

The Cationic Rearrangement of (3-Hydroxy-1-propenyl)tris(trimethylsilyl)silanes into (1-Trimethylsilyl-2-propenyl)bis(trimethylsilyl)silanol – Experimental and Theoretical Studies

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(3-Hydroxy-1-propenyl)tris(trimethylsilyl)silanes $(\text{Me}_3\text{Si})_3\text{-SiCH=CHCR}_2\text{OH}$ (**8b,c**) (**b**: R = Me; **c**: R = Ph) undergo a rapid rearrangement involving a 1,2-Si,C migration of one trimethylsilyl group from the central silicon atom to a cationic neighboring carbon atom and a shift of the olefinic double bond, in the presence of acid, to afford (1-trimethylsilyl-2-propenyl)bis(trimethylsilyl)silanol $(\text{Me}_3\text{Si})_2\text{Si(OH)CH-(SiMe}_3\text{)CH=CR}_2$ (**13b,c**). Treatment of **8b,c** with sulfuric acid in methanol gives the methoxysilanes $(\text{Me}_3\text{Si})_2\text{Si(OMe)CH-(SiMe}_3\text{)CH=CR}_2$ (**14b,c**). In a related reaction, **8b,c** are con-

verted by boron trifluoride into the fluorosilanes $(\text{Me}_3\text{Si})_2\text{-SiFCH(SiMe}_3\text{)CH=CR}_2$ (**15b,c**). A possible mechanism of the isomerization reaction, involving the rearrangement of the silylcarbenium ions $[(\text{Me}_3\text{Si})_3\text{SiCH=CHCR}_2]^+$ into the silylium ions $[(\text{Me}_3\text{Si})_2\text{SiCH(SiMe}_3\text{)CH=CR}_2]^+$, is proposed. This is supported by calculations, which indicate the higher stability of the silylium ion **10b** compared with the isomeric silylcarbenium cation **9b**. For **14c** the results of an X-ray structural analysis are given.

Introduction

Recently we found that 1-hydroxyalkyltris(trimethylsilyl)silanes (**1**) undergo a rapid isomerization in the presence of strong acids into 1-trimethylsilylalkylbis(trimethylsilyl)silanol (**6**) (Scheme 1).^[1] The reaction path was interpreted in terms of a cationic rearrangement initiated by an acid-catalyzed elimination of water from the alcohol **1** and formation of the carbenium ion **2**. The subsequent 1,2-Si,C migration of one trimethylsilyl group, and attack of X^- , the conjugate base of the acid used as the catalyst, at the central silicon atom produces the intermediate **5**, which after hydrolytic workup affords the silanol **6**. A decision as to whether the reaction involves a synchronous nucleophilic attack by X^- on the central silicon atom and migration of one trimethylsilyl group from silicon to carbon (**3**) or, alternatively, proceeds through a silylium ion intermediate **4**, could not be made. It is very likely that the isomerization is facilitated by the greater stability of the silylium ion **4** than the carbenium cation **2**, and we consider the crucial step of the conversion **1**→**6** to be the isomerization of the silyl-substituted carbenium ion into the silylium ion by 1,2-migration of one SiMe_3 group from the tetracoordinated

silicon center to the neighboring carbon atom. Some reactions of this type have recently been described,^[2,3] and confirm expectations from theoretical work, according to which α -silyl carbenium ions should generally be less stable than the isomeric silylium ions.^[4]

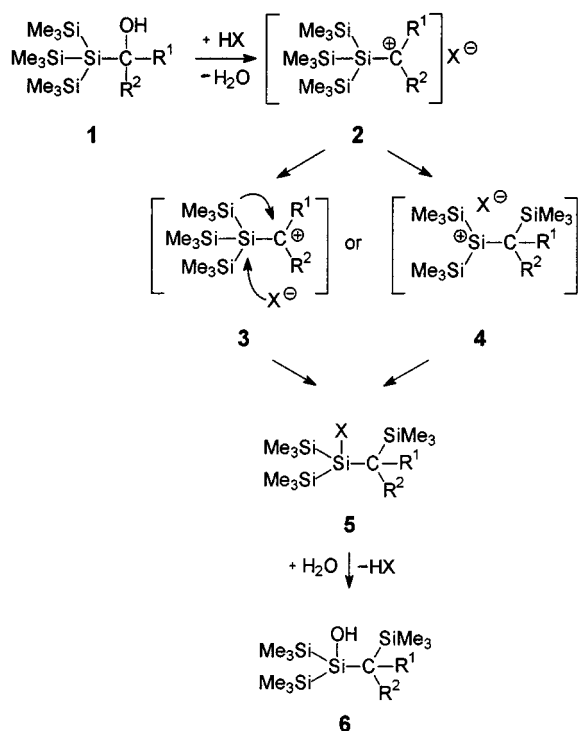
Continuing these studies we extended our experiments to vinylogous derivatives of the alcohols **1**, and in the present paper we report on the related behavior of (3-hydroxy-1-propenyl)tris(trimethylsilyl)silanes **8**, which rearrange in the presence of acid to give the (1-trimethylsilyl-2-propenyl)bis(trimethylsilyl)silanol **13**.

