CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201202124

Synthesis of 2,2,5,5-Tetrasubstituted 1,4-Dioxa-2,5-disilacyclohexanes via Organotin(IV)-Catalyzed Transesterification of (Acetoxymethyl)alkoxysilanes

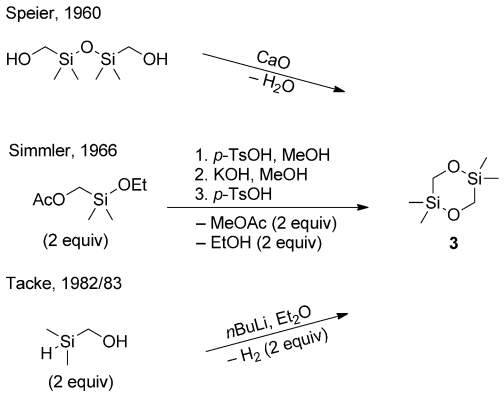
Sascha A. Erhardt,[a] Florian Hoffmann,[b] Jürgen O. Daiß,[b] Jürgen Stohrer,[b] Eberhardt Herdtweck,[c] and Bernhard Rieger*[a]

Abstract: (Acetoxymethyl)silanes **2**, **7a–c**, and **10a–c** with at least one alkoxy group, of the general formula $(AcOCH_2)Si(OR)_{3-n}(CH_3)_n$ (R: Me, Et, *i*Pr; $n=0$, 1, 2), were synthesized from the corresponding (chloromethyl)silanes **1**, **6a–c**, and **9a–c** by treatment with potassium acetate under phase-transfer-catalysis conditions. These compounds were found to provide 2,2,5,5-organo-substituted 1,4-dioxa-2,5-disilacyclohexanes **3**, **8a–c**, and **11a–c** if treated with organotin(IV) catalysts such as dioctyltin oxide. The reaction proceeds through transesterification of the acetoxy and alkoxy units followed by ring-closure to form a dimeric six-membered ring. The corresponding alkyl acetates are formed as the reaction by-products. With these mild conditions, the method overcomes the drawbacks of previously reported synthetic routes to furnish 2,2,5,5-tetramethyl-1,4-dioxa-2,5-disilacyclohexane (**3**) and even allows the synthesis of 1,4-dioxa-2,5-disilacyclohexanes bearing hydrolytically labile alkoxy substituents at the silicon atom in good yields and high purity. These new materials were fully characterized by NMR spectroscopy, elemental analysis, mass spectrometry, and X-ray analysis (*trans*-**8a**).

Keywords: cyclization · phase-transfer catalysis · silanes · synthetic methods · transesterification

Introduction

The synthesis of cyclic alkoxy silanes has received a lot of interest due to the widespread applications of these compounds.[1] They are useful precursors for the organofunctionalization of polysiloxanes,[2] as well as being monomers in the field of ring-opening polymerization.[3] 2,2,5,5-Substituted 1,4-dioxa-2,5-disilacyclohexanes are literature-known examples[4–6] that attracted our attention. The most prominent derivative is 2,2,5,5-tetramethyl-1,4-dioxa-2,5-disilacyclohexane (**3**), which was first described by Speier et al.[4] Dehydration of 1,3-bis(hydroxymethyl)tetramethyldisiloxane was caused by heating with lime (CaO) to afford silane **3** in yields of 40–60% (Scheme 1). An alternative route was reported by Simmler et al.:[5] the reaction of (acetoxymethyl)ethoxydimethylsilane with acidic methanol gave (hydroxymethyl)ethoxydimethylsilane as an intermediate (exchange of the alkoxy groups is likely but was not reported), which was treated with potassium hydroxide followed by work-up with *para*-toluenesulfonic acid to give **3** in 68% yield (Scheme 1). Tacke et al. used hydroxymethyl(dimethyl)silane as the starting material, which underwent cyclization in 31% yield by reaction with catalytic amounts of *n*-butyllithium and with the evolution of hydrogen (Scheme 1).[6,7]



Scheme 1. Previously reported synthetic routes to **3**. *p*-Ts: *para*-toluenesulfonyl.

[a] Dipl.-Chem. S. A. Erhardt, Prof. Dr. B. Rieger
Wacker-Lehrstuhl für Makromolekulare Chemie
Institut für Siliciumchemie
Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13562
E-mail: rieger@tum.de

[b] Dr. F. Hoffmann, Dr. J. O. Daiß, Dr. J. Stohrer
Wacker Chemie AG, Consortium für Elektrochemische Industrie
Zielstattstrasse 20, 81379 München (Germany)

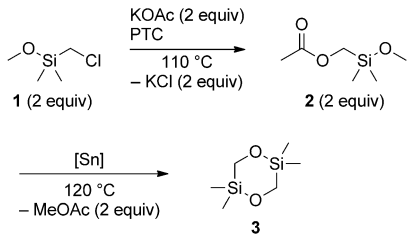
[c] Dr. E. Herdtweck
Anorganisch-chemisches Institut, Lehrstuhl für Anorganische Chemie
Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)

However, in all of these synthetic pathways, the non-neutral reaction conditions, that is, acidic or basic catalysis, lead to rapid rearrangement of the cyclic structure of **3** after distillation due to traces of the catalyst, to give oligomeric or polymeric products.[4–6] However, for applications as precursors of functionalized polysiloxanes, stable monomeric compounds are desirable. Additionally, if compounds with hydrolyzable alkoxy side groups are to be synthesized, anhydrous reaction conditions are required.

Organotin(IV) reagents are known to catalyze transesterifications of alcohols and esters under mild and neutral conditions.[8] This methodology was also used to achieve ring closures by which lactones were formed in the tin-promoted reaction of a carboxyl group with a hydroxy group,[9] as well as by the intramolecular reaction of a *tert*-butyl ester and a hydroxy group.[10] The methodology is also applicable to (acetoxymethyl)alkoxysilanes and, surprisingly, yields dioxadisilacycles through tin-catalyzed transesterification of the acetoxy and alkoxy units. Herein, we present a new route to 2,2,5,5-organo-substituted 1,4-dioxa-2,5-disilacyclohexanes, which leads to a stable product under neutral, anhydrous conditions.[11]

Results and Discussion

(Acetoxymethyl)methoxydimethylsilane (**2**) was synthesized from (chloromethyl)methoxydimethylsilane (**1**) by treatment with potassium acetate (Scheme 2). Commonly, *N*,*N*-dimethylformamide (DMF) is used as the solvent at high temperatures (reflux conditions) for the conversion of (chloromethyl)silanes into the corresponding (acetoxymethyl)silanes in the presence of a large excess of sodium or potassium acetate.[12] In order to increase yields and the reaction speed, various phase-transfer catalysts were tested (Table 1).[13,14] In lieu of DMF, high-temperature-boiling solvents (diphenyl ether and the hydrocarbon mixture Hydroseal G 400 H) were used to simplify the workup procedure. Aliquat 336 or tetrabutylphosphonium bromide in Hydroseal G 400 H afforded the highest conversions of 92 and 89%, respectively (Table 1, entries 4 and 5). A slight excess (1.18 equiv) of potassium acetate was sufficient.



Scheme 2. Synthesis of (acetoxymethyl)silane **2** followed by cyclization to **3**. PTC: phase-transfer catalyst.

Table 1. Synthesis of **2** by using phase-transfer catalysis under different conditions.

Entry	Solvent	PTC[a]	t [h][b]	Yield [%][c]
1	Hydroseal G 400 H	Bu_4NBr	8	72
2	Hydroseal G 400 H	Bu_4PCl	5	79
3	diphenyl ether	Bu_4PBr	4	78
4	Hydroseal G 400 H	Aliquat 336	9	92
5	Hydroseal G 400 H	Bu_4PBr	5	89
6	diphenyl ether	Aliquat 336	6	88

[a] 2 mol% catalyst was used. Aliquat 336: trioctylmethylammonium chloride. [b] Reactions were run until GC analysis showed a conversion of at least 99%. [c] Yields of isolated products after distillation.

