2,2-Dihydroxy-methylcyclosiloxanes and other 2,2-difunctional methylcyclosiloxanes

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Abstract

Starting from 2,2-dichloro-methylcyclosiloxanes [$-OSiCl_2-(OSiMe_2)_n-$] (**1a–c**) [n: 1, 2, 3] the corresponding 2,2-dihydroxy-methylcyclosiloxanes [$-OSi(OH)_2-(OSiMe_2)_n-$] (**2a–c**), the 2,2-dimethoxy-methylcyclosiloxanes [$-OSi(OMe)_2-(OSiMe_2)_n-$] (**3a–c**), the 2,2-difluoro-methylcyclosiloxanes [$-OSiF_2-(OSiMe_2)_n-$] (**4a,b**) [n: 2, 3], the 2,2-dihydrido-methylcyclosiloxanes [$-OSiH_2-(OSiMe_2)_n-$] (**5a,b**) [n: 2, 3] and two spirosiloxanes [$-(OSiMe)_m-OSi-$][$-OSi-(OSiMe_2)_n-$] (**6a,b**) [m,n: **a**: 3, 1; **b**: 2, 3] have been synthesized and characterized by NMR-, MS and partly by IR spectroscopy. **2a** is stable in diluted solution only. **2b** forms a crystalline 1:1 adduct with H_2O characterized by X-ray analysis as a highly organized tube like structure. © 2001 Elsevier Science B.V. All rights reserved.

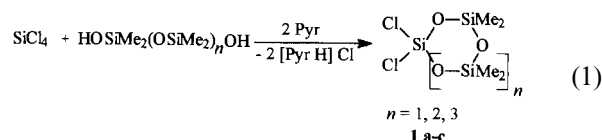*Keywords:* Cyclisations; Cyclosiloxanes; Silanols; Spirosiloxanes; X-ray crystal structures

1. Introduction

Continuing investigations on synthesis, reactivity and structure of silanols and siloxanols [1] we were interested in geminal methylcyclosiloxanediols. Such compounds exist up to now only with phenyl or *t*-butyl substituents at Si [2], probably due to their higher condensation stability.

According to our experiences in silanol synthesis it should be possible to synthesize the methylcyclosiloxanediols also from the corresponding 2,2-dichloro-cyclosiloxanes by improved methods of cautious hydrolysis [3]. The 2,2-dichloro-cyclosiloxanes are also suitable starting products for the synthesis of other geminal difunctional methylcyclosiloxanes.

2. Results and discussion

First we have reinvestigated the synthesis of 2,2-dichloro-methylcyclosiloxanes (**1a–c**) by the cyclocondensation of $SiCl_4$ with methylsiloxane-α,ω-diols Eq. (1).

$$SiCl_4 + HOSiMe_2(OSiMe_2)_nOH \xrightarrow[-2\,[\text{Pyr H}]\,Cl]{2\,\text{Pyr}} \quad (1)$$

$n = 1, 2, 3$
1 a–c

We could not reconfirm the results of Zachernyuk et. al [4] that sufficient yields could be obtained only with *p*-nitraniline as HCl-acceptor. We got yields up to 66% also with other amines (pyridine, Et_3N) depending only on a slow and strictly simultaneous reaction of equimolar amounts of the reactants under conditions according to the dilution principle.

Surprisingly we did not succeed in getting the corresponding 2-chloro-2-hydrido-methylcyclosiloxanes with $SiHCl_3$ as starting product instead of $SiCl_4$.

The 2,2-dichloro-cyclosiloxanes (**1a–c**) have been converted according to Scheme 1 to get other 2,2-difunctional methylcyclosiloxanes, preferably the cyclosiloxanediols.

The hydrolysis in the two phase system ether/water with ammonium carbamate as HCl acceptor gave quantitatively the expected cyclosiloxane-2,2-diols (**2a–c**). Whereas **2b** and **2c** could be separated as stable compounds, **2b** as crystals, **2c** as an oil, **2a** was stable in solution only. After evaporation of the solvent crystals of **2a** are formed, but they decompose within some