Results and Discussion

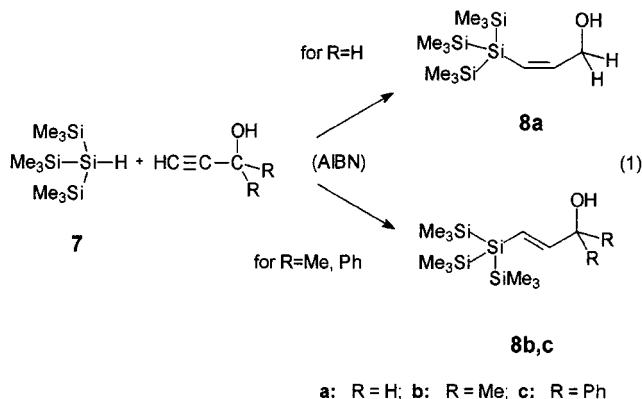
The aim of the studies described in this paper was to examine whether tris(trimethylsilyl)silyl-substituted carbenium ions with a delocalized positive charge also undergo 1,2-Si,C trimethylsilyl migrations as discussed above for the isomerization of **2** into **5**. As model compounds we have chosen tris(trimethylsilyl)silylcarbocations, which were intended to be generated by the acid-induced elimination of water from the respective 3-hydroxy-1-propenylsilanes. For that purpose we prepared the alcohols **8a–c** by addition of tris(trimethylsilyl)silane (**7**) across the triple bonds of propargylic alcohol, 2-methyl-3-butyn-2-ol and 1,1-diphenyl-2-propyn-1-ol (Scheme 2). This method, and its application to the synthesis of **8a**, has already been described,^[5] and proved to be suitable also for the reaction of **7** with the above-mentioned propynols.

‡ Theoretical calculations

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Scheme 1. The acid-induced rearrangement of 1-hydroxyalkyltris(trimethylsilyl)silanes **1** into bis(trimethylsilyl)-1-trimethylsilylalkylsilanols **6**



Scheme 2

In agreement with the literature data, the addition of **7** to the triple bond of propargylic alcohol led to the *Z*-olefin **8a**.^[5] In contrast, the coupling constants of the olefinic protons in **8b** and **8c** unambiguously revealed an *E*-configuration for both olefins. This difference is due to the different space filling properties of the C(OH)R₂ substituents (R = Me, Ph) in **8b,c**.

The Acid-Induced Isomerization of the (3-Hydroxy-1-propenyl)tris(trimethylsilyl)silanes into (1-Trimethylsilyl-2-propenyl)bis(trimethylsilyl)silanols

The alcohols **8a–c**, dissolved in ether, were treated with hydrochloric acid or, alternatively, pentane solutions of **8a–c** were stirred with a few drops of sulfuric acid at room temperature. In all experiments with **8a** the alcohol was al-

ways recovered unchanged. Under the same conditions, however, **8b** and **8c** underwent rapid rearrangements and after aqueous workup of the reaction mixtures we obtained the silanols **13b** and **13c**, respectively. Sulfuric acid proved to be most effective for the acid-catalyzed isomerization of 1-hydroxyalkyl-tris(trimethylsilyl)silanes (**1**).^[1] Therefore — and also because of the convenient experimental procedure — we used only this catalyst in all the studies described below.

