Preparation, Characterization, and Thermal and Surfactant Studies of Polyfluorinated Amphiphilic Carbosilane Dendrimers

Bamidele A. Omotowa and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

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ABSTRACT: The synthesis of amphiphilic carbosilane dendrimers that contain perfluoroalkyl and hydroxy groups at terminal positions is explored in this work. Zeroth- and first-generation hydroxyallyl dendrimers were reacted with a heptadecafluorodecane hydrosilane to produce the new first- and second-generation derivatives in 58% and 55% yields, respectively. The reaction of a zeroth-generation carbosilane dendrimer with four terminal ester groups with 1,1,2-trifluorobut-1-enyl-4-magnesium bromide gave another type of the first-generation polyfluorinated amphiphilic derivative under mild conditions in 58% yield. Their compositions were confirmed by NMR and IR spectroscopy as well as mass spectrometry and elemental analyses. The thermal stabilities were evaluated by differential scanning calorimetry and thermogravimetric analysis. Polyfluoroalkylation increased the thermal stability of the amphiphilic carbosilane dendrimers relative to their nonfluorinated precursors. IR results showed that the amphiphatic dendrimers were useful for solubilizing pentoxyfylline (antibiotic) in perfluoro solvents (perfluorobenzene, perfluorodecalin, and perfluorooctyl bromide).

Introduction

Perfluoro solvents have been used in several bi- or triphase heterogeneous combinations with water and/or organic solvents.[1,2] These heterogeneous systems allow the use of highly fluorinated organic and organometallic compounds as reagents in syntheses and catalysis and as surfactants in separation science.[3] Control of reaction rates, product separation, and yields is better in a number of reactions when undertaken in heterogeneous solvent systems.[3b−e,l,4] The polyfluorinated analogues of Wilkinson and Vaska catalysts,[5] triarylphosphines,[3a,h,m,o,t] and organotin reagents, e.g., $XSnCH_2CH_2CH_2C_6F_{13}$ (X = H, Br, or Ar),[3b,f,6] are some of the better known categories of compounds that are used in heterogeneous applications. The polyfluorinated reagents in heterogeneous-phase applications act essentially as amphiphiles, since they can be manipulated to dissolve in either the organic or aqueous phase, particularly at elevated temperatures.[3] We began to investigate the syntheses and properties of polyfluorinated amphiphiles[7] since they find use in a variety of fields, e.g., as gene carriers and as secondary surfactants in drug delivery.[8] Polyfluorinated dendrimers with a peripheral hydroxy functionality represent a new class of compounds that may possess unique surface and surfactant properties.

Dendrimers have peculiar properties that were recognized early by Vögtle, Tomalia, Newkome, and Fréchet,[9] and have been the subject of many reviews.[10] There are very few amphiphilic dendrimers in the literature,[11] and they were mostly used at aqueous−organic interfaces. Highly fluorinated dendrimers built on polyaminopolyamide (PAMAM) cores are useful for applications in supercritical carbon dioxide ($SC\text{-}CO_2$) or perfluorinated solvents.[12] The PAMAM core is highly functionalized, containing N−H and/or C═O groups that are useful for possible hydrogen bonding to facilitate the transfer of chemical units across solvent interfaces. Evidence that organic molecules can be held in the core regions was obtained earlier.[13] The carbosilane dendrimers have basically an inert core, but their surfaces have been diversely functionalized,[14] and include the water-soluble,[15] hydroxy-terminated,[16] or perfluoroalkyl-terminated[17] carbosilane dendrimers. Tethered multifunctionalities on the surface of carbosilane dendrimers may result in unique solvent-dependent surface properties. It could be difficult to free a molecule that has been transported across solvent phases from the core regions of PAMAM dendrimers.[13] Ideally, the localized peripheral functionalization would make it easier to free organic molecules after an interfacial transfer has been effected. We now report high-yield syntheses of such compounds by known procedures, and have explored their surface properties, and interfacial activity.

* To whom correspondence should be addressed. E-mail: jshreeve@uidaho.edu.

Experimental Section

The solvents, tetrahydrofuran (THF) and diethyl ether, were dried with sodium and distilled over a purple solution of benzophenone and dimethyl sulfoxide (DMSO) over calcium hydride. Chloroplatinic acid and all other chemicals were used as received from Aldrich, Acros, or Lancaster. Pentoxyfylline was obtained from Fischer, and used without further purification. The equipment for NMR, IR, MALDI-TOF, ApCI, and FAB+ experiments was as described elsewhere.[7,17,18]

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments TA10 differential scanning calorimeter equipped with an autocool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from +40 to −80 °C and heating to 400 or 550 °C at 10 °C/min. Transition temperatures, T_m, were taken as peak maxima. The onset of decomposition was taken as the point at which the abnormal section of the plot began. Thermogravimetric analysis (TGA) measurements were made using a TA Instrument TA50. Samples were heated at 10 °C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate 70 mL/min).

Syntheses. Compounds 1−3. The syntheses of compounds **1**−**3**, ending in chloromethyl(dimethyl)silane units, were achieved by hydrosilylation reaction of the respective carbosilane dendrimers that terminated in allylsilane units[19] with $HSiMe_2CH_2Cl$, following procedures described earlier in the literature.[14] A description of the synthesis of **1** is given.

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$Si(CH_2CH_2CH_2SiMe_2CH_2Cl)_4$ (1). Tetraallylsilane (1.92.g, 9.98 mmol) was placed, under an inert atmosphere, in a two-necked 50 mL Schlenk flask that was equipped with a magnetic stir bar and a side arm to control the nitrogen inlet flow or vacuum. To the stirring liquid were added 5 mL of THF, 2 drops of 10^{-3} M chloroplatinic acid, and 5 mL of a THF solution of chloromethyl(dimethyl)silane (7.55 g, 60.0 mmol). After the mixture was stirred, under nitrogen for 1 h at 25 °C, the temperature of the reaction was raised to cause gentle reflux at ∼70 °C for 12 h. The reaction mixture was then cooled to ambient temperature, and the volatile contents were removed under vacuum. Further purification involved pentane/CH_2Cl_2 (9:1) elution of the crude over silica gel to give pure **1**.

