Conformationally Stable 1-Substituted 1-Methyl-4-*t*-butyl-1-silacyclohexanes, a New Organosilicon System Suitable for Stereochemical Studies

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Ten 1-methyl-4-*t*-butyl-1-silacyclohexyl derivatives ($C_{10}H_{21}Si\text{-}X$, X=H, Cl, $OCH(CH_3)_2$, OCH_3, $OC(CH_3)_3$, C_6H_5, *p*-Br–C_6H_4, *p*-Cl–C_6H_4, $Si(CH_3)_2H$, F) were synthesized and separated into conformationally stable *cis* and *trans* isomers. The stereochemistry of these compounds has been determined on the basis of NMR and GLC. They were found to behave stereochemically like acyclic optically active silanes.

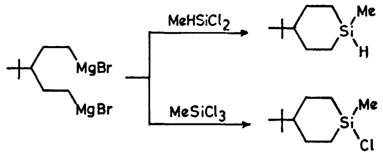
Sommer and Frye prepared the first optically active organosilicon compounds, 1-naphthylphenylmethylsilane derivatives (1-NaPhMeSi*X) in 1959.[1)]

Since then several reports have been made on other optically active organosilicon compounds.[2–5)] They are of importance for the study of the stereochemical behavior of reactions at silicon centers. Several other types of optically active ring compounds are also known.[6,7)] However, the majority of optically active organosilicon compounds so far prepared have at least one bond between an aromatic moiety and silicon. Such a structure is often inconvenient for a certain stereochemical research of reactions in which the bond of silicon to aromatic groups cleaves or forms. Cleavage of the bond of silicon to aromatic groups with electrophiles (desilylation)[8)] and substitution reactions of silyl radicals on an aromatic nucleus (homolytic aromatic silylation)[9)] are examples of such reactions. Moreover, accurate measurement of optical activity requires a large amount of pure sample. In some cases, separation of optically active product(s) from a reaction mixture is infeasible because of extensive racemization.[10)]

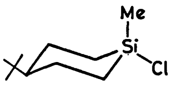
Conformationally stable compound such as *t*-butylcyclohexane derivatives are also useful in stereochemical investigations. However, no silicon analog of such a class of compounds has been prepared. During the course of a study on the stereochemistry of unstable organosilicon intermediates such as silyl radicals and silylenes,[11)] it became necessary to find aliphatic silicon compounds suitable for the stereochemical study. This paper describes the synthesis and reactions of new 4-*t*-butyl-1-methyl-1-silacyclohexane derivatives.[12)] Numerous stereochemical studies on the corresponding carbon analogs, 4-*t*-butylcyclohexanes, have been published since the first proposal of the *t*-butyl function as a holding group.[13)] The conformationally stable organosilicon compounds are also proved to be useful in the stereochemical study of almost all kinds of reactions on silicon.

Results and Discussion

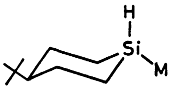
Preparation and Stereochemistry. The reaction of the di-Grignard reagent from 3-*t*-butyl-1,5-dibromopentane (**1**)[14)] with methyldichlorosilane and with methyltrichlorosilane afforded 4-*t*-butyl-1-methyl-1-silacyclohexane (**2**, *cis*/*trans*=1.0) and 4-*t*-butyl-1-methyl-1-chloro-1-silacyclohexane (**3**, *cis*/*trans*=1/2.3), respectively.



Since all the compounds so far prepared have a methyl group on silicon, 4-*t*-butyl and 1-methyl groups are referred to as *cis* and *trans* respectively, throughout this paper. Suffix a is added to the *cis* compounds and b to the *trans*, as illustrated in the following.



3a (*cis*)



2b(*trans*)

By reduction of **3** (*cis*/*trans*=1/2.3) with lithium aluminum hydride, **2** (*cis*/*trans*=2.8/1) was obtained. The *cis* and *trans* mixtures of **2** and **3** could not be separated into individual isomers by means of GLC. However, alkoxy derivatives, prepared by the direct alcoholysis of **3** or alcoholysis of **2** catalyzed by palladium on charcoal, can be used for separation. The isopropoxysilane (**4**) was the most convenient for separation of *cis* and *trans* isomers by preparative TLC. These isomeric alkoxysilanes can be reduced to **2** with lithium aluminum hydride with retention of configuration as in reduction of optically active alkoxysilanes.[2)] Several derivatives were prepared from **2** and **3** the usual organosilicon transformations (Table 1).