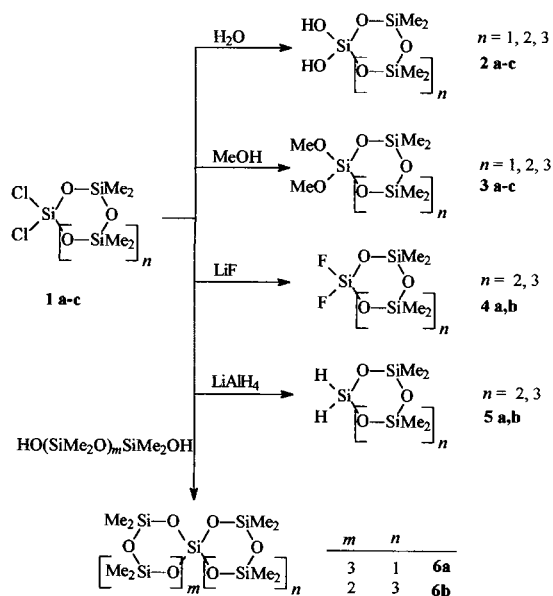* Corresponding author. Tel.: +49-381-4981755; fax: +49-381-4981763.

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minutes. This decomposition is not or not only a con-densation. The strained six membered siloxane ring is cleaved, indicated by the shift of the very characteristic ^{29}Si-NMR signals for the Me$_2$SiO-groups from $\delta = -8$ (cyclotrisiloxane) to values at about $\delta = -20$ for un-strained rings (compare the corresponding signals for **2b** and **2c**) or open chain siloxanes.

The structure of **2a–c** was confirmed preferably by ^{29}Si-NMR and IR-spectra completed by ^{1}H-, ^{13}C-NMR and MS data and for **2b** by X-ray diffraction.

The OH-stretching band position (v_{OH}) in diluted CCl$_4$-solution and the shift of this band at association of the diols with diethylether (Δv_{OH}) were determined, the (Δv_{OH}) as a measure of the relative acidity [5]. The results are given in Table 1 compared with the corre-sponding values for other silane- and siloxane-diols measured before [6].

While the v_{OH} are nearly constant the Δv_{OH} values increase with increasing number of siloxy-substituents at the Si(OH)$_2$ group. The cyclosiloxanediols have gen-erally higher Δv_{OH} than the noncyclic compounds.
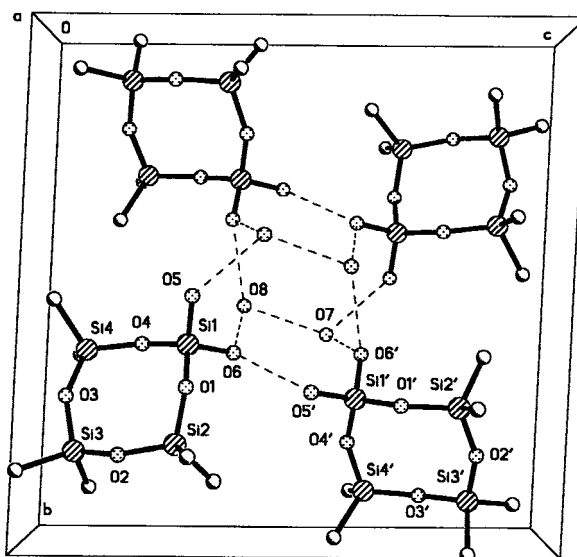

Fig. 1. Molecular structure of **2b** with two slightly different molecules and two molecules of water in the asymmetric unit connected via four H-bonds and crystallographic arrangement of the two asymmetric units in the unit cell connected via four additional H-bonds.

Within the cyclosiloxanediols the strained cyclotrisilox-anediol **2a** has the highest acidity.

The cyclotetrasiloxanediol **2b** is slightly soluble in water (0.02 M at 25°C). It crystallizes from aqueous solution as a 1:1 adduct with water in very fine needles. We got the same adduct from aqueous nitromethane solution in crystals well suited for an X-ray analysis giving the following results:

The asymmetric unit is formed by two slightly differ-ent siloxanediol molecules and two molecules of water, connected by four hydrogen bonds, one between silanol and silanol (271 pm), two between silanol and water (269, 272 pm) and one between water and water (278 pm), as shown in Fig. 1.

Two asymmetric units form the unit cell by inversion. The asymmetric units are connected with each other by four silanol–water hydrogen bonds (275 pm) forming a highly organized tube like structure with the water molecules and the Si–OH groups inside the tube as shown in Fig. 2.

Selected bond lengths and bond angles are given in Table 2. Both molecules of **2b** have slightly different Si–O–Si angles between 148 and 154°. All these angles are greater than for octamethylcyclotetrasiloxane (142.5°) [7].

