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Methylchlorooligosilanes as products of the basecatalysed disproportionation of various methylchlorodisilanes

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Abstract

The methylchlorodisilanes $SiCl_2Me$-$SiCl_2Me$ (**1**), $SiCl_2Me$-$SiClMe_2$ (**2**) and $SiClMe_2$-$SiClMe_2$ (**3**) disproportionate in the presence of a basic catalyst into methylchloromonosilanes and various methylchlorooligosilanes. Oligosilanes involving up to seven silicon atoms were identified by means of ^{29}Si-, ^{13}C- ^{1}H-NMR and GC-MS measurements. Formation of methylchlorooligosilanes is thought to take place via silylene intermediates.

Keywords: Silicon; Disilanes; Methylchlorooligosilanes; Oligosilane; Base catalysis; Disproportionation

1. Introduction

The disproportionation of methylchlorodisilanes is the focus of attention for certain technical applications. It offers the possibility to convert the methylchlorodisilanes of the 'disilane fraction' of the Müller Rochow process into monosilanes and polysilanes, avoiding alkaline metal condensation. The methylchlorooligosilanes and polysilanes formed are reactive polymers owing to the remaining Si–Cl functions of these compounds and can further be converted into silicon carbide. It is known [1] that hexachlorodisilane easily disproportionates in presence of amines:

$$4Si_2Cl_6 \longrightarrow 3SiCl_4 + Si(SiCl_3)_4 \text{ and}$$
$$5Si_2Cl_6 \longrightarrow 4SiCl_4 + Si_2Cl_5\text{-}Si(SiCl_3)_3 \quad (1)$$

Only branched oligosilanes are obtained in this reaction. Trandell and Urry [2] have also investigated the disproportionation of Si_2Cl_5Me and **1** using Me_3N as a catalyst. These branched oligosilanes $SiCl_2Me$-$Si(SiCl_3)_3$ and $SiMe(SiCl_2Me)_3$, respectively, could be isolated from the product mixture. The disproportionation of **1** required a reaction time of 17 days at 65 °C whereas Si_2Cl_6 and Si_2Cl_5Me were converted within a few hours at room temperature. **3** did not react under any conditions.

Baney et al. [3] prepared polymers from the components of the 'disilane fraction' $SiCl_2Me$-$SiCl_2Me$ and $SiCl_2Me$-$SiClMe_2$, respectively, adding small amounts of tetrabutylphosphoniumchloride. Based on the chemical analysis, a crude picture of the polymer structure was given which was characterized by a highly branched silicon atom framework. Elucidating investigations which deliver information about the nature of the prepolymer intermediates are missing until now.

2. Results and discussion

In order to find out the mechanism of the disproportionation reaction and to test preparative applications we investigated the disproportionation reaction of **1**, **2** and **3**. The procedure with the disilane **1** was carried out under 'homogeneous' as well as 'heterogeneous' conditions. 'Homogeneous' means that the catalyst is added to the disilane, forming a homogeneous reaction mixture, whereas in the 'heterogeneous' case we used a catalyst with bis-(dimethylamido)-phosphoric acid

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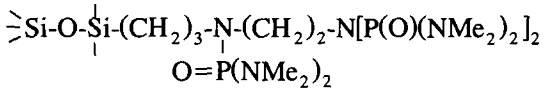
groups grafted onto the surface of a silicate carrier [4–6]:



$$\geqslant\mathrm{Si{-}O{-}\overset{|}{\underset{|}{Si}}{-}(CH_2)_3{-}\underset{\underset{O=P(NMe_2)_2}{|}}{N}{-}(CH_2)_2{-}N[P(O)(NMe_2)_2]_2} \qquad (2)$$

Using this procedure it was possible to obtain oligosilanes as well as polysilanes free of the catalyst. This is important for their further polymer conversion into silicon carbide fibers for instance [7,8]. Those polymers which contain the stored catalyst undergo random crosslinking reactions when the polymer is heated again.

Our previous studies checking various Lewis-base compounds have shown that 1-methylimidazole (**4**) is a very effective catalyst [9]. Therefore we used **4** for all 'homogeneous' experiments.

2.1. Disproportionation of $SiCl_2MeSiCl_2Me$ (1)

In Fig. 1 a typical ^{29}Si-NMR spectrum of the oligosilane mixture, which was obtained by the heterogeneous disproportionation is shown. As described earlier [10] it was possible to assign the resonances to certain oligosilanes, comparing the signal intensities between different samples and using the $^1J_{SiSi}$ coupling constants and the intensities of the ^{29}Si satellites (see Table 1). GC-MS investigations (see Table 2) confirm the obtained results. Since any absorption bands in the 1000–1100 cm^{-1} region of the registrated IR spectra of the oligosilane mixtures are not observed, a formation of compounds with Si–CH$_2$–Si units at temperatures up to 200 °C should be neglected.

