

# Improved Synthesis of HOPh<sub>2</sub>Si-SiPh<sub>2</sub>OH and Crystal Structure Analyses of HOPh<sub>2</sub>Si-SiPh<sub>2</sub>OH and HOPh<sub>2</sub>Si-SiPh<sub>2</sub>-O-Ph<sub>2</sub>Si-SiPh<sub>2</sub>OH·1/2C<sub>6</sub>H<sub>6</sub>

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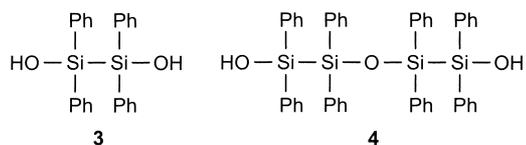
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Disilanes, Silanols, Siloxanes

1,1,2,2-Tetraphenyldisilane-1,2-diol (**3**) was prepared in a two-step synthesis, starting from 1,2-bis(diethylamino)-1,1,2,2-tetraphenyldisilane (**1**). Treatment of **1** with acetyl chloride yielded 1,2-dichloro-1,1,2,2-tetraphenyldisilane (**2**), which upon hydrolysis gave **3** (total yield 83%). Compounds **2** and **3** were characterized by elemental analyses (C, H) and solution NMR experiments (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si; CDCl<sub>3</sub>). In addition, compound **1** and its condensation product, 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane (**4**; studied as the hemibenzene solvate **4**·1/2C<sub>6</sub>H<sub>6</sub>), were structurally characterized by single-crystal X-ray diffraction.

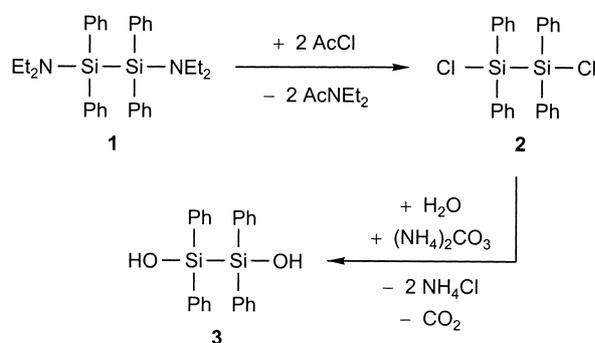
## Introduction

1,1,2,2-Tetraphenyldisilane-1,2-diol (**3**) is a versatile difunctional building block for the synthesis of siloxane systems with Si-Si bonds (for a recent example, see ref. [1]). In 1961 Winkler and Gilman reported on the first synthesis of compound **3**, starting from chlorodiphenylsilane and using a coupling reaction with magnesium to form the Si-Si bond [Ph<sub>2</sub>Si(H)Cl → HPh<sub>2</sub>Si-SiPh<sub>2</sub>H → ClPh<sub>2</sub>Si-SiPh<sub>2</sub>Cl → HOPh<sub>2</sub>Si-SiPh<sub>2</sub>OH] [2]. As this synthetic method is characterized by unsatisfactory yields and limited reliability, we have worked out an alternative approach for the synthesis of **3**, using a method for the Si-Si bond formation developed by Tamao *et al.* [3]. We report here on an improved and reliable synthesis of compound **3** and the crystal structure analyses of **3** and its condensation product 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane (**4**; studied as the hemibenzene solvate **4**·1/2C<sub>6</sub>H<sub>6</sub>).



## Results and Discussion

The title compound **3** was prepared according to Scheme 1 in a two-step synthesis, starting



Scheme 1.

from 1,2-bis(diethylamino)-1,1,2,2-tetraphenyldisilane (**1**) [3, 4]. Thus, treatment of **1** with acetyl chloride in dichloromethane afforded 1,2-dichloro-1,1,2,2-tetraphenyldisilane (**2**) (yield 89%), which upon hydrolysis in a mixture of dichloromethane, diethyl ether, water, and ammonium carbonate gave the disilane diol **3** (yield 93%; total yield 83%). Compounds **2** and **3** were isolated as crystalline solids, and their identities were established by elemental analyses (C, H) and solution NMR studies (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si; CDCl<sub>3</sub>). In addition, **3** and its condensation product **4** (studied as the hemibenzene solvate **4**·1/2C<sub>6</sub>H<sub>6</sub>) were structurally characterized by single-crystal X-ray diffraction. Compound **4**·1/2C<sub>6</sub>H<sub>6</sub> [2] was isolated in minor amounts as a by-product in the crystallization of **3**.

