SYNTHESIS OF CYCLOALKYL SUBSTITUTED CYCLOTETRASILANES

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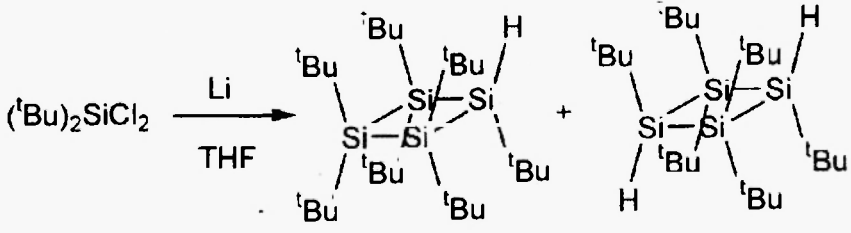
Abstract
1,2,3,4-Tetracycloalkyl-1,2,3,4-tetraphenylcyclotetrasilanes (**5**, **6**) were prepared by Wurtz-coupling reactions from cycloalkylphenyldichlorosilanes (**3**, **4**) with sodium-dispersion. A preliminary single crystal X-ray structure analysis of the cis-cis-trans isomer of 1,2,3,4-tetracyclopentyl-1,2,3,4-tetraphenylcyclotetrasilane (**5a**) reveals a folded four membered ring of silicon atoms as core structure. Ring opening reactions with bromine gave 1,4-dibromo substituted 1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenyltetrasilanes (**7**, **8**). Subsequent reactions with H_2O in THF resulted in the formation of 2,3,4,5-tetracycloalkyl-2,3,4,5-tetraphenyl-1-oxa-2,3,4,5-tetrasilacyclopentanes (**9**, **10**). The treatment of **5** or **6** with $AlCl_3$/AcCl substitutes all phenyl groups with chlorine and cleaves the four membered silicon ring into a mixture of mono-, di-, tri- and tetrasilanes $Cl(SiClR)_xCl$ (x = 1, 2, 3, 4, R = cycloalkyl). All products were characterized by ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

1. Introduction

In general, cyclo- and polysilanes are produced by reductive coupling reactions of diorganodichlorosilanes with sodium in toluene. Cyclosilanes are the thermodynamically preferred products. The ring size formed is depending on the kind and bulkiness of the substituents at silicon. The presence of large and sterically demanding substituents gives rise to the stabilization of small rings. For instance, the reaction of *t*-Bu_2SiI_2 with Li yielded hexa-*t*-butylcyclotrisilane[1] while a similiar treatment of *t*-Bu_2SiCl_2 resulted in the formation of cyclotetrasilanes but under cleavage of one or two *t*-Bu-substituents[2]:



(1)

A cyclotetrasilane (*i*-Pr_8Si_4) is also formed in high yield by reaction of *i*-Pr_2SiCl_2 with Li, however in the cases of the less bulky substituents Et or Ph, i. e. in the reductions of Et_2SiCl_2 or Ph_2SiCl_2 with Li in THF cyclopentasilanes are formed as main products but besides small amounts of the corresponding cyclotetrasilanes. The formed ring size may depend also on the synthetic route: while treatment of *t*-Bu(*c*-Hex)SiI_2 with alkaline metals yields the corresponding cyclotrisilane [*t*-Bu(*c*-Hex)Si]$_3$, exclusively, reductions starting from the disilane Cl[*t*-Bu(*c*-Hex)Si]$_2$Cl produced mainly the four membered ring compound [*t*-Bu(*c*-Hex)Si]$_4$ [3]

Crystal structure analyses of cyclotetrasilanes have shown both, planar and folded four membered rings of silicon atoms[2,5]. In general, cyclotetrasilanes bearing different substituents on each silicon atom adopt conformations with folded Si_4-rings while cyclotetrasilanes like Si_4Ph_8[4] or Si_4Cl_8[5] possess a planar Si_4-ring.

