Identification of the Stereoisomers of 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane

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Received January 26, 1994®

The configurations of three synthetically available stereoisomers (tttt, ttcc, and tctc) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane have been unambiguously assigned by using spin labeling techniques and by preparing chemical derivatives. $^1J_{C-Si}$, $^2J_{C-Si}$, and $^3J_{C-Si}$ values were determined for the three stereoisomers with ^{13}C-labeled methyl groups. The dominating isomer resulting from the synthesis possesses an all-trans structure and can be isolated in up to 95% purity.

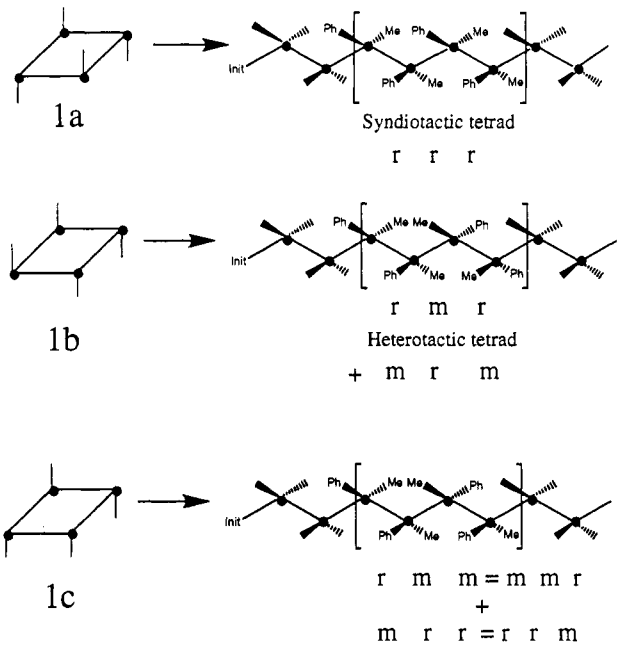
Introduction

Properties of polysilanes depend not only on the structure of substituents but also on their configurations, because they affect the conformation of the backbone.[1-3] Therefore, the preparation of stereoregular polysilanes is essential for definitive structure–property relationships to be obtained. For example, syndiotactic poly(methylphenylsilylene), PMPS, was predicted to exist in the planar zigzag or all-trans conformation, which could result in a higher λ_{max} for this structure than for the heterotactic and isotactic ones.[4] We have focused our efforts on the synthesis of well-defined polysilanes with a special emphasis on the ring-opening process.[5-7]

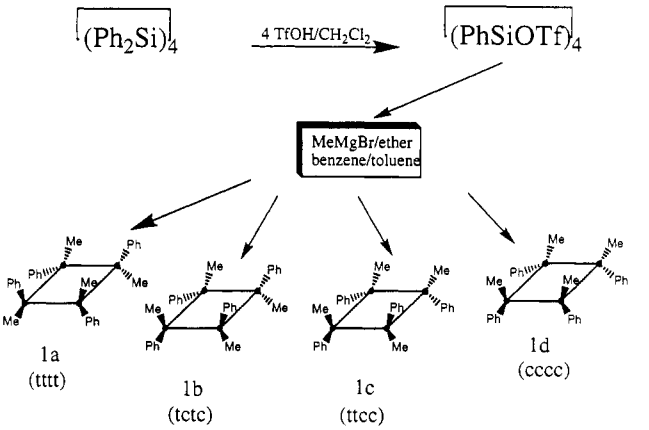
A retrosynthetic analysis for the preparation of stereoregular PMPS indicates that the ring-opening polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (1) affords the possibility of controlling the microstructure of the resulting polymer (Scheme 1). Ring-opening polymerization of all-trans cyclotetrasilane (tttt) **1a**, in a stereoregular fashion, should lead to a polymer with syndiotactic tetrads. Ring opening of **1b** and **1c** should yield nonstereoregular heterotactic structures.

