calculations. Nevertheless, even though relativistic results may better approach a quantitative description of the electronic structure, it is presently unclear whether such demanding computational efforts are worthwhile. In the case of far simpler molecules, such calculations improve the interpretation of PE data to only a limited extent. The matter, however, still remains open to question, and further studies will be reported in a forthcoming paper.[10c]

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Registry No. $U(\eta^5\text{-}C_5H_5)_3CH_3$, 37205-28-0; $U(\eta^5\text{-}C_5H_5)_3NH_2$, 112196-34-6; $U(\eta^5\text{-}C_5H_5)_3BH_4$, 37298-62-7; $U(\eta^5\text{-}C_5H_5)_3NCS$, 69526-48-3.

Supplementary Material Available: Orbitals, eigenvalues, and population analysis of Cp_3ThOCH_3 in C_s symmetry (Table SI) and in C_{3v} symmetry (Table SII) and relativistic orbitals, eigenvalues, and population analysis of Cp_3ThOCH_3 in C_{3v} symmetry (Table SIII) (2 pages). Ordering information is given on any current masthead page.

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^{19}F NMR Studies of the Reaction of Octaphenylcyclotetrasilane with Triflic Acid

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The chemo- and stereoselectivity of the dearylation reaction of octaphenylcyclotetrasilane with trifluoromethanesulfonic acid was studied using ^{19}F NMR. Up to four triflate groups could be easily introduced to the ring. Substitution of the fifth phenyl group was accompanied by ring cleavage. Dearylation competes with the exchange of silyl triflates with triflic acid and leads to the thermodynamic distribution of stereoisomers.

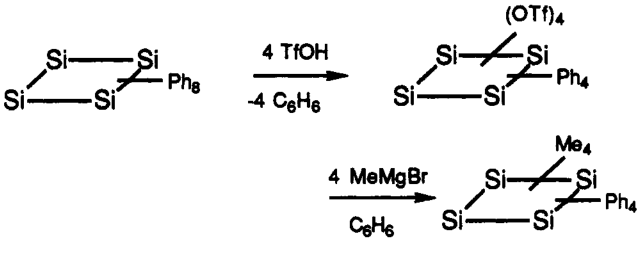
Introduction

Arylsilanes are known to undergo electrophilic displacement of aryl groups by strong protonic acids.[1-3] The first step of the reaction involves a reversible protonation of the ipso-carbon atom, followed by nucleophilic attack of the resulting anion on the silicon atom with cleavage of the C_{Ar}–Si bond.[1] Although this reaction is often referred to as *protodesilylation* in organic chemistry literature, we prefer the "silicocentric" term, *dearylation*, which is more suitable to discussions of reactions on the silicon backbone.

Labile functional groups such as halogens and perchlorate can be introduced onto silicon by silane dearylation, thus enabling further modification by a variety of nucleophilic reagents.[4-6] For example, functional silanes react with $LiAlH_4$, organometallic reagents, alcohols, and primary or secondary amines yielding silicon hydrides and organo-, alkoxy-, and aminosilanes, respectively.

Trifluoromethanesulfonic (triflic) acid is a versatile and very efficient dearylating reagent.[6,7] The resulting silyl triflates are among the most reactive silylating agents.[5,6] They also initiate the cationic polymerization of some vinyl and heterocyclic monomers[8] and can be converted to silyl ketene acetals for initiation of group transfer polymerization.[9] Thus, poly(tetrahydrofuran) and poly(methyl methacrylate) have been grafted onto poly(methylphenylsilylene) backbones which were dearylated with triflic acid.[9-11]

Scheme I



The kinetics of dearylation of dimethyldiphenylsilane[6] and α,ω-diphenylpermethyloligosilanes[12] have been studied. Although substitution of the first phenyl group is very fast, substitution of the second phenyl group in dimethyldiphenylsilane is several orders of magnitude slower due to deactivation by the electron-withdrawing triflate group. The reaction rate is 23 times lower when the TfO group is bound to the α Si atom in a disilane. Although this effect decreases with increasing separation of the phenyl and triflate groups, it is still significant at distances up to four Si–Si bonds. For example dearylation of the first Ph group in 1,5-diphenyldecamethylpentasilane is 7 times faster than dearylation of the second one.[12]

The replacement of aryl by alkyl groups in cyclotetrasilanes provides a route for the synthesis of strained rings such as 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetra-

