Macrocyclic Siloxanes with Two Exocyclic *trans*-Silanol and Two Exocyclic *trans*-Amino Functions − Stereoselective Syntheses and Structures

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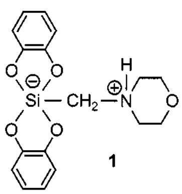
A simple preparative method for the stereoselective synthesis of ten- and twelve-membered cyclosiloxanes with two exocyclic *trans*-silanol and two exocyclic *trans*-amino functions has been developed. Thus, treatment of trimethoxy(morpholinomethyl)silane (**5**) with two molar equivalents of $HOPh_2Si–SiPh_2OH$ and $HOPh_2Si–O–SiPh_2OH$, respectively, yielded *trans*-1,6-bis(2-hydroxy-1,1,2,2-tetraphenyldisilan-1-yloxy)-1,6-bis(morpholinomethyl)-3,3,4,4,8,8,9,9-octaphenyl-2,5,7,10-tetraoxa-1,3,4,6,8,9-hexasilacyclodecane (**6**, 10-membered ring) and *trans*-2,8-bis(3-hydroxy-1,1,3,3-tetraphenyldisiloxan-1-yloxy)-2,8-bis(morpholinomethyl)-4,4,6,6,10,10,12,12-octaphenylcyclohexasiloxane (**7**, 12-membered ring). In contrast, treatment of **5** with two molar equivalents of $HOPh_2C–CPh_2OH$ afforded (morpholiniomethyl)bis[tetraphenylethane-1,2-diolato(2–)]silicate (**3**), a zwitterionic spirocyclic λ^5*Si*-silicate. Compounds **3**, **6**·EtOAc, and **7**·PhMe were characterized by elemental analyses (C, H N), solid-state ^{29}Si VACP/MAS NMR studies, solution NMR experiments (^1H, ^{13}C, ^{29}Si; $CDCl_3$), and crystal structure analyses.

Introduction

Various organic *vic*-diols (e.g. 1,2-dihydroxybenzene and glycolic acid derivatives) have been used to prepare zwitterionic spirocyclic λ^5*Si*-silicates with two bidentate diolato(2−) ligands,[1] such as compounds **1** and **2**. Following the strategy applied to the syntheses of **1** and **2**, we attempted to prepare the related zwitterionic λ^5*Si*-silicates **3** and **4**.



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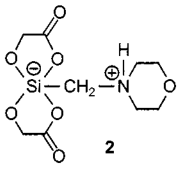

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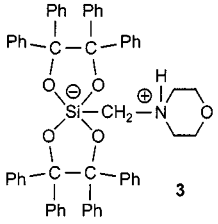

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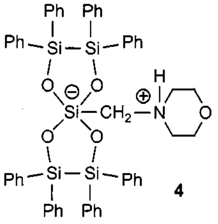

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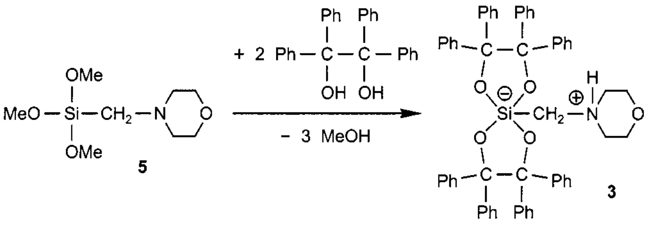
Results and Discussion

To synthesize compounds **3** and **4**, trimethoxy(morpholinomethyl)silane[2] (**5**) was treated with two molar equivalents of the respective *vic*-diol, tetraphenylethane-1,2-diol or tetraphenyldisilane-1,2-diol[3] (Scheme 1 and 2). Both reactions were performed in acetonitrile at room temperature, and compound **3** was obtained in 93% yield as a colorless crystalline solid. However, to our great surprise treatment of **5** with $HOPh_2Si{-}SiPh_2OH$ under the same conditions as applied to the synthesis of **3** did not yield the expected product **4**, we instead obtained the ten-membered cyclosiloxane **6**. This compound was isolated, after recrystallization from ethyl acetate, as the solvate **6**·EtOAc (yield 70%).