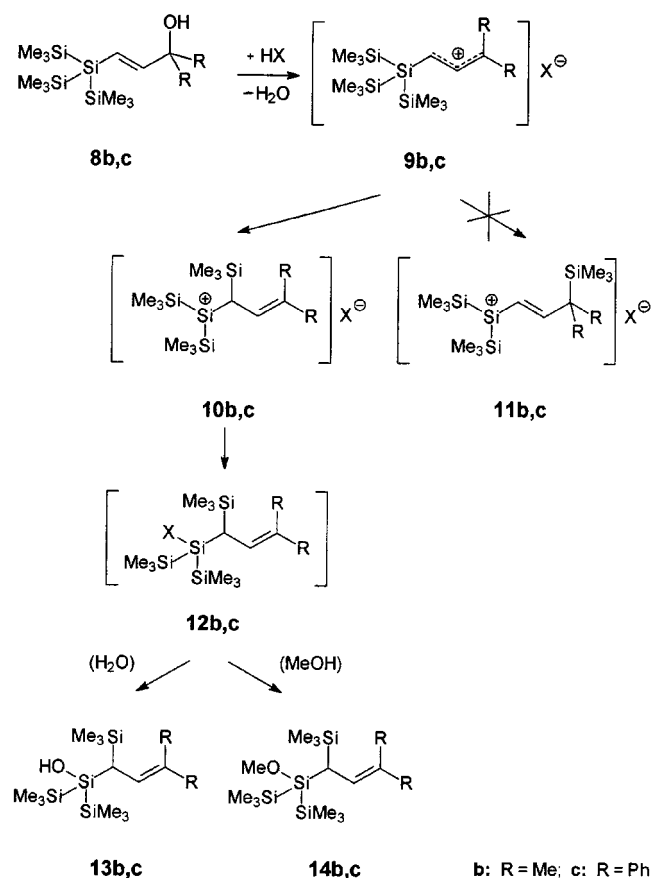
The suggested mechanism of the reaction is outlined in Scheme 3. Protonation of **8b,c** and elimination of water leads to the carbenium ions **9b,c**. (3-Hydroxy-1-propenyl)-tris(trimethylsilyl)silane (**8a**) is reluctant to undergo the rearrangement. Obviously, elimination of water from the primary alcohol failed under our conditions and therefore no reaction occurs. Despite delocalization of the positive charge in **9b,c**, which is expected to enhance the stability of the carbocations, one trimethylsilyl group migrates from the central silicon atom to the adjacent carbon atom generating the transient silylium ions **10b,c**. As already mentioned, Apeloig et al. found that α -silyl-substituted carbenium ions are generally less stable than the isomeric silylium ions.^[3,4] This is confirmed by ab initio calculations, described below, which indicate a significantly higher stability of the silylium ion **10b** than the carbenium ion **9b**; this energy difference is supposed to be the driving force of the rearrangement **9b,c** → **10b,c**. Addition of X⁻ to the silylium silicon atoms results in formation of the silanes **12b,c**, which during the aqueous workup hydrolyse to give the silanols **13b,c**. Of course, a synchronous process involving an attack of X⁻ at the central silicon atom of **9b,c** and a simultaneous shift of one Me₃Si group to the α -carbon atom of the alkyl substituent affording **12b,c** cannot be excluded.

For the reaction of **8c** with ethereal HCl the intermediate chlorosilane **12c** (R = Cl) was isolated; this compound can easily be converted into the silanol **13c** by addition of water. Attempts to isolate the silyl sulfates **12b,c** (R = OSO₃H) after reaction of **8b,c** with sulfuric acid failed. Due to rapid hydrolysis, the products obtained always contained considerable amounts of the silanols **13b,c**. When the isomerization of **8b,c** was carried out with sulfuric acid in methanol, solvolysis of the silylsulfates **12b,c** (X = OSO₃H) afforded the methoxysilanes **14b,c** (Scheme 3).

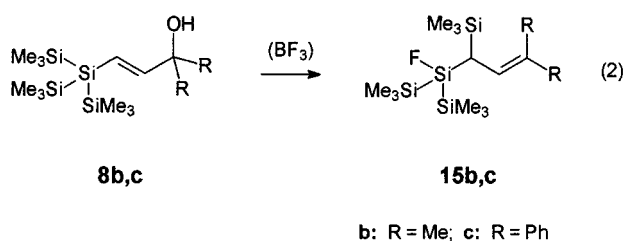
Of course, a 1,4-migration of one trimethylsilyl group of **9b,c** producing the silylium ions **11b,c** may be possible (Scheme 3), although products originating from conversions of **11b,c** were not observed. This is in agreement with the results of the calculations described below.

According to a related mechanism, treatment of **8b,c** with boron trifluoride produced the fluorosilanes **15b,c** (Scheme 4).

The structures of **8b,c** and **13b,c–15b,c** were elucidated by a full spectral analysis (¹H, ¹³C and ²⁹Si NMR spectroscopy, IR spectroscopy, MS and elemental analysis). For the methoxysilane **14c** an X-ray structural analysis was performed, which confirmed the compound as a crowded silane (Figure 1). Thus, the Si1–C1 bond in **14c** is slightly elongated (1.906 Å) and the angle C1–Si1–Si3 (112.53 °)



Scheme 3. The acid-induced conversion of the 3-hydroxy-1-propenyltris(trimethylsilyl)silanes **8b,c** into the silanols **13b,c** or the methoxysilanes **14b,c**



Scheme 4

is widened. The other bond lengths and angles are in the expected range.

The reaction sequence **8**→**10** can be considered to be possibly a useful method for the generation of sterically congested silylium ions just by operating in the unprotected periphery of the molecule.

