# Selective Formation of Functionalized Disiloxanes from Terphenylfluorosilanes

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The reactivity of the sterically hindered organofluorosilane 2,6-$Mes_2C_6H_3$-$SiF_3$ (**1**) (Mes = 2,4,6-trimethylphenyl) under hydrolytic conditions differs substantially from that of the corresponding organo chlorosilane. During the hydrolysis of **1** the combination of thermodynamic (increased Si−F bond strengths compared to Si−Cl) and kinetic aspects (steric hindrance) favors condensation of intermediately formed silanol over the hydrolysis to give a silanetriol. In the course of the reaction no evidence for a silanetriol could be found, while the corresponding difluorosilanol seems to be a key intermediate. The condensation of this difluorosilanol leads to a tetrafluorodisiloxane, which can be isolated. Further displacement of the remaining fluorine atoms in this siloxane is possible with organolithium reagents or base. In the latter case the deprotonated disiloxanetetrol is formed, which due to its fourfold silanol functionality is a suitable precursor for metallasiloxanes. The deprotonated disiloxanetetrol forms a dimeric structure in the solid state, which is stabilized by hydrogen bonding and potassium aryl interactions

## Introduction

Oligomeric and polymeric organosiloxanes as well as sophisticated cage compounds such as silasesquioxanes lead the way between industrial application and modern research.[1−5] Usually, they are generated starting from chloro- or alkoxysilanes under hydrolytic conditions, which involves silanols as labile intermediates.[6] To obtain a specific siloxane selectively, it is crucial to control the competition between silanol formation and silanol condensation.[7] The presence of a sterically demanding substituent can successfully slow the condensation reaction which allowed the synthesis of stable silanols, silanediols, and silanetriols.[8−12] By controlled condensation of such monomeric silanediols or triols the fascinating class of metallasiloxanes is accessible.[13−15] The primary condensation products of di- or trifunctional silanols such as disiloxane 1,3-diols or disiloxane 1,3-tetrols[16] are functionalized siloxanes themselves and recently have been identified as valuable synthons for various metal and nonmetal siloxane derivatives.[17]

Considerably less is known about organofluorosilanes as precursors for silanols and siloxanes.[18,19] Due to the higher dissociation energy of the Si−F bond compared to Si−Cl, in the hydrolysis of fluorosilanes condensation should be more favored than hydrolysis. Here we report our investigations of the hydrolytic behavior of a sterically hindered trifluorosilane, which show that the siloxane formation does not involve an intermediate silanetriol, as in the case of chlorosilanes. In contrast, an organo difluoro silanol seems to be a likely intermediate, whose dimer could be isolated and identified. Moreover, the reactivity of this primary condensation product has been explored, which gives access to the selective formation of a disiloxane-1,3-tetrol in its singly deprotonated form.

## Results and Discussion

Earlier we noticed the unprecedented hydrolytic stability of 2,6-$Mes_2C_6H_3$-$SiF_3$ (**1**).[20] The compound can

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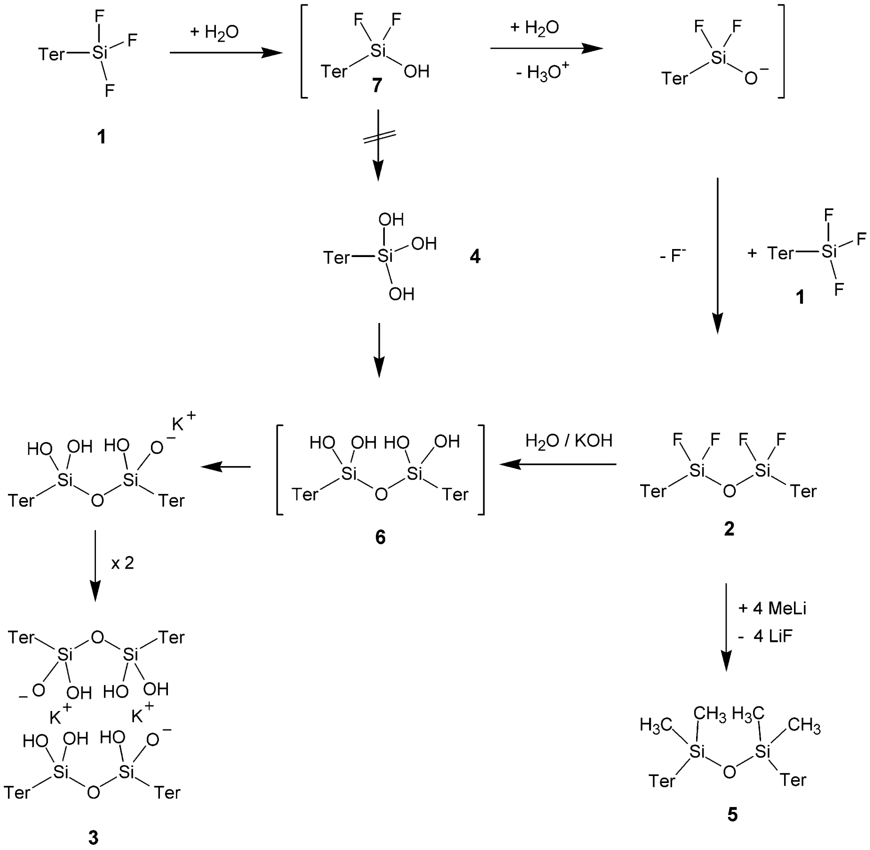
**Scheme 1. Hydrolysis of 1 under Neutral and Basic Conditions (Ter = 2,6-$Mes_2C_6H_3$)**



