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SYNTHESIS AND PROPERTIES OF SUBSTITUTED METHYLCYCLOPOLYSILANES

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Summary

Co-condensation of five equivalents Me_2SiCl_2 and one equivalent $RR'SiCl_2$ with lithium provides the five- and six-membered rings $RR'Si(Me_2Si)_4$ and $RR'Si(Me_2Si)_5$. This method provides a direct route to the phenyl substitued methylcyclopolysilanes (R,R' = Me, Ph) which can be used for further functionalization of the silicon rings. It also provides several new sterically hindered methylcyclopolysilanes (R,R' = Ph, Ph; Me, t-Bu; t-Bu, t-Bu) which could not be synthesized by the conventional demethylation routes. These products have all been isolated and characterized by their ultraviolet, ^1H-, ^{13}C- and ^{29}Si-NMR spectra.

Introduction

The unique electron properties of permethylcyclosilanes have been the subject of considerable study [1]. Syntheses of five- and six-membered rings, $(Me_2Si)_5$ (**1a**) and $(Me_2Si)_6$ (**1b**), have been well established [2,3] (eq. 1 and 2), and several substituted compounds have also been prepared. The usual route to derivatives of **1b** involves chlorodemethylation with HCl and $AlCl_3$ [4a], or $HSiCl_3$ and $PtCl_4$ [5], to give a mixture which can be separated by phenylation, recrystallization of the phenyl derivative **3b**, and chlorodephenylation to give the chloro derivative **2b** (eq. 3). An even lengthier sequence of reactions involving ring-contraction and Si—Si bond cleavage leads to the chloro five-membered ring **2a** [4b]. These chloro compounds are starting materials for the synthesis

$$Me_2SiCl_2 \xrightarrow[\text{THF, 0°C}]{\text{Li}} \underset{\textbf{(1a)}}{(Me_2Si)_5} + \underset{\textbf{(1b)}}{(Me_2Si)_6} + \text{polymer} \qquad (1)$$

$$\underset{\textbf{(1b)}}{(Me_2Si)_6} \xrightarrow[\text{254 nm}]{h\nu} \underset{\textbf{(1a)}}{(Me_2Si)_5} + Me_2Si: \qquad (2)$$

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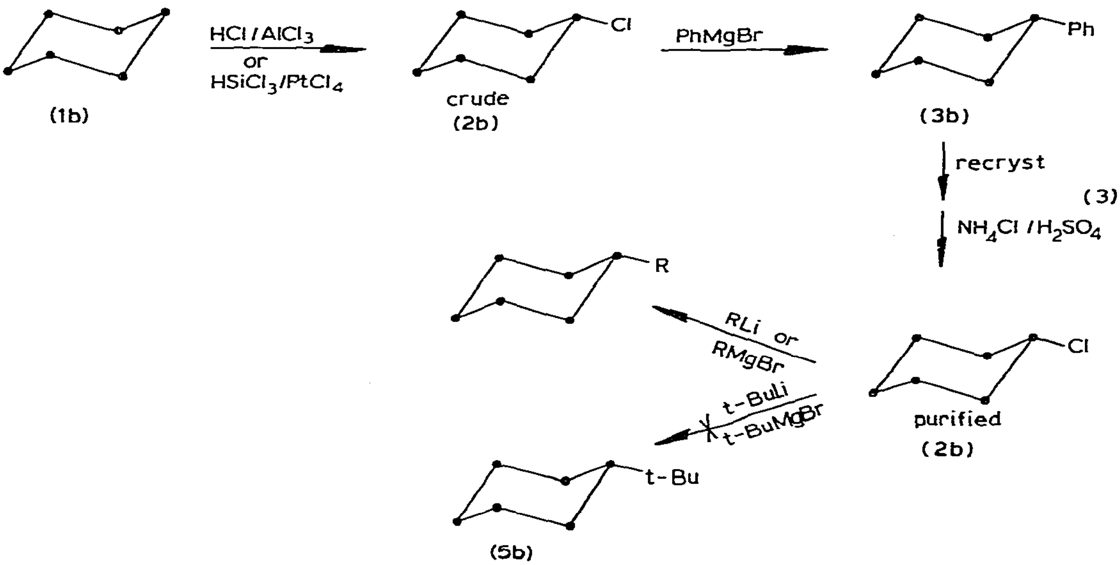


(3)

Each dot represents a silicon atom with sufficient methyl groups attached to bring the total valency of silicon to four.

of other derivatives, but bulky substituents cannot be introduced (for example, t-BuLi does not react with **2b**).