Theoretical Studies

Since there is no direct experimental evidence that the rearrangement of **8b,c** → **13b,c** proceeds through the intermediates **9b,c** and **10b,c**, we have used ab initio calculations to predict the relative stabilities of the carbenium ion **9b** and the isomeric silylium ion **10b**. To estimate the probab-

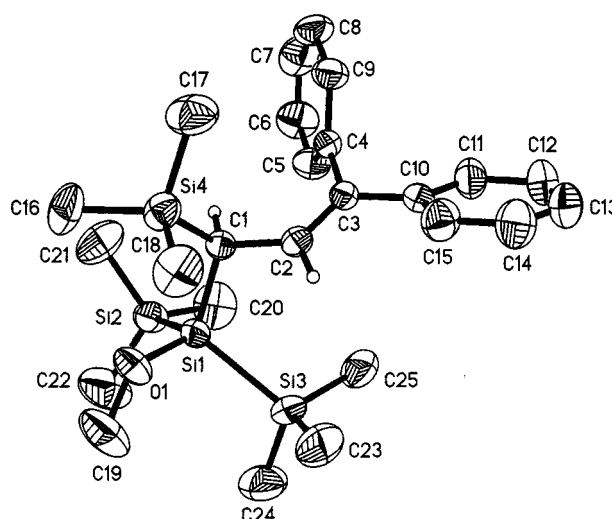


Figure 1. Molecular structure of **14c** in the crystal (H atoms omitted, except C1H and C2H, ORTEP plot with 30% probability of the thermal ellipsoids); selected bond lengths [Å] and angles [°]: Si1–C1 1.906(4), Si1–Si2 2.3621(19), Si1–Si3 2.3630(18), Si1–O1 1.645(4), C1–Si4 1.898(4), C1–C2 1.496(5), C2–C3 1.338(5); Si2–Si1–Si3 111.27(7), Si1–C1–Si4 114.60(19), Si1–O1–C19 131.6(5), Si3–Si1–C1 112.53(13), Si2–Si1–C1 109.54(13), O1–Si1–C1 105.74(19)

ity of a 1,4-trimethylsilyl migration in **9b**, we also included the silylium ion **11b** in these studies (Scheme 3). The calculations were performed for isolated species using the Gaussian 98 program package.^[6] The following procedure was applied. First, we made a geometry optimization of **9b**, **10b** and **11b** at the HF/6-31G(d) level. Based on these geometric structures single point energy calculations were performed at the HF/6-31G(d) and MP2/6-31G(d) levels. Secondly, geometry optimizations with single point energy calculations were performed at the HF/6-31++G(d,p) level.^[7] The values of the absolute energies obtained by these procedures are shown in Table 1. Table 2 shows the energy differences in kcal/mol. The differences of the absolute energies obtained at the different levels indicate a stabilization of **10b** of between 9.9 and 22.7 kcal·mol^{−1} compared with **9b** depending on the method indicated in Table 2. The values obtained are close to the stabilization energies of other silylium ions over their isomeric α-silyl-substituted carbenium ions reported by Apeloig.^[4] The other possible intermediate **11b** is energetically disfavoured by between 3.6

Table 1. Sum of electronic energies and nuclear repulsion energies E [Hartrees]^[a] of isomers **9b**, **10b** and **11b**, without corrections due to zero-point energies, thermal energies and solute-solvent interactions

Method	E(9b)	E(10b)	E(11b)
HF/6-31G(d)	−1706.05509	−1706.07197	−1706.06543
MP2/6-31G(d) ^[b]	−1708.20490	−1708.24102	−1708.22252
HF/6-31++G(d,p)	−1706.12505	−1706.14087	−1706.13510

^[a] 1 Hartree = 627.5095 kcal·mol^{−1}. ^[b] Single point energy calculation based on an HF/6-31G(d) geometry optimization.

kcal·mol⁻¹ [HF/6-31++G(d,p)] and 11.6 kcal·mol⁻¹ [MP2/6-31G(d)] compared with **10b**. These results clearly indicate a higher stability of **10b** compared with **9b** and **11b**, supporting the reaction mechanism suggested in Scheme 3.

Table 2. Differences in the total energies [kcal·mol⁻¹] of the three isomeric cations **9b**, **10b** and **11b**

Method	E(9b) – E(10b)	E(11b) – E(10b)
HF/6-31G(d)	10.6	4.1
MP2/6-31G(d) ^[a]	22.7	11.6
HF/6-31++G(d,p)	9.9	3.6

^[a] Single point energy calculation based on a HF/6-31G(d) geometry optimization.

Experimental Section

General: All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402. (Me₃Si)₃SiH (**7**) was prepared using the method described by Marschner;^[8] **8a** was synthesized following the procedure given by Utimoto,^[5] but the reaction was induced by AIBN instead of triethylborane. Due to the formation of SiC, the results of the elemental analyses of some compounds were unsatisfactory. In these cases HRMS data are given.