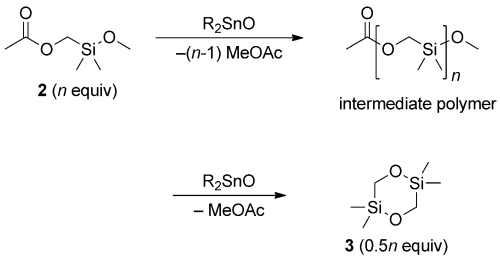
The subsequent ring closure was promoted by tin(IV) compounds. The catalyst (0.5 mol%) was suspended in silane **2**, and the reaction mixture was stirred at 120°C. The evolving methyl acetate was distilled off at reduced pressure over a period of 6 h to shift the equilibrium of the reaction toward the desired product. After distillation, silane **3** was obtained in high purity in 86% yield. Various organotin(IV) compounds were tested as catalysts, with yields ranging from 72 to 86% (Table 2). Dioctyltin oxide and dibutyltin oxide were the most efficient catalysts.

Table 2. Synthesis of dioxadisilacyclohexane **3** by using different catalysts.

Entry	Catalyst[a]	t [h][b]	Yield [%][c]
1	dibutyldimethoxy tin	7	72
2	dibutyltin dilaurate	8	79
3	dimethyltin oxide	6	80
4	dioctyltin oxide	6	86
5	dibutyltin oxide	6	86

[a] 0.5 mol% catalyst was used. [b] Reactions were run until GC analysis showed a conversion of at least 98%. [c] Yields of isolated products after distillation.

The formation of silane **3** proceeds in two steps. Firstly, silane **2** condenses by transesterification and removal of methyl acetate into linear oligomers with $[SiMe_2–CH_2–O]$ repeating units and methoxy or acetyl end groups, respectively (Scheme 3). These oligomers are in a dynamic thermal equilibrium with cyclic compounds $[SiMe_2–CH_2–O]_m$ ($m \geq 2$; the three-membered ring with $m = 1$ is not stable towards oligomerization under these conditions and was therefore

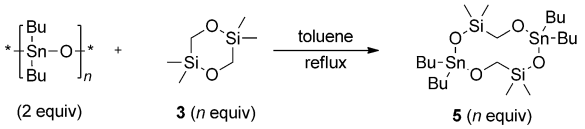


Scheme 3. Tin(IV)-catalyzed synthesis of cyclic silane **3**. R: *n*-butyl or *n*-octyl.

not observed). Analysis by GC and GC-MS showed linear ($n \leq 9$) and cyclic ($m \leq 12$) homologues in the reaction mixture.[15] Upon completion of the polymer formation, the average ratio of repeating units (linear and cyclic) to end groups (methoxy and acetyl) was found to be in the range 15–30:1 (as determined by ^{1}H NMR spectroscopy). From this reaction mixture, the most volatile cyclic product **3** ($m=2$) is then separated by distillation. The thermal equilibration of the reaction induces the formation of further quantities of **3** until nearly all of the [$SiMe_2$–CH_2–O] units are converted into this stable ring structure.

It is noteworthy that the use of a long distillation column was necessary to prevent contamination of **3** with the next higher homologue, 2,2,5,5,8,8-hexamethyl-1,4,7-trioxa-2,5,8-trisilacyclononane (**4**, $m=3$), in the distillate. However, for most applications, this mixture can be used just as pure silane **3**.

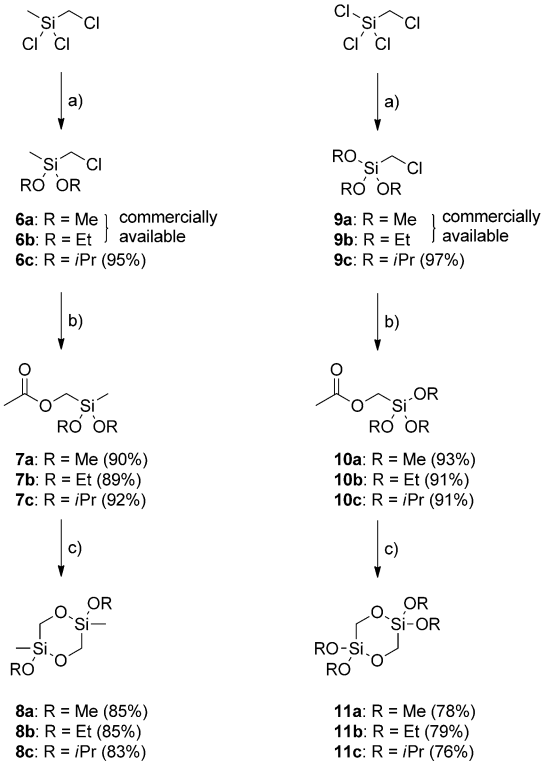
From the brown liquid distillation residue, a white solid precipitated upon cooling; this was identified as a cyclic silastannoxane by NMR spectroscopy and FAB-MS. When dibutyltin oxide was used as the catalyst, the compound 2,2,7,7-tetrabutyl-4,4,9,9-tetramethyl-1,3,6,8-tetraoxa-4,9-disila-2,7-distannacyclodecane (**5**) was formed. Compound **5** could also be synthesized from silane **3** and dibutyltin oxide by simply heating stoichiometric amounts in toluene (Scheme 4). The respective silastannoxanes are the only tin



Scheme 4. Synthesis of silastannoxane **5** from silane **3** and dibutyltin oxide.

compounds observed by ^{119}Sn NMR spectroscopy throughout the reaction. After the reaction, they comprise up to 90% of the tin catalyst in the distillation residue (as judged by ^{1}H NMR spectroscopy). It is not clear if these compounds are intermediates from the catalytic cycle or just by-products formed from silane **3** and the catalyst. Indeed, as silastannoxane **5** is a very effective catalyst for the formation of **3** from **2**, it is assumed that **5** is at least in a dynamic equilibrium with the reactive species. Attempts to obtain single crystals for X-ray structure determination were not successful.

Notably, degradation of **3**, especially by polymerization as previously reported,[4–6] could not be detected when it was stored at room temperature with exclusion of moisture. The silane remained stable (as judged by NMR spectroscopy) even after one year, due to the synthetic method that does not contaminate the product with traces of acids or bases, which can lead to decomposition. Inspired by these results, we adapted the protocol outlined above for the synthesis of dioxadisilacyclohexanes bearing labile alkoxy groups at the silicon atom.[16]



Scheme 5. Synthesis of silanes **8a–c** and **11a–c**. a) ROH, imidazole, DMAP, CH_2Cl_2, 0°C to room temperature, 12 h; b) KOAc, Bu_4PBr (2 mol%), 110°C; c) Oct_2SnO (0.5 mol%), 120–125°C. DMAP: 4-(dimethylamino)pyridine.

(Acetoxymethyl)silanes **7a–c** and **10a–c** with methoxy, ethoxy, and the sterically more demanding isopropoxy substituents were synthesized as precursors by using the optimized protocol as previously described (Scheme 5). (Chloromethyl)silanes **6c** and **9c** were synthesized by alcoholysis of (chloromethyl)dichloromethylsilane and (chloromethyl)trichlorosilane with isopropanol in 95 and 97% yields, respectively. Imidazole was used in excess as an HCl scavenger and DMAP was used as the catalyst.[17] Treatment of silanes **6a–c** and **9a–c** with potassium acetate and tetrabutylphosphonium bromide as the phase-transfer catalyst afforded the corresponding (acetoxymethyl)silanes **7a–c** and **10a–c** in high yields. Silanes with purities of at least 99.8%, as verified by GC analysis, were used for the subsequent cyclization reactions. (Acetoxymethyl)silanes were stored over molecular sieves to prevent moisture-driven generation of alcohols because contamination of the cyclic silanes with alcohols would lead to slow polymerization by ring opening.