	<b>3</b>	<b>4·1/2C<sub>6</sub>H<sub>6</sub></b>
Empirical formula	C <sub>24</sub> H <sub>22</sub> O <sub>2</sub> Si <sub>2</sub>	C <sub>51</sub> H <sub>45</sub> O <sub>3</sub> Si <sub>4</sub>
Formula mass [g mol <sup>-1</sup> ]	398.60	818.23
Collection <i>T</i> [K]	173(2)	173(2)
λ(Mo-K <sub>α</sub> ) [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group (no.)	<i>P</i> $\bar{1}$ (2)	<i>C</i> 2/ <i>c</i> (15)
<i>a</i> [Å]	13.229(3)	23.502(5)
<i>b</i> [Å]	14.664(3)	16.755(3)
<i>c</i> [Å]	19.394(4)	24.508(5)
α [°]	103.96(3)	90
β [°]	100.83(3)	110.99(3)
γ [°]	113.64(3)	90
<i>V</i> [Å <sup>3</sup> ]	3168.9(11)	9011(3)
<i>Z</i>	6	8
<i>D</i> (calcd.) [g cm <sup>-3</sup> ]	1.253	1.206
μ [mm <sup>-1</sup> ]	0.185	0.173
<i>F</i> (000)	1260	3448
Crystal dimensions [mm]	0.2×0.2×0.2	0.4×0.3×0.3
2θ Range [deg]	5.74–52.86	4.16–46.54
Index ranges	–16 ≤ <i>h</i> ≤ 16, –18 ≤ <i>k</i> ≤ 17, –24 ≤ <i>l</i> ≤ 24	–26 ≤ <i>h</i> ≤ 26, –18 ≤ <i>k</i> ≤ 18, –27 ≤ <i>l</i> ≤ 27
No. of collected reflections	46146	35777
No. of independent reflections	12536	6457
<i>R</i> <sub>int</sub>	0.0387	0.0759
No. of reflections used	12536	6457
No. of restraints	6	4
No. of parameters	775	536
<i>S</i> <sup>[a]</sup>	0.888	1.009
Weight parameters <i>a/b</i> <sup>[b]</sup>	0.0442/0.0000	0.0554/0.5681
<i>R</i> 1 <sup>[c]</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0419	0.0360
<i>wR</i> 2 <sup>[d]</sup> (all data)	0.0893	0.0934
Max./min. residual electron density [e Å <sup>-3</sup> ]	+0.319/–0.290	+0.285/–0.185

Table 1. Crystal data and experimental parameters for the crystal structure analyses of **3** and **4·1/2C<sub>6</sub>H<sub>6</sub>**.

<sup>[a]</sup>  $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{0.5}$ ; *n* = no. of reflections; *p* = no. of parameters; <sup>[b]</sup>  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , with  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ ; <sup>[c]</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>[d]</sup>  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{0.5}$ .

Compound **3** crystallizes in the space group *P* $\bar{1}$ , with three molecules in the asymmetric unit (molecules **3A**, **3B**, and **3C**). Compound **4·1/2C<sub>6</sub>H<sub>6</sub>** crystallizes in the space group *C*2/*c*, with one half each of molecules **4A** and **4B** and one half of a benzene molecule in the asymmetric unit. The crystal data and the experimental parameters used for the crystal structure analyses of **3** and **4·1/2C<sub>6</sub>H<sub>6</sub>** are summarized in Table 1. The structures of molecules **3A**, **3B**, **3C**, **4A**, and **4B** are depicted in Figures 1–4.

The Si–Si (Si–O) distances of **3** are in the range 2.3617(9) – 2.3790(11) Å [1.6482(19) – 1.6584(17) Å], and the Si–C bond lengths amount to 1.864(2) – 1.8808(19) Å. All silicon atoms are tetrahedrally coordinated, with bond angles at the silicon atoms in the range 101.42(8) – 117.53(7)° (for crystal structures of other disilane-1,2-diols, see refs. [5] and [6]). The conformations of the three

crystallographically different molecules are characterized by gauche arrangements, with O–Si–Si–O dihedral angles amounting to –68.56(10)° (**3A**), –70.56(11)° (**3B**), and –66.71(11)° (**3C**). The three conformations differ mainly in the arrangement of their phenyl groups (different degrees of torsion around the respective Si–C bonds).