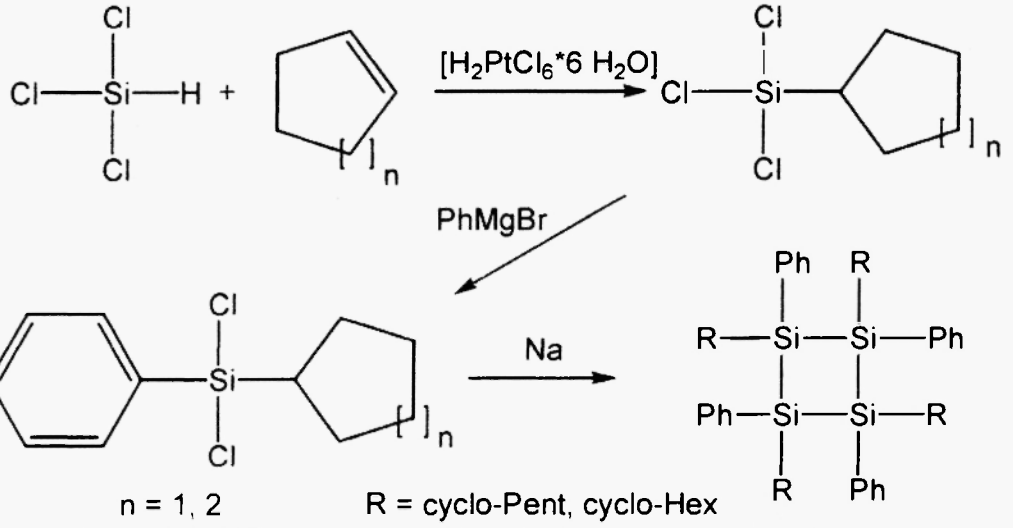
However, octacyclohexylcyclotetrasilane, prepared by Weidenbruch et al.[6] starting from Cl[*c*-Hex_2Si]$_4$Cl and potassium, revealed a folded Si_4 ring (folding angle: 27.6°). Starting from phenylcycloalkyldichlorosilanes the reaction with alkaline metals should give mainly cyclotetrasilanes because the steric demand of a cycloalkylgroup is in between those of *t*-butyl and phenyl substituents and comparable whith an isopropyl group.

Cyclotetrasilanes show an increased reactivity in comparison with five or six membered cycles because of ring strain. Ring opening reactions with bromine[7], lithium[8] and $AlCl_3$/AcCl[9] are known.

The resulting functional substituted tetrasilanes may serve as starting materials for further syntheses.

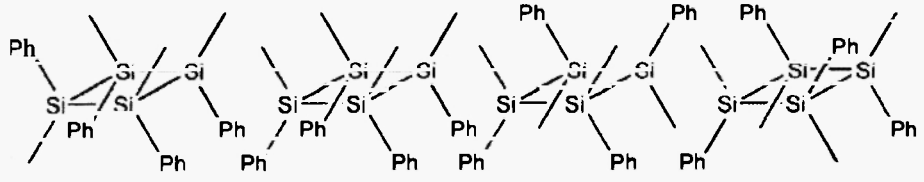
2. Results and discussion

Cyclopentyl- and cyclohexylphenyldichlorosilane (**3**, **4**) were synthesized in two steps starting from trichlorosilane. The first step is a hydrosilylation of the corresponding cycloalkene with trichlorosilane catalyzed by hexachloroplatinic acid[10] followed by treatment with phenylmagnesium bromide, see scheme 1. Wurtz-coupling reactions of **3** or **4** with sodium dispersion in toluene engendered the 1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenylcyclotetrasilanes **5** and **6** besides small quantities of the corresponding cyclopenta- and cyclohexasilanes which was proven by GPC measurements. The GPC results showed also that in these cases no polysilanes have been formed.



Scheme 1, Synthesis of 1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenylcyclotetrasilanes (**5**, **6**)

Due to the two different substituents at each silicon atom the cyclotetrasilanes **5** and **6** can occur in four different stereoisomers, see scheme 2. Mixtures of all four stereoisomers should give rise to six signals in the ^{29}Si NMR spectra what was found indeed in both cases. That means, that all expected stereoisomers were formed although in different amounts, as displayed in figure 1.



number of signals in the ^{29}Si NMR spectra	3	1	1	1

Scheme 2, The four stereoisomeres of the 1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenylcyclotetrasilanes and the expected number of signals in ^{29}Si NMR spectroscopy. The cycloalkyl substituents are omitted for clarity.