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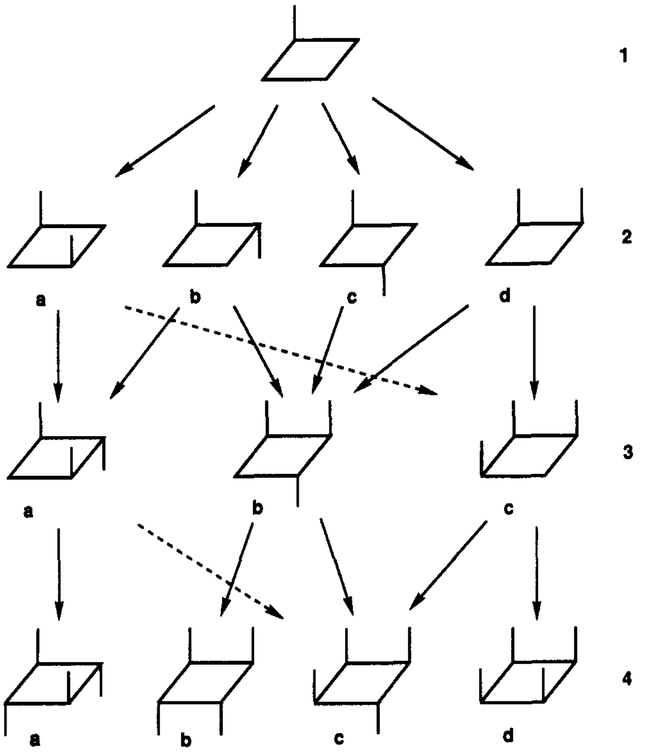
Scheme II



silane[13-15] which are less sterically hindered upon ring opening and therefore polymerizable. This new monomer is polymerized by ring opening polymerization using anionic initiators. Its synthesis involves triflation of octaphenylcyclotetrasilane and subsequent methylation of the 1,2,3,4-tetraphenyl-1,2,3,4-tetrakis(trifluoromethylsulfonoxy)cyclotetrasilane with methylmagnesium bromide (Scheme I). Only one triflate group can be successfully introduced at each silicon atom, resulting in over 90% yield of the 1,2,3,4-tetramethyl-substituted derivative as a mixture of stereoisomers.

Our objective is to obtain well-defined polysilanes with controlled molecular weight, polydispersity, and tacticity. The chemo-, regio- and stereoselectivity of the monomer synthesis is therefore of primary importance. In order to better understand this process and to optimize the synthesis, we have studied the reaction of $(SiPh_2)_4$ with triflic acid using ^{19}F NMR spectroscopy. The reaction products are analyzed as a mixture of isomers because the triflate derivatives are quite unstable and cannot be separated into individual isomers by chromatography.

Because it is difficult to assign absolute configurations to specific isomers obtained in the dearylation, it is necessary to make intuitive assignments based on the steric and electronic effects of substituents, as reported previously.[16,17] Analysis of more stable methylphenyl isomers will be reported in a subsequent paper.

