_2H_{6-n}Cl_n + n\ Hg + n\ HCl$$

Equation 13

2.2.1.4 With HX / $AlCl_3$

Disilane could be converted into a mixture of higher halogenated products with HCl or HBr in the presence of the corresponding aluminium halide[83]. Already in 1923 *Stock* reacted Si_3H_8 with $CHCl_3/AlCl_3$ to a mixture of higher chlorinated species[84]. Later *MacDiarmid* was able to isolate monoiododisilane from the reaction of Si_2H_6 with AlI_3[85]. In the same manner monobromo- and monochlorodisilane[86], 1,1-dichlorodisilane and 1,1,2-trichlorodisilane[87] could be prepared from Si_2H_6 and $AlBr_3$ or $AlCl_3$, respectively.

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[78] R. P. Hollandsworth, W. M. Ingle, M. A. Ring, *Inorg. Chem*. 1967, 6, 844

[79] A. J. Vanderwielen, M. A. Ring, *Inorg. Chem*. 1972, 11, 246

[80] R. P. Hollandsworth, M. A. Ring, *Inorg. Chem*. 1968, 7, 1635

[81] J. E. Drake, N. Goddard, N. P. C. Westwood, *J. Chem. Soc. (A)*, 1971, 3305

[82] D. Schulz, X. Dai, K. J. Nelson, P. Boudjouk 2009, WO 2009/148878 A2

[83] A. Stock, K. Somieski, *Ber. Deut. Chem. Ges*. 1920, 53, 759

[84] A. Stock, P. Stiebeler, *Ber. Deut. Chem. Ges*. 1923, 56, 1087

[85] L. G. L. Ward, A. G. MacDiarmid, *J. Am. Chem. Soc*. 1960, 82, 2151

[86] M. Abedini, C. H. Van Dyke, A. G. MacDiarmid, *J. Inor. Nucl. Chem*. 1963, 25, 307

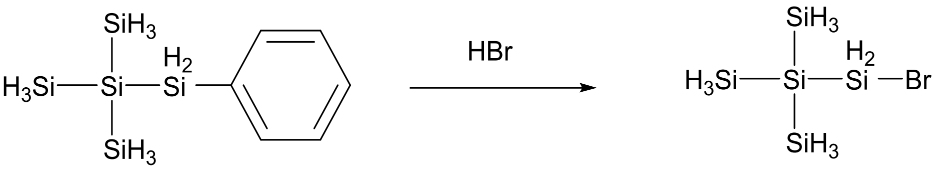
[87] R. P. Hollandsworth, M. A. Ring, *Inorg. Chem*. 1968, 7, 1635

2.2.2 Selective Halogenation of Heteroatom-H-Silanes

As already mentioned the direct halogenation of higher silanes frequently affords unseparable mixtures of several halohydrosilanes. The selectivity of the halogenation reaction can be greatly improved by employing structurally well-defined heterosubstituted hydrosilane starting materials.

2.2.2.1. Halogenative Dearylation of Aryl-H-Silanes

In contrast to hydrosilanes, arylated silanes $Ar_ySi_nH_{2n+2-y}$ are much better suitable for the selective preparation of chlorohydrosilanes $Cl_ySi_nH_{2n+2-y}$ (n = 2 - 7) as the scission of silicon-aryl-bonds with HX (X = halogen) can be easily accomplished[88]. *Fehér et al.* obtained the bromohydrosilanes $BrSiH_2SiH(SiH_3)_2$, $BrSiH_2Si(SiH_3)_3$ and $BrSiH_2Si(SiH_3)_2SiH_3$ from the corresponding phenyl substituted derivatives after treatment with an excess of liquid anhydrous HBr (Equation 14)[89].



Equation 14

The reaction of 1,2-diphenyldisilane with HCl in the presence of catalytic amounts of $AlCl_3$ afforded a mixture of several chlorinated disilane species due to $AlCl_3$-catalyzed redistribution reactions. Formation of an azeotropic mixture of the products with benzene prevented the isolation of individual species by distillation[90]. This problem can be circumvented by the employment of p-tolyl-, mesityl- or α-naphtyl substitued educts or by the execution of the reaction in a high pressure vessel without a catalyst. *Hassler*

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[88] J. Y. Corey, in S. Patai, Z. Rappoport (Ed.): The Chemistry of Organic Silicon Compounds, Wiley, John Sons, Inc. 1989, 1

[89] F. Fehér, R. Freund, *Inorg. Nucl. Chem. Letters* 1973, 9, 937

[90] H. Söllradl, E. Hengge, *J. Organomet. Chem*. 1983, 243, 257

was able to isolate a series of bromo-, iodo- and chloro- substituted di-, tri- and tetrasilanes using this method[91,92,93,94,95,96].

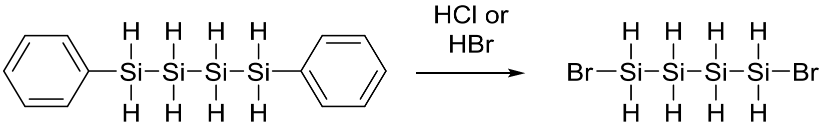
$$Ar_ySi_nH_{2n+2-y} \xrightarrow{HX} X_ySi_nH_{2n+2-y} + ArH$$

X = Cl, Br, I   y = 1 - 9

Ar = Ph, naphtyl, mesityl, *p*-tolyl

Equation 15

Stüger et al. were able to isolate 1,4-dichloro- and 1,4-dibromotetrasilane after treatment of 1,4-diphenyltetrasilane with liquid HX in absence of a catalyst at low temperatures[97].



Equation 16

In a similar fashion 2,3-dibromotetrasilane and 1,4-dibromo-2,3-bis(bromosilyl)tetrasilane could be isolated. The compounds 2,3-dichlorotetrasilane and 1,4-dichloro-2,3-bis(chlorosilyl)tetrasilane were synthesized in an autoclave[98,99].

Another approach for halogenative dearylation of phenylsilanes employs stoichiometric amounts of trifluoromethanesulfonic acid instead of excess HX gas. Further reaction of the silyltrifluoromethansulfonates thus obtained with triethylammoniumchloride or LiCl

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[91] K. Hassler, M. Pöschl, *J. Organomet. Chem*. 1990, 398, 225
[92] K. Schenzel, K. Hassler, *Spectrochim. Acta* 1994, 50A, 139
[93] K. Hassler, W. Köll, K. Schenzel, *J. Mol. Struct*. 1995, 348, 353
[94] A. Gupper, K. Hassler, *Eur. J. Inorg. Chem*. 2001, 2007
[95] K. Hassler, U. Katzenbeisser, *J. Organomet. Chem*. 1994, 480, 173
[96] K. Hassler, W. Köll, *J. Organomet. Chem*. 1997, 540, 113
[97] H. Stüger, *J. Organomet. Chem*. 1992, 433, 11
[98] H. Stüger, *J. Organomet. Chem*. 1993, 458, 1
[99] H. Stüger, P. Lassacher, *J. Organomet. Chem*. 1993, 450, 79

affords the respective chlorosilanes[100]. The unsymmetrical chlorodisilanes $H_3SiSiCl_3$ and $H_3SiSiHCl_2$ could be prepared successfully this way[101].

2.2.2.2 Halogenative Scission of Si-N- or Si-O bonds

A selective method for the synthesis of chlorodisilanes starting from Si_2Cl_6 was reported by *Stüger et al.* who introduced amino protective groups into the molecule to avoid complete hydrogenation of the chlorosilane. After hydrogenation the protective groups were easily cleaved off by treatment with HCl and the respective chlorodisilanes were obtained in good yields.[102]

$$\begin{tikzcd}
Si_nCl_{2n+2} \arrow[r, "LiN(SiMe_2Ph)_2"] & {[N(SiMe_2Ph)_2]_ySi_nCl_{2n+2-y}} \arrow[r, "LiAlH_4"] & {[N(SiMe_2Ph)_2]_ySi_nH_{2n+2-y}} \arrow[d, "HCl"] \\
 & & Cl_ySi_nH_{2n+2-y}
\end{tikzcd}$$

This method has also been applied to tri-, tetra- and pentasilanes[103]. In this cases, however, the target compounds contained inseparable small amounts of Si-Si bond scission products.

Equation 17 shows the formation of monofluorodisilane by the reaction of tris(disilyl)amine and boron trifluoride[104].

$$(Si_2H_4)_3N + BF_3 \longrightarrow Si_2H_5F + (Si_2H_5)_2NBF_2$$

Equation 17

In a similar way *MacDiarmid* and *Van Dyke* reacted bis(disilanyl)ether with boron trichloride to obtain monochlorodisilane[105].

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[100] W. Uhlig, Chem. Ber. 1996, 129, 733 - 739
[101] W. Uhlig, *Z. Anorg. Allg. Chem.* 1993, 619, 1479
[102] H. Stueger, P. Lassacher, E. Hengge, *J. Organomet. Chem.* 1997, 547, 227
[103] W. Gollner, K. Renger, H. Stüger, *Inorg. Chem.* 2003, 42, 4579
[104] M. Abedini, A. G. MacDiarmid, *Inorg. Chem.* 1963, 2, 608

$$3\ (Si_2H_4)_2O + 2\ BCl_3 \longrightarrow 6\ Si_2H_5Cl + B_2O_3$$

Equation 18

2.2.2.3 Halogen Exchange Reactions

Monobromodisilane and monochlorodisilane can be obtained after treatment of monoiododisilane with AgBr[106] or AgCl[107].

$$Si_2H_5I + AgX \xrightarrow[X\ =\ Cl,\ Br]{} Si_2H_5X + AgI$$

Equation 19

Antimony trifluoride was used as a halogen exchange reagent to obtain 1,1-difluorodisilane and 1,1,1-trifluorodisilane from the corresponding chlorosilanes[108].

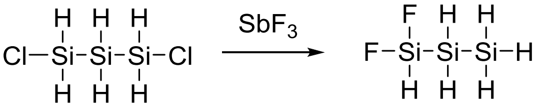
$$Si_2H_{6-m}Cl_m \xrightarrow{SbF_3} Si_2H_{6-n}F_n$$

Equation 20

Surprisingly, the reaction of 1,3-dichlorotrisilane with SbF_3 afforded the isomer 1,1-difluorotrisilane instead of the expected halogen exchange product (Equation 21)[109].

---

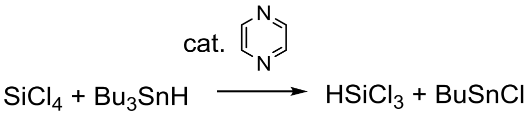
[105] C. H. Van Dyke, A. G. Macdiarmid, *Inorg. Chem*. 1964, 3, 747
[106] L. G. L. Ward, A. G. MacDiarmid, *J. Inorg. Nucl. Chem*. 1961, 20, 345
[107] A. D. Craig, J. V. Urenovitch, A. G. MacDiarmid, *J. Chem. Soc*. 1962, 548
[108] J. E. Drake, N. Goddard, *J. Chem. Soc. (A)* 1970, 2587
[109] J. E. Drake, N. Goddard, N. P. C. Westwood, *J. Chem. Soc. (A)* 1971, 3305



Equation 21

2.2.3 Partial Hydrogenation of Higher Chlorosilanes

Known procedures published in the patent literature for the catalytic convertion of $SiCl_4$ to $HSiCl_3$ with H_2 or HCl are not suitable for chlorinated polysilanes like Si_2Cl_6, due to the fact that Si-Si bonds are not stable at the necessary reaction conditions at $T \geq 500°C$. *Roewer et al.* introduced the method of partial hydrogenation of $SiCl_4$ or organochlorosilanes Me_nSiCl_{4-n} with Bu_3SnH in the presence of a lewis base catalyst[110].



Equation 22

Under the same conditions Si_2Cl_6 reacts to monochlorosilanes H_nSiCl_{4-n} and complex mixtures of partially chlorinated disilanes[111]. Neither of these methods has been applied to the synthesis of higher Cl/H-silanes from chlorooligosilanes Si_nCl_{2n+2} with $n > 2$ so far.

2.2.4 Further Methods

Besides the above mentioned methods there are a few approaches for the preparation of partially halogenated hydrosilanes described in the literature, which represent only special cases or have a limited scope in preparative chemistry.

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[110] U. Pätzold, G. Roewer, U. Herzog, *J. Organomet. Chem*. 1996, 508, 147
[111] U. Herzog, G. Roewer, U. Pätzold, *J. Organomet. Chem*. 1995, 494, 143

For instance, it has been found that Me_3SnH hydrogenates selectively Si-Cl or Si-Br bonds in the presence of Si-F linkages. Based on this fact the synthesis of certain fluorosilanes could be accomplished (Equation 23).[112].

$$F_3SiSiHBr_2 \xrightarrow{Me_3SnH} F_3SiSiH_3$$

Equation 23

Furthermore, it has been shown that mixtures of halogenated di- and trisilanes are formed when fluoro-, chloro- or bromomonosilanes were exposed to silent electrical discharges[113,74].

SiF_2, finally, was shown to be a potential precursor for the synthesis of fluorinated silanes like H_3SiSiF_3, $HSiF_2SiF_3$ and $H_2Si(SiF_3)_2$, which were obtained after treating SiF_2 with different hydrogen compounds such as H_2S[114], HBr[115,116], B_2H_6[117] or PH_3[118,119].

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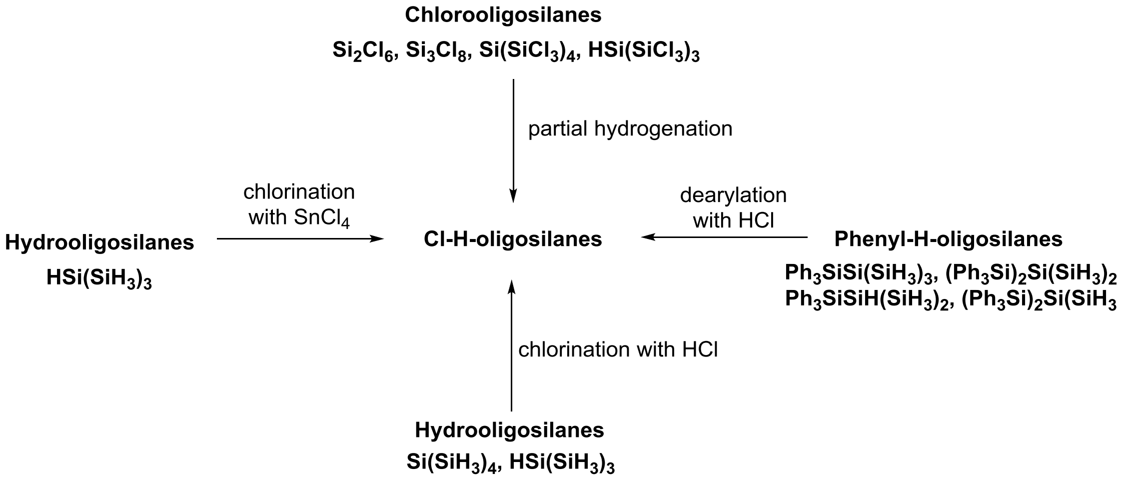
[112] J.J. D´Errico, K. G. Sharp, *Inorg. Chem.* 1989, 28, 2886
[113] J. E. Drake, N. P. C. Westwood, *J. Chem. Soc. (A)* 1971, 3300
[114] K. G. Sharp, J. L. Margrave, *Inorg. Chem*. 1969, 8, 2655
[115] K.G. Sharp, J. F. Bald jr., *Inorg. Chem*. 1975, 14, 2553
[116] J. F. Bald jr., K. G. Sharp, A. G. MacDiarmid, *J. Fluorine Chem*. 1973/74, 3, 433
[117] D. Solan, A. B. Burg, *Inorg. Chem*. 1972, 11, 1253
[118] G. R. Langford, D. C. Moody, J. D. Odom, *Inorg. Chem*. 1975, 14, 134
[119] J. C. Thompson, A. P. G. Wright, *Can. J. Chem*. 1979, 57, 994

3. Results and Discussion

As already mentioned in the introductory chapter the aim of this master thesis is to develop different possible and technically viable synthetic pathways to partially chlorinated higher silicon hydrides with improved properties and less unfavourable characteristics for deposition processes. Scheme 1 shows a synthesis plan for the different approaches which were investigated. The required synthesis steps and results will be discussed in more detail in the following chapter.



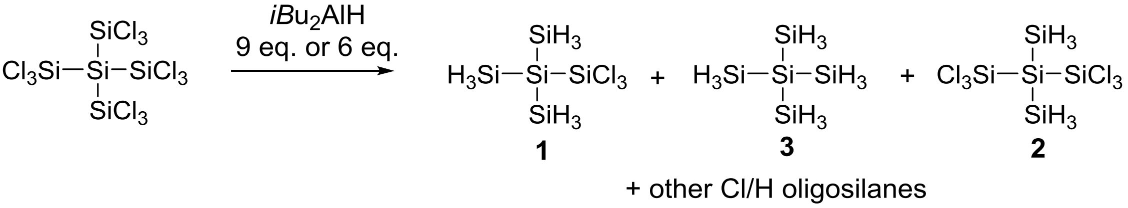
Scheme 1 Investigated pathways to partially chlorinated higher silicon hydrides

3.1 Partial Hydrogenation of Chlorooligosilanes

Previously it has been shown that the partial hydrogenation of higher chlorinated silanes with $LiAlH_4$ only affords unseparable mixtures of various Cl/H-silanes. The selectivity of partial hydrogenation, however, might be improved by using iBu$_2$AlH for hydrogenation. The increased steric bulk of iBu$_2$AlH should reduce the rate of the hydrogenation reaction thus increasing selectivity. Furthermore, the presence of only one hydride atom per molecule facilitates the performance of the hydrogenation reaction under strictly sub-stoichiometric conditions. Thus, we hydrogenated various perchlorooligosilanes with linear and branched structures with sub-stoichiometric amounts of iBu$_2$AlH in order to synthesize partially hydrogenated species as selectively as possible.

3.1.1 Reaction of Dodecachloroneopentasilane with *i*Bu$_2$AlH

The reaction of $Si(SiCl_3)_4$ with sub-stoichiometric amounts of iBu$_2$AlH afforded the partially chlorinated neopentasilanes 1,1,1-trichloroneopentasilane **1** and bis-trichlorosilyltrisilane **2** as the major products along with neopentasilane **3** and smaller amounts of other Cl/H-oligosilanes (Equation 24). Furthermore, we found, that the product ratio can be influenced by the relative amount of the added iBu$_2$AlH.