The following silanes could be identified:

5 $SiCl_2Me–SiClMe–SiCl_2Me$
6 $SiMe(SiCl_2Me)_3$
7 $(SiCl_2Me)_2SiMe–SiClMe–SiCl_2Me$
8 $[SiMe(SiCl_2Me)_2]_2$
9 $SiClMe[SiMe(SiCl_2Me)_2]_2$

Our homogeneous disproportionation experiments with **1** led to the same oligosilanes which were obtained using heterogeneous catalysis regime. There are only some differences in the relative product distribution. In both cases the only monosilane formed is $MeSiCl_3$. One point worth mentioning is that the catalyst **4** gives oligosilane mixtures very rich in **6**. On this new route the tetrasilane **6** and further derivatives are readily accessible. It should be noted too that the monosilane $MeSiCl_3$, together with the catalyst **4** (NMI) formes a white precipitate, having the composition $MeSiCl_3 \cdot 2NMI$. The ^{29}Si CP/MAS NMR spectrum of the substance shows a sharp line at −180 ppm (that means a shift of −193 ppm, compared to $MeSiCl_3$) which is characteristic for a sixfold (octahedral) coordinated silicon atom.

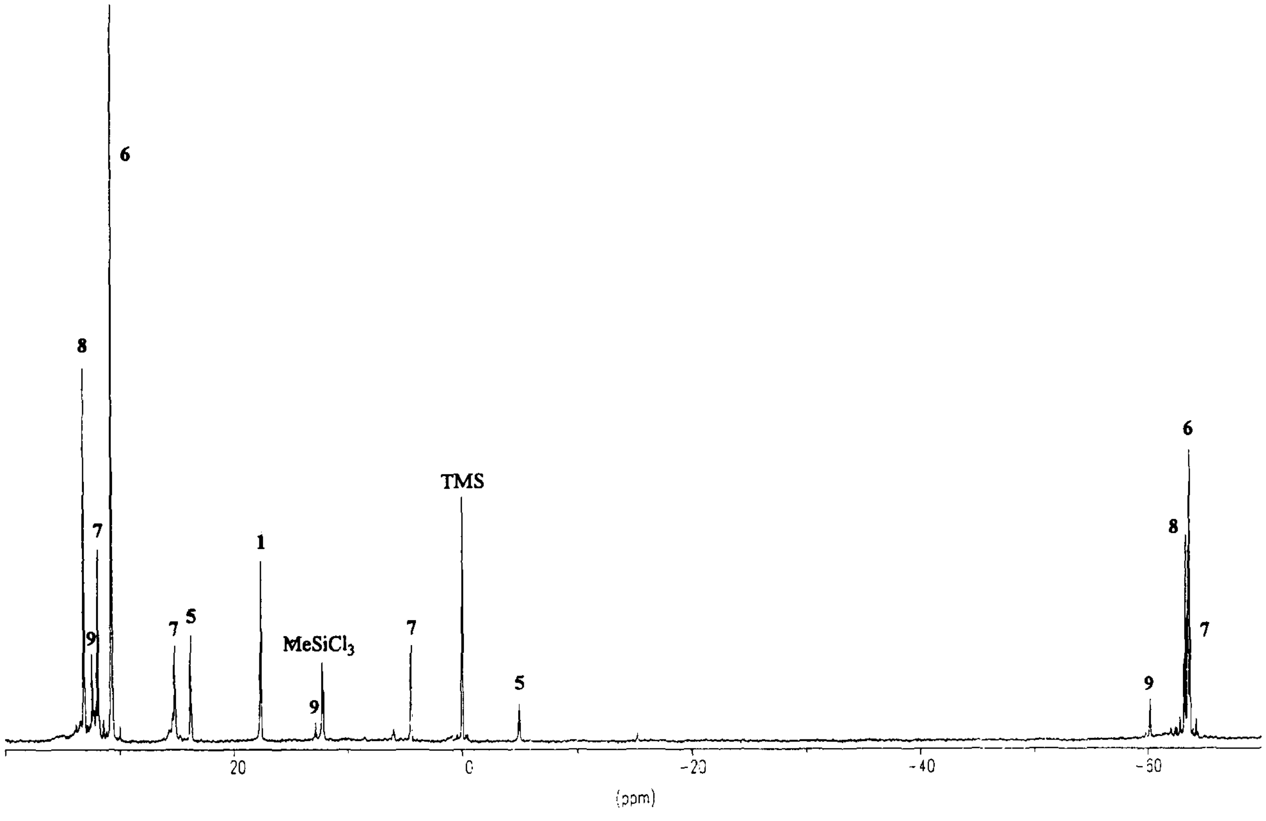
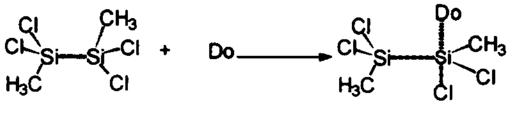


Fig. 1. ^{29}Si NMR spectrum of the oligosilane mixture obtained by heterogeneous disproportionation of **1**.