Nomenclature

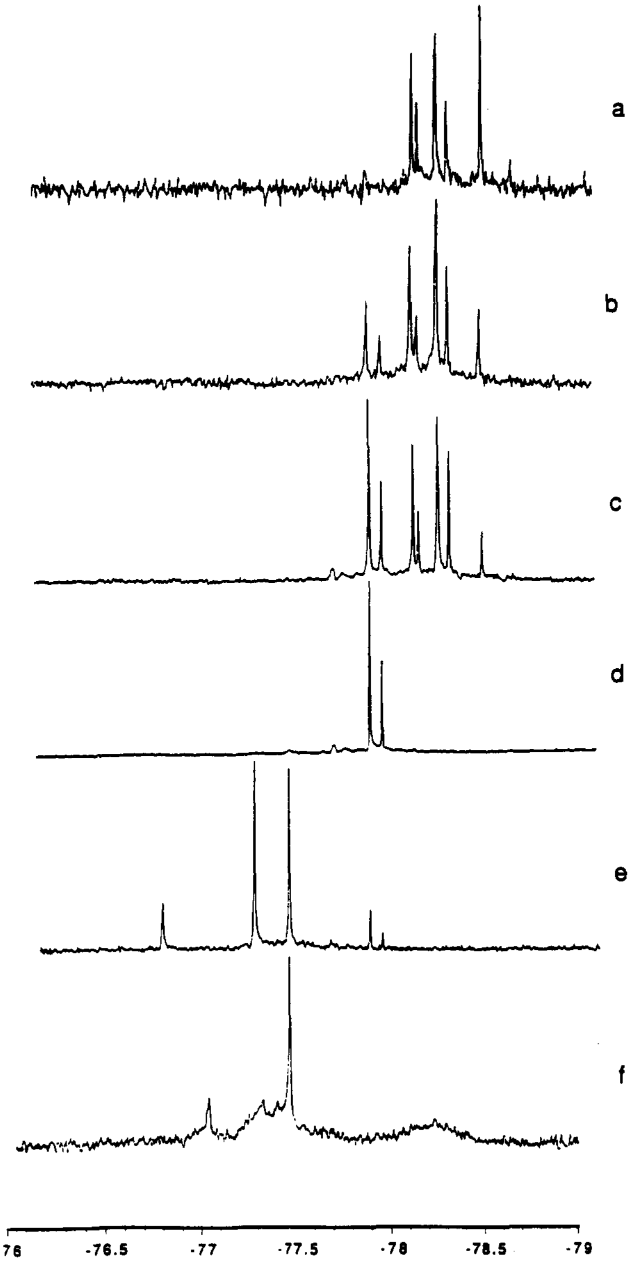


Figure 1. ^{19}F NMR spectra (in $CDCl_3$) of the reaction mixtures of $(Ph_2Si)_4$ ($[(Ph_2Si)_4]_0$ = 0.05 mol/L) with TfOH in CH_2Cl_2: (a) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 0.5; (b) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 1; (c) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 2; (d) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 3; (e) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 4; (f) $[TfOH]_0/[(Ph_2Si)_4]_0$ = 5.

Simplified terminology analogous to that of porphyrin derivatives[18] will be used hereafter to describe the geometric isomers of triflated cyclotetrasilanes. This nomenclature is based on the relative positions of the triflate groups above (up) or below (down) the plane of the ring. For example, the trans-1,2 isomer in Scheme II (**2b**) is named 1-up-2-down, while the other three ditriflates are referred to as 1,3-up (**2a**), 1-up-3-down (**2c**), and 1,2-up (**2d**). The three possible tritriflates shown in Scheme II are named 1,3-up-2-down (**3a**), 1,2-up-3-down (**3b**), and 1,2,3-up (**3c**). The four tetratriflates are named 1,3-up-2,4-down (**4a**), 1,2-up-3,4-down (**4b**), 1,2,3-up-4-down (**4c**), and 1,2,3,4-up (**4d**).

Results

Dearylation of octaphenylcyclotetrasilane was performed in a drybox by slowly adding TfOH to a stirred suspension of $(Ph_2Si)_4$ in CH_2Cl_2 using the following $[TfOH]_0/[(Ph_2Si)_4]_0$ ratios: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, and 5. In all cases, a pale yellow color appeared within 30 s. The so-

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Table I. ^{19}F and ^{29}Si NMR Chemical Shifts of Triflated Cyclotetrasilanes and ^1H NMR Chemical Shifts of Methylated Cyclotetrasilanes, $X_nPh_{8-n}Si_4$[a]

isomer (*n*)	^{19}F (in $CDCl_3$)	^{29}Si (in $CDCl_3$)	^1H (in C_6D_6)
1 (1)	−78.5	33.5, −21.6, ...	0.88
2a–d (2)	−78.1	27.8, −22.6	0.84
	−78.33	26.5, −27.9	0.775
	−78.26	26.6, −31.6	0.875
	−78.14	25.6, −24.2	0.78
3a (3)	−77.9, −77.97	20.5, 19.4, −31.4	0.82, 0.68 (2:1)
3b,c (3)	−78.2, −78.26, ...	18.2, 16.9, −29.6, ...	0.85, 0.64, 0.6 (1:1:1), 0.92, 0.74 (2:1)
4a (4)	−77.5	14.0	0.72
4b (4)	−77.3	13.3	0.75
4c (4)	−76.8, −77.3, −77.5		0.73, 0.68, 0.67 (1:1:2)

[a] Tentative assignments made by comparison of relative signal intensity with the predicted thermodynamic stability due to steric effects (ppm).

lutions became homogeneous only when at least 2 equiv of TfOH was used. Figure 1 presents the ^{19}F NMR spectra of equilibrated samples taken from each reaction mixture, and Table I summarizes the resonances and their assignments to the isomers shown in Scheme II. The resonances appear further downfield as the number of triflate groups on the ring increases.

One singlet at −78.5 ppm corresponding to $(TfO)Ph_7Si_4$ and four singlets at −78.1 to −78.33 ppm (with 7:4:3:2 relative intensities) corresponding to the four $(TfO)_2Ph_6Si_4$ isomers are observed when 0.5 equiv of TfOH is used. Although substitution of a second phenyl group by triflate is deactivated by the first triflate group, formation of the ditriflates is not surprising considering that the system is heterogeneous with some unreacted $(Ph_2Si)_4$ remaining out of solution. Since the reaction mixture does not become homogeneous until at least 2 equiv of TfOH is added, the product mixture of reactions using less than this is evidently kinetically controlled. However, a small resonance due to the monotriflate is still observed in the reaction mixture containing 2 equiv of TfOH, as are resonances due to the di- and tritriflates. As shown in Figure 2d, the extent of dearylation corresponds to the reactant stoichiometry only when 3 equiv of TfOH is used. That is, resonances due to $(TfO)Ph_7Si_4$, $(TfO)_2Ph_6Si_4$, and $(TfO)_4Ph_4Si_4$ are essentially absent. The two signals at −77.9 and −77.97 ppm (relative intensity 2:1) are ascribed to only one of the $(TfO)_3Ph_5Si_4$ isomers.