The mechanism of the cyclization reactions of silanes **7a–c** and **10a–c** is assumed to be analogous to that outlined above for silane **3**. There is more than one reactive group at the silicon atom, so the intermediate polymer can also be branched or cross-linked, which would thus lead to the formation of branched or cross-linked cyclic compounds. Dioctyltin oxide was used throughout in the reactions. Thereby, 2,5-dialkoxy-2,5-dimethyl-1,4-dioxa-2,5-disilacyclohex-

anes **8a–c** could be obtained in yields of 83–85% by starting from silanes **7a–c**, respectively. The products were isolated after distillation as a mixture of isomers, with the alkoxy groups in *cis* or *trans* positions relative to each other on the six-membered ring (**8a**: *cis*:*trans* ratio ≈ 1:1, as determined by NMR spectroscopy). This can also be seen in the ^{29}Si NMR spectra (INEPT experiment)[18] of **8a–c**, which clearly show two distinct peaks with similar chemical shifts ($\Delta\delta = 0.2$–0.3 ppm; Figure 1). The *trans* isomer of **8a** could be separated by crystallization at −20 °C. *trans*-2,5-Dimethoxy-2,5-dimethyl-1,4-dioxa-2,5-disilacyclohexane (*trans*-**8a**) crystallizes in a chair conformation (Figure 2). A mixture of isomers is formed because the alkoxy substituents are relatively small. If bulky phenyl substituents are present, only the *trans* isomer is formed, as in the case of 2,5-dimethyl-2,5-diphenyl-1,4-dioxa-2,5-disilacyclohexane.[6] Significantly, upon standing at room temperature, both isomers of **8a** (*cis*: enriched in the mother liquor; *trans*: melted crystals) rearrange into the original ratio of isomers within several weeks (Figure 3), with simultaneous polymerization being observed. Apparently, both isomers are in a dynamic equilibrium. At −20 °C, no rearrangement was observed within the same period of time.

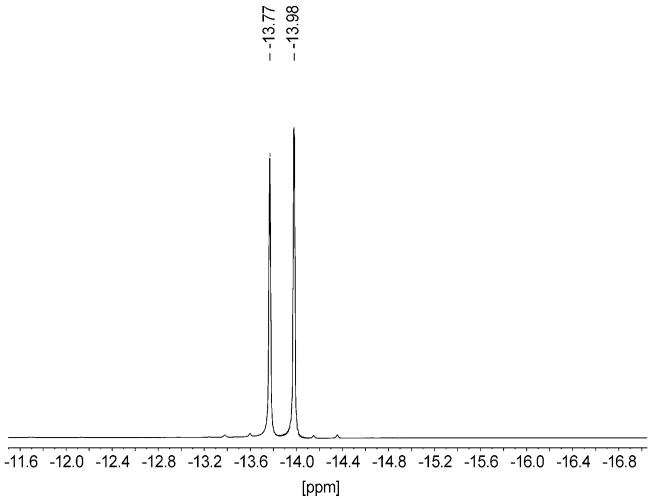


Figure 1. ^{29}Si NMR spectrum of **8a** showing signals for both isomeric products.

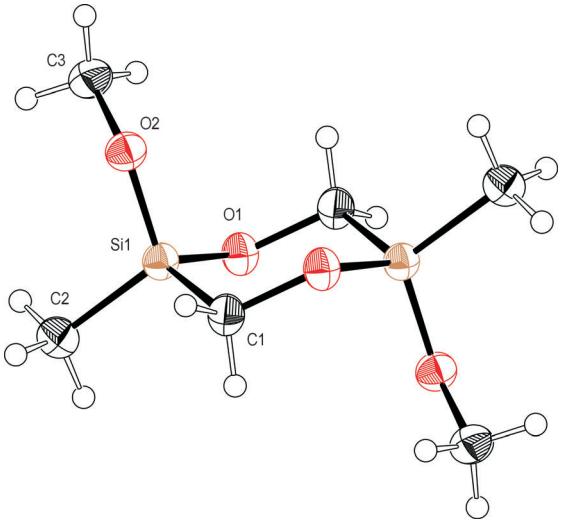


Figure 2. ORTEP-style plot of compound *trans*-**8a** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Si1–O1 1.655(2), Si1–O2 1.652(2), Si1–C1 1.891(2), Si1–C2 1.851(3), O1–C1′ 1.467(3), O2–C3 1.445(3); O1–Si1–O2 110.7(1), O1–Si1–C1 107.8(1), O1–Si1–C2 106.9(1), O2–Si1–C1 104.9(1), O2–Si1–C2 112.9(1), C1–Si1–C2 113.6(1), Si1–O1–C1′ 120.5(1), Si1–O1–C3 122.5(2), Si1–C1–O1′ 111.8(2). Operator for generating equivalent atoms: $-x$, $1-y$, $-z$.

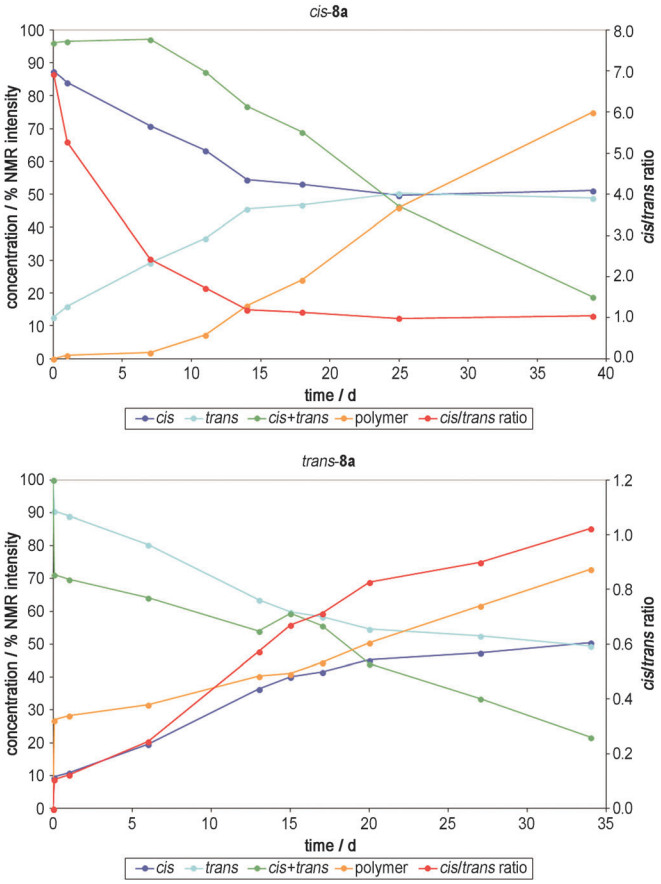


Figure 3. Kinetics of the equilibration of *cis* and *trans* isomers of **8a**.

The synthetically challenging hydrolytically labile tetraalkoxy-substituted cyclic silanes **11a–c** were synthesized in an analogous manner to **8a–c** from (acetoxymethyl)trialkoxysilanes **10a–c** in good yields. In addition, it was found that "mixed" ring structures could also be accessed by this synthetic route, if mixtures of (acetoxymethyl)silanes are used. Thus, commercially available **9a**, which contains impurities of **6a**, leads through **10a** and **7a** to **11a** with an impurity of 2,2,5-trimethoxy-5-methyl-1,4-dioxa-2,5-disilacyclohexane (**12**). Admittedly, the synthetic usefulness of this reaction is limited because poorly separable statistical mixtures of cyclic compounds are formed if stoichiometric mixtures of (acetoxymethyl)silanes are used.

If the hydrolytic stabilities of the different cyclic silanes are compared, the (dialkoxy)dimethyl-substituted rings are considerably more stable than those bearing four alkoxy substituents. As expected,[19] the methoxy derivatives are the most labile, whereas the ethoxy and isopropoxy derivatives are more stable towards hydrolysis. More precisely, if handled under argon at −20 °C, silanes **8a–c** remain intact for several months, whereas some oligomerization products can be detected in **11b** and **11c** by NMR spectroscopy within several weeks. The tetramethoxy-substituted silane **11a** is the least stable and shows traces of oligomers after several days.

Conclusion

2,2,5,5-Substituted 1,4-dioxa-2,5-disilacyclohexanes can be synthesized in high yield and purity from (acetoxymethyl)alkoxysilanes in a tin-catalyzed two-step transesterification reaction of the acetoxy and alkoxy units through intermolecular condensation followed by ring closure. The (acetoxymethyl)alkoxysilanes are accessible from (chloromethyl)alkoxysilanes in high-temperature-boiling solvents with phase-transfer catalysis. Due to the mild, neutral, and anhydrous reaction conditions, hydrolytically labile alkoxy substituents at the silicon atom are tolerated and the obtained compounds are much more stable than those obtained by alternative synthetic routes. These novel cyclic silanes are interesting monomers and precursors. Investigations to explore their chemistry are in progress.