be stored in air for years without signs of decomposition or hydrolysis. In contrast the analogous chlorosilane 2,6-$Mes_2C_6H_3$-$SiCl_3$ is known to hydrolyze as expected.[21] Consequently, simply the size of the ligand cannot be the reason for the unusual hydrolytic stability of **1**. To understand this peculiar behavior, we investigated the displacement of the fluorine atoms by hydroxyl groups in **1** in more detail.

In contrast to the solid state—where no reaction occurs—in solution **1** very slowly reacts with water. From mixtures of THF or acetone solutions of **1** and water after very long reaction times (weeks) tiny amounts of a single product can be isolated, whereas the rest of the trifluorosilane can be recovered unchanged. The only product is the corresponding tetrafluorodisiloxane (**2**), which can be identified spectroscopically. In the $^{29}$Si NMR spectra it shows a signal at −75.5 ppm with a characteristic triplet splitting due to the coupling with the adjacent fluorine atoms ($^1J_{SiF}$ = 263 Hz). The corresponding signal in the $^{19}$F NMR spectra appears at −128.4 ppm. Under more basic conditions all fluorine atoms at the silyl group can be displaced by hydroxyl groups. To achieve this, either **2** or trifluorosilane **1** has to be treated with an excess of KOH in THF solution. From this reaction a singly deprotonated terphenyl-substituted disiloxane-1,3-tetrol (**3**) is formed selectively. Despite the presence of three labile silanol groups in this product, no further polycondensation is observed. However, this cannot be a consequence of the steric situation, since linear polymeric arrangements involving 2,6-dimesitylphenylsilanes are known from the literature.[22] Disiloxane-1,3-tetrol **3** shows a singlet at −58.8 ppm in the $^{29}$Si NMR spectra, which proves that all fluorine atoms have been displaced.

In addition to spectroscopic evidence for its formation, we have been able to obtain the crystal structure of **3**. In the solid state two disiloxane units form an adduct that is bridged by the alkali metal cations. As in the case of the related polymeric tetrafluorosilicate [2,6-$Mes_2C_6H_3$-$SiF_4K]_n$ ,[22] the interaction of the potassium cation with the aromatic $\pi$-systems of the terphenyl ligand seems to significantly stabilize aggregation, in this case to form a dimeric structure (Figure 1). The relevant potassium carbon distances are generally 3.19−3.22 Å shorter than the ones found in the related $K^+$ benzene complex (3.37 Å).[23] Moreover, hydrogen bonds formed by half of the silonol units contribute to the stability of the inorganic core unit. The O−H distances of the silanol units that are involved in hydrogen bonding are significantly longer (1.201(9)−1.224(17) Å) than the ones that show no such interaction (0.805(5)−0.898(7) Å).