In this paper we report the direct synthesis of phenylsubstituted five- and six-membered rings, **3a** and **3b**, from monosilane precursors. The same method was used for syntheses of sterically hindered and *gem* disubstituted methylcyclosilanes (**4a**, **4b**, **5a**, **5b**, **6a**, **6b**).

Results and discussion

Synthesis

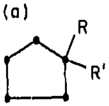
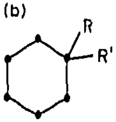
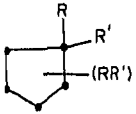
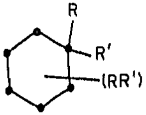
Substituted cyclopolysilanes were prepared by co-condensation of Me_2SiCl_2 and a substituted dichlorosilane with lithium. In each case a mixture of five- and six-membered rings was obtained (Table 1). The total isolated yield of cyclic products in each of the substituted systems (**3**—**6**; 72—85%) was quite high, and none of the insoluble polymer often produced in syntheses of the permethyl rings was observed for the substituted systems.

In the monosubstituted systems (**3**, **5**) the substituted six-membered rings made up nearly one-half of the product mixture. In the 1,1-disubstituted systems (**4**, **6**) this percentage was somewhat reduced, with the yield of 1,1-di-t-butyl five-membered ring (**6a**) nearly equaling the yield of 1,1-di-t-butyl six-membered ring (**6b**). These changes in product distribution are probably due to conformational distortions brought about by the bulky geminal substituents which deter the closure of the six-membered ring.

The mixtures were separated by Kugelrohr distillation followed by recrystallization or by preparative HPLC or GC. **2a** and **2b** ($R = Me$; $R' = Cl$) were prepared by dephenylation of **3a** and **3b** respectively with NH_4Cl and H_2SO_4. Each of the substituted rings is an air-stable solid.

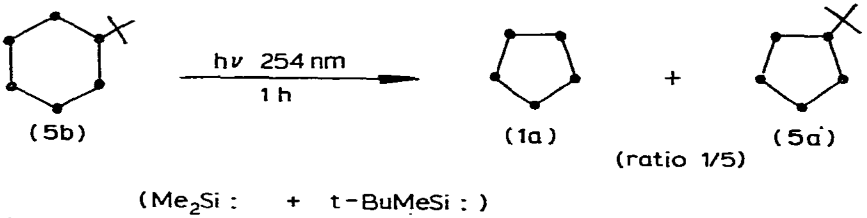
TABLE 1

PROPORTION OF CYCLIC PRODUCTS FROM THE REACTION 5 $Me_2SiCl_2 + RR'SiCl_2 \xrightarrow[0^\circ C]{Li,\ THF}$

Compound	R,R′	Yield [a]	$(SiMe_2)_5$	$(SiMe_2)_6$	(a) 	(b) 		
1	Me, Me	70	7	93	—	—	—x	—
3	Ph, Me	84	3	34	6	44	4	9
4	Ph, Ph	72	5	37	6	36	4	12
5	t-Bu, Me	79	2	34	7	45	4	8
6	t-Bu, t-Bu [b]	78	4	40	27	29	0	0

[a] Total isolated yield of mixture of cyclosilanes. [b] Run at $Me_2SiCl_2/t\text{-}Bu_2SiCl_2$ 10/1.

1b and **5a** in the reaction mixture could not be separated by chromatographic methods, so **5a** was prepared instead by photolysis of **5b** (eq. 4). This method



(4)

however was not effective for the preparation of **3a** or **4a**, both because the phenyl-substituted silylene unit appears to be eliminated preferentially from **3b** and **4b**, and because **3a** and **4a** themselves undergo rapid photolysis.

Attempted synthesis of 1,2-disubstituted rings by reaction of the disubstituted disilanes $(PhSiMeCl)_2$ and $(t\text{-}BuSiMeCl)_2$ with excess Me_2SiCl_2 gave randomization of substituents and product distributions similar to those in Table 1.