However, the attempted synthesis of **1a** is complicated by the concurrent formation of two other stereoisomers, **1b** and **1c**; formation of **1d** is not observed (Scheme 2). Assignment of **1c** is evident from the distinctive 1:2:1 intensity pattern of peaks present in the ^{29}Si NMR spectrum (cf. Figure 4). Due to the similarity of stereoisomers **1a** and **1b**, a definitive spectroscopic assignment of these isomers was not apparent. This problem was solved by a combination of synthetic modification and isotopic labeling. When they are taken together, the results of these experiments provide conclusive evidence that theall-trans isomer **1a** is the major product of the synthesis.

Scheme 1



Scheme 2



Polymerization of **1a** does in fact lead to highly syndiotactic PMPS in excellent yields,[8] in good accord with Scheme 1.

Results and Discussion

A. Synthetic Modification of 1. Because of the similar symmetries of isomers **1a** and **1b** (D_{2d} and C_{2h},

* Abstract published in *Advance ACS Abstracts,* April 1, 1994.

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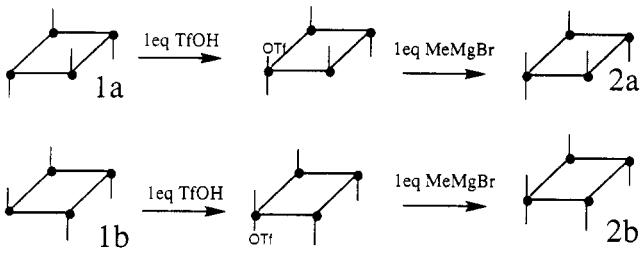
Scheme 3[a]



[a] Phenyl groups are not shown.

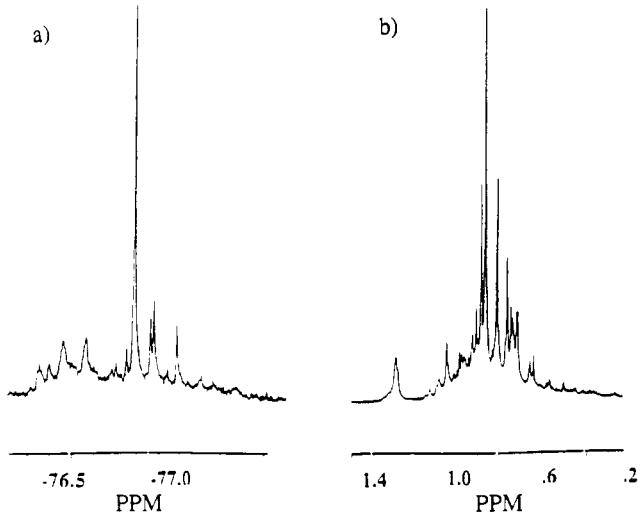


Figure 1. 284.2-MHz ^{19}F NMR spectrum (a) and 300-MHz ^{1}H NMR spectrum (b) of the products of the reaction of **1a** with 1.2 equiv of trifluoromethanesulfonic acid. The reaction was carried out in CD_2Cl_2 and the solution transferred to the NMR tube for analysis.

respectively, in idealized flat structures), all of the observable NMR nuclei appear equivalent under the conditions employed.[9] Lowering or completely breaking the symmetry of the two compounds through chemical derivatization should lead to discernable differences in the NMR spectra, from which the structures of the parent compounds can be deduced. Repeated crystallizations of the mixture of stereoisomers of **1** from cold hexane yield over 95% of a single pure stereoisomer (by ^{1}H NMR), either **1a** or **1b**. The expected results of chemical modification carried out on this pure isomer are shown in Scheme 3.