The pure cis-cis-trans-isomer of **5** could be isolated by crystallization from hexane/THF solutions. The prelimary result of an X-ray structure analysis of the cis-cis-trans isomer revealed a folded four membered ring skeleton formed by the silicon atoms (figure 2).The three ^{29}Si NMR signals belonging to the cis-cis-trans-isomer of **5** could be assigned by a measurement of the redesolved crystals of the pure isomer, see table 1.

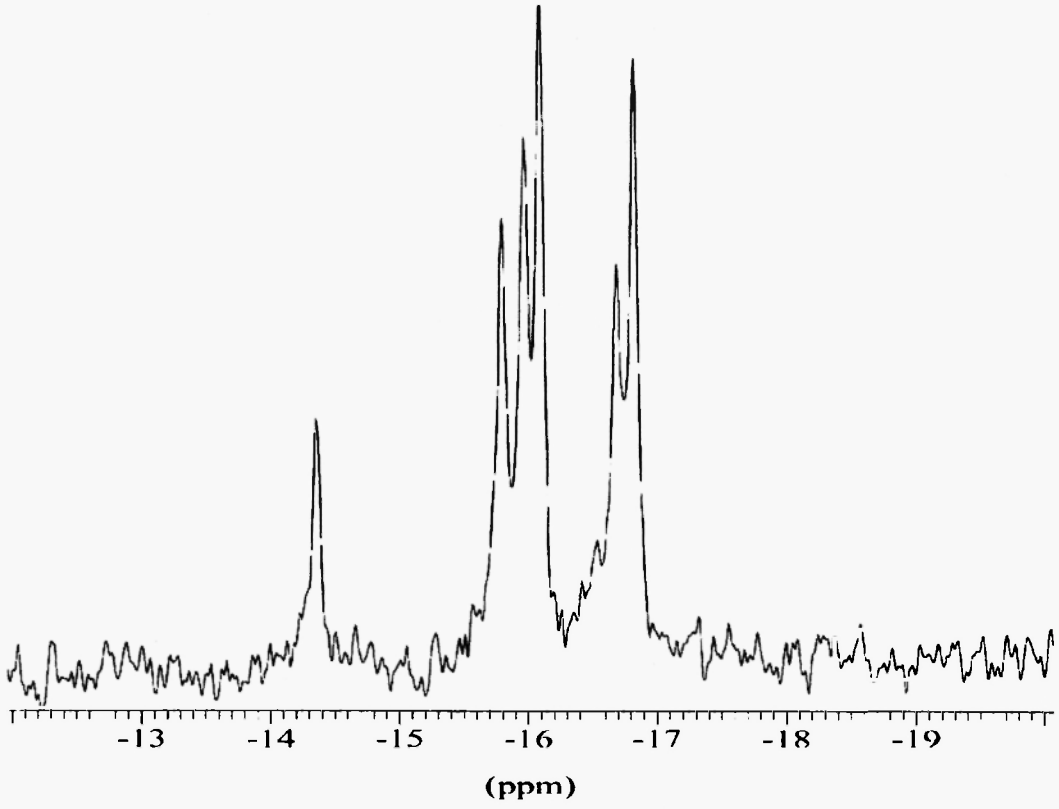
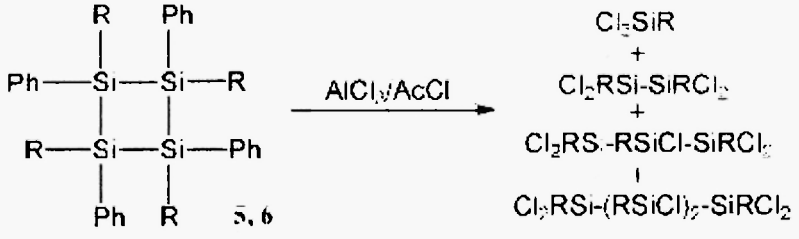


Figure 1, ^{29}Si NMR spectrum of a mixture of all stereoisomers of **6**

A Wurtz-coupling reaction with an equimolar mixture of *c*-HexPhSiCl$_2$ (**4**) and Me$_2$SiCl$_2$, however, gave instead of cyclotetrasilanes, a polysilane in 8 % yield with a molecular weight of M_w = 90000 g/mol. This as formed co-polymer contained 18.9 % Me$_2$Si- besides 81.1 % *c*-HexPhSi groups as determined by signal intensity integration from the ^{1}H NMR spectra. Thus in average four *c*-HexSiPh units per one Me$_2$Si unit are present in the polymer backbone.