Triflation is very fast and moderately exothermic when up to 3 equiv of acid are added. For example, reaction with 0.5 equiv of TfOH was complete before its first NMR spectrum was recorded. Reaction with a fourth equivalent of TfOH is considerably slower due to the deactivation by three triflate groups. As shown in Figure 2, it takes approximately 6 h at 25 °C to consume the fourth equivalent of TfOH. The position of free acid varies with concentration and in this case is detected by the broadening of each resonance until it is consumed. The fact that some tritriflate is still detected when all the acid is consumed, without any resonances due to products substituted with more than four triflate groups, indicates that slightly less than 4:1 $[TfOH]_0/[(Ph_2Si)_4]_0$ stoichiometry was actually used. In the case of $[TfOH]_0/[(Ph_2Si)_4]_0 = 5$, free acid was present in the mixture even after 24 h. Similar results were obtained in chloroform. However, dearylation in benzene is much slower and does not go to 100% conversion with 4 equiv of TfOH even after 24 h.

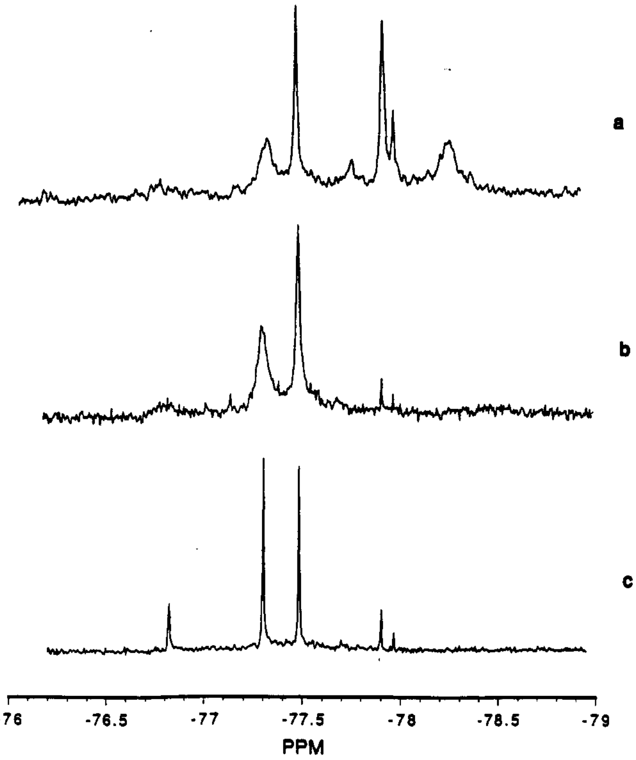

Figure 2. ^{19}F NMR spectra (in $CDCl_3$) of the reaction mixture of $(Ph_2Si)_4$ with TfOH in CH_2Cl_2 ($[(Ph_2Si_4]_0 = 0.05$ mmol/L; $[TfOH]_0/[(Ph_2Si)_4]_0 = 4$): (a) after 20 min; (b) after 2 h; (c) after 6 h.

The samples dearylated with 2–5 equiv of TfOH were subsequently reacted with 1–1.02 equiv of MeMgBr (relative to the triflate groups) in a mixture of benzene and ether. Correlation of the ^1H NMR spectra (Figure 3) of the resulting methylcyclotetrasilanes with the ^{19}F NMR spectra of their triflated precursors enabled most of the resonances to be assigned. The ^1H NMR spectrum of the 3:1 mixture reveals the presence of small amounts of two other trimethylcyclotetrasilane isomers in addition to the **3a** isomer (Scheme I) detected by ^{19}F NMR of the corresponding triflate derivative. The ^1H NMR spectrum of the 4:1 reaction mixture shown in Figure 3c includes the same five resonances due to tetramethylcyclotetrasilane isomers reported previously.[14] The ^1H NMR spectrum of the 5:1 mixture (Figure 3d) reveals that 55% of the mixture contains tetramethylcyclotetrasilanes. We believe that the resonances at 0.0–0.06 ppm correspond to linear 1,1,2,3,4-pentamethyl-1,2,3,4-tetraphenyltetrasilane (15%) and that those at 0.3–0.5 ppm correspond to pentamethylcyclotetrasilanes. A Si–H multiplet at 4.15 ppm confirms that a fifth equivalent of triflic acid may react by opening the ring, as well as by dearylation. The broad resonance centered at −78.2 ppm in Figure 1f is also presumably due to linear ring-opened silanes. Although resonances due to pentatriflate cyclics were not assigned in Figure 1f, they may overlap those of the tetratriflate and be the source of the broadening of those peaks.