The *cis* and *trans* structures of hydrosilanes (**2**) can be identified unequivocally even as a mixture by NMR, and spectral assignment done with the mixture was confirmed again with pure isomers, **2a** and **2b**. Figure 1 shows the NMR spectra of **2**. Figures 2 and 3 show Si–H region of NMR spectra of **2b**, and **2a**, respectively.

The structures of **2a** and **2b** were assigned as follows from SiH–CH_2 coupling constants. Irradiation of the $SiCH_3$ signal of **2b** revealed $J_{SiH(ax)CH(ax)}$ and $J_{SiH(ax)CH(eq)}$ to be 6.5 and 1.7 Hz, respectively, and $J_{SiH(ax)CH(ax)}$ to be *ca.* 1.0 Hz for **2a**. The value of $J_{SiH(ax)CH(ax)}$ observed in the present compound is relatively smaller than the $J_{SiH(ax)CH(ax)}$ values (8—13 Hz) observed for carbon analogs. It should be noted that the present analysis of the coupling constants may not be accurate for complex systems such as AA′BB′X. Thus, we do not claim accuracy of the absolute values of the coupling constant. However, the relative values are sufficient to

TABLE 1. PROTON MAGNETIC RESONANCE DATA FOR 4-*t*-BUTYL-1-METHYL-1-SILACYCLOHEXYL DERIVATIVES ($X(CH_3)SiCH_2CH_2CH(t\text{-}Bu)CH_2CH_2$)

Compound		δ, ppm[a]		
No.	X	$SiCH_3$	$C(CH_3)_3$	Si-X
2a	H	0.12 (d) (J=3.5 Hz)	0.86 (s)	3.95—3.78 (m) (3.91)[d]
2b	H	0.07 (d) (J=3.5 Hz)	0.86 (s)	3.93—3.53 (m) (3.80)[d]
3a[b]	Cl	0.42 (s)	0.86 (s)	
3b[b]	Cl	0.38 (s)	0.87 (s)	
4a	$OCH(CH_3)_2$	0.10 (s)	0.86 (s)	1.10 (d), 3.96 (sep) (J=6.0 Hz)
4b	$OCH(CH_3)_2$	0.02 (s)	0.86 (s)	1.14 (d), 3.99 (sep) (J=6.0 Hz)
5a	OCH_3	0.10 (s)	0.86 (s)	3.36 (s)
5b	OCH_3	0.01 (s)	0.85 (s)	3.41 (s)
6a	$OC(CH_3)_3$	0.13 (s)	0.86 (s)	1.21 (s)
6b	$OC(CH_3)_3$	0.06 (s)	0.85 (s)	1.26 (s)
7a	C_6H_5	0.35 (s)	0.96 (s)	7.63—7.22 (m)
7b	C_6H_5	0.26 (s)	0.84 (s)	7.73—7.25 (m)
8a	p-Br-C_6H_4	0.27 (s)	0.89 (s)	7.37—7.41 (m)
8b	p-Br-C_6H_4	0.12 (s)	0.80 (s)	7.42—7.44 (m)
9a	p-Cl-C_6H_4	0.22 (s)	0.84 (s)	7.31—7.34 (m)
9b	p-Cl-C_6H_4	0.09 (s)	0.77 (s)	7.36—7.42 (m)
10a[c]	$Si(CH_3)_2H$	0.10 (s)	0.84 (s)	0.10 (d), 3.56 (sep) (J=4.5 Hz)
10b[c]	$Si(CH_3)_2H$	0.04 (s)	0.84 (s)	0.16 (d), 3.69 (sep) (J=4.5 Hz)
11a[b]	F	0.25 (d) (J=7.3 Hz)	0.88 (s)	
11b[b]	F	0.18 (d) (J=7.3 Hz)	0.88 (s)	

a) NMR spectra were taken as carbon tetrachloride solution with Varian Associates HA-100 and A-60D. b) Isomers were not separated, chemical shift being determined with a mixture. c) Preparation and determination of this material were described in the previous paper.[12] Details will be published later. d) Center of the chemical shift determined by decoupling.