Equation 24

After the addition of 9 eq. of neat iBu$_2$AlH to $Si(SiCl_3)_4$ at 0 °C a clear solution was obtained. The proton-decoupled ^{29}Si-INEPT-NMR-spectrum (Figure 3) of the reaction mixture shows typical signals for **3** (δ^{29}Si = -165.5 and -89.7 ppm)[120] and the partially chlorinated species **1** (δ^{29}Si = -165.5 and -89.7 ppm)[64] and **2** (δ^{29}Si = -101.5, -95.5 and 13.0 ppm) along with several resonance lines with low intensity arising from other unidentified products. **1** could be isolated from the crude product by distillation at 50 °C and 0.01 mbar as a colourless oil in 38 % yield. The product contained small amounts of hydrosilane impurities with presumably **3** as the major species and traces of iBu$_2$AlH or iBu$_2$AlCl.

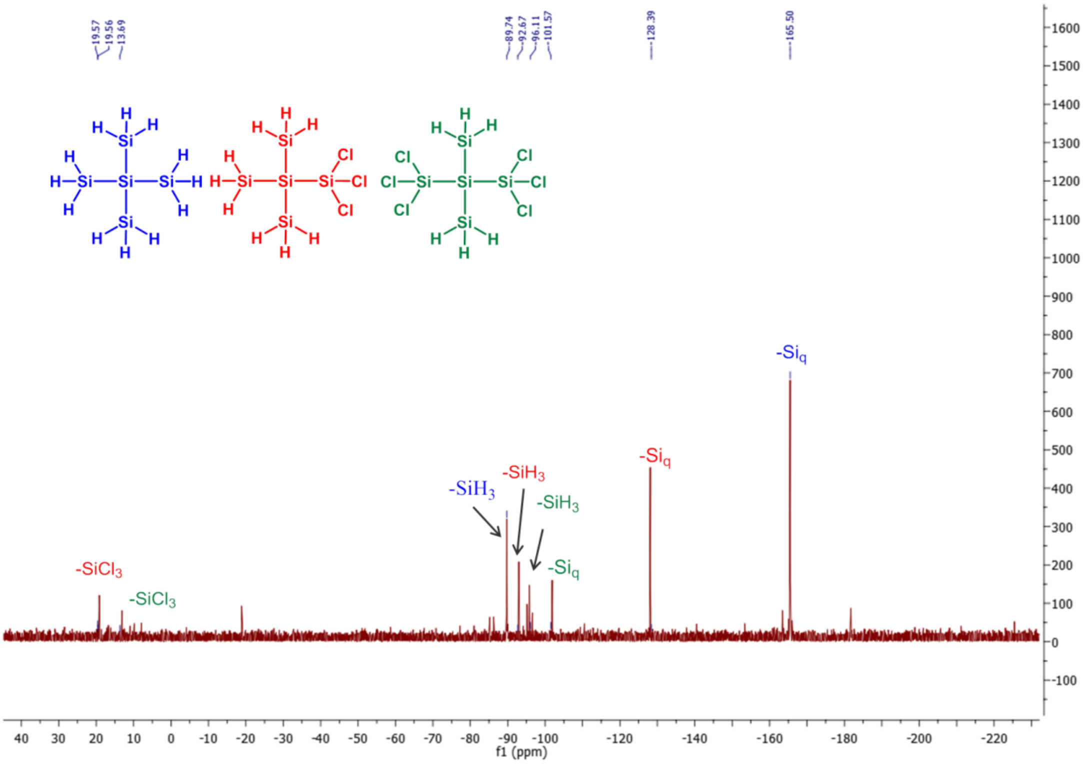


Figure 3 ^{29}**Si-INEPT-NMR-spectrum (**^{1}**H decoupled) of the reaction mixture obtained after addition of 9 eq. of** i**Bu**$_2$**AlH to Si(SiCl**$_3$**)**$_4$ **at 0 °C.**

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[120] J. Hahn, Z. Naturforsch. 1980, 35b, 282

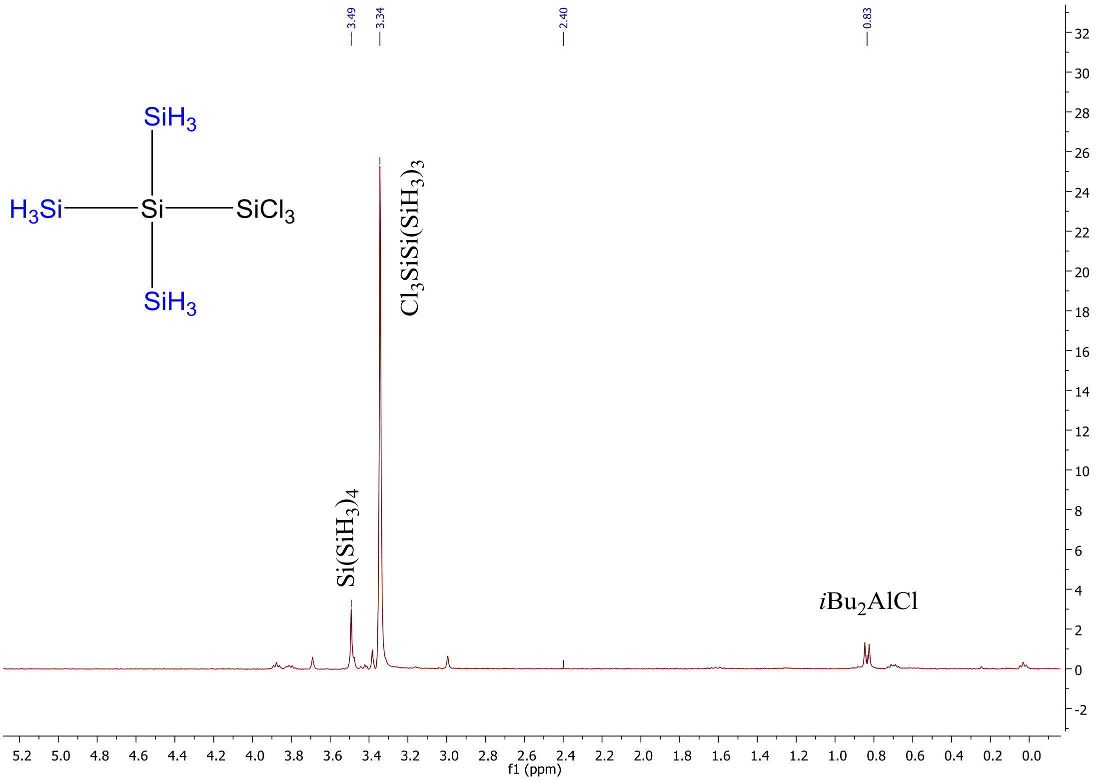


Figure 4 ^{1}H-NMR spectrum of compound 1 after isolation by fractional recondensation

NMR spectra clearly prove the structural identity of compound **1**. The ^{1}H-NMR spectrum (Figure 4 ^{1}H-NMR spectrum of compound 1) shows a singulet peak at 3.34 ppm in the typical range for the SiH_3 groups. The signal at 3.49 ppm is easily assigned to neopentasilane **3**. In the proton-coupled ^{29}Si-NMR spectrum (Figure 5) a quartet of the SiH_3-groups appears centered at around -93 ppm (^{1}JSi-H = 208.6 Hz). Each signal is further split into a septet (^{3}JSi-H = 2.9 Hz), due to long-range-coupling to the adjacent SiH_3-groups. The resonance line centered at 20.2 ppm can be assigned to the $SiCl_3$-group, which is significantly broadened by long-range-coupling to the SiH_3-moieties. Due to coupling with the protons of the SiH_3-groups (^{2}JSi-H = 5.7 Hz) the signal of the quaternary Si at -127.9 ppm atom also appears as a multiplet. The additional quartet centered at around -90 ppm indicates the presence of neopentasilane **3**.

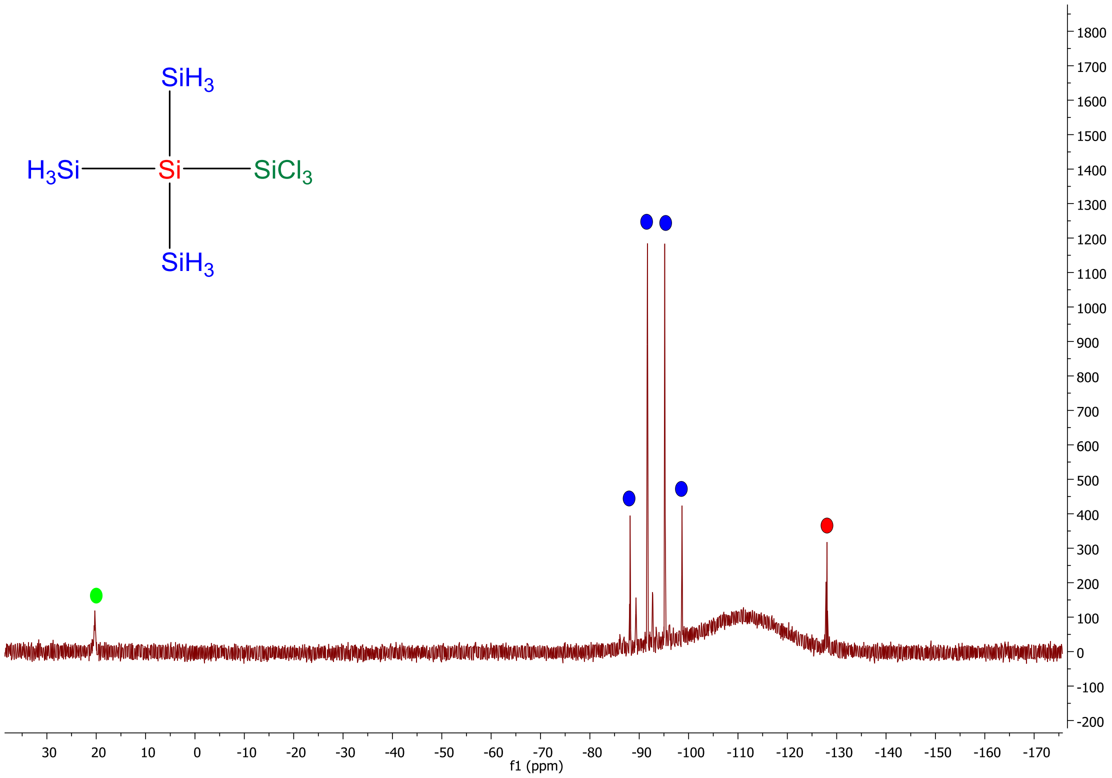


Figure 5 Proton-coupled ^{29}Si-NMR spectrum of compound 1 after isolation by fractional recondensation

If only 6 equivalents of *i*Bu$_2$AlH were added to Si(SiCl$_3$)$_4$ the resulting reaction mixture contained larger quantities of **2**. After removal of **1** and **3** from the crude product, **2** could be obtained from the high boiling residue by distillation at 90 °C and 0.01 mbar as a colourless liquid in 25% yield. The product contained considerable amounts of hydrosilane impurities of unidentified structure and *i*Bu$_2$AlCl.

NMR spectra obtained for compound **2** again are consistent with the proposed structure. The ^{1}H-NMR spectrum of **2** (Figure 6 ^{1}H-NMR spectrum of compound shows a singulett peak at 3.36 ppm which is in the estimated range for the SiH$_3$-group. Additional signals of other unidentified hydrosilane species are visible in this area. Furthermore, several signal groups characteristic for *i*Bu$_2$AlCl can be identified in the area around 1 ppm. Figure 7 ^{29}Si-INEPT-NMR spectrum (^{1}H decoupled) of 2 after isolation by fractional recondensationshows the ^{29}Si-INEPT-NMR spectrum of **2**. The signal of the quaternary Si-atom appears at -101.3 ppm. The resonance line of the SiH$_3$-groups is located at -95.9 ppm, while the SiCl$_3$-signal was found at 13.9 ppm. In the proton-coupled ^{29}Si-NMR (Figure 8) all lines exhibit characteristic splitting patterns. The SiH$_3$-signal forms a quartet (^{1}JSi-H = 215.8 Hz) with further quartet splitting of the individual lines (^{3}JSi-H = 3.6 Hz). The $SiCl_3$-signal is split into a poorly resolved multiplett due to long-range coupling to the SiH_3-groups. The signal of the quaternary Si-atom could not be clearly identified due to its low intensity. Additionally the ^{29}Si spectra of **2** show several peaks in the SiH_3 area arising from unseparable by-products of unidentified structure.

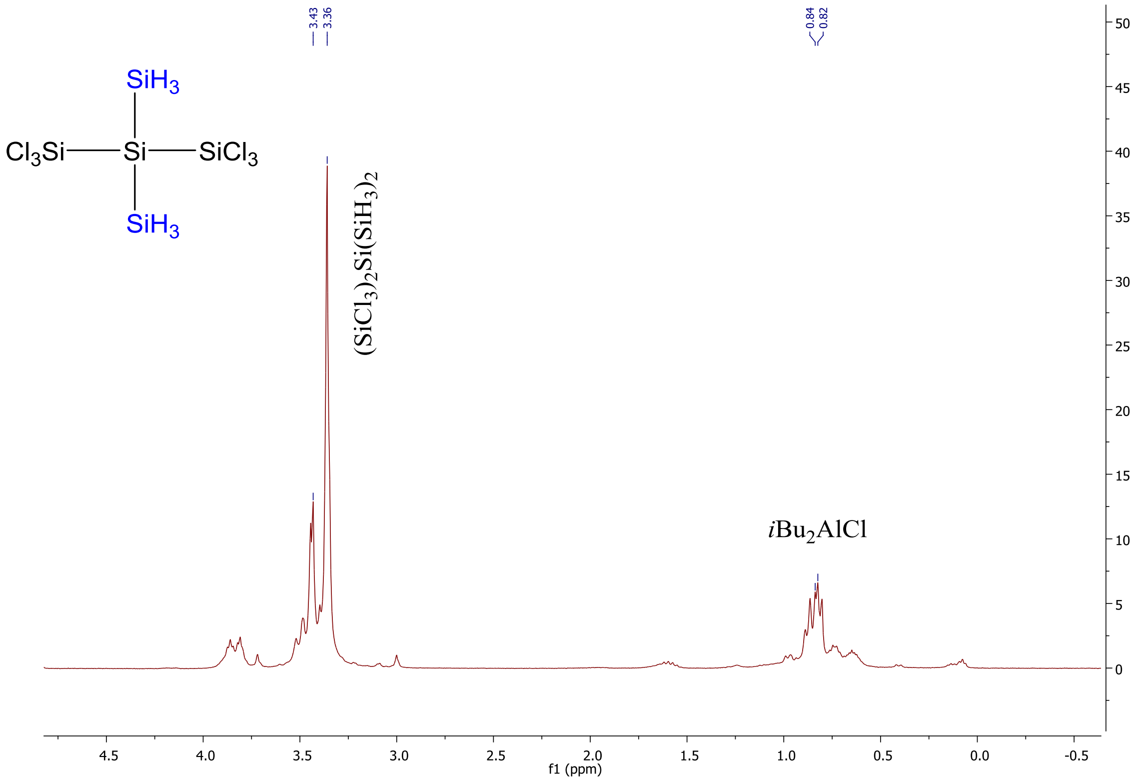


Figure 6 ^{1}H-NMR spectrum of compound 2 after isolation by fractional recondensation

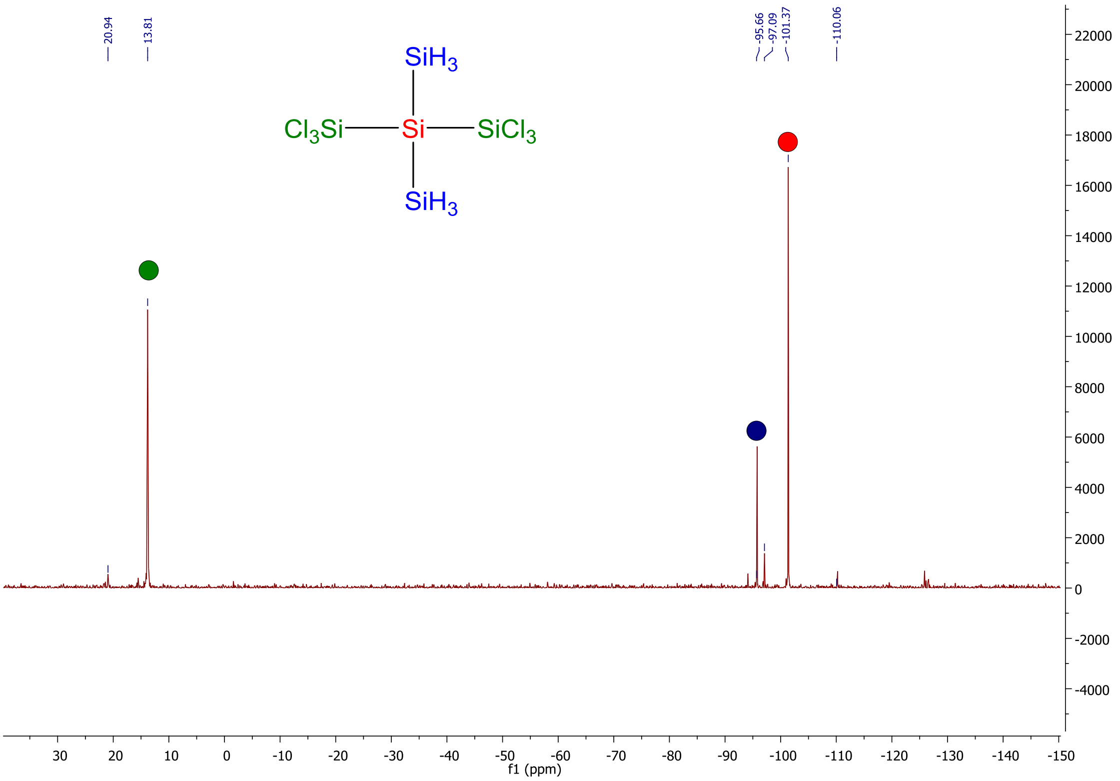


Figure 7 ^{29}Si-INEPT-NMR spectrum (^{1}H decoupled) of 2 after isolation by fractional recondensation