The silicon atoms in the structure of **3** deviate only slightly from the tetrahedral geometry with bond angles of C1−Si1−O1 (112.24(18)°), C1−Si1−O2 (112.81(19)°), O1−Si1−O2 (107.95(17)°), O5−Si2−C24 (105.11(18)°), C24−Si2−O4 (112.38(19)°), C24−Si2−O3 (112.18(19)°), O3−Si2−O4 (107.87(17)°), O4−Si2−O5 (107.45(18)°), and O5−Si2−O3 (111.79(16)°). The central Si1#1−O5−

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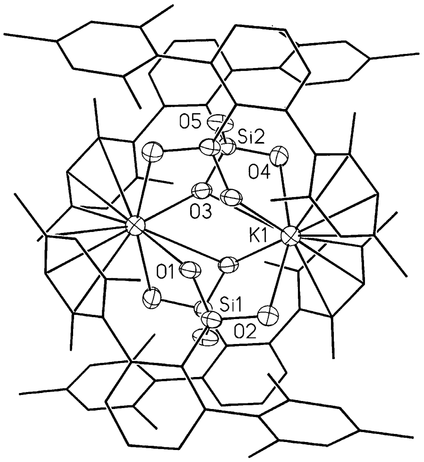

**Figure 1.** X-ray crystal structure of **3** with schematic terphenyl substituents and hydrogen atoms omitted. Thermal ellipsoids are shown at the 50% probability level.

Si2 angle within the disiloxane unit is 129.82(17)°. The Si−O (1.571−1.656(4) Å) and Si−C (1.893−1.894(4) Å) bond distances compare to Si−O (1.600−1.626 Å) and Si−C (1.840 Å) bond distances reported for the single known crystal structure of a tetrahydroxodisiloxane.[24] The crystal structure of **3** is the first example of a singly deprotonated tetrahydroxodisiloxane.

As already mentioned, an excess of KOH is necessary to completely convert trifluorosilane **1** into disiloxane **3**. If stoichiometric amounts of KOH are applied, one could imagine that initially the silanetriol **4** is formed, which in an additional step condenses to **3**. However, this does not seem to be the case since the use of stoichiometric amounts of KOH simply results in lower yields of **3** along with only partially defluorinated byproducts, as is evident from the Si−F coupling patterns in the $^{29}$Si NMR. This mixture can then be converted to **3** with additional base. Obviously the tendency of KOH to deprotonate the intermediate disiloxane-1,3-tetrol **6** or difluorosilanol **7** seems to be greater than to further displace fluorine.

The formation of **2** as well as the occurrence of the above-mentioned partially defluorinated byproducts indicate that at least in the case of fluorosilanes the hydrolysis leading to disiloxanes does not necessarily involve silanetriols. In contrast we believe that disiloxane **3** is formed via a difluorosilanol which should form from the trifluorosilane and base or water. As is known from gas phase studies, difluorosilanols possess considerable acidity.[25] Consequently also the terphenyl-substituted difluorosilanol should be prone to lose a proton and to subsequently attack another trihalosilane. In this step tetrafluorodisiloxane **2** is then formed, which can be isolated under neutral conditions. Especially under neutral conditions also a homofunctional condensation of 2 equiv of difluorosilanol to **2** seems possible. In the presence of strong base the remaining fluorine atoms are then exchanged successively, resulting in the formation of **3**.

The fluorine atoms in disiloxane **2** can also be displaced by nucleophiles other than hydroxide. For instance in the reaction of **2** with methyllithium all four fluorine atoms are exchanged by methyl groups, while the central Si−O bond of the disiloxane remains intact. This tetramethyl-substituted disiloxane **5** shows a resonance at −7.8 ppm in the $^{29}$Si NMR spectra and no fluorine coupling. A crystal of **5** was studied by X-ray diffraction, and its structure is shown in Figure 3. Selected bond distances and angles are given in Table 2.

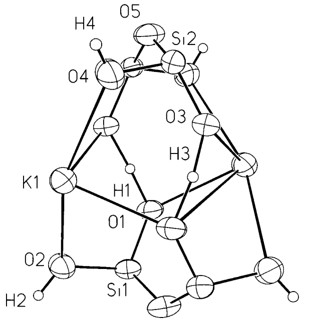

**Figure 2.** Detail of the X-ray crystal structure of **3** showing the central unit with hydrogen bonding (organic ligands omitted for clarity). Thermal ellipsoids are shown at the 50% probability level.