Scheme 1. Synthesis of the zwitterionic λ^5*Si*-silicate **3**

From a formal point of view, the formation of **6** could be rationalized in terms of a dimerization of **4**; however, there is no experimental evidence for this assumption. The reaction mechanism is still under investigation and it is an open question as to whether the zwitterion **4** is an intermediate in this reaction or not. Nevertheless, it appears that we have discovered an efficient stereoselective synthetic method for the preparation of macrocyclic siloxanes with two exocyclic *trans*-silanol groups and two exocyclic *trans*-amino functions. As a further example of this method, we have succeeded in synthesizing the twelve-membered cyclosiloxane **7**. This compound was obtained analogously to the synthesis of **6** by treatment of **5** with two molar equivalents of tetraphenyldisiloxane-1,3-diol[4] in acetonitrile at room

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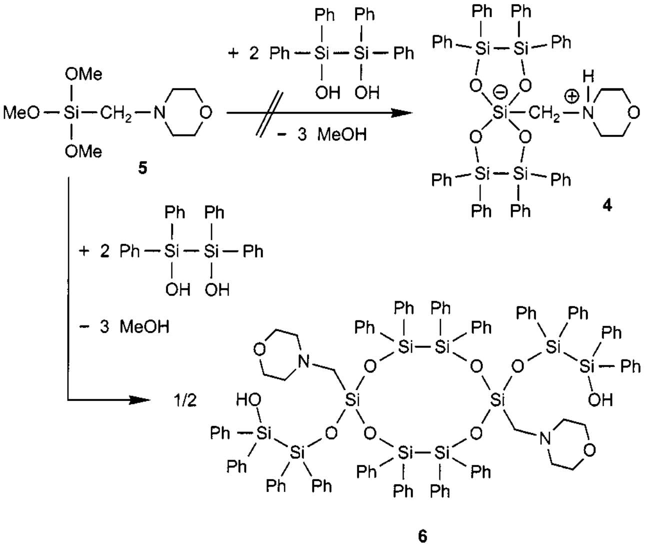
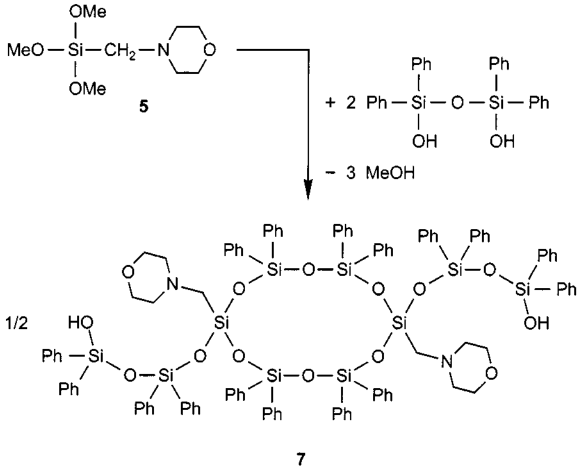


Scheme 2. Synthesis of the ten-membered cyclosiloxane **6**

temperature (Scheme 3). The product was isolated, after recrystallization from toluene/petroleum ether, as the solvate **7**·PhMe (yield 72%).



Scheme 3. Synthesis of the twelve-membered cyclosiloxane **7**

Compounds **3**, **6**·EtOAc, and **7**·PhMe were characterized by elemental analyses (C, H N), solid-state ^{29}Si VACP/MAS NMR studies, solution NMR experiments (^{1}H, ^{13}C, ^{29}Si; $CDCl_3$),[5] and crystal structure analyses.