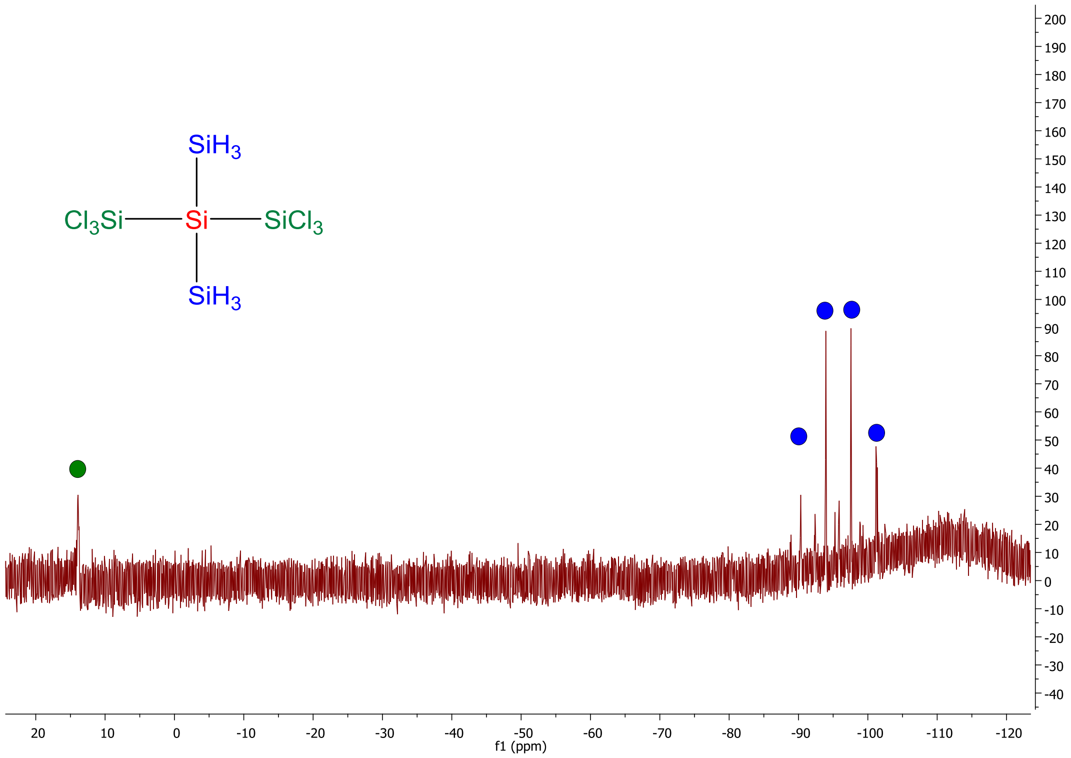
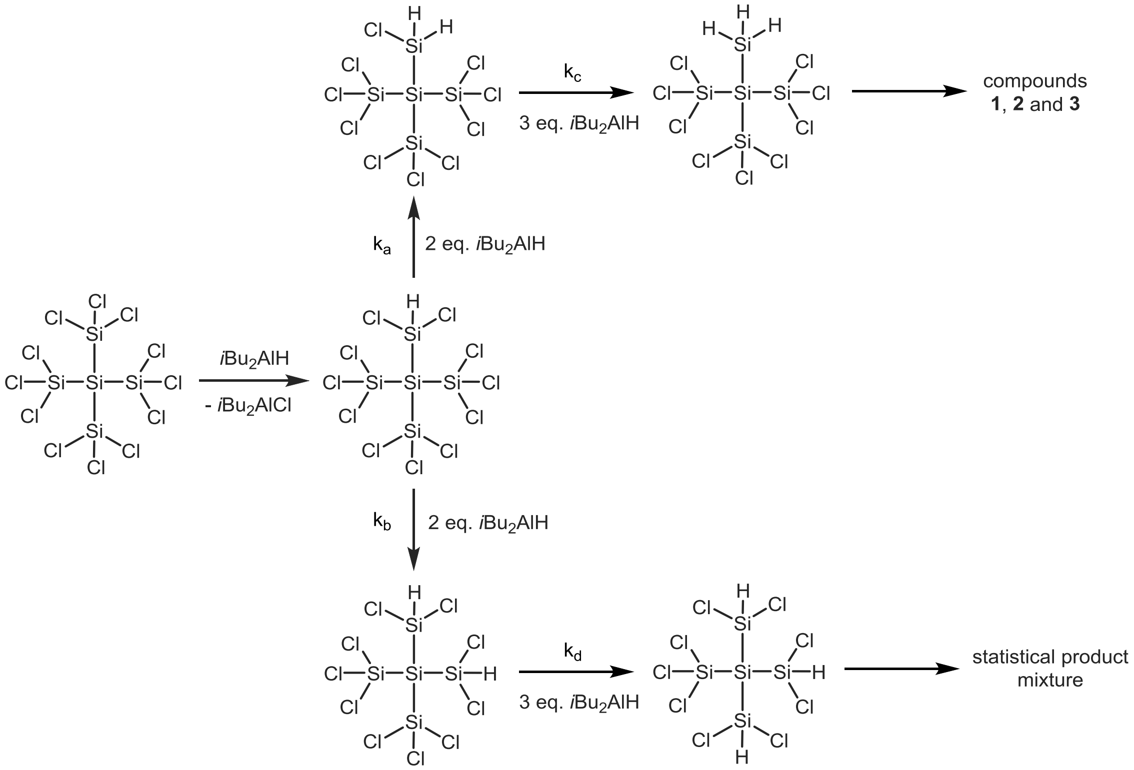


Figure 8 Proton-coupled ^{29}Si-NMR spectrum of 2 after isolation by fractional recondensation

Scheme 2 shows a possible reaction mechanism responsible for the unexpected selectivity with respect to the formation of compounds **1** and **2**. After hydrogenation of the first Si-Cl bond the second hydrogenation step can occur either at the same Si atom or at an adjacent $SiCl_3$ group. Both competing pathways exhibit different rate constants k_a and k_b. We assume that k_a is significantly larger than k_b, which causes the predominant formation of SiH_2Cl groups. The same picture holds for the subsequent hydrogenation step taking place primarily at the SiH_2Cl groups. Again only the hydrogenation with the rate constant k_c is the major pathway observed because the rate constant k_c is significantly larger than k_d and k_a. As a consequence the formation of the products **1** and **2** containing exclusively SiH_3 and $SiCl_3$ groups is favored over the formation of species with SiH_2Cl and $SiHCl_2$ moieties.



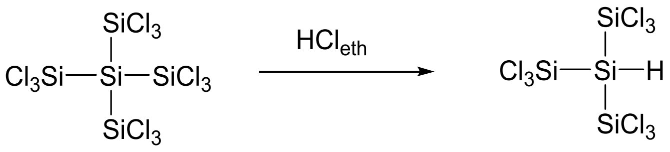
Scheme 2. Proposed reaction mechanism responsible for the selective formation of compounds 1 and 2.

3.1.2 Reaction of Nonachloroisotetrasilane with *i*Bu_2AlH

3.1.2.1. Synthesis of Nonachloroisotetrasilane 4

Older work claims that nonachloroisotetrasilane **4** is easily accessible by bubbling dry HCl gas through a solution of dodecachloroneopentasilane dissolved in $SiCl_4$ in the presence of catalytic amounts of amines[121]. During attempts to reproduce the results of this study, however, we always observed complete degradation of the educt to $HSiCl_3$ as the major product.

A patent by Gelest describes a different synthetical protocol for the synthesis of **4.** They also used $SiCl_4$ as a solvent, but instead of gaseous HCl a diethyl ether solution of HCl was used. In this case ether also serves as an auxiliary base, thus, making the addition of any amino base unnecessary. In the course of our attempts to synthesize **4** we additionally discovered, that compound **4** also can be obtained in very good yields without the use of $SiCl_4$ as a solvent (Equation 25).



4

Equation 25

$Si(SiCl_3)_4$ was dissolved in diethyl ether and 1.5 equiv. of etheral HCl was added. The starting material was consumed usually within 10 min (depending on the used amount of starting material) and **4** was obtained after distillation at 60°C (0.01 mbar) nearly without any detectable by-products. The reaction pathway depends strongly on the

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[121] a.) W. Raml, E. Hengge, Monatshefte für Chemie, 1980, 111, 29. b) F. Höfler, R. Jannach, W. Raml, *Z. anorg. allg. Chem.* 1977, 428, 75. c.) B. C. Arkles, Y. Pan, G. L. Larson, From U.S. Pat. Appl. Publ. 2012, US 20120071678 A1 20120322. d.) N. Auner, M. C. Holthausen, F. Neumeyer, From PCT Int. Appl. 2016, WO 2016011993 A1 20160128.

purity of $Si(SiCl_3)_4$. If the catalyst of the synthesis from $Si(SiCl_3)_3$ is not separated carefully the further reaction shows decomposition to $HSiCl_3$.

NMR data of 4 are consistent with literature values[121]. A proton-coupled ^{29}Si-NMR spectrum of 4 is shown in Figure 9.

A doublet for the Si-H group appears centered around -80 ppm (^{1}JSi-H = 214 Hz). The resonance line at 4.45 ppm can be assigned to the $SiCl_3$ group.

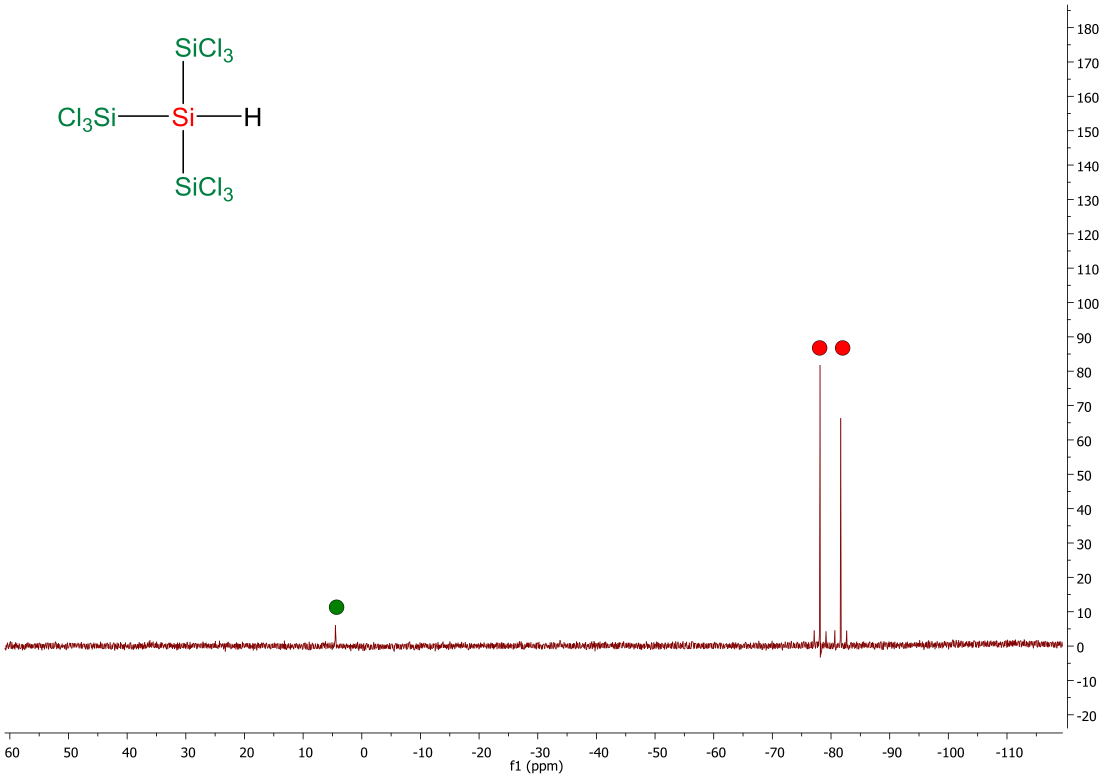
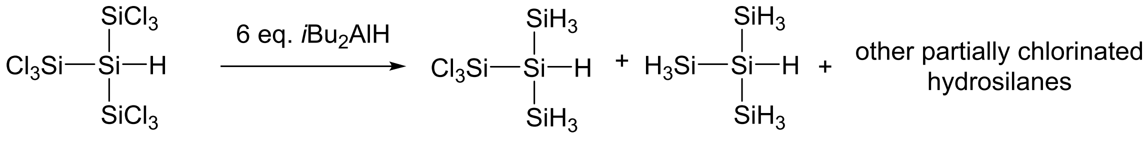


Figure 9 Proton-coupled ^{29}Si-NMR spectrum of 4

3.1.2.2. Partial Hydrogenation of 4

With the primary aim to partially hydrogenate the isotetrasilane skeleton we reacted compound **4** with 6 equivalents of *i*Bu_2AlH (Equation 26). After the addition of the hydrogenating agent a clear solution was obtained. After removal of **6** from the crude product, compound **5** could be isolated after distillation at 50°C at 0.01 mbar as a colourless liquid with a purity of about 70%. The product contained considerable amounts of hydrosilane impurities which could not be separated.



5 **6**

Equation 26

The ^{1}H-NMR-spectrum of **5** (Figure exhibits a doublet for the SiH$_3$-group at 3.24 ppm and a multiplet for the SiH group at 3.05 ppm. The additional signals between 3.30 and 3.5 ppm indicate the presence of hydrosilane impurities of unknown structure. Figure 11 displays the ^{29}Si-INEPT-NMR spectrum of **5**. The resonance line at -97.7 ppm can be assigned to the SiH$_3$-groups. The signal for the tertiary Si-atom appears at -105.9 ppm. The peak of the SiCl$_3$-group could not be identified in the spectrum. Additional lines between -90 to -100 ppm arise from unidentified hydrosilane by-products.

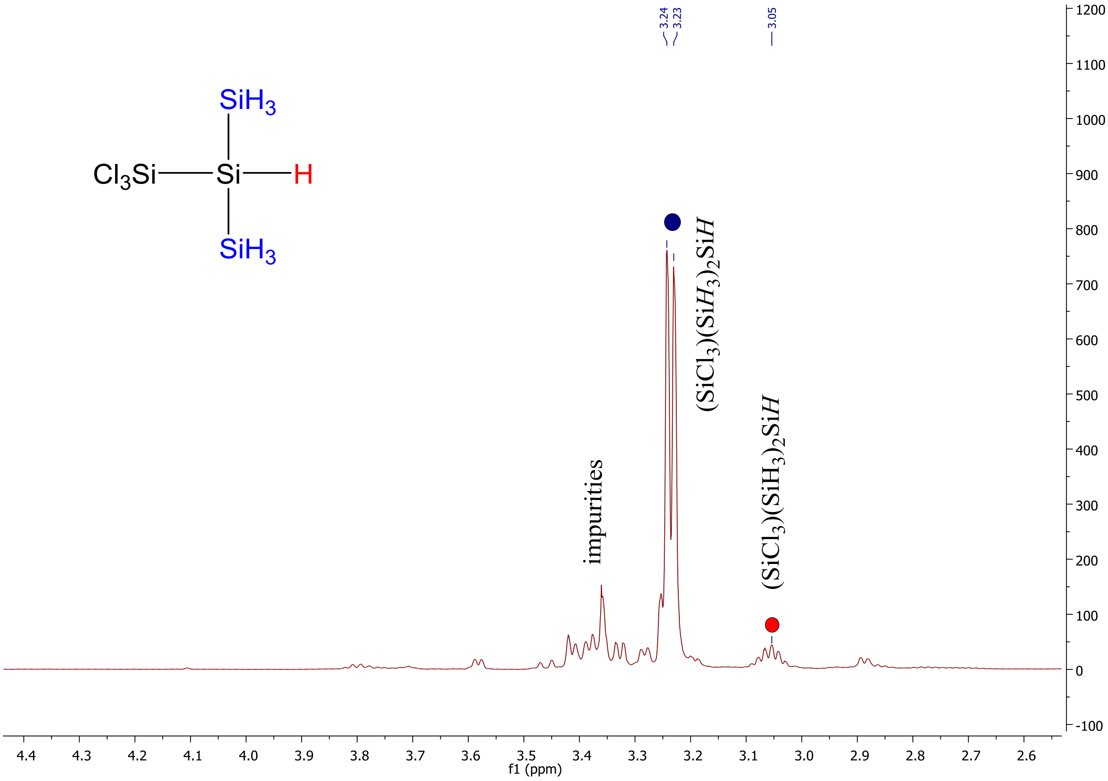


Figure 10 ^{1}H-NMR spectrum of 5 after isolation by fractional recondensation

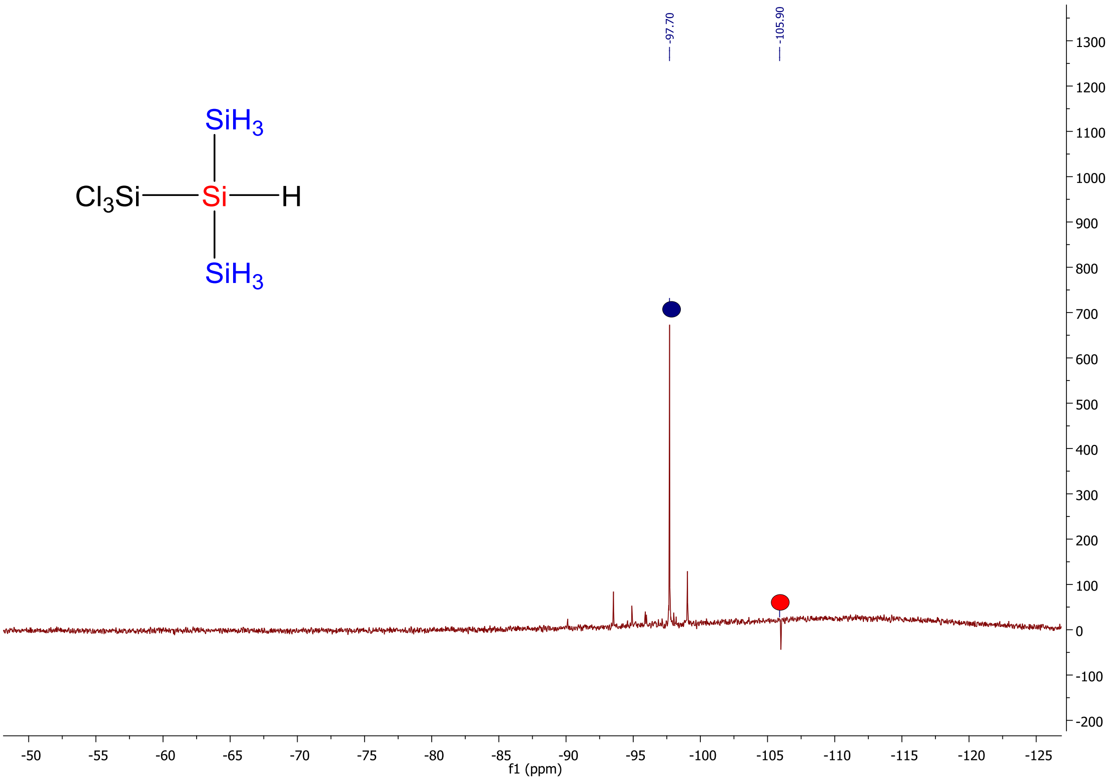
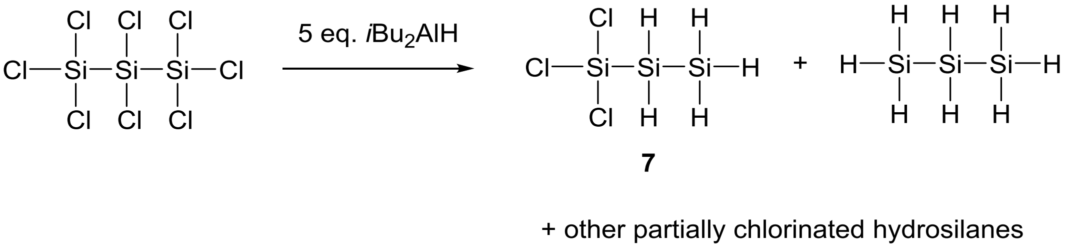


Figure 11 ^{29}Si-INEPT-NMR spectrum (^{1}H decoupled) of 5 after isolation by fractional recondensation

3.1.3 Reaction of Octachlorotrisilane with *i*Bu_2AlH

Si_3Cl_8 conveniently can be partially hydrogenated with sub-stoichiometric amounts of *i*Bu_2AlH. The best selctivity was observed when 5 equivalents of *i*Bu_2AlH were used. In this case 1,1,1-trichlorotrisilane $H_3SiSiH_2SiCl_3$ **7** and Si_3H_8 were obtained along with smaller amounts of other Cl/H-oligosilanes (Equation 27).