2.1.2. Reaction mechanism

In our opinion the first step of the heterogeneous, as well as the homogeneous catalytic disproportionation, should be an electron pair donor acceptor interaction of the catalyst with the disilane molecule, giving rise to the formation of a pentacoordinated transition state:



(2)

Such adducts of disilanes are instable in general. Only a few isolable adducts are known so far, for instance the Lewis-base adducts of Si_2Cl_6, **1** and **2** with 2.2′-bipyridyl and 1.10-phenanthroline, respectively [11].

As can be seen from the crystal structure analysis of **1** · bipy [12] one silicon atom is hexacoordinated, in contrast to the other silicon atom that remains tetracoordinated. To confirm this feature of the structure we recorded a ^{29}Si CP/MAS spectrum of the adduct. It exhibited two resonances at 13 and − 136 ppm, belonging to the fourfold and sixfold coordinated silicon, respectively.

Another important feature of the structure is the lengthening of the Si–Cl bonds at the hexacoordinated silicon atom and of the Si–Si bond too. Kummer and Köster [13] investigated the decomposition of the analogous base adduct of Si_2Cl_6. By increasing the temperature the adduct decomposes easily in the presence of excess bipy to $SiCl_4$ · bipy (colorless) and $SiCl_2$ · 2bipy (dark green). The last can be regarded as a basestabilized silylene.

Table 1

Compound	$\delta\ ^{29}Si$ (ppm)	$\delta\ ^{13}C$ (ppm)	$\delta\ ^{1}H$ (ppm)	$^{1}J_{SiSi}$ (Hz)	$^{1}J_{SiC}$ (Hz)
$(Cl_2MeSi^A)_2Si^BClMe$	A + 23.77	+ 6.5	+ 0.988	111.7	
	B − 4.93	− 2.7	+ 0.820		
$(Cl_2MeSi^A)_3Si^BMe$	A + 30.73	+ 9.01	+ 1.038	86.4	56.0
	B − 63.51	− 12.62	+ 0.575		40.1
$(Cl_2MeSi^A)_2Si^BMe$-Si^CClMe-Si^DCl_2Me	A 32.08	+ 9.44	+ 1.050	AB 84.02	
	B − 63.66	− 11.87	+ 0.623	BC 60.64	
	C + 4.45	+ 0.52	+ 0.845	CD 108.2	
	D + 25.22	+ 6.58	+ 0.993		
$[(Cl_2MeSi^A)_2Si^BMe]_2$	A + 33.14	+ 9.68	+ 1.084	83.23	54.9
	B − 63.22	− 10.04	+ 0.684		38.4
$[(Cl_2MeSi^A)_2Si^BMe$-$]_2$ Si^CClMe	A + 32.4	+ 9.62		AB 83.23	
	B − 60.25	− 10.98		BC 59.45	
	C + 12.8	+ 4.25			
Cl_2MeSi^A-Si^BMe_2Cl	A + 24.55	+ 5.65	+ 0.881	127.2	54.7
	B + 14.98	+ 0.72	+ 0.624		51.5
$(Cl_2MeSi^A)_2Si^BMe$-Si^CClMe_2	A + 33.63				
	B − 66.80				
	C + 23.90				
$(Cl_2MeSi^A)_2Si^BMe$-$Si^CMe(Si^DCl_2Me)$-(Si^EMe_2Cl)	A + 34.14/ + 34.22 [a]				
	B − 62.83				
	C − 68.22				
	D + 35.82				
	E + 26.23				
$(SiClMe_2)_2$	+ 17.15	+ 1.12	+ 0.531		49.4
$(ClMe_2Si^A$-$)_2Si^BMe_2$	A + 25.15		+ 0.520	82.1	47.0
	B − 43.66		+ 0.252		41.5
$(ClMe_2Si^A$-Si^BMe_2-$)_2$	A + 26.57		+ 0.498	78.7	46.4
	B − 42.60		+ 0.252		40.3
$(ClMe_2Si^A$-$Si^BMe_2)_2Si^CMe_2$	A + 26.76				
	B − 41.01				
	C − 41.59				
$ClMe_2Si^A$-Si^BMe_2-Si^CCl_2Me	A + 23.59				
	B − 39.17				
	C + 32.80				
$ClMe_2Si^A$-Si^BMe_2-$Si^CMe(Si^DCl_2Me)_2$	A + 25.62				
	B − 39.95				
	C − 65.59				
	D + 35.44				