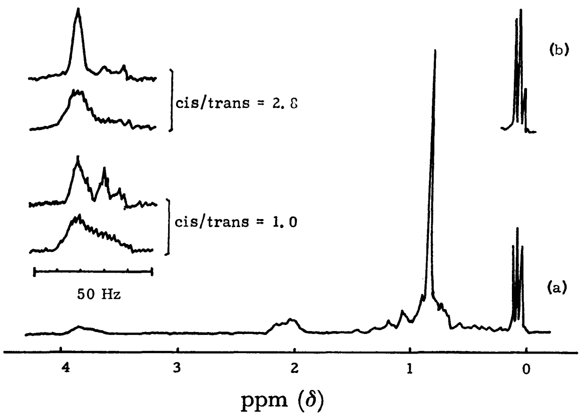


Fig. 1. (a) NMR spectra of **2** (1: 1 *cis-trans* mixture) prepared from di-Grignard reagent from **1** and methyldichlorosilane and (b) methyl signals of **2** (2.8: 1 *cis-trans* mixture) prepared by reduction of **3** with $LiAlH_4$. Left part of the spectra shows each SiH signals in addition to decoupling signals of **2** irradiated at Si–CH_3.

assign the stereochemistry. The axial Si–Me (*e.g. cis* compounds) gives rise to a resonance at lower field (δ 0.12) than the equatorial SiMe (δ 0.07), whereas the axial hydrogen (δ 3.80) appears at higher field than the equatorial hydrogen (δ 3.91). A similar relationship has been observed for cyclohexane derivatives. Incidentally, West proposed the structure of silacyclohexane ring as a deformed chair form.[15]

Many observations show that the chemical shifts of protons in the functional groups attached to six-membered rings are related to their configuration and that these relations afford a reasonable basis for stereochemical assignments as shown in Table 2.[16] Compounds listed in Table 1 were assigned for their *cis* and *trans* structures on the basis of NMR spectra assuming that the compound with a methyl signal of NMR appearing at lower

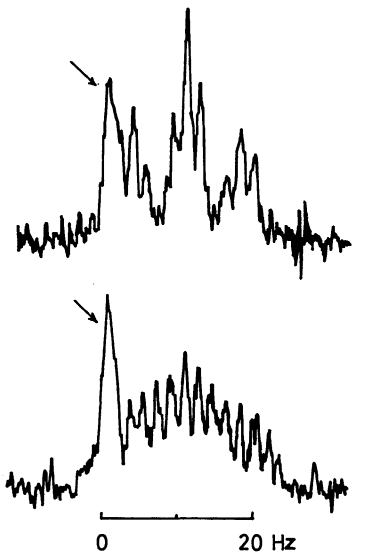


Fig. 2. SiH signal of **2b** (lower) and SiH signal irradiated at the $SiCH_3$ signal of **2b** (upper). The arrows indicate a signal due to unknown impurity.

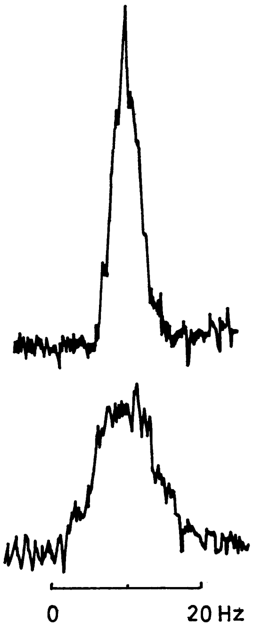
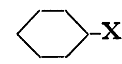
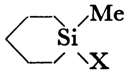


Fig. 3. SiH signal of **2a** (lower) and SiH signal irradiated at the $SiCH_3$ signal of **2a** (upper).

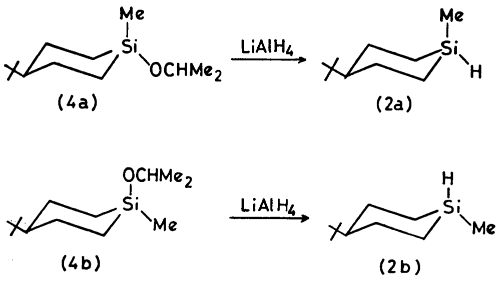
Table 2. CHEMICAL SHIFTS AND CONFIGURATION OF FUNCTIONAL GROUP ATTACHED TO SIX-MEMBERED RING IN THE CHAIR CONFORMATION