Equation 27

Complete separation and isolation of the products by distillation at room temperature and 0.01 mbar was not possible. The ^{1}H-NMR spectrum of the major fraction (Figure 12) clearly showed the presence of Si_3H_8 (triplet at 3.63 ppm, multiplet at 3.45 ppm)[122] and compound **7** (triplet at 3.75 ppm, quartet at 3.92 ppm) as the major products in an approximate ratio of 1 : 2. The structure proposed for compound **7** is additionally established by the proton-coupled ^{29}Si-NMR spectrum of the resulting product mixture (Figure 13). Besides the signals of Si_3H_8 (triplet at 115.3 ppm, ^{1}JSi-H = 193.8 Hz; quartet centered at 97.2, ^{1}JSi-H = 205.2 Hz)[120] the spectrum shows a quartet of triplets (^{1}JSi-H = 207.6 Hz, ^{2}JSi-H = 3.4 Hz) around -100 ppm, which can be assigned to the SiH_3 group of **7**. The SiH_2 group of **7** appears as a triplet of quartets at 91 ppm (^{1}JSi-H = 205.4 Hz, ^{2}JSi-H = 5.3 Hz). The low field shift of this triplet relative to Si_3H_8 is as expected for a SiH_2 group adjacent to an $SiCl_3$ moiety. The $SiCl_3$ signal (not shown in Figure 13), finally, is found at 15.9 ppm in a typical range for $SiCl_3$ groups. Residual low intensity lines arise from further Cl/H silane by-products.

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[122] AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))

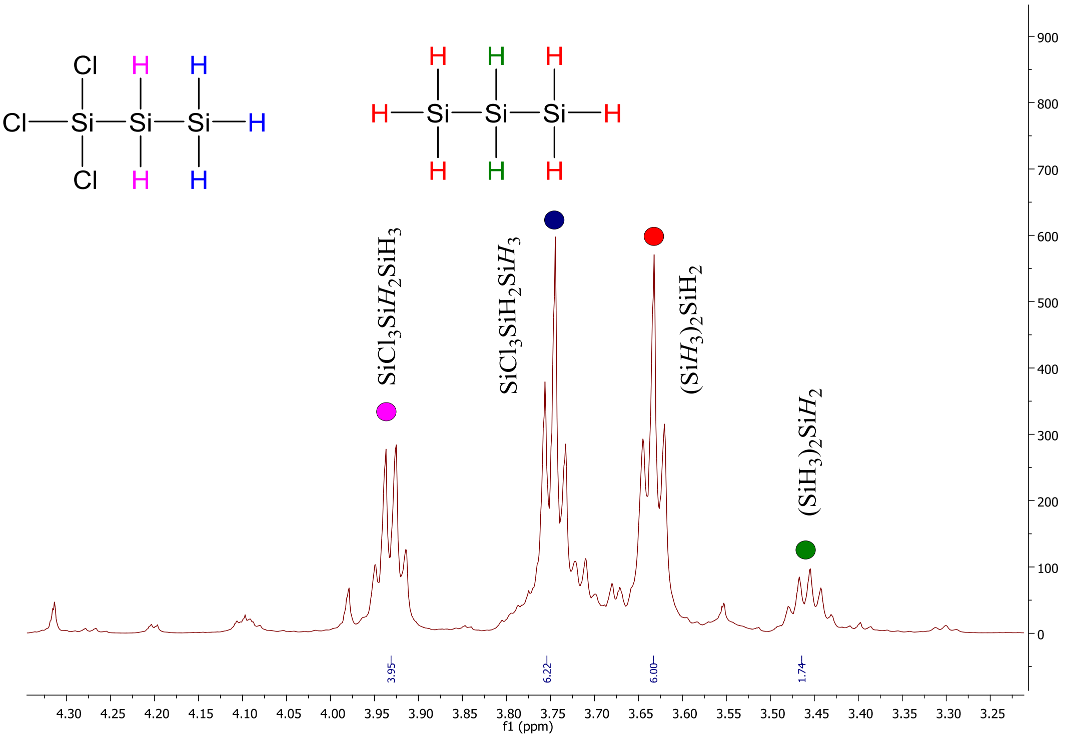


Figure 12 ^{1}**H-NMR spectrum of the volatile products of the reaction of** Si_3Cl_8 **with 5 eq. of** ***i*****Bu**$_2$**AlH.**

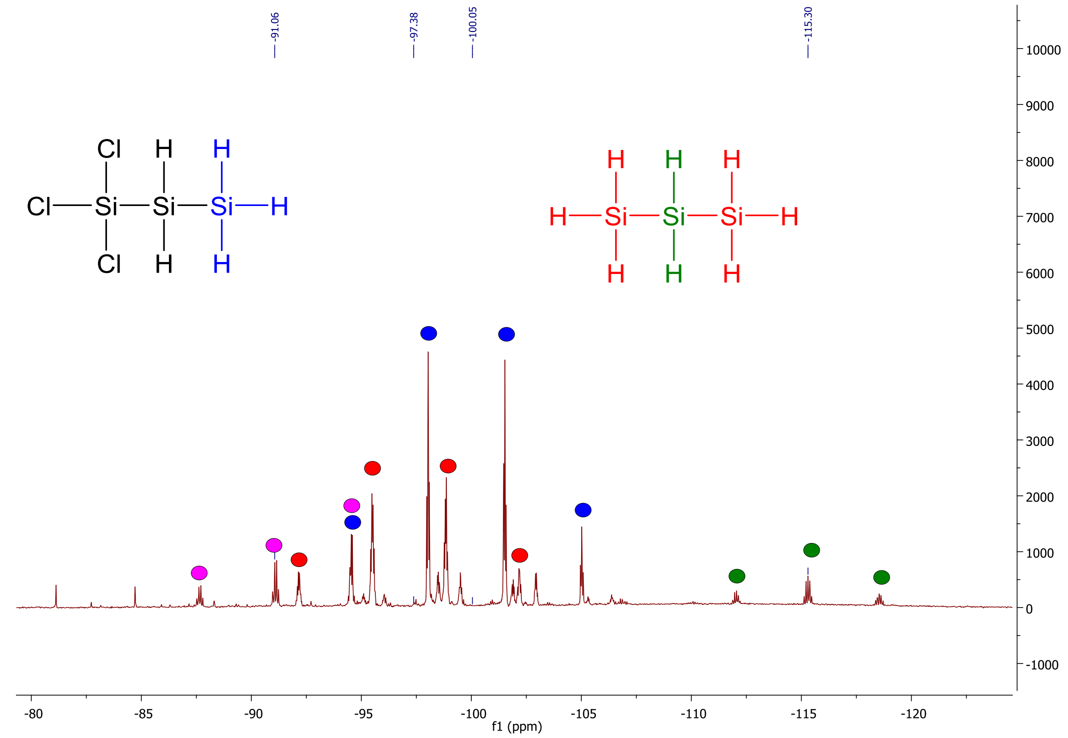
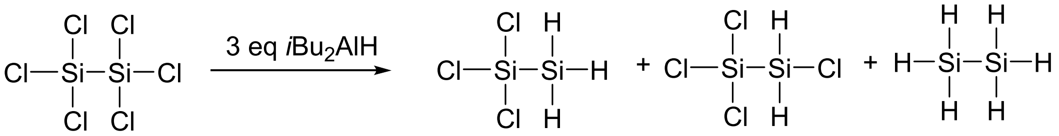


Figure 13 Proton-coupled ^{29}**Si-NMR spectrum of the volatile products of the reaction of** Si_3Cl_8 **with 5 eq. of** ***i*****Bu**$_2$**AlH.**

3.1.4 Reaction of Hexachlorodisilane with *i*Bu_2AlH

Treatment of Si_2Cl_6 with sub-stoichiometric amounts of *i*Bu_2AlH under identical conditions as described in the preceding section for Si_3Cl_8 afforded mixtures of several Cl/H-disilanes (Equation 28). With three equivalents of the hydrogenating agent 1,1,1-trichlorodisilane $H_3SiSiCl_3$ **8** and 1,1,1,2-tetrachlordisilane **9** were formed as the major products in a ratio of approximately 55 % : 40 % along with 5 % of Si_2H_6 (estimated by integration of the ^{1}H-NMR signals) and could not be separated further. When larger or smaller amounts of *i*Bu_2AlH were used the complexity of the resulting product mixture increased.



8 **9**

+ other partially chlorinated hydrosilanes

Equation 28

Besides several unidentified signals with low intensity ^{1}H-NMR analysis (Figure 14) of the colourless liquid obtained after recondensation of the crude product showed characteristic resonances for **8**[123], **9**[124] and Si_2H_6 ($\delta^1H = 3.1$ ppm)[122] All products were additionally identified by their ^{29}Si chemical shifts and splitting patterns (Figure 15). Detailed NMR data can be found in the Experimental Section.

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[123] a.) Haas, A.; Suellentrup, R.; Krueger, C. *Z. Anorg. Allg. Chem.* 1993, 619, 819. b.) Uhlig, W. *Z. Anorg. Allg. Chem.* 1993, 619, 1479–1482 c.) Stueger, H.; Lassacher, P.; Hengge, E. *J. Organomet. Chem.* 1997, 547, 227.

[124] Soellradl, H.; Hengge, E. *J. Organomet. Chem.* 1983, 243, 257.

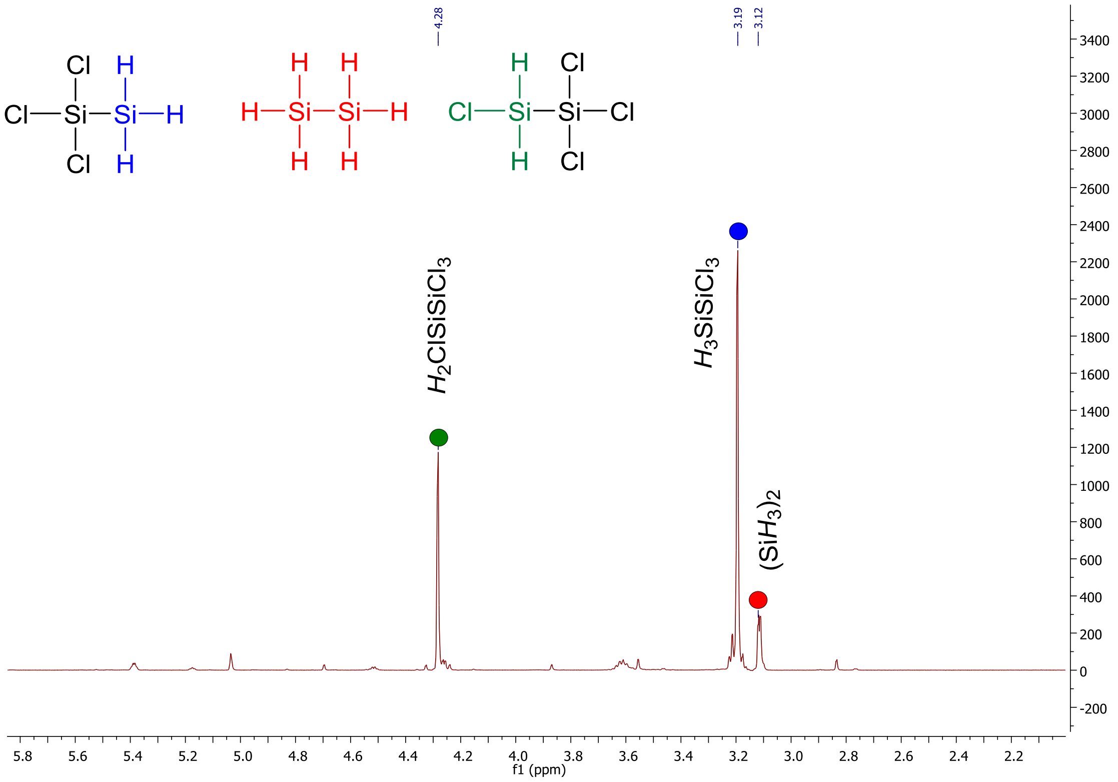


Figure 14 ^{1}H-NMR spectrum of the volatile products of the reaction of Si_2Cl_6 with 3 eq. of *i*Bu_2AlH.

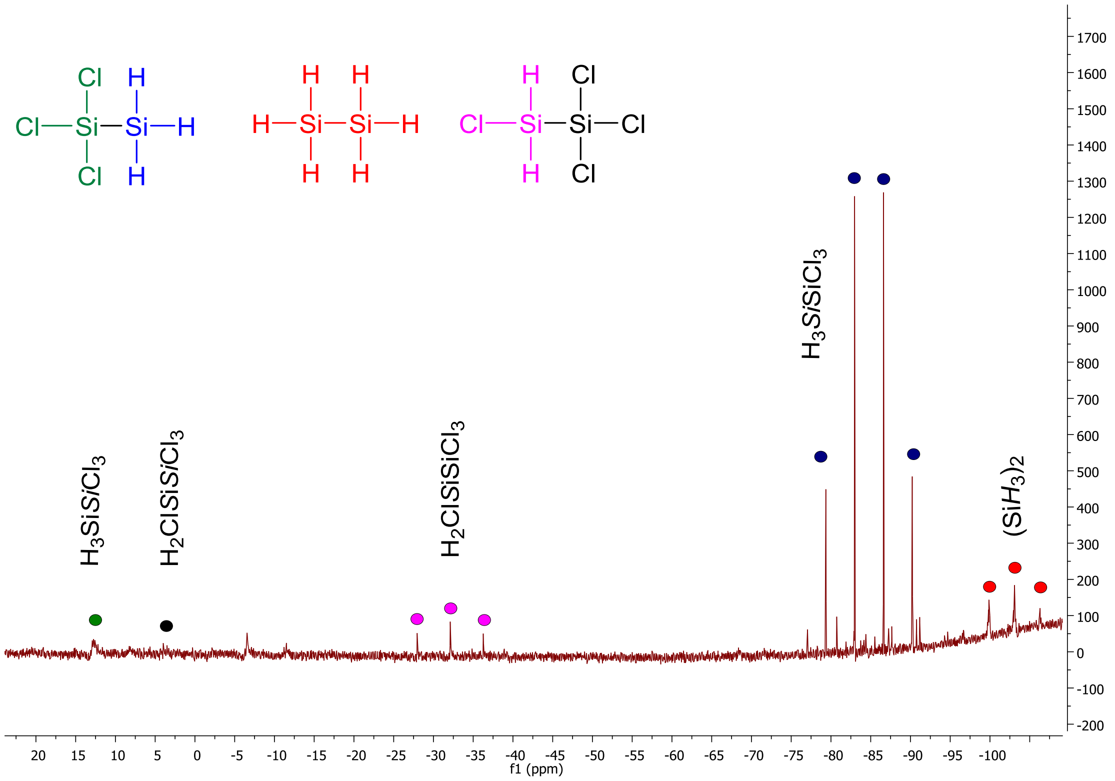


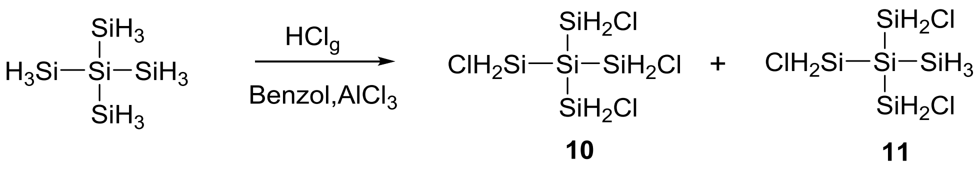
Figure 15 Proton coupled ^{29}Si-NMR spectrum of the volatile products of the reaction of Si_2Cl_6 with 3 eq. of *i*Bu_2AlH.