Ultraviolet spectra

The ultraviolet spectra of the cyclopolysilanes **1a**—**6a** and **1b**—**6b** are shown in Fig. 1 and 2 respectively, and the absorption maxima are listed in Table 2. All of the compounds studied have absorptions in the near ultraviolet region attributable to their silicon framework. Absorption in the permethyl rings

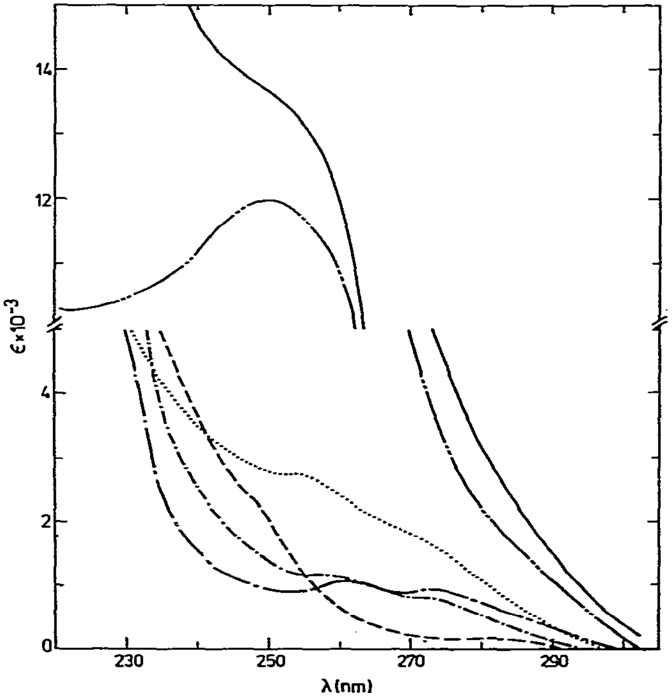


Fig. 1. Ultraviolet absorption spectra of substituted methylcyclopentasilanes $RR'Si(Me_2Si)_4$: R,R' = Me, Me (1a), — — — —; Me, Cl (2a), — — — —; Me, Ph (3a), — - - — - - —; Ph, Ph (4a), ————; Me, t-Bu (5a), — · — · —; t-Bu, t-Bu (6a), · · · · · · · · ·.

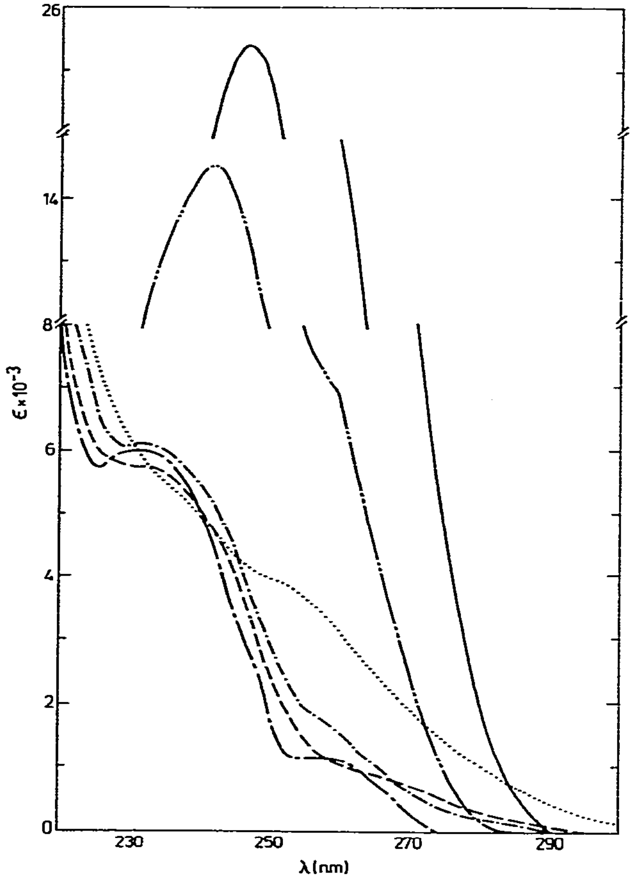


Fig. 2. Ultraviolet absorption spectra of substituted methylcyclohexasilanes $RR'Si(Me_2Si)_5$: R,R' = Me, Me (1b), — - — - —; Me, Cl (2b), — — — —; Me, Ph (3b) — - - — - - —; Ph, Ph (4b), ————; Me, t-Bu (5b), — • — • —; t-Bu, t-Bu (6b), • • • • • • • • •.