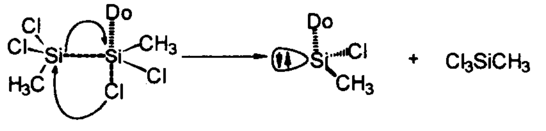
[a] Both Si^ACl_2Me groups are diastereotopic with different chemical shifts.

Table 2
Relative intensities of the obtained fragment ions

Ion [+]	Major peak m/e	**5**	**6**	**7**	**8**	**10**	**12**	**13**
$SiCH_3$	43	15	23	32	25	30	11	14
SiCl	63	36	45	33	22	32	11	11
$Si(CH_3)_3$	73	5	66	72	63	100	100	100
$SiCH_3Cl$	78	7	5	4		3	2	2
$Si(CH_3)_2Cl$	93	100	55	64	36	71	21	33
$SiCH_3Cl_2$	113	23	28	23	21			
$Si_2(CH_3)_3Cl$	136		15	25	23	59	23	25
$Si_2(CH_3)_4Cl$	151		5	38	16	76	54	36
$Si_2(CH_3)_2Cl_2$	156	29	12		2			
$Si_2(CH_3)_3Cl_2$	171	1	57	17	9	12	2	
$Si_2(CH_3)_2Cl_3$	193	31	2	1	3			
$Si_3(CH_3)_6Cl$	209							9
$Si_3(CH_3)_4Cl_2$	214			4				
$Si_3(CH_3)_5Cl_2$	229				26	6	4	50
$Si_3(CH_3)_3Cl_3$	236	1	11	6	10	37		19
$Si_3(CH_3)_4Cl_3$	251		2	79	7	73	1.3	3
$Si_3(CH_3)_5Cl_3$	266						0.7 [a]	
$Si_3(CH_3)_3Cl_4$	271	3	100	17	3	11		
$Si_3(CH_3)_2Cl_5$	291	1						
$Si_4(CH_3)_5Cl_3$	294				2			
$Si_3(CH_3)_3Cl_5$	306	2 [a]						
$Si_4(CH_3)_6Cl_3$	309				1			
$Si_4(CH_3)_5Cl_4$	329			2	41	6		73
$Si_4(CH_3)_4Cl_5$	349		5	100	3	1.6		
$Si_4(CH_3)_5Cl_5$	364					0.4 [a]		
$Si_4(CH_3)_3Cl_6$	369		1					
$Si_4(CH_3)_4Cl_6$	384		0.4 [a]					
$Si_5(CH_3)_6Cl_4$	387							3
$Si_5(CH_3)_5Cl_5$	407				0.8			1.1
$Si_5(CH_3)_6Cl_5$	422							0.3
$Si_5(CH_3)_4Cl_6$	427			3	100			
$Si_5(CH_3)_4Cl_7$	449			0.5				
$Si_6(CH_3)_6Cl_7$	507				2			
$Si_6(CH_3)_5Cl_8$	527				0.5			
$Si_6(CH_3)_6Cl_8$	542				0.1 [a]			

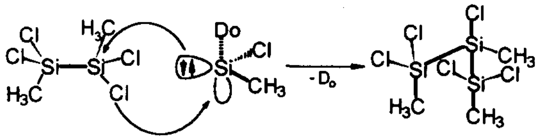
[a] Molpeak.

Closely related to this reaction pathway the intermediate baseadduct should be decomposed generating a basestabilized silylene species:



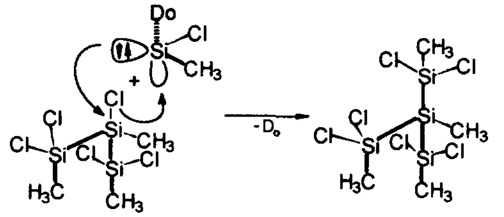
(3)

Therefore the formation of the first disproportionation product can be explained via an insertion of the methylchlorosilylene into the Si–Cl bond of **1** according to the reaction



(4)

The second insertion of the :SiClMe silylene should generate the tetrasilane **6**:

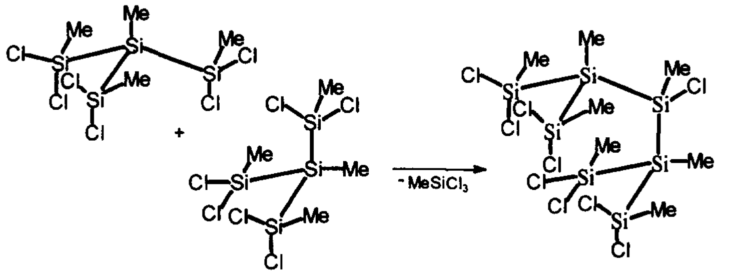


(5)

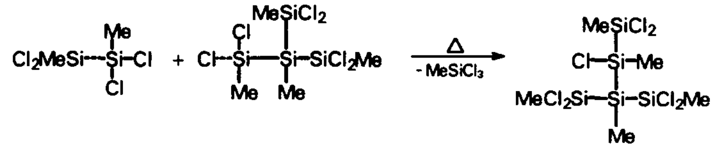
Linear tetrasilanes were not found. This means that the insertion of a silylene takes place exclusively into the Si–Cl bond of the middle silicon atom. From our own investigations of the basecatalysed hydrogenation of trisilanes having a –SiClMe– middle group (for instance $SiClMe_2$–SiClMe–$SiClMe_2$) with trialkylstannanes it is known that hydrogenation also takes place first and exclusively in the middle –SiClMe– group [14]. Consequently both the hydrogenation and insertion start at the silicon atom with the highest acceptor strength [15]. The order of the stability of 2.2′-bipyridyl adducts of methylchloromono- and disilanes displays the electron drawing effect of silylgroups in comparison with chlorine substituents [11]:

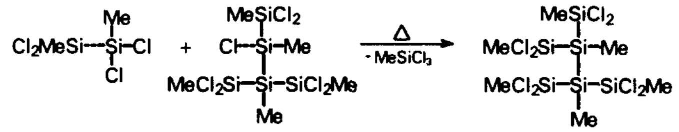
$$Me < SiMe_3 = Cl < SiClMe_2 < SiCl_2Me < SiCl_3$$

The electron withdrawing effect of the two $SiCl_2Me$ groups at the middle Si atom in **5** overcomes the influence of the second chlorine atom at the terminal Si atoms. A step by step insertion sequence of the :SiClMe silylene should lead to the pentasilane **7** and hexasilane



(6)


(7)


(8)

8. The heptasilane **9** could arise from the reaction of two molecules of the tetrasilane **6** (see Eqn. (6)).

The extraordinary acceptor strength of the middle silicon atom in the trisilane and pentasilane makes the molecules very sensitive to a nucleophilic attack. For this reason only small amounts of these compounds are present in the oligosilane mixtures.

Due to the relatively high boiling points the oligosilanes involving four or more silicon atoms, these compounds are not able to come into contact with the catalyst during the heterogeneous reaction regime. Therefore, we assume that at higher temperatures (150–175 °C) the formation of the penta-, hexa and heptasilane (**7**–**9**) also proceeds without the catalyst (see Eqn. (7) and (8)).

In principle a thermal treatment of the oligosilane mixture according to reaction (**6**) gives rise to further crosslinking of the oligosilanes, whereby a polymer skeleton is generated, which is constructed predominately of $\geq$SiMe and $-SiCl_2Me$ units.

2.2. *Disproportionation of $SiCl_2Me-SiClMe_2$ (2)*

It is very difficult to synthesize the pure compound **2**. For this reason several mixtures containing **2** as the main component were reacted. First a mixture containing 81 mol% of **2** and 19 mol% of **1** was examined.

A ^{29}Si NMR spectrum of the filtrated liquid showed besides the monosilane Me_2SiCl_2 peak, the signals of the same oligosilanes as during the disproportionation of pure **1** and additional signals due to the tetrasilane $SiMe(SiCl_2Me)_2SiClMe_2$ **10** and the hexasilane $(SiCl_2Me)_2SiMe-SiMe(SiCl_2Me)SiClMe_2$ **11**.

It seems that **2** is preferentially cleaved into the silylene : SiClMe and the monosilane Me_2SiCl_2, but the insertion of the formed silylene takes place predominantely on **1** because of its higher acceptor strength. Thus, mainly the same oligosilanes as during the disproportionation of pure **1** are formed.

To prevent the formation of the disproportionation products from the disilane **1**, a mixture containing only **2** and **3** was used for further disproportionations.