Dearylation of any one of the four equivalent sites in isomer **1a**, followed by methylation, should result in compound **2a**. The same process carried out with **1b** should give **2b**. Previous results indicated that in the reaction of octaphenylcyclotetrasilane (Ph_8Si_4) with 5 equiv of triflic acid, dearylation competes with ring cleavage.[10] However, ring cleavage does not occur when only 4 equiv of triflic acid is added to Ph_8Si_4, and the intermediate is methylated to yield **1**, followed by a single dearylation and methylation to yield **2**. The stereochemistry of the methylation of the monotriflated derivative $Me_4(OTf)Ph_3Si_4$ is not important because an achiral dimethyl-substituted silicon atom is formed.

Figure 1 shows the ^{19}F and ^{1}H NMR spectra of the intermediate product of the reaction shown in Scheme 3. The ^{19}F NMR spectrum (Figure 1a) displays one dominating signal, which is assigned to the monotriflated product of either **1a** or **1b**. The ^{1}H NMR spectrum (Figure 1b) shows four major signals, one of which is assigned to unreacted starting material, leaving the three other major peaks present in the ratio 1:2:1. This is the expected pattern of the product derived from **1a**. It was previously established that the chemoselectivity of the dearylation is less than 100%,[10] which results in a mixture of unreacted **1** and monotriflated and ditriflated species. The ditriflated species account for the other minor peaks observed in Figure 1. According to integration of the ^{1}H NMR spectrum, less than 10% of unreacted **1** remains.

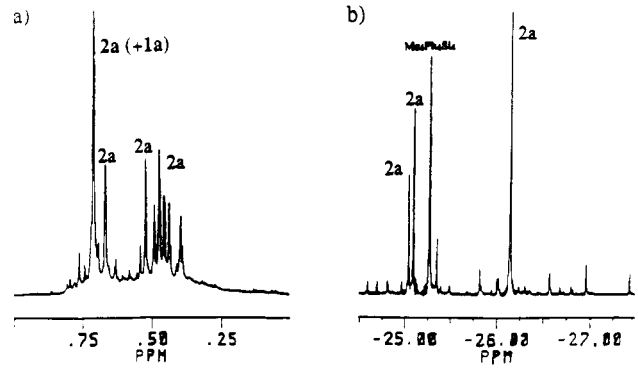


Figure 2. 300-MHz ^{1}H NMR spectrum (a) and 59.6-MHz ^{29}Si NMR spectrum (b) of the products of the reaction of **1a** with 1.2 and 1.0 equiv of trifluoromethanesulfonic acid, followed by methylation with a stoichiometric amount of methylmagnesium bromide. Spectra were recorded in C_6D_6.

Upon methylation of the monotriflated species and purification of the products, the ^{1}H and ^{29}Si NMR spectra shown in Figure 2 were obtained. One of the strongest peaks is assigned to the unreacted **1a**, and the lower intensity peaks are assigned to various isomers of the hexamethyl derivatives, $Me_6Ph_2Si_4$; no specific assignments have been made at present. This was confirmed by allowing the same reaction to proceed using 2 equiv of triflic acid and methylmagnesium bromide. The peaks assigned to $Me_6Ph_2Si_4$ were dominating, and no unreacted starting material was detected.

The ^{1}H NMR spectrum (Figure 2a) contains four strong signals in the ratio 2:1:1:1, while the ^{29}Si NMR spectrum (Figure 2b) displays three signals in the ratio 2:1:1. These are the expected patterns for compound **2a**, which confirms the assignment of the dominating isomer in the synthesis of **1** to **1a**. This is in accord with previously reported assignments which were based on thermodynamic considerations and chemical intuition.[10]

B. Isotopic Labeling of 1. Isotopic labeling methods provide a more subtle means of creating observable NMR spectral differences for **1a** and **1b**, as opposed to chemical modifications, which can strongly perturb the system. In the synthesis of **1** (Scheme 2), the triflated intermediates were treated with ^{13}C-labeled methylmagnesium iodide, yielding compound **1***, with 99% ^{13}C labeling of the methyl groups.