TABLE 2

ULTRAVIOLET SPECTRAL DATA FOR SUBSTITUTED PERMETHYLCYCLOPOLYSILANES

Compound	λ_{max}(nm) (ϵ(l mol^{-1} cm^{-1}))		
$(Me_2Si)_5$ (1a)	261(1100)	272(970)	
$ClMeSi(Me_2Si)_4$ (2a)	246(2600)sh	284(80)	
$PhMeSi(Me_2Si)_4$ (3a)	249(12,000)	280(2200)sh	
$Ph_2Si(Me_2Si)_4$ (4a)	250(13,700)	264(9000)sh	284(2300)sh
$t\text{-}BuMeSi(Me_2Si)_4$ (5a)	257(1200)	273(820)sh	
$t\text{-}Bu_2Si(Me_2Si)_4$ (6a)	254(2700)	268(1900)sh	
$(Me_2Si)_6$ (1b)	231(6000)	253(1200)	
$ClMeSi(Me_2Si)_5$ (2b)	232(5700)	266(800)	
$PhMeSi(Me_2Si)_5$ (3b)	245(14,000)	263(7000)sh	
$Ph_2Si(Me_2Si)_5$ (4b)	247(25,000)	264(12,000)sh	
$t\text{-}BuMeSi(Me_2Si)_5$ (5b)	231(6100)	257(1800)sh	
$t\text{-}Bu_2Si(Me_2Si)_5$ (6b)	232(6000)sh	253(3900)sh	

TABLE 3

^{1}H CHEMICAL SHIFTS OF SOME SUBSTITUTED CYCLOPOLYSILANES

Compounds	δ, ppm (No. of methyls)							Other
1a	0,225(10)							
2a	0,614(1)	0,360(2)	0,242(2)	0.133(2)	0,132(2)			
3a	0,476(1)	0,253(2)	0,244(4)	0.241(2)				Ph 7,51(*o*), 7,22(*m*+*p*)
4a	0,325(4)	0,230(4)						Ph 7,59(*o*), 7,17(*m*+*p*)
5a	0,315(2)	0,258(2)	0,210(4)	0.150(1)				t-Bu 1,08
6a	0,360(4)	0,246(4)						t-Bu 1,17
1b	0,207(12)							
2b	0,607(1)	0,351(2)	0,247(2)	0,213(2)	0,193(1)	0,160(1)	0,134(2)	
3b	0,501(1)	0,298(2)	0,245(1)	0,243(2)	0,239(1)	0,225(2)	0,195(2)	Ph 7,52(*o*), 7,22(*m*+*p*)
4b	0,364(4)	0,219(2)	0,165(4)					Ph 7,62(*o*), 7,21(*m*+*p*)
5b	0,324(2)	0,289(2)	0,219(1)	0,207(5)	0,191(1)			t-Bu 1,08
6b	0,367(4)	0,244(4)	0,217(2)					t-Bu 1,17

TABLE 4

^{13}C CHEMICAL SHIFTS OF SOME SUBSTITUTED CYCLOPOLYSILANES

Compounds	δ, ppm (No. of carbons)							Other
1a	−6,25(10)							
2a	−0,72(1)	−6,21(2)	−6,36(2)	−6,87(4)				
3a	−5,25(2)	−5,94(2)	−6,24(4)	−7,11(1)				Ph[a] 137,82(*i*), 135,28(*o*), 128,24(*m*)
4a	−5,00(4)	−5,89(4)						Ph[b] 136,64(*o*), 128,69(*p*), 128,24(*m*)
5a	−3,67(2)	−5,74(2)	−5,84(2)	−6,42(2)	−8,27(1)			t-Bu 29,97(3), 21,14(1)
6a	−1,68(4)	−5,47(4)						t-Bu 32,46(3), 23,92(1)
1b	−5,93(12)							
2b	−0,08(1)	−5,86(1)	−5,90(2)	−6,20(2)	−6,24(1)	−6,27(2)	−6,80(2)	
3b	−4,53(2)	−5,29(2)	−5,36(1)	−6,16(2)	−6,31(1)	−6,35(2)	−6,59(1)	Ph[a] 137,87(*i*), 135,12(*o*), 128,19(*m*)
4b	−4,45(4)	−5,74(2)	−5,80(4)					Ph[b] 136,56(*o*), 128,61(*p*), 128,02(*m*)
5b	−2,87(2)	−4,60(2)	−5,07(2)	−5,23(1)	−6,50(1)	−6,73(2)	−7,40(1)	t-Bu 30,47(3), 22,73(1)
6b	−1,69(4)	−4,52(2)	−4,59(4)					t-Bu 32,19(3), 23,98(1)

[a] *Para* resonance obscured by solvent. [b] *Ipso* resonance not observed, may be accidentally equivalent to *ortho*.