Yield: 76%. IR (cm^{-1}): $\nu_s(CH_3)$ 2918 (vs), $\nu_a(CH_2)$ 2957 (s), $\nu_s(CH_2)$ 2872 (m). UV (λ_{max}): 231, 267 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.07 (s, 24H, Si*Me*$_2$), 0.50−0.85 [dt, 6H, Si(C*H*$_2$-CH$_2$C*H*$_2$Si)], 1.32 [m, 8H, Si(CH$_2$C*H*$_2$CH$_2$Si)], 2.74 (s, 8H, SiMe$_2$C*H*$_2$Cl); ^{13}C, δ 0.8, 17.3, 18.3, 18.6, 30.4 (J_{Si-C} = 13 Hz); ^{29}Si, δ 0.64, 3.14. MS: *m*/*z* calcd (M) ($C_{24}H_{56}Cl_4Si_5$) 626.94, found (EI) 477 (M^+ − one arm), with the expected isotopic pattern. Anal. Calcd for $C_{24}H_{56}Cl_4Si_5$: C, 45.98; H, 9.00. Found: C, 44.91; H, 8.88.

$Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2Cl)_2]_4$ (2). Yield: 70%. IR (cm^{-1}): $\nu_a(CH_3)$ 2955 (vs), $\nu_s(CH_3)$ 2913 (vs), $\nu_a(CH_2)$ 2874 (vs), $\nu_s(CH_2)$ 2792 (m). UV (λ_{max}): 234, 273 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.04 (s, 24H, Si*Me*$_2$), 0.11 (s, 12H, Si*Me*), 0.58 and 0.71 [dt, 48H, Si(C*H*$_2$CH$_2$C*H*$_2$Si)], 1.37 [br, 24H, Si(CH$_2$C*H*$_2$CH$_2$Si)], 2.78 (s, 00H, SiMe$_2$C*H*$_2$Cl); ^{13}C, δ −4.9, −4.4, 18.3, 18.5, 18.7, 30.5 (J_{Si-C} = 13 Hz); ^{29}Si, δ 0.72, 1.28, 3.22. MS: *m*/*z* calcd (M) ($C_{68}H_{148}Cl_8Si_{13}$) 1644.64, found (MALDI-TOF) 1607.16. Anal. Calcd for $C_{68}H_{148}Cl_8Si_{13}$: C, 50.00; H, 9.13. Found: C, 50.88; H, 9.91.

$Si\{CH_2CH_2CH_2Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2Cl)_2]_3\}_4$ (3). Yield: 68%. IR (cm^{-1}): $\nu_s(CH_3)$ 2915 (vs). UV (λ_{max}): 237, 266 (sh), 295 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.04 (s, 24H, Si*Me*), 0.10 (s, 24H, Si*Me*$_2$), 0.56 and 0.71 [dt, 160H, Si(C*H*$_2$CH$_2$C*H*$_2$Si)], 1.37 [m, 80H, Si(CH$_2$C*H*$_2$CH$_2$Si)], 2.79 (s, 48H, SiMe$_2$C*H*$_2$Cl); ^{13}C, δ −4.3, 17.8, 18.5, 19.3, 30.4 (J_{Si-C} = 13 Hz); ^{29}Si, δ 0.58, 1.29, 3.22. MS: *m*/*z* calcd (M) ($C_{204}H_{444}Cl_{24}Si_{41}$) 4900, $(M + Na)^+$ 4923, found (MALDI-TOF) 4930. Anal. Calcd for $C_{204}H_{444}Cl_{24}Si_{41}$: C, 50.11; H, 8.95. Found: C, 49.09; H, 9.24.

Compounds 4−6. A description of the synthesis of **4** is given below. The same method was utilized for the syntheses of **5** and **6**.

$Si(CH_2CH_2CH_2SiMe_2CH_2SCH_2COOCH_2CH_3)_4$ (4). 1 (0.80 g, 1.28 mmol), 25 mL of ethanol, thioglycolic acid (0.53 g, 5.76 mmol), and a magnetic stir bar were placed in a 50 mL round-bottomed one-necked flask. Potassium hydroxide (1.4 g, 25 mmol) in 3 mL of water was added until pH ≈ 12−14. The flask was connected to a reflux condenser, and the reaction mixture was warmed to 80 °C and held at reflux for 24 h. On cooling, concentrated hydrochloric acid was added carefully to the reaction mixture until the pH was reduced to ∼1−2. The magnetic stir bar was removed, and ethanol and other volatile compounds were removed on a rotary evaporator at 50 °C. Two 20 mL portions of diethyl ether were added to the flask, the flask was shaken thoroughly, and the two portions were separated using a separating funnel. The combined organic phase was evaporated to leave the crude product and some unreacted thioglycolic acid. The latter was removed by washing the contents of the flask with two 10 mL portions of water. The contents of the flask were then taken up in 20 mL of diethyl ether, dried using anhydrous sodium sulfate, filtered, and dried in vacuo over 24 h to give a mixed [COOH (ca. 80%) and COOEt (ca. 20%)] functional dendrimer. An inspection of the crude product by ^1H NMR spectroscopy confirmed complete substitution of the chloromethyl functionality in **1**. This product was held at reflux for 8 h with anhydrous ethanol (20 mL) containing 3 g of sulfuric acid. On cooling, most of the ethanol was removed on the rotary evaporator at 50 °C. An aqueous solution (15 mL) containing 3 g of potassium carbonate was added to neutralize the acid. The aqueous solution was then shaken three times with 20 mL portions of ethyl ether. The combined ether solution was dried over sodium sulfate and filtered and the volatile solvent removed in vacuo over 24 h to yield **4** in 88% yield (based on **1**).

Yield: 90%. IR (cm^{-1}): $\nu(H_2O)$ 3445 (w, br), $\nu_a(CH_3)$ 2955 (vs), $\nu_s(CH_3)$ 2914 (vs), $\nu_a(CH_2)$ 2877 (vs), $\nu_s(C{=}O)$ 1733 (vs). UV (λ_{max}): 234, 278 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.05 (s, 24H, Si*Me*$_2$), 0.55 (t), 0.64 (t) and 1.32 (m) (6H, SiCH$_2$CH$_2$-CH$_2$Si), 1.28 [t, 12H, C(O)OCH$_2$C*H*$_3$], 1.92 (s, 8H, SiMe$_2$C*H*$_2$S), 3.18 [s, 8H, SC*H*$_2$C(O)OCH$_2$CH$_3$], 4.19 [q, 8H, C(O)OC*H*$_2$CH$_3$]; ^{13}C, δ −3.3, 14.3, 17.4, 18.2, 18.4, 19.8, 37.7, 61.2, 170.4; ^{29}Si, δ 0.89, 1.69. MS: *m*/*z* calcd (M) ($C_{40}H_{86}O_9S_4Si_5$) 961, found ($APcI^+$) 961. Anal. Calcd for $C_{40}H_{86}O_9S_4Si_5{\cdot}H_2O$: C, 49.03; H, 8.91. Found: C, 49.09; H, 8.91.

$Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2SCH_2COOCH_2CH_3)_2]_4$ (5). Yield: 78%. IR (cm^{-1}): $\nu(H_2O)$ 3445 (m, br), $\nu_a(CH_3)$ 2955 (vs), $\nu_s(CH_3)$ 2914 (vs), $\nu_a(CH_2)$ 2877 (vs), $\nu_s(C{=}O)$ 1733 (vs). UV (λ_{max}): 238 nm. NMR ($CDCl_3$) (ppm): ^1H, δ −0.07 (s, 12H, Si*Me*), 0.08 (s, 48H, Si*Me*$_2$), 0.55 (br) and 0.64 (t) (48H, SiC*H*$_2$CH$_2$C*H*$_2$Si), 1.32 (br, 24H, SiCH$_2$C*H*$_2$CH$_2$-Si), 1.27 [t, 24H, C(O)OCH$_2$C*H*$_3$], 1.94 (s, 16H, SiMe$_2$C*H*$_2$S), 3.19 [s, 16H, SC*H*$_2$C(O)OCH$_2$CH$_3$], 4.19 [q, 16H, C(O)OC*H*$_2$-CH$_3$]; ^{13}C, δ −5.0, −3.3, 14.3, 18.3, 18.7, 19.7, 37.8, 61.1, 170.4; ^{29}Si, δ 0.54, 1.25, 1.73. MS: *m*/*z* calcd (M) ($C_{96}H_{204}O_{16}S_8Si_{13}$) 2232.28, $(M + Ag)^+$ 2343.28, found (electrospray) 2343.10. Anal. Calcd for $C_{96}H_{206}O_{17}S_8Si_{13}$: C, 51.10; H, 9.14. Found: C, 50.84; H, 9.03.

$Si\{CH_2CH_2CH_2Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2SCH_2COOCH_2CH_3)_2]_3\}_4$ (6). Yield: 72%. IR (cm^{-1}): ν(OH) 3400 (s, br), $\nu_a(CH_3)$ 2958 (vs), $\nu_s(CH_3)$ 2918 (vs), $\nu_s(C{=}O)$ 1725 (vs). UV (λ_{max}): 230, 273 (sh), 295 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.08 (s, 180H, Si*Me* and Si*Me*$_2$), 0.55 (t), 0.65 (t), and 1.32 (m) (240H, SiCH$_2$CH$_2$CH$_2$Si), 1.27 [t, 72H, C(O)-OCH$_2$C*H*$_3$], 1.91 (s, 48H, SiMe$_2$C*H*$_2$S), 3.17 [s, 48H, SC*H*$_2$C(O)OCH$_2$-CH$_3$], 4.16 [q, 48H, C(O)OC*H*$_2$CH$_3$]; ^{13}C, δ −3.3, 14.3, 18.3, 18.5, 19.9, 37.7, 61.1, 170.4; ^{29}Si, δ 0.72, 1.65. Anal. Calcd for $C_{300}H_{636}O_{48}S_{24}Si_{41}$: C, 50.60; H, 9.22. Found: C, 50.30; H, 9.35.

Compounds 7−9. The reactions of **4**−**6** with allylmagnesium bromide led to the syntheses of **7**−**9**, respectively. A description of the synthesis of **7** is given below. The same method led to the syntheses of **8** and **9**.

$Si[CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH{=}CH_2)_2]_4$ (7). Into a 50 mL two-necked flask (the type described for the synthesis of **1** above) were placed compound **4** (2.0 g, 2.08 mmol) and 10 mL of THF, under an atmosphere of nitrogen. A solution of 2.0 M allylmagnesium bromide in THF (25.0 mL, 50 0 mmol) was added dropwise to the stirring solution at 25 °C. A white precipitate was formed as the addition proceeded. After the Grignard reagent was added, the flask was fitted with a reflux condenser and the reaction mixture was maintained at 40 °C with stirring for 2 h. On cooling, 2 mL of concentrated HCl was added dropwise to the reaction mixture. The magnetic stir bar was removed, the solvent was evaporated on a rotary evaporator, and the contents were washed with two portions of 10 mL of water. The product **7** was taken up in 20 mL of diethyl ether, dried using anhydrous sodium sulfate, filtered, and evaporated in vacuo for 24 h.

Yield: 97%. IR (cm^{-1}): ν(OH) 3445 (m, br), ν_a(olefin CH) 3076 (m), $\nu_a(CH_3)$ 2954 (s), $\nu_s(CH_3)$ 2914 (vs), $\nu_a(CH_2)$ 2877 (s). UV (λ_{max}): 240, 282 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.08 (s, 24H, Si*Me*$_2$), 0.57 (br), 0.65 (t), and 1.34 (br) (24H, SiC*H*$_2$C*H*$_2$C*H*$_2$Si), 1.87 (s, 8H, SiMe$_2$C*H*$_2$S), 2.25 (dt, 16H, C*H*$_2$-CH=CH$_2$), 2.69 [s, 8H, SC*H*$_2$C(OH)CH$_2$CH=CH$_2$], 5.10 (dd, 16H, CH$_2$CH=C*H*$_2$), 5.84 (m, 8H, CH$_2$C*H*=CH$_2$); ^{13}C, δ −3.3, 17.4, 18.5, 19.9, 20.3, 43.3, 47.3, 73.8, 118.8, 133.6; ^{29}Si, δ 0.93, 1.59. MS: *m*/*z* calcd (M) ($C_{56}H_{108}O_4S_4Si_5$) 1114.15, found (MALDI-TOF) 1112.5, (FAB+) 1113.4. Anal. Calcd for $C_{56}H_{108}$-$O_4S_4Si_5$: C, 60.37; H, 9.77. Found: C, 60.70; H, 9.93.

$Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH{=}CH_2)_2)_2]_4$ (8). Yield: 94%. IR (cm^{-1}): ν(OH) 3442 (m, br), ν_a(olefin CH) 3076 (m), $\nu_a(CH_3)$ 2954 (s), $\nu_s(CH_3)$ 2913 (vs), $\nu_a(CH_2)$ 2878 (s). UV (λ_{max}): 239, 300 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.05 and 0.06 (s, 36H, Si*Me*), 0.07 (s, 144H, Si*Me*$_2$), 0.56 (br), 0.65 (t), and 1.33 (br) (240H, SiCH$_2$-CH$_2$CH$_2$Si), 1.85 (s, 48H, SiMe$_2$C*H*$_2$S), 2.27 (t, 96H, C*H*$_2$CH=CH$_2$), 2.32 (br, 24H, OH), 2.66 [s, 48H, SC*H*$_2$C(OH)CH$_2$CH=CH$_2$], 5.10 (dd, 96H, CH$_2$CH=C*H*$_2$), 5.84 (m, 48H, CH$_2$C*H*=

CH_2); ^{13}C, δ −3.2, −1.0, 17.4, 18.5, 19.9, 20.3, 43.4, 47.3, 73.8, 118.9, 133.6; ^{29}Si, δ 0.77, 1.54. MS: *m/z* calcd (M) ($C_{128}H_{252}O_8S_8Si_{13}$) 2541.01, $(M + Ag)^+$ 2649.01, found (electrospray) 2648.71. Anal. Calcd for $C_{128}H_{252}O_8S_8Si_{13}$: C, 60.50; H, 10.00. Found: C, 62.39; H, 10.21.

Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH{=}CH_2)_2)_2]_3$}$_4$ (9). Yield: 92%. IR (cm^{-1}): ν(OH) 3445 (m, br), ν_a(olefin CH) 3076 (m), $\nu_a(CH_3)$ 2954 (s), $\nu_s(CH_3)$ 2914 (vs), $\nu_a(CH_2)$ 2877 (s). UV (λ_{max}): 235 nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.05 and 0.06 (s, 36H, Si*Me*), 0.07 (s, 144H, $SiMe_2$), 0.56 (br), 0.65 (t), and 1.33 (br) (240H, $SiCH_2CH_2CH_2Si$), 1.85 (s, 48H, $SiMe_2CH_2S$), 2.27 (t, 96H, $CH_2CH{=}CH_2$), 2.32 (br, 24H, OH), 2.66 [s, 48H, $SCH_2C(OH)CH_2CH{=}CH_2$], 5.10 (dd, 96H, $CH_2CH{=}CH_2$), 5.84 (m, 48H, $CH_2CH{=}CH_2$); ^{13}C, δ −3.2, −1.0, 17.4, 18.5, 19.9, 20.3, 43.4, 47.3, 73.8, 118.9, 133.6; ^{29}Si, δ 0.77, 1.54. Anal. Calcd for $C_{396}H_{756}O_{24}S_{24}Si_{41}$: C, 60.80; H, 9.74. Found: C, 60.46; H, 10.05.

Si[$CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH_2CF{=}CF_2)_2]_4$ (10). Compound **4** was reacted with 1,1,2-trifluorobut-1-enyl-4-magnesium bromide following the procedure described for **7**, to obtain the polyfluorinated dendrimer **10**.

Yield: 58%. IR (cm^{-1}): ν(OH) 3440 (m, br), $\nu_a(CH_3)$ 2957 (s), $\nu_s(CH_3)$ 2917 (vs), $\nu_a(CH_2)$ 2881 (s). UV (λ_{max}): 232, 290 (sh) nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.01 (s, 24H, $SiMe_2$), 0.50 (br) and 0.59 (t) (16H, $SiCH_2CH_2CH_2Si$), 1.26 (br, 8H, $SiCH_2CH_2CH_2Si$), 1.67 (t, J_{H-H} = 7 Hz, 16H, $CH_2CH_2CF{=}CF_2$), 1.79 (s, 8H, $SiMe_2CH_2S$), 2.31 (br, 16H, $CH_2CH_2CF{=}CF_2$), 2.39 (br, 4H, OH), 2.65 [s, 8H, $SCH_2CH(OH)(CH_2CH_2CF{=}CF_2)_2$]; ^{13}C, δ −3.4, 17.3, 18.4, 19.8, 20.3 (d, J_{C-F} = 20.5 Hz), 20.5, 34.1, 47.2, 72.7, 128.7 (dd, J_{C-F} = 235.4 Hz, J_{C-F} = 54.7 Hz), 152.9 (td, J_{C-F} = 238.8, J_{C-F} = 47.16 Hz); ^{19}F, δ −105.6 (dd, J_{F-F} = 89.0 Hz, J_{F-F} = 33.9 Hz), −124.7 (dd, J_{F-F} = 112.96 Hz, J_{F-F} = 90.37 Hz), −174.7 (dm, J_{F-F} = 110.1 Hz); ^{29}Si, δ 0.90, 1.75. Anal. Calcd for $C_{64}H_{100}O_4S_4F_{24}Si_5{\cdot}3H_2O$: C, 44.39; H, 6.13. Found: C, 44.23; H, 6.45.

Compounds 11 and 12. The hydrosilylation reactions of **8** and **9** with 1*H*,1*H*,2*H*,2*H*-perfluorooctyl(dimethyl)hydrosilane, $C_6F_{13}CH_2CH_2SiMe_2H$, led to the syntheses of **11** and **12**, respectively. A description of the synthesis of **11** is given below. The same method was employed for the synthesis of **12**.

Si[$CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13})_2]_4$ (11). Into a two-necked 50 mL flask equipped with a magnetic stir bar and connected to a nitrogen inlet were added 0.50 g (0.45 mmol) of **7**, 2.92 g (7.20 mmol) of $C_6F_{13}CH_2CH_2SiMe_2H$, and three drops of 1 M chloroplatinic acid solution in 2-propanol. The reaction mixture was stirred at 25 °C for 0.5 h and subsequently warmed to reflux at 65−70 °C. NMR spectra indicated that the olefins in **7** had been completely reduced over 18 h. On cooling, the volatile contents of the flask were removed under vacuum while the flask was held in a water bath at 40 °C for 20 h to give crude **11**. Pentane, dichloromethane, and diethyl ether were used in successive chromatographic elutions over a silica gel column. The product was in the diethyl ether fraction. Repeated chromatographic elution produced analytically pure **11**.

