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# Hydroxy- and boronic-acid-functionalized carbosilanes: Synthesis and solid state structure of $Si(C_6H_4-4-SiMe_2((CH_2)_3OH))_4$

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#### ABSTRACT

Consecutive synthesis methodologies for the preparation of carbosilanes (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>)<sub>2</sub> (**2**), Si (C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>2</sub>((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>))<sub>4</sub> (**5**), (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>OH)<sub>2</sub> (**3**), and Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>3-n</sub>((CH<sub>2</sub>)<sub>3</sub>OH)<sub>n</sub>)<sub>4</sub> (**6a**, n = 1; **6b**, n = 2; **6c**, n = 3) are reported. Boronic acids **2** and **5** are accessible by treatment of (Ph)(Me)Si (CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> (**1**) or Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>2</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>))<sub>4</sub> (**4a**) with HBBr<sub>2</sub>·SMe<sub>2</sub> followed by addition of water, while **3** and **6** are available by the hydroboration of **1** or Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>3-n</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>n</sub>)<sub>4</sub> (**4a**, n = 1; **4b**, n = 2; **4c**, n = 3) with H<sub>3</sub>B·SMe<sub>2</sub> and subsequent oxidation with H<sub>2</sub>O<sub>2</sub>.

The single molecular structure of **6a** in the solid state is reported. Representative is that **6a** crystallized in the chiral *non*-centrosymmetric space group  $P2_12_12_1$  forming 2D layers due to intermolecular hydrogen bond formation of the HO functionalities along the crystallographic *a* and *c* axes. © 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Molecular tectonics based on molecular recognition events and their iteration is the approach dealing with the design and preparation of molecular networks in the solid state. This includes the formation of molecular networks from molecules consisting of multiple peripheral recognition groups, which are capable to form revisable intermolecular forces including van-der-Waals, electrostatic and  $\pi$ - $\pi$  interactions, as well as hydrogen and coordination bonds affording diverse connectivities and topologies, respectively [1–3]. Possible molecular tectons are, for example, M(C<sub>6</sub>H<sub>4</sub>-4-B (OH)<sub>2</sub>)<sub>4</sub> (M = C, Si) and Si(C<sub>6</sub>H<sub>4</sub>-4-OH)<sub>4</sub>, which build open 3-dimensional structures with significant internal volumes for the inclusion of guest molecules [3].

Optically inactive molecules can induce crystallization into a chiral crystal structure [4]. Matsuura and others reported about the probability to generate chirality in the crystallization of achiral molecules in a chiral conformer, helical arrangement and formation of, *e. g.*, head-to-head stacking columnar arrangements [4].

Against this background, we recently got interested in the synthesis of molecular network packing structures by molecular recognition processes including hydrogen-bond formation of carbosilanes featuring terminal hydroxy or boronic acid functionalities. We here report on subsequent synthesis procedures to prepare carbosilanes of type (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>)<sub>2</sub>, Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>2</sub>((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>))<sub>4</sub>, (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>OH)<sub>2</sub>, and Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>3-n</sub>((CH<sub>2</sub>)<sub>3</sub>OH)<sub>n</sub>)<sub>4</sub> (n = 1, 2, 3), respectively.

#### 2. Results and discussion

The synthesis methodology to prepare hydroxy- and boronicacid-functionalized carbosilanes was established for (Ph)(Me)Si ((CH<sub>2</sub>)<sub>3</sub>X)<sub>2</sub> (**2**, X = B(OH)<sub>2</sub>; **3**, X = OH) using (Ph)(Me)Si(CH<sub>2</sub>CH= CH<sub>2</sub>)<sub>2</sub> (**1**) and HBBr<sub>2</sub>·SMe<sub>2</sub>/H<sub>2</sub>O or H<sub>3</sub>B·SMe<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> as key starting materials (Scheme 1).

Hydroboration of **1** with HBBr<sub>2</sub>·SMe<sub>2</sub> in boiling dichloromethane gave (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>BBr<sub>2</sub>)<sub>2</sub> which by subsequent treatment with water at 0 °C produced the boronic acid (Ph)(Me)Si ((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>)<sub>2</sub> (**2**) in very good yield (Scheme 1, Experimental Part) [5]. After appropriate work-up, carbosilane **2** could be isolated as a colorless solid which only dissolves in common polar solvents including tetrahydrofuran and diethyl ether. For the synthesis of **3**, carbosilane **1** was added to a tetrahydrofuran solution containing H<sub>3</sub>B·SMe<sub>2</sub> at 0 °C. *In-situ* formed (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>BH<sub>2</sub>)<sub>2</sub> was thereafter oxidized with hydrogen peroxide to afford colorless liquid **3** in 91% isolated yield [6].

Based on these studies  $Si(C_6H_4-4-SiMe_{3-n}(CH_2CH=CH_2)_n)_4$  (**4a**, n = 1; **4b**, n = 2; **4c**, n = 3) was subjected to hydroboration—hydrolysis and hydroboration—oxidation cycles as shown in Scheme 2, whereby identical reaction conditions were applied as discussed earlier (see synthesis of **2** and **3**, Scheme 1). After appropriate work-up, carbosilane Si( $C_6H_4-4$ -SiMe<sub>2</sub>((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>))<sub>4</sub> (**5**)



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Scheme 1. Synthesis of 2 and 3 from 1 and HBBr<sub>2</sub>·SMe<sub>2</sub>/H<sub>2</sub>O or H<sub>3</sub>B·SMe<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>.

was isolated in quantitative yield as a colorless solid, *non*-soluble in protic organic solvents. The hydroxy end-capped molecules  $Si(C_6H_4-4-SiMe_{3-n}((CH_2)_3OH)_n)_4$  (**6a**, n = 1; **6b**, n = 2; **6c**, n = 3) were isolated in moderate to excellent yields (Experimental Part). It has to be emphasized that carbosilane **6a** with its four terminal HO functionalities dissolves in benzene, dichloromethane and diethyl ether, while **6b** containing eight end-capped hydroxy groups dissolves in more polar solvents including tetrahydrofuran and dimethyl sulfoxide. Carbosilane **6c** with its twelve terminal hydroxy units is only sparely soluble in, for example, dimethyl sulfoxide.

