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New olefinic functionalized disilanes. Synthesis and NMR spectroscopical investigations

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Abstract

The new olefinic substituted aminodisilanes, which are obtained from the reaction of organometallic reagents with aminochlorodisilanes, are converted into the chlorodisilanes by equilibration reactions or treatment with HCl. The resulting olefinic functionalized disilanes are identified by means of ²⁹Si, ¹³C, ¹H NMR and GC MS measurements. © 1997 Elsevier Science S.A.

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1. Introduction

We have recently reported the synthesis of aminochlorodisilanes containing several chlorine atoms [1]:

$$[Cl_2 MeSi]_2 + 2nEt_2 NH$$

$$\rightarrow (Et_2 N)_n Cl_{4-n} Me_2 Si_2 + nEt_2 NH^* HCl$$

$$n = 1,2,3$$
(1)

Reactions between chlorodisilanes and dialkylamines were also studied by Wan and Verkade [2]. In contrast to the route via condensation of chloromonosilanes with lithium recommended by Tamao et al. [3] or Matsumoto and coworkers [4], any numbers of chlorine atoms can be preserved and used in subsequent reactions. This way offers an access to anchor olefin functions at definite positions at the 1,1,2,2-tetrachlorodimethyldisilane (TCDMDS) and thus to obtain two various reactive sites in this disilane molecule. The diethylamino groups primarily introduced into the disilane are able to act as protecting groups which can be removed by HCl or equilibration reactions.

2. Results and discussion

Using the dialkylamino function as protecting group in the synthesis of organochlorodisilanes is a very successful method to generate definitely substituted molecules. So the silicon chlorine bonds in aminochloromethyldisilanes are quite reactive against organometallic reagents containing Mg, Li, Na (Eq. (2)).

$$Me(R_{2}^{a}N)_{2}Si-Si(R_{2}^{a}N)MeCl + M-R^{b}-CH_{2}=CH_{2}$$

$$\rightarrow Me(R_{2}^{a}N)_{2}Si-Si(R_{2}^{a}N)Me(R^{b}-CH_{2}=CH_{2})$$
(2)

We used this general route to prepare olefinic substituted alkylaminochlorodisilanes. The conversion of the resulting organoaminodisilanes in the corresponding chloro compounds succeeds by equilibration with chlorosilanes or by treatment with HCl. Double bonds in the organic group are preserved by either method.

2.1. Olefin substituted aminodisilanes

The aminochlorodisilanes are synthesized by the reaction of diethylamine with 1,1,2,2-tetrachlorodimethyldisilane [1]. Using this method the monosubstituted (1),

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Compound	R	$\delta_{\rm Si}^{\rm A}$ (ppm)	δ ^B _{Si} (ppm)	¹ J _{SiSi} (Hz)	$^{1}J_{\rm SiC}$ (Hz)
$\overline{\left[Me(Et_2N)RSi\right]_2(2)}$	Cl a	2.1			60.0
	α-Allyl	-7.07			
	Vinyl	-13.55			
$[Me(Et_2N)RSi]_2$ (3)	Cl ^a	-0.05			
	α-Allyl	-7.18			
	Vinyl	-13.61			
$Me(Et_2N)_2Si^{A}-Si^{B}Me(Et_2N)R (4)$	Cl ^a	4.5	-12.4	149.8	$53.1 (^{1}J_{Si^{B}C})$
	α-Allyl	-8.35	- 8.8		
	β-Allyl	- 8.85	- 15.4	129.2	
	Vinyl	-9.87	- 15.3	149.3	
	Me	-7.75	- 8.96		

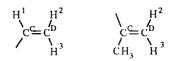
Table 1 ²⁹Si NMR shifts of substituted aminosilanes