The methyl regions of the 300-MHz ^{1}H NMR spectra of **1*** and **1** (mixtures of stereoisomers) are shown in Figure 3; the aromatic regions of both spectra are similar. The methyl region of **1*** displayed the same pattern of five signals as seen for **1**, except split into doublets ($^{1}J_{C-H}$ = 123 Hz), which confirmed the preparation of **1***. This spectrum, however, contained no discernable information which could be used for identification of stereoisomers **1a*** and **1b***.

(9) ^{1}H and ^{13}C NMR spectra were recorded at 300 and 500 MHz and 79.4 and 125.7 MHz, respectively, with no observable spectral differences.

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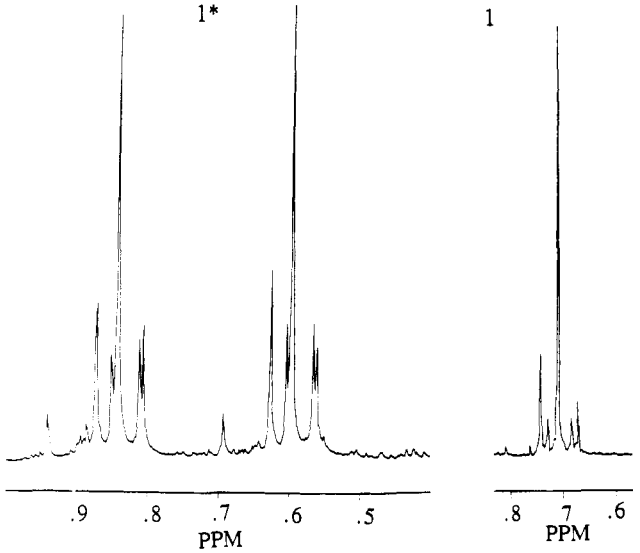


Figure 3. Methyl regions of the 300-MHz ^1H NMR spectra (C_6D_6) of compounds **1** and **1*** prepared by the route in Scheme 2 and by substituting ^{13}C-labeled methylmagnesium iodide in the second step, respectively.

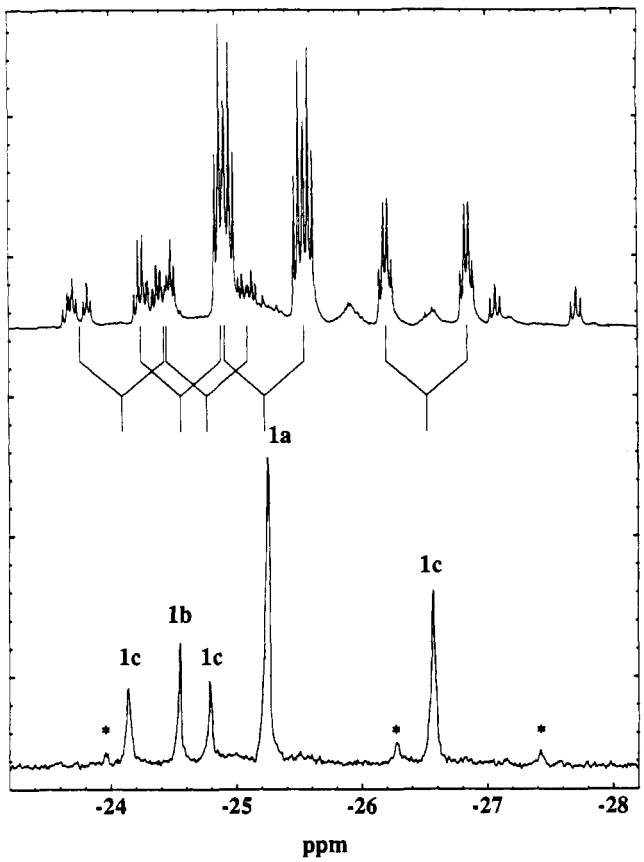


Figure 4. 59.6-MHz ^{29}Si NMR spectra of (bottom) **1** and (top) **1*** showing the correlation of peaks from the unlabeled compound with those in the ^{13}C-labeled one. Peaks labeled with asterisks are assigned to impurities, most likely $Me_3Ph_5Si_4$ derivatives, which are not assigned in the upper spectrum.