The 2,2-dimethoxy-methylcyclosiloxanes **3a–c** were obtained using the common method for the alkoxysi-lane synthesis by the reaction of the corresponding 2,2-dichlorosilanes **1a–c** with two equivalents of methanol in diethylether using pyridine as HCl-accep-tor. All three compounds are liquids at room tempera-ture. The structure was confirmed by ^{29}Si- and ^{1}H-NMR as well as by MS data.

Scheme 1.

Table 1
Band position of the OH streching IR bands (v_{OH}) and OH band shift at association with diethyleher (Δv_{OH}) for **2a–c** and other siloxanediols

Compound	v_{OH} (cm^{-1})	Δv_{OH} (cm^{-1})
2a	3699	349
2b	3701	315
2c	3700	324
Me$_2$Si(OH)$_2$	3697	273
(Me$_3$SiO)MeSi(OH)$_2$	3699	290
(Me$_3$SiO)$_2$Si(OH)$_2$	3701	308

The preparation of the 2,2-difluoro-methylcyclosiloxane **4a,b** was realized by the reaction of the corresponding dichloro-compounds **1b,c** with LiF in tetrahydrofurane at room temperature. While these eight- resp. ten-membered rings are formed quantitatively we did not succeed with the preparation of the corresponding cyclotrisiloxane. Also at temperatures below 0°C Si–O cleavage was the preferred reaction due to the less stable Si–O–Si bonds in the strained ring. The unstrained cycles **4a,b** are stable at room temperature, but attempts at vacuum distillation gave partial decomposition above 40°C already.

The structure was confirmed by ^{19}F- and ^{29}Si-NMR as well as by mass spectroscopic data. The high field shifted ^{29}Si-NMR signals of the SiF_2 group ($d = -106.6$ for **4a**, $d = -108.0$ for **4b**) have the characteristic triplett structure for the direct Si–F coupling ($J = 164.5$ resp. 166.5 Hz).

The 2,2-dihydrido-methylcyclosiloxanes **5a,b** were obtained by the reaction of the dichloro-cyclosiloxanes **1b,c** with $LiAlH_4$ in tetrahydrofurane. As for the difluoro compounds it was impossible to get the corresponding cyclotrisiloxane due to the less stable Si–O–Si bond in the sixmembered ring. The structure was confirmed by ^{1}H and ^{29}Si-NMR, MS and IR data. The ^{29}Si-NMR signals of the SiH_2 groups ($\delta -50.6$ for **5a**, -53.8 for **5b**) have the characteristic triplet structure for the direct Si–H coupling ($J = 250.8$ resp. 248.9 Hz). The Si–H characteristic IR bands show a doublett structure due to the antisymmetric and symmetric SiH_2 stretching vibrations.

Using the same principle as for the preparation of **1a–c** the cyclocondensation of the 1.1-dichlorocyclosiloxanes with α,ω-siloxanediols should be an appropriate method for the synthesis of both symmetric and asymmetric spirosiloxanes (see Scheme 1). While some symmetric spirosiloxanes are already known [8] we prepared the asymmetric compounds **6a,b** with six- and ten-membered resp. eight- and ten-membered siloxane rings by this method. **6a** was obtained by reaction of **1a** with octamethyltetrasiloxane-1,7-diol and **6b** by reaction of **1c** with hexamethyltrisiloxane-1,5-diol. **6a,b** were characterized by ^{1}H-, ^{13}C- and ^{29}Si-NMR and MS.
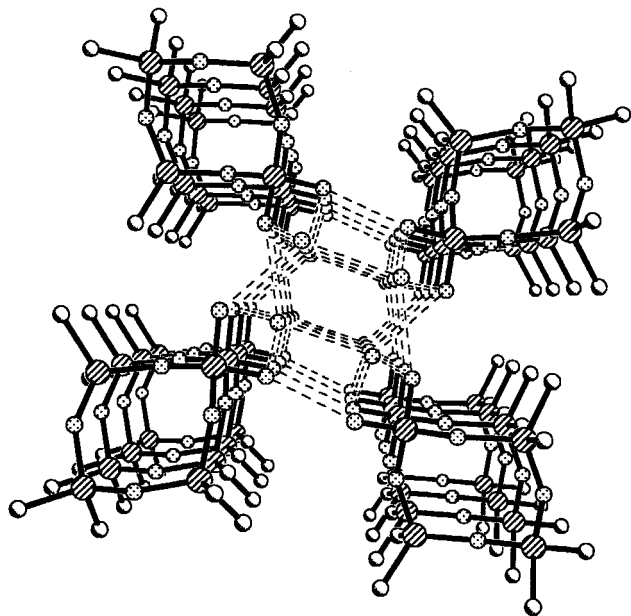

Fig. 2. Tube like arrangement of the **2b** molecules and water with the Si–OH groups and water inside the tube. View along the crystallographic *a*-axis.