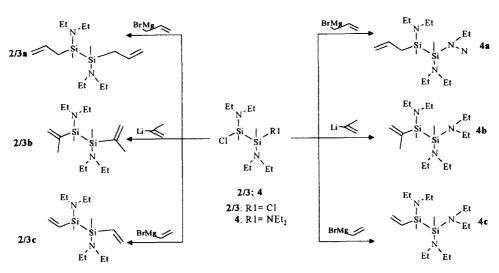
^a Ref. [1].

the symmetrical two-fold (2/3) and the three-fold (4) aminosubstituted products are obtained. Beside these expected amino compounds, we also detected the byproducts Me(Et₂N)₂Si-Si(Et₂N)Me₂, Me₂(Et₂N)Si-Si(Et₂N)MeCl, Cl(Et₂N)₂Si-Si(Et₂N)MeCl, which occur in very small amounts, by GC MS and ²⁹Si NMR spectroscopy (Table 1).

The aminochlorodisilanes are able to react with organometallic compounds to form the corresponding organosubstituted aminodisilanes. The reaction of the starting compounds 2/3 and 4 with allyllithium leads to the β -bonded allylaminodisilane (4b). The α -bonded species (2/3a, 4a) are obtained in amounts less then 4% yield. The pure α -allylaminodisilanes are generated using the allylmagnesium reagent. In this case the β -allylaminodisilane is not observed. The vinyl compounds (2/3c, 4c) are prepared by the reaction of the vinyl-magnesiumbromide with 2/3 or 4 (Scheme 1).

The 1,2-dichloro-1,2-bis(diethylamino)dimethyldisilane (2/3) forms two diastereotopic isomers which always occur in the ratio 2:3. Generally, the stereoisomerism is preserved in the allyl and vinyl compounds which result from the reaction of the organometallic reagent with 2/3. But the concentration ratio is near 1:1. In every case we have identified two different Si atoms, but the ¹³C NMR spectra of the olefinic species, in contrast to those of the chloro functionalized compounds, do not exhibit any indication of diastereomers related to the diethylamino groups. In the ¹³C NMR spectra of $[(C_2H_3)Me(Et_2N)Si]_2$ there is no distinction between the chemical shifts of the Si-CH₃ groups, but the ¹H NMR spectra demonstrate that the hydrogens are not equal. Also, the hydrogen atoms bonded to the vinyl groups exhibit differences of about 1.7 to 2.9 Hz. The $[(\alpha-C_3H_5)Me(Et_2N)Si]_2$ shows two different Si-CH₂ and Si-CH₃ groups, belonging to the two diastere-omers. The results of the ²⁹Si, ¹³C, ¹H NMR measurements are summarized in Tables 1-3, the hydrogen atoms in the olefinic groups are labeled as follows:





Scheme 1.

R	δ ₆ (nnm)										
1											
	Si ^A –CH ₃	Si ^B CH ₃	$N \sim CH_3^A$	$N \sim CH_3^A$	$N \sim CH_3^B$	-CH, /-CH, N-CH ^A	N-CH ^A	N-CHA	N-CH ^B	من	UU UU
RMe(Et ₂ N	RMe(Et ₂ N ₂) ₂ Si ^A $-$ Si ^B Me(Et ₂ N),	N),				e /7	7		11 2112		
CI "	-0.8	3.2	14.7	14.9	15.1		39.55	39.61	40.5		
b-Allyl	-0.1	-1.0	15.5		15.6	22.6	39.9		41.0	0 1 1 1	1276
α-Allyl	0.4	- 2.0	15.5		15.6	26.6	10 05		0110		0.201
Vinyl	- 0.2	-1.4	15.4		15.5	2	39.9		41.0	112.2	141.6
	Si-CH ₃	$N \sim CH_3$	$-CH_2/-CH_3$	N-CH ₂	CD	Cc					
$[Me(Et_2N_2)RSi]_2$)RSi]2										
CI ^{a,b}	1.6/1.7	14.88/14.90		40.8 / 40.3							
α-Allyl ^b	-2.4/-2.3	15.8/15.8	26.1/26.4	41.0/41.0	112.6/112.6	135 5/135 5					
Vinyl ^b	-2.2/-2.2	15.7/15.7		41.1/41.1	131.1/131.1	140.3/140.3					
^a Ref. [1].											