(3-Hydroxy-3-methyl-1-butenyl)tris(trimethylsilyl)silane (8b): 2-Methyl-3-buten-2-ol (1.2 g, 14.0 mmol) and AIBN (0.2 g) were gradually added at room temperature to a solution of **7** (3.0 g, 12.1 mmol) in toluene (30 mL). The mixture was heated under reflux for 5 h, and then water was added and the organic phase separated, dried and the solvents evaporated. The residue was purified by kugelrohr distillation at 75–100 °C/7·10⁻³ mbar to afford 3.0 g (74.7%) of **8b**. Colorless crystals, m.p. 58–63 °C. IR (nujol): $\tilde{\nu}$ = 3407 cm⁻¹ (OH). ¹H NMR ([D₆]benzene): δ = 0.27 (s, 27 H, SiCH₃), 0.98 (s, 1 H, OH), 1.15 (s, 6 H, CCH₃), 5.92 (d, ³J = 18.6 Hz, 1 H, CH), 6.29 (d, ³J = 18.6 Hz, 1 H, CH). ¹³C NMR ([D₆]benzene): δ = 0.9 (SiCH₃), 29.7 (CCH₃), 71.9 (COH), 115.4 and 156.9 (olef. C). ²⁹Si NMR ([D₆]benzene): δ = –85.5 (SiSiMe₃), –13.1 (SiMe₃). MS (70 eV): *m/z* (%) = 317 (3) [M – CH₃]⁺, 315 (3) [M – OH]⁺, 259 (12) [M – SiMe₃]⁺, 73 (100) [SiMe₃]⁺. C₁₄H₃₆OSi₄ (332.8): calcd. C 50.53, H 10.90; found C 50.79, H 10.85.

(3-Hydroxy-3,3-diphenyl-1-propenyl)tris(trimethylsilyl)silane (8c): Following the procedure given for **8b**, 3.0 g (12.1 mmol) of **7**, 2.50 g (12.1 mmol) of 1,1-diphenyl-2-propyn-1-ol and 0.2 g of AIBN gave 2.7 g (49%) of **8c** after kugelrohr distillation (200 °C/3·10⁻² mbar). Colorless oil. IR (cap.): $\tilde{\nu}$ = 3462 cm⁻¹ (OH_{ass.}), 3556 and 3601 cm⁻¹ (OH_{free}). ¹H NMR ([D₆]benzene): δ = 0.23 (s, 27 H, SiCH₃), 1.84 (s, 1 H, OH), 6.12 (d, ³J = 18.6 Hz, 1 H, CH), 6.82 (d, ³J = 18.6 Hz, 1 H, CH), 7.03–7.49 (m, arom. 10 H, CH). ¹³C NMR ([D₆]benzene): δ = 1.0 (SiCH₃), 81.0 (COH), 119.6 and 153.3 (olef. C), 127.3, 127.5 and 128.3 (arom. CH), 146.8 (arom. C). ²⁹Si NMR ([D₆]benzene): δ = –85.0 (SiSiMe₃), –12.8 (SiMe₃). MS (70 eV): *m/z* (%) = 456 (2) [M]⁺, 441 (2) [M – CH₃]⁺, 439 (2) [M – OH]⁺, 383 (7) [M – SiMe₃]⁺, 73 (100) [SiMe₃]⁺. C₂₄H₄₀OSi₄ (456.9): calcd. C 63.09, H 8.82; found C 63.47, H 8.86.

Chloro(3,3-diphenyl-2-propenyl-1-trimethylsilyl)bis(trimethylsilyl)silane (12c): Compound **8c** (0.5 g, 1.1 mmol) was dissolved in

30 mL of ether containing excess hydrogen chloride, and the solution was stirred at room temperature for 8 h. After addition of solid NaHCO₃ and filtration, the solution was evaporated. Chromatographic separation of the residue (silica gel, heptane/ethyl acetate 20:1) gave 0.14 g (26%) of the chlorosilane **12c** and 0.15 g (30%) of the silanol **13c**.

12c: Colorless oil. ¹H NMR ([D₆]benzene): δ = 0.18, 0.22 and 0.27 (3s, 3 × 9 H, SiCH₃), 2.51 (d, ³J = 13.4 Hz, 1 H, SiCH), 6.43 (d, ³J = 13.4 Hz, 1 H, olef. CH), 6.98–7.48 (m, arom. 10 H, CH). ¹³C NMR ([D₆]benzene): δ = –0.9, –0.6 and 0.3 (SiCH₃), 22.8 (CH), 126.9, 127.1, 127.2, 127.4, 128.6, 128.7, 130.7, 139.4, 140.3 and 143.5 (arom. and olef. C). ²⁹Si NMR ([D₆]benzene): δ = –14.3 and –13.7 (SiSiMe₃), 3.3 (CSiMe₃), 9.6 (SiCl). MS (70 eV): *m/z* (%) = 474 (5) [M]⁺, 459 (4) [M – CH₃]⁺, 439 (1) [M – Cl]⁺, 401 (2) [M – SiMe₃]⁺, 73 (100) [SiMe₃]⁺. C₂₄H₃₉ClSi₄ (475.4): calcd. C 60.64, H 8.27, Cl 7.46; found C 61.18, H 8.24, Cl 8.07. HRMS: calcd. 474.18173; found 474.18510.