3.2 Partial Chlorination of Branched Higher Silicon Hydrides

As already pointed out in section 2 of this work the partial chlorination of linear silanes including di- and trisilane usually affords complex mixtures of several Cl/H silanes. Branched substrates offer better opportunities for a selective reaction course. Earlier studies from our group, for instance, showed, that neopentasilane **3** selectively can be chlorinated to 1,2,3,4-tetrachloroneopentasilane **10** with $SnCl_4$[63]. In continuation of these studies we thus decided to perform further investigations concerning the selectivity of partial chlorination reactions of neopentasilane **3** and isotetrasilane **4** using HCl and $SnCl_4$ as halogenating reagents.

3.2.1 Partial Chlorination of Neopentasilane with HCl

When dry HCl gas was bubbled through a benzene solution of **3** containing catalytic amounts of $AlCl_3$ at 80 °C for 15 minutes 1,2,3,4-tetrachloroneopentasilane **10** and 1,2,3-trichloroneopentasilane **11** were formed with remarkable selectivity (Equation 29). After removal of the solvent and the catalyst an approximately 12 : 1 mixture of pure **9** and **10** were obtained. Attempts to separate both components by distillation or crystallization unfortunately were unsuccessful. It is interesting to note that complex mixtures of partially chlorinated hydrosilanes were obtained without any product selectivity if toluene was used as a solvent instead of benzene under otherwise identical conditions.



Equation 29

Besides the resonance line for the SiH_2Cl-group of **10** at 4.85 ppm[63] the ^{1}H-NMR spectrum of the resulting volatile product fraction (Figure 16) showed two further signals at 4.84 and 3.37 ppm which can be assigned to the SiH_2Cl and the SiH_3 group of

11. The respective ^{29}Si-INEPTH-NMR spectrum (Figure 17) also exhibits three signals. The resonace line at -24.6 ppm represents the SiH_2Cl-group of **10**[63] while the signals at -25.7 and -98.5 ppm belong to the SiH_2Cl and the SiH_3 groups of **11**, respectively.

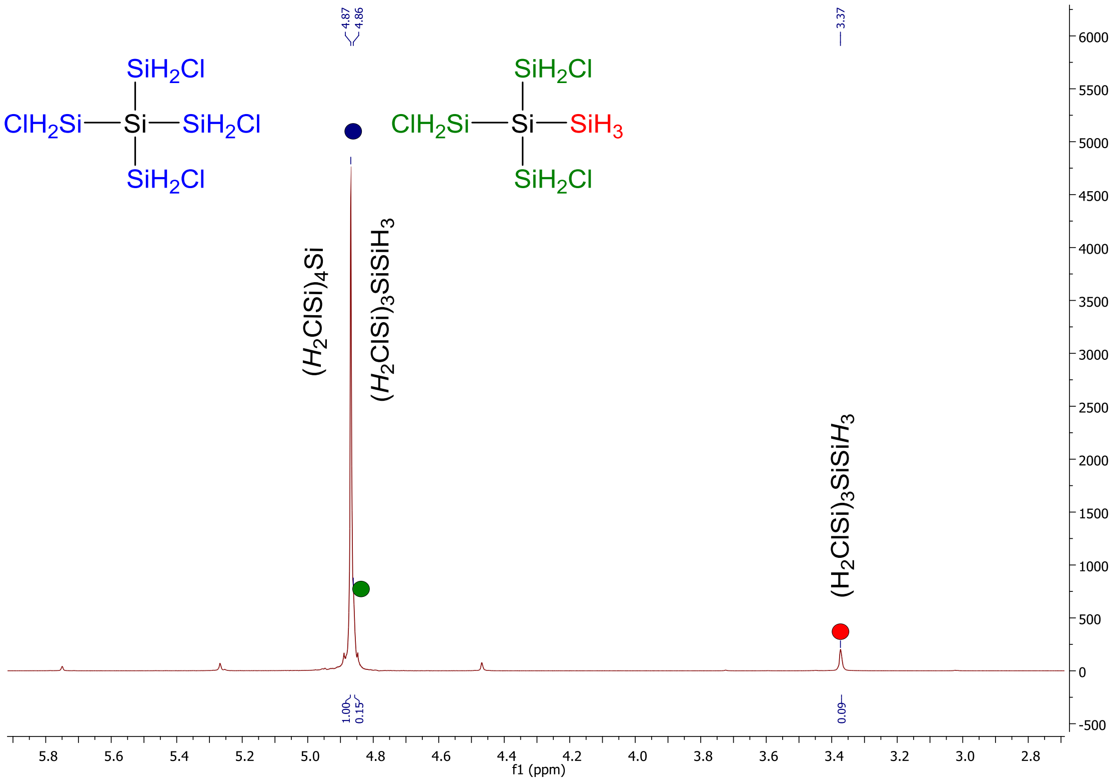


Figure 16 ^{1}H-NMR spectrum of the volatile products of the reaction of 3 with $HCl/AlCl_3$.

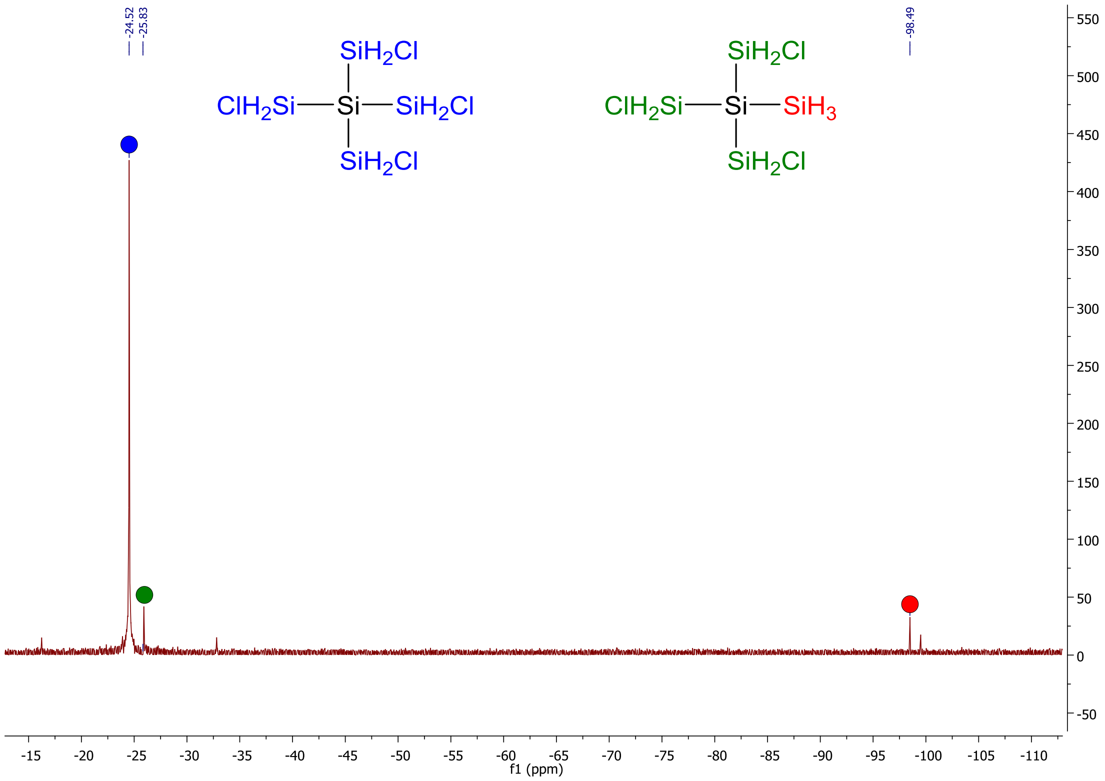
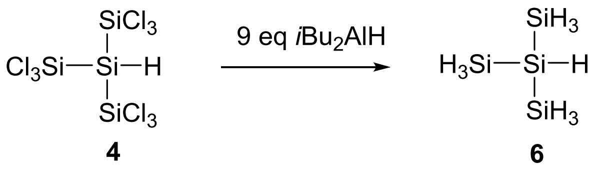


Figure 17 ^{29}Si-INEPTH-NMR spectrum (^{1}H decoupled) the volatile products of the reaction of 3 with HCl/AlCl$_3$.

3.2.2 Partial Chlorination of Isotetrasilane

3.2.2.1. Synthesis of Isotetrasilane

Isotetrasilane **6** is conveniently synthesized by the hydrogenation of nonachloroisotetrasilane **4** (Equation 30) prepared according to section 3.1.2.1 of this work with 9 equivalents of *i*Bu$_2$AlH. After distillation at room temperature and 0.01 mbar the target compound was obtained as a colourless liquid with a yield of about 60%.

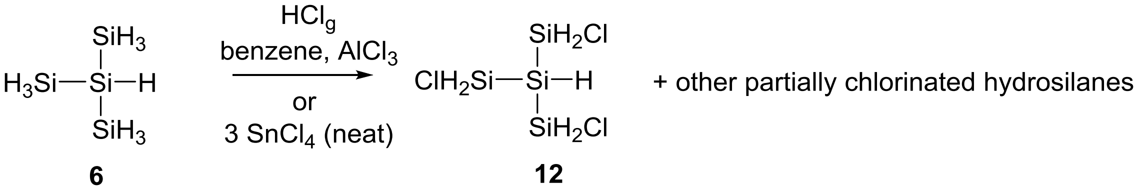


Equation 30

NMR data of the product are consistent with literature[120].

3.2.2.2. Chlorination Reactions

When **6** was reacted with HCl/$AlCl_3$ in an analogous manner as described above for neopentasilane, 1,2,3-trichloroisotetrasilane **12** was obtained as the major product along with unidentified partially chlorinated hydrosilanes. If $SnCl_4$ was used as a halogen source a nearly identical course of the reaction was observed.



Equation 29

Attempts to isolate pure **12** by fractional recondensation or crystallization were unsuccessful in both cases. NMR analysis of the crude products, however, clearly established the structure of compound **12**. In the ^{1}H-NMR spectra (Figure 18) the SiH_2Cl resonance is found at 4.71 ppm as a doublet resulting from coupling to the central SiH moiety. The SiH resonance appears as a multiplet centered at 2.88 ppm. The ^{29}Si-INEPTH-NMR spectra (Figure 20) show the signal of the SiH_2Cl group at -26.3 ppm and the signal of the tertiary Si-atom at -109.6 ppm. All SiH_2Cl chemical shifts are found close to the values observed for the partially chlorinated neopentasilanes **10** and **11**. The SiH resonances are shifted downfield as compared to the unsubstituted compound **6** by ~0.2 ppm in the ^{1}H- and by ~30 ppm in the ^{29}Si spectrum due to the impact of the electronegative Cl substituents at the adjacent Si atoms.

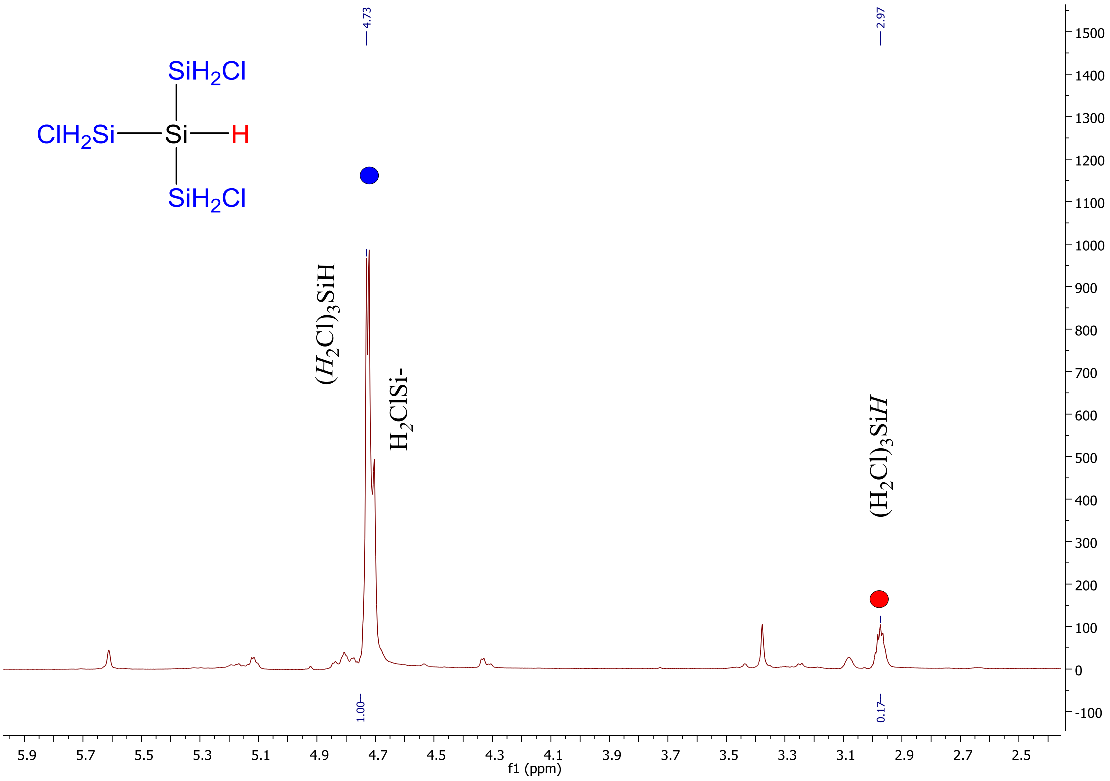


Figure 18 ^{1}**H-NMR spectrum of the volatile products of the reaction of 6 with HCl/AlCl$_3$.**

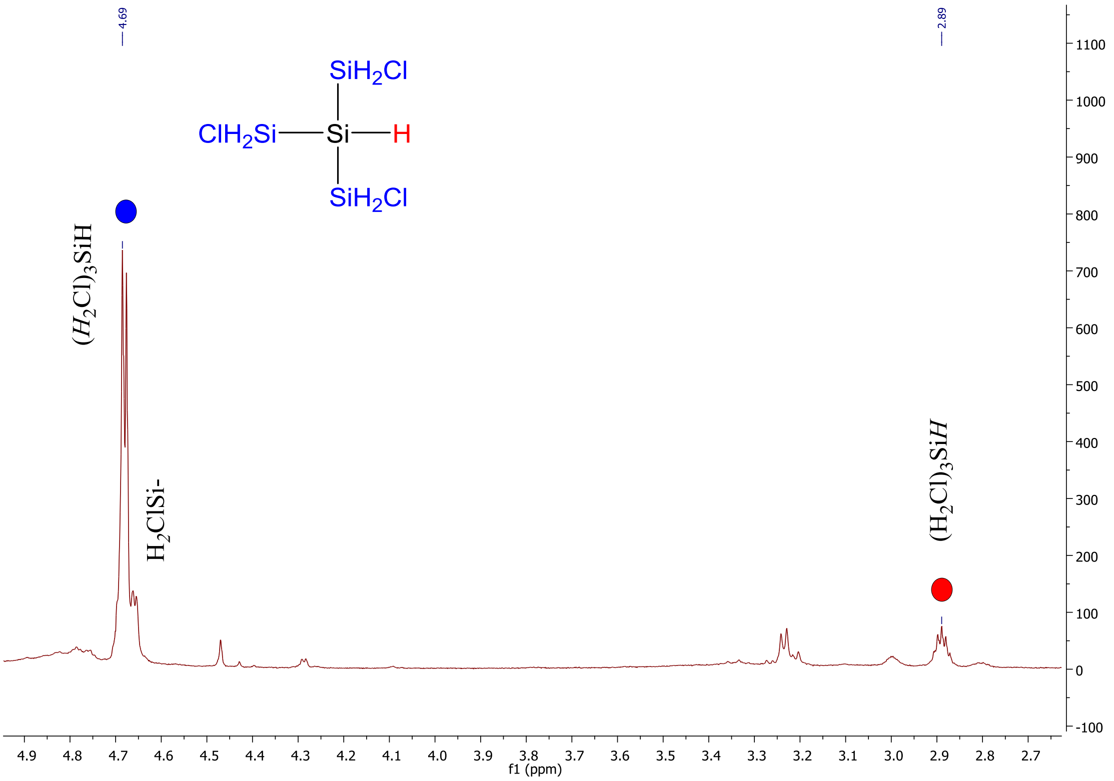


Figure 19 ^{1}**H-NMR spectrum of the volatile products of the reaction of 6 with** $SnCl_4$**.**

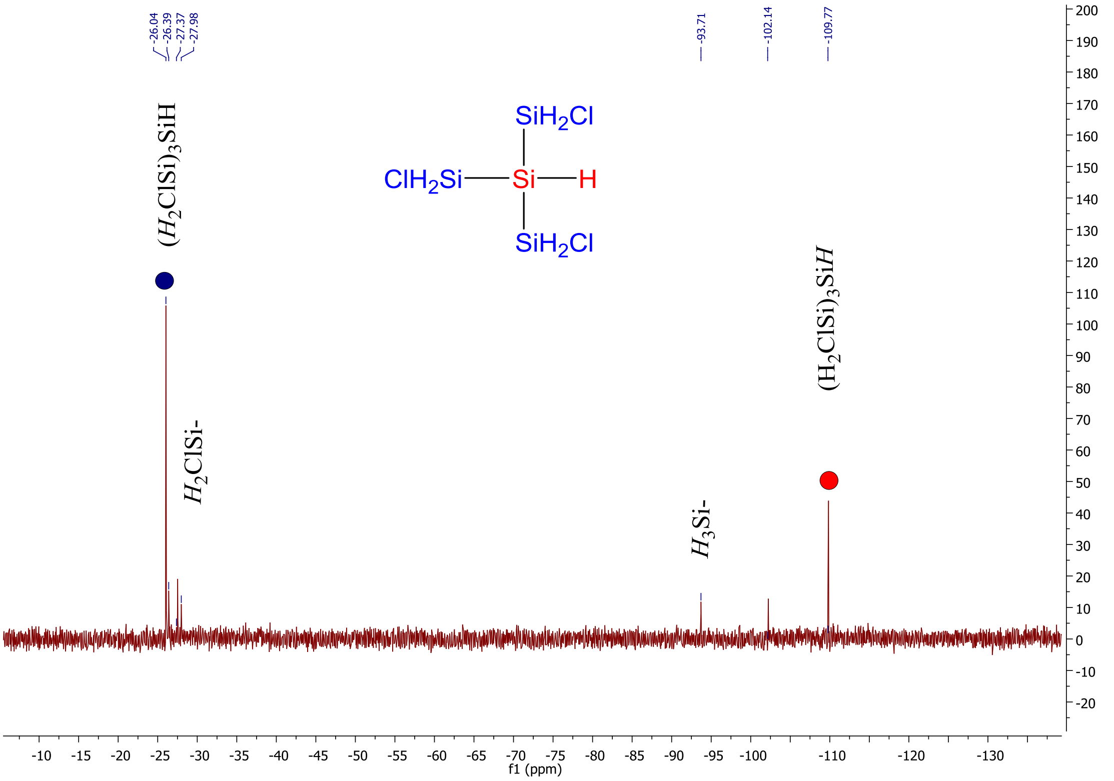
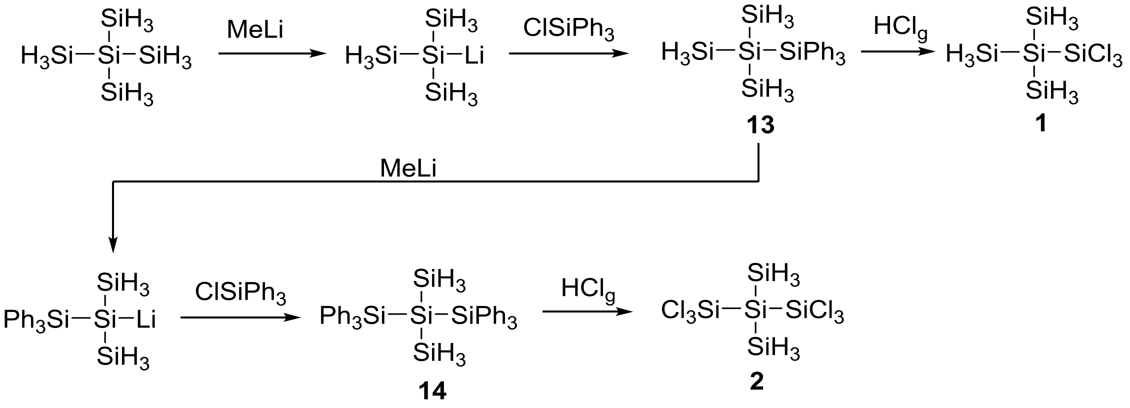


Figure 20 ^{29}**Si-INEPTH-NMR spectrum (**^{1}**H decoupled) of the volatile products of the reaction of 6 with** $HCl/AlCl_3$**.**

3.3 Chlorodephenylation of Phenyl-H-Oligosilanes

3.3.1 Synthesis of Tri- and Hexachloroneopentasilane 1 and 2

Because compound **1** and **2** prepared according to section 3.1.1 of this work always contained minor amounts of impurities which could not be separated we decided to synthesize **1** and **2** independently by the chlorodephenylation method starting from the Ph/H oligosilanes **13** and **14** (Scheme 3).