Table 2 13 C NMR shifts of substituted aminosilanes 2/3 and 4

^b Two existing stereoisomers.

Compound	ж	δ _H (ppm) Si-CH ₃	$\delta_{\rm H} (\rm ppm) J_{\rm H-H}$ $\rm N \sim CH_3 (Hz)$	J _{H-H} (Hz)	$\delta_{\rm H}$ (ppm) $\delta_{\rm H}$ (ppm) -CH ₂ N-CH ₂	δ _H (ppm) N-CH ₂	<i>J</i> _{н-н} (Hz)	$ \begin{array}{ll} J_{H-H} & \delta_{H} & (ppm) \\ (Hz) & = CH^{1} \end{array} $	<i>J</i> _{н-н} (Hz)	$\delta_{\rm H} (\rm ppm) = CH^2$	$J_{\rm H-H}$ (Hz)	$\delta_{\rm H} (\rm ppm) = CH^3$	<i>J</i> _{Н-Н} (Hz)	
[Me(Et ₂ N)RSi] ₂ ^a	CI (a) (b) α -Allyl (a) (b) Vinyl (a) (b)	0.74 0.66 0.19 0.16 0.22 0.20	1.17 T 1.17 T 0.98 T 0.98 T 0.98 T 0.98 T	6.9 6.9 7.0 7.0 7.0	1.70 ^b M 1.59 ^b M	3.08 M 3.08 M 2.83 Q 2.86 Q 2.86 Q	6.9 6.9 7.0 7.0	5.80 ^b M 5.81 ^b M 6.17 ^b D/D 2 6.17 ^b D/D 2	20.0/14.4 20.2/14.5	4.82 M 4.82 M 5.917 ^b D/D 14.5/4.0 5.924 ^b D/D 14.5/4.0	14.5/4.0 14.5/4.0	4.83 D 4.83 D 4.83 D 5.67 ^b D/D	18.9 18.9 20.0/3.8 20.0/3.8	
		δ _H (ppm) Si ^A -CH ₃	$ \begin{array}{c c} \delta_{H} & (ppm) & \delta_{H} & (ppm) & \delta_{H} & (ppm) \\ \text{Si}^{A} - \text{CH}_{3} & \text{Si}^{B} - \text{CH}_{3} & \text{N} \sim \text{CH}_{3} \end{array} $	$\frac{\delta_{\rm H}~(\rm ppm)}{\rm N\sim CH_3}$	J _{H-H} (Hz)	$\delta_{\rm H}$ (ppm) $J_{\rm H-H}$ -CH ₂ /-CH ₃ (Hz)		δ _H (pm) N-CH ₂	J _{H-H} (Hz)	$\delta_{\rm H}$ (pm) =CH ¹	$\delta_{\rm H} (\rm pm) = CH^2$	J _{H-H} (Hz)		J _{H-H} (Hz)
Me(Et ₂ N) ₂ Si ^A Si ^B Me(Et ₂ N)R	Cl α-Allyl	0.45 0.16	0.66	1.22 bT/ 1.20 bT 0.97 bT/ 0.90 bT	6.9/6.9 6.6/6.6	1.65 M		3.09 M 2.86 M		5.82 M	4.79 D	9.5	4.80 D	18.2
	β-Allyl Vinyl	0.54 0.17	0.57 0.22	1.35 T 0.98 T	6.7 7.0	2.2 D	5.4	3.24 Q 2.9 Q	6.5 7.0	6.2 M	6.06 D 5.9 D/D	18.3 14.5/4.1	6.4 M 5.7 D/D	20.0/3.