Identification of molecules **2**, **3**, **5**, and **6a**–**6c** described herein has followed from their spectroscopic studies (IR; <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si {<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H} **(2, 5)** NMR spectroscopies). Correct elemental microanalyses were obtained for all complexes. Additionally, ESI-TOF mass-spectrometric measurements were carried out. The structure of **6a** in the solid state was determined by single X-ray structure determination.

IR spectroscopy can be used to monitor the progress of the hydroboration of **1** and **4** since the  $\nu_{C=C}$  vibration of the allyl group(s)

in **1** and **4a**–**4c** appearing at  $1630 \text{ cm}^{-1}$  disappears upon addition of the appropriate boron H–B unit to the carbon–carbon double bond. The terminal hydroxy functionalities in **2**, **3**, **5**, and **6a**–**6c** give rise to a broad characteristic band centered at  $3330 \text{ cm}^{-1}$ . The shape of this absorption indicates hydrogen bridge formation and hence, the origin of a molecular network by self-assembly. For the Si–C bonds a representative frequency is observed at ca. 1250 cm<sup>-1</sup> [7]. The C–B and B–O units present in **2** and **5** show distinctive vibrations between 620–1270 and 1310–1380 cm<sup>-1</sup> [7] (Experimental Part).

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy is also a favored analytical method to show the success of the hydroboration reactions. The representative resonance signals for the SiCH<sub>2</sub>CH=CH<sub>2</sub> units in **1** and **4a** at 1.80 (SiCH<sub>2</sub>), 4.90 (H<sub>2</sub>C=), and 5.80 ppm (CH=) vanish on addition of the HBBr<sub>2</sub> SMe<sub>2</sub> reagent and water and new signals at 0.68 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>B(OH)<sub>2</sub>), 0.76 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>B(OH)<sub>2</sub>), 1.40 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>B(OH)<sub>2</sub>), and 7.39 ppm (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>B(OH)<sub>2</sub>) are found for **2** and **5**. The appropriate alcohols **3** and **6a**–**6c** show new resonances at 0.75 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.44 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 3.36 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), and 4.4 ppm (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH). Similar trends are found in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2**, **3**, **5**, and **6a**–**6c** (Experimental Part).

<sup>29</sup>Si<sup>1</sup>H} NMR spectroscopic measurements were carried out with all newly synthesized compounds. For example, the spectrum of carbosilane **4a** shows two signals at -14.6 and -4.4 ppm which can be assigned to the core silicon atom and the outer silicons (Experimental Part) [8]. For **5a** and **6a**–**6c** the resonance signal for the inner Si atom appears at the same chemical shift (-15.5 ppm). In contrast, the outer silicons of these molecules are observed at lower field (**5**, -3.5; **6b**, -1.2; **6a**/**6c**, -0.5 ppm) (Experimental Part). The respective Si resonances for the boronic acids **2** and **5** are found at higher field, when compared with the appropriate HO end-capped carbosilanes **3** and **6a**–**6c**, respectively (Experimental Part).

The formation of the boronic acid derivatives was additionally proven by  ${}^{11}B{}^{1}H$  NMR spectroscopy, the signal at 30 ppm is representative for this type of units.



Scheme 2. Synthesis of carbosilanes 5 and 6a-6c from 4a-4c.

Furthermore, ESI-TOF mass-spectrometric measurements were carried out with all compounds. Ionization was achieved by doping with K<sup>+</sup>. Carbosilanes **3** and **6a**–**6c** show unequivocally their molecular ion peak  $[M + K^+]$  (Experimental Part). For **2** and **5**, when measured in tetrahydrofuran and doped with KSCN,  $[M + KSCN - 2H]^+$  is characteristic.

The molecular structure of **6a** in the solid state was determined by single X-ray structure determination. Single crystals could be obtained by vapor-phase diffusion of *n*-hexane into a dichloromethane solution containing **6a** at ambient temperature. The molecular structure of **6a** is presented in Fig. 1 together with selected bond distances (Å) and angles (°). Experimental and structural refinement data are given in Table 2 (Experimental Part).

Carbosilane 6a crystallized in the non-centrosymmetric chiral space group  $P2_12_12_1$ . The chirality results from the crystallization of achiral **6a** in form of a chiral conformer, a phenomenon, which only has been recently recognized [4a]. The absolute structure of 6a was established by anomalous dispersion effects with respect to the absolute structure parameter [9]. Most probably and in agreement with the argumentation of Matsuura and Koshima, [4a] the mutual interactions of 6a by formation of intermolecular hydrogen bonds (Figs. 2 and 3, Table 1) are responsible for this observation. Thus, 6a forms in the solid state 1D chains with intertectonic distances among consecutively arranged tetrahedral silicon atoms of 7.476 Å, i. e., the silicon atoms Si1, Si1A, Si1B and Si1C (Fig. 2). Above and below a chain, further 1D chains of **6a** are arranged, which are symmetry generated by 21 screw axes. Within these 1D chains only one intermolecular interaction between adjacent molecules of **6a** can be found (Entry 4, Table 1: Fig. 2), however, between individual 1D chains a number of different intermolecular interactions can be observed. These intermolecular interactions are hydrogen bonds giving rise to the formation of 2D layers of **6a** along the crystallographic *a* and *c* axes (Fig. 2). An assignment of these intermolecular hydrogen bonds is complicated, due to the disorder of all terminal CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH groups of **6a**. The occupation factors of these disordered groups –