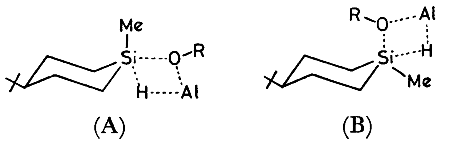
Group	Relationship in  -X[16]	Relationship in  Me Si X
Me	Equatorial upfield	Equatorial upfield
OMe	Equatorial upfield[a]	Equatorial upfield
H	Axial upfield	Axial upfield
	$J_{CHax-CHax}$ 8—13 Hz	$J_{SiHax-CHax}$ 6.5 Hz
	$J_{CHax-CHeq}$ 2—6 Hz	$J_{SiHax-CHeq}$ 1.7 Hz
		$J_{SiHeq-CHax}$ 1 Hz

a) Some exceptions have been given.[16]

field is the *cis* isomer.

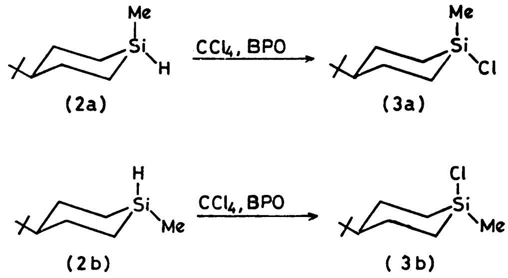
Reaction. The isomeric alkoxy derivatives were reduced to **2** with lithium aluminum hydride with retention of configuration. It seems of interest that the *cis* isopropoxysilane, **4a**, was more reactive than the *trans* one, **4b**, toward reduction. Thus, **4a** was reduced easily with lithium aluminum hydride by reflux for a few hours in ether. However, **4b** could not be reduced completely at the temperature of refluxing ether even after 10 h, and was only reduced in refluxing tetrahydrofuran. To this type of reaction, Sommer and coworkers[17] suggested a four-centered mechanism. The present result on the silacyclohexane series can also be explained in terms of such a four-centered mechanism. The reaction intermediate or the transition state (B) leading to **2b** should be much more crowded than (A) which should lead to **2a**. Thus it is reasonable to consider that **4b** is less reactive than **4a** toward reduction.





(A) (B)

The free radical chlorination of **2** with carbon tetrachloride in the presence of benzoyl peroxide gave **3** in almost quantitative yields with retention of configuration.



Since the free-radical chlorination in this reaction has been shown to go through a silyl radical intermediate with retention of configuration,[18] the chlorosilane (**3**) should have the same configuration as **2**.[7] This is a strong indication that the stereochemical assignments based on NMR are valid.

Reactions of **3** (*cis*/*trans*=1/2.3) with lithium aluminum hydride gave **2** (*cis*/*trans*=2.8/1), namely, an inversion of configuration. 4-*t*-Butyl-1-methyl-1-phenyl-1-silacyclohexane (**7**, *cis*/*trans*=1.6/1) was also prepared from **3** (*cis*/*trans*=1/2.3) by phenylation with phenyllithium. Methanolysis of **3** (*cis*/*trans*=1/2.3) gave 4-*t*-butyl-1-methyl-1-methoxy-1-silacyclohexane (**5**, *cis*/*trans*=1.7/1), with inversion of configuration in both reactions. Thus, the stereochemical courses of these three reactions were in good agreement with the results studied by using optically active silicon compounds.[2] Recently it has been demonstrated that the angle-strained asymmetric silicon center shows remarkable stereochemical crossover to retention of configuration.[7] However, it can be concluded that the strainless silicon centers in six-membered rings behave stereochemically like acyclic organosilicon compounds.

Several derivatives listed in Table 4 were prepared and separated by preparative GLC. As an example, phenyl derivatives **7a** and **7b** could be separated by GLC, typical examples of GLC and NMR spectra being shown in Fig. 4. The ratio of **7a** and **7b** determined by GLC agreed completely with that obtained by NMR. Silacyclohexyl derivatives which have bulky groups attached to silicon at the equatorial position, *i.e.* *cis* compounds, were separated systematically from