Yield: 55%. IR (cm^{-1}): ν(OH) 3446 (m, br), $\nu_a(CH_3)$ 2959 (s), $\nu_s(CH_3)$ 2913 (vs), $\nu_a(CH_2)$ 2883 (s). UV (λ_{max}): 234 nm. NMR ($CDCl_3$) (ppm): ^1H, δ 0.04 (s, 24H, $SiMe_2CH_2S$), 0.08 (s, 48H, $SiMe_2CH_2CH_2C_6F_{13}$), 0.55 and 0.69 (br, 16H, $SiCH_2CH_2CH_2Si$), 0.75 (t, 16H, $SiMe_2CH_2CH_2C_6F_{13}$), 0.93 (t, 16H, $CH_2SiMe_2CH_2CH_2C_6F_{13}$), 1.31 [br, 24H, $SiCH_2CH_2CH_2Si$ and $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13}$], 1.48 [dt, 16H, $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13}$], 1.84 (s, 8H, $SiMe_2CH_2S$), 2.05 [br, 16H, $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2CF_2C_5F_{11}$], 2.68 [s, 8H, $SCH_2C(OH)$]; ^{13}C, δ −2.9, −2.2, 15.5, 16.4, 17.8, 18.8, 19.2, 19.5, 20.1, 20.5, 21.4, 26.6 (t, $^2J_{C-F}$ = 23 Hz), 42.0, 49.0, 74.7; ^{19}F, δ −83.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 48F), −116.6 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −122.5 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −123.4 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −123.8 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −126.7 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F); ^{29}Si, δ 0.72, 1.60, 3.92. Anal. Calcd for $C_{136}H_{196}O_4S_4F_{104}Si_{13}$: C, 37.43; H, 4.50. Found: C, 37.96; H, 5.46.

Si{$CH_2CH_2CH_2Si\{CH_2CH_2CH_2SiMe[CH_2CH_2CH_2SiMe_2CH_2SCH_2C(OH)(CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13})_2]_2\}_3$}$_4$ (12). **12** was prepared from 1.0 g (0.394 mmol) of **8** and 5.12 g (12.61 mmol) of $C_6F_{13}CH_2CH_2SiMe_2H$, following the procedure described for **11**.

Yield: 58%. IR (cm^{-1}): ν(OH) 3446 (m, br), $\nu_a(CH_3)$ 2959 (s), $\nu_s(CH_3)$ 2913 (vs), $\nu_a(CH_2)$ 2883 (s). UV (λ_{max}): 237 nm. NMR ($CDCl_3$) (ppm): ^1H, δ −0.06 (s, 12H, Si*Me*), 0.04 (s, 48H, $SiMe_2CH_2S$), 0.07 (s, 96H, $SiMe_2CH_2CH_2C_6F_{13}$), 0.55 and 0.69 (br, 48H, $SiCH_2CH_2CH_2Si$), 0.75 (t, 32H, $SiMe_2CH_2CH_2C_6F_{13}$), 0.93 (t, 32H, $CH_2SiMe_2CH_2CH_2C_6F_{13}$), 1.31 [br, 64H, $SiCH_2CH_2CH_2Si$ and $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13}$], 1.48 [dt, 32H, $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2C_6F_{13}$], 1.84 (s, 16H, $SiMe_2CH_2S$), 2.05 [br, 32H, $C(OH)CH_2CH_2CH_2SiMe_2CH_2CH_2CF_2C_5F_{11}$], 2.68 [s, 16H, $SCH_2C(OH)$]; ^{13}C, δ −4.2, −3.0, −2.5, 15.4, 16.2, 17.9, 18.6, 19.2, 19.4, 20.0, 20.6, 21.2, 26.7 (t, $^2J_{C-F}$ = 23 Hz), 41.9, 43.6, 49.0, 74.9; ^{19}F, δ −83.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 48F), −116.6 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −122.5 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −123.4 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −123.8 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F), −126.7 ($CF_3CF_2CF_2CF_2CF_2CF_2CH_2$, 32F); ^{29}Si, δ 1.27, 1.60, 3.92. Anal. Calcd for $C_{288}H_{428}O_8S_8F_{208}Si_{29}$: C, 38.26; H, 4.74. Found: C, 38.34; H, 5.08.

General Description of the Procedure Followed in Solubilization Experiments. (1) A 0.1 g sample of pentoxyfylline and 2 mL of (i) hexafluorobenzene [or (ii) perfluorodecalin or (iii) perfluorooctyl bromide] were placed in a 4 mL vial, and the vial was shaken vigorously to dissolve as much as possible at 25 °C. The mixture or solution formed was allowed to settle. A pipet was used to place about 4−5 drops of the clear solution phase on a KBr plate. The respective perfluoro solvent evaporated gradually in open air, and the IR spectrum of the residue was recorded. The plate was the blank reference in all measurements. (2) (a) A 2 mL sample of a 1 M aqueous solution of pentoxyfylline was shaken with 2 mL of the perfluoro solvent at 25 °C. (b) The IR spectrum of the evaporated perfluoro chemical phase was recorded, following the procedure for KBr plate preparation in step 1 above. (3) (a) A 2 mL sample of a 1 M aqueous solution of pentoxyfylline was shaken with 2 mL of the perfluoro solvent, containing 5% v/v dendrimer. (b) The IR spectrum of the residue of the perfluoro chemical phase was recorded.

Results and Discussion

To investigate the syntheses and properties of polyfluorinated amphiphiles, we gradually converted **1**−**3** to **4**−**6** and then to the amphiphiles **7**−**13** via a divergent synthetic strategy.[11,13−17] Carbosilane dendrimers terminating in $-SiMe_2CH_2Cl$, and on which small, bifunctional mercaptoalkyl groups, such as $HSCH_2CH_2OH$, $HSCH_2CH_2SO_3Na$, and $HSCH_2CH_2NMe_2$ were derivatized, have been reported.[15] The silicon atoms situated at branching locations in these dendrimers were linked by $-(CH_2)_{2-}$ chains, resulting from hydrosilylation of vinylsilane precursors.[15] Dispersion of reactive terminal sites is an advantage for reaction with sterically demanding ligands. Therefore, we employed allylsilane precursors to obtain new carbosilane cores linked by $-(CH_2)_{3-}$ chains, **1**−**3**, shown in Figure 1.

The reactions of **1**−**3** with thioglycolic acid (mercaptoacetic acid), $HSCH_2COOH$, proceeded at pH 12−14

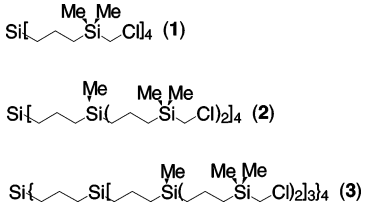


Figure 1.

