An efficient synthetic route to primary and secondary condensation products of silanetriols starting from (arylamino)trichlorosilanes

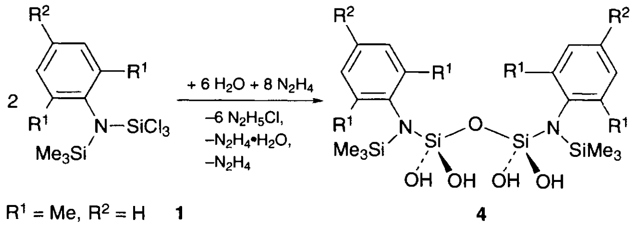
Ramaswamy Murugavel, Peter Böttcher, Andreas Voigt, Mrinalini G. Walawalkar, Herbert W. Roesky,*
Emilio Parisini, Markus Teichert and Mathias Noltemeyer

Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany

Stoichiometry dependent hydrolysis of (arylamino)silyltrichlorides using anhydrous N_2H_4 as the HCl acceptor and dehydrating agent leads to the formation of the primary and secondary condensation products of silanetriols, tetrahydroxydisiloxanes $[Ar(SiMe_3)NSi(OH)_2]_2O$ and cyclotrihydroxytrisiloxanes $[Ar(SiMe_3)NSi(OH)O]_3$, respectively.

There has been considerable interest in the chemistry of silanols[1] containing more hydroxy groups in view of their use as building blocks for two- and three-dimensional heterosiloxanes[2] which would find applications in materials chemistry and catalysis. A number of synthetic routes have been described for the hydrolysis of organotrichlorosilanes. The use of normal hydrolysis conditions leads to polyhedral silasesquioxanes[3] and a wide variety of polymeric silicone materials[4] through the self-condensation of the *in situ* formed silanols. On the other hand, the use of milder hydrolysis conditions often leads to the clean formation of silanetriols $RSi(OH)_3$.[5] There are no convenient synthetic routes for the hydrolysis of trichlorosilanes resulting in the primary and secondary condensation products of silanetriols. The only known synthetic route for this purpose employs aqueous alkali-metal hydroxides (KOH or NaOH) for the preparation of tetrahydroxydisiloxanes.[6–8] However, application of this route to silyltrichlorides containing Si–N or Si–O bonds leads to untractable products. During the course of our studies on the hydrolysis of trichlorosilanes, we found that the N_2H_4 assisted hydrolysis directly yields both the primary and secondary condensation products of the silanetriols, depending upon the stoichiometry of the hydrazine used. The preliminary results of this investigation are reported here.

The hydrolysis of (arylamino)trichlorosilanes **1–3**[5a] in the presence of 3 equiv. of H_2O and 4 equiv. of N_2H_4 (anhydrous) in Et_2O at 0 °C leads to the exclusive formation of new organic-soluble tetrahydroxydisiloxanes **4–6** in nearly quantitative yields (Scheme 1). The anhydrous hydrazine, in these reactions, acts both as an HCl acceptor and as a dehydrating agent of the silanetriol formed in the course of the reaction. In order to confirm this supposition, we reacted 2 equiv. of the silanetriol $(2,6\text{-}Me_2C_6H_3)N(SiMe_3)Si(OH)_3$[5a] with 1 equiv. of anhydrous N_2H_4 in Et_2O at 25 °C. This procedure exclusively leads to the formation of **4** (Scheme 2).



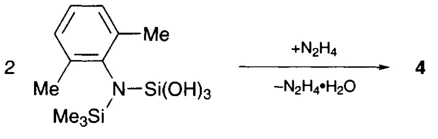
$R^1 = Me, R^2 = H$ **1** **4**
$R^1 = Me, R^2 = Me$ **2** **5**
$R^1 = Pr^i, R^2 = H$ **3** **6**