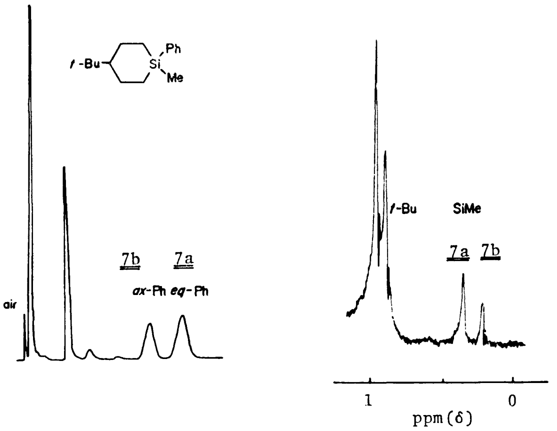


Fig. 4. GLC chart (left) and NMR spectrum (right) of 4-*t*-butyl-1-methyl-1-phenyl-1-silacyclohexane (**7**).

their *trans* compounds on GLC with a longer retention time as observed for carbon analogs.[12]

It should be noted that the compounds possess some advantages as substrates in the stereochemical study; (a) separation of *cis* and *trans* isomer is relatively easy: (b) the stereochemical course can be monitored by NMR and/or GLC; hence each reaction requires only a small amount of reactant: (c) a mixture simply enriched with either of the two isomers can be used satisfactorily: (d) absence of the phenyl or naphthyl group makes some reactions, such as photolysis in the presence of **2** and halodesilylation of **7**, possible.

Experimental

Materials. Reduction of *t*-butylphenol followed by chromic acid oxidation was employed for the preparation of 4-*t*-butylcyclohexanone according to the literature.[19] Preparation of 1,5-dibromo-3-*t*-butylpentane (**1**) has been described elsewhere.[20] Other materials were commercially available and were used without further purification.

NMR spectra were obtained at 100 MHz using a Varian HA-100 spectrometer. IR spectra were taken with a Hitachi EPI spectrometer.

*Preparation of 4-*t*-Butyl-1-methyl-1-silacyclohexane (2).* *Method A*: A mixture of 5 g (0.2 g-atom) of magnesium and 100 ml of tetrahydrofuran (THF) was placed in a 500 ml three-necked flask. Then 28.6 g (0.10 mol) of **1** and 11.5 g (0.10 mol) of methyldichlorosilane in 100 ml of THF were added over a period of 1 h. The mixture was stirred with reflux for several hours to complete the reaction. The mixture was then hydrolyzed and extracted with petroleum ether. After the solvent was removed, fractional distillation gave 5 g (0.03 mol, 29% yield) of **2** (*cis*/*trans*=1) as a colorless oil, bp 95 °C (35 mmHg); n_D^{20} 0.8424; IR (neat, cm^{-1}): 2120 (ν_{SiH}), 1250 (δ_{SiMe}) 800 (ν_{Si-Me}). Found: C, 70.37; H, 12.89%. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.01%.

Method B: Reduction of 1 g (4 mmol) of **3** (*cis*/*trans*=1/2.3) with 1 g (26.3 mmol) of lithium aluminum hydride gave **2** (*cis*/*trans*=2.8/1) in an almost quantitative yield (by GLC). The compound was identified by comparing its NMR and IR spectra and GLC with those of **2** prepared by method A.

*Preparation of 4-*t*-Butyl-1-methyl-1-chloro-1-silacyclohexane (3).* A mixture of 4 g (0.2 g-atom) of magnesium and 100 ml of THF was placed in a 500 ml three-necked flask. Then 28.5 g (0.10 mol) of **1** and 15 g (0.10 mol) of methyltrichlorosilane in 100 ml of THF were added in a period of 1 h. After the reaction was completed, THF was distilled as completely as possible and 200 ml of diethyl ether was added. The precipitated magnesium salts were filtered from the ethereal solution. After the solvent was removed, fractional distillation gave 10 g (0.148 mol, 48% yield) of **3** (*cis*/*trans*=1/2.3) as a colorless oil, bp 103 °C (20 mmHg). Found: C, 58.32; H, 10.6%. Calcd for $C_{10}H_{21}SiCl$: C, 58.64; H, 10.33%.

*Preparation of 4-*t*-Butyl-1-methyl-1-fluoro-1-silacyclohexane (11).* A volatile residue in the preparation of **3** [5.8 g bp ≈120 °C (3 mmHg)] was added drop by drop to 50 ml of concd sulfuric acid at −10 °C with vigorous stirring over a period of 30 min. After additional stirring for 1 h, 4 g (0.07 mol) of ammonium hydrogen fluoride was added several portions. The organic layer was extracted with petroleum ether. Evaporation of the solvent gave 5.1 g of a residue. Fractional distillation of the residue gave 3.7 g of **11** (*cis*/*trans*=1) as a colorless oil, bp 98 °C (55 mmHg); n_D^{20} 0.9127. IR (neat cm^{-1}): 1260 (ν_{SiMe}), 800 (ν_{SiMe}). Found: F, 10.3%. Calcd for $C_{10}H_{21}SiF$: F, 10.1%.