The crystal structure of **3** is characterized by a complex one-dimensional hydrogen bonding system with six intermolecular O–H⋯O interactions along the base vector [00 1] (Table 2, Fig. 5). All six OH groups are involved as donor functions, and the oxygen atoms O1, O2 (2-fold), O3, O4, and O6 act as acceptor atoms. These hydrogen bonds lead to an infinite tube-like arrangement of the molecules in the crystal, with the hydrophilic SiOH groups inside and the hydrophobic phenyl groups outside the tube.

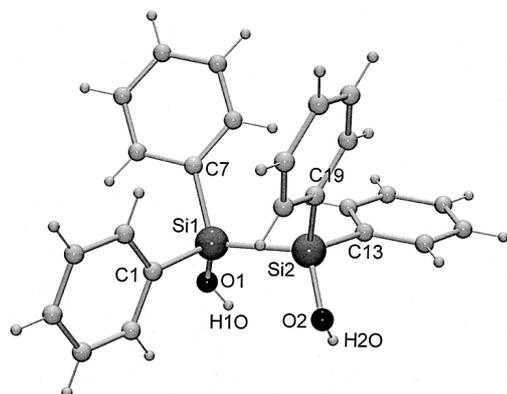


Fig. 1. Structure of molecule **3A** in the crystal of **3**. Selected distances [Å] and angles [°] (standard deviations in parentheses): Si1-Si2 2.3708(10), Si1-O1 1.6584(17), Si1-C1 1.869(3), Si1-C7 1.8808(19), Si2-O2 1.6544(15), Si2-C13 1.871(3), Si2-C19 1.871(2); Si2-Si1-O1 110.64(6), Si2-Si1-C1 111.89(7), Si2-Si1-C7 110.39(7), O1-Si1-C1 106.78(10), O1-Si1-C7 110.49(9), C1-Si1-C7 106.51(10), Si1-Si2-O2 110.56(7), Si1-Si2-C13 112.26(7), Si1-Si2-C19 106.89(7), O2-Si2-C13 109.15(9), O2-Si2-C19 107.73(9), C13-Si2-C19 110.13(10).

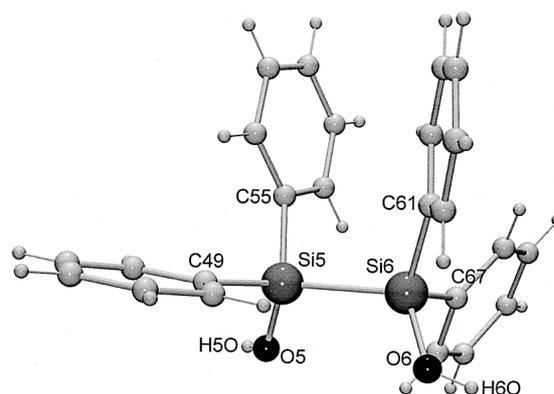


Fig. 3. Structure of molecule **3C** in the crystal of **3**. Selected distances [Å] and angles [°] (standard deviations in parentheses): Si5-Si6 2.3617(9), Si5-O5 1.6545(15), Si5-C49 1.864(2), Si5-C55 1.869(2), Si6-O6 1.6482(19), Si6-C61 1.877(2), Si6-C67 1.873(2); Si6-Si5-O5 109.64(7), Si6-Si5-C49 117.24(7), Si6-Si5-C55 101.42(8), O5-Si5-C49 108.42(9), O5-Si5-C55 111.23(9), C49-Si5-C55 108.73(10), Si5-Si6-O6 114.80(7), Si5-Si6-C61 107.61(7), Si5-Si6-C67 103.77(7), O6-Si6-C61 108.36(9), O6-Si6-C67 109.15(10), C61-Si6-C67 113.23(10).