Scheme 1

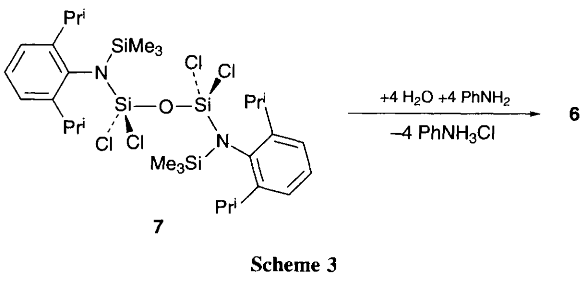
In an independent experiment, starting from the hexachlorodisiloxane $Cl_3SiOSiCl_3$ and 2 equiv. of $(2,6\text{-}Pr^i{}_2C_6H_3)(SiMe_3)NLi$, we synthesised the tetrachlorodisiloxane $RSiCl_2OSiCl_2R$ **7** which is quantitatively hydrolysed to the tetrahydroxydisiloxane **6** in the presence of aniline and H_2O (Scheme 3).

The products **4–7** have been characterised by elemental analyses and MS, IR and NMR spectroscopic data.† All the compounds show peaks due to the M^+ ion by EIMS and the other spectroscopic data are consistent with the proposed structure. Single crystals suitable for X-ray diffraction studies were grown from methanol–1,4-dioxane for **4** and from Et_2O–pentane for **7**.‡ There are essential differences between the structure of **4** (Fig. 1) and the previously reported tetrol $[Bu^tSi(OH)_2]_2O$ **8**.[6] While the average Si–O–Si angle of the siloxane linkage in **4** is only 141.9(2)°, the corresponding linkage is linear in **8** (180°) where molecules of **8** associate themselves in the form of hydrogen-bonded sheets in the solid state. By contrast, the three molecules of **4** in the asymmetric unit form a cage structure through intermolecular O–H···O hydrogen bonds as depicted in Fig. 1. There is very little difference between the terminal and bridging Si–O distances in **4**. In the molecular structure of **7** (Fig. 2), surprisingly the Si–O–Si siloxane linkage is linear as in the case of **8**. The Si–O bridging distance [1.595(1) Å] is slightly shorter than that found in **4**. The $SiMe_3$ and aryl substituents on the nitrogen exist in a *trans* orientation in this centrosymmetric molecule.

In order to investigate whether other siloxanes could be obtained using the same synthetic strategy, we varied the stoichiometry of the N_2H_4. Thus, the treatment of $RSiCl_3$ **1** with >6 equiv. of N_2H_4 results in the formation of cyclotrihydroxytrisiloxane, $[(2,6\text{-}Me_2C_6H_3)N(SiMe_3)Si(OH)O]_3$ **9**, the secondary condensation product of silanetriols (Scheme 4). Compound **9** has been characterised by EIMS (M^+ at m/z 759) and other spectroscopic and analytical data.† However, we were not able to obtain single crystals suitable for X-ray diffraction studies. The ^{29}Si NMR spectrum shows two peaks at δ −75.5



Scheme 2



7

Scheme 3

and −76.5 in a 2 : 1 integral ratio suggesting that the six-membered siloxane ring in **9** might exist in a boat conformation analogues to that observed for *trans*-cyclotriphosphazanes.[9] To our knowledge, **9** represents the first example of a cyclotrihydroxytrisiloxane, bearing free hydroxy groups on a six-membered siloxane ring.

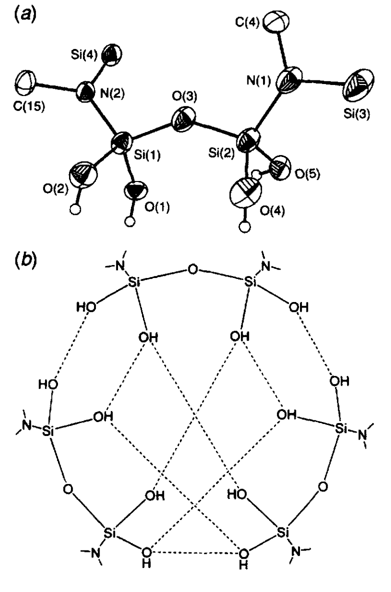


Fig. 1 (*a*) The core and (*b*) the schematic hydrogen-bonded cage structure of **4** [av. Si–O$_{\text{terminal}}$ 1.628 Å, av. Si–O$_{\text{bridging}}$ 1.621 Å, Si–O–Si 140.7(2)°]