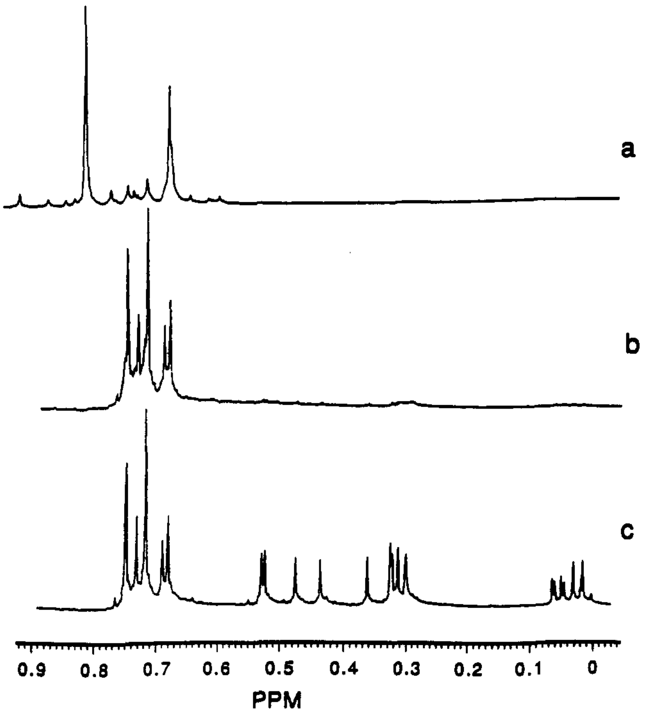

Figure 3. ^{1}H NMR spectra (in C_6D_6) of the products of the reaction of slight excess of MeMgBr with (trifluoromethylsulfonoxy)phenylcyclotetrasilanes in C_6H_6: (a) $[TfOH]_0/[(Ph_2Si)_4]_0 = 3$; (b) $[TfOH]_0/[(Ph_2Si)_4]_0 = 4$; (c) $[TfOH]_0/[(Ph_2Si)_4]_0 = 5$.

Table I also summarizes the INEPT ^{29}Si NMR chemical shifts of the triflated cyclotetrasilanes. Although INEPT is not quantitative with respect to the number of Si atoms causing a signal, the relative intensities of signals arising from Si atoms having the same substituents is comparable and therefore was used to assign peaks. In addition, the intensities of signals arising from diphenyl-substituted Si are somewhat higher than those from >SiPh(OTf) due to more efficient polarization transfer from the ortho protons of the two phenyl rings. The resonances shift upfield as the number of triflate groups in the ring increases. Signals at 13–33 ppm correspond to >SiPh(OTf) moieties, while the resonances at −20 to −30 ppm correspond to $>SiPh_2$ groups. As expected, no resonances due to $>SiPh_2$ are observed for the tetratriflates. The monotriflate and all four ditriflate isomers were identified. Four signals corresponding to tritriflate isomers are observed in the range for >SiPh(OTf) resonances, with the two major peaks at 20.5 and 19.4 ppm assigned to the **3a** isomer. Only two resonances are observed for the tetratriflates.

Discussion

Selectivity of the Triflation Reaction. Earlier studies concerning the reactivity of phenyl silanes toward triflic acid were performed on linear permethylsilanes with terminal phenyl groups.[6,12] The reactivity of octaphenylcyclotetrasilane toward triflic acid should differ from that of the above linear oligosilanes for two reasons. First, the steric and electronic factors determining substitution are altered by the conformation of the strained ring. Second, the reactivity of an aryl group in $>SiPh_2$ will be different than that of an aryl group in >SiPh(alkyl). Nevertheless, the presence of a triflate moiety should still inhibit a second displacement at the same silicon atom and should reduce the rate of dearylation at neighboring silicon atoms.

The NMR experiments confirm that the rate of dearylation decreases as additional triflate groups are introduced onto the cyclotetrasilane. The selectivity of the reaction therefore increases with increasing substitution. Thus, ditriflates are obtained in approximately 70% yield, while the tri- and tetratriflates are formed in over 90% yield (NMR). The selective formation of the monotriflate is low, not only because the rates are faster at this stage but also because the reaction is heterogenous with less than 1% of octaphenylcyclotetrasilane in solution in CH_2Cl_2. The monotriflate is more soluble and therefore undergoes further triflation in solution. However, cyclotetrasilane containing five triflate groups is not obtained selectively since a second substitution at >SiPh(OTf) is very slow and competes with ring cleavage by the acid.