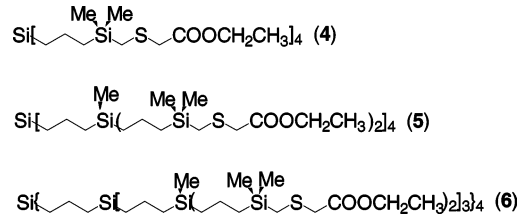


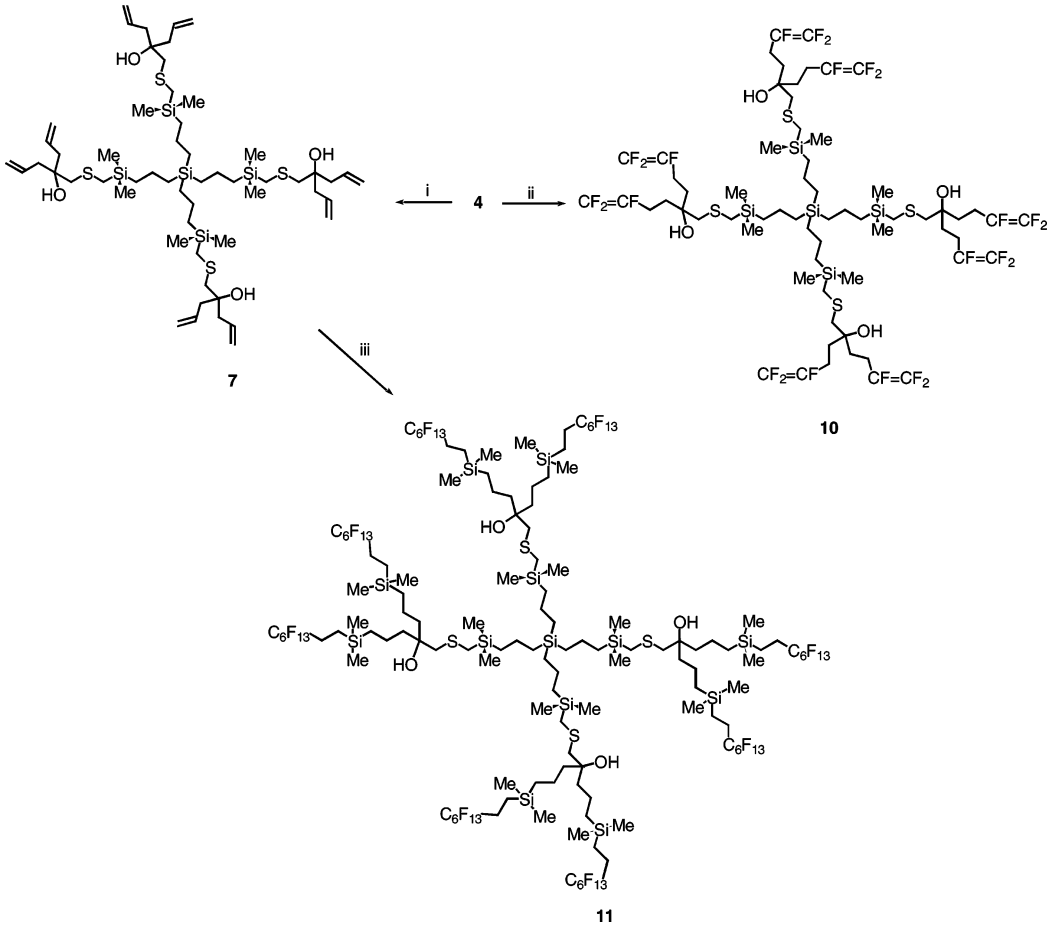
Figure 2.

using KOH, and after workup gave the respective partly acid terminated dendrimers. Even though thioglycolic acid is readily oxidized (resulting in loss of CO_2!) on standing for a long time in air,[20] the new dendrimers were formed in high yields. Apparently, both the formation of potassium thioglycolate from acid−base neutralization reaction of the −COOH groups and KOH and the mercapto substitution of the chloromethylsilane proceeded at high pH, precluding possible oxidation of thioglycolic acid reagent. The unreacted thioglycolic acid was removed by washing with water during the subsequent workup. Because this involved acidification (to pH 1−2) of the reaction mixture in aqueous alcohol, ca. 20% esterification usually occurred (on the basis of relative integrations in the ^{1}H NMR spectra). Since our target was complete esterification, the carboxylic acid terminal dendrimers were not isolated. Rather, acid-catalyzed esterification of the partly acid terminated dendrimers was continued. The methylene signals of $SiMe_2CH_2Cl$ in the ^{1}H and ^{13}C NMR spectra of **1**−**3** were shifted from δ 2.80 (s, ^{1}H) and δ 30.4 (^{13}C) ppm to δ 1.95 and δ 41.3 ppm, respectively, in those of **4**−**6**. Complete conversion of **3** to **6** occurred over a longer reaction time (ca. 72 h) than for the conversion of **1** to **4** or **2** to **5** (ca. 8 and 24 h, respectively). These results are comparable with those of closely related compounds.[15] The compositions of **4**−**6** (Figure 2) were confirmed by elemental analysis. Atmospheric pressure chemical ionization mass spectrometry (APcI-MS) showed the M^+ signal for **4** at *m*/*z* 961. When the methanol solution of **5** was spiked with silver triflate, the $(M + Ag)^+$ peak was seen at *m*/*z* 2343 in electrospray MS.

It is noteworthy that repeated attempts to react thioglycolic acid with $Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2SiMe_2CH_2Cl)_3]_4$[21] at 90 °C over several days did not succeed. Although it is not clear why reaction does not proceed, no mercapto-functional carbosilane dendrimers have been synthesized from a precursor with $-Si[(CH_2)_nSiMe_2Cl]_3$ terminal groups. At least, one methyl group was present in the $-SiMe[(CH_2)_nSiMe_2CH_2SCH_2R]_2$- or $-SiMe_2[(CH_2)_nSiMe_2CH_2SCH_2R]$-type compounds known to date.[15]