(3-Methyl-1-trimethylsilyl-2-butenyl)bis(trimethylsilyl)silanol (13b): Concentrated sulfuric acid (0.15 g, 1.5 mmol) was added gradually to a solution of **8b** (0.5 g, 1.5 mmol) in pentane (30 mL) and the mixture was stirred at room temperature for 8 h. After neutralization with aqueous NaHCO₃ solution, washing with water and drying, the solvent was removed in vacuo and the residue purified by column chromatography (silica gel, heptane/ethyl acetate 20:1) to give 0.09 g (18%) of **13b**. Colorless oil. IR (nujol): $\tilde{\nu}$ = 3454 cm⁻¹ (SiOH_{ass.}), 3649 cm⁻¹ and 3677 cm⁻¹ (SiOH_{free}). ¹H NMR ([D₆]benzene): δ = 0.19 (s, 18 H, SiSiCH₃), 0.24 (s, 9 H, SCSiCH₃), 0.52 (s, 1 H, OH), 1.54 and 1.70 (2d, ⁴J = 1.2 Hz, 2 × 3 H, CCH₃), 1.97 (d, ³J = 12.8 Hz, 1 H, SiCH), 5.24 (dpseudoquart, ³J = 12.8, ⁴J = 1.2 Hz, 1 H, olef. CH). ¹³C NMR ([D₆]benzene): δ = –1.1, –0.3 and –0.1 (SiCH₃), 17.9 and 26.0 (CCH₃), 22.8 (CH), 121.6 and 127.8 (olef. C). ²⁹Si NMR ([D₆]benzene): δ = –19.4 and –19.6 (SiSiMe₃), 2.0 (CSiMe₃), 8.4 (SiSiMe₃). MS (70 eV): *m/z* (%) = 332 (2) [M]⁺, 317 (4) [M – CH₃]⁺, 259 (19) [M – SiMe₃]⁺, 73 (100) [SiMe₃]⁺. HRMS: calcd. 332.18433; found 332.18365.

(3,3-Diphenyl-1-trimethylsilyl-2-propenyl)bis(trimethylsilyl)silanol (13c): Following the procedure described above but using ether instead of pentane as the solvent, 0.5 g (1.1 mmol) of **8c** and 0.3 g (0.3 mmol) of sulfuric acid afforded 0.22 g (45%) of **13c**. Colorless crystals from heptane/ethyl acetate, m.p. 96–98 °C. IR (nujol): $\tilde{\nu}$ = 3463 cm⁻¹ (SiOH_{ass.}), 3646 and 3677 cm⁻¹ (SiOH_{free}). ¹H NMR ([D₆]benzene): δ = 0.12, 0.21 and 0.23 (3s, 3 × 9 H, SiCH₃), 0.57 (s, 1 H, OH), 2.47 (d, ³J = 13.4 Hz, 1 H, CH), 6.52 (d, ³J = 13.4 Hz, 1 H, CH), 6.98–7.41 (m, arom. 10 H, CH). ¹³C NMR ([D₆]acetone): δ = –1.0, –0.5 and 0.0 (SiCH₃), 25.8 (CH), 126.5, 127.0, 127.2, 128.6, 128.8, 129.7, 130.9, 137.2, 140.8 and 144.0 (arom. and olef. C). ²⁹Si NMR ([D₆]benzene): δ = –19.1 and –18.8 (SiSiMe₃), 2.1 (CSiMe₃), 8.8 (SiSiMe₃). MS (70 eV): *m/z* (%) = 456 (2) [M]⁺, 441 (5) [M – CH₃]⁺, 338 (20) [M – SiMe₃]⁺, 73 (100) [SiMe₃]⁺. C₂₄H₄₀OSi₄ (456.9): calcd. C 63.09, H 8.82; found C 62.92, H 8.88.