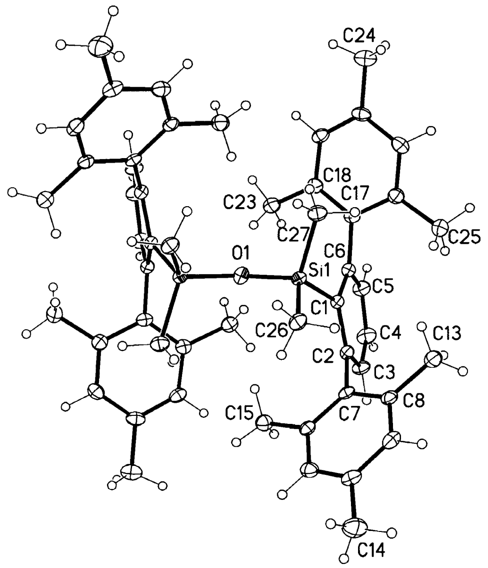

**Figure 3.** X-ray crystal structure of **5** with thermal ellipsoids shown at the 50% probability level.

Compound **5** crystallizes in the monoclinic space group *C*2/*c* ($Z = 4$). The structure of **5** deviates only slightly from the tetrahedral geometry at the silicon atoms with O1−Si1−C27 (108.35(6)°), O1−Si1−C26 (108.41(7)°), C26−Si1−C27 (106.18(8)°), O1−Si1−C1 (103.83(7)°), C1−Si1−C27 (114.65(8)°), and C1−Si1−C26 (115.14(8)°) bond angles. The Si−O (1.6499(7) Å) and Si−C (1.8597−1.9055(18) Å) bond distances are normal and fall within the region of Si−O (1.626−1.663 Å) and Si−C (1.84−1.899 Å) bond distances reported for acyclic tetramethyl diaryl disiloxanes.[26,27] Somewhat surprising, the Si−C bond length between silicon and the sp$^2$ carbon atom (1.9055(18) Å (Si−C(aryl)) is longer than the Si−C distance from silicon to the sp$^3$ carbon

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3**

| | | | | | |
|---|---|---|---|---|---|
| Si1#1−O1 | 1.574(3) | K1−O1#1 | 2.620(4) | O3−Si2−O5 | 111.79(16) |
| Si1−O5#1 | 1.645(4) | K1−O3#1 | 2.635(4) | O3−Si2−O4 | 107.87(17) |
| Si1−O2 | 1.651(4) | K1−O2 | 2.869(4) | O5−Si2−O4 | 107.45(18) |
| Si1−C1 | 1.894(4) | K1−O4 | 2.900(4) | O3−Si2−C24 | 112.18(19) |
| Si2−O3 | 1.571(3) | K1−C45 | 3.185(5) | O5−Si2−C24 | 105.11(18) |
| Si2−O5 | 1.638(4) | K1−C50 | 3.223(5) | O4−Si2−C24 | 112.38(19) |
| Si2−C24 | 1.893(4) | O1−Si1−O5#1 | 111.79(17) | O5#1−Si1−O2 | 107.41(18) |
| Si2−O4 | 1.656(4) | O1−Si1−O2 | 107.95(17) | O1−Si1−C1 | 112.24(19) |
| O3−H3 | 1.224(17) | O5−Si1−C1 | 104.58(18) | O2−Si1−C1 | 112.81(19) |
| O1−H1 | 1.201(9) | O4−H4 | 0.805(5) | O3−H3−O3#1 | 162.24(17) |
| O2−H2 | 0.898(7) | | | O1−H1−O1#1 | 172.14(17) |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5**

| | | | |
|---|---|---|---|
| Si(1)−O(1) | 1.6499(7) | O(1)−Si(1)−C(27) | 108.35(6) |
| Si(1)−C(1) | 1.9055(18) | O(1)−Si(1)−C(26) | 108.41(7) |
| Si(1)−C(26) | 1.8656(18) | C(27)−Si(1)−C(26) | 106.18(8) |
| Si(1)−C(27) | 1.8597(18) | O(1)−Si(1)−C(1) | 103.83(7) |
| C(1)−C(2) | 1.419(2) | C(27)−Si(1)−C(1) | 114.65(8) |
| C(1)−C(6) | 1.426(2) | C(26)−Si(1)−C(1) | 115.14(8) |
| | | Si(1)−O(1)−Si(1)#1 | 141.90(11) |