Previous studies[4-11] have shown that it is possible to substitute all phenyl groups of cyclosilanes like Si$_4$Ph$_8$ for chlorine or bromine without cleavage of the four membered ring.

However, our attempts to synthezise 1,2,3,4-tetracycloalkyl-1,2,3,4-tetrachlorocyclotetrasilanes by treatment with acetyl chloride plus equimolar amounts of aluminium chloride failed until now. Indeed, all phenyl groups were exchanged for chlorine, but it occurred a complete cleavage of the cyclosilanes **5** and **6** into a mixture of mono-, di-, tri- and in the case of **6** tetrasilanes.



(2)

It seems to be impossible to realize such substitution reactions without cleavage of the Si$_4$-ring by this method. The assignment of the signals in the ^{29}Si NMR spectra was simplified by the fact that the chemical shifts of the cycloalkyl substituted silanes Cl(SiRCl)$_x$Cl (x = 1, 2, 3, 4; R = *cyclo*-Pent, *cyclo*-Hex) are very similar to those of already known methyl substituted silanes Cl(SiMeCl)$_x$Cl (x = 1, 2, 3, 4)[12, 13].

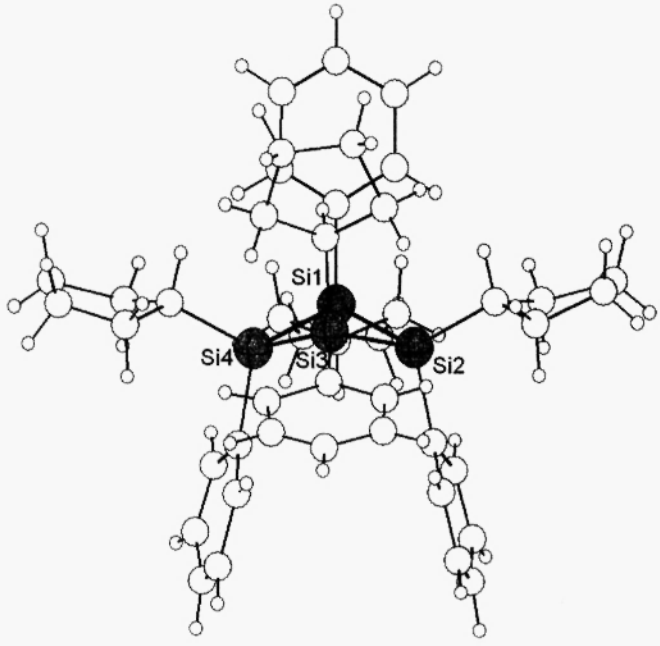


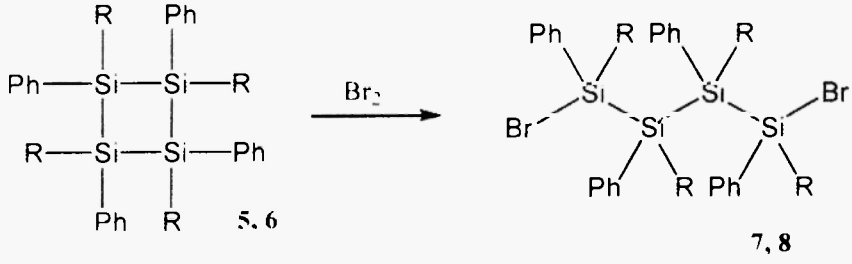
Figure 2, Structural representation of the cis-cis-trans isomer of **5** exhibiting a folded four membered ring of silicon atoms.