Scheme 3: Synthesis of compounds 1 and 2 by the chlorodephenylation route

The precursors **13** and **14** were prepared according to literature procedures [125,126]. The corresponding precursor was then dissolved in benzene and a catalytic amount of $AlCl_3$ was added. The solution was cooled to 10 °C and HCl was bubbled through for about 15 minutes. After separation of the catalyst and fractional recondensation in vacuo the pure chlorodephenylation products **1** and **2** were obtained with yields of about 42 % and 39 %, respectively[64]. NMR data of the products are identical to the ones prepared according to section 3.1.1. ^{1}H-NMR analysis (Figures 21 and 22) clearly established the purity of the samples.

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[125] H. Stüger, T. Mitterfellner, R. Fischer, C. Walkner, M. Patz, S. Wieber, *Chem. Eur. J.* 2012, 18, 7662 – 7664

[126] A. Temmel, Master Thesis, TU Graz, 2012

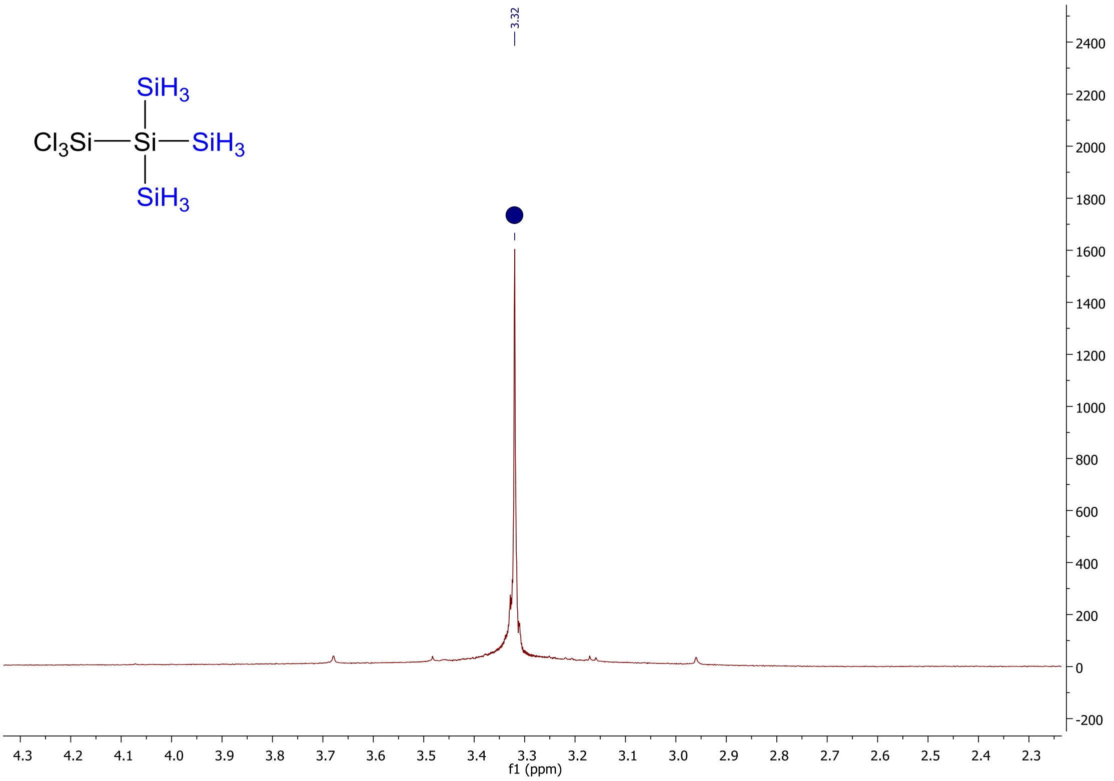


Figure 21 ^{1}H- NMR spectrum of pure 1

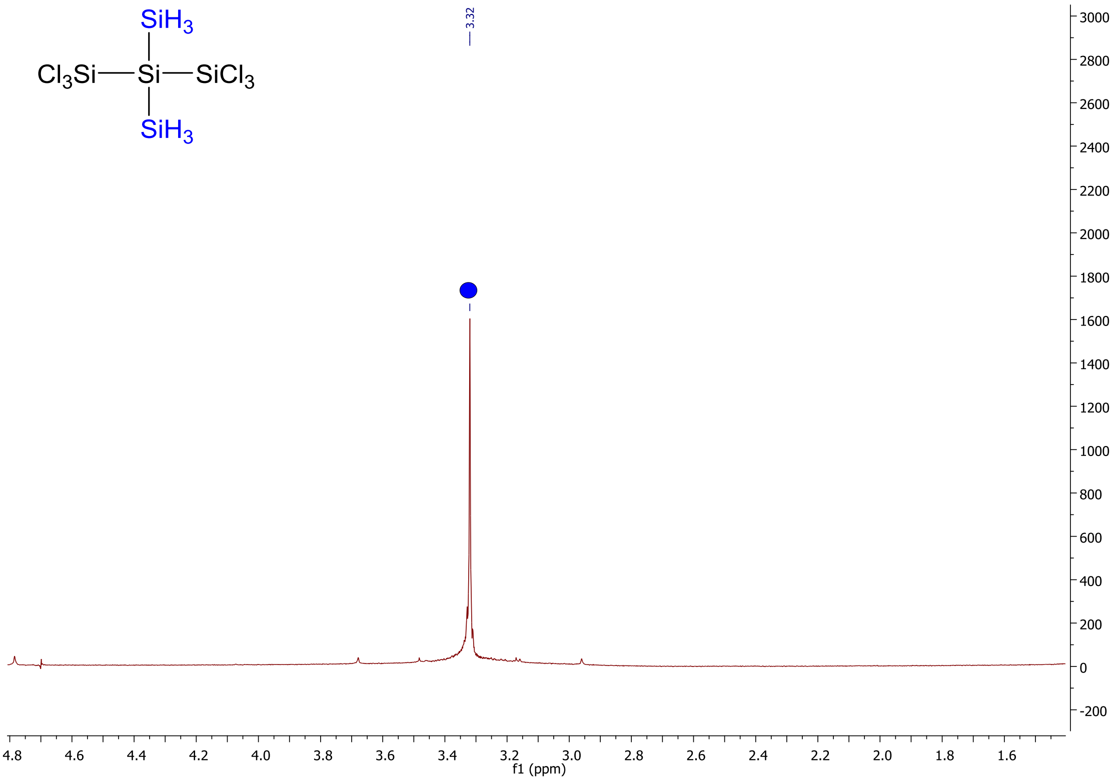
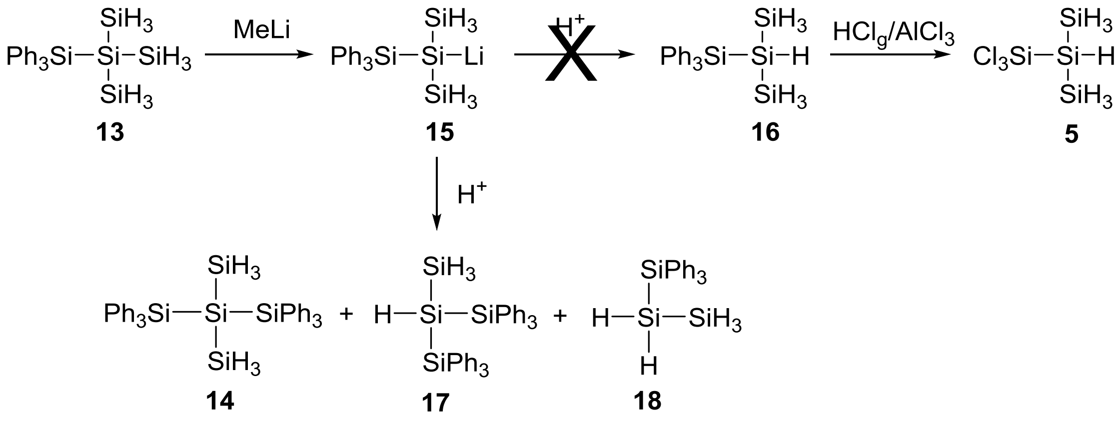


Figure 22 ^{1}H-NMR spectrum of pure 2

3.3.2 Attempted Synthesis of Chloroisotetrasilane 5

The basic approach for the attempted synthesis of 1,1,1-trichloroisotetrasilane is depicted in Scheme 4.



Scheme 4: Route for the attempted synthesis of compound 5 by chlorodephenylation

In the first step the isotetrasilanide **15** should be protonated to give 1,1,1-triphenylisotetrasilane **16** which subsequently should be transformed to the target compound **5** by treatment with HCl gas in the presence of a catalytic amount of $AlCl_3$. Our experiments, however, clearly demonstrated that the precursor molecule **16** and thus also the target compound **5** are synthetically not accessible as proposed in Scheme 4. NMR analysis of the crude product of the acid hydrolysis of the silanide **15** showed, that instead of **16** a mixture of the isotetrasilanes **14**, **17** and **18** was formed. Furthermore, it has been found that the relative amounts of **14**, **17** and **18** strongly depend on the experimental performance of the reaction. When the proton source was added to the isotetrasilanide solution compound **14** was obtained nearly exclusively as shown by its characteristic ^{1}H-NMR resonance at 3.61 ppm (Figure 23). Addition of the isotetrasilanide solution to the acid, however, afforded compounds **17** and **18** as the major products along with only minor amounts of **14**. In this case the ^{1}H-NMR spectrum showed a triplet ($\delta^1H = 3.29$ ppm, SiH_3) and a quartet ($\delta^1H = 3.54$ ppm, SiH_2) for **18** along with a doublet ($\delta^1H = 3.39$ ppm, SiH_3) and a quartet ($\delta^1H = 3.84$ ppm, SiH) for **17** and the characteristic resonance line at 3.61 ppm for **14** (Figure 24). By integration of the resonances a product ratio of 4% **14**, 48 % **17** and 48% **18** could be estimated.

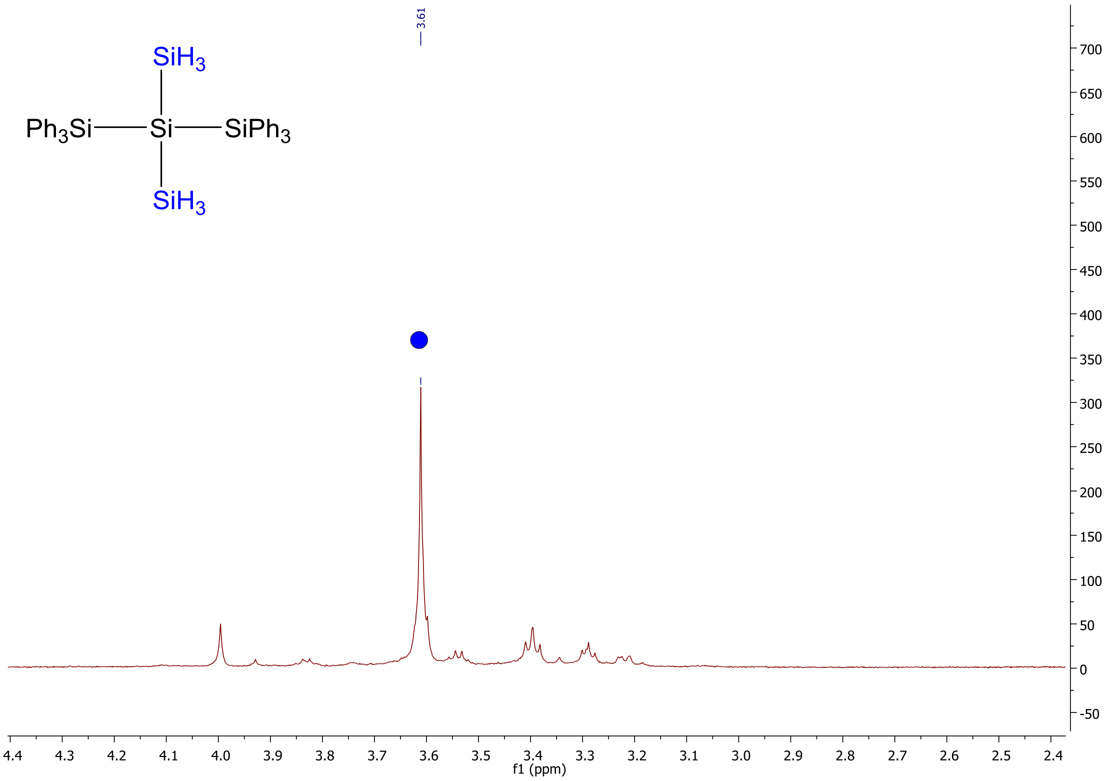


Figure 23 ^{1}H-NMR spectrum of the product mixture obtained after addition of $PhSO_3H$ to an ether solution of the isotetrasilanide 15