(**1a**, **1b**) is believed to involve excitation from a delocalized σ-bonding orbital to an unfilled orbital having σ^* or π character (or both) [1a]. The nature of this first excited state is dependent on orbital overlap, and therefore on the geometry of the molecule.

Substitution with t-butyl groups would be expected to cause mainly steric effects on the electronic transitions. Substitution with a single t-butyl group (**5a**, **5b**) has little effect on the absorption spectra of either permethyl ring. Addition of a second t-butyl group on the same silicon in compounds **6a**, **6b** leads to marked increases in the extinction coefficients for the low-energy transitions in both systems, as well as a significant bathochromic shift of the longest wavelength absorption for **6b**. These effects can be understood in terms of ring conformations. In going from the permethyl to the mono-t-butyl systems, the five- and six-membered rings can retain envelope and chair conformations, respectively, with t-butyl groups equatorial. When *gem* t-butyl groups are present, however, the rings are probably forced to twist to avoid 1,3-diaxial interactions. The low-energy transitions evidently become more permitted in these distorted rings. Twisting in **6b** may lead to improved orbital overlap between neighboring silicons, decreasing the energy of the first excited state.

Chlorine and phenyl substituents may be expected to have electronic as well as steric effects on the UV absorptions. Substitution with chlorine in **2b** leads to a modest bathochromic shift of the lowest-energy transition compared to **1b**. The major effect of chlorine in **2a**, compared with **1a**, is to decrease the extinction coefficient for the lowest-energy absorption, but the position and intensity of other bands are also changed (Fig. 1). Phenyl groups, in **3a**, **3b** and **4a**, **4b**, have a much more pronounced effect on the spectra of the permethyl rings, leading to bathochromic shifts and marked intensification of absorption bands. Similar spectral changes have been observed upon phenyl substitution in linear polysilanes, and attributed to mixing between the π^* orbitals of the benzene rings and the polysilane (σ^*) excited state orbitals. In the phenyl substituted cyclosilanes, these effects may be augmented by conformational changes, especially in **4a** and **4b**.

Nuclear Magnetic Resonance (NMR)

Substitution of one of the methyls in $(Me_2Si)_6$ with some other group R produces four nonequivalent silicons designated α, β, γ, δ, where R is attached to the α-silicon. Since the resulting methyls can be *cis* or *trans* to the substituent there are seven nonequivalent methyls in a ratio of 1/2/2/2/2/1/1. This should lead to seven methyl resonances in both ^{1}H- and ^{13}C-NMR. Similarly, monosubstituted five-membered rings should have three distinct silicons (1/2/2) and five distinct methyls (1/2/2/2/2). While the methyl resonances are resolved in many cases, some are too similar to be assigned to particular positions.

The 1,1-disubstituted six-membered rings (**4b**, **6b**) have three different methyls (4/4/2) and the five-membered rings (**4a**, **6a**) have two (4/4). In the following sections changes in chemical shifts relative to the parent compounds (**1a** and **1b**) are discussed and designated as $\Delta\delta$.

^{1}*H NMR*

^{1}H NMR chemical shifts for the cyclopolysilanes **1a**—**6a** and **1b**—**6b** are given in Table 3. Chlorine substitution (**2a**, **2b**) causes a downfield shift ($\Delta\delta$ 0.44 ppm) of the α-methyls. A similar but smaller effect is seen for phenyl substitution (**3a**, **3b**). The 1,1-disubstituted compounds (**4a**, **4b** and **6a**, **6b**) show a slight downfield shift ($\Delta\delta$ = 0.10—0.16 ppm) for the β-methyls.

^{13}*C NMR*

^{13}C NMR chemical shifts for the cyclopolysilanes **1a**—**6a** and **1b**—**6b** are given in Table 4. The changes in chemical shifts (again $\Delta\delta$ relative to **1a**, **1b**) are similar to those in the proton spectra, but more pronounced. For example **2a** and **2b** show downfield shifts of the α-methyl ($\Delta\delta = +5.5$ and $+5.9$ ppm respectively). This is consistent with the results of Stanislawski and West [9] on linear polysilanes, and arises mainly from deshielding by the electronegative chlorine substituent.