Experimental Section

General methods: All reactions were performed under an atmosphere of argon by using standard Schlenk techniques, unless otherwise stated. Solvents were dried by employing standard methods. Chemicals were purchased from commercial suppliers and used as received. Hydroseal G 400 H was obtained from Total. (Chloromethyl)silanes **1**, **6a**, **6b**, **9a**, and **9b** were obtained from Wacker Chemie AG. ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded on a Bruker Avance 500 cryospectrometer (^{1}H: 500 MHz; ^{13}C: 126 MHz; ^{29}Si: 99 MHz), Bruker Avance 360 spectrometer (^{1}H: 360 MHz; ^{29}Si: 72 MHz), or Bruker Avance 300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz; ^{29}Si: 60 MHz; ^{119}Sn: 112 MHz) at ambient temperature. Chemical shifts are reported in δ (ppm) and were determined relative to internal [D$_5$]benzene (^{1}H NMR: $\delta = 7.16$ ppm), internal [D$_6$]benzene (^{13}C NMR: $\delta = 128.06$ ppm), internal $CHCl_3$ (^{1}H NMR: $\delta = 7.27$ ppm), internal $CDCl_3$ (^{13}C NMR: $\delta = 77.00$ ppm), external tetramethylsilane (^{29}Si NMR: $\delta = 0$ ppm, in C_6D_6 or $CDCl_3$), or external tetramethylstannane (^{119}Sn NMR: $\delta = 0$ ppm, in C_6D_6); coupling constants are reported in Hz. ^{13}C NMR spectra were assigned with the aid of DEPT 135 experiments. GC-MS analysis was measured on a Varian CP-3800 GC unit coupled with a Varian Saturn 2100 T mass spectrometer. FAB-MS analysis was performed on a Finnigan MAT 90 mass spectrometer. IR spectra were recorded on a Nicolet Avatar 370 FT-IR spectrometer. Elemental analyses were performed by using the Vario EL analyzer (Elementar) at the Department of Inorganic Chemistry, Technische Universität München.

Rearrangement of *cis*- and *trans*-8a: The rearrangement of *cis*- and *trans*-**8a** was monitored by GC analysis and ^{1}H NMR spectroscopy. The absolute GC data turned out to be distorted by the polymerization of **8a** (formation of nonvolatile compounds), but the *cis*/*trans* ratio was in good agreement with the NMR data. The kinetic data shown in Figure 3 were derived from the ^{1}H NMR signals (in $CDCl_3$) of the methoxy groups because they did not superimpose with the signals of the polymer like the silicon-bound methyl groups did. The concentrations of *cis*- and *trans*-**8a** are shown in relation to each other, that is, their sum is 100 %. Their ratio is derived from these data. The concentrations of the sum of the isomers of **8a** and the polymer are shown in relation to the theoretical number of protons (6 or 10, respectively), that is, their sum may differ slightly from 100 %.

Single-crystal X-ray structure determination of compound *trans*-8a:[20] Suitable single crystals for the X-ray diffraction study were grown by cooling a mixture of *cis*- and *trans*-**8a** to −20 °C. A clear colorless fragment was fixed on the top of a glass fiber with perfluorinated ether and transferred to the diffractometer. Preliminary examination and data collection was carried out on an area-detecting system with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, Bruker AXS, APEX II, rotating anode, FR591). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection was performed at low temperature ($T = 123$ K, Oxford Cryosystems cooling device). The crystal was measured with eleven/nine data sets in rotation scan mode ($\Delta\phi/\Delta\omega = 0.50°$; $dx = 55/35$). Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined by using a riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual-electron-density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[20] CCDC-866726 (*trans*-**8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for *trans*-**8a**: Formula: $C_6H_{16}O_4Si_2$; $M_r = 208.37$; colorless fragment; crystal size: $0.17 \times 0.18 \times 0.23$ mm; monoclinic; space group: $C2/c$ (no. 15); $a = 12.1313(17)$, $b = 6.8248(7)$, $c = 17.045(3)$ Å; $\beta = 130.098(9)°$; $V = 1079.5(3)$ Å^3; $Z = 4$; $\mu(Mo_{K\alpha}) = 0.307$ mm^{-1}; $\rho_{calcd} = 1.282$ g cm^{-3}; θ range = 3.12–25.36°; 11940 data collected; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 857/965/0.061; data/restraints/parameters: 965/0/57; $R1$ [$I_o > 2\sigma(I_o)$/all data]: 0.0416/0.0465; $wR2$ [$I_o > 2\sigma(I_o)$/all data]: 0.1082/0.1097; GOF = 1.157; $\Delta\rho_{max/min}$: 0.48/−0.21 e Å^{-3}.

General procedure A for the synthesis of (acetoxymethyl)silanes: Potassium acetate (1.18 equiv) and tetrabutylphosphonium bromide (0.02 equiv) were suspended in the appropriate (chloromethyl)silane (1 equiv) and heated at 110 °C with vigorous stirring for 4–8 h, until GC-MS analysis showed full conversion. After cooling of the mixture to room temperature, anhydrous dichloromethane was added and the mixture was filtered. The solvent was removed by distillation at ambient pressure. The residue was then purified by distillation under reduced pressure to afford the pure product.

General procedure B for the synthesis of (acetoxymethyl)silanes: Potassium acetate (1.18 equiv) and tetrabutylphosphonium bromide (0.02 equiv) were suspended in the appropriate (chloromethyl)silane (1 equiv). A high-temperature-boiling solvent was added (diphenyl ether or Hydroseal G 400 H), and the reaction mixture was heated at 110 °C with vigorous stirring for 4–8 h, until GC-MS analysis showed full conversion. The (acetoxymethyl)silanes were purified by distillation under reduced pressure.

General procedure C for the synthesis of (acetoxymethyl)silanes: Potassium acetate (1.18 equiv) and tetrabutylphosphonium bromide (0.02 equiv) were suspended in the appropriate (chloromethyl)silane (1 equiv) and heated at 110 °C with vigorous stirring for 4–8 h, until GC-MS analysis showed full conversion. After being cooled to room temperature, the mixture was diluted with dichloromethane and poured into water. The organic phase was separated, the aqueous layer was extracted with di-

chloromethane, and the combined organic extracts were washed with water and saturated NaCl solution. After drying over $MgSO_4$, the dichloromethane was removed by distillation at ambient pressure. For purification, the crude silanes were distilled under reduced pressure.

General procedure D for the synthesis of 2,2,5,5-functionalized 1,4-dioxa-2,5-disilacyclohexanes: (Acetoxymethyl)silanes were distilled prior to cyclization reactions, to purities of at least 99.8% (as determined by GC analysis) and stored over molecular sieves (4 Å). Dioctyltin oxide (0.5 mol%) was suspended in the appropriate silane, and the mixture was heated at 120–125°C. Evolving alkyl esters were removed by distillation under vacuum. The pressure was continuously decreased over a period of approximately 6 h. After complete removal of the alkyl esters, the dioxadisilacyclohexanes were distilled from the reaction mixture.

(Acetoxymethyl)methoxydimethylsilane (2): General procedure B, silane **1** (101 g, 731 mmol), potassium acetate (84.6 g, 862 mmol), tetrabutylphosphonium bromide (4.96 g, 14.6 mmol), Hydroseal G 400 H (100 mL), 110°C, 5 h. Distillation at 92°C (100 mbar) afforded **2** as a colorless liquid (105 g, 648 mmol, 89%); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.80$ (s, 2H; Si–CH_2–O), 3.24 (s, 3H; OCH_3), 1.68 (s, 3H; Ac CH_3), 0.07 ppm (s, 6H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.7$ (C=O), 56.3 (Si–CH_2–O), 50.4 (OCH_3), 20.3 (Ac CH_3), −3.7 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -12.4$ ppm; MS (70 eV): m/z (%): 146.9 [M^+–CH_3] (38.4); elemental analysis: calcd (%) for $C_6H_{14}O_3Si$ (162.07): C 44.41, H 8.70, Si 17.31; found: C 44.95, H 8.77, Si 17.23.