Methoxy(3-methyl-1-trimethylsilyl-2-butenyl)bis(trimethylsilyl)silane (14b): Compound **8b** (0.5 g, 1.5 mmol) and sulfuric acid (0.4 g, 3.6 mmol) were dissolved in 30 mL of methanol. The solution was stirred at room temperature for 8 h, neutralized with solid NaHCO₃ and washed with cold water. The product was extracted with ether, the solution evaporated and the residue purified by chromatography (silica gel, heptane/ethyl acetate 20:1) to afford 0.21 g (40%) of **14b**. Colorless crystals, m.p. 54–58 °C. IR (nujol): $\tilde{\nu}$ = 1087 cm⁻¹ (SiOC). ¹H NMR ([D₆]benzene): δ = 0.22, 0.24 and 0.29 (3s, 3 × 9 H, SiCH₃), 1.56 and 1.70 (2d, ⁴J = 1.2 Hz, 2 × 3 H, CCH₃), 2.01 (d, ³J = 12.8 Hz, 1 H, SiCH), 3.31 (s, 3 H, OCH₃), 5.25 (dpseudoquart, ³J = 12.8, ⁴J = 1.2 Hz, 1 H, olef.

CH). ^{13}C NMR ($[\text{D}_6]\text{benzene}$): $\delta = -0.2, -0.1$ and 0.6 (SiCH_3), 17.9 and 26.0 (CCH_3), 21.3 (CH), 53.6 (OCH_3), 121.7 and 127.7 (olef. C). ^{29}Si NMR ($[\text{D}_6]\text{benzene}$): $\delta = -19.6$ and -19.8 (SiSiMe_3), 2.4 (CSiMe_3), 12.2 (SiOMe). MS (70 eV): m/z (%) = 346 (2) $[\text{M}]^+$, 331 (7) $[\text{M} - \text{CH}_3]^+$, 273 (15) $[\text{M} - \text{SiMe}_3]^+$, 73 (100) $[\text{SiMe}_3]^+$. $\text{C}_{15}\text{H}_{38}\text{OSi}_4$ (346.8): calcd. C 51.95, H 11.04; found C 51.82, H 10.89. HRMS: calcd. 346.19998; found 346.19792.

Methoxy(3,3-diphenyl-1-trimethylsilyl-2-propenyl)bis(trimethylsilyl)silane (14c): As described for **14b**, 0.5 g (1.1 mmol) of **8c** gave 0.4 g (78%) of **14c** after treatment with H_2SO_4 in methanol. The purification was performed by chromatography (silica gel, heptane); single crystals were obtained by recrystallization from heptane, m.p. $83-87^\circ\text{C}$. IR (nujol): $\tilde{\nu} = 1090\text{ cm}^{-1}$ (SiOC). ^1H NMR ($[\text{D}_6]\text{benzene}$): $\delta = 0.17, 0.24$ and 0.29 (3s, 3×9 H, SiCH_3), 2.52 (d, $^3J = 13.4$ Hz, 1 H, SiCH), 3.28 (s, OCH_3 , 1 H), 6.54 (d, $^3J = 13.4$ Hz, 1 H, olef. CH), $7.01-7.42$ (m, 10 H, arom. CH). ^{13}C NMR ($[\text{D}_6]\text{benzene}$): $\delta = 0.1, 0.2$ and 0.7 (SiCH_3), 24.9 (CH), 53.6 (OCH_3), $126.6, 127.0, 127.2, 128.5, 128.6, 128.9, 130.9, 137.9, 140.6$ and 144.0 (arom. and olef. C). ^{29}Si NMR ($[\text{D}_6]\text{benzene}$): $\delta = -19.26$ and -19.31 (SiSiMe_3), 2.7 (CSiMe_3), 13.2 (SiOMe). MS (70 eV): m/z (%) = 470 (2) $[\text{M}]^+$, 450 (10) $[\text{M} - \text{CH}_3]^+$, 397 (15) $[\text{M} - \text{SiMe}_3]^+$, 73 (100) $[\text{SiMe}_3]^+$. $\text{C}_{25}\text{H}_{42}\text{OSi}_4$ (471.0): calcd. C 63.76, H 8.99; found C 63.75, H 8.78.

Fluoro(3-methyl-1-trimethylsilyl-2-butenyl)bis(trimethylsilyl)silane (15b): Boron trifluoride diethyl ether complex (0.22 g, 1.6 mmol) was added gradually at -78°C to a solution of **8b** (0.50 g, 1.5 mmol) in diethyl ether (30 mL) and the mixture was stirred for 2 h. After warming to room temperature stirring was continued for 4 h, water was added and the organic phase was separated, dried and the solvents evaporated. Column chromatography (silica gel, heptane) of the residue gave 0.40 g (79.5%) of **15b**. Colorless oil. IR (nujol): $\tilde{\nu} = 1011\text{ cm}^{-1}$ (SiF). ^1H NMR ($[\text{D}_6]\text{benzene}$): $\delta = 0.21$ (s, 18 H, SiSiMe_3), 0.25 (s, 9 H, CSiMe_3), 1.51 and 1.67 (2d, $^4J = 1.53$ Hz, 2×3 H, CCH_3), 2.18 (dd, $^3J = 5.8$, $^3J = 12.8$ Hz, 1 H, CH), 5.27 (dpseudoquart, $^3J = 12.8$, $^4J = 1.53$ Hz, olef. CH, 1 H). ^{13}C NMR ($[\text{D}_6]\text{benzene}$): $\delta = -1.5, -0.6$ and -0.5 (SiCH_3), 17.8 and 25.9 (CCH_3), 22.9 (d, $^2J = 15.0$ Hz, SiCH), 120.3 (d, $^3J = 4.7$ Hz, olef. CH), 128.3 (olef. C). ^{29}Si NMR ($[\text{D}_6]\text{benzene}$): $\delta = -19.0$ and -19.4 (SiSiMe_3), 2.6 (CSiMe_3), 33.5 (d, $^1J = 334$ Hz, SiF). ^{19}F NMR ($[\text{D}_6]\text{benzene}$): $\delta = -198.1$ (SiF). MS (70 eV): m/z (%) = 335 (5) $[\text{M} + \text{H}]^+$, 319 (5) $[\text{M} - \text{CH}_3]^+$, 261 (15) $[\text{M} - \text{SiMe}_3]^+$, 73 (100) $[\text{SiMe}_3]^+$. Due to the ease of fragmentation an HRMS could not be obtained.