The Si coordination polyhedron of **3** is a strongly distorted trigonal bipyramid (Berry distortion 42.3%),[6] each bidentate tetraphenylethane-1,2-diolato(2−) ligand spanning one axial and one equatorial site (Figure 1). The zwitterion forms an intramolecular N−H···O1 hydrogen bond in the crystal [N−H 0.85(3), H···O1 2.31(2), N···O1 2.746(2) Å, N−H···O1 112(2)°].[7]

Compounds **6**·EtOAc and **7**·PhMe show some common structural features (Figure 2 and 3). With respect to the positions of their silicon atoms, the ten- and twelve-membered rings adopt a chair conformation, both ring systems being characterized by a center of symmetry. The two morpholinomethyl substituents occupy axial positions, whereas the two $OPh_2Si-SiPh_2OH$ (**6**·EtOAc) or $OPh_2Si-O-SiPh_2OH$ (**7**·PhMe) groups occupy equatorial sites. Thus, each of the two pairs of identical exocyclic functional groups (two silanol and two amino moieties) are in *trans*-position to each other. The conformations present in the crystal allow the formation of intramolecular O−H···N hydrogen bonds [**6**·EtOAc: O4−H 0.8198, H···N 1.9325, O4···N 2.737(3) Å, O4−H···N 166.75°; **7**·PhMe: O4−H 0.78(7), H···N 2.02(7), O4···N 2.787(5) Å, O4−H···N 172(8)°].[7] The three Si1−O distances of **6**·EtOAc [1.6034(17)−1.6092(16) Å] and **7**·PhMe [1.603(3)−1.605(3) Å] are somewhat shorter than the other Si−O distances [**6**·EtOAc: 1.6369(16)−1.6482(18) Å; **7**·PhMe: 1.620(3)−1.635(3) Å]. The Si−O−Si angles of the ring systems amount to 157.13(11) and 164.18(12)° (**6**·EtOAc) and to 152.1(2)−153.9(2)° (**7**·PhMe). The Si−C distances are in the range 1.866(2)−1.882(2) Å (**6**·EtOAc) and 1.843(5)−1.859(5) Å (**7**·PhMe), and the Si−Si distances (**6**·EtOAc) amount to 2.3610(11) and 2.3907(11) Å.

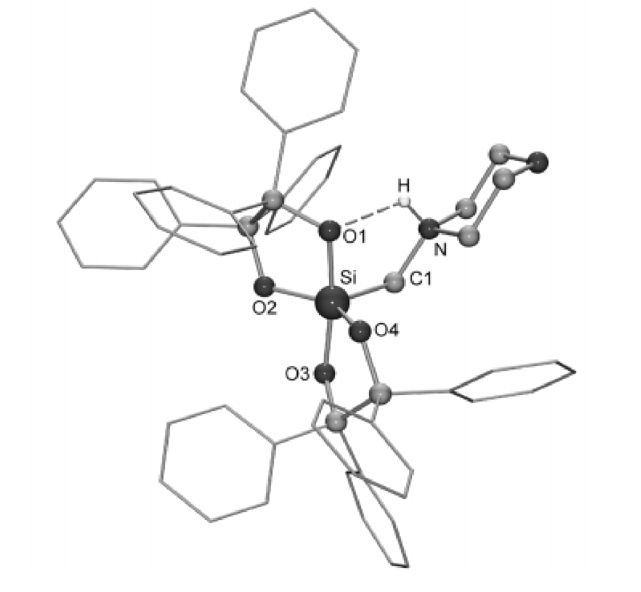


Figure 1. Molecular structure of **3** in the crystal (hydrogen atoms, except for N*H*, are omitted for clarity); selected distances [Å] and angles [°] (standard deviations in parentheses): Si−O1 1.7728(15), Si−O2 1.6992(15), Si−O3 1.7303(15), Si−O4 1.6987(15), Si−C1 1.909(2); O1−Si−O2 86.67(7), O1−Si−O3 170.44(7), O1−Si−O4 89.05(7), O1−Si−C1 94.32(8), O2−Si−O3 88.95(7), O2−Si−O4 136.82(7), O2−Si−C1 111.01(9), O3−Si−O4 88.33(7), O3−Si−C1 95.18(9), O4−Si−C1 112.15(9)

In conclusion, contrary to the reaction of silane **5** with two molar equivalents of $HOPh_2C-CPh_2OH$ (which gives formation of the zwitterionic λ^5*Si*-silicate **3**), treatment of **5** with two molar equivalents of $HOPh_2Si-SiPh_2OH$ or $HOPh_2Si-O-SiPh_2OH$ leads to the formation of macrocyclic siloxanes. With the syntheses of compounds **6** and **7** we have discovered an efficient stereoselective synthesis of ten- and twelve-membered macrocyclic siloxanes with two exocyclic silanol and two exocyclic amino functionalities in mutual *trans*-positions. To the best of our knowledge, functionalized cyclic siloxanes of this particular formula type have not been described in the literature.[8] Due to these exocyclic functionalities, in addition to the characteristic chemical reactivity of the Si−O−Si and