In the case of t-butyl substituted rings (**5a**, **5b**) α-methyls show an upfield shift ($\Delta\delta = -2.0$ and -1.5 ppm). In both **5a** and **5b** another resonance is observed substantially downfield ($\Delta\delta = +2.6$ and $+3.1$ ppm) corresponding to two methyl groups. These resonances are assigned to the methyl groups which are β and *cis* to the t-butyls. This assignment is supported by the fact that the 1,1-di-t-butyl substituted rings (**6a**, **6b**) show a large downfield shift ($\Delta\delta = +4.6$ and $+4.2$ ppm) for the β-methyls.

The effects of phenyl substitution (**3a**, **3b** and **4a**, **4b**) are very similar to those for t-butyl, but smaller. The results suggest that the major factors involved in perturbation by phenyl and t-butyl groups are steric in origin.

Although **1b** exists in a chair conformation as a solid [10], its ^{1}H- and ^{13}C-NMR spectra show single resonances [11] instead of distinct axial and equatorial methyls. In the present study, no evidence for rigid chair conformations of **1b**—**6b** was observed at 30°C by ^{1}H- or ^{13}C-NMR. In the cases of **1b**, **4b** and **5b**, lowering the temperature to —80°C gave no changes in the ^{13}C NMR spectra. For **6b** the $C(CH_3)_3$ ^{13}C NMR resonance broadens at —80°C. This implies a

TABLE 5

^{29}Si CHEMICAL SHIFTS OF SOME SUBSTITUTED CYCLOPOLYSILANES

Compound	δ, ppm (No. of silicons)			
1a		—41.90(5)		
2a	18.37(1)	—41.50(2)	—42.81(2)	
3a	—39.33(1)	—41.12(2)	—42.25(2)	
4a	—31.48(1)	—40.86(2)	—42.40(2)	
5a	—24.66(1)	—41.42(2)	—42.81(2)	
6a	—8.79(1)	—40.52(2)	—41.70(2)	
1b		—41.86(6)		
2b	16.94(1)	—39.10(2)	—41.75(1)	—41.97(2)
3b	—40.32(1)	—41.34(2)	—41.38(2)	—41.77(1)
4b	—33.24(1)	—40.89(2)	—41.69(2)	—42.00(1)
5b	—27.10(1)	—40.83(2)	—41.17(2)	—42.68(1)
6b	—10.51(1)	—40.16(2)	—42.50(2)	—43.71(1)

slowed rate of exchange of these methyl carbons, but does not indicate what process is responsible.

^{29}Si NMR

The ^{29}Si NMR chemical shifts for cyclopolysilanes **1a**—**6a** and **1b**—**6b** are shown in Table 5. These resonances are spread over an even wider range than the ^{13}C NMR methyl resonances. The α-Si resonances of **2a** and **2b** show a dramatic downfield shift ($\Delta\delta$ = +60.3 and +58.8 ppm), and the β-silicons show a slight downfield shift ($\Delta\delta$ = +0.4 and +2.8 ppm). These effects can again be attributed to deshielding by the electronegative chlorine substituent [9].

The monophenyl rings (**3a**, **3b**) show a slight downfield shift of the α-silicon ($\Delta\delta$ = +2.8 and +1.5 ppm), while a larger effect is seen for the 1,1-diphenyl rings (**4a**, **4b**: $\Delta\delta$ = +10.4, +8.7 ppm). In all four cases the effect on the β-silicon is small ($\Delta\delta$ = +0.6 + 1.2 ppm).

The downfield shift of the α-silicon by a single t-butyl substituent (**5a**, **5b**: $\Delta\delta$ = +17.2, +14.8 ppm) is about half that of the disubstituted cases (**6a**, **6b**: $\Delta\delta$ = +33.1, +31.4 ppm). Small downfield shifts are also seen for the β-silicon ($\Delta\delta$ = +1—+1.7 ppm).

Experimental

Dichlorosilanes Me_2SiCl_2, $PhMeSiCl_2$ and Ph_2SiCl_2 are commercially available, and t-$BuMeSiCl_2$ and t-Bu_2SiCl_2 were prepared by known methods [6,7]. Tetrahydrofuran was distilled from lithium aluminum hydride prior to use. All reactions were carried out under an atmosphere of dried nitrogen.