2,2,5,5-Tetramethyl-1,4-dioxa-2,5-disilacyclohexane (3): General procedure D, dioctyltin oxide (965 mg, 2.67 mmol), silane **2** (86.7 g, 534 mmol), 120°C (pressure was decreased from 650 to 100 mbar). Silane **3** (40.6 g, 230 mmol, 86%) was obtained as a colorless liquid by distillation at 42°C (12 mbar); m.p. 19–21°C; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.51$ (s, 4H; Si–CH_2–O), 0.10 ppm (s, 12H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta =$ 56.8 (Si–CH_2–O), −3.1 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta =$ 9.1 ppm; MS (70 eV): m/z (%): 176.2 [M^+] (92.9); elemental analysis: calcd (%) for $C_6H_{16}O_2Si_2$ (176.07): C 40.86, H 9.14, Si 31.85; found: C 40.61, H 9.12, Si 31.56.

NMR data for the intermediate polymer in the formation of 3: ^{1}H NMR (300/500 MHz, C_6D_6): $\delta = 4.1$–3.9 (Si–CH_2–OAc), 3.6–3.0 ([Si–CH_2–O]$_x$, OCH_3), 1.86–1.82 ppm (Ac CH_3); ^{1}H NMR (300/500 MHz, $CDCl_3$): $\delta =$ 3.77–3.67 (Si–CH_2–OAc), 3.46–3.37 (OCH_3), 3.37–3.16 ([Si–CH_2–O]$_x$), 2.03 ppm (Ac CH_3).

2,2,5,5,8,8-Hexamethyl-1,4,7-trioxa-2,5,8-trisilacyclononane (4): Occasionally contained as an "impurity" in silane **3** (see text); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 3.34$ (s, 18H; Si–CH_2–O), 0.15 ppm (s, 6H; Si–CH_3); MS (70 eV): m/z (%): 264.1 [M^+] (2.3).

2,2,7,7-Tetrabutyl-4,4,9,9-tetramethyl-1,3,6,8-tetraoxa-4,9-disila-2,7-distannacyclodecane (5): Dibutyltin oxide (9.8 g, 39.4 mmol), silane **3** (3.5 g, 19.8 mmol), and toluene (5 mL) were heated to reflux (120–125°C, complete dissolution) for some hours until ^{1}H NMR monitoring showed that the signals of the starting materials had disappeared and only product signals were present. The mixture was first cooled to room temperature and then in a refrigerator overnight. The white precipitate was separated, washed with pentane, and dried in vacuo. Compound **5** (9.7 g, 14.4 mmol, 73%) was obtained as a white microcrystalline powder, which was moderately soluble in tetrahydrofuran or toluene. From the mother liquor, no further product could be obtained; m.p.: 98–100°C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 3.13$ (s, ^1J(H,C) = 132.5, ^3J(H,Sn) = 35.7 Hz, 4H; Si–CH_2–O), 1.91 (m, ^3J(H,Sn) = 95.4 Hz, 8H; nBu CH_2), 1.55 (m, 8H; nBu CH_2), 1.45 (t, ^3J(H,H) = 7.6, ^2J(H,Sn) = 70 Hz, 8H; Sn–CH_2), 1.08 (t, ^3J(H,H) = 7.3, ^1J(H,C) = 125.8 Hz, 12H; nBu CH_3), 0.37 ppm (s, ^1J(H,C) = 118.0, ^1J(H,Si) = 6.4 Hz, 12H; Si–CH_3); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 55.2$ (Si–CH_2–O), 28.1 (^2J(C,Sn) = 34 Hz; nBu CH_2), 27.5 (^3J(C,Sn) = 79 (^{117}Sn) and 82 Hz (^{119}Sn); nBu CH_2), 21.1 (^1J(C,Sn) = 598 (^{117}Sn) and 623 Hz (^{119}Sn); Sn–CH_2), 14.3 (nBu CH_3), 1.8 ppm (^1J(C,Si) = 58.3 Hz; Si–CH_3); ^{29}Si NMR (60 MHz, C_6D_6): $\delta = 0.01$ ppm (^2J(Si,Sn) = 20 Hz); ^{119}Sn NMR (112 MHz, C_6D_6): $\delta = -141.8$ ppm (br ($\Delta\nu_{1/2} = 70$ Hz), ^1J(Sn,C) = 616, ^3J(C,Sn) = 85, ^3J(Sn,Si) = 172 Hz); IR (KBr): $\tilde{\nu} = 2955$ (s), 2926 (s), 2895 (w, sh), 2870 (m), 2857 (s), 2798 (m), 2725 (vw), 1464 (m), 1456 (m), 1423 (w), 1375 (w), 1341 (vw), 1285 (vw), 1261 (vw, sh), 1244 (s), 1207 (w), 1194 (vw), 1155 (w), 1075 (w), 982 (s), 926 (s), 883 (m), 869 (m), 824 (s), 803 (m), 741 (m), 690 (m), 673 (m), 634 (w), 619 (w), 595 cm^{-1} (w); FAB-MS: m/z (%): 675.2 [M+H$^+$] (16.4); elemental analysis: calcd (%) for $C_{22}H_{52}O_4Si_2Sn_2$ (674.25): C 39.19, H 7.77, Si 8.33, Sn 35.21; found: C 38.91, H 7.58, Si 8.29, Sn 35.3.

(Chloromethyl)(diisopropoxy)methylsilane (6c): Dry isopropanol (32.0 mL, 422 mmol) was added to a solution of imidazole (30.7 g, 452 mmol) and 4-(dimethylamino)pyridine (2.4 g, 20 mmol) in dry dichloromethane (350 mL). The solution was cooled to 0°C. At that temperature, dichloro(chloromethyl)methylsilane (32.1 g, 196 mmol) was added dropwise, which resulted in precipitation of imidazole hydrochloride. The suspension was allowed to warm to room temperature and stirred overnight (12 h). After filtration, ammonium chloride solution (10% in water, 200 mL) was slowly added. The organic phase was separated, the aqueous layer was extracted with dichloromethane (2×75 mL), and the combined organic extracts were washed with water (100 mL) and saturated NaCl solution (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Compound **6c** (39.1 g, 186 mmol, 95%) was obtained as a colorless liquid by distillation under reduced pressure; b.p. 70°C (20 mbar); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.03$ (sept, ^3J(H,H) = 6.1 Hz, 2H; iPr CH), 2.62 (s, 2H; Si–CH_2–O), 1.11 (d, ^3J(H,H) = 6.1 Hz, 18H; iPr CH_3), 0.23 ppm (s, 3H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 65.74$ (iPr CH), 27.9 (Si–CH_2–O), 25.8 (iPr CH_3), −5.2 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -19.0$ ppm; MS (70 eV): m/z (%): 209.0 [M^+–H] (3.1); elemental analysis: calcd (%) for $C_8H_{19}ClO_2Si$ (210.08): C 45.59, H 9.09, Si 13.32; found: C 45.25, H 9.29, Si 13.25.

(Acetoxymethyl)dimethoxymethylsilane (7a): General procedure B, potassium acetate (64.4 g, 656 mmol), tetrabutylphosphonium bromide (3.85 g, 11.1 mmol), silane **6a** (86.0 g, 556 mmol), diphenyl ether (100 mL), 110°C, 8 h. After distillation, silane **7a** was obtained as a colorless liquid (89.4 g, 501 mmol, 90%); b.p. 70°C (20 mbar); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.85$ (s, 2H; Si–CH_2–O), 3.33 (s, 6H; OCH_3), 1.68 (s, 3H; Ac CH_3), 0.14 ppm (s, 3H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.7$ (C=O), 53.7 (Si–CH_2–O), 50.2 (OCH_3), 20.2 (Ac CH_3), −6.1 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -11.2$ ppm; MS (70 eV): m/z (%): 177.7 [M^+] (1.2); elemental analysis: calcd (%) for $C_6H_{14}O_4Si$ (178.07): C 40.43, H 7.92, Si 15.76; found: C 40.27, H 7.54, Si 15.63.