*Preparation and Separation of 4-*t*-Butyl-1-methyl-1-methoxy-1-silacyclohexane (5).* *Method A*: Methanolysis of 0.99 g (4.9 mmol) of **3** (*cis*/*trans*=1/2.3) with 10 ml (0.25 mol) of methanol in the presence of 20 ml (0.2 mol) of cyclohexylamine in 50 ml of petroleum ether gave 1.03 g of a crude product. This was purified by chromatography on a silica gel column to yield 0.65 g (3.3 mmol, 67% yield) of **5** (*cis*/*trans*=1.7/1). The *cis* and *trans* mixture can be separated into each isomer by preparative GLC (PEG 20 M, ratio of the retention times: *cis*/*trans*=1.14). Physical data are: **5a**, n_D^{20} 1.4530; d_4^{20} 0.8891 and **5b**, n_D^{20} 1.4520; d_4^{20} 0.8908. IR (neat, cm^{-1}): 1090 (ν_{SiO}), 1255 (ν_{SiMe}), 820 (ν_{SiMe}). Found **5a**: C, 66.14; H, 12.25%. **5b**: C, 66.18; H, 11.86%. Calcd for $C_{11}H_{24}SiO$: 65.93; H, 12.07%.

Method B: Methanolysis of 1.39 g (8.19 mmol) of **2** (*cis*/*trans*=1) with 0.35 ml (8.7 mmol) of methanol in dry pentane in the presence of 0.09 g of 10% palladium on charcoal (10% Pd–C) gave **5** (1.7 g) as a crude product, which was subsequently treated with a silica gel column. Fractional distillation gave 0.89 g (4.5 mmol, 54% yield) of pure **5**, bp 120 °C (70 mmHg). The substance was identified by comparing its NMR, IR, and GLC with those of **5** prepared by method A.

*Preparation and Separation of 4-*t*-Butyl-1-methyl-1-isopropoxy-1-silacyclohexane (4).* 3.69 g (21.6 mmol) of **2** (*cis*/*trans*=1) was treated with 2 g (*ca.* 20 mmol) of isopropyl alcohol in 50 ml of dry pentane in the presence of 0.5 g of 10% Pd–C. After further work-up as described above, fractional distillation gave 2.60 g (10.7 mmol, 49.5% yield) of **4**, bp 108 °C (24 mmHg). The product was isolated and purified by preparative GLC (Apiezon L, ratio of retention times: **4a**/**4b**=1.25) to give 0.49 g of **4b**, n_D^{20} 1.4483; d_4^{20} 0.8714 and 0.57 g of **4a**, n_D^{20} 1.4486; d_4^{20} 0.8710, IR (neat cm^{-1}) 1030 (ν_{SiO}), 1255 (ν_{SiMe}), 815 (ν_{SiMe}). Found **4a**: C, 68.14; H, 12.25%. **4b**: C, 68.32; H, 12.25%. Calcd for $C_{13}H_{28}SiO$: C, 68.35; H, 12.35%.

*Preparation and Separation of 4-*t*-Butyl-1-methyl-1-*t*-butoxy-1-silacyclohexane (6).* 25 ml of pentane, 0.4 ml (2.5 mmol) of triethylsilane and 3 ml (30 mmol) of *t*-butyl alcohol were treated with 0.5 g of 10% Pd–C. When vigorous evolution of hydrogen ceased 1.7 g (9.8 mmol) of **2** (*cis*/*trans*=1) was added to the mixture which was kept standing overnight under nitrogen. After a similar work-up, fractional distillation gave 2.1 g (8.7 mmol, 85% yield) of **6**, bp 145 °C (70 mmHg). This was separated to each isomer with preparative GLC (Apiezon L, ratio of retention times: **6a**/**6b**=1.22), giving 0.41 g of **6a**, n_D^{20} 1.4484, d_4^{20} 0.8680; and 0.22 g of **6b**, n_D^{20} 1.4510, d_4^{20} 0.8727.