Table 2
Selected bond lengths (Å) and bond angles (°) for the two molecules of **2b** in the asymmetric unit

	Molecule 1	Molecule 2
Bond lengths		
Si1–O1	1.600(2)	1.598(2)
Si2–O1	1.635(2)	1.624(2)
Si2–O2	1.618(2)	1.613(2)
Si3–O2	1.628(2)	1.605(2)
Si3–O3	1.624(3)	1.623(2)
Si4–O3	1.639(4)	1.614(2)
Si4–O4	1.617(2)	1.617(2)
Si1–O4	1.593(2)	1.602(2)
Si1–O5	1.609(2)	1.616(2)
Si1–O6	1.619(2)	1.617(2)
Bond angles		
Si1–O1–Si2	149.4(2)	148.3(2)
Si2–O2–Si3	148.4(2)	153.7(2)
Si3–O3–Si4	147.9(5)	153.0(2)
Si4–O4–Si1	152.3(2)	149.8(2)
H bonds		
O5'–H–O6	2.712(3)	
O6–H–O8	2.722(3)	
O6'–H–O7	2.688(3)	
O7–H–O8	2.784(3)	

3. Experimental

3.1. General

All operations except the chlorosiloxane hydrolysis were carried out in carefully dried solvents under argon. The methylsiloxane-α,ω-diols, $HOSiMe_2(OSiMe_2)_nOH$ ($n = 1–3$) were prepared according to procedures described previously [6]. IR: Nicolett 205. The v_{OH} for **2a–c** were detertmined in 0.01 M CCl_4-solutions and the Δv_{OH} in 0.01 CCl_4-solutions containing 0.25 M diethylether. NMR: Bruker AC 250 (250 MHz for ^{1}H, 235.3 MHz for ^{19}F) and ARX 400 (100.6 MHz for ^{13}C, 79.5 MHz for ^{29}Si) with tetramethylsilane resp. trichlorofluoromethane as internal standards. MS: Intectra AMD 402 (70 eV).

3.2. Synthesis of the 2,2-dichloro-methylcyclosiloxanes (1 a–c)

Approximately 0.1 mol of the corresponding methyl-siloxane-α,ω-diol, $HOSiMe_2(OSiMe_2)_nOH$ ($n = 1–3$) and one equivalent of $SiCl_4$ separately solved in 100 ml ether were simultaneously given to a stirred solution of 2.02 equivalents of pyridine in 700 ml ether in the course of 1 h. After filtration of the pyridine hydrochloride and evaporation of ca. 90% of the ether 100 ml of pentane were added. Residual hydrochloride was filtered, the solvent was evaporated. The dichlorocyclosiloxanes were separated by Kugelrohr distillation resp. sublimation.

1a: 16.5 g (99 mmol) of $SiCl_4$ and 16.4 g (99 mmol) of 1,3-hydroxy-tetramethyldisiloxanediol gave after sublimation (75°C at 20 mbar) 10.4 g (40%) of a crystalline product, m.p. 66°C. ^{1}H-NMR (C_6D_6): δ 0.51 (s, $2(CH_3)_2Si$, 12H). ^{13}C-NMR (C_6D_6): δ 0.17 ($2(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): $\delta = -60.6$ ($SiCl_2$), -3.5 ($2(CH_3)_2Si$). MS (m/z, %): 247 (100) [$M^+ - CH_3$]. Anal. Calc. for $C_4H_{12}O_3Cl_2Si_3$ (263.3): C, 18.25; H, 4.59. Found: C, 18.16; H, 4.39%.

1b: 16 g (95 mmol) of $SiCl_4$ and 22.8 g (95 mmol) of 1,3-dihydroxy-hexamethyl-trisiloxane gave after distillation (68°C at 5 mbar) 14.9 g (66%) of a crystalline product, mp. 30°C. ^{1}H-NMR (C_6D_6): δ 0.03 (s, $(CH_3)_2Si$, 6H), 0.10 (s, $2(CH_3)_2Si$, 12H). ^{13}C-NMR (C_6D_6): δ 0.19 (2 $(CH_3)_2Si$), 0.57 ($(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): δ -60.6 ($SiCl_2$), -17.6 (Me_2Si), -14.5 (2 Me_2Si). MS (m/z, %): 321 (66) [$M^+ - CH_3$], 301 (100) [$M^+ - Cl$]. Anal. Calc. for $C_6H_{18}O_4Cl_2Si_4$ (337.5): C 21.36; H 5.38. Found: C 21.66; H 5.20%.

