



First cyclotrisiloxanes with three different R_2Si -units of the general formula $R_2^1Si(OSiR_2^2)(OSiR_2^3)O$ ($R_2^1 = Me_2Si(NSiMe_3)_2$, $R^2 = Cl$, $Ot-Bu$, $R^3 = Me$)

Andreas Rammo*

Institute of Inorganic Chemistry, Saarland University, Campus C4 1, 66123 Saarbrücken, Germany

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ABSTRACT

The reaction of compound $Me_2Si(NSiMe_3)_2Si(OH)Cl$ with Me_2SiCl_2 leads to the disiloxane $Me_2Si(NSiMe_3)_2Si(Cl)OSi(Me_2)Cl$ (**1**). Hydrolysis of **1** in the presence of pyridine results in $Me_2Si(NSiMe_3)_2Si(OH)OSi(Me_2)OH$ (**2**), which is allowed to react with $SiCl_4$ to give cyclotrisiloxane $[Me_2Si(NSiMe_3)_2Si](OSiMe_2)(OSiCl_2)O$ (**3**). The treatment of **1** with $(t-BuO)_2Si(OH)_2$ forms cyclotrisiloxane $[Me_2Si(NSiMe_3)_2Si](OSiMe_2)[OSi(Ot-Bu)_2]O$ (**4**). Compound **3** is obtained as a crystalline solid while **4** is an oily liquid. The ring size of these new types of cyclotrisiloxanes with three different R_2Si -units is confirmed by cryoscopy in benzene, ^{29}Si NMR chemical shifts and in case of **3**, additionally by a single X-ray diffraction study. The different electronegativities of the substituents in the R_2Si -units lead to different bond lengths and bond angles within the Si_3O_3 cycle, which are discussed in detail in the molecular structure of **3**.

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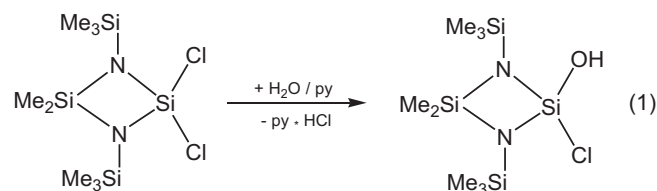
1. Introduction

For more than 50 years, ring-opening polymerisation of cyclic siloxanes has extensively been used in industry and chemical laboratories as the basic method for the synthesis of high molecular weight linear polysiloxanes [1,2]. In contrast to the almost strain-free eight-membered cyclosiloxanes, which provide less successful results by the kinetically controlled ring-opening polymerisation [3–6], the six-membered cyclosiloxanes can easily and successfully be polymerised. The driving force is the relief of ring strain present within cyclotrisiloxanes [7]. Cyclotrisiloxanes with similar R_2Si -units of the general formula $(R_2SiO)_3$ have already been known since the early 20th century [8–11] and such as $(R_2Si^1)(OSiR_2^2)_2O$ with two different R_2Si -units have been synthesised and characterised in the last decades [7,12–16]. Few Si_3O_3 cycles with different R^1R^xSi -units ($x = 1–3$) have been mentioned in literature [17–19]. However cyclotrisiloxanes with three different R_2Si -units have so far not been reported.

2. Results

2.1. Synthesis

The formation of the cyclotrisiloxanes, **3** and **4** can be achieved in a stepwise synthesis. The starting compound, $Me_2Si(NSiMe_3)_2SiCl_2$ [20], is converted into $Me_2Si(NSiMe_3)_2Si(OH)Cl$ [15,21] by partial hydrolysis in the presence of pyridine (equation (1)).



The substitution of one chlorine atom can easily be detected by NMR spectroscopy. In $Me_2Si(NSiMe_3)_2SiCl_2$ (C_{2v} -symmetry) the two methyl groups of the Me_2Si -moiety are homotopic giving only one signal in 1H and ^{13}C NMR spectra. The substitution of one chlorine atom by a hydroxyl group results in a second singlet in the NMR spectra [15,21], each representing one diastereotopic methyl group of the compound $Me_2Si(NSiMe_3)_2Si(OH)Cl$ (C_s -symmetry) (Fig. 1).

* Tel.: +49 681 302 2965; fax: +49 681 302 3995.

E-mail address: a.rammo@mx.uni-saarland.de.