**Fig. 1.** ORTEP diagram of the molecular structure of **6a** (50% probability level) with the atom numbering scheme. Except O-bonded hydrogen atoms all hydrogen atoms and disordered CH<sub>3</sub> groups have been omitted for clarity. Disordered atoms have been labeled with the suffix '. Selected bond distances (Å) and angles (°): Si1–C1 1.869(6), Si1–C7 1.889(6), Si1–C13 1.870(6), Si1–C19 1.871(6); C1–Si1–C7 110.3(3), C1–Si1–C13 108.0(3), C1–Si1–C19 111.3(2), C7–Si1–C13 110.3(3), C7–Si1–C19 110.7(3).



**Fig. 2.** Top-view on a selected part of one 2D layer formed by **6a** in the solid state due to intermolecular hydrogen bonds and its orientation with respect to the unit cell. Except O-bonded hydrogen atoms, all other hydrogen atoms and the disordered  $CH_3$  groups have been omitted for clarity. Labels "A" to "G" refer to a 1st to 7th symmetry generated molecule of **6a**. Suffix ' refers to disordered atomic positions.

although freely pre-refined with SHELXS-97 [10] — were finally adjusted to fixed values in order to ensure that the sum of the occupation factors of interacting OH<sup>...</sup>O units does not exceed 1.0.

In addition, O-bonded hydrogen atoms could not be located in different Fourier maps but were added on calculated positions. Therefore, for the assignment of intermolecular hydrogen bonds the sum of the occupation factors of interacting OH<sup>...</sup>O atoms and the distance criteria [11] has been taken into account. Dotted lines between oxygen atoms indicate that both requirements are fulfilled (Fig. 2). As shown in Fig. 2, the hydrogen atoms of interacting OH<sup>...</sup>O units are then not always located on expected positions. Fig. 3 shows the packing mode of the 2D layers of **6a** with its orientation with respect to the unit cell.

#### 3. Conclusion

In this study, allyl-functionalized carbosilanes of type (Ph)(Me)Si  $(CH_2CH=CH_2)_2$  and Si $(C_6H_4$ -4-SiMe<sub>3-n</sub> $(CH_2CH=CH_2)_n)_4$  were converted to the appropriate alcohols (Ph)(Me)Si $((CH_2)_3X)_2$  and Si $(C_6H_4$ -4-SiMe<sub>3-n</sub> $((CH_2)_3X)_n)_4$  (X = OH, B(OH)\_2; n = 1, 2, 3) by hydroboration—oxidation or hydroboration—hydrolysis cycles. The therefore necessary boron derivatives have been synthesized by treatment of (Ph)(Me)Si $(CH_2CH=CH_2)_2$  and Si $(C_6H_4$ -4-SiMe<sub>3-n</sub> $(CH_2CH=CH_2)_2$  and Si $(C_6H_4$ -4-SiMe<sub>3-n</sub> $(CH_2CH=CH_2)_n)_4$  with HBBr<sub>2</sub>·SMe<sub>2</sub> and H<sub>3</sub>B·SMe<sub>2</sub>, respectively, reaction of the appropriate BBr<sub>2</sub> or BH<sub>2</sub> compounds with water or hydrogen peroxide produced the respective boronic acid or alcohol-functionalized carbosilane species. Achiral **6a** crystallized in chiral crystals in a 2D network. The hydroxyl functionalities of **6a** are responsible for the network formation by means of intermolecular hydrogen bonds and most probably these intermolecular contacts are responsible for the chiral nature of the 2D network.

#### 4. Experimental part

#### 4.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen (O<sub>2</sub> traces: CuO catalyst, BASF AG, Ludwigshafen; H<sub>2</sub>O:



Fig. 3. Top (left) and side view (right) on selected parts of 2D layers formed by carbosilane 6a in the solid state. All hydrogen atoms and disordered CH<sub>3</sub> groups are omitted for clarity.

molecular sieve 4 Å) using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were purified by distillation from sodium/benzophenone ketyl; petroleum ether and dichloromethane from calcium hydride. Infrared spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer. <sup>1</sup>H NMR spectra were recorded with a Bruker spectrometer (AC 250) operating at 250.13 MHz in the Fourier transform mode; <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 50.323 MHz. Chemical shifts are reported in  $\delta$  units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal (D<sub>6</sub>-acetone/CDCl<sub>3</sub>:<sup>1</sup>H NMR,  $\delta = 2.05/$ 7.26 ppm;  ${}^{13}C{}^{1}H$  NMR,  $\delta = 30.83$ , 205.87/77.00 ppm).  ${}^{29}Si{}^{1}H$  NMR spectra were recorded at 49.662 MHz (external standard relative to  $SiMe_4$ ,  $\delta = 0.00$  ppm); <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded at 80.252 MHz (external standard relative to BF<sub>3</sub>,  $\delta = 0.00$  ppm). ESI-TOF mass spectra were recorded with a Mariner Biospectrometry workstation 4.0 from Applied Biosystems. Melting points were determined using sealed nitrogen purged capillaries and a Büchi MP 510 melting point apparatus. Microanalyses were performed by the Institute of Organic Chemistry, University Heidelberg and the Institute of Organic Chemistry, Chemnitz, Technical University.