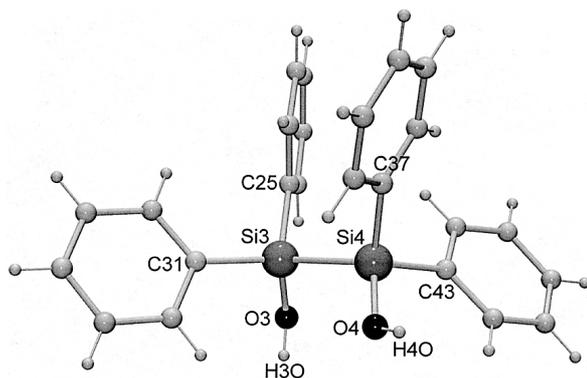


Fig. 2. Structure of molecule **3B** in the crystal of **3**. Selected distances [Å] and angles [°] (standard deviations in parentheses): Si3-Si4 2.3790(11), Si3-O3 1.6494(18), Si3-C25 1.877(2), Si3-C31 1.879(2), Si4-O4 1.6526(17), Si4-C37 1.876(2), Si4-C43 1.880(2); Si4-Si3-O3 108.58(7), Si4-Si3-C25 104.61(7), Si4-Si3-C31 117.53(7), O3-Si3-C25 108.57(10), O3-Si3-C31 108.58(9), C25-Si3-C31 108.64(10), Si3-Si4-O4 114.23(6), Si3-Si4-C37 111.57(7), Si3-Si4-C43 106.45(7), O4-Si4-C37 106.23(9), O4-Si4-C43 108.85(10), C37-Si4-C43 109.44(9).

The Si-Si (Si-O) distances of **4**·1/2C<sub>6</sub>H<sub>6</sub> are in the range 2.3510(9) - 2.3527(9) Å [1.6277(7) - 1.6502(15) Å], and the Si-C bond lengths amount to 1.867(2) - 1.873(2) Å. All silicon atoms are tetrahe-

drally coordinated, with bond angles at the silicon atoms in the range 103.62(6) - 116.31(7)° (for the crystal structure of a related cyclic condensation product, see ref. [7]). The conformations of the two crystallographically different molecules can each be described as eight-membered rings, including one of the two OH hydrogen atoms.

Attempts to localize the OH hydrogen atoms in the difference Fourier synthesis failed. Thus, the O-H distances were constrained in the refinement to result in a chemically acceptable hydrogen-bonding situation. Due to symmetry requirements of the unit cell, the OH hydrogen atoms are disordered on two equally occupied positions. The hydrogen-bonding system depicted in Fig. 4 represents one of the two possible arrangements (intramolecular O2A-H2OD...O2 and O4-H4OB...O4A interactions as well as intermolecular O2-H2OA...O4 and O4A-H4OC...O2A interactions; second arrangement: intramolecular O2-H2OB...O2A and O4A-H4OD...O4 interactions as well as intermolecular O2A-H2OC...O4A and O4-H4OA...O2 interactions). As a result, this hydrogen-bonding system leads to the formation of dimers of **4A** and **4B** in the crystal of **4**·1/2C<sub>6</sub>H<sub>6</sub>.