(Acetoxymethyl)diethoxymethylsilane (7b): General procedure A, potassium acetate (56.7 g, 578 mmol), tetrabutylphosphonium bromide (3.32 g, 9.80 mmol), silane **6b** (89.5 g, 490 mmol), 110°C, 8 h. Silane **7b** (90.1 g, 437 mmol, 89%) was obtained by distillation at 77°C (16 mbar) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.90$ (s, 2H; Si–CH_2–O), 3.66 (q, ^3J(H,H) = 7.0 Hz, 4H; Et CH_2), 1.69 (s, 3H; Ac CH_3), 1.10 (t, ^3J(H,H) = 7.0 Hz, 6H; Et CH_3), 0.20 ppm (s, 3H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.7$ (C=O), 58.6 (Et CH_2), 54.3 (Si–CH_2–O), 20.3 (Ac CH_3), 18.6 (Et CH_3), −5.1 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -15.0$ ppm; MS (70 eV): m/z (%): 206.1 [M^+] (0.4); elemental analysis: calcd (%) for $C_8H_{18}O_4Si$ (206.10): C 46.57, H 8.79, Si 13.61; found: C 46.43, H 8.90, Si 13.47.

(Acetoxymethyl)diisopropoxymethylsilane (7c): General procedure C, potassium acetate (22.0 g, 224 mmol), tetrabutylphosphonium bromide (1.31 g, 3.80 mmol), silane **6c** (40.0 g, 190 mmol), 110°C, 6 h. Purification by distillation provided **7c** (41.0 g, 175 mmol, 92%) as a colorless liquid; b.p. 70°C (6 mbar); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.07$ (sept, ^3J(H,H) = 6.1 Hz, 2H; iPr CH), 3.90 (s, 2H; Si–CH_2–O), 1.71 (s, 3H; Ac CH_3), 1.12 (d, ^3J(H,H) = 6.1 Hz, 12H; iPr CH_3), 0.22 ppm (s, 3H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.6$ (C=O), 65.5 (iPr CH), 54.9 (Si–CH_2–O), 25.8 (iPr CH_3), 20.4 (Ac CH_3), −4.1 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -17.9$ ppm; MS (70 eV): m/z (%): 234.0 [M^+] (0.2); elemental analysis: calcd (%) for $C_{10}H_{22}O_4Si$ (234.13): C 51.25, H 9.46, Si 11.98; found: C 51.40, H 9.26, Si 12.16.

2,5-Dimethoxy-2,5-dimethyl-1,4-dioxa-2,5-disilacyclohexane (8a): General procedure D, dioctyltin oxide (200 mg, 0.553 mmol), silane **7a** (19.7 g, 111 mmol), 120°C (pressure was decreased from 650 to 20 mbar). The crude product was distilled at 36°C (2×10^{-1} mbar) to provide **8a** (9.83 g, 47.2 mmol, 85%) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta =$ 3.69 (m, 4H; Si–CH_2–O), 3.51 and 3.35 (s, 6H; OCH_3), 0.08 and 0.00 ppm (s, 6H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 54.9$ and 54.4

(Si–CH_2–O), 50.4 and 50.3 (OCH_3), −5.4 and −5.5 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -13.8$ and −14.0 ppm; MS (70 eV): *m/z* (%): 208.1 [M^+] (44.2); elemental analysis: calcd (%) for $C_6H_{16}O_4Si_2$ (208.06): C 34.59, H 7.74, Si 26.96; found: C 34.55, H 7.59, Si 26.83.

Separation of isomers of 8a: *trans*-**8a** crystallized upon storage of the isomeric mixture at −20 °C for some days. The mother liquor (mainly *cis*-**8a**) was removed with a syringe and the colorless crystals were washed with cold pentane and dried in vacuo. An 11.2 g amount of **8a** gave 3.85 g (34 %) of *trans*-**8a** and 4.97 g (44 %) of enriched *cis*-**8a**. Both isomers should be stored under an inert atmosphere at low temperature to retain their isomeric composition. *cis*-**8a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.83$ (m, 0.8 H; Si–CH_2–O), 3.78 (m, 1.2 H; Si–CH_2–O), 3.60 (s, 1.2 H; Si–CH_2–O), 3.55 (s, 0.8 H; Si–CH_2–O), 3.52 (s, ^1J(H,C) = 143.1 Hz, 6 H; OCH_3), 0.168 (s, ^1J(H,C) = 119.9, ^2J(H,Si) = 7.4 Hz, 3 H; Si–CH_3), 0.166 ppm (s, ^1J(H,C) = 119.7, ^2J(H,Si) = 7.4 Hz, 3 H; Si–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 54.3$ (OCH_3), 50.4 (Si–CH_2–O), −5.66 ppm (s, ^1J(C,Si) = 76.0 Hz, Si–CH_3); ^{29}Si NMR (60 MHz, $CDCl_3$): $\delta = -13.0$ ppm (s, ^1J(Si,C) = 76.5 Hz). *trans*-**8a**: m.p.: 20–22 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.694$ (s, 2 H; Si–CH_2–O), 3.690 (s, 2 H; Si–CH_2–O), 3.56 (s, ^1J(H,C) = 143.0 Hz, 6 H; OCH_3), 0.12 ppm (s, ^1J(H,C) = 119.9, ^2J(H,Si) = 7.3 Hz, 6 H; Si–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 54.8$ (OCH_3), 50.5 (Si–CH_2–O), −5.75 ppm (s, ^1J(C,Si) = 75.6 Hz, Si–CH_3); ^{29}Si NMR (60 MHz, $CDCl_3$): $\delta = -13.1$ ppm (s, ^1J(Si,C) = 75.4 Hz).

2,5-Diethoxy-2,5-dimethyl-1,4-dioxa-2,5-disilacyclohexane (8b): General procedure D, dioctyltin oxide (198 mg, 547 μmol), silane **7b** (22.6 g, 109 mmol), 120 °C, 6 h (pressure was continuously decreased from 600 to 10 mbar). Distillation at 46 °C (1.4×10^{-1} mbar) afforded the cyclic product (11.0 g, 46.7 mmol, 85 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.72$ (m, 8 H; Et CH_2, Si–CH_2–O), 1.14 and 1.10 (t, ^3J(H,H) = 7.0 Hz, 6 H; Et CH_3), 0.14 and 0.06 ppm (s, 6 H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 58.8$ and 58.7 (Et CH_2), 55.2 and 54.7 (Si–CH_2–O), 18.7 and 18.6 (Et CH_3), −4.90 and −4.86 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -15.5$ and −15.2 ppm; MS (70 eV): *m/z* (%): 236.2 [M^+] (26.8); elemental analysis: calcd (%) for $C_8H_{20}O_4Si_2$ (236.09): C 40.64, H 8.53, Si 23.76; found: C 40.69, H 8.80, Si 23.91.

2,5-Diisopropoxy-2,5-dimethyl-1,4-dioxa-2,5-disilacyclohexane (8c): General procedure D, dioctyltin oxide (92.2 mg, 255 μmol), silane **7c** (12.0 g, 51.0 mmol), 125 °C (pressure was continuously decreased from 600 to 5 mbar). Distillation at 36 °C (1.6×10^{-2} mbar) provided **8c** (5.58 g, 21.1 mmol, 83 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta =$ 4.18 and 4.09 (sept, ^3J(H,H) = 6.1 Hz, 2 H; *i*Pr CH), 3.72 (m, 4 H; Si–CH_2–O), 1.16 and 1.12 (dd, ^3J(H,H) = 6.1 Hz, 12 H; *i*Pr CH_3), 0.16 and 0.09 ppm (s, 6 H; Si–CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 65.7$ and 65.7 (*i*Pr CH), 55.3 and 55.0 (Si–CH_2–O), 25.9 and 25.9 (*i*Pr CH_3), −4.3 and −4.4 ppm (Si–CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -16.7$ and −17.0 ppm; MS (70 eV): *m/z* (%): 264.2 [M^+] (7.0); elemental analysis: calcd (%) for $C_{10}H_{24}O_4Si_2$ (264.12): C 45.41, H 9.15, Si 21.24; found: C 45.40, H 9.26, Si 21.16.