In the experiment with a low amount of 1-methylimidazole (**4**) (0.05 g g^{-1} disilane mixture) the only disproportionation product was the tetrasilane **10**, besides the unreacted disilanes and the monosilane Me_2SiCl_2. Approximately 70% of **2** and none of **3** were disproportionated.

In a second experiment (0.10 g **4**/ g disilane mixture) **2** was completely converted. Besides the known oligomers **10** (16 mol% of the oligosilanes) and **11** (11 mol%), two new products were found: a trisilane $SiCl_2Me-SiMe_2-SiClMe_2$ (**12**, 30 mol%) and a pentasilane $(SiCl_2Me)_2SiMe-SiMe_2-SiClMe_2$ (**13**, 42 mol%). A GC-MS of the silane mixture confirmed the NMR results.

The formation of the tetrasilane **10** and the hexasilane **11** follows from the insertion of the :SiClMe silylene into $SiCl_2Me-SiClMe_2$ (see Eqn. (9)).

The first step should be the formation of a trisilane $(SiCl_2Me-SiClMe-SiClMe_2)$ but due to its highly re-


(9)


(10)

active middle silicon atom (see 2.1) a second silylene insertion proceeds very fast. For this reason the tetrasilane **10** formation is preferred. Apparently, the same effects steer the conversion of the tetrasilane **10** into the hexasilane **11**.

The formation of the trisilane **12** and the pentasilane **13** can be explained by the insertion of the :SiClMe silylene into the $SiClMe_2$–$SiClMe_2$ (see Eqn. (10)).

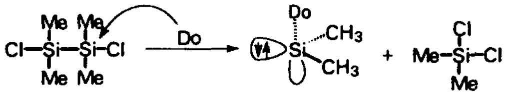
The found product distribution, especially the preferred formation of the products **10** through to **13** supports our proposed picture of the mechanism of the disilane disproportionation. As described for Si_2Cl_5Me, unsymmetric disilanes disproportionate exclusively into a monosilane, including the silicon atom with the higher number of methyl groups and a silylene with the minimal number of methyl groups. This can be concluded from the acceptor strength order of the chlorinated silyl groups. The insertion of the silylene also takes place exclusively on the silicon atom with the highest acceptor strength being the higher chlorinated silicon atom (in **2**, **10** and **12** the $SiCl_2Me$ group).

2.3. Disproportionation of $SiClMe_2$–$SiClMe_2$ (3)

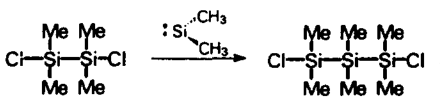
Using **4** as the catalyst we were even able to stimulate the disproportionation of **3**. Therefore the reaction conditions had to be changed to higher temperatures to force the reaction to proceed with an acceptable rate.

The monomer produced is exclusively Me_2SiCl_2, which forms a precipitate $Me_2SiCl_2 \cdot 2NMI$ with the catalyst. Contrary to the adduct with $MeSiCl_3$ the silicon atom is coordinated fourfold in this compound. This is concluded from the ^{29}Si CP/MAS NMR spectrum (signals at 2.9 and 1.1 ppm) suggesting an ionic structure $[Me_2Si(NMI)_2]Cl_2$.

Besides some **3** and the monosilane Me_2SiCl_2 the ^{29}Si NMR spectrum (Fig. 2) of the liquid manifests the formation of $SiMe_2Cl$–$SiMe_2$–$SiMe_2Cl$ (**14**, 78 mol% of the oligosilanes), $SiMe_2Cl$–$(SiMe_2)_2$–$SiMe_2Cl$ (**15**, 20 mol%) and $SiMe_2Cl$–$(SiMe_2)_3$–$SiMe_2Cl$ (**16**, 2 mol%). As calculated from the registrated concentration of the disilane and the corresponding higher oligomers, 76% of the disilane is converted according to the eqns. (11) and (12):



(11)



(12)

Besides its mechanistic aspects this reaction offers the possibility to synthesize linear, α,ω-dichloromethyl-