Table 1, ^{29}Si NMR chemical shifts (ppm) of the stereoisomers of **5** and **6**

compound	δ_{Si}
5	-18.71[a], -19.73, -20.26, -20.40, -21.12[b], -21.30[a]
6	-14.35, -15.78, -15.96, -16.08, -16.68, -16.81

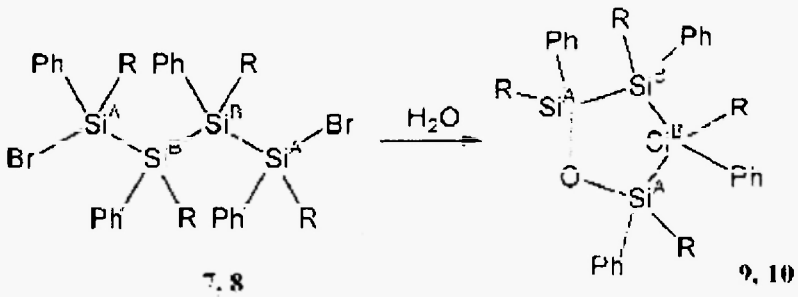
a) cis-cis -trans-isomer, Si1 and Si3
b) cis-cis -trans-isomer, Si2 and Si4 (assignment, see figure 2)

Ring opening reactions of **5** or **6** with bromine gave 1,4-dibromo-1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenyltetrasilanes (**7**, **8**) in high yields without any by-products. The formed six different stereoisomers all together should give rise to eight signals in ^{29}Si NMR spectra for both, the middle and terminal silicon atoms, see table 2. Indeed, at least for Si^B of **7** and **8** eight signals emerged, while only seven could be resolved for Si^A, see table 4. Thus, all six stereoisomers of **7** and **8** were formed.



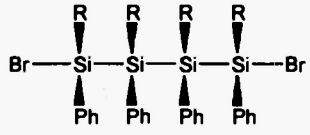
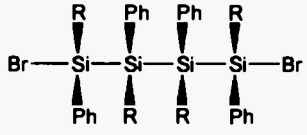
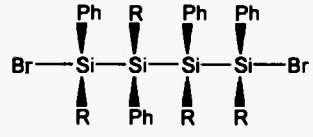
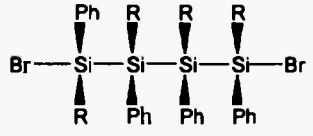
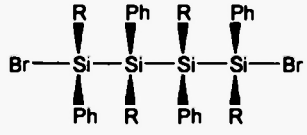
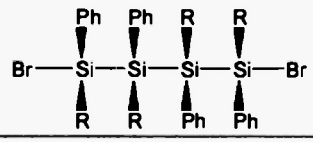
(3)

As described previously for $Br(SiMe_2)_4Br$[14] hydrolysis of **7** and **8** with H_2O in THF yielded 2,3,4,5-tetracycloalkyl-2,3,4,5-tetraphenyl-1-oxa-2,3,4,5-tetrasilacyclopentanes (**9**, **10**), see equation 4.



7, 8 9, 10 (4)

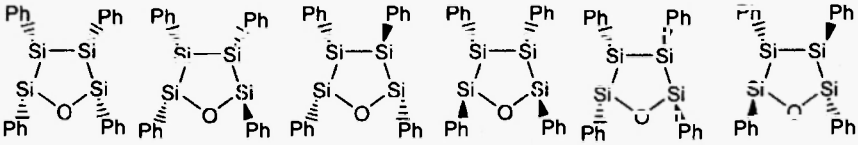
Table 2, Stereoisomers of 1,2-dibromo-1,2,3,4-tetracycloalkyl-1,2,3,4-tetraphenyltetrasilanes (**7**, **8**) and the resulting number of signals in ^{29}Si NMR spectra

	conformation	signals in ^{29}Si NMR	
		middle Si	random Si
	SSRR	1	1
	SRSR	1	1
	RSSS	2	2
	RSRR	2	2
	SRRS	1	1
	SSSS	1	1

In contrast to other siloxanes, the Si-O-Si unit in oxatetrasilacyclopentanes, e. g. Me_8Si_4O[14] has been shown to give a strong absorption in the IR spectra at approximately 950 cm^{-1} as a result of ring strain. Such a strong absorption in this IR region is also arising in case of compounds **9** and **10** proving the formation of a five-membered ring Si_4O.