**Table 3. Crystal Data and Structure Refinement for 3 and 5**

| | 3 | 5 |
|---|---|---|
| formula | $C_{96}H_{106}K_2O_{10}Si_4$ | $C_{52}H_{62}OSi_2$ |
| fw | 1610.37 | 759.20 |
| temp, K | 213(2) | 133(2) |
| wavelength | 0.71073 | 0.71073 |
| cryst syst | orthorhombic | monoclinic |
| space group | *Fdd*2 | C12/*c*1 |
| unit cell dimens | | |
| *a*, Å | 30.03(3) | 26.251(2) |
| *b*, Å | 45.54(5) | 13.0494(9) |
| *c*, Å | 12.788(11) | 14.9190(10) |
| α, deg | 90 | 90.00 |
| β, deg | 90 | 120.065(2) |
| γ, deg | 90 | 90.00 |
| volume, Å$^3$ | 17487(30) | 4423.0(5) |
| *Z* | 8 | 4 |
| density(calcd), Mg/m$^3$ | 1.223 | 1.140 |
| *F*(000) | 6848 | 1640 |
| θ range for data collection, deg | 2.25 to 25.04 | 1.79 to 28.38 |
| goodness-of-fit on $F^2$ | 1.059 | 0.923 |
| final *R* indices | $R = 0.0514$ | $R = 0.0429$ |
| $[I > 2\sigma(I)]$ | 4997 | 3275 |
| *R* indices (all data) | $R_w = 0.1424$ | $R_w = 0.1106$ |

atoms (1.8597−1.8656(18) Å (Si−$CH_3$)). Moreover, the Si−O−Si angle of 141.90(11)° is somewhat smaller than the Si−O−Si angle in the less hindered $(CH_3)_3Si-O-Si(CH_3)_3$ (148.8(2)°).[28] Only few tetrafluorodisiloxanes have been reported so far, which throughout carry bulky substituents.[29,30] Up to now, their reactivity has not been explored in detail. As we could show, the fluorine atoms can be displaced smoothly under retention of the central disiloxane unit.

In summary, it has been shown that the hydrolysis of trihalosilanes resulting in the formation of oligosiloxanes does not necessarily involve silanetriols. By combining steric hindrance with the thermodynamic stability of an Si−F bond we were able to slow the hydrolysis of trihalosilanes, which allows the identification of intermediates in the condensation process. For terphenyl trifluorosilane we found indications that the corresponding difluorosilanol is likely to be a key intermediate in the subsequent condensation reaction. Its primary condensation product, the stable tetrafluorodisiloxane, could be isolated, and its reactivity was explored. Generally, condensation seems to be much faster than the hydrolysis of the starting fluorosilanes, which is just the opposite situation with chlorosilanes. The deprotonated disiloxane-1,3-tetrol (**3**) is likely to be a valuable precursor for the generation of new metallasiloxanes.

## Experimental Section

**General Procedures.** The syntheses of **2** and **3** were carried out under ambient conditions without exclusion of oxygen and moisture. The synthesis of **5** was performed under an atmosphere of dry, oxygen-free argon with solvents freshly distilled from the appropriate drying agent. $Mes_2C_6H_3SiF_3$ (**1**) was prepared according to ref 20. NMR spectra were recorded on a Bruker DPX 250 spectrometer at room temperature and referenced externally versus TMS or $CFCl_3$. Analyses have been performed at the microanalytical divisions of the Universities of Bochum and Bonn. Mass spectra (EI) were recorded on a Masslab VG 12-250. Melting points are uncorrected and have been measured on a Mettler FP61.

**Synthesis of Tetrafluorodisiloxane 2.** In a round-bottom flask 2.0 g (5 mmol) of **1** is dissolved in 100 mL of acetone. To this solution 10 mL (0.56 mol) of water is added under stirring. Stirring is continued for 3 weeks. During this time a white solid precipitates at the walls of the reaction flask. The clear solution is decanted from the precipitate and can be used to recover unreacted starting material. The remaining precipitate is isolated, washed with hexanes, and dried under vacuum (yield: 0.06 g, 3%). Mp: 241 °C. $^{29}$Si NMR ($CDCl_3$): −75.5 ppm (t, $^1J_{SiF} = 263$ Hz). $^{19}$F NMR ($CDCl_3$): −128.4 ppm. $^1$H NMR ($CDCl_3$): 7.63 (t, $^3J_{HH} = 7.7$ Hz, 1H), 7.14 (d, $^3J_{HH} = 7.7$ Hz, 2H), 6.96 (s, 4H), 2.45 (s, 6H), 1.95 (s, 12H). MS (EI): 774 (5%, $M^+$), 398 (100%, $M^+$ − TerSiOF), 379 (7%, $M^+$ −$TerSiOF_2$), 312 (41%, $Ter^+$). Anal. Calcd for $C_{48}H_{50}F_4OSi_2$ (775.07): C, 74.38; H, 6.50. Found: C, 74.44; H, 6.52.