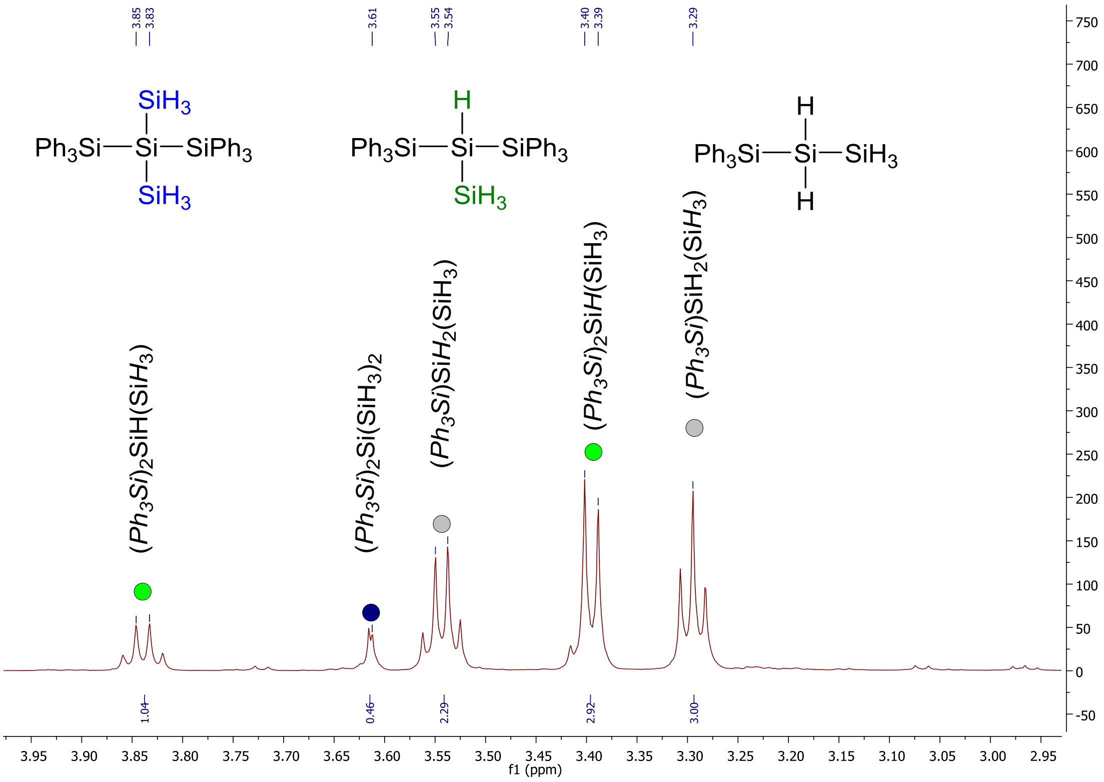
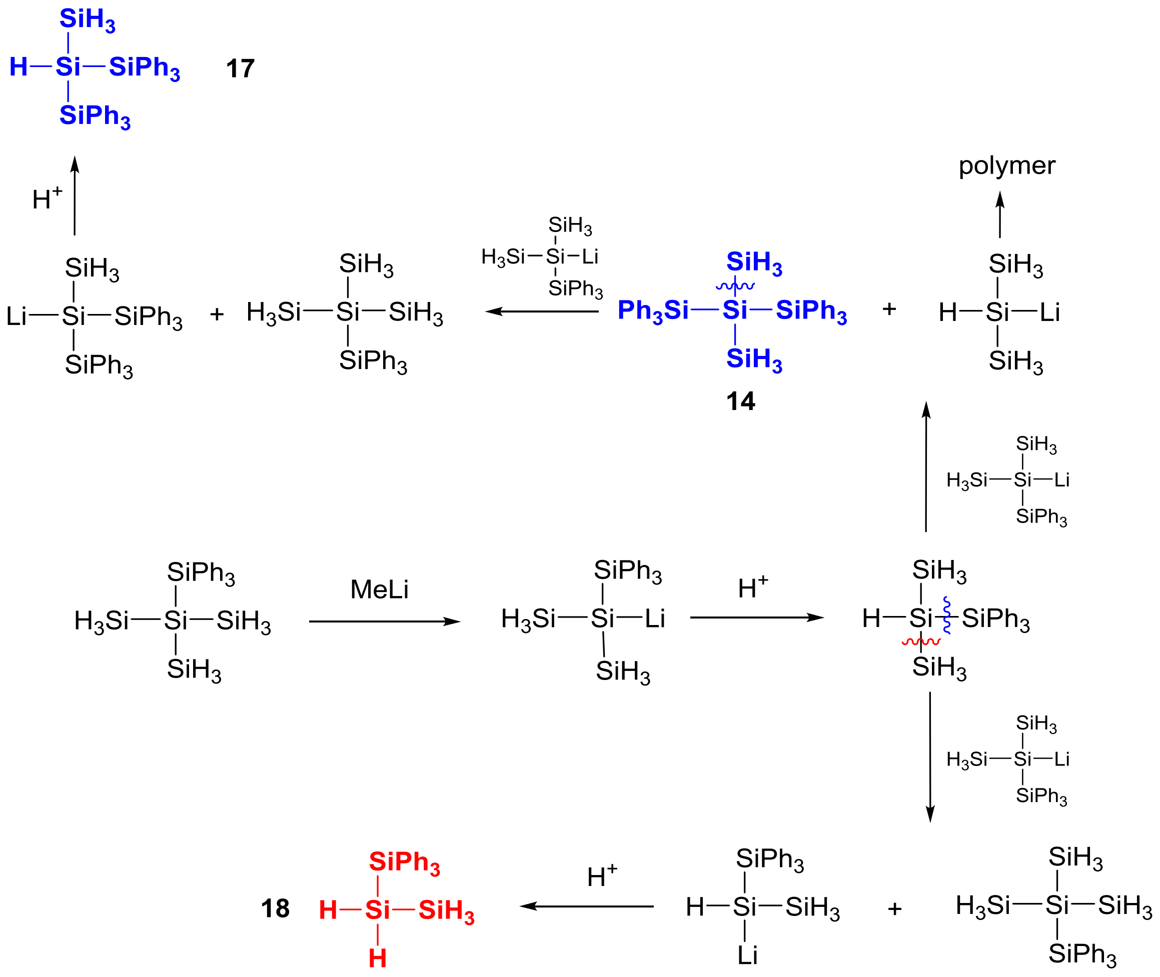


Figure 24 ^{1}H-NMR spectrum of the product mixture obtained after addition of an ether solution of the isotetrasilanide 15 to $PhSO_3H$

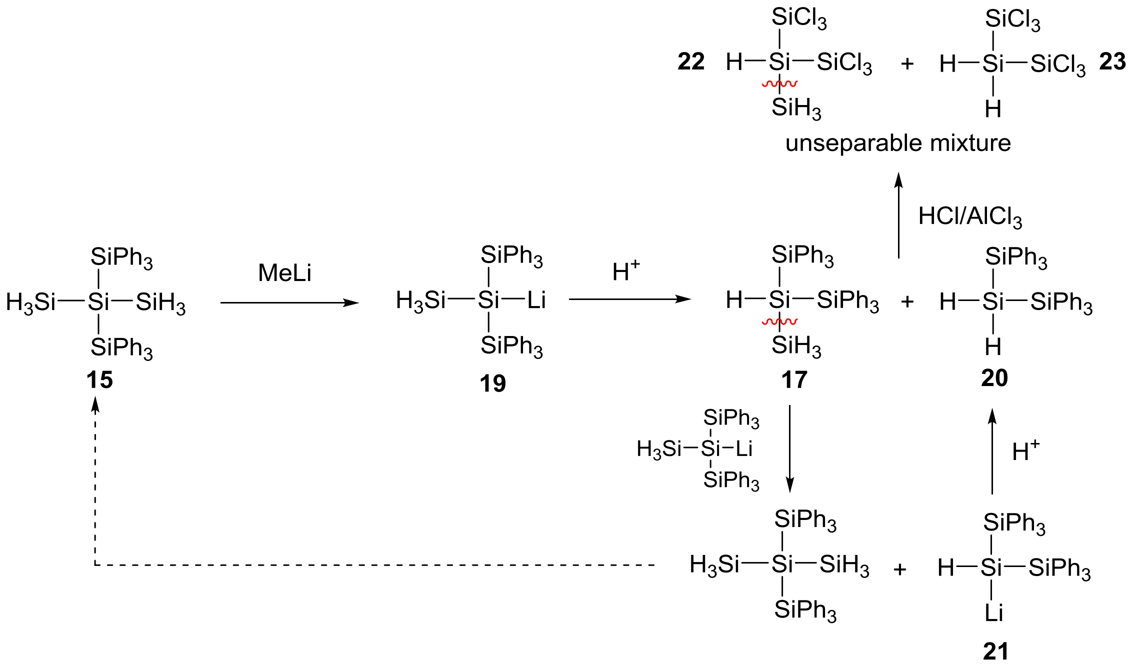
Scheme 5 displays a proposed reaction mechanism responsible for the formation of **14**, **17** and **18**.



Scheme 5. Proposed reaction mechanism for the formation of 15, 17 and 18

3.3.3 Attempted Synthesis of Chloroisotetrasilane 23

Using a closely related reaction sequence as described in the preceding section we also attempted to synthesize the hexachloroisotetrasilane **23** (Scheme 6).



Scheme 6: Route for the attempted synthesis of compound 23 by chlorodephenylation

Addition of an ether solution of the silanide **19** to $PhSO_3H$ dissolved in diethyl ether, however, afforded an inseparable mixture of the isotetrasilane **17** with the hexaphenyltrisilane **20** in an approximate ratio of 2 : 3 (estimated by integration of the ^1H-NMR resonances) making the preparation of pure **22** by subsequent chlorodephenylation impossible. The ^1H-NMR spectrum of the resulting mixture (Figure 25) showed a doublet (δ^1H = 3.39 ppm, SiH_3) and a quartet (δ^1H = 3.84 ppm, SiH) for **17** and a singulet at 4.0 ppm for **20**. Apparently the target compound **17**, once formed, partly reacts with excess of the silanide **19** by scission of the Si-SiH_3 bond to hexaphenylneopentasilane **15** and the silanide **21**. Subsequent reaction of **21** with H^+ finally affords the trisilane by-product **20**.

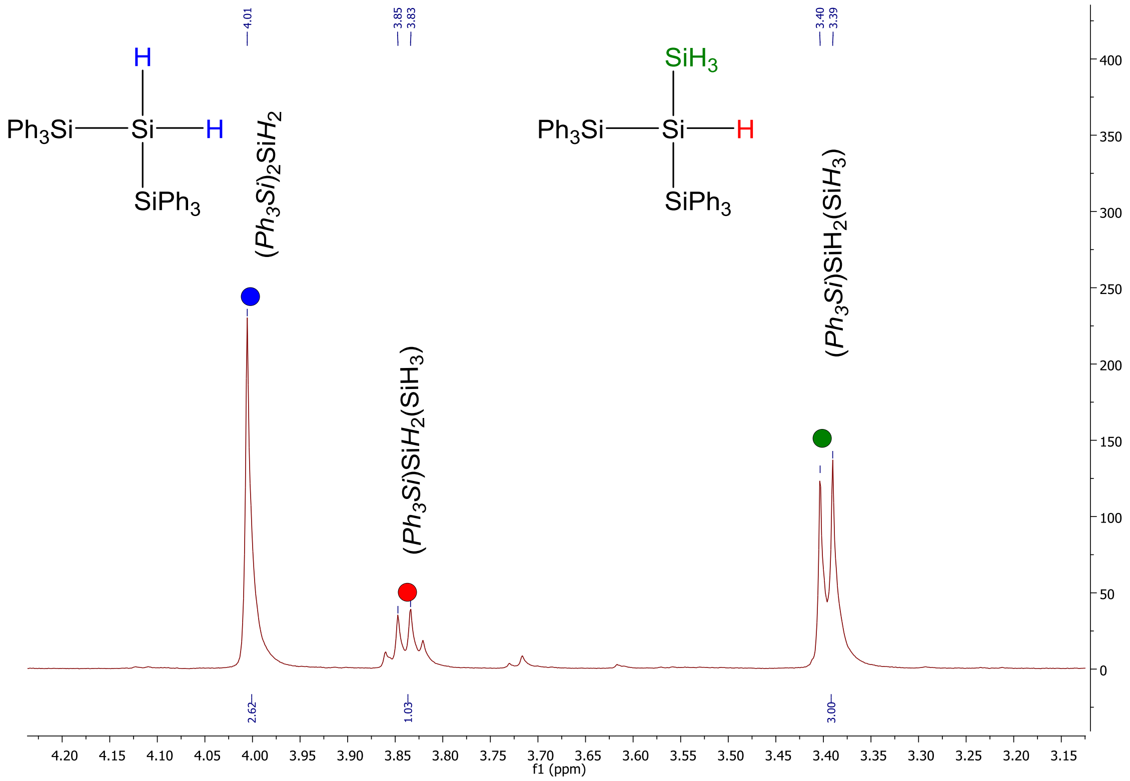


Figure 25 ^{1}**H-NMR spectrum of the product mixture obtained after addition of an ether solution of the isotetrasilanide 19 to** $PhSO_3H$

4 Summary and Conclusion

The primary objective of this master thesis was the synthesis of partially chlorinated hydrosilanes using different approaches. The most promising results were obtained for the partial hydrogenation of oligochlorosilanes with sub-stoichiometric amounts of *i*$BuAl_2H$, which was performed successfully with different educts. In all cases a strong preference for the formation of products with intact $SiCl_3$-groups was observed. Starting from dodecachloroneopentasilane, thus, the trichlorosilylsilanes $Cl_3SiSi(SiH_3)_3$ (**1**) and $(Cl_3Si)_2Si(SiH_3)_2$ (**2**) could be synthesized with remarkable selectivity and isolated in reasonable purity. Related transformations involving Si_2Cl_6, Si_3Cl_8 or $HSi(SiCl_3)_3$ also primarily gave the corresponding trichlorosilylsilanes.

The chlorination of neopentasilane and isotetrasilane with HCl /$AlCl_3$ or $SnCl_4$, on the contrary, afforded Cl/H-silanes with different substitution patterns. In both cases the ClH_2Si-silanes $Si(SiH_2Cl)_4$ (**10**) and $HSi(SiH_2Cl)_3$ (**12**), respectively, were obtained as the primary products.

In conclusion, although the target compounds could not be separated completely from minor amounts of by-products in all cases, the outcome of this work enables the targeted synthesis of various Cl/H-oligosilanes in particular with branched structures in reasonable purity. Additional studies will be necessary to show whether or not those previously unaccessible materials exhibit potential as precursors for CVD processes with improved performance.

5 Experimental Part

5.1 Working Technique

Due to the sensitivity of starting materials and products all experiments were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system[127]. NPS, DCNPS, HCDS and OCTS were kindly provided by Evonik Industries AG. Commercially available chemicals were used unless otherwise noted.

5.2 Analytical methods

^{1}H (299.95 MHz) and ^{29}Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer in C_6D_6 or with a D_2O capillary as an internal lock and referenced versus TMS using the internal ^{2}H-lock signal of the solvent. Mass spectra were run either on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 µm poly(dimethylsiloxane)). Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR Spectrometer from the solid sample. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus.

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[127] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, *15*, 1518

5.3 Syntheses

5.3.1 Starting Materials

5.3.1.1. 1,1,1,3,3,3-Hexachloro-2-(trichlorosilyl)trisilane (4)

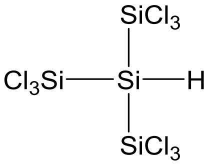

Table 1 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
70 g	$Si(SiCl_3)_4$	142.22 g/mol	124 mmol	1

70 g (0.124 mmol) of $Si(SiCl_3)_4$ were dissolved in 50 mL of diethylether and cooled to 0°C. 1.5 molar equivalents of a solution of 2.5 M HCl in ether were added within 10 minutes. Subsequently the reaction solution was allowed to warm to room temperature and then the solvent was stripped off in vacuum. The compound was purified by distillation. Silicon tetrachloride was removed from the yellow to orange mixture at atmospheric pressure without allowing pot temperature to exceed 80°C. Subsequent distillation at 60-65°C (0.01 mBar) afforded 37.5 g (70 %) of pure **4**. Analytical data are consistent with literature[128].

^{29}Si-NMR: -79.9 ppm (d, H*Si*($SiCl_3$)$_3$, ^{1}JSi-H = 214 Hz)

-4.5 ppm (s, *Si*Cl_3)

^{1}H-NMR: 3.74 (s, 1H, *H*Si($SiCl_3$))

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[128] H. C. Marsmann, W. Raml, E. Hengge, *Z. Naturforsch*. 1980, 35b, 1541.

5.3.1.2 iso-Tetrasilane (6)

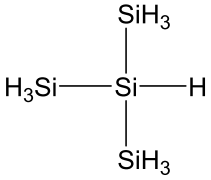


Table 2 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
74 ml	$i\mathrm{Bu_2AlH}$	142.22 g/mol	374.6 mmol	9
18 g	$\mathrm{HSi(SiCl_3)_3}$	432.4 g/mol	41.6 mmol	1

74 ml (374.6 mmol) of $i\mathrm{Bu_2AlH}$ was slowly added to 18 g (41.6 mmol) of $\mathrm{HSi(SiCl_3)_3}$ at 0°C. During this addition the suspension became a clear solution. The resulting mixture was allowed to warm to room temperature and stirred overnight. Recondensation of the mixture at room temperature and 0.01 mbar afforded 3 g (59%) of **6** as a colourless liquid. Analytical data are consistent with literature**Fehler! Textmarke nicht definiert.**.

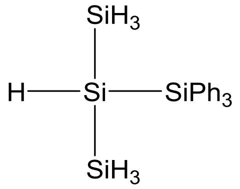
^{29}Si-NMR: -136.8 ppm (dm, $\mathit{Si}(\mathrm{SiH_3})_2$,)

-94.7 ppm (q, $\mathit{Si}\mathrm{H_3}$)

^{1}H-NMR: 2.69 (m, 1H, SiH)

3.33 (d, 9H, SiH_3)

5.3.1.3 Attempted Synthesis of 1,1,1-Triphenyl-2-silyltrisilane (16)



Method A:

Table 3 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
0.5 g	$Ph_3SiSi(SiH_3)_3$	380.82 g/mol	1.8 mmol	1
0.8 ml	Methyllithium (MeLi)	1.6 mol/l	1.8 mmol	1
0.5 ml	$HCl_{eth.}$	4.2 mol/l	2.1 mmol	1.6

1 eq. of a 1.6 M solution of MeLi (0.8 ml) in Et_2O were slowly added to a solution of 0.5 g of $Ph_3SiSi(SiH_3)_3$ in 20 ml of diethyl ether at -30°C. The resulting mixture was allowed to warm to room temperature and stirred for an hour. Afterwards the solution was slowly added via a syringe to a solution of 0.5 ml HCl_{eth} (4.2 mol/l) in 15 ml of diethyl ether at 0°C. After stirring for 30 min the solvent was evaporated in vacuo and 30 ml of pentane were added and the salts were filtered off. The pentane was evaporated in vacuo and the product was obtained as a white solid. ^{1}H- and ^{29}Si-NMR analysis of the product showed the predominate formation of 2,2-bistriphenylsilyltrisilane **14**[126].

Method B:

Table 4 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
0.5 g	$Ph_3SiSi(SiH_3)_3$	380.82 g/mol	1.8 mmol	1
0.8 ml	Methyllithium (MeLi)	1.6 mol/l	1.8 mmol	1
10 ml	H_2SO_4 10%			

1 eq. of MeLi (0.8 ml, 1.6mol/l solution in Et_2O) were slowly added to a solution of 0.5 g of $Ph_3SiSi(SiH_3)_3$ in 20 ml of diethyl ether at -30°C. The resulting mixture was allowed to warm to room temperature and stirred for an hour. Afterwards the solution was slowly added via a syringe to a mixture of 10 ml of degassed H_2SO_4 (10%) with 20 ml of toluene at 0°C. After phase separation, two-fold washing of the aqueous phase with 10 ml of toluene, drying of the combined organic layers with Na_2SO_4 and evaporation of the solvents in vacuo a white solid remained. ^1H- and ^{29}Si-NMR analysis of the product showed the predominate formation of 2,2-bistriphenylsilyltrisilane **14**[126].