Six different stereoisomers of **9** as well as **10** were formed in these reactions, see scheme 3. Two of these should give rise to two sets of signals for Si^A as well as Si^B. Thus, a total of eight ^{29}Si NMR signals for both,

Si^A and Si^B, should be originated. But only seven signals were observed that means that in our synthesis either one isomer was not formed or two signals were not resolved, see table 3.

							
Signals in ^{29}Si NMR spectra	Si^A	1	2	2	1	1	1
	Si^B	1	2	2	1	1	1

Scheme 3, All stereoisomers of 2,3,4,5-tetracycloalkyl-2,3,4,5-tetraphenyl-1-oxatetrasilacyclopentanes (9, 10) and the resulting number of signals in ^{29}Si NMR spectroscopy.
The cycloalkyl substituents are omitted for clarity.

Table 3, ^{29}Si NMR chemical shifts (ppm) of **7 - 10**

compound		δ_{Si}
7	Si^A	15.5, 15.79, 16.08, 16.25, 16.71, 17.37, 17.72
	Si^B	-36.00, -35.53, -34.43, -33.93, -33.84, -33.58, -33.34, -32.94
8	Si^A	15.83, 15.93, 16.16, 16.37, 16.55, 17.33, 18.00
	Si^B	-31.74, -31.36, -31.27, -30.76, -30.75, -29.34, -28.67
9	Si^A	5.17, 5.25, 5.32, 5.53, 5.66, 5.95, 6.24
	Si^B	-38.75, -37.43, -36.27, -36.00, -35.73, -35.49, -34.92
10	Si^A	4.09, 4.40, 4.59, 4.89, 5.36, 5.84, 6.59
	Si^B	-35.15, -34.09, -33.14, -32.83, -31.94, -31.66, -31.22

3. Experimental

3.1. Preparation of cycloalkylphenyldichlorosilanes RPhSiCl$_2$ (R = cyclo-C$_5$H$_9$ (3), cyclo-C$_6$H$_{11}$ (4))

a) Cyclopentyltrichlorosilane (**1**) was obtained by treatment of 51 g (0.75 mol) cyclopentene and 100.7 g (0.75 mol) trichlorosilane with 10 mg (0.02 mmol) of hexachloroplatinic acid. After 6 days with stirring the product was distilled in vacuo to give 76.3 g (0.38 mol, 64 %) cyclopentyltrichlorosilane as a colorless liquid.
1, bp_2: 27 °C; ^{29}Si NMR: 13.5 ppm; ^{13}C NMR: 26.8 ppm, 27.1 ppm, 32.8 ppm (ipso); ^1H NMR: 1.64 ppm, 1.67 ppm, 1.91 ppm.
Cyclohexyltrichlorosilane (**2**) was obtained via the same procedure.
2, bp_2: 48 °C, 88 % yield; ^{29}Si NMR: 12.9 ppm; ^{13}C NMR 25.47 ppm, 26.03 ppm, 26.57 ppm (para), 33.91 ppm (ipso); ^1H NMR: 1.28 ppm, 1.35 ppm, 1.75 ppm, 1.84 ppm, 1.97 ppm.
b) Phenylcycloalkyldichlorosilanes
0.13 mol of the corresponding cycloalkyltrichlorosilane was dissolved in 30 ml diethyl ether. 0.16 mol phenylmagnesium bromide (prepared from 25.1 g (0.16 mol) C_6H_5Br and 3.9 g (0.16 mol) magnesium in 200 ml diethylether) were added slowly to the stirred solution. After removal of the magnesium salts the products were distilled.
(*c*-PentPhSiCl$_2$) (**3**): bp_2: 119 °C, 19.11 g (78 mmol, 60 % yield);
^{29}Si NMR: 19.64 ppm; ^{13}C NMR: *c*-Pent: 26.83 ppm, 27.28 ppm, 29.58 ppm (ipso); Ph: 128.15 ppm (meta), 131.33 ppm (para), 132.41 ppm (ipso), 133.57 ppm (ortho); ^1H NMR: 1.79 ppm, 1.89 ppm, 2.04 ppm, 7.56 ppm, 7.72 ppm, 7.88 ppm;
GC/MS: 244 (M^+, 24), 175 ($PhSiCl_2$, 85), 166 ($C_5H_8Cl_2$, 48), 141 (7), 104 (9), 77 (Ph, 54), 68 (C_5H_8, 100).
(*c*-HexPhSiCl$_2$) (**4**): bp_2: 128 °C, 30.2 g (0.11 mol, 89.7 % yield);
^{29}Si NMR: 18.76 ppm; ^{13}C NMR: *c*-Hex: 25.79 ppm, 26.26 ppm (para), 27.13 ppm, 30.41 ppm (ipso); Ph: 128.2 ppm (meta), 131.39 ppm (para), 131.51 ppm (ipso), 133.85 ppm (ortho); ^1H NMR: 1.2 ppm, 1.28 ppm, 1.68 ppm, 1.73 ppm, 1.68 ppm, 7.38 ppm (ortho), 7.41 ppm (para), 7.69 ppm (meta);
GC/MS: 258 (M^+, 24), 180 ($C_6H_{10}SiCl_2$, 85), 175 ($PhSiCl_2$, 75), 141 (9), 115 (4), 104 (6), 82 (C_6H_{10}, 100), 77 (Ph, 66).