#### 4.2. General remarks

The starting materials were purchased from commercial providers and were used as received. Carbosilanes  $(Ph)(Me)Si(CH_2CH=CH_2)_2$ 

## Table 1 Selected O<sup>...</sup>O distances of crystallographically different intermolecular hydrogen bonds of **6a**.<sup>a</sup>

Entry	Oxygen	Oxygen on the adjacent molecule	Distance (Å)
1	04C	O3D	2.795
2	01'A	O3D	2.444
3	04'	O2F	2.731
4	04'G	01'E	2.577
5	04	02′F	2.914

<sup>a</sup> Labels on the oxygen atoms refer to labels given in Fig. 2.

(1) [12] and Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe<sub>3-n</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>n</sub>)<sub>a</sub> (**4a**, **4c**) [8d] were prepared according to synthesis methods described elsewhere.

#### 4.2.1. Synthesis of (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>B(OH)<sub>2</sub>)<sub>2</sub> (**2**)

To HBBr<sub>2</sub>·SMe<sub>2</sub> dissolved in dichloromethane (11.0 mmol, 1.0 M, 11.0 mL) was drop-wise added **1** (1.01 g, 5.00 mmol) in 9.0 mL of dichloromethane. The reaction mixture was refluxed for 2 h and was then cooled to 0 °C and carefully hydrolyzed with water (20 mL). Stirring was continued for 30 min at ambient temperature and then all volatile materials were removed in *oil-pump vacuum*.

Та	bl	e 2	

Experimental data for the X-ray diffraction studies of 6a.

-		
	Empirical formula	C <sub>44</sub> H <sub>68</sub> O <sub>4</sub> Si <sub>5</sub>
	Formula weight	801.42
	T (K)	188 (2)
	Crystal system	Orthorhombic
	Space group	$P2_{1}2_{1}2_{1}$
	a (Á)	7.4759 (5)
	b (Å)	23.0324 (17)
	c (Å)	28.278 (2)
	V (Á <sup>3</sup> )	4869.1 (6)
	Ζ	4
	$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.093
	$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.183
	F (000)	1736
	Crystal size (mm)	0.5  imes 0.3  imes 0.2
	$\theta_{\min}, \theta_{\max}$ (°)	1.14, 25.50
	Limiting indices	$-9 \le h \le 9$ ; $0 \le k \le 27$ ; $0 \le l \le 34$
	Number of reflections collected	33276
	Number of unique reflections (R <sub>int</sub> )	9041 (0.1040)
	Completeness to $\theta$ (%)	99.9 ( $ heta = 25.50^{\circ}$ )
	Absorption correction	None
	Number of parameters	334
	Goodness of fit (GOF) on $F^2$	1.023
	Final <i>R</i> indices $(I > 2(I))^{a,b}$	$R_1 = 0.0936, wR_2 = 0.2307$
	R indices (all data) <sup>a,b</sup>	$R_1 = 0.1807, wR_2 = 0.2687$
	Largest difference peak and hole (e $Å^{-3}$ )	-0.305, 0.728

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$ 

<sup>b</sup>  $wR_2 = \sqrt{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2}$  with  $w = 1/(\sigma^2(F_o^2) + (g_1P)^2 + g_2P)$ ;  $P = (\max(F_o^2, 0) + 2F_c^2)/3$ .

The product was isolated by suction filtration and washed with distilled water (50 mL) to give 2 as a colorless solid 1.31 g (4.46 mmol, 89% based on 1).

M.p.: 195 °C. IR (KBr): 3293 (s), 3062 (w), 2916 (m), 2876 (m), 1378 (s, B–O), 1358 (s, B–O), 1248 (m, CH<sub>3</sub> bending), 824 (m, C–Si), 792 (m, C–Si). <sup>1</sup>H NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 7.51 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.38 (m, 3H, C<sub>6</sub>H<sub>4</sub>), 7.38 (bs, 4H, OH), 1.38 (m, 8H, BCH<sub>2</sub>), 0.75 (m, 8H, CH<sub>2</sub>), 0.67 (t, 7.70 Hz, 8H, SiCH<sub>2</sub>), 0.26 (s, 24H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 139.5 (1C, Ar C–Si), 134.5 (2C, Ar C–H), 129.6 (1C, Ar C–H) 128.6 (2, Ar C–H), 20.9 (br, 2C, BCH<sub>2</sub>), 19.8 (2C, CH<sub>2</sub>), 18.3 (4C, SiCH<sub>2</sub>), -2.1 (8C, SiCH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = -3.3. <sup>11</sup>B {<sup>1</sup>H} NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 30.3. ESI-TOF-MS (THF/CH<sub>3</sub>CN/KSCN): m/z 389.05 [M + KSCN – 2H]<sup>+</sup>. Anal. Calc. for C<sub>13</sub>H<sub>24</sub>B<sub>2</sub>O<sub>4</sub>Si (294.16): C, 53.10; H, 8.23. Found: C, 53.24; H, 8.36.

#### 4.2.2. Synthesis of (Ph)(Me)Si((CH<sub>2</sub>)<sub>3</sub>OH)<sub>2</sub> (3)

To BH<sub>3</sub>·SMe<sub>2</sub> (11.0 mmol, 2.0 M, 5.5 mL) in tetrahydrofuran (50 mL), compound **1** (5.00 mmol, 1.01 g) dissolved in tetrahydrofuran (75 mL) was added during 10 min at 0 °C. After stirring the reaction mixture at this temperature for 2 h, it was quenched with aqueous NaOH (3 M, 3.75 mL) and was allowed to stir for another 15 min. Then H<sub>2</sub>O<sub>2</sub> (30%, 3.75 mL) was added in a single portion and the reaction mixture was stirred for 30 min at 25 °C. Afterwards, a saturated potassium carbonate solution (30 mL) was added. Extraction with diethyl ether (2 × 100 mL) was carried out and the combined organic layers were dried over brine (30 mL) and then over magnesium sulfate. All volatiles were removed by rotary evaporator and the obtained residue was purified by chromatography (column size: 2 × 35 cm, dichloromethane, silica gel) to gave **3** as a colorless solid. Yield: 1.09 g (4.57 mmol, 91% based on **1**).