Method C:

Table 5 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$Ph_3SiSi(SiH_3)_3$	380.82 g/mol	2.6 mmol	1
1.6 ml	Methyllithium (MeLi)	1.6 mol/l	2.6 mmol	1
0.41 g	$PhSO_3H$	158.18 g/mol	2.6 mmol	1

1 eq. of MeLi (1.6 ml, 1.6mol/l solution in Et_2O) were slowly added to a solution of 1 g of $Ph_3SiSi(SiH_3)_3$ in 20 ml of diethyl ether at -30°C. The resulting mixture was allowed to warm to room temperature and stirred for an hour. Afterwards a solution of 0.41 g of $PhSO_3H$ (2.6 mmol) in 15 ml of diethyl ether and 10 ml of toluene were slowly added via a syringe at -20°C. The resulting mixture was allowed to warm to room temperature

and stirred for an hour. Now the solvent was evaporated in vacuo and 30 ml of toluene were added and the salts were filtered off. The toluene was evaporated in vacuo and a white solid remained. ^{1}H- and ^{29}Si-NMR analysis of the product showed the predominate formation of 2,2-bistriphenylsilyltrisilane **14**[126]

Method D:

Table 6 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1.3 g	$Ph_3SiSi(SiH_3)_3$	380.82 g/mol	3.41 mmol	1
2.1 ml	Methyllithium (MeLi)	1.6 mol/l	3.41 mmol	1
0.54 g	$PhSO_3H$	158.18 g/mol	3.41 mmol	1

1 eq. of MeLi (2.1 ml, 1.6mol/l solution in Et_2O) were slowly added to a solution of 1.3 g of $Ph_3SiSi(SiH_3)_3$ in 20 ml of diethyl ether at -30°C. The resulting mixture was allowed to warm to room temperature and stirred for an hour. Afterwards the solution was slowly added via a syringe to a solution of 0.54 g $PhSO_3H$ in 30 ml diethyl ether at -30°C. After stirring for 30 min the solvent was evaporated in vacuo and 30 ml of toluene were added and the salts were filtered off. The toluene was evaporated in vacuo and the product was obtained as a white solid. ^{1}H- and ^{29}Si-NMR analysis of the product showed the formation of a mixture of 2,2-bistriphenylsilyltrisilane **14**, 1,1,1,3,3,3-hexaphenyl-2-silyltrisilane **17** and 1,1,1-triphenyltrisilane **18** in an approximate ratio of 4% :48% :48% , which could not be separated by crystallization.

17: ^{1}H-NMR: 3.39 (d, 3H, SiH_3)

3.33 (q, 1H, SiH)

18:

^{1}H-NMR: 3.29 (d, 3H, SiH_3)

3.54 (q, 2H, SiH_2)

5.3.1.4 Attempted Synthesis of 1,1,1,3,3,3-Hexaphenyl-2-silyltrisilane (17)

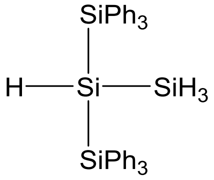


Table 7 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1.5 g	$(Ph_3Si)_2Si(SiH_3)_2$	609.11 g/mol	2.5 mmol	1
1.55 ml	Methyllithium (MeLi)	1.6 mol/l	2.5 mmol	1
0.4 g	Benzenesulfonic acid	158.18 g/mol	2.5 mmol	1

1 eq. of MeLi (1.55 ml, 1.6mol/l in Et_2O) were slowly added to a solution of 1.5 g 2,2-$(Ph_3Si)_2Si(SiH_3)_2$ in 20 ml of diethyl ether at -30°C. The resulting mixture was allowed to warm to room temperature and stirred for an hour. Afterwards the solution was slowly added via a syringe to a solution of 0.4 g benzenesulfonic acid in 30 ml diethyl etherat -30°C. After stirring for 30 min the solvent was evaporated in vacuo and 30 ml toluene were added and the salts were filtered off. The toluene was evaporated in vacuo and the product was obtained as white solid. ^{1}H- and ^{29}Si-NMR analysis of the product showed the formation of a mixture of 1,1,1,3,3,3-hexaphenyl-2-silyltrisilane **17** and 1,1,1,3,3,3-hexaphenyltrisilane **20** in an approximate ratio of 2 : 3 which could not be separated by crystallization.

17:

^{1}H-NMR: 3.39 (d, 3H, Si*H₃*)

3.33 (q, 1H, Si*H*)

20:

^{1}H-NMR: 4.01 (s, 2H, Si*H₂*)

5.3.2 Cl/H Oligosilanes

5.3.2.1 1,1,1-Trichloroneopentasilane (1) from $Si(SiCl_3)_4$

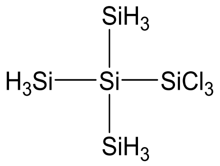


Table 8 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
204 ml	*i*Bu_2AlH	142.22 g/mol	1145 mmol	9
72 g	$Si(SiCl_3)_4$	565.83 g/mol	127 mmol	1

204 ml (1145mmol) of *i*Bu_2AlH were slowly added to 72 g (127 mmol) of $Si(SiCl_3)_4$ at 0 °C. During this addition the suspension became a clear solution. The resulting mixture was allowed to warm to room temperature and stirred overnight. The by-product neopentasilane was evaporated at room temperature and 0.01 mbar. Fractional recondensation of the remaining mixture at 50 °C and 0.01 mbar afforded 7.2 g (38%) of **1** as a colourless oil. Small amount of other hydrosilane species were also detected in the final product.

5.3.2.2 1,1,1-Trichloroneopentasilane (1) from $Ph_3SiSi(SiCl_3)_3$

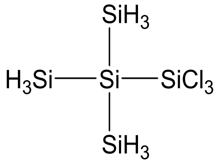


Table 9 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$Ph_3SiSi(SiH_3)_3$	380.82 g/mol	2.63 mmol	1

1.00 g (2.63 mmol) of $Ph_3SiSi(SiH_3)_3$ were dissolved in 15 ml of benzene and a catalytic amount of $AlCl_3$ was added. The reaction solution was cooled to 0°C and subsequently anhydrous gaseous HCl was bubbled through the reaction solution. The start of the reaction is marked by a colour change from colourless to yellow. After a reaction time of 15 min the solvent and the products were evaporated from the catalyst in vacuo at 40 °C. After removal of the benzene at 90°C (1013 mbar) fractional recondensation of the remaining colourless liquid at 50 °C and 0.05 mbar afforded 0.23 g (42%) of pure **1** as a colourless oil.

^{29}Si-NMR: -127.9 ppm (m, ^{2}JSi-H = 5.7 Hz, *Si*(SiH$_3$)$_{3)}$

-93.1 ppm (q, ^{1}JSi-H = 208.6 Hz, ^{3}JSi-H = 2.9 Hz, *Si*H$_3$)

20.2 ppm (m, SiCl$_3$)

^{1}H-NMR: 3.32 (s, 9H, Si*H*$_3$)

IR : ν(Si-H) = 2145 (s) cm^{-1}

MS ($Cl_3H_9Si_5$, M^{+}): 254.8 (found)

255.85 (calc)

Analysis ($Cl_3H_9Si_5$) calc. H: 3.60 %

found: 3.55 %

5.3.2.3 2,2-Bistrichlorosilyltrisilane (2) from $Si(SiCl_3)_4$

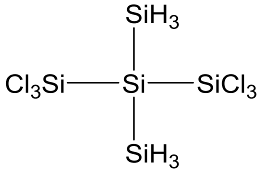


Table 10 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
136 ml	*i*Bu_2AlH	142.22 g/mol	1145 mmol	6
72 g	$Si(SiCl_3)_4$	565.83 g/mol	127 mmol	1

204 ml (1145mmol) of *i*Bu_2AlH were slowly added to 72 g (127 mmol) of $Si(SiCl_3)_4$ at 0°C. During this addition the suspension became a clear solution. The resulting mixture was allowed to warm to room temperature and stirred overnight. The volatile side products were removed by distillation at 50 °C and 0.01 mbar. Distillation of the remaining residue at 90°C and 0.01 mbar afforded 8.2 g (25%) of **2** as a colourless liquid. Small amounts of hydrosilane impurities were detected in the final product by NMR-spectroscopy.

5.3.2.4 2,2-Bistrichlorosilyltrisilane (2) from $Ph_3SiSi(SiCl_3)_3$

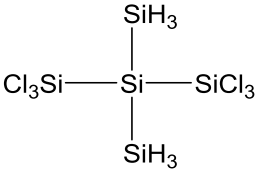


Table 11 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$(Ph_3Si)_2Si(SiH_3)_2$	609.11 g/mol	1.64 mmol	1

1.00 g (1.64 mmol) of $(Ph_3Si)_2Si(SiH_3)_2$ were dissolved in 15 ml of benzene and a catalytic amount of $AlCl_3$ was added. The reaction solution was cooled to 0°C and subsequently anhydrous gaseous HCl was bubbled through the reaction solution. The start of the reaction is marked by a colour change from colourless to yellow. After a reaction time of 15 min the solvent was evaporated in vacuo. Now 15 ml of pentane were added and the precipitated $AlCl_3$ was filtered off. Pentane was evaporated at room temperature in vacuo and 0.23 g (39%) of pure **2** were obtained as a colourless wax-like solid.

^{29}Si-NMR: -101.3 ppm (m, *Si*$(SiH_3)_3$)

-95.9 ppm (q, ^{1}JSi-H = 215.8 Hz, ^{3}JSi-H = 3.6 Hz, *Si*H_3)

13.9 ppm (m, $SiCl_3$)

^{1}H-NMR: 3.34 (s, 6H, SiH_3)

IR : ν(Si-H) = 2139 (s) cm^{-1}

Analysis ($Cl_6H_6Si_5$) calc. H: 1.68 %

found: 1.71 %

5.3.2.5 2-Trichlorosilyltrisilane (5) from $HSi(SiCl_3)_3$

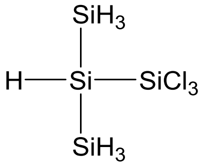


Table 12 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
42 ml	$i\mathrm{Bu_2AlH}$	142.22 g/mol	222 mmol	6
16 g	$HSi(SiCl_3)_3$	432.4 g/mol	37 mmol	1

42 ml (222 mmol) of $i\mathrm{Bu_2AlH}$ was slowly added to 16 g (37 mmol) of $HSi(SiCl_3)_3$ at 0°C. During this addition the suspension became a clear solution. The resulting mixture was allowed to warm to room temperature and stirred overnight. The volatile side product including $HSi(SiH_3)_3$ were removed in vacuo at room temperature and 0.01 mbar. Recondensation of the remaining mixture at 50 °C and 0.01 mbar afforded 3.2 g (38%) of a colourless liquid. NMR analysis showed that the final product contained compound **5** along with ~ 25% of other Cl/H silanes which could not be removed by further distillation.

^{29}Si-NMR: -106.0 ppm (dm, *Si*$(SiH_3)_2$, $^2J_{Si-H}$ = 5.7 Hz)

-97.7 ppm (q, $^1J_{Si-H}$ = 209 Hz, $^3J_{Si-H}$ = 2.1 Hz, *Si*H_3)

^{1}H-NMR: 3.24 (d, 6H, SiH_3)

3.05 (m, 1H, Si*H*)

5.3.2.6 Partial Hydrogenation of Si_2Cl_6

Table 13 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
19.8 ml	*i*Bu_2AlH	142.22 g/mol	112 mmol	3
10 g	Si_2Cl_6	268.87 g/mol	37 mmol	1

19.8 ml (112 mmol) of *i*Bu_2AlH were slowly added to 10 g (37 mmol) of Si_2Cl_6 at 0°C. The resulting mixture was allowed to warm to room temperature and stirred overnight. Now the volatile components were separated by recondensation at room temperature and 0.01 mbar to give 4.5 g of a clear and colourless liquid. NMR analysis of the volatile fraction showed the formation of $H_3SiSiCl_3$ **8**, $H_2ClSiSiCl$ **9** and H_3SiSiH_3 as the major products in a ratio of approximately 55 % : 40 % : 5 % (estimated by integration of the ^{1}H-NMR signals) along with small amounts of other Cl/H-disilanes (compare Table 14). Fractional recondensation of the obtained mixture brought no further improvement.

Table 14. NMR lines identified in the reaction mixture

$H_3SiSiCl_3$	^{1}H-NMR:	3.2 ppm ($\mathit{H}_3SiSiCl_3$)
	^{29}Si-NMR:	-84.8 ppm ($H_3\mathit{Si}SiCl_3$); 12.9 ppm ($H_3Si\mathit{Si}Cl_3$)
H_3SiSiH_3	^{1}H-NMR	3.10 (H_3SiSiH_3); ^{29}Si-NMR: -101.5 ppm ($H_3\mathit{SiSi}H_3$)
$H_2ClSiSiCl_3$	^{1}H-NMR	4.28 ppm ($\mathit{H}_2ClSiSiCl_3$)
	^{29}Si-NMR:	4.0 ppm ($H_2Cl\mathit{Si}SiCl_3$)
$H_2ClSiSiH_3$	^{29}Si-NMR:	-89.2 ppm ($H_2ClSi\mathit{Si}H_3$)
$Cl_3SiSiCl_3$	^{29}Si-NMR:	-6.5ppm ($Cl_3\mathit{SiSi}Cl_3$)

5.3.2.7 Partial Hydrogenation of Si_3Cl_8

Table 15 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
24.5 ml	$i\mathrm{Bu_2AlH}$	142.22 g/mol	135 mmol	5
10 g	Si_3Cl_8	367.86 g/mol	27 mmol	1

24.5 ml (135 mmol) of $i\mathrm{Bu_2AlH}$ was slowly added to 10 g (27 mmol) of Si_3Cl_8 at 0°C. The resulting mixture was allowed to warm to room temperature and stirred overnight. Now the volatile components were separated by recondensation at room temperature and 0.01 mbar to give 2.4 g of a clear and colourless liquid. NMR analysis of the volatile fraction showed the formation of $H_3SiSiH_2SiCl_3$ **7** and Si_3H_8 as the main products. GC/MS analysis additionally showed the presence of 1,1-dichlorotrisilane, 2,2-dichlorotrisilane, monochlorotrisilane, and smaller amounts of other Cl/H-silanes of unidentified structure in the reaction mixture. Fractional recondensation brought no further improvement.

Table 16. NMR lines identified in the reaction mixture

$H_3SiSiH_2SiCl_3$	^{1}H-NMR: 3.75 ppm (H_3SiSiH$_2$SiCl$_3$); 3.92 ppm (H$_3$SiSiH_2SiCl$_3$) ^{29}Si-NMR: -99.8 ppm (H$_3$$SiSiH_2$SiCl$_3$); 15.9 ppm (H$_3$SiSiH$_2$$SiCl_3$)
$H_3SiSiH_2SiH_3$	^{1}H-NMR 3.45 ppm (SiH_2(SiH$_3$)$_2$); 3.64 ppm (SiH$_2$(SiH_3)$_2$); ^{29}Si-NMR: -115.3 ppm (SiH$_2$(SiH$_3$)$_2$); -97.2 ppm (SiH$_2$(SiH$_3$)$_2$)

5.3.2.8 Partial Chlorination of $Si(SiH_3)_4$ with $HCl/AlCl_3$

Table 17 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$Si(SiH_3)_4$	152.52 g/mol	6.55 mmol	1

1.00 g (6.55 mmol) of $Si(SiH_3)_4$ were dissolved in 15 ml of benzene and a catalytic amount of $AlCl_3$ was added. The reaction solution was heated to 70°C and subsequently anhydrous gaseous HCl was bubbled through for 15 min. After evaporation of the solvent in vacuo 15 ml of pentane were added and the precipitated $AlCl_3$ was filtered off. Pentane was evaporated at room temperature in vacuo and 1.2 g (63%) of $Si(SiH_2Cl)_4$ **10** were obtained as a colourless liquid containing about 7 % of $(H_2ClSi)_3SiSiH_3$ **11**. NMR data of **10** are consistent with literature values[77]. If toluene was used as a solvent instead of benzene only an undefined mixture of several Cl/H-silanes was obtained.

$(SiH_2Cl)_4Si$ (**10**):

^{1}H-NMR: 4.87 ppm $(Si\mathit{H}_2Cl)_4Si)$

^{29}Si-NMR: -24.58 ppm $((\mathit{Si}H_2Cl)_4Si)$

$(SiH_2Cl)_3Si(SiH_3)$ (**11**):

^{1}H-NMR 4.86 ppm $((Si\mathit{H}_2Cl)_3Si(SiH_3))$

3.37 ppm $((SiH_2Cl)_3Si(Si\mathit{H}_3))$

^{29}Si-NMR: -25.7 ppm $((\mathit{Si}H_2Cl)_3Si(SiH_3))$

-98.5 ppm$((SiH_2Cl)_3Si(\mathit{Si}H_3))$

5.3.2.9 Partial Chlorination of $HSi(SiH)_3$ with HCl

Table 18 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$HSi(SiH)_3$	122.42 g/mol	8.19 mmol	1

1.00 g (8.19 mmol) of $HSi(SiH)_3$ were dissolved in 15 ml of benzene and a catalytic amount of $AlCl_3$ was added. The reaction solution was heated to 70°C and subsequently anhydrous gaseous HCl was bubbled through for 15 min. Now the solvent and the products were evaporated from the salts in vacuo. After removal of the benzene at 90°C (1013 mbar) distillation of the remaining colourless liquid at room temperature and 0.01 mbar afforded 0.8 g of a colourless oily liquid containing $HSi(SiH_2Cl)_3$ **12** as the major product along with minor amounts of partially chlorinated isotetrasilane species as shown by NMR analysis. Attempts to isolate pure $HSi(SiH_2Cl)_3$ by distillation or crystallization were not successful.

5.3.2.10 Partial Chlorination of $HSi(SiH)_3$ with $SnCl_4$

Table 19 Quantity of reagents used for synthesis

Quantity	Reagent	Molar mass/molarity	Mole	Equiv.
1 g	$HSi(SiH)_3$	122.42 g/mol	8.19 mmol	1
5.58 g	$SnCl_4$	260.5 g/mol	21.42	2.6

3.19 g (12.24 mmol) of $SnCl_4$ were added via a syringe to a solution of 1 g (8.19 mmol) of $HSi(SiH)_3$ in 30 ml of pentane at 0°C. After stirring overnight another 2.39 g (9.18 mmol) of $SnCl_4$ were added. The mixture was stirred for another 48 h. Subsequent filtration and concentration in vacuo afforded 0.9 g of a colourless oily liquid containing $HSi(SiH_2Cl)_3$ **12** as the major product along with minor amounts of partially chlorinated isotetrasilane species as shown by NMR analysis. Attempts to isolate pure $HSi(SiH_2Cl)_3$ by distillation or crystallization were not successful

$(SiH_2Cl)_3SiH$ (**12**):

^{1}H-NMR: 4.87 ppm (d, $(Si\mathit{H}_2Cl)_3SiH$)

2.97 ppm (m, $(SiH_2Cl)_3Si\mathit{H}$)

^{29}Si-NMR: -26.32 ppm ($(\mathit{Si}H_2Cl)_4Si$)

-109.63 ppm ($(SiH_2Cl)_3\mathit{Si}H$)