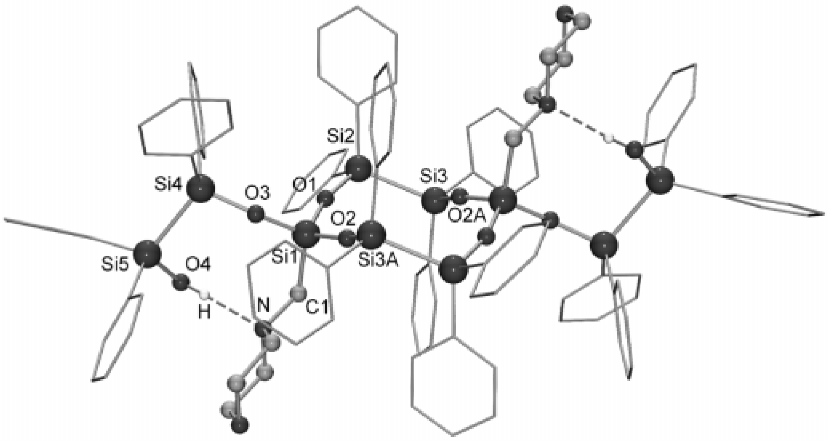


Figure 2. Molecular structure of **6** in the crystal of **6**·EtOAc (hydrogen atoms, except for O*H*, are omitted for clarity); selected distances [Å] and angles [°] (standard deviations in parentheses): Si1−O1 1.6073(16), Si1−O2 1.6092(16), Si1−O3 1.6034(17), Si1−C1 1.875(2), Si2−Si3 2.3610(11), Si2−O1 1.6448(15), Si3−O2A 1.6369(16), Si4−Si5 2.3907(11), Si4−O3 1.6482(18), Si5−O4 1.6378(17), Si−C(Ph) 1.866(2)−1.882(2); Si1−O1−Si2 157.13(11), Si1−O2−Si3A 164.18(12), Si1−O3−Si4 157.64(11), Si2−Si3−O2A 108.51(7), Si3−Si2−O1 109.68(7), Si4−Si5−O4 101.71(8), Si5−Si4−O3 104.16(7), O1−Si1−O2 108.99(9), O1−Si1−O3 109.37(9), O1−Si1−C1 109.90(10), O2−Si1−O3 110.29(9), O2−Si1−C1 105.79(9), O3−Si1−C1 112.40(10), Si−Si−C(Ph) 107.44(9)−119.51(9), O−Si−C(Ph) 105.05(10)−109.57(10), C(Ph)−Si−C(Ph) 107.81(12)−109.34(10)