M.p.: 237 °C. IR (KBr): 3338 (s, O-H), 3068 (w), 3050 (w), 3019 (w), 2930, (s), 2873 (s), 1427 (m), 1253 (m), 1053, (s), 1012 (s), 860 (m, C–Si), 805 (m, C–Si), 787 (m, C–Si). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.49$ (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.34 (m, 3H, C<sub>6</sub>H<sub>5</sub>), 3.56 (t, 6.62 Hz, 4H, CH<sub>2</sub>O, 1.97 (brs, 2H, OH), 1.56 (m, 4H, CH<sub>2</sub>), 0.97 (m, 4H, CH<sub>2</sub>Si), 0.29 (s), 3H, SiCH<sub>3</sub>). <sup>1</sup>H NMR (DMSO- $D_6$ ):  $\delta = 7.52$  (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.40 (m, 3H, C<sub>6</sub>H<sub>5</sub>), 4.43 (t, 5.30 Hz, 2H, OH), 3.36 (td, 6.72 Hz, 5.30 Hz, 4H, CH<sub>2</sub>O), 1.43 (m, 4H, CH<sub>2</sub>), 0.74 (m, 4H, SiCH<sub>2</sub>), 0.27 (s, 24H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 137.7 (Ar C–Si, 1C), 133.7 (Ar C–H, 2C), 129.0 (Ar C-H, 1C), 127.8 (Ar, C-H, 2C), 65.5 (CH<sub>2</sub>OH, 2C), 26.9 (CH<sub>2</sub>, 2C), 9.6 (SiCH<sub>2</sub>, 2C), -5.3 (SiCH<sub>3</sub>, 1C). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO- $D_6$ ):  $\delta = 138.9$  (Ar C–Si, 1C), 134.5 (Ar C–H, 2C), 129.8 (Ar C–H, 1C), 128.7 (Ar C-H, 2C), 64.7 (CH<sub>2</sub>OH, 2C), 27.9 (CH<sub>2</sub>, 2C), 10.5 (SiCH<sub>2</sub>, 2C), -4.2 (SiCH<sub>3</sub>, 1C). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -1.2$ . <sup>29</sup>Si{<sup>1</sup>H} NMR (DMSO- $D_6$ ):  $\delta = -1.3$ . ESI-TOF-MS (THF/CH<sub>3</sub>CN/KSCN): m/z 277.09 (100)  $[M + K]^+$ . Anal. Calc. for  $C_{13}H_{22}O_2Si$  (238.40): C, 65.50; H, 9.30. Found: C, 65.87; H, 9.06.

#### 4.2.3. Synthesis of Si(C<sub>6</sub>H<sub>4</sub>-4-SiMe(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>)<sub>4</sub> (**4b**)

4.2.3.1. 1-Br-C<sub>6</sub>H<sub>4</sub>-4-SiMeCl<sub>2</sub>. 4-Bromophenylmagnesium bromide was prepared by the drop-wise addition of 1,4-dibromobenzene (1.00 mol, 236 g) dissolved in diethyl ether (600 mL) to magnesium turnings (1.05, 25.5 g) in diethyl ether (100 mL) during 3 h. Stirring was continued at 25 °C for 17 h and afterwards the reaction mixture was refluxed for 5 h. The Grignard solution was drop-wise added to MeSiCl<sub>3</sub> dissolved in diethyl ether (250 mL) over 1.5 h. The reaction mixture was refluxed for 5 h. The solution was then transferred via canula from the precipitated magnesium salts and the residue was extracted with diethyl ether (3 × 100 mL). The combined fractions were concentrated in *oil-pump vacuum* to give 1-Br-C<sub>6</sub>H<sub>4</sub>-4-SiMeCl<sub>2</sub> (used without further purification).

#### 4.2.3.2. 1-Br-4-(Si(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>Me)-C<sub>6</sub>H<sub>4</sub>. Allyl

bromide was prepared by slow addition of allyl bromide (2.00 mol, 242.0 g) dissolved in diethyl ether (2000 mL) to a suspension of

magnesium

magnesium turnings (3.00 mol, 72.90 g) in diethyl ether (120 mL) during 8 h. After 2 h of stirring, the Allyl magnesium bromide was transferred via a canula from the excess of magnesium. To this solution, 1-Br-C<sub>6</sub>H<sub>4</sub>-4-SiMeCl<sub>2</sub> (1.0 mol, 270.0 g) dissolved in diethyl ether (200 mL) was drop-wise added during 2 h. The obtained reaction mixture was refluxed for 5 h and then quenched with 10% of HCl (250 mL). The organic layer was extracted with water (200 mL), dried over magnesium sulfate, concentrated in *oil-pump vacuum* and purified by fractional vacuum distillation to give 1-Br-4-(Si(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>Me)-C<sub>6</sub>H<sub>4</sub> as a colorless liquid. Yield: 93.50 g (0.33 mol, 33% based on 1-Br-C<sub>6</sub>H<sub>4</sub>-4-SiMeCl<sub>2</sub>).