3.2. Wurtz Coupling Reactions

1,2,3,4-Tetracyclopentyl-1,2,3,4-tetraphenylcyclotetrasilane (**5**)

7 g (0.3 mol) Na and 70 ml toluene were heated up to 110 °C and stirred vigorously. 35 g (0.15 mol) **3** were added to the resulting Na dispersion . The reaction mixture turned deep blue within one minute. After 1 h of intense stirring at 110 °C the mixture was cooled down to room temperature, and 200 ml MeOH were added carefully. The residues were extracted with 70 ml toluene and filtered. The cyclosilane was precipitated from the filtrate by addition of 200 ml MeOH. 7.4 g (11 mmol, 28 %) of crude **5** was collected after drying *in vacuo*.

GPC: (*c*-PentSiPh)$_4$ (**5**): 83.7 %, (*c*-PentSiPh)$_5$: 9.3 %, (*c*-PentSiPh)$_6$: 7 %

5: ^{13}C NMR: 25.06 ppm, 26.9 ppm, 31.1 ppm, 127.39 ppm, 128.34 ppm, 135.19 ppm, 137.54 ppm; ^{1}H NMR: 1.38 ppm, 1.57 ppm, 2.1 ppm, 6.96 ppm, 7.2 ppm, 7.33 ppm, 7.71 ppm;

Anal. calcd. for **5**: C: 75.79, H: 8.10. Found: C: 75.61, H: 8.17.

1,2,3,4-Tetracyclohexyl-1,2,3,4-tetraphenylcyclotetrasilane (**6**) was prepared by essentially the same procedure. Yield 9.8 g (13 mmol, 34.6 %).

GPC: (*c*-HexSiPh)$_4$ (**6**): 84.8 %, (*c*-HexSiPh)$_5$: 13.4 %, (*c*-HexSiPh)$_6$: 1.7 %

6: ^{13}C NMR: 26.4 ppm, 28.22 ppm, 28.77 ppm, 30.9 ppm, 127.61 ppm, 134.4 ppm, 136.1 ppm, 137.49 ppm; ^{1}H NMR: 1.17 ppm, 1.41 ppm, 1.68 ppm, 2.08 ppm, 6.82 ppm, 7.0 ppm, 7.28 ppm, 7.71 ppm; Anal. calcd. for 6: C: 76.52, H: 8.56. Found: C: 75.14, H: 8.53.

Poly(cyclohexylphenylsilane)co(dimethylsilane)

This copolysilane was produced applying the procedure described above starting with 19.9 g (77 mmol) c-HexPhSiCl$_2$, 9.9 g (77mmol) Me_2SiCl_2 and 7 g (0.3 mol) Na. Addition of MeOH to the solution of the crude product in toluene yielded a white precipitation of the copolysilane in 8 % yield.