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Compound	R	δ _H (ppm) Si-CH ₃	$\delta_{\rm H}$ (ppm) -CH ₂	J _{Н-Н} (Нz)	δ _H (ppm) =CH ¹	$\delta_{\rm H}$ (ppm) =CH ²	J _{Н-Н} (Нz)	$\delta_{\rm H}$ (ppm) =CH ³	$J_{\rm H-H}$ (Hz)
[MeClRSi] ₂ ^a	α-Allyl (a)	0.528	1.97	7.9	5.77 M	5.0 D	9.8	5.01	18.0
-	(b)	0.535	1.97	7.9	5.77 M	5.0 D	9.8	5.01	18.0
	Vinyl (a)	0.62		c		c		c	
	(b)	0.60		с		с		с	
		$\delta_{\rm H}$ (ppm) Si ^A -CH ₃	δ _H (ppm) Si ^B -CH ₃	$\delta_{\rm H}$ (ppm) -CH ₂ /-CH ₃	J _{Н-Н} (Нz)	δ _H (pm) -CH ¹	J _{Н-Н} (Нz)	δ _H (pm) –CH ²	δ _H (pm) -CH ³
MeCl ₂ Si ^A – Si ^B MeClR	α-Allyl	0.90	0.61	2.05 D	7.9	5.79 M		5.03 M	5.06 M
	β-Allyl	0.90	0.66	1.91 D	4.7	5.75 D	22.2	6.44 M	
	Vinyl	0.89	0.68			с		с	с

Table 4 ¹H NMR shifts of olefinic chlorosilanes (couplings are indexed by D, doublet; T, triplet; O, quartet; M, multiplet)

^a The two existing diastereomers of the compounds are marked (a) and (b).

^b No unambiguous assignment to one of the stereoisomers possible.

^c Multiplet between 5.9 and 6.3 ppm.

2.2. Cleavage of the Si-N bond

The exchange of dialkylamino groups for chlorine is achieved by equilibration reactions with chlorosilanes (TCDMDS, trichlormethylsilane TCMS) or by treatment with dry HCl [3]. In the last case the chlorination of the double bond has to be taken into consideration. To investigate the reaction of TCDMDS with 4a the compounds are mixed at room temperature in the molar ratio 3:1. In this way all diethylamino groups should be exchanged for chlorine and the 1-(α -allyl)1,2,2-trichlorodimethyldisilane (5a) should result. The ²⁹Si NMR spectra indicate that in the equilibration experiment Cl₂MeSi-Si(Et₂N)MeCl and two various disilane species are generated. The aminodisilane 2/3 is formed in lower yields.

The equilibration with trichloromethylsilane (4 mol) forms a mixture of the completely chlorinated product **5a** exclusively besides residual TCMS and its mono-aminated derivative $MeSiCl_2(NEt_2)$.

After the treatment of $Me(Et_2N)_2Si-Si(Et_2N)Me(\alpha-allyl)$ (5a) with dry HCl we observe only one silicon containing compound without any diethylamino groups, however the allyl function is preserved. The cleavage of the silicon nitrogen bond by HCl gives pure products without fractional distillation. NMR data of the olefinic chlorodisilanes are given in Tables 4 and 5. Interpretations of the ²⁹Si IGATED and ¹H NMR spectra lead to Scheme 2.

3. Experimental details

NMR spectra were recorded on a Bruker MSL 300 spectrometer at 59.627 MHz (29 Si), 75.47 MHz (13 C) and 300.13 MHz (1 H) with TMS as internal standard using the IGATED (29 Si, 13 C) or QUADCYCL (13 C, 1 H) pulse sequence.

GC MS measurements were performed on a Hewlett Packard 5971.