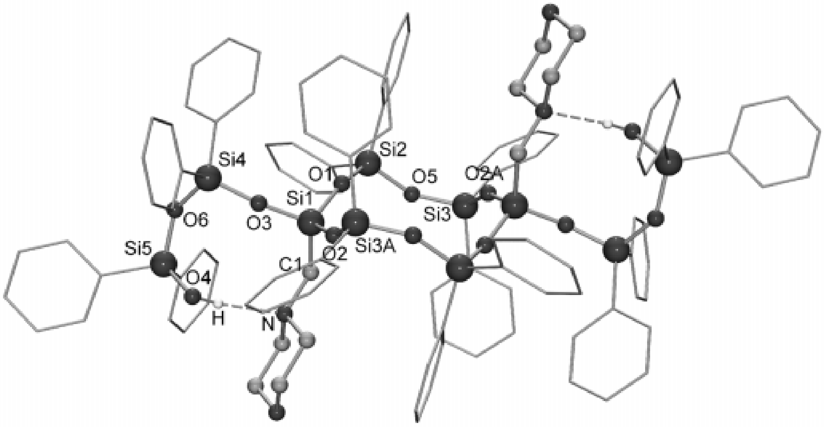


Figure 3. Molecular structure of **7** in the crystal of **7**·PhMe (hydrogen atoms, except for O*H*, are omitted for clarity); selected distances [Å] and angles [°] (standard deviations in parentheses): Si1−O1 1.603(3), Si1−O2 1.603(3), Si1−O3 1.605(3), Si1−C1 1.844(5), Si2−O1 1.628(3), Si2−O5 1.625(3), Si3−O2A 1.623(3), Si3−O5 1.620(3), Si4−O3 1.622(3), Si4−O6 1.622(3), Si5−O4 1.621(4), Si5−O6 1.635(3), Si−C(Ph) 1.843(5)−1.859(5); Si1−O1−Si2 152.1(2), Si1−O2−Si3A 153.9(2), Si1−O3−Si4 166.1(2), Si2−O5−Si3 153.8(2), Si4−O6−Si5 137.3(2), O1−Si1−O2 108.6(2), O1−Si1−O3 110.0(2), O1−Si1−C1 107.2(2), O2−Si1−O3 108.4(2), O2−Si1−C1 111.2(2), O3−Si1−C1 111.3(2), O1−Si2−O5 108.9(2), O2A−Si3−O5 110.6(2), O3−Si4−O6 109.5(2), O4−Si5−O6 111.1(2), O−Si−C(Ph) 106.3(2)−112.0(2), C(Ph)−Si−C(Ph) 110.3(2)−112.4(2)

Si−Si bonds in the ring skeletons, such compounds represent promising starting materials for the preparation of novel polymeric SiO-based materials.[9] Future studies will elucidate the synthetic potential of the title compounds.

Experimental Section

General: 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 DuPont Instruments differential scanning calorimeter, type Thermal-Analyzer 910. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H: 300.1 MHz; ^{13}C: 75.5 MHz; ^{29}Si: 59.6 MHz). CDCl$_3$ was used as solvent. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H: $\delta = 7.24$), CDCl$_3$ (^{13}C: $\delta = 77.0$), or external TMS (^{29}Si: $\delta = 0$). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO$_2$ (diameter 7 mm) containing ca. 300 mg of sample [79.5 MHz; TMS as external standard ($\delta = 0$); spinning rate: 5 kHz (**3**, **6**·EtOAc) or 7 kHz (**7**·PhMe); contact time: 5 ms; 90° ^{1}H transmitter pulse length: 3.6 μs; repetition time: 4 s].

Synthesis of (Morpholiniomethyl)bis[tetraphenylethane-1,2-diolato(2−)]silicate (3): Compound **5** (1.04 g, 4.70 mmol) was added at 20 °C to a stirred solution of tetraphenylethane-1,2-diol (3.44 g, 9.39 mmol) in acetonitrile (250 mL) and the mixture then kept undisturbed for 4 days at the same temperature. The resulting precipitate was isolated by filtration, washed with acetonitrile (2 × 10 mL), and dried in vacuo (0.01 Torr, 1 h) to give 3.83 g (4.46 mmol) of colorless crystals (yield 95%). M.p. 260 °C (dec.). − Due to the poor solubility of **3**, solution NMR experiments failed. − ^{29}Si VACP/MAS NMR: δ = −98.9. − $C_{57}H_{51}NO_5Si$ (858.1): calcd. C 79.78, H 5.99, N 1.63; found C 79.8, H 5.9, N 1.8.