Stereoselectivity of Substitution. Scheme II shows all isomers which may be generated at each triflation or methylation step. The 1-up-2-down ditriflate and the 1,2-up-3-down tritriflate are chiral isomers. They both appear as racemic mixtures of enantiomers and cannot be distinguished by NMR. The other isomers are optically inactive.

The reaction of triflates with Grignard reagent is presumably stereoselective. We therefore assume that the relative proportion of isomers should be preserved during methylation and that the proportion of isomers is established during the triflation process. The relative proportion of isomers does not correspond to the statistical distribution of 2:4:5:2 of **4a**:**4b**:**4c**:**4d** (Scheme II). This implies that steric effects determine the proportion of isomers formed, especially during triflation since triflate is larger ($r \approx 3$ Å)[19] than either phenyl or methyl. Although it is not possible at this stage to directly correlate the NMR signals with isomers of absolute configuration, we can assume that the relative proportion of different isomers is related to the relative steric hindrance of the substituents. This is especially true for the triflate derivatives not only because their size is larger but also because the triflate groups of trisubstituted and tetrasubstituted isomers, and probably disubstituted isomers, can exchange. Exchange is not possible once the triflates are replaced by methyl substituents. The relative ratio of isomers of 1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetramethylcyclotetrasilane also conforms to relative stabilities based on the steric effects of the *tert*-butyl groups.[16,17]

In the case of disubstituted rings, the 1-up-3-down isomer should be the most stable isomer and therefore the predominant product. Two other isomers, presumably 1,3-up and 1-up-2-down, appear in smaller, but similar, amounts. The most hindered 1,2-up isomer should account for the isomer formed in the smallest quantity (Figure 1). The small regioselectivity between 1,3- vs 1,2-substitution can be explained by electronic effects operating on both sides of the ring. While 1,2-substitution can be formally considered as a substitution in the α position from one side of the ring and γ from the other, 1,3-substitution is β from both sides. According to the data for α,ω-diphenylpermethyloligosilanes,[12] the ratio of the rate constants of dearylation of the first and second phenyl group is 23, 13, and 10 for the α, β, and γ positions, respectively. Assuming that the electronic effects in the ring are similar to those in linear silanes, the rates of 1,2- and 1,3-substitution may be comparable.

In the case of tritriflate, three isomers are possible, two of which (**3a**, 1,3-up-2-down, and **3c**, 1,2,3-up) would give two singlets (2:1), and the third one (**3b**, 1,2-up-3-down) which should give three signals (1:1:1). The ^{19}F spectrum of $[TfOH]_0/[(Ph_2Si)_4]_0 = 3$ mixture shows two dominating signals (−77.90 and −77.97 ppm, ca. 85% by integration,

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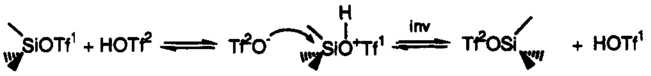
[19] Yao, N. P.; Benion, D. N. *J. Electrochem. Soc.* **1971**, *118*, 1079.

Scheme III



presumably 1,3-up-2-down). Small signals downfield from the main two peaks can be attributed to isomers **3b** and **3c**. The signal of the triflate group in position 3 of the isomer **3b**, 1,2-up-3-down, may overlap with the signals of those in positions 1 and 3 of the isomer **3a** (1,3-up-2-down) due to similar shielding. The ^{1}H spectrum of the methylated analog shows resonances due to all of the tritriflates with one strongly dominating over the others (ca. 85% by integration).

The ^{19}F spectrum of the $[\mathrm{TfOH}]_0/[(\mathrm{Ph_2Si})_4]_0 = 4$ mixture shows only three tetratriflate signals, while there are five signals in the ^{1}H spectrum. There are four isomers of tetrasubstituted rings possible, which should give six signals total, but the most hindered one, 1,2,3,4-up (all-cis, **4d**) is probably not formed. The most likely explanation for this inconsistency is that some fluorine signals for tetratriflate isomers coincidentally overlap each other. In fact, shielding of the triflate groups in positions 1 and 3 in the 1,2,3-up-4-down isomer is similar to that in the 1,2-up-3,4-down isomer (compare **4b** and **4c** is Scheme II), while the triflate group in position 4 of 1,2,3-up-4-down would be shielded as in the 1,3-up-2,4-down isomer (**4a**). Only the triflate group in position 2 is different and appears downfield from the others.