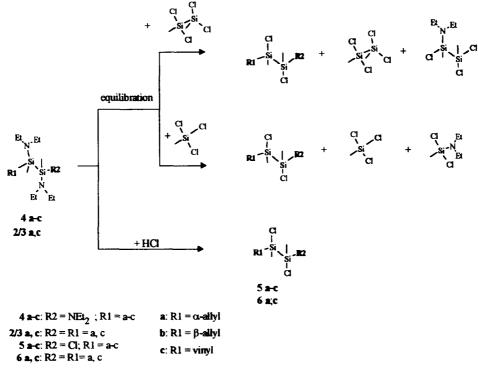
 Table 5

 ²⁹Si, ¹³C NMR shifts of the olefinic chlorodisilanes

Compound	R	δ (ppm)		$J_{\text{Si-Si}}$ (Hz)	δ _C (ppm)				
		SiA	Si ^B		Si ^A -CH ₃	Si ^B -CH ₃	C ^c	CD	CH ₂ /-CH ₃
Me(R)ClSi ^A -Si ^B MeCl ₂	Et ₂ N ^b	- 19.0	21.2	161.3	0.0	6.7			
	α-Āllyl	11. 9	24.1		-1.2	6.7	130.1	117.1	24.1
	β-Allyl	1.1	24.3	130.7	-0.7	5.9	149.5	122.7	22.6
	Vinyl	1.8	23.5	129.3	- 1.0	5.9	137.4	131.5	
[Me(R)ClSi] ₂ ^a	Et ₂ N ^b	2.1 / - 0.1			1.6/1.7				
-	α-Āllyl	14.8/14.5			-0.321		130.9/131.0	116.1	25.0
	Vinyl	4.5/4.3			-0.431		135.8	133.4	

^a Diastereotopic compound.

^b Ref. [1].



Scheme 2.

3.1. Synthesis of olefin substituted aminodisilanes

3.1.1. $(\beta - C_3 H_5)(Et_2 N)MeSi - SiMe(Et_2 N), (4b)$

To a solution of 65.3 ml allyllithium/THF (0.68 M) prepared by cleavage of the allylphenylether with lithium [5] 15 g Me(Et₂N)₂Si-Si(Et₂N)MeCl (0.044 mol, 12.8 ml) in 20 ml THF was added dropwise. After the complete addition the mixture was kept under reflux for 13 h. By removing the THF and stirring the residue with pentane a white precipitate was obtained. After filtration and evaporation of the solvent, distillation under reduced pressure gave 8g of the pure compound (58% yield). $K_p = 117-120$ °C/1.5 torr GC MS 343 (M⁺) 329 (M⁺ - Me) 270 (Si₂(Et₂N)₃) 241 (Si₂(Et₂N)₂(C₃H₅)) 198 (Si₂Me₂(Et₂N)(C₃H₅)) 187 (SiMe₂(Et₂N)₂) 156 (SiMe(Et₂N)(C₃H₅)) 116 (SiMe(Et₂N)).

3.1.2. $(\alpha - C_3 H_5)(Et_2 N)MeSi-SiMe(Et_2 N)_2$ (4a)

15 g Me(Et₂N)₂Si-Si(Et₂N)MeCl (0.044 mol, 12.8 ml) was added dropwise to 66 ml of an allylmagnesiumbromide/diethylether solution (1 M) and the resulting mixture was refluxed for 12 h. The two phases formed were not separated. After removing the ether the residue was stirred with hexane under reflux for 2 h. The precipitate obtained was filtered and the solvent evaporated. The crude product was distilled under reduced pressure to give 8.3 g pure compound (55% yield). $K_p = 125 ^{\circ}C/1.0 \text{ torr GC MS 343 (M^+) 302}$ (Si₂Me₂(Et₂N)₃) 229 (Si₂Me₂(Et₂N)₂) 198 $(Si_2Me_2(Et_2N)(C_3H_5))$ 187 $(SiMe_2(Et_2N)_2)$ 156 $(SiMe(Et_2N)(C_3H_5))$ 116 $(SiMe(Et_2N))$.