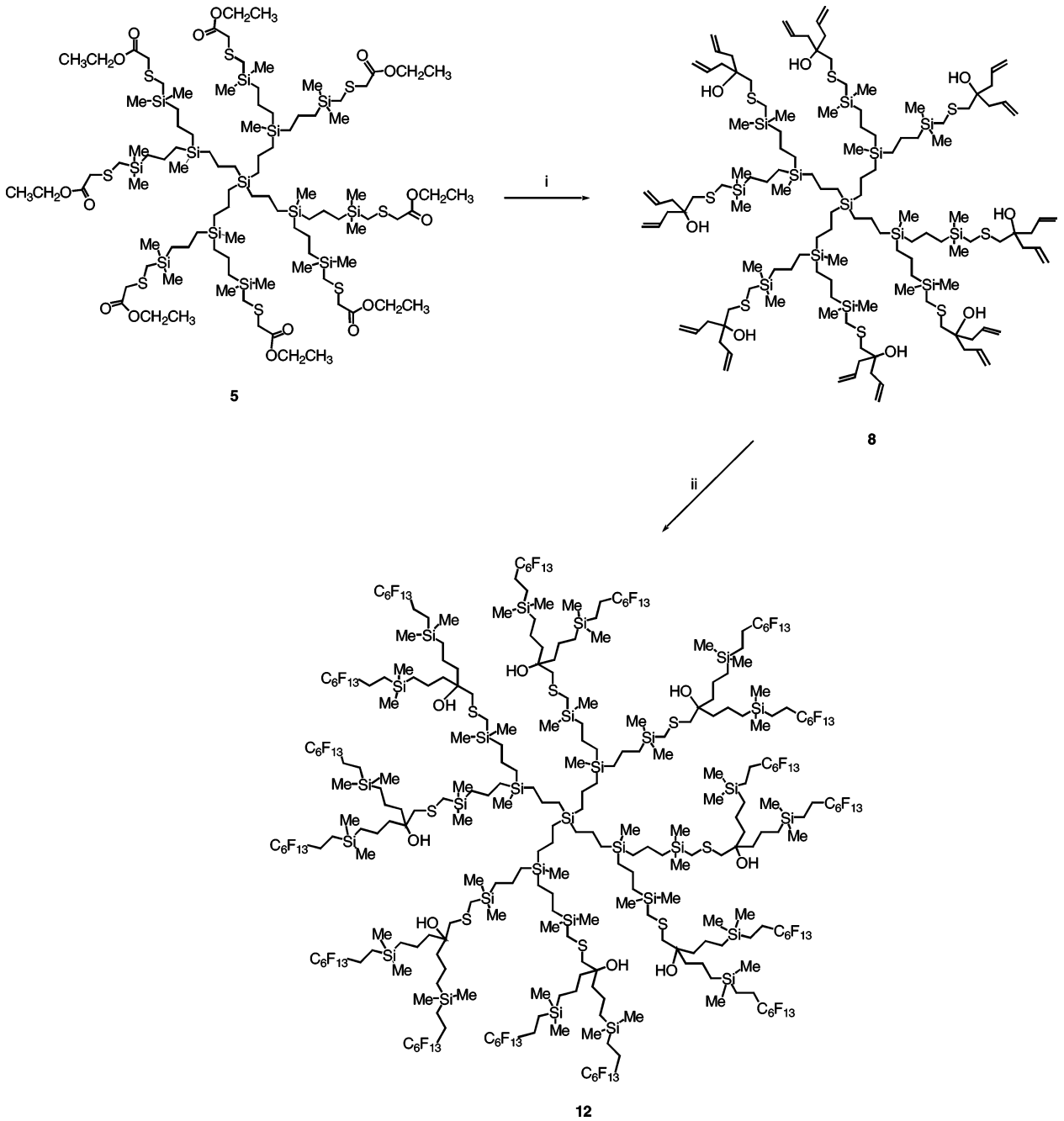
Compounds **4**−**6** were useful templates for the syntheses of the hydroxy-functional dendrimers **7**−**10** in Schemes 1−3. The carboxylic ester moieties in **4**−**6** underwent reactions with either allylmagnesium bromide or 1,1,2-trifluorobut-1-enyl-4-magnesium bromide to give **7**−**9** or **10**. The Grignard reagents used in this paper were selected merely as representatives of many analogues possible.

Scheme 1[a]



[a] Reagents and conditions: (i) CH_2=$CHCH_2MgBr$/THF/25 °C, 2 h; (ii) CF_2=$CFCH_2CH_2CH_2MgBr$/THF/25 °C, 2 h; (iii) $C_6F_{13}CH_2CH_2SiMe_2H$/THF/$[H_2PtCl_6 \cdot xH_2O]$/reflux, 18 h.

Scheme 2[a]



[a] Reagents and conditions: (i) $CH_2{=}CHCH_2MgBr$/THF/40 °C, 2 h; (ii) $C_6F_{13}CH_2CH_2SiMe_2H$/[$H_2PtCl_6{\cdot}xH_2O$]/reflux, 18 h.

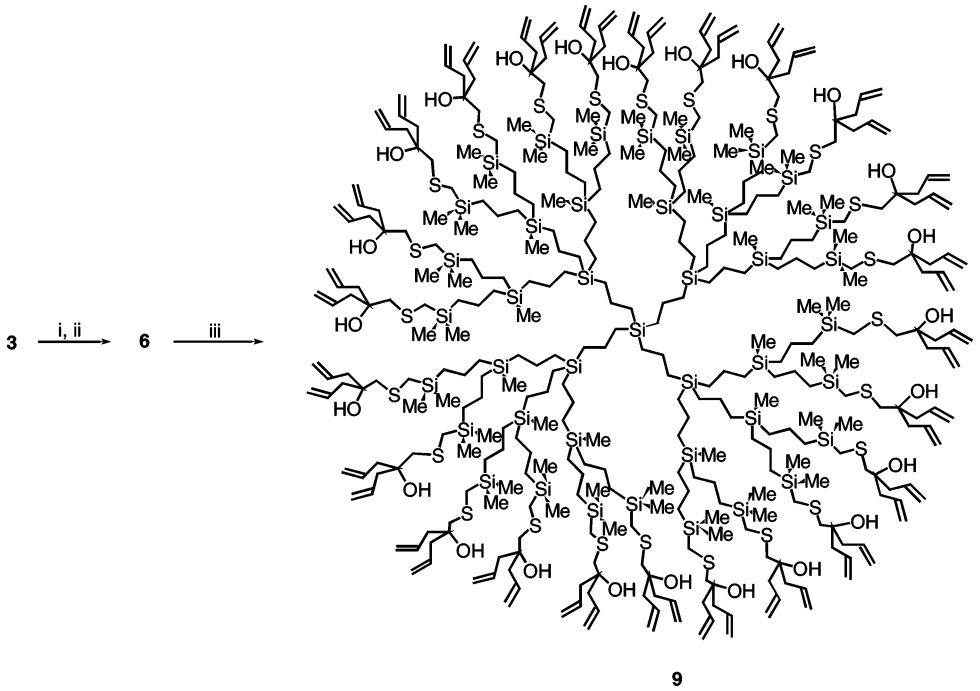
Evidence from NMR spectroscopy confirms that complete reaction of the ester groups was achieved, and gave the respective tertiary alcohols **7**−**10**. Formation of **7**−**10** was accompanied by the disappearance of the ethoxy signals at δ 1.32 (CH_3) and 4.20 (CH_2O) ppm in the ^{1}H NMR spectra and at δ 14.0 (CH_3) and 61.0 (CH_2O) ppm that were present in the ^{13}C NMR spectra of **4**−**6**. New signals for the respective organic moiety, either $CH_2CH{=}CH_2$ or $CH_2CH_2CF{=}CF_2$, were seen.