B.p.: 93–96 °C/0.5 mmHg. IR (film): 3076, 3050, 2993, 2971, 2901, 2885, 1630 (m, C=C), 1254 (m, CH3 bending), 820 (s, Si–C), 803 (s, Si–C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.50 (dt, 8.20 Hz, 1.84 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.37 (dt, 8.20 Hz, 1.84 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 5.75 (m, 2H, CH<sub>2</sub>CH= CH<sub>2</sub>), 4.89 (m, 2H, CH=CH<sub>2</sub>), 4.87 (m, 2H, CH=CH<sub>2</sub>), 1.80 (dt, 8.08 Hz, 1.15 Hz, 4H, SiCH<sub>2</sub>CH), 0.29 (s, 3H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 135.6 (Ar C–Si, 1C), 135.5 (Ar C–H, 2C), 133.7 (CH<sub>2</sub>CH= CH<sub>2</sub>, 2C), 130.9 (Ar C–H, 2C), 124.1 (Ar Br–C, 1C), 114.2 (CH=CH<sub>2</sub>, 2C), 21.4 (SiCH<sub>2</sub>CH, 2C), -5.9 (SiCH<sub>3</sub>, 1C). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -5.3 (1 Si). Anal. Calc. for C<sub>13</sub>H<sub>17</sub>BrSi (281.26): C, 55.51; H, 6.09. Found: C, 55.45; H, 6.08.

4.2.3.3.  $Si(C_6H_4$ -4- $SiMe(CH_2CH=CH_2)_{2/4}$  (**4b**). <sup>n</sup>BuLi (2.5 M, 11.85 mmol, 4.74 mL, *n*-hexane) was added drop-wise to 1-Br-4-(*Si* (*CH<sub>2</sub>CH=CH<sub>2</sub>*)<sub>2</sub>*Me*)-*C*<sub>6</sub>*H*<sub>4</sub> (11.85 mmol, 3.33 g) dissolved in diethyl ether (60 mL) at -30 °C. The reaction mixture was stirred below -10 °C for 30 min and then SiCl<sub>4</sub> (2.962, 0.5033 g, 0.339 mL) was added in a single portion. The reaction mixture was stirred for 30 min at this temperature and then 24 h at 25 °C. Afterwards, it was quenched with water (100 mL) and the resulting mixture was extracted with diethyl ether (100 mL). The organic layer was dried over magnesium sulfate and all volatile materials were removed in *oil-pump vacuum*. The product was purified by silica gel column chromatography (*n*-hexane – 20% dichloromethane/*n*-hexane, column size 4 × 25 cm) to give **4b** as a colorless solid. Yield: 0.850 g (1.020 mmol, 34% based on SiCl<sub>4</sub>).

M.p.: 235–237 °C. IR (KBr): 3070, 3047, 2989, 2967, 2907, 2878, 1630 (s, C=C), 1252(m, CH<sub>3</sub> bending), 1132, 820 (s, Si–C), 805 (s, Si–C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.53 (m, 16H, C<sub>6</sub>H<sub>4</sub>), 5.79 (ddt, 16.86 Hz, 10.18 Hz, 8.06 Hz, 8H, CH<sub>2</sub>CH=CH<sub>2</sub>), 4.90 (ddt, 16.86 Hz, 2.76 Hz, 1.50 Hz, 16H, CH=CH<sub>2</sub>), 4.87 (ddt, 10.10 Hz, 2.76 Hz, 1.50 Hz, 8H, CH=CH<sub>2</sub>), 1.82 (dt, 8.06 Hz, 1.50 Hz, 16H, SiCH<sub>2</sub>CH), 0.29 (s, 12H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 138.6 (Ar C–Si, 4C), 135.5 (Ar C–H, 8C), 134.9 (Ar C–Si, 4C), 134.1 (CH<sub>2</sub>CH=CH<sub>2</sub>, 8C), 133.2 (Ar C–H, 8C), 113.9 (CH=CH<sub>2</sub>, 8C), 21.5 (SiCH<sub>2</sub>CH, 8C), -5.9 (SiCH<sub>3</sub>, 4C). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -5.8 (4 Si, Si terminal), -14.8 (1 Si, Si core). ESITOF-MS (THF/CH<sub>3</sub>CN/KSCN): m/z (rel. intensity) = 871.39 (100) [M + K]<sup>+</sup>. Anal. Calc. for C<sub>52</sub>H<sub>68</sub>Si<sub>5</sub> (833.52): C, 74.93; H, 8.22. Found: C, 74.35; H, 8.24.

#### 4.2.4. Synthesis of $Si(C_6H_4-4-SiMe_2((CH_2)_3B(OH)_2))_4$ (5)

To HBBr<sub>2</sub>·SMe<sub>2</sub> dissolved in dichloromethane (1.26 mmol, 1.0 M, 1.26 mL) a dichloromethane solution (4 mL) containing **4a** (0.20 g, 0.27 mmol) was drop-wise added and the reaction mixture was refluxed for 2 h. Afterwards, the reaction solution was cooled to 0 °C, hydrolyzed with water (5 mL) and stirring was continued for 30 min at ambient temperature. The organic solvent was removed in *oil-pump vacuum* and the obtained solid was isolated by suction filtration and washed with distilled water (50 mL) to give **5**. Yield: 0.23 g (0.25 mmol, 92% based on **4a**).