^{29}Si: -37.5 ppm ($SiMe_2$), -21.3 ppm (*c*-HexSiPh); ^{13}C: 26.73 ppm, 28.63 ppm, 30.84 ppm; 127.31 ppm, 136.22 ppm; ^{1}H: -0.26 ppm, 0.06 ppm, 0.91 ppm, 1.04 ppm, 1.31 ppm; 6.95 ppm, 7.04 ppm, 7.05 ppm.

3.3. Reaction of 5 and 6 with aluminium chloride and acetyl chloride

0.5 g (0.7 mmol) **5**, 10 ml n-hexane and 0.76 g (5.7 mmol) $AlCl_3$ were added. The mixture was cooled down to 0 °C and with stirring 0.45 g (5.7 mmol) acetyl chloride were added dropwise. After stirring overnight the hexane phase was separated. Removal of the solvent *in vacuo* yielded an oily mixture of Cl[Si(*c*-Pent)Cl]$_x$Cl, x = 1, 2, 3.

^{29}Si NMR: *c*-PentSiCl$_3$: 13.37 ppm, (*c*-PentSiCl$_2$)$_2$: 16.67 ppm, (*c*-PentSi^{A}Cl$_2$)$_2$(*c*-PentSi^{B}Cl): 3.63 ppm (Si^B), 21.28 ppm (Si^A).

An anologous reaction with 6 yielded an oily mixture of Cl[Si(*c*-Hex)Cl]$_x$Cl, x = 1, 2, 3, 4.

^{29}Si NMR: *c*-HexSiCl$_3$: 12.83 ppm, (*c*-HexSiCl$_2$)$_2$: 17.67 ppm, (*c*-HexSi^{A}Cl$_2$)$_2$(*c*-HexSi^{B}Cl): -4.09 ppm (Si^B), 22.03 ppm (Si^A), [*c*-HexSi^{A}Cl$_2$-Si^{B}Cl(c-Hex)-]$_2$: 22.7 / 23.1 ppm (Si^A), 1.5 / 3.6 ppm (Si^B) (two diastereomers).

3.4. Ring opening reactions of 5 and 6 with bromine

1,4-Dibromo-1,2,3,4-tetracyclopentyl-1,2,3,4-tetraphenyltetrasilane (7)

0.5 g (0.7 mmol) **5** was dissolved in 5 ml CCl_4 and 0.11 g (0.7 mmol) Br_2 were added. The reaction mixture was stirred for 4 h while the colour of Br_2 disappeared. After drying *in vacuo* an oily residue was obtained. Yield: 0.54 g, 0.6 mmol, 90 %.

1,4-Dibromo-1,2,3,4-tetracycohexyl-1,2,3,4-tetraphenyltetrasilane (**8**) was produced via the same procedure. Yield: 0.58 g, 0.6 mmol, 90 %.

^{29}Si NMR of 7 and **8**: see table 4.

3.5. Formation of oxatetrasilacyclopentanes

2,3,4,5-Tetracyclopentyl-2,3,4,5-tetraphenyl-1-oxa-2,3,4,5-tetrasilacyclopentane (9)

0.6 g (0.7 mmol) Br(*c*-Pent)PhSi-(*c*-PentSiPh)$_2$-SiPh(*c*-Pent)Br (7) were dissolved in 5 ml THF and some drops H_2O were added to the stirred solution. After stirring overnight and removal of the solvent a white amorphous solid was obtained.

IR: ν(Si-O-Si): 958 cm^{-1}

2,3,4,5-Tetracyclohexyl-2,3,4,5-tetraphenyl-1-oxa-2,3,4,5-tetrasilacyclopentane (**10**) was obtained by an analogous reaction of **8**.

^{29}Si NMR of **9** and **10**: see table 4.

IR: ν(Si-O-Si): 957 cm^{-1}

3.6. NMR, GC/MS and IR spectroscopy

All NMR spectra were recorded on a BRUKER DPX 400 in $CDCl_3$ solution. ^{29}Si NMR spectra were obtained applying an IGATED pulse sequence.

GC/MS measurements were carried out on a Hewlett Packard 5971. Ionisation energy: 70 eV, column: 30 × 0.25 × 0.25 m coated with phenylmethylpolysiloxane. Flow: He 0.5 ml/min.

IR spectra were recorded on a Nicolet 510 FT-IR spectrometer using KBr tablets.

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