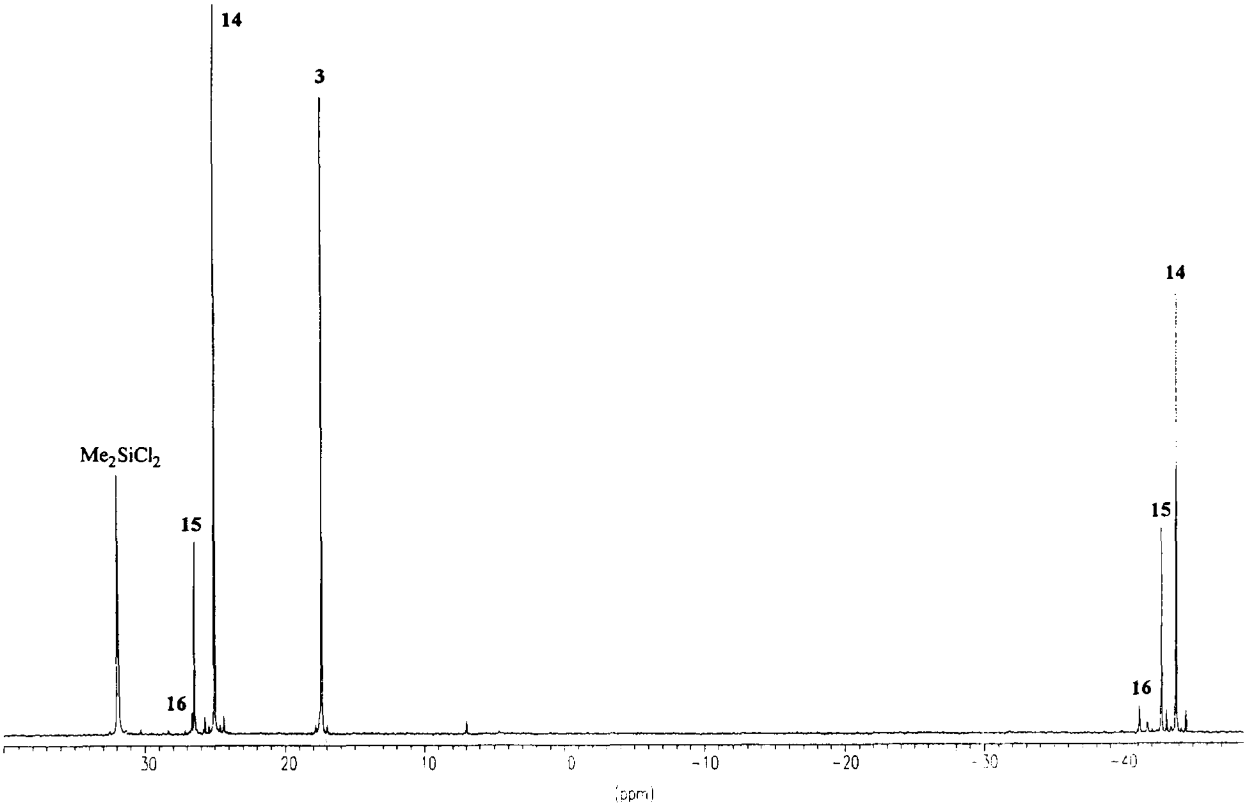


Fig. 2. ^{29}Si NMR spectrum of the oligosilane mixture obtained by homogeneous disproportionation.

oligosilanes without using metal condensation. Pure 1.3-dichlorohexamethyltrisilane could be isolated from the reaction mixture by fractional distillation.

It should be possible to obtain even higher oligosilanes by simply increasing the amount of **4** and/or the reaction time. The ^{1}H and ^{29}Si NMR chemical shift data of the found, $\alpha\omega$-dichloroligosilanes are in accordance with the values published earlier by Stanislawski and West [16].

3. Experimental details

3.1. ^{29}Si, ^{13}C and ^{1}H NMR

The measurements were performed on a BRUKER MSL 300 spectrometer at 59.627, 75.47 and 300 MHz, respectively. The ^{29}Si and ^{13}C NMR spectra were recorded using inverse gated decoupling. The coupling constants $^1J_{\mathrm{SiSi}}$ were obtained either directly from the spectra or by applying the INADEQUATE pulse sequence. TMS was used as internal reference for all NMR data.

3.2. GC-MS

GC MS spectra were recorded on a Hewlett Packard 5971. Ionisation energy: 70 eV Column: 30 m × 0.25 mm × 0.25 μm coated with phenylmethylpolysiloxane Temp.: Injector 280 °C. Detector 280 °C. Column 45 280 °C (5 °C min^{-1}). Flow: Helium 0.5 ml min^{-1}.

3.3. Synthesis of Methylchlorodisilanes

3.3.1. $SiCl_2Me–SiCl_2Me$ (1)

1 was prepared from the disilane fraction by treatment with acetylchloride and aluminiumchloride as described in [17]. yield: 90–98%, Kp. 153 °C, F. 9 °C.

3.3.2. $SiCl_2Me–SiClMe_2$ (2)

2 was obtained by chlorination of hexamethyldisilane (14.6 g, 100 mmol) with aluminiumchloride and acetylchloride in a 1:3:3-molar ratio. After the addition of the $AlCl_3$ and CH_3COCl the mixture was heated to 125 °C and stirred for 1 h. Condensation of the disilanes into a trap gave 13 g of a mixture of 81 mol% 1.1.2-trichlorotrimethyldisilane and 19 mol% 1.1.2.2-tetrachlorodimethyldisilane (product a).