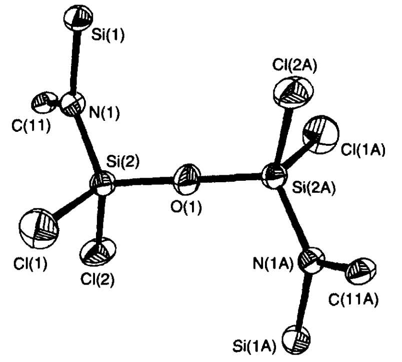
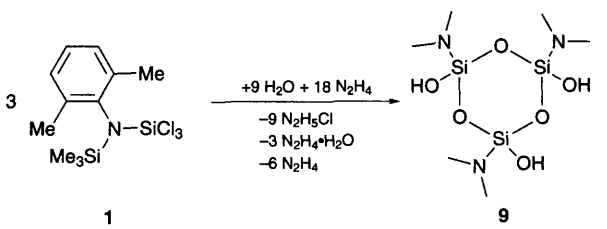


Fig. 2 The core structure of **7** in the solid state [Si–O 1.595(1) Å, av. Si–Cl 2.025 Å, Si–O–Si 180°]



Scheme 4

The (poly)hydroxy compounds described here are promising starting materials for the synthesis of multi-dimensional metallasiloxanes. Compound **9** especially would serve as a starting material for metal-containing siloxane polymers.

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Footnotes

† All the compounds yielded satisfactory analytical data. *Selected spectroscopic data*: **4**; IR [ν(Si–OH)] 3322, 3350, 3552 cm^{-1}, EIMS *m/z* 524 (M$^+$), ^{29}Si NMR (CDCl$_3$) δ −73.4 (SiO$_3$), 7.4 (SiMe$_3$). **5**; IR [ν(Si–OH)] 3320, 3350, 3587 cm^{-1}, EIMS *m/z* 552 (M$^+$), ^{29}Si NMR (CDCl$_3$) δ −73.4 (SiO$_3$), 6.9 (SiMe$_3$). **6**; IR [ν(Si–OH)] 3339, 3581 cm^{-1}, EIMS *m/z* 636 (M$^+$), ^{29}Si NMR (CDCl$_3$) δ −65.3 (SiO$_3$), 7.5 (SiMe$_3$). **7**; EIMS *m/z* 710 (M$^+$), ^{29}Si NMR (CDCl$_3$) δ −50.2 (SiOCl$_2$), 11.5 (SiMe$_3$). **9**; IR [ν(Si–OH)] 3291, 3587 cm^{-1}, EIMS *m/z* 759 (M$^+$), ^{29}Si NMR (CDCl$_3$) δ −75.5, −76.5 (2 : 1, SiO$_3$), 7.6, 7.9 (2 : 1, SiMe$_3$).

‡ *Crystal data*: **4**; $C_{22}H_{40}N_2O_5Si_4$, M = 524.92, monoclinic, space group $P2_1/c$, a = 24.787(5), b = 13.527(3), c = 27.633(6) Å, β = 93.65(3)°, U = 9246(3) Å^3, Z = 12, D_c = 1.196 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), T = 153 K, R = 0.0528, R_w = 0.1235 for 12010 reflections with $I > 2\sigma(I)$.

7; $C_{30}H_{52}Cl_4N_2OSi_4$, M = 710.90, monoclinic, space group $P2_1/c$, a = 8.362(5), b = 15.387(3), c = 14.717(6) Å, β = 97.68(3)°, U = 1876.6(7) Å^3, Z = 2, D_c = 1.258 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), T = 153 K, R = 0.0464, R_w = 0.0957 for 3273 reflections with $I > 2\sigma(I)$.

Common data: reflections were measured on a Stoe-Siemens-AED four-circle diffractometer. Full-matrix least-squares refinement on F^2 with all data using SHELXL-93 for **4** and SHELXL-96 for **7**. Hydrogen atoms included in calculated positions and refined using a riding model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/239.

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