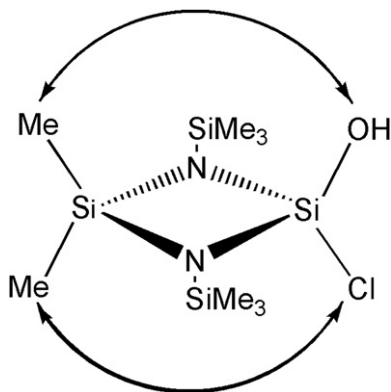
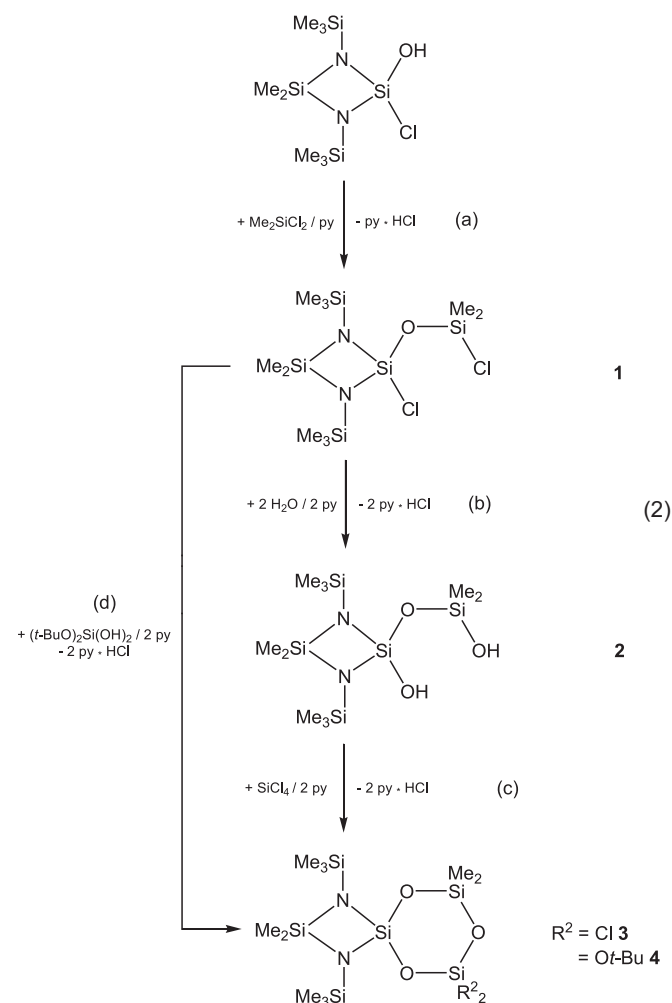


Fig. 1. The different substituents, Cl and OH influence the terminal methyl groups to give two separate singlets in the ^1H and ^{13}C NMR spectra.

The colourless solid $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$ is a stable material. No self-condensation reactions releasing HCl or water are observed [21]. On the other hand, if the sterically less demanded dichlorodimethylsilane is allowed to react with $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$ in the presence of the hydrochloride acceptor pyridine, the disiloxane **1** can be prepared (equation (2a)).



In order to suppress an undesirable concurrence reaction between the desired product **1** and $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$, the mixture of $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$ /pyridine in the solvent diethyl ether is slowly added to an excess of Me_2SiCl_2 under vigorous stirring. The disiloxane **1** gives an oily colourless liquid, which can be isolated by distillation at 55°C under reduced pressure (10^{-2} Torr) yielding 68%. In the ^1H and ^{13}C NMR spectra for **1** the two diastereotopic methyl groups show two singlets like in the compound $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$ (Fig. 1) and the integration ratio of the NMR signals in the proton resonance spectrum is fully consistent with the structure of compound **1**.

The treatment of **1** with two equivalents of water in the presence of pyridine forms the 1,3-disiloxandiol **2** (equation (2b)). In order to have a homogeneous reaction and to keep constant the necessary small amounts of water when hydrolysing **1**, a dioxane solution of definite water content is used. As derived from the ^1H and ^{13}C NMR spectra of the reaction solution, **2** turns out to be an unstable compound. Obviously, the silanol groups of **2** tend to inter- and/or intramolecular condensation reactions. The attempt to isolate **2** by removing the solvent under reduced pressure results in an oily liquid leading to a huge number of signals in the NMR spectra. For this reason, after generating **2** and filtration of the ammonium salt, the ethereal solution of **2** is immediately allowed to react with tetrachlorosilane to provide the cyclic compound **3** (equation (2c)). In order to prefer an intramolecular ring cyclisation and to reduce intermolecular reactions the dilution principle is used [22].

Compound **4** is formed by the treatment of disiloxane **1** with the equimolar amount of $(\text{t-BuO})_2\text{Si}(\text{OH})_2$ [23] in the presence of the hydrochloride acceptor pyridine (equation (2d)). NMR spectra reveal a very slow reaction and it is necessary to reflux the ethereal solution for 12 h to complete the generation of **4**.

The cyclotrisiloxanes, **3** and **4** can be isolated by vacuum distillation in yields of 70%, and 72%, respectively. Contrarily to compound **4**, obtained as a colourless and viscous liquid, the oily distillate of **3** crystallises out while cooling down to room temperature.

Whereas in the ^1H NMR spectra of the compounds $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Si}(\text{OH})\text{Cl}$, **1** and **2**, the diastereotopic methyl groups give two separate singlets, while in the cyclic compounds **3** and **4**, respectively, the two methyl groups are isochronous and consequently only one singlet is observed with an integration of six protons. However, in the ^{13}C NMR spectrum each methyl group results in the expected singlet.

2.2. Spectroscopy

^{29}Si NMR resonances show a significant shift to lower field for six-membered cyclosiloxanes compared to eight-membered cyclosiloxanes and thus allow to distinguish between ring sizes (Table 1).

The observed low-field shift for smaller ring sizes [28,29] is deduced from the increasing ring strain energy in comparison to eight- and higher-membered cycles [7]. In Table 2, additionally to the recorded ^{29}Si NMR chemical resonances for the cycles **3** and **4**,

Table 1
Comparison of ^{29}Si NMR chemical shifts for some cyclo six- and cyclo eight-membered siloxanes.

Cyclosiloxanes	$n = 3$	$n = 4$
$(\text{Cl}_2\text{SiO})_n$	-58.3	-69.3 [24]
$(\text{Me}_2\text{SiO})_n$	-9.2	-20.0 [25]
$(\text{Ph}_2\text{SiO})_n$	-33.5	-42.7 [26]
$[(\text{EtO})_2\text{SiO}]_n$	-88.0	-95.1 [27]

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