M.p.: 231 °C. IR (KBr): 3368 (s), 3050 (w), 2997 (w), 2953 (m), 2922 (m), 2874 (w), 1378 (s, B–O), 1249 (m), 1133 (m), 827 (s), 804 (m), 779 (m). <sup>1</sup>H NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 7.58 (bd, 7.51 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.49 (bd, 7.51 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.40 (bs, 4H, O–H), 1.42 (m, 8H, BCH<sub>2</sub>),

0.76 (m, 8H, CH<sub>2</sub>), 0.68 (t, 7.60 Hz, 8H, SiCH<sub>2</sub>), 0.26 (s, 24H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 142.1 (Ar C–Si, 4C), 135.9 (Ar C–H, 8C), 134.8 (Ar C–Si, 4C), 133.9 (Ar C–H, 8C), 20.9 (br, 4C, BCH<sub>2</sub>), 19.7 (CH<sub>2</sub>, 4C), 19.5 (SiCH<sub>2</sub>, 4C), -2.1 (SiCH<sub>3</sub>, 8C). <sup>29</sup>Si{<sup>1</sup>H} NMR (DMSO- *D*<sub>6</sub>):  $\delta$  = -3.5 (4 Si, Si terminal), -15.5 (1 Si, Si core). <sup>11</sup>B{<sup>1</sup>H} NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 30.1. ESI-TOF-MS (THF/CH<sub>3</sub>CN/KSCN): m/z (rel. intensity) = 1007.66 (100) [M + KSCN - 2H]<sup>+</sup>, 1021.68 (92) [M + THF + K - 2H]<sup>+</sup>. Anal. Calc. for C<sub>44</sub>H<sub>72</sub>B<sub>4</sub>O<sub>8</sub>Si<sub>5</sub> · H<sub>2</sub>O (930.72): C, 56.78; H, 8.01. Found: C, 56.48; H, 7.80.

#### 4.2.5. Synthesis of $Si(C_6H_4-4-SiMe_2((CH_2)_3OH))_4$ (**6a**)

To BH<sub>3</sub>·SMe<sub>2</sub> (2.2 mL, 2.0 M, 4.4 mmol) dissolved in tetrahydrofuran (20 mL) a tetrahydrofuran solution (30 mL) containing carbosilane **4a** (0.73, 1.00 mmol) was added during 10 min at 0 °C. After 2 h of stirring, the reaction mixture was treated with aqueous NaOH (3 M, 1.8 mL) and stirring was continued for 15 min. Then H<sub>2</sub>O<sub>2</sub> (30%, 1.8 mL) was added in a single portion and the reaction mixture was stirred at 25 °C for 30 min. Afterwards, a saturated aqueous potassium carbonate solution (25 mL) was added and then extracted with diethyl ether (2 × 75 mL). The combined organic layers were dried over magnesium sulfate. All volatiles were removed by rotary evaporation to give **6a** as a colorless solid. Yield: 0.79 g (0.98 mmol, 98% based on **4a**).

M.p.: 220 °C. IR (KBr): 3323 (s, O-H), 3049 (w), 2998 (w), 2950 (m), 2930, (m), 2871 (m), 1248 (s, CH<sub>3</sub> bending), 1133, (s), 864 (m, C–Si), 835 (m, C–Si), 768 (m, C–Si). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.52 (m, 16H, C<sub>6</sub>H<sub>4</sub>), 3.58 (t, 6.76 Hz, 8H, CH<sub>2</sub>O), 1.57 (m, 12H, CH<sub>2</sub> and OH), 0.75 (m, 8H, CH<sub>2</sub>Si), 0.28 (s, 24H, SiCH<sub>3</sub>). <sup>1</sup>H NMR (DMSO- $D_6$ ):  $\delta = 7.54$  (d, 7.49 Hz, 8H, C<sub>6</sub>H<sub>4</sub>), 7.46 (bd, 7.49 Hz, 8H, C<sub>6</sub>H<sub>4</sub>), 4.41 (t, 5.30 Hz, 4H, OH), 3.36 (td, 6.72 Hz, 5.30 Hz, 8H, CH<sub>2</sub>O), 1.45 (m, 8H, CH<sub>2</sub>), 0.72 (m, 8H, SiCH<sub>2</sub>), 0.26 (s, 24H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 140.5$  (Ar C–Si, 4C), 135.6 (Ar C–H, 8C), 134.6 (Ar C–H, 4C), 132.9 (Ar C-H, 8C), 65.6 (CH<sub>2</sub>OH, 4C), 27.1 (CH<sub>2</sub>, 4C), 11.3 (SiCH<sub>2</sub>, 4C), -3.2 (SiCH<sub>3</sub>, 8C). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO- $D_6$ ):  $\delta = 141.7$  (Ar C–Si, 4C), 136.0 (Ar C–H, 8C), 134.8 (Ar C–Si, 4C), 133.89 (Ar C–H, 8C), 64.6 (CH<sub>2</sub>OH, 4C), 27.9 (CH<sub>2</sub>, 4C), 11.9 (SiCH<sub>2</sub>, 4C), -2.2 (SiCH<sub>3</sub>, 8C). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -2.4$  (4 Si, Si terminal), -14.9 (1 Si, Si core). <sup>29</sup>Si{<sup>1</sup>H} NMR (DMSO- $D_6$ ):  $\delta = -2.5$  (4 Si, Si terminal), -15.4 (1 Si, Si core). ESI-TOF-MS (THF): m/z 839.51  $[M + K]^+$ . Anal. Calc. for C<sub>44</sub>H<sub>68</sub>O<sub>4</sub>Si<sub>5</sub>: C, 65.94; H, 8.55. Found: C, 65.68; H, 8.72.

#### 4.2.6. Synthesi of $Si(C_6H_4-4-SiMe((CH_2)_3OH)_2)_4$ (**6b**)

Compound **6b** was synthesized in a similar manner as **6a** (see above) with following details:  $BH_3 \cdot SMe_2$  (2.64 mmol, 2.0 M, 1.32 mL) dissolved in tetrahydrofuran (5 mL), carbosilane **4b** (0.30 mmol, 0.25 g) dissolved in tetrahydrofuran (20 mL), aqueous NaOH (3 M, 1.08 mL),  $H_2O_2$  (30%, 1.8 mL), saturated aqueous  $K_2CO_3$  (15 mL) and diethyl ether (25 mL). After appropriate work-up, compound **6b** could be isolated as a colorless solid. Yield: 0.24 g (0.25 mmol, 82% based on **4b**).