IR (neat cm^{-1}) 1050 (ν_{Si-O}), 1250 (ν_{SiMe}), 820 (ν_{SiMe}). Found: **6a**: C, 69.69, H, 12.56%. **6b**: C, 69.14; H, 12.45%. Calcd for $C_{14}H_{30}SiO$: C, 69.35; H, 12.47%.

*Preparation and Separation of 4-*t*-Butyl-1-methyl-1-phenyl-1-silacyclohexane (7).* *Method A:* Phenylation of 3.1 g (16.4 mmol) of **11** with 25 ml (0.87 M, 20.1 m eq.) of phenyllithium in ether, followed by fractional distillation, gave 2.5 g (9.5 mmol, 58% yield) of **7**, bp 145 °C (35 mmHg). This was further purified by preparative GLC (Apiezon L, ratio of retention times: **7a**/**7b**=1.26) to give 0.78 g of **7a**: n_D^{20} 1.5173; d_4^{20} 0.9345, and 0.36 g of **7b**: n_D^{20} 1.5174; d_4^{20} 0.9333, IR (neat, cm^{-1}): 1436, 1115 (SiPh); 1250 (ν_{SiMe}), 800 (ν_{SiMe}). Found **7a**: C, 77.79, H, 10.72%. **7b**: C, 77.72; H, 10.92%. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63%.

*Preparation and Separation of 4-*t*-Butyl-1-methyl-1-(*p*-bromophenyl)-1-silacyclohexane (8).* *p*-Bromophenyllithium was prepared from 10.5 g (10.5 mmol) of 1,4-dibromobenzene and 10 m eq. of butyllithium in ether by Gilman's method.[21] To the ethereal solution of *p*-bromophenyllithium was added 1.5 g (8.0 mmol) of **11**. The reaction mixture was refluxed overnight under nitrogen. Further work-up and evaporation of the solvent gave 3.3 g of a residual material. This was purified with a silica gel column to give 2.6 g (8.0 mmol, 100% yield) of **8** (*cis*/*trans*=1.86/1) as a pale yellow oil which solidified readily. Further purification of 1.2 g of **8** by preparative GLC (Apiezon L, ratio of retention times: **8a**/**8b**=1.24) gave 176 mg of **8a** (mp 39—40 °C after recrystallization from ethanol) and 77 mg of **8b** (mp 84—85 °C, after recrystallization from ethanol). Found **8a**: C, 59.24; H, 7.78%. **8b**: C, 59.31; H, 8.01%. Calcd for $C_{16}H_{25}SiBr$; C, 59.06; H, 7.74%.

*Preparation and Separation of 4-*t*-Butyl-1-*p*-Chlorophenyl-1-methyl-1-silacyclohexane (9).* *p*-Chlorophenylmagnesium chloride in THF was prepared from 7 g (47.5 mmol) of 1,4-dichlorobenzene and 1 g (40 mg-atom) of magnesium. By a similar procedure to that given above, followed by purification by preparative GLC (Apiezon L, ratio of retention times: **9a**/**9b**=1.20), 0.85 g (4.5 mmol) of **11** gave *ca.* 40 mg of **9a** (mp 30 °C) and 10 mg of mixture of **9a** and **9b**. Calcd for $C_{16}H_{25}SiCl$: C, 68.41; H, 9.06%. Mixture of **8a** and **8b**; C, 68.49; H, 9.20%.

Preparation of cis-*4-*t*-Butyl-1-methyl-1-silacyclohexane (2a).* A mixture of 0.56 g (2.26 mmol) of **4a** and 1 g (26.4 mmol) of lithium aluminum hydride in 100 ml of ether was refluxed for 10 h and hydrolyzed. After work-up, 0.26 g (1.54 mmol, 68% yield) of pure **2a** was obtained. The structure of **2a** was confirmed by its IR and NMR spectra, and retention time of GLC.

Preparation of trans-*4-*t*-Butyl-1-methyl-1-silacyclohexane (2b).* Reduction of 0.44 g (1.8 mmol) of **4b** with 1 g (26.4 mmol) of lithium aluminum hydride by refluxing in THF for 10 h gave 0.23 g (1.3 mmol 75% yield) of pure **2b**. The structure of **2b** was confirmed by its IR and NMR spectra, and retention time of GLC.

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