**Synthesis of Substituted Potassium Trihydroxooxodisiloxane 3.** In a round-bottom flask 1.0 g (2.5 mmol) of **1** is dissolved in a mixture of 100 mL of diethyl ether and 25 mL of benzene. To this solution 0.56 g (10 mmol) of solid KOH is added under stirring. Stirring is continued until the KOH is completely dissolved. Then the solution is allowed to stand until solid KF starts to precipitate. The supernatant solution is separated, the solvent is removed in a vacuum, and the residue is extracted with cyclohexane. This extract is filtered, and the solvent is removed (yield: 0.92 g, 91.0%). Alternatively, **3** can also be prepared starting from **2** following the same procedure by reacting it with 4 equiv of KOH. Mp: 280 °C (dec). $^{29}$Si NMR ($C_6D_6$): −58.8 ppm. $^1$H NMR ($C_6D_6$): 7.22 (t, $^3J_{HH} = 7.5$ Hz, 1H), 6.88 (d, $^3J_{HH} = 7.5$ Hz, 2H), 6.77 (s, 4H), 2.12 (s, 6H), 2.10 (s, 12H). $^{13}$C NMR ($C_6D_6$): 149.40 ($C_q$), 148.85 (CH), 141.23 ($C_q$), 137.08 ($C_q$), 131.92 ($C_q$), 131.02 ($C_q$), 137.33 (CH), 137.19 (CH), 21.38 (*ortho*-$CH_3$), 21.26 (*para*-$CH_3$). MS(EI): 767 (33%, $M^+$ − K), 436 (100%, $M^+$ − Ter), 313 (32%,

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$Ter^+$). Anal. Calcd for $C_{48}H_{53}KO_5Si_2$ (805.2): C, 71.60; H, 6.63. Found: C, 71.50; H, 6.49.

**Synthesis of Tetramethyldisiloxane 5.** In a flame-dried flask 1.0 g (1.3 mmol) of **2** is dissolved in 20 mL of 1,2-dimethoxyethane. This solution is cooled to −78 °C, and under stirring 3.6 mL (5.8 mmol) of MeLi in diethyl ether is added slowly. Stirring is continued at that temperature for 15 min, and then the mixture is allowed to slowly warm to room temperature. Subsequently the solvent is removed in a vacuum, and the residue is extracted twice with 10 mL of benzene. This extract is filtered, and the solvent is removed (yield: 0.86 g, 87 0%). Mp: 202 °C. $^{29}Si$ NMR ($C_6D_6$): −7.8 ppm (s). $^1H$ NMR ($C_6D_6$): 7.59 (m, 1H), 7.37 (m, 2H), 7.20 (s, 4H), 2.56 (s, 6H), 2.42 (s, 12H), 0.12 (s, 6H). $^{13}C$ NMR ($C_6D_6$): 130.18 ($C_q$), 129.67 ($C_q$), 129.38 (CH), 129.10 ($C_q$), 128.93 ($C_q$), 128.70 (CH), 128.50 (CH), 126.00 ($C_q$), 21.79 (*ortho*-$CH_3$), 21.58 (*para*-$CH_3$), 2.47 (Si-$CH_3$). MS: 758 (2%, $M^+$), 357 (5%, $TerSiO^+$), 354 (2%, $TerSiCH^+$), 342 (25%, $TerSiH^+$), 312 (100%, $Ter^+$). Anal. Calcd for $C_{52}H_{62}OSi_2$ (759.22): C, 82.26; H, 8.23. Found: C, 81.97; H, 8.38.

**Supporting Information Available:** Complete crystallographic details of the X-ray structures of **3** and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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