Synthesis of *trans*-1,6-Bis(2-hydroxy-1,1,2,2-tetraphenyldisilan-1-yloxy)-1,6-bis(morpholinomethyl)-3,3,4,4,8,8,9,9-octaphenyl-2,5,7,10-tetraoxa-1,3,4,6,8,9-hexasilacyclodecane−Ethyl Acetate (6·EtOAc): Compound **5** (27.8 mg, 126 μmol) was added at 20 °C to a stirred solution of tetraphenyldisilane-1,2-diol (100 mg, 251 μmol) in acetonitrile (5 mL). Stirring was continued for 1 h and the mixture then kept undisturbed for 2 days at the same temperature. The resulting precipitate was isolated by filtration, washed with acetonitrile (2 × 1 mL), recrystallized from ethyl acetate, and dried in vacuo (0.01 Torr, 1 h) to give 85.3 mg (44.1 μmol) of colorless crystals (yield 70%). M.p. 212 °C (loss of ethyl acetate at ca. 127 °C). − ^{1}H NMR: δ = 1.25 (t, 3 H, OCH_2CH_3), 1.40 (s, 4 H, $SiCH_2N$), 1.83−2.05 (m, 8 H, CCH_2N), 2.03 [s, 3 H, C(O)CH_3, overlapping with the multiplet for CCH_2N], 3.29−3.42 (m, 8 H, CCH_2O), 4.10 (q, 2 H, OCH_2CH_3), 6.77−6.86, 6.87−7.01, and 7.06−7.36 (m, 80 H, SiC_6H_5), 8.3 (br. s, 2 H, SiOH). − ^{13}C NMR: δ = 14.2 (OCH_2CH_3), 21.1 [C(O)CH_3], 48.0 ($SiCH_2N$), 56.9 (CCH_2N), 60.4 (OCH_2CH_3), 65.6 (CCH_2O), 127.5, 127.6, 127.7, and 127.9 (C-2/C-6 or C-3/C-5, SiPh), 129.1, 129.3, 129.65, and 129.71 (C-4, SiPh), 134.6 (two non-equivalent sites, not resolved), 135.1, and 135.2 (C-2/C-6 or C-3/C-5, SiPh), 135.8, 136.2, 136.6, and 138.0 (C-1, SiPh), *C*(O)CH_3 resonance not found. − ^{29}Si NMR: δ = −73.7 (SiO_3C), −17.1, −16.1, and −15.3 (Si*Si*OC_2). − ^{29}Si VACP/MAS NMR: δ = −75.6 (SiO_3C), −17.4, −15.2, −14.1, and −10.7 (Si*Si*OC_2). − $C_{110}H_{110}N_2O_{12}Si_{10}$ (1932.9): calcd. C 68.35, H 5.74, N 1.45; found C 68.6, H 5.8, N 1.5.

Synthesis of *trans*-2,8-Bis(3-hydroxy-1,1,3,3-tetraphenyldisiloxan-1-yloxy)-2,8-bis(morpholinomethyl)-4,4,6,6,10,10,12,12-octaphenylcyclohexasiloxane−Toluene (7·PhMe): Compound **5** (133 mg, 601 μmol) was added at 20 °C to a stirred solution of tetraphenyldisiloxane-1,3-diol (500 mg, 1.21 mmol) in acetonitrile (4 mL). Stirring was continued at the same temperature for 1 day, and the resulting precipitate was isolated by filtration, washed with acetonitrile (2 × 1 mL), crystallized from toluene/petroleum ether [1:1 (v/v); addition of petroleum ether (b.p. 40−60 °C) to a solution of **7** in toluene at 20 °C], and dried in vacuo (0.01 Torr, 1 h) to give 434 mg (217 μmol) of colorless crystals (yield 72%). M.p. (dec.) 169−170 °C (loss of toluene at ca. 90 °C). − ^{1}H NMR: δ = 1.38 (s, 4 H, $SiCH_2N$), 1.65−1.80 (m, 8 H, CCH_2N), 2.32 (s, 3 H, CCH_3), 3.02−3.16 (m, 8 H, CCH_2O), 6.98−7.44 (m, 85 H, SiC_6H_5, $C_6H_5CH_3$), 8.9 (br. s, 2 H, SiOH). − ^{13}C NMR: δ = 21.8 ($PhCH_3$), 47.5 ($SiCH_2N$), 57.1 (CCH_2N), 66.1 (CCH_2O), 125.3 (C-4, PhMe), 127.5, 127.6 (two non-equivalent sites, not resolved), and 127.8 (C-2/C-6 or C-3/C-5, SiPh), 128.2 and 129.0 (C-2/C-6 or C-3/C-5, PhMe), 129.6, 130.0 (two non-equivalent sites, not resolved), and 130.2 (C-4, SiPh), 133.8 and 134.1 (C-1, SiPh), 134.3 (two non-equivalent sites, not resolved), 134.5, and 134.6 (C-2/C-6 or C-3/C-5, SiPh), 134.9 (C-1, PhMe), 136.0 (C-1, SiPh), one resonance signal (C-1, SiPh) not found. − ^{29}Si NMR: δ = −77.3 (SiO_3C), −47.0, −44.4, and −37.2 (Si*Si*OC_2). − ^{29}Si VACP/MAS NMR: δ = −77.6 (SiO_3C), −48.8, −47.7, −42.9, and −35.3 (Si*Si*OC_2). − $C_{113}H_{110}N_2O_{14}Si_{10}$ (2000.9): calcd. C 67.83, H 5.54, N 1.40; found C 67.9, H 5.9, N 1.3.