The ^{29}Si NMR spectra of the mixtures of stereoisomers of **1** and **1*** are shown in Figure 4. In the spectrum of **1**, the three peaks in the consistent ratio of 1:2:1 are assigned to isomer **1c**; the remaining singlets at −24.59 and −25.26 ppm must therefore be assigned to **1a** and **1b**. In contrast to the spectrum of **1**, the spectrum for **1*** contains fine structure which provides deeper insight into the stereochemistry of each isomer.

Table 1. Carbon–Silicon Coupling Constants for the Stereoisomers of 1*[a]

stereoisomer	^1J, Hz	^2J, Hz	^3J, Hz
1a*	37.6 ± 0.2	2.1 ± 0.2	4.6 ± 0.2
1b*	37.8 ± 0.2	2.1 ± 0.2	1.9 ± 0.2
1c*-Si_b (×2)	38.6 ± 0.2	2.1 ± 0.2	1.8 ± 0.2
1c*-Si_a	38.5 ± 0.2	1.8 ± 0.2	4.5 ± 0.2
1c*-Si_d	39.8 ± 0.2	1.7 ± 0.2	6.8 ± 0.2

[a] $^1J_{C\text{-}Si}$ is the coupling constant between the observed silicon atom and the methyl carbon directly attached. $^2J_{C\text{-}Si}$ is the coupling to the methyl carbons on two neighboring α-silicon atoms, and $^3J_{C\text{-}Si}$ is the coupling constant to the methyl carbon on the β-silicon atom.

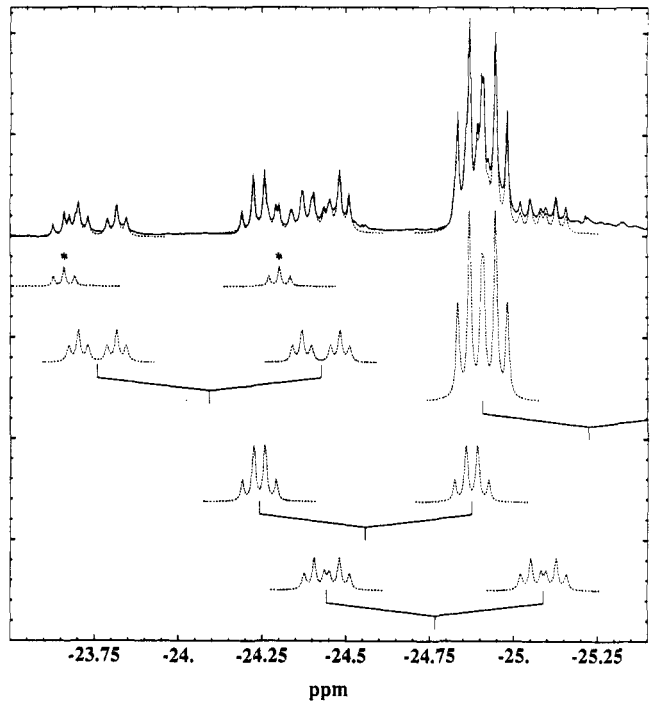


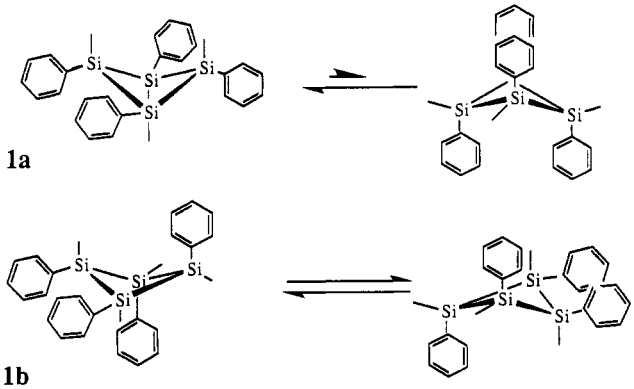
Figure 5. Fit of the fine structure present in the ^{29}Si NMR spectrum of **1*** using a simple splitting scheme with Lorentzian line shapes. Coupling constants derived from the fit are listed in Table 1.