Mass spectra were recorded on a Varian AEI MS 902 at 70 eV. Ultraviolet spectra were run in spectrograde cyclohexane, and were recorded using a Varian Cary 118. Analytical GLC analyses were carried out using a Hewlett Packard 5720A gas chromatograph equipped with a 6′ X 1/8″ QF1 column (10% on Chromosorb W). Preparative GLC was carried out using a Varian Aerograph Model 90-P chromatograph equipped with a 6′ × 3/8″ QF1 column (20% on Chromosorb W). Preparative HPLC separations were accomplished using a Waters Associates liquid chromatograph equipped with an Altex Model 153 UV detector and a Whatman M-9 column containing Partisil-100DS-2 with a 90% MeOH/10% THF mobile phase.

All NMR spectra were run using benzene-d_6 as solvent and TMS as an internal standard. ^{1}H NMR spectra were recorded on a Brücker 270 MHz spectrometer. ^{13}C- and ^{29}Si-NMR spectra were obtained using a JEOL FX-200 NMR spectrometer (50.1 and 39.6 MHz respectively). ^{29}Si NMR spectra were run in 10 mm tubes with a small amount of $Cr(acac)_3$ added to shorten the silicon spin-lattice relaxation times and eliminate the negative NOE from proton decoupling.

Preparation of $Me_{10}RR'Si_6$ and $Me_8RR'Si_5$

A solution of 5 equiv. of Me_2SiCl_2 and 1 equiv. $RR'SiCl_2$ in THF was added dropwise to 13.2 equiv. (10% excess) Li wire clippings in THF. The mixture was stirred and the temperature was maintained below 5°C with an ice-salt water bath. The solution was warmed to room temperature overnight and developed a deep blue-black color. After aqueous workup and drying, the solvent was stripped off to yield an oily solid. All distillations indicated below are Kugelrohr distillations.

*Si_5Me_9Ph (**3a**) and $Si_6Me_{11}Ph$ (**3b**)*

Using the procedure above, Me_2SiCl_2 (60.6 ml, 500 mmol) and $PhMeSiCl_2$ (16.1 ml, 100 mmol) in 100 ml THF were added to Li (1.32 mol, 9.2 g) in 900 ml THF to yield 41.6 g of pale yellow solid. Kugelrohr distillation at 120—200°C/1 Torr, gave 34.5 g of white solid; this is an 84% yield of a mixture of cyclic compounds (Table 1). Recrystallization of the fraction rich in **3b** (~160°C) with 3/1 THF/EtOH yielded purified **3b** as a white solid, m.p. 110—111°C; mass spectrum, selected *m/e* (relative intensity) 412(10.7), 411(18.7), 410(47.3, M^+), 337(4.4), 336(9.3), 321(2.7), 275(2.5), 263(13.7), 260(10.6), 201(6.7), 135(27.8), 73(100); exact mass: measured 410.1579, calcd. 410.1578, dev. 0.24 ppm.

Preparative HPLC of the distillation fraction (~140°C) rich in **3a** gave purified **3a**, m.p. 64—68°C; mass spectrum, selected *m/e* (relative intensity) 354(1.6), 353(5.6), 352(12.9, M^+), 279(3.4), 278(12.1), 264(1.6), 263(6.5), 233(4.2), 217(1.8), 135(23.9), 73(100); exact mass: measured 352.1351, calcd. 352.1341, dev. 2.8 ppm.

*$Si_5Me_8Ph_2$ (**4a**) and $Si_6Me_{10}Ph_2$ (**4b**)*

Using the procedure above, Me_2SiCl_2 (121.2 ml, 1 mol) and Ph_2SiCl_2 (41.4 ml, 200 mmol) in 200 ml THF were added to Li (18.3 g, 2.64 mol) in 1.4 l THF to yield 97.2 g of crude product. Distillation at 150°C/1 Torr, yielded 28.6 g of a mixture of **1a** and **1b**. Distillation at 210°C/1 Torr, yielded 26 g of a mixture of **4a** and **4b** (1/6). Recrystallization of this mixture gave purified **4b** as a white crystalline solid, m.p. 98—99°C; mass spectrum, selected *m/e* (relative intensity) 474(7.7), 473(13.9), 472(30.0, M^+), 337(2.9), 336(4.2), 325(14.4), 324(17.6), 322(3.2), 260(24.3), 197(7.0), 135(62.6), 73(100); exact mass: measured 472.1744, calcd. 472.1734, dev. 2.1 ppm.