1c: 16.5 g (95 mmol) of $SiCl_4$ and 29.8 g (95 mmol) of 1,5-dihydroxy-octamethyltetrasiloxane gave after distillation (85–87°C at 1.7 mbar) 16 g (41%) of a colourless liquid. ^{1}H-NMR (C_6D_6): δ 0.14 (s, $2(CH_3)_2Si$, 12H), 0.17 (s, $2(CH_3)_2Si$, 12H). ^{13}C-NMR (C_6D_6): δ 0.33 (2 $(CH_3)_2Si$), 0.88 ($2(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): δ -73.6 ($SiCl_2$), -20.3 (2 Me_2Si), -16.7 ($2Me_2Si$). MS (m/z, %): 395 (59) [$M^+ - CH_3$], 287 (100) [$M^+ - Si(CH_3)_3$, $-CH_3Cl$]. Anal. Calc. for $C_8H_{24}O_5Cl_2Si_4$ (411.6): C 23.34; H 5.88. Found: C 23.36; H 6.10%.

3.3. Synthesis of the 2,2-dihydroxy-methylcyclosiloxanes (2a–c)

Approximately 10 mmol of the corresponding dichlorocyclosiloxane **1a–c** solved in 10 ml ether were added dropwise within 15 min to a well stirred mixture of 35 ml ether, 35 ml water saturated with NaCl and 1.2 equivalents of ammoniumcarbaminate. After separation of the ether layer, two times extraction of the water layer with 20 ml ether and drying the unified ether solutions with Na_2SO_4 the ether was removed by distillation in vacuo. The remaining products are the diols **2a–c**.

2a: 2.6 g (9.9 mmol) of **1a** gave 2.2 g (97%) of the crystalline diol which decomposes within some minutes but can be stored in 1 M solutions (diethylether, benzene, CCl_4) for a longer time. IR: see Table 1. ^{1}H-NMR (C_6D_6): δ 0.22 (s, 2 $(CH_3)_2Si$, 12H), 5.05 (s, $Si(OH)_2$, 2H). ^{13}C-NMR (C_6D_6): δ 1.28 ($2(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): δ -84.0 ($Si(OH)_2$), -8.2 ($2(CH_3)_2Si$).

2b: 3.7 g (11 mmol) of **1b** gave 2.9 g (88%) of the crystalline diol, m.p. 41°C. IR(CCl_4 resp. CCl_4/ether): see Table 1. ^{1}H-NMR (C_6D_6): δ 3.56 (s, $Si(OH)_2$, 2H), 0.20 (s, $(CH_3)_2Si$, 6H), 0.26 (s, $2(CH_3)_2Si$, 12H). ^{13}C-NMR (C_6D_6): δ 0.63 ($2(CH_3)_2Si$), 0.79 ($(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): δ -88.8 ($Si(OH)_2$), -18.4 (Me_2Si), -17.1 ($2(CH_3)_2$). MS (m/z, %): 301 (100) [$M^+ + H$], 283 (78) [$M^+ - OH$]. Anal. Calc. for $C_6H_{20}O_6Si_4$ (300.6): C 23.98; H 6.71. Found: C 24.11; H 6.67%.

2c: 4.1 g (10 mmol) of **1c** gave 3.5 g (93%) of the liquid diol. − IR (CCl_4 resp. CCl_4/ether): see Table 1. ^{1}H-NMR (C_6D_6): δ 0.21 (s, $2(CH_3)_2Si$, 12H), 0.28 (s, $2(CH_3)_2Si$, 12H), 3.69 (s, OH, 2H). ^{13}C-NMR (C_6D_6): δ 0.81 ($2(CH_3)_2Si$), 1.02 ($2(CH_3)_2Si$). ^{29}Si-NMR (C_6D_6): δ -89.9 ($Si(OH)_2$), -20.7 ($2Me_2Si$), -19.3 ($2Me_2Si$). MS (m/z, %): 375 (42) [$M^+ + H$], 357 (100) [$M^+ - OH$]. Anal. Calc. for $C_8H_{26}O_7Si_5$ (374.7): C 25.64; H 6.99. Found: C 25.65; H 6.88%.