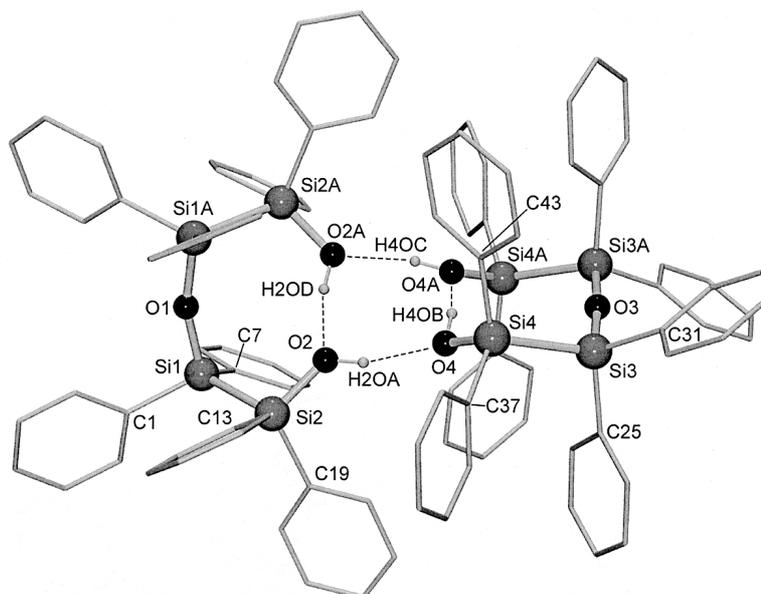


Fig. 4. Structures of molecules **4A** and **4B** in the crystal of **4**·1/2C<sub>6</sub>H<sub>6</sub> (phenyl groups represented as stick models for clarity). Selected distances [Å] and angles [°] (standard deviations in parentheses) for **4A**: Si1-Si2 2.3510(9), Si1-O1 1.6277(7), Si1-C1 1.867(2), Si1-C7 1.871(2), Si2-O2 1.6492(16), Si2-C13 1.869(2), Si2-C19 1.871(2); Si2-Si1-O1 105.03(6), Si2-Si1-C1 116.31(7), Si2-Si1-C7 111.98(7), O1-Si1-C1 105.17(10), O1-Si1-C7 110.09(8), C1-Si1-C7 107.92(9), Si1-Si2-O2 104.23(6), Si1-Si2-C13 111.37(7), Si1-Si2-C19 115.60(7), O2-Si2-C13 109.43(10), O2-Si2-C19 108.96(9), C13-Si2-C19 107.14(9), Si1-O1-Si1A 161.50(14). Data for **4B**: Si3-Si4 2.3527(9), Si3-O3 1.6307(8), Si3-C25 1.873(2), Si3-C31 1.871(2), Si4-O4 1.6502(15), Si4-C37 1.867(2), Si4-C43 1.871(2); Si4-Si3-O3 108.25(7), Si4-Si3-C25 107.87(6), Si4-Si3-C31 112.40(7), O3-Si3-C25 108.07(7), O3-Si3-C31 108.39(9), C25-Si3-C31 111.71(9), Si3-Si4-O4 103.62(6), Si3-Si4-C37 113.85(7), Si3-Si4-C43 112.79(7), O4-Si4-C37 106.85(9), O4-Si4-C43 109.10(9), C37-Si4-C43 110.17(10), Si3-O3-Si3A 175.70(14).

Table 2. Hydrogen-bonding geometries in the crystal of **3** (distances [Å] and angles [°])<sup>[a]</sup>.

D-H...A	D...A	D-H	H...A	D-H...A
O1-H1O...O4	2.676(3)	0.83(3)	1.84(3)	179(3)
O2-H2O...O2	2.737(3)	0.80(3)	1.97(3)	163(3)
O3-H3O...O6	2.699(2)	0.83(2)	1.92(2)	156(2)
O4-H4O...O2	2.764(2)	0.809(18)	1.956(18)	177(3)
O5-H5O...O3	2.736(2)	0.82(3)	1.93(2)	168(3)
O6-H6O...O1	2.735(2)	0.83(3)	1.91(3)	170(3)

<sup>[a]</sup> Data calculated by using the program PLATON [8].

### Experimental Section

*General procedures.* All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (<sup>1</sup>H, 300.1 MHz; <sup>13</sup>C, 75.5 MHz; <sup>29</sup>Si,

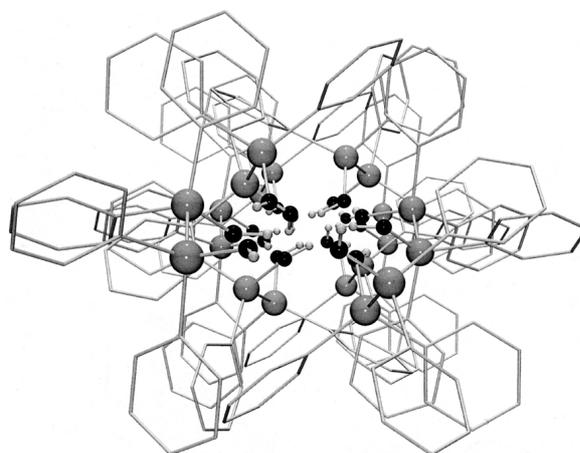


Fig. 5. Infinite tube-like arrangement of molecules **3A**, **3B**, and **3C** in the crystal of **3** (projection along [001]), with the hydrophilic SiOH groups inside and the hydrophobic phenyl groups outside the tube. The phenyl groups are represented as stick models for clarity.