A simple splitting scheme with Lorentzian line shapes and spectral superposition was employed to derive the coupling constants shown in Table 1 and, also, to generate the fit shown in Figure 5.

In order to facilitate the discussion of the coupling constants in the stereoisomers, it is necessary to emphasize that each of the three different types of silicon atoms in isomer **1c** are in environments resembling those of the silicon atoms in **1a**, **1b**, or **1d**. Two silicon atoms in isomer **1c** (**1c***-Si_b) are in an environment similar to that of the silicon atoms in isomer **1b** and, therefore, should be present with twice the intensity of the silicon atoms which are in environments similar to those in **1a** and **1d** (**1c***-Si_a and **1c***-Si_d, respectively).

Analysis of the coupling constants presented in Table 1 indicates very large values of ^1J for all systems. Apparently, values of ^1J for **1c** are higher than those for **1a** and **1b**, regardless of the stereochemical environment. It is possible that these values are strongly dominated by the hybridization of the corresponding Si–C bonds. Values of ^2J are quite similar in all cases and smaller than ^3J values. The latter provide the most important information for structural determination. The ^3J value for the **1c***-Si_b

Scheme 4



1a

1b

atoms is the smallest (1.8 Hz). The values of ^3J for silicon atoms Si_a and Si_d are 4.6 and 6.8 Hz, respectively. The two identical silicon atoms, **1c***-Si_b, are attached to essentially the same ring fragment as are the silicon atoms in isomer **1b***; therefore, the set of ^2J and ^3J coupling constants which most nearly match those of **1c***-Si_b must belong to isomer **1b***. By analogy, the set of ^2J and ^3J coupling constants determined for silicon atom **1c***-Si_a matches best those from **1a***, leading to the conclusion that they exist in similar environments. The remaining silicon atom, **1c***-Si_d, possesses quite different coupling constants, indicating a unique environment not present in either of the synthetically available isomers; however, it is anticipated that the ^2J and ^3J values for isomer **1d** could be similar to those for **1c***-Si_d.

It is recognized that cyclotetrasilanes exist as rapidly interconverting puckered rings rather than flat structures.[11] The flipping of the rings is faster than the NMR time scale, and therefore, one average value of the chemical shift as well as of the coupling constant for the stereoisomers is observed. It is expected that **1a** can adopt a preferred conformation with the bulky phenyl groups in equatorial positions, which would have a lower energy than the conformer with all phenyl groups in axial positions (Scheme 4). On the other hand, methyl and phenyl groups on two neighboring Si atoms in **1b** will be in both equatorial and axial positions. These structures should be energetically equivalent and should show no conformational preference. It seems that at the lowest temperatures (~−80 °C) some broadening of the signals assigned to **1b** is noticed, whereas signals assigned to **1a** remain fairly sharp. However, the low signal to noise ratio makes any definitive measurements of the dynamics of the ring flipping impossible.

Conclusions

It can be concluded that the chemical derivatization, as well as the isotopic labeling methods, indicate that the stereoisomer which is formed in the highest yield in the synthesis of **1** can be assigned to **1a**. This isomer possesses an all-trans configuration of its substituents. Assignment of the other isomers to **1b** and **1c** was also accomplished; however, separation of the two compounds has not yet been achieved. Isolation of **1a** allows the synthesis of highly syndiotactic PMPS.