Crystal Structure Analyses of 3, 6·EtOAc, and 7·PhMe: Suitable single 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_α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 with all unique reflections (SHELXL-97).[10] For the hydrogen atoms, a riding model was employed, except for the N*H* atom of **3** and O*H* atom of **7**·PhMe, which were refined freely.

Selected Data for 3: Single crystal (0.4 × 0.3 × 0.3 mm) obtained from the reaction mixture, $C_{57}H_{51}NO_5Si$, $M_r = 858.08$, analysis at 173(2) K, monoclinic, space group $P2_1/n$, $a = 14.930(3)$, $b = 16.257(3)$, $c = 18.462(4)$ Å, $\beta = 99.54(3)°$, $V = 4419.2(15)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.290$ g cm^{-3}, $\mu = 0.107$ mm^{-1}, $F(000) = 1816$, $2\theta_{max} = 49.62°$, 36433 collected reflections, 7550 unique reflections ($R_{int} = 0.0682$), 581 parameters, $R_1 = 0.0433$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1117, $S = 0.889$, largest difference peak and hole +0.285 and −0.447 e Å^{-3}.

Selected Data for 6·EtOAc: Single crystal (0.4 × 0.4 × 0.2 mm) obtained from ethyl acetate at 20 °C, $C_{106}H_{102}N_2O_{10}Si_{10}$·EtOAc, $M_r = 1932.90$, analysis at 253(2) K, triclinic, space group $P\bar{1}$, $a = 14.274(2)$, $b = 14.363(3)$, $c = 14.459(2)$ Å, $\alpha = 61.057(19)$, $\beta = 87.579(19)$, $\gamma = 82.08(2)°$, $V = 2568.4(7)$ Å^3, $Z = 1$, $\rho_{calcd.} = 1.250$ g cm^{-3}, $\mu = 0.189$ mm^{-1}, $F(000) = 1020$, $2\theta_{max} = 53.84°$, 29307 collected reflections, 10267 unique reflections ($R_{int} = 0.0757$), 599 parameters, $R_1 = 0.0457$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1267, $S = 0.906$, largest difference peak and hole +0.692 and −0.510 e Å^{-3}. The crystal contains ethyl acetate molecules located on a center of inversion.

Selected Data for 7·PhMe: Single crystal (0.4 × 0.3 × 0.1 mm) obtained from toluene/petroleum ether at 20 °C, $C_{106}H_{102}N_2O_{14}Si_{10}$·PhMe, $M_r = 2000.93$, analysis at 173(2) K, triclinic, space group $P\bar{1}$, $a = 13.832(2)$, $b = 14.207(2)$, $c = 16.989(2)$ Å, $\alpha = 74.54(2)$, $\beta = 71.44(2)$, $\gamma = 64.97(2)°$, $V = 2833.6(7)$ Å^3, $Z = 1$, $\rho_{calcd.} = 1.173$ g cm^{-3}, $\mu = 0.175$ mm^{-1}, $F(000) = 1054$, $2\theta_{max} = 46.62°$, 20277 collected reflections, 7726 unique reflections ($R_{int} = 0.0738$), 683 parameters, 581 restraints, $R_1 = 0.0545$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1525, $S = 0.861$, largest difference peak and hole +0.551 and −0.374 e Å^{-3}. The crystal contains tubes along [1 0 0] which are occupied by the toluene molecules.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-158876 (**3**), CCDC-158877 (**6**·EtOAc), and CCDC-158878 (**7**·PhMe). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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