3.1.3. $(C_2H_3)(Et_2N)MeSi-SiMe(Et_2N)_2$ (4c)

The vinyl compound was synthesized in the same manner as mentioned for the α -allyl compound. Because the vinyl Grignard reagent was diluted in THF, the separation of two phases did not occur. The THF was removed before adding the hexane and stirring at reflux for 2 h. The pure product was obtained by distillation in 59% yield. $K_p = 115 \text{ }^{\circ}\text{C}/2.25 \text{ torr GC MS } 330$ $(M^+) 302 (Si_2 Me_2(Et_2 N)_3) 256$ $(Si_2 Me_2(Et_2 N)_2(C_2 H_3)) 229 (Si_2 Me_2(Et_2 N)_2) 187$ $(SiMe_2(Et_2 N)_2) 184 (Si_2 Me_2(Et_2 N)(C_2 H_3)) 158$ $(Si_2 Me_2(Et_2 N)) 142 (SiMe(Et_2 N)(C_2 H_3)) 116$ $(SiMe(Et_2 N)).$

3.1.4. $(\alpha - C_3 H_5)(Et_2 N)MeSi-SiMe(Et_2 N)(\alpha - C_3 H_5)$ (2 / 3a)

The synthesis was carried out as described for 4a. $K_p = 105 \text{ °C}/1.0 \text{ torr } (61\% \text{ yield}) \text{ GC MS } 312 \text{ (M}^+)$ 271 (M⁺-(C₂H₃)) 198 (Si₂Me₂(Et₂N)(C₃H₅)) 156 (SiMe(Et₂N)(C₃H₅)) 129 (SiMe₂(Et₂N)).

3.1.5. $(C_2H_3)(Et_2N)MeSi-SiMe(Et_2N)(C_2H_3)$ (2/3c) The synthesis was carried out analogously to 4c. $K_p = 86-90 \text{ °C}/2.25 \text{ torr} (51\% \text{ yield}) \text{ GC MS } 286 (\text{M}^+)$ 269 $(\text{M}^+ - \text{Me}) 256 (\text{M}^+ - (C_2H_3)) 212$ $(Si_2Me_2(Et_2N)(C_2H_3)_2) 184 (Si_2Me_2(Et_2N)(C_2H_3))$ 168 $(Si_2Me(Et_2N)(C_2H_3)) 158 (Si_2Me_2(Et_2N)) 142$ $(SiMe(Et_2N)(C_2H_3))$ 126 $(Si(Et_2N)(C_2H_3))$ 116 $(SiMe(Et_2N))$.

3.2. Equilibration reactions

3.2.1. TCDMDS

To 4.35×10^{-3} mol (0.99 g, 0.78 ml) TCDMDS 1.45 $\times 10^{-3}$ mol (0.5 g) **4a** was added. The mixture was stirred overnight at room temperature and for the NMR measurement diluted with CDCl₃/TMS.

3.2.2. TCMS

A mixture of 5.8×10^{-3} mol (0.87 g, 0.686 ml) TCMS and 1.46×10^{-3} mol (0.5 g) **4a** was stirred overnight at room temperature. TMS was used as internal standard for the NMR spectroscopy.

3.3. Cleavage of the Si-N bond by HCl

HCl was bubbled through a mixture of the olefinic aminodisilanes in dry CCl_4 . The solution became cloudy and warmed up. At the end of the reaction the formed precipitate dissolved and two phases were obtained. The solvent (CCl_4) of the lower phase containing the prod-

uct was evaporated. The resulting chlorodisilane can be purified by distillation:

Compound	B.p. _{1 torr} (°C)	Yield (%)
(a-C ₃ H ₅)ClMeSi-	44	70
SiMeCl ₂ 5a		
$(\beta - C_3 H_5)$ ClMeSi-	41	33
SiMeCl ₂ 5b		
$(C_2H_3)ClMeSi-$	35	60
SiMeCl ₂ 5c		
$(\alpha - C_3 H_5)$ ClMeSi-	65	81
SiMeCl(α -C ₃ H ₅) 6a		
$(C_2H_3)ClMeSi-$	40	62
$SiMeCl(C_2H_3)$ 6c		

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