(Chloromethyl)triisopropoxysilane (9c): Dry isopropanol (48.0 mL, 627 mmol) was added to a solution of imidazole (43.4 g, 637 mmol) and 4-(dimethylamino)pyridine (3.7 g, 30 mmol) in dry dichloromethane (350 mL). (Chloromethyl)trichlorosilane (36.6 g, 199 mmol) was added dropwise at 0 °C, which resulted in precipitation of imidazole hydrochloride. The suspension was allowed to warm to room temperature and stirred overnight (12 h). After filtration, ammonium chloride solution (10 % in water, 200 mL) was slowly added. The organic phase was separated, the aqueous layer was extracted with dichloromethane (2 × 75 mL), and the combined organic layers were subsequently washed with water (100 mL) and saturated NaCl solution (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was distilled to furnish **9c** (49.0 g, 192 mmol, 97 %) as a colorless liquid; b.p. 60 °C (5 mbar); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.28$ (sept, ^3J(H,H) = 6.1 Hz, 3 H; *i*Pr CH), 2.69 (s, 2 H; Si–CH_2–O), 1.19 ppm (d, ^3J(H,H) = 6.1 Hz, 18 H; *i*Pr CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 66.2$ (*i*Pr CH), 25.6 (*i*Pr CH_3), 25.2 ppm (Si–CH_2–O); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -61.3$ ppm; MS (70 eV): *m/z* (%): 253.0 [M^+–H] (3.4); elemental analysis: calcd (%) for $C_{10}H_{23}ClO_3Si$ (254.11): C 47.13, H 9.10, Si 11.02; found: C 47.61, H 9.26, Si 11.07.

(Acetoxymethyl)trimethoxysilane (10a): General procedure B, potassium acetate (95.2 g, 558 mmol), tetrabutylphosphonium bromide (3.79 g, 11.2 mmol), silane **9a** (86.0 g, 556 mmol), Hydroseal G 400 H (150 mL), 110 °C, 4 h. After purification by distillation, silane **10a** was obtained as a colorless liquid (101 g, 520 mmol, 93 %); b.p. 85 °C (20 mbar); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.93$ (s, 2 H; Si–CH_2–O), 3.42 (s, 9 H; OCH_3), 1.66 ppm (s, 3 H; Ac CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.5$ (C=O), 50.8 (Si–CH_2–O), 50.6 (OCH_3), 20.2 ppm (Ac CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -53.3$ ppm; MS (70 eV): *m/z* (%): 193.8 [M^+] (0.1); elemental analysis: calcd (%) for $C_6H_{14}O_5Si$ (194.06): C 40.43, H 7.92, Si 15.76; found: C 37.45, H 7.42, Si 14.43.

(Acetoxymethyl)triethoxysilane (10b): General procedure A, potassium acetate (52.5 g, 535 mmol), tetrabutylphosphonium bromide (3.08 g, 9.03 mmol), silane **9b** (96.4 g, 453 mmol), 110 °C, 7 h. Distillation at 84 °C (10 mbar) provided **10b** (97.2 g, 411 mmol, 91 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.99$ (s, 2 H; Si–CH_2–O), 3.80 (q, ^3J(H,H) = 7.0 Hz, 6 H; Et CH_2), 1.69 (s, 3 H; Ac CH_3), 1.13 ppm (t, ^3J(H,H) = 7.0 Hz, 9 H; Et CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.5$ (C=O), 59.0 (Et CH_2), 51.7 (Si–CH_2–O), 20.3 (Ac CH_3), 18.5 ppm (Et CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -56.5$ ppm; MS (70 eV): *m/z* (%): 236.5 [M^+] (0.5); elemental analysis: calcd (%) for $C_9H_{20}O_5Si$ (236.11): C 45.74, H 8.53, Si 11.88; found: C 46.12, H 8.74, Si 11.96.

(Acetoxymethyl)triisopropoxysilane (10c): General procedure C, potassium acetate (18.2 g, 185 mmol), tetrabutylphosphonium bromide (1.09 g, 3.14 mmol), silane **9c** (40.0 g, 157 mmol), 110 °C, 8 h. The crude product was distilled (b.p. 80 °C, 6 mbar) to provide **10c** (39.6 g, 142 mmol, 91 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.27$ (sept, ^3J(H,H) = 6.1 Hz, 3 H; *i*Pr CH), 3.98 (s, 2 H; Si–CH_2–O), 1.71 (s, 3 H; Ac CH_3), 1.18 ppm (d, ^3J(H,H) = 6.1 Hz, 18 H; *i*Pr CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 170.5$ (C=O), 65.8 (*i*Pr CH), 52.4 (Si–CH_2–O), 25.6 (*i*Pr CH_3), 20.4 ppm (Ac CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -59.5$ ppm; MS (70 eV): *m/z* (%): 278.1 [M^+] (0.5); elemental analysis: calcd (%) for $C_{12}H_{26}O_5Si$ (278.15): C 51.77, H 9.41, Si 10.09; found: C 51.68, H 9.23, Si 10.40.

2,2,5,5-Tetramethoxy-1,4-dioxa-2,5-disilacyclohexane (11a): General procedure D, dioctyltin oxide (166 mg, 459 μmol), silane **10a** (17.8 g, 91.8 mmol), 120 °C (pressure was decreased from 650 to 10 mbar). Silane **11a** (8.62 g, 35.8 mmol, 78 %) was obtained by distillation at 40 °C (1.0×10^{-3} mbar) as a colorless liquid; ^{1}H NMR (360 MHz, C_6D_6): $\delta = 3.80$ (br, 4 H; Si–CH_2–O), 3.40 ppm (br, 12 H; OCH_3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, ^2J(H,Si) = 4.5 Hz, 4 H; Si–CH_2–O), 3.58 ppm (s, 12 H; OCH_3); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 52.4$ (Si–CH_2–O), 50.5 ppm (OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 51.8$ (s, ^1J(C,Si) = 103.5 Hz; Si–CH_2–O), 50.2 ppm (OCH_3); ^{29}Si NMR (72 MHz, C_6D_6): $\delta = -53.3$ ppm; ^{29}Si NMR (60 MHz, $CDCl_3$): $\delta = -53.8$ ppm (s, ^1J(Si,C) = 103.2 Hz); MS (70 eV): *m/z* (%): 240.2 [M^+] (43.9); elemental analysis: calcd (%) for $C_6H_{16}O_6Si_2$ (240.05): C 29.98, H 6.71, Si 23.37; found: C 30.30, H 6.95, Si 23.57.

2,2,5-Trimethoxy-5-methyl-1,4-dioxa-2,5-disilacyclohexane (12): Occasionally obtained as an "impurity" in silane **11a** (see text); NMR signals partially hidden by those of **11a**; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.60$ (s), 3.57 (s), 3.56 (s), 0.16 ppm (s, ^2J(H,Si) = 7.2 Hz; Si–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.3$ (SiMe–OCH_3), 51.0 (MeSi–CH_2–O), −6.3 ppm (Si–CH_3); ^{29}Si NMR (60 MHz, $CDCl_3$): $\delta = -13.5$ (Si(Me)OMe), −53.6 ppm ($Si(OMe)_2$); MS (70 eV): *m/z* (%): 224.1 [M^+] (18.6).

2,2,5,5-Tetraethoxy-1,4-dioxa-2,5-disilacyclohexane (11b): General procedure D, dioctyltin oxide (131.4 mg, 364 μmol), silane **10b** (17.2 g, 72.8 mmol), 120 °C, 9 h (pressure was continuously decreased from 600 to 5 mbar). Distillation at 47 °C (1.6×10^{-2} mbar) gave the title compound **11b** (8.52 g, 28.7 mmol, 79 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.80$ (m, 12 H; Et CH_2, Si–CH_2–O), 1.12 ppm (m, 12 H; Et CH_3); ^{13}C NMR (126 MHz, C_6D_6): $\delta = 59.1$ (Et CH_2), 53.3 (Si–CH_2–O), 18.5 ppm (Et CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -55.3$ ppm; MS (70 eV): *m/z* (%): 296.1 [M^+] (25.9); elemental analysis: calcd (%) for $C_{10}H_{24}O_6Si_2$ (296.11): C 40.51, H 8.16, Si 18.95; found: C 40.42, H 8.15, Si 18.97.