The C=O signals of ester groups seen in the ^{13}C NMR spectra of **4**−**6** at ca. δ 170 ppm disappeared, and new signals at ca. δ 73.0 ppm were found. This is indicative of new tertiary alcohol carbon atoms in **7**−**10**. The conversions of **4**−**6** to **7**−**9**, respectively, were also accompanied by changes in the chemical shifts for $SiMe_2CH_2SCH_2$– with magnitudes of Δ = ca. −0.49 ppm (^{1}H) and +9.6 ppm (^{13}C) in their NMR spectra. The NMR spectra did not reflect any significant changes for the other proton and carbon atoms of the moiety as a result of this transformation.

During the conversion of **4**−**6** to **7**−**9**, the intermediates were polymagnesium bromides (Figure 3, left) that were subsequently acid-hydrolyzed to give the respective polyols. The polymagnesium bromides were stable white solids at room temperature or waxy when warmed to 40 °C in ethyl ether or in THF. The polyols **7**−**9** reacted with potassium hydride to form the polypotassium derivatives (Figure 3, right). However, the polypotassium salts were poor nucleophiles and did not react with chlorotrimethylsilane and alkyl halides.

Very little or no reaction of the ester groups with Grignard or organolithium reagents at 0 °C or lower temperatures was observed; e.g., the ester groups did not react with perfluoroalkylmagnesium halides[18a] with

Scheme 3[a]



[a] Reagents and conditions: (i) $HSCH_2CH_2COOH/KOH/EtOH/H_2O/80$ °C, 24 h; (ii) catalytic $H_2SO_4/EtOH$/reflux, 8 h; (iii) $CH_2{=}CHCH_2MgBr/THF/40$ °C, 2 h.

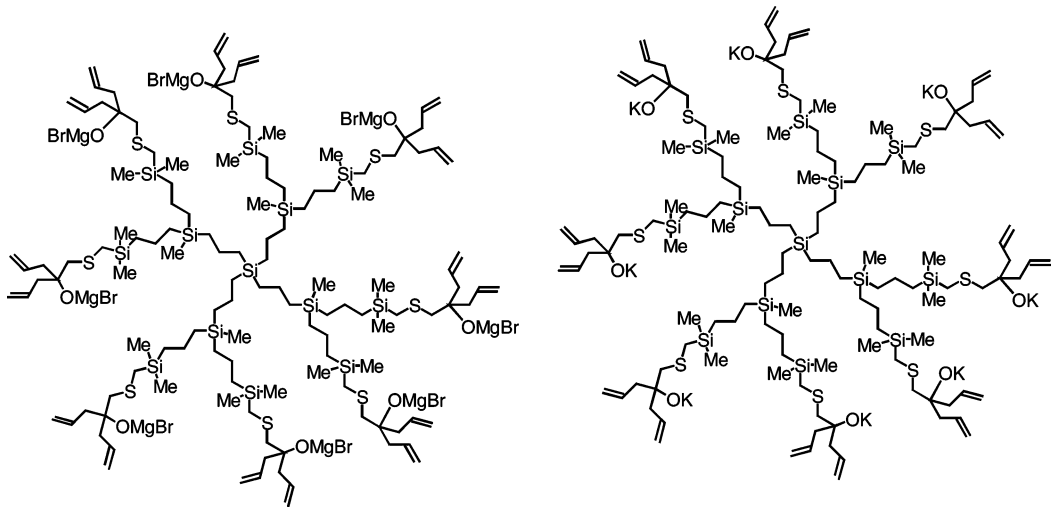


Figure 3.

stirring at between −50 and −10 °C over 6 h. They were unreactive toward *n*-butyllithium under the same conditions.

Although the reactions of **4** with Grignard reagents to form **7** and **10** proceeded at 25 °C, complete reaction of **5** and **6** required 40 °C for complete transformation of the ester groups to the allyl derivatives **8** and **9** to occur.

The Grignard reagents of polyfluorinated alkyl halides can also be reacted with the esters to form stable analogous polyols. For example, the reaction of 1,1,2-trifluorobut-1-enyl-4-magnesium bromide, $CF_2{=}CFCH_2$-CH_2MgBr, with **4** resulted in **10**. The hydrolysis of $BrC^aH^a{}_2C^bH^b{}_2CF{=}CF_2$ to $C(OH)(C^aH^a{}_2C^bH^b{}_2CF{=}CF_2)_2$ in **10** was accompanied by changes in NMR shifts: Δ(chemical shift) = −1.83 ppm (^{1}H) and −6.2 ppm (^{13}C) for $C^aH^a{}_2$ and −0.53 ppm (^{1}H) and +4.6 ppm for $C^bH^b{}_2$.

When **4** was reacted with freshly prepared pentafluorophenylmagnesium bromide in THF, the changes in the ^{1}H and ^{13}C NMR spectra of the product indicated that the ester function had reacted completely. However, the ^{19}F NMR spectrum showed a number of new and unexpected signals. No attempt was made to purify the crude product by chromatography. Although the reason for this observation is not clear, the fluorine atoms in the perfluorophenyl group are known to be very susceptible to nucleophilic attack.[18]

We also investigated the use of trifluoromethyl(trimethyl)silane to effect possible mono- or bis(trifluoromethylation) of esters.[23] The expected CsF-catalyzed reaction of 1:1 Me_3SiCF_3/COOEt with **4**−**6** in MeCN (or THF) at 25 °C or at reflux did not result in the transformation of COOEt to $-C(O)CF_3$ or $-C(OH)(CF_3)_2$ derivatives. Nor did the transformation occur in nonpolar hydrocarbons, such as pentane, hexane, or cyclohexane. Others have observed that, even in the presence of a fluoride ion catalyst, reaction of Me_3SiCF_3 with nonactivated esters was sluggish at room temperature.[24]