Possibility of Isomerization. The exchange of triflate groups occurs very rapidly in less sterically hindered silyl triflates such as $\mathrm{Me_3SiOTf}$. Only one sharp signal is seen in the ^{19}F spectrum of a mixture of $\mathrm{Me_3SiOTf}$ and TfOH, indicating that exchange is fast compared to the NMR time scale. A similar exchange occurs with trimethylsilyl perchlorate and perchloric acid.[20] The mechanism of the exchange probably involves protonation of the $\mathrm{Tf^1O}$ ester leaving group and the attack of the $\mathrm{Tf^2O^-}$ triflate anion on silicon. As shown in Scheme III, this reaction would proceed with inversion of configuration. The exchange may also occur with retention of configuration if it occurs within a six-membered transition state, but this process would not result in isomerization. In the case of phenyl(triflate)cyclotetrasilanes, fast exchange would lead to a thermodynamic mixture of stereoisomers at each stage of substitution. For example, although only the ditriflates **2a** and **2b** can form the tritriflate **3a** directly and although they constitute only 50% of the ditriflates, the tritriflates are composed of over 85% of isomer **3a**.

The dearylation reaction at $[\mathrm{TfOH}]_0/[(\mathrm{Ph_2Si})_4]_0 < 3$ is too fast for the exchange to be observed by NMR, since the acid is consumed very rapidly. However, substitution of the fourth phenyl group is slow enough to make such observations possible. Triflate groups in tetratriflate cyclotetrasilanes undergo much slower exchange than trimethylsilyl triflate does, and no coalescence of the ^{19}F NMR signals is observed. However, the signals are broad at room temperature at shorter reaction times (Figure 2a,b). The rate constant of the exchange process is roughly estimated from the line shape to be $k_{ex} \approx 10^3$ mol^{-1}·L·s^{-1} under these conditions. The lines of some isomers and of the free acid are broadened, while the others remain sharp (Figure 2). This may be either because the isomers react with the acid at different rates or because the differences in the chemical shifts of the protonated and nonprotonated species are different for various isomers. The sharp signal at −77.5 ppm is attributed to the thermodynamically most stable 1,3-up-2,4-down isomer of tetratriflates (**4a**, Scheme II). This assumption is consistent with the fact that the signals assigned to the corresponding precursor tritriflate (−77.90 and −77.97 ppm), 1,3-up-2-down isomer (**3a**), are also sharp under these conditions. This might indicate that the isomers having a triflate group in the cis position undergo faster exchange than those having the all-trans configuration.

Dearylation and ester group exchange evidently compete, leading to a thermodynamically preferred mixture of isomers. A kinetic isomer distribution should be observed at low $[\mathrm{TfOH}]_0/[\mathrm{silane}]_0$ ratios (<3). The differences in the isomer composition determined by ^{19}F vs ^{1}H NMR may correspond to the different reaction times of the triflation experiments (compare Figure 2a,b with Figure 2c). Long reaction times for $[\mathrm{TfOH}]_0/[(\mathrm{Ph2Si})]_0 = 4$ lead to high yields of all-trans $\mathrm{Me_4Si_4Ph_4}$.

Solvent Effect. The reaction in benzene is much slower than in chlorinated solvents. After 24 h, free acid is still present in the solution. The reaction is also less selective in benzene and in all cases leads to a mixture of di-, tri-, and tetratriflates. This is mainly due to the low dielectric constant of benzene which disfavors polar transition states. Strong protonic acids such as perchloric and triflic acids are more aggregated and less reactive in nonpolar solvents than in $\mathrm{CH_2Cl_2}$.[21]

Conclusions

Although the rate of dearylation of octaphenylcyclotetrasilane in $\mathrm{CH_2Cl_2}$ is relatively fast when up to 3 equiv of TfOH is added, it decreases gradually as the number of triflate groups on the cyclotetrasilane ring increases. Complete substitution of the fourth phenyl group requires ca. 6 h (25 °C, $[(\mathrm{Ph_2Si})_4]_0 = 0.05$ mol/L) and either a slight excess of TfOH (5 mol %) or longer reaction times.

The selectivity of the triflation is relatively low for the monotriflate due to the heterogeneity of the system but increases with the degree of substitution and is ca. 70% for di- and over 90% for tri- and tetratriflate cyclotetrasilanes (based on NMR). Pentatriflate cyclotetrasilane cannot be obtained in high yield because ring cleavage by triflic acid competes with dearylation. The dearylation process in nonpolar solvents such as benzene is slower and less selective than in chlorinated solvents.

Isomerization via exchange of triflate groups is fast compared to substitution of the fourth phenyl group and leads to the thermodynamic ratio of isomers.

A comparison of the fluorine and proton spectra for various $[\mathrm{TfOH}]_0/[(\mathrm{Ph_2Si})_4]_0$ ratios shows that there is no significant change in the relative concentration of triflate and methyl stereoisomers. This indicates a high stereoselectivity in the reaction of silyl triflates with Grignard reagents.