3.4. Synthesis of the 2.2-dimethoxy-methylcyclosiloxanes (3a–c)

A total of 2.1 equivalents of methanol in 10 ml ether were added dropwise to a stirred solution of ca. 10 mmol of the corresponding 2,2-dichlorocyclosiloxane **1a–c** and 2.1 equivalents of pyridine in 30 ml ether. After 30 min. stirring the pyridine hydrochloride was separated by filtration, and the ether was removed by distillation. The remaining liquids were estimated as the expected dimethoxy compounds **3a–c** in high purity. Distillation in vacuo was possible but did not improve the purity.

3a: 2.6 g (9.9 mmol) of **1a** gave 2.4 g (95%) of a colourless liquid, b.p. 100°C (10 mbar). ^{1}H-NMR (C_6D_6): δ 0.16 (s, $2(CH_3)_2Si$, 12H), 3.47 (s, $2CH_3O$, 6H). ^{13}C-NMR (C_6D_6): δ 0.58 ($(CH_3)_2Si$), 50.72 (CH_3O). ^{29}Si-NMR (C_6D_6): δ -86.3 ($(CH_3O)_2Si$), -6.3 (Me_2Si). MS (m/z, %): Anal. Calc. for $C_6H_{18}O_5Si_3$ (254.5): C, 28.32; H 7.13. Found: C, 28.51; H 7.04%.

3b: 3.4 g (10 mmol) of **1b** gave 3.0 g (91%) of a colourless liquid, b.p. 50°C (0.8 mbar). ^{1}H-NMR (C_6D_6): δ 0.19 (s, $(CH_3)_2Si$, 6H), 0.21 (s, $2(CH_3)_2Si$, 12H), 3.49 (s, OCH_3, 6H). ^{13}C-NMR (C_6D_6): δ 0.58 ($2(CH_3)_2Si$), 0.79 ($(CH_3)_2Si$), 50.74 (OCH_3). ^{29}Si-NMR (C_6D_6): δ -91.4 ($(CH_3O)_2Si$), -18.6 (Me_2Si), -17.3 ($2Me_2Si$). MS (m/z, %): 313 (100) [$M^+ - CH_3$], 283 (29) [$M^+ - CH_3OCH_2$]. Anal. Calc. for $C_8H_{24}O_6Si_4$ (328.6): C 29.24; H 7.36. Found: C, 29.33; H, 7.42%.

3c: 4.1 g (10 mmol) of **1c** gave 3.7 (92%) of a colourless liquid, b.p. 70°C (0.5 mbar). ^{1}H-NMR (C_6D_6): δ 0.19 (s, 2(CH$_3$)$_2$Si, 12H), 0.23 (s, 2(CH$_3$)$_2$Si, 12H), 3.48 (s, OCH$_3$, 6H). ^{13}C-NMR (C_6D_6): δ 0.72 (2(CH$_3$)$_2$Si), 0.98 (2(CH$_3$)$_2$Si), 50.68 (OCH$_3$). ^{29}Si-NMR (C_6D_6): δ −92.5 ((CH$_3$O)$_2$Si), −21.09 (2Me$_2$Si), −19.7 (2Me$_2$Si). MS (m/z, %): 387 (100) [M$^+$ − CH$_3$]. Anal. Calc. for C$_{10}$H$_{30}$O$_7$Si$_5$ (402.8): C, 29.85; H, 7.51. Found: C, 29.81; H, 7.49%.

3.5. Synthesis of the 2,2-difluoro-methylcyclosiloxanes (4a,b)

A mixture of ca. 10 mmol of the corresponding dichlorocyclosiloxane **1b,c**, 2.3 equivalents of LiF and 50 ml THF was stirred under reflux for 12 h. After removing the solvent in vacuo 35 ml of ether were added. LiCl was filtrated, and the ether was removed at room temperature in vacuo. The remaining colourless liquids were estimated as the desired compounds **4a,b**. Attempts of distillation in vacuo gave no higher purity (ca. 95%) due to partial decomposition above 40°C.

4a: 3.4 g (10 mmol) of **1b** gave 2.8 g (92%) of a colourless liquid. ^{1}H-NMR (C_6D_6): δ 0.08 (s, (CH$_3$)$_2$Si, 6H), 0.09 (s, 2(CH$_3$)$_2$Si, 12H). ^{13}C-NMR (C_6D_6): δ −0.01 (2(CH$_3$)$_2$Si), 0.47 ((CH$_3$)$_2$Si). ^{29}Si-NMR (C_6D_6): δ −106.6 (t, $J = 164.5$ Hz, SiF$_2$), −17.7 (Me$_2$Si), −14.2 (2Me$_2$Si). ^{19}F-NMR (235.3 MHz), (C_6D_6): δ −151.2. MS (m/z, %): 304 (11) [M$^+$], 285 (14) [M$^+$ − F). Anal. Calc. for C$_6$H$_{18}$F$_2$O$_4$Si$_4$ (304.54): C, 23.66; H, 5.69. Found: C, 23.96; H, 5.84%.