M.p.: 241 °C. IR (KBr): 3337 (s, OH), 3049 (w), 2996 (w), 2928 (s), 2870 (s), 1252 (m), 1133 (s), 1051 (s), 860 (m), 802 (s), 782 (s). <sup>1</sup>H NMR (DMSO- $D_6$ ):  $\delta$  = 7.58 (bd, 7.42 Hz, 8H, C<sub>6</sub>H<sub>4</sub>), 7.50 (bd, 7.42 Hz, 8H, C<sub>6</sub>H<sub>4</sub>), 4.42 (t, 5.20 Hz, 8H, O-H), 3.37 (td, 6.68 Hz, 5.20 Hz, 16H, CH<sub>2</sub>O), 1.45 (m, 16H, CH<sub>2</sub>), 0.75 (m, 16H, SiCH<sub>2</sub>), 0.27 (s, 12H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO- $D_6$ ):  $\delta$  = 140.9 (Ar C–Si, 4C), 135.9 (Ar C–H, 8C), 134.8 (Ar C–Si, 4C), 134.2 (Ar C–H, 8C), 64.7 (CH<sub>2</sub>O, 8C), 27.9 (CH<sub>2</sub>, 8C), 10.4 (SiCH<sub>2</sub>, 8C), -4.3 (SiCH<sub>3</sub>, 4C). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -1.2 (4 Si, Si terminal), -15.5 (1 Si, Si core). ESI-TOF-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN/KSCN): m/z 1015.50 [M + K]<sup>+</sup>. Anal. Calc. for C<sub>52</sub>H<sub>84</sub>O<sub>8</sub>Si<sub>5</sub> (977.65): C, 63.88; H, 8.66. Found: C, 63.55; H, 8.89.

#### 4.2.7. Synhesis of Si(C<sub>6</sub>H<sub>4</sub>-4-Si((CH<sub>2</sub>)<sub>3</sub>OH)<sub>3</sub>)<sub>4</sub> (**6c**)

Compound **6c** was synthesized as described earlier (see preparation of **6a**):  $BH_3 \cdot SMe_2$  (3.53 mmol, 2.0 M, 1.76 mL) in tetrahydrofuran

(5 mL), **4c** (0.25 g, 0.27 mmol) in tetrahydrofuran (30 mL), aqueous NaOH (3 M, 1.44 mL), H<sub>2</sub>O<sub>2</sub> (30%, 1.44 mL), saturated aqueous K<sub>2</sub>CO<sub>3</sub> (15 mL), tetrahydrofuran (2 × 75 mL). After appropriate work-up, compound **6c** could be isolated as a colorless solid. Yield: 0.22 g (0.193 mmol, 72% based on **4c**).

M.p.: 260 °C. IR (KBr): 3371 (s), 3048 (w), 2997 (w), 2929 (s), 2871 (s), 1133 (s), 1053 (s), 857 (m, C–Si). <sup>1</sup>H NMR (DMSO-*D*<sub>6</sub>):  $\delta$  = 7.57 (bd, 7.58 Hz, 8H, C<sub>6</sub>H<sub>4</sub>), 7.50 (bd, 7.58 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 4.42 (t, 5.16 Hz, 12H, O–H), 3.36 (td, 6.77 Hz, 5.16 Hz, 24H, CH<sub>2</sub>O), 1.44 (m, 24H, CH<sub>2</sub>), 0.76 (m, 24H, SiCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 140.1 (Ar C–Si), 135.9 (Ar C–H), 134.7 (Ar C–Si), 134.5 (Ar C–H), 64.8 (CH<sub>2</sub>O), 27.9 (CH<sub>2</sub>), 8.7 (SiCH<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -0.5 (4 Si, Si terminal), -15.5 (1 Si, Si core). ESI-TOF-MS (EtOH/CH<sub>2</sub>Cl<sub>2</sub>/KSCN): m/z 1191.14 [M + K]<sup>+</sup>. Anal. Calc. for C<sub>60</sub>H<sub>100</sub>O<sub>12</sub>Si<sub>5</sub> (1153.86): C, 62.46; H, 8.74. Found: C, 62.14; H, 8.98.

#### 4.3. Single X-ray structure determination

Experimental crystallographic data for **6a** are given in Table 2. The data were collected with a Bruker Smart 1 k CCD diffractometer by using graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For protection against oxygen and moisture, the preparation of single crystals was performed in perfluoro alkyl ether (ABCR GmbH & Co KG, viscosity 1600 cSt). The structure was solved by direct methods with the program SHELXS-97 [10] and structure refinement was done on least-square based  $F^2$  using SHELXL-97 [13].

All non-hydrogen atoms were fully refined anisotropically in their local positions. The positions of the hydrogen atoms have been refined with a riding model. All 3-hydroxypropyl substituents are disordered and were refined on two atomic positions. In first stages the occupation factors have been freely refined. They were finally adjusted to idealized factors based on preliminary obtained values. The differences are thus less than 5% and are as follows: 0.40/0.60 (C(28) - O(1)), 0.60/0.40 (C(32) - O(2)), 0.40/0.60 (C (39) - O(3)), 0.60/0.40 (C(42) - O(4)). In addition, several methyl groups are disordered and were refined on two atomic positions with the following occupation factors:0.37/0.63 (C(26)) and 0.55/ 0.45 (C(40), C(41)), respectively.

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#### Supplementary material

The crystallographic data for **6a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication under the CCDC number 761190. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

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