Experimental Section

Techniques. The NMR measurements were performed using an IBM NR-300 spectrometer. The ^{19}F spectra (in $\mathrm{CDCl_3}$) were recorded in $\mathrm{CDCl_3}$ at 282.4 MHz and the chemical shifts are reported relative to $\mathrm{CFCl_3}$ using trifluoroacetic acid (−78.5 ppm) as an external standard. The ^{29}Si spectra (in $\mathrm{CDCl_3}$) were recorded at 59.6 MHz using a standard Bruker INEPT microprogram. The delay values applied were D1 = 3.0 s, D2 = 0.014 s, D3 = 0.007 s. Chemical shifts are reported relative to external TMS.

All synthetic experiments were performed in a nitrogen atmosphere VAC HE-43 drybox. The concentrations of $\mathrm{H_2O}$ and $\mathrm{O_2}$ were below 1 ppm.

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Materials. Dichloromethane (Fisher) was washed with fuming sulfuric acid, water, and aqueous $NaHCO_3$ and then distilled twice from CaH_2 under nitrogen. Benzene (Fisher) was refluxed over and distilled from CaH_2 under nitrogen and stored over sodium/potassium alloy. Triflic acid (3M, Chemistry Division) was distilled under vacuum. Methylmagnesium bromide, 3.0 M in Et_2O (Aldrich) was used as received. Octaphenylcyclotetrasilane was prepared according to a literature procedure.[22]

Synthesis of 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. In a typical experiment 1,2,3,4-tetraphenyl-1,2,3,4-tetrakis(trifluoromethylsulfonoxy)cyclotetrasilane was first prepared by adding triflic acid (43.7 μL, 0.494 mmol) dropwise with a microsyringe to a stirred suspension of $(Ph_2Si)_4$ (~90 mg, 0.123 mmol) in CH_2Cl_2 (2 mL). The reaction mixture became homogeneous. After ^{19}F NMR demonstrated that the reaction was complete (~6 h), CH_2Cl_2 was removed by trap-to-trap distillation. The crude intermediate was dissolved in benzene (2 mL), and a 3.0 M solution of MeMgBr in Et_2O (0.165 mL, 0.494 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and was then filtered through a 0.2-μm filter. The solvent was removed by trap-to-trap distillation to yield 0.053 g (90%) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane.

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Reactions of 2-Furyl, 2-Thienyl, and *N*-Methyl-2-pyrrolyl Mercurials with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ Complexes. Synthesis of $Fe_2(CO)_6$ Complexes with Bridging $\eta^1{:}\eta^2$-Furyl and Thienyl Ligands

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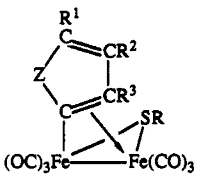
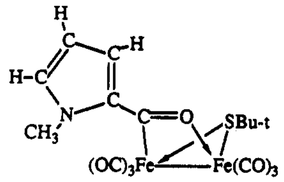
Reactions of furyl- and methyl-substituted furyl-, thienyl-, and methyl-substituted thienyl mercurials with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ gave products of type A



A

Z = O or S

in which the organic ligands are σ-bonded to iron via an α-carbon atom and π-bonded to the other iron atom via a C=C bond. On the other hand, 1-methyl-2-pyrrolyl mercurials reacted with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ to give B.



B

The compound $(\mu\text{-}\sigma,\pi\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-}PhS)Fe_2(CO)_6$ (**10c**) crystallizes in the monoclinic space $P2_1/c$ with $a = 7.805$ (1) Å, $b = 17.091$ (2) Å, $c = 13.344$ (2) Å, $\beta = 96.90$ (1)°, $V = 1767.1$ Å^3, and $Z = 4$. Refinement by full-matrix, least-squares techniques has resulted in residuals of $R = 0.027$ and $R_w = 0.036$, based on 248 parameters refined and 2403 unique observations. The furyl group in the compound bridges the two iron centers, being σ-bound to one metal while π-bonded to the other via the adjacent olefin linkage. The oxygen atom and the other olefin linkage in this group point away from the metals and remain uncomplexed.

Introduction

We have reported recently concerning reactions of vinylic mercuric halides with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes.[1] Two types of products were obtained in such reactions, $(\mu\text{-}\eta^1{:}\eta^2$-vinyl)(μ-alkanethiolato)hexacarbonyldiiron(Fe–Fe) (1) and (μ-α,β-unsaturated acyl)-(μ-alkanethiolato)hexacarbonyldiiron(Fe–Fe) (2) complexes. Scheme I shows their probable method of formation. Which type of product was formed depended on the nature of the substituents on the vinylic carbon atoms. With $CH_2{=}CHHgBr$, $ClCH{=}CHHgCl$, and $PhCH{=}$

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