4b: 4.1 g (10 mmol) of **1c** gave 3.5 g (92%) of a colourless liquid. ^{1}H-NMR (C_6D_6): δ 0.118 (s, 2(CH$_3$)$_2$Si, 12H), 0.121 (s, 2(CH$_3$)$_2$Si, 12H). ^{13}C-NMR(C_6D_6): δ 0.13 (2(CH$_3$)$_2$Si), 0.74 (2(CH$_3$)$_2$Si). ^{29}Si-NMR (C_6D_6): δ −108.0 (t, $^1J = 166.5$ Hz, SiF$_2$), −20.1 (Me$_2$Si), −16.5 (2Me$_2$Si). ^{19}F-NMR (235.3 MHz), (C_6D_6): δ −150.5. MS (m/z, %): 378 (5) [M$^+$], 663 (14) [M$^+$ − CH$_3$], 73 (100) [Si(CH$_3$)$_3^+$]. Anal. Calc. for C$_8$H$_{24}$F$_2$O$_5$Si$_5$ (378.69: C, 25.37; H, 6.39. Found: C, 25.56; H, 6.60%.

3.6. Synthesis of the 2,2-dihydrido-methylcyclosiloxanes (5a,b)

A mixture of ca. 10 mmol of the corresponding chlorosilane **1b,c** and 5.1 mmol of LiAlH$_4$ and 50 ml tetrahydrofurane was stirred 12 h under reflux. After removing the THF at room temperature, addition of 35 ml pentane, filtration and distillation of the pentane in vacuo remains a colourless oil.

5a: 3.3 g (9.8 mmol) of **1b** gave 2.4 g (91%) of a colourless liquid. IR (cap.) ν_{OH} 2184/2168 cm^{-1} (SiH$_2$ strech). ^{1}H-NMR(C_6D_6): δ 0.16 (s, (CH$_3$)$_2$Si, 6H), 0.17 (s, 2(CH$_3$)$_2$Si, 12H), 4.96 (s, SiH$_2$, 2H). ^{13}C-NMR (C_6D_6): δ 0.33 (2(CH$_3$)$_2$Si), 0.74 ((CH$_3$)$_2$Si). ^{29}Si-NMR

(C_6D_6): δ −51.6 (t, $^1J = 250.7$ Hz, SiH$_2$), −18.8 (Me$_2$Si), −16.5 (2Me$_2$Si). MS (m/z, %): 267 (11) [M$^+$ − H], 253 (100) [M$^+$ − CH$_3$], 73 (19) [Si(CH$_3$)$_3^+$]. Anal. Calc. for C$_6$H$_{20}$O$_4$Si$_4$ (268.56): C, 26.83; H, 7.51. Found: C, 27.04; H, 7.46%.

5b: 4.1 g (10 mmol) of **1c** gave 3.2 g (94%) of a colourless liquid. IR (cap.) ν_{OH} 2179/2166 cm^{-1} (SiH$_2$ stretch). ^{1}H-NMR (C_6D_6): δ 0.17 (s, 2(CH$_3$)$_2$Si, 12H), 0.18 (s, 2(CH$_3$)$_2$Si, 12H), 4.96 (s, SiH$_2$, 2H). ^{13}C-NMR (C_6D_6): δ 0.65 (2(CH$_3$)$_2$Si), 0.94 (2(CH$_3$)$_2$Si). ^{29}Si-NMR (C_6D_6): δ −53.8 (t, $^1J = 250.7$ Hz, SiH$_2$), −20.9 (2 Me$_2$Si), −18.5 (2Me$_2$Si). MS (m/z, %): 341 (100) [M$^+$ − H], 327 (50) [M$^+$ − CH$_3$], 73 (25) [Si(CH$_3$)$_3^+$]. Anal. Calc. for C$_8$H$_{26}$O$_5$Si$_5$ (342.71): C, 28.04; H, 7.65. Found: C, 28.47; H, 7.73%.