Preparative HPLC provided **4a**, m.p. 48—50°C; mass spectrum, selected *m/e* (relative intensity) 416(5.5), 415 (13.3), 414(32.4, M^+), 341(3.5), 340(5.1), 326(2.2), 325(6.8), 279(9.0), 278(20.3), 264(8.0), 197(6.4), 135(76.5), 73(100); exact mass: measured 414.1508, calcd. 414.1497, dev. 2.7 ppm.

*$Si_6Me_{11}t$-Bu (**5b**)*

Using the procedure above, Me_2SiCl_2 (30.5 ml, 250 mmol) and t-$BuMeSiCl_2$ (8.55 g, 50 mmol) in 50 ml THF were added to Li (4.6 g, 660 mmol) in 450 ml THF to yield 19.3 g of an oily yellow solid. Recrystallization from 3/1 THF/EtOH gave 15.4 g (79% yield) of a crystalline mixture containing mainly **1b** and **5b**. Preparative HPLC yielded purified **5b**, m.p. 173—177°C; mass spectrum, selected *m/e* (relative intensity) 392(3.5), 391(7.8), 390(16.0, M^+), 333(20.4), 260(14.4), 259(38.0), 243(1.7), 201(2.8), 115(3.8), 73(100): exact mass: measured 390.1903, calcd. 390.1902, dev. 0.26 ppm.

*Si_5Me_8t-Bu_2 (**6a**) and $Si_6Me_{10}t$-Bu_2 (**6b**)*

Using a variation on the above procedure Me_2SiCl_2 (14.2 ml, 117 mmol) and t-Bu_2SiCl_2 (2.5 g, 12 mmol) in 30 ml THF were added to Li (2.0 g, 0.29 mol) in 250 ml THF. The reaction was run overnight at 0°C, then allowed to warm to room temperature and stirred for an additional three days. Workup provided 8.8 g of crude product which was distilled (160—180°C/1 Torr) to yield a mixture of **1b**, **6a** and **6b**. Preparative HPLC yielded **6a** and **6b**.

6a. M.p. 116—122°C; mass spectrum, selected *m/e* (relative intensity) 375(0.6), 374(2.3, M^+), 317(3.3), 261(13.8), 207(29.4), 157(3.9), 115(9.7), 73(100); exact mass: measured 374.2130, calcd. 374.2123, dev. 1.9 ppm.

6b. M.p. 125—128°C; mass spectrum, selected *m/e* (relative intensity) 434(0.9), 433(1.5), 432(3.2, M^+), 375(11.0), 319(16.7), 317(1.8), 302(3.9), 301(13.6), 245(28.7), 157(5.3), 115(2.8), 73(100); exact mass: measured 432.2371, calcd. 432.2360, dev. 2.5 ppm.

*Si_5Me_9Cl (**2a**) and $Si_6Me_{11}Cl$ (**2b**)*

2a and **2b** were prepared by dephenylation of **3a** and **3b** respectively, with NH_4Cl and H_2SO_4 according to Kumada's procedure [4]. Preparative GLC yielded purified **2a** and **2b**.

2a. M.p. 142—145°C, mass spectrum, selected *m/e* (relative intensity) 312(22.3), 311(14.2), 310(48.0, M^+), 295(2.0), 237(3.4), 217(7.4), 202(14.2), 157(12.2), 93(3.0), 73(100); exact mass: measured 310.0647, calcd. 310.0640, dev. 2.3 ppm.

2b. M.p. 205—207°C; mass spectrum, selected *m/e* (relative intensity) 371 (1.1), 370(3.8), 369(2.3), 368(6.3, M^+), 296(1.0), 260(3.2), 215(1.8), 201(3.8), 93(1.3), 73(100); exact mass: measured 368.0880, calcd. 368.0877, dev. 0.8 ppm.

Si_5Me_9t-Bu (**5a**)

5a was prepared by photolysis of 460 mg of **5b** in 80 ml of distilled, degassed cyclohexane at 254 nm for 1 h (yield 50% by GLC). Preparative GLC of the resulting mixture gave **5a**, m.p. 118—122°C; mass spectrum, selected *m/e* (relative intensity) 334(5.1), 333(8.5), 332(32.3, M^+), 276(11.6), 275(26.5), 215(20.2), 202(19.4), 201(47.3), 73(100); exact mass: measured 332.1164, calcd. 332.1653, dev. 3.3 ppm.

By comparison photolysis of 25 mg of **3b** in 5 ml of distilled, degassed cyclohexane at 254 nm for 1 h gave only a 15% yield (by GC) of **3a**.

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