Experimental Section

All experiments were performed in a Vacuum Atmospheres HE-43 dry box under a nitrogen atmosphere with O_2 and H_2O concentrations below 1.0 ppm. CH_2Cl_2 was stirred over fuming H_2SO_4 for several days, neutralized with Na_2CO_3, refluxed over CaH_2 for several days under argon, and finally distilled before use. Benzene and toluene were refluxed over Na under argon and distilled prior to use. CD_2Cl_2 was stored over CaH_2 for several hours in the drybox prior to use. Trifluoromethanesulfonic acid was vacuum-transferred prior to use. Hexane was refluxed over CaH_2 for a minimum of 12 h under argon and distilled prior to use. MeMgBr (Aldrich) was used as received. Ph_8Si_4 was prepared using the method reported by Gilman.[12]

1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. To a stirred slurry of 9.5 g (0.0130 mol) of Ph_8Si_4 in 200 mL of CH_2Cl_2 at room temperature was added 4 equiv of triflic acid (4.61 mL) dropwise. At 2 equiv the reaction mixture became homogeneous. After the addition was completed, the reaction mixture, now yellow, was stirred for 12–16 h further. CH_2Cl_2 was removed via trap to trap distillation, and the resulting yellow powder was dried under vacuum for several hours. The solid was dissolved in a 2:1 mixture of toluene/benzene and the temperature lowered to −30 °C in a cooling bath. To this was added, in a dropwise fashion, 4 equiv of methylmagnesium bromide, 3.0 M in ether. The mixture was stirred for 3 h while being warmed to ambient temperature, at which time the salts were filtered off using a 0.2-μm filter and the solvents removed by trap-to-trap distillation. The remaining off-white oil was dissolved in hexane, which precipitated more white inorganic salts that were again filtered. The hexane was removed by trap-to-trap distillation, and the procedure was repeated three times, yielding 5.95 g (95%) of a mixture of stereoisomers of **1**, in the form of a white powder. Upon recrystallization from cold hexane, **1a**, up to 95% pure, was obtained.

1*: **^{13}C-Labeled $Me_4Ph_4Si_4$.** This compound was prepared by the same procedure as above, except with ^{13}C-labeled methylmagnesium iodide being used.

1,1,2,3,4-Pentamethyl-2,3,4-triphenylcyclotetrasilane (2a). **1a** (0.250 g) was dissolved in 1 mL of CD_2Cl_2, and 46.0 μL (1 equiv) of triflic acid was added dropwise. After the mixture was stirred for 30 min, a sample was taken for ^{19}F and ^{1}H NMR experiments. The sample was returned and the mixture stirred overnight. The solvent was removed by trap-to-trap distillation and the remaining yellow oil dried for several hours under vacuum. This oil was then methylated as described above. After a workup similar to that discussed previously, approximately 0.2 g of $Me_4Ph_4Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$ was obtained. This mixture was stored in cold hexane, and small portions were dried under vacuum for NMR experiments.

NMR Experiments. Except for ^{19}F and ^{1}H NMR experiments on the triflated derivatives, which were performed in CD_2Cl_2, all other spectra were recorded in C_6D_6 using C_6H_6 as an internal reference for ^{1}H and ^{13}C and TMS as an external reference for ^{29}Si. All experiments were carried out on an IBM NR-300 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra were recorded at 75.4 MHz, and ^{29}Si NMR spectra were recorded at 59.6 MHz using a standard Bruker DEPT micro program. ^{19}F NMR spectra were recorded at 282.4 MHz, and the chemical shifts are reported relative to methyl triflate. ^{1}H and ^{13}C NMR spectra of **1*** were also determined on an IBM NR-500 spectrometer at 500 and 125.7 MHz, respectively.

Acknowledgment. Support of the Office of Naval Research and the National Science Foundation for this work is appreciated. K.M. acknowledges support via matching funds from DuPont, Xerox, and PPG Inc. within the Presidential Young Investigator Award. We also thank Dr. Jim Maxka for many helpful discussions.

OM940069D

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