Fluoro(3,3-diphenyl-1-trimethylsilyl-2-propenyl)bis(trimethylsilyl)silane (15c): As described above, treatment of 0.50 g (1.1 mmol) of **8c** with 0.16 g (1.1 mmol) of boron trifluoride diethyl ether complex in ether (30 mL) afforded 0.22 g (43%) of colorless crystals, m.p. $76-79^\circ\text{C}$. IR (nujol): $\tilde{\nu} = 1021\text{ cm}^{-1}$ (SiF). ^1H NMR ($[\text{D}_6]\text{benzene}$): $\delta = 0.13, 0.23$ and 0.27 (3s, 3×9 H, SiCH_3), 2.57 (dd, $^3J = 8.8$, $^3J = 13.4$ Hz, 1 H, SiCH), 6.57 (d, $^3J = 13.4$ Hz, 1 H, olef. CH), $7.01-7.39$ (m, 10 H, arom. CH). ^{13}C NMR ($[\text{D}_6]\text{benzene}$): $\delta = -1.3, -0.7$ and -0.3 (SiCH_3), 26.2 (d, $^2J = 15.9$ Hz, CH), $126.8, 126.9, 127.2, 128.3, 128.7, 130.6, 138.8, 140.6, 143.3$ and 148.7 (arom. and olef. C). ^{29}Si NMR ($[\text{D}_6]\text{benzene}$): $\delta = -18.6$ (SiSiMe_3), 3.0 (CSiMe_3), 34.7 (d, $^1J = 334$ Hz, SiF). ^{19}F NMR ($[\text{D}_6]\text{benzene}$): $\delta = -197.5$ (SiF). MS (70 eV): m/z (%) = 458 (5) $[\text{M}]^+$, 443 (2) $[\text{M} - \text{CH}_3]^+$, 385 (2) $[\text{M} - \text{SiMe}_3]^+$, 73 (100) $[\text{SiMe}_3]^+$. $\text{C}_{24}\text{H}_{39}\text{FSi}_4$ (458.9): calcd. C 62.81, H 8.57; found C 62.82, H 8.50.

X-ray Structure Determination of 14c: X-ray diffraction data were collected with a Bruker P4 four-circle diffractometer, Mo- $K\alpha$ radiation, graphite monochromator, crystal size $0.48 \times 0.44 \times 0.41$ mm 3 , $T = 293(2)\text{K}$, $\text{C}_{25}\text{H}_{42}\text{OSi}_4$, $M = 470.95$, colorless prism, monoclinic, $a = 9.205(2)$, $b = 12.684(7)$, $c = 13.226(4)$ Å, $\beta = 94.78(3)^\circ$, $V = 1538.8(10)$ Å 3 , $Z = 2$, space group Pn , $\rho_{\text{ber}} = 1.016$ Mg m $^{-3}$, $\mu = 0.206$ mm $^{-1}$, $F(000) = 512$, data collection range: $4.46 \leq 2\theta \leq 44.00$, $-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$, 4054 reflections collected, 3776 independent and 3156 observed [$I > 2\sigma(I)$], $R_1 = 0.0452$ (obs.), $wR_2 = 0.1073$ (obs.), $\text{GOF}(F^2) = 1.033$; max./min. residual electron density: $+0.122/-0.105$ eÅ $^{-3}$. The weighting scheme was calculated according to $w^{-1} = \sigma^2(F_0^2) + (0.0485P)^2 + 0.000P$ with $P = (F_0^2 + 2F_c^2)/3$. The structure was solved by direct methods (Bruker SHELXTL). All non-hydrogen atoms were refined anisotropically, with the hydrogen atoms introduced into theoretical positions and refined using a riding model.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156379. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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