59.6 MHz). CDCl<sub>3</sub> was used as solvent. Chemical shifts (ppm) were determined relative to internal CHCl<sub>3</sub> (<sup>1</sup>H,  $\delta$  = 7.24), internal CDCl<sub>3</sub> (<sup>13</sup>C,  $\delta$  = 77.0), or external TMS (<sup>29</sup>Si,  $\delta$  = 0).

#### 1,2-Bis(diethylamino)-1,1,2,2-tetraphenyldisilane (**1**)

This compound was synthesized according to ref. [3].

#### 1,2-Dichloro-1,1,2,2-tetraphenyldisilane (**2**)

Acetyl chloride (1.60 g, 20.4 mmol) was added to a stirred solution of **1** (5.00 g, 9.83 mmol) in dichloromethane (40 ml) at 0 °C and the mixture then stirred for 1 d at r.t. The solvent was removed under reduced pressure and the resulting solid recrystallized from toluene / petroleum ether (40 - 60 °C) [1:1 (v/v)] to give 3.81 g (8.75 mmol) of a colorless crystalline product (yield 89%). – M. p. 106 - 109 °C. – <sup>1</sup>H NMR:  $\delta$  = 7.26 - 7.69 (m, 20 H, SiPh). – <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 128.2 (C-2/C-6 or C-3/C-5, SiPh), 130.8 (C-4, SiPh), 132.2 (C-1, SiPh), 135.0 (C-2/C-6 or C-3/C-5, SiPh). – <sup>29</sup>Si{<sup>1</sup>H} NMR:  $\delta$  = -4.6. – C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>Si<sub>2</sub> (435.5): calcd. C 66.19, H 4.63; found C 66.2, H 4.7.

#### 1,1,2,2-Tetraphenyldisilane-1,2-diol (**3**)

A solution of **2** (2.00 g, 4.59 mmol) in dichloromethane (7 ml) was added dropwise at 0 °C to a stirred mixture of water (17 ml), diethyl ether (5 ml), and ammonium carbonate (618 mg, 6.43 mmol). Stirring was continued for 1 h at the same temperature and the aqueous phase then saturated with sodium chloride. The two phases were separated, and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude product was recrystallized from benzene / petroleum ether (60 - 70 °C) [1:1 (v/v); cooling of a boiling saturated solution to room temperature] to give 1.70 g (4.26 mmol) of a colorless crystalline product (yield 93%). – M. p. 138 - 140 °C. – <sup>1</sup>H NMR:  $\delta$  = 2.65 (br. s, 2 H, SiOH), 7.21 -

7.40 and 7.45 - 7.54 (m, 20 H, SiPh). – <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 127.8 (C-2/C-6 or C-3/C-5, SiPh), 129.7 (C-4, SiPh), 134.2 (C-1, SiPh), 136.2 (C-2/C-6 or C-3/C-5, SiPh). – <sup>29</sup>Si{<sup>1</sup>H} NMR:  $\delta$  = -10.4. – C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>Si<sub>2</sub> (398.6): calcd. C 72.32, H 5.56; found C 72.2, H 5.6.

#### 1,5-Dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane-Hemibenzene (**4**·1/2C<sub>6</sub>H<sub>6</sub>)

Compound **4**·1/2C<sub>6</sub>H<sub>6</sub> was formed in minor amounts as a by-product in the crystallization of **3**. A procedure for the synthesis of **4**·1/2C<sub>6</sub>H<sub>6</sub> has been reported elsewhere [2].

#### Crystal structure analyses of **3** and **4**·1/2C<sub>6</sub>H<sub>6</sub>

Suitable single crystals of **3** and **4**·1/2C<sub>6</sub>H<sub>6</sub> were obtained by crystallization of **3** from benzene/petroleum ether (60 - 70 °C) (see preparation). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) [9] and refined by full-matrix least-squares on  $F^2$  with all unique reflections (SHELXL-97) [10]. For the CH hydrogen atoms of **3** and **4**·1/2C<sub>6</sub>H<sub>6</sub>, a riding model was employed. The OH hydrogen atoms of **3** were localized in the Fourier synthesis and refined freely. The OH hydrogen atoms of **4**·1/2C<sub>6</sub>H<sub>6</sub> were placed on ideal positions and refined using distance restraints. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-181214 (**3**) and CCDC-181215 (**4**·1/2C<sub>6</sub>H<sub>6</sub>). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

#### Acknowledgments

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