2,2,5,5-Tetraisopropoxy-1,4-dioxa-2,5-disilacyclohexane (11c): General procedure D, dioctyltin oxide (77.5 mg, 215 μmol), silane **10c** (12.0 g, 42.9 mmol), 125 °C, 8 h (pressure was continuously decreased from 600 to 5 mbar). Distillation at 52 °C (1×10^{-3} mbar) afforded silane **11c** (6.78 g, 16.4 mmol, 76 %) as a colorless liquid; ^{1}H NMR (500 MHz, C_6D_6): $\delta=$ 4.43 (sept, ^3J(H,H) = 6.1 Hz, 4H; *i*Pr CH), 3.92 (m, 4H; Si−CH_2−O), 1.19 ppm (d, ^3J(H,H) = 6.4 Hz, 24H; *i*Pr CH_3); ^{13}C NMR (126 MHz, C_6D_6): δ = 66.1 (*i*Pr CH), 53.8 (Si−CH_2−O), 25.7 ppm (*i*Pr CH_3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta=-56.9$ ppm; MS (70 eV): *m*/*z* (%): 352.2 [M^+] (20.1); elemental analysis: calcd (%) for $C_{14}H_{32}O_6Si_2$ (352.17): C 47.69, H 9.15, Si 15.93; found: C 47.64, H 9.07, Si 15.82.

Acknowledgements

F.H., J.O.D., and J.S. thank Karin Reußwig for performing the experimental work at Wacker Chemie AG. S.A.E. and B.R. thank Wacker Chemie AG for generous financial support, as well as for their kind donation of chemicals, and Katrin Deller and Dr. Carly Anderson for helpful discussions.

[1] a) R. H. Krieble, C. A. Burkhard, *J. Am. Chem. Soc.* **1947**, *69*, 2689–2692; b) W. H. Knoth, R. V. Lindsey, *J. Am. Chem. Soc.* **1958**, *80*, 4106–4108; c) W. Simmler, *Chem. Ber.* **1963**, *96*, 349–356; d) G. Rossmy, G. Koerner, *Makromol. Chem.* **1964**, *73*, 85–108; e) V. F. Mironov, N. S. Fedotov, V. L. Kozlikov, *Chem. Heterocycl. Compd.* **1970**, *4*, 261–263; f) D. Seyferth, T. F. O. Lim, *J. Am. Chem. Soc.* **1978**, *100*, 7074–7075; g) W. Ando, M. Ikeno, A. Sekiguchi, *J. Am. Chem. Soc.* **1978**, *100*, 3613–3615; h) D. Tzeng, W. P. Weber, *J. Org. Chem.* **1982**, *47*, 1976–1977; i) V. Chvalovsky, W. S. El-Hamouly, *Tetrahedron* **1983**, *39*, 1195–1197; j) L. I. Makarova, N. V. Sergienko, L. A. Leites, T. S. Yadritseva, A. A. Zhdanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1989**, *38*, 2405–2409; k) R. Shchepin, C. Xu, P. Dussault, *Org. Lett.* **2010**, *12*, 4772–4775.

[2] J. Daiß, S. Jungermann, E. Fritz-Langhals, J. Cremer, PCT Int. Appl. WO 2011051108 A1 20110505, **2011**.

[3] a) A. P. Dove in *Handbook of Ring-Opening Polymerization* (Eds.: P. Dubois, O. Coulembier, J.-M. Raquez), WILEY-VCH, Weinheim, **2009**, pp. 357–378; b) J. Penelle in *Handbook of Ring-Opening Polymerization* (Eds.: P. Dubois, O. Coulembier, J.-M. Raquez), WILEY-VCH, Weinheim, **2009**, pp. 329–356.

[4] J. L. Speier, M. P. David, B. A. Eynon, *J. Org. Chem.* **1960**, *25*, 1637–1640.

[5] W. Simmler, H. Niederprüm, H. Sattlegger, *Chem. Ber.* **1966**, *99*, 1368–1383.

[6] R. Tacke, H. Lange, A. Bentlage, W. S. Sheldrick, L. Ernst, *Z. Naturforsch. B: Chem. Sci.* **1983**, *38*, 190–193.

[7] R. Tacke, H. Lange, A. Bentlage, *Chem. Ber.* **1982**, *115*, 3673–3677.

[8] a) J. Otera, T. Yano, A. Kawabata, H. Nozaki, *Tetrahedron Lett.* **1986**, *27*, 2383–2386; b) J. Otera, N. Danoh, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5307–5311; c) J. Otera, *Chem. Rev.* **1993**, *93*, 1449–1470; d) O. A. Mascaretti, L. E. Furlán, *Aldrichimica Acta* **1997**, *30*, 55–68.

[9] J. Otera, T. Yano, Y. Himeno, H. Nozaki, *Tetrahedron Lett.* **1986**, *27*, 4501–4504.

[10] S. L. Schreiber, D. Desmaele, J. A. Porco, Jr., *Tetrahedron Lett.* **1988**, *29*, 6689–6692.

[11] S. A. Erhardt, F. Hoffmann, J. O. Daiß, B. Bechlars, J. Stohrer, B. Rieger, *16th International Symposium on Silicon Chemistry*, Hamilton (Canada), **2011**, Book of Abstracts, Poster 67.

[12] Selected relevant publications dealing with the conversion of chloromethyl silanes into acetoxymethyl silanes: a) R. Tacke, T. Kornek, T. Heinrich, C. Burschka, M. Penka, M. Pülm, C. Keim, E. Mutschler, G. Lambrecht, *J. Organomet. Chem.* **2001**, *640*, 140–165; b) R. Ilg, D. Troegel, C. Burschka, R. Tacke, *Organometallics* **2006**, *25*, 548–551; c) D. Troegel, F. Möller, C. Burschka, R. Tacke, *Organometallics* **2009**, *28*, 5765–5770; d) A. Sunderkötter, S. Lorenzen, R. Tacke, P. Kraft, *Chem. Eur. J.* **2010**, *16*, 7404–7421.

[13] Selected relevant examples: a) E. V. Dehmlow, S. S. Dehmlow, *Phase Transfer Catalysis*, WILEY-VCH, Weinheim, **1993**; b) S. Ambasht, S. K. Chiu, P. E. Peterson, J. Queen, *Synthesis* **1980**, 318–320; c) R. Tacke, V. I. Handmann, *Organometallics* **2002**, *21*, 2619–2626; d) T. Schmid, J. O. Daiss, R. Ilg, H. Surburg, R. Tacke, *Organometallics* **2003**, *22*, 4343–4346.

[14] J. Daiß, J. Stohrer, PCT Int. Appl. WO 2011101278 A1 20110825, **2011**.

[15] It is very likely that higher homologues are also present in the reaction mixture but they cannot be detected by GC or GC-MS because their vapor pressure is too low. Cyclic compounds can undergo ring-opening polymerization to form linear oligomers and polymers. These cyclic and linear intermediates interact with each other in equilibrium reactions.

[16] J. Daiß, S. Schmid, PCT Int. Appl. WO 2011117071 A1 20110929, **2011**.

[17] S. K. Chaudhary, O. Hernandez, *Tetrahedron Lett.* **1979**, *20*, 99–102.

[18] a) G. A. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, *101*, 760–762; b) B. J. Helmer, R. West, *Organometallics* **1982**, *1*, 877–879.

[19] a) B. Arkles, J. R. Steinmetz, J. Zazyczny, P. Mehta, *J. Adhes. Sci. Technol.* **1992**, *6*, 193–206; b) S. Altmann, J. Pfeiffer, *Monatsh. Chem.* **2003**, *134*, 1081–1092.

[20] a) Bruker APEX suite of crystallographic software, APEX 2 (Version 2008.4), Bruker AXS Inc., Madison, WI, USA, **2008**; b) Bruker SAINT (Version 7.56a) and SADABS (Version 2008/1), Bruker AXS Inc., Madison, WI, USA, **2008**; c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435, SIR92; d) *International Tables for Crystallography, Vol. C*, (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199); e) G. M. Sheldrick, SHELXL-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, **1998**; f) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2010**; g) L. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838, WinGX (Version 1.70.01, January 2005); h) K. Brandenburg, DIAMOND (Version 3.2f), Crystal Impact GbR, Bonn, Germany, **2010**.

Received: June 15, 2012
Revised: January 11, 2013
Published online: February 18, 2013