3.7. Synthesis of the Spirosiloxanes (6a,b)

Approx. 5 mmol of a 2,2-dichloro-methylcyclosiloxane **1a,c** and one equivalent of a corresponding methylsiloxane-α,ω-diol, both solved separately in 25 ml diethylether, were dropped simultaneously to a stirred solution of two equivalents of pyridine in 50 ml ether. After filtration of the pyridinehydrochloride and evaporation of the ether 30 ml of pentane were added. The residual hydrochloride was removed by filtration. After evaporation of the pentane a Kugelrohr destillation in vacuo allowed the spirosiloxanes to separate as colourless oils.

6a: 2.6 g (9.9 mmol) of **1a** and 3.1 g (9.9 mmol) of octamethyltetrasiloxane-α,ω-diol gave 2 g (40%) of a colourless oil, b.p. 65°C (0.06 mbar). ^{1}H-NMR (C_6D_6): δ 0.19 (s, 2(CH$_3$)$_2$Si, 12H), 0.20 (s, 2(CH$_3$)$_2$Si, 12H), 0.24 (s, 2(CH$_3$)$_2$Si, 12H). ^{13}C-NMR (C_6D_6): δ 0.76 (2(CH$_3$)$_2$Si), 0.78 (2(CH$_3$)$_2$Si), 0.99 (2(CH$_3$)$_2$Si). ^{29}Si-NMR (C_6D_6): δ −102.1 (SiO$_4$), −21.1 (2Me$_2$Si), −19.9 (2Me$_2$Si), −7.0 (2Me$_2$Si in the six-membered ring). MS (m/z, %): 489 (57) [M$^+$ − CH$_3$]. Anal. Calc. for C$_{12}$H$_{36}$O$_8$Si$_7$ (505.01): C, 28.54; H, 7.19. Found: C, 28.59; H, 7.06%.

6b: 4.1 g (10 mmol) of **1c** and 2.4 g (10 mmol) of hexamethyltrisiloxane-α,ω-diol gave 4 g (70%) of a colourless oil, b.p. 70°C (0.01 mbar). ^{1}H-NMR (C_6D_6): δ 0.19 (s, (CH$_3$)$_2$Si, 6H), 0.20 (s, 2(CH$_3$)$_2$Si, 12H), 0.23 (s, 2(CH$_3$)$_2$Si, 12H), 0.25 (s, 2(CH$_3$)$_2$Si, 12H). ^{13}C-NMR (C_6D_6): δ 0.72 (2(CH$_3$)$_2$Si), 0.85 (3(CH$_3$)$_2$Si), 1.02 (2(CH$_3$)$_2$Si). ^{29}Si-NMR (C_6D_6): δ −107.2 (SiO$_4$), −21.1 (2Me$_2$Si), −20.4 (2Me$_2$Si), −18.8 (Me$_2$Si), −18.1 (2Me$_2$Si). MS (m/z, %): 563 (50) [M$^+$ − CH$_3$]. Anal. Calc. for C$_{14}$H$_{42}$O$_9$Si$_8$ (579.16): C, 29.03; H, 7.31. Found: C, 29.11; H, 7.26%.

3.8. Crystal structure determination of 2b

The data collection was done on a STOE IPDS with graphite monochromator using Mo−K$_\alpha$ radiation. The

structure was solved with direct methods (SHELXS-86, G.M. Sheldrick, SHELXS-86, Universität Göttingen, 1986) and refined by the full-matrix least-squares method of SHELXL-97 (G.M. Sheldrick, SHELXL-97, Universität Göttingen, 1997). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions and refined using the riding model.

Further data: temperature: 200 K; wavelength: 0.71073 Å; crystal system: triclinic; space group: $P\bar{1}$; unit cell dimensions: $a = 6.6850(13)$ Å, $b = 16.020(3)$ Å, $c = 16.227(3)$ Å, $\alpha = 92.62(3)°$, $\beta = 90.43(3)°$, $\gamma = 90.76(3)°$; $V = 1735.8(6)$ Å^3; $Z = 4$; D_{calc}: 1.219 g cm^{-3}; absorption coefficient: 0.357 mm^{-1}; $F(000) = 680$; crystal size: $0.45 \times 0.38 \times 0.3$ mm^3; Θ range for data collection: 2.51–22.00°; index range: $-7 \leq h \leq 6$, $-16 \leq k \leq 16$, $0 \leq l \leq 17$; reflections collected: 4052; independent reflections: 4052; data/restraints/parameters: 4052/0/328; goodness-of-fit on F^2: 0.946; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0342$, $wR_2 = 0.0804$; R indices (all data): $R_1 = 0.0484$, $wR_2 = 0.0835$; largest difference peak and hole: $0.270/-0.166$ e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139866. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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