In a second experiment the reaction mixture (same as above) was heated only for a few minutes. A product containing 1.2-dichlorotetramethyldisilane and 1.1.2-trichlorotrimethyldisilane in a molar ratio 2: 3.5 was obtained (product b).

A separation into pure disilanes by distillation has not been successful because of the almost equal boiling points.

3.3.3. $SiClMe_2$-$SiClMe_2$ (3)

1.2-dichlorotetramethyldisilane was prepared by chlorination of hexamethyldisilane (29.2 g, 200 mmol) with aluminiumchloride (53.4 g, 400 mmol) and acetylchloride (31.4 g, 400 mmol) at 0 °C. After stirring for two hours the 1.2-dichlorotetramethyldisilane was condensed into a trap at −78 °C. Redistillation gave 27.7 g (74%) pure 1.2-dichlorotetramethyldisilane. Kp. 147.5 °C, F. 12 °C.

3.4. Heterogeneous disproportionation of 1

The dried and securated glass apparatus consists of a 500 ml three necked flask equipped with a magnetic stirrer, an argon inlet tube, thermometer and a 15 × 7 cm column in which 10 g of the catalyst mixed with Raschig rings are stored. The top of the column is connected with a distillation bridge and a refluxing condensor.

The flask is charged with 200 g (0.877 mol) of **1**. The disilane is evaporated and carried to the catalyst. The disproportionation reaction is observed at the catalyst surface at temperatures between 120–135 °C. The reaction products are separated due to their distinctive boiling ranges. The gaseous methyltrichlorosilane $MeSiCl_3$ (Kp. 66 °C) is removed by distillation in the argon stream during the reaction. The formed methylchlorooligosilanes and **1** flowed down to the heated flask. A mixture of different oligosilanes can be isolated after a reaction time of 15 min at temperatures up to 175 °C. A crosslinking due to the high reactivity of the oligomers strongly controlled by the applied heating schedule (temperatures between 175 and 350 °C) finally lead to methylchloropolysilanes, which differed from each other by their crosslinking degree.

Yield methylchloropolysilanes: 20–25 mass% of the initial **1**.

3.5. Homogeneous disproportionation of methylchlorodisilanes

3.5.1. Disproportionation of 1

100 g **1** were diluted with 70 g toluene. A mixture of 19 g 1-methylimidazole (**4**) and 30 g toluene was added dropwise, during stirring, to this solution. A white precipitate was obtained immediately. After stirring overnight the solution was separated. A ^{29}Si-NMR-spectrum showed, beside some unreacted **1**, the formation of $MeSiCl_3$, as well as the oligosilanes **6** (70 mol% of oligosilanes), **7** (14 mol%), **8** (13 mol%) and **5** (3 mol%). Relatively pure (95%) **6** could be obtained by separation of the volatiles (toluene, $MeSiCl_3$, **1**) by condensation at room temperature in a vacuum and a distillation of the tetrasilane at 80 °C/0.01 kPa.

The white precipitate occuring during the reaction was found to be $MeSiCl_3 \cdot 2NMI$. Elemental analysis:

C: 34.18%, H: 4.75%, N: 17.92% ($C_9H_{15}Cl_3N_4Si$: C: 34.46%, H: 4.82%, N: 17.85%).

3.5.2. Disproportionation of 2

0.2 g **4** was added to 1 g of the product a (see Section 4.3.2.) diluted in 3 ml toluene. A white precipitate formed immediately. A ^{29}Si-NMR-spectrum of the filtrated solution was recorded. As described above 1 g of product b was treated with a) 0.05 g **4** and b) 0.10 g **4**. ^{29}Si NMR and GC/MS of the resulting mixtures were recorded.

3.5.3. Disproportionation of 3

0.5 g **4** was added to 4.29 g **3** and the mixture was heated and refluxed for 3 h. After cooling down to room temperature a white crystalline pecipitate occured, which was found to be $Me_2SiCl_2 \cdot 2$ NMI. Elemental analysis: C: 41.08%, H: 6.90%, N: 17.47% ($C_{10}H_{18}Cl_2N_4Si$: C: 40.96%, H: 6.19%, N: 19.10%).

Fractional distillation of the filtrated solution under reduced pressure gave 1 g pure $SiMe_2Cl$-$SiMe_2$-$SiMe_2Cl$ (Kp. 75–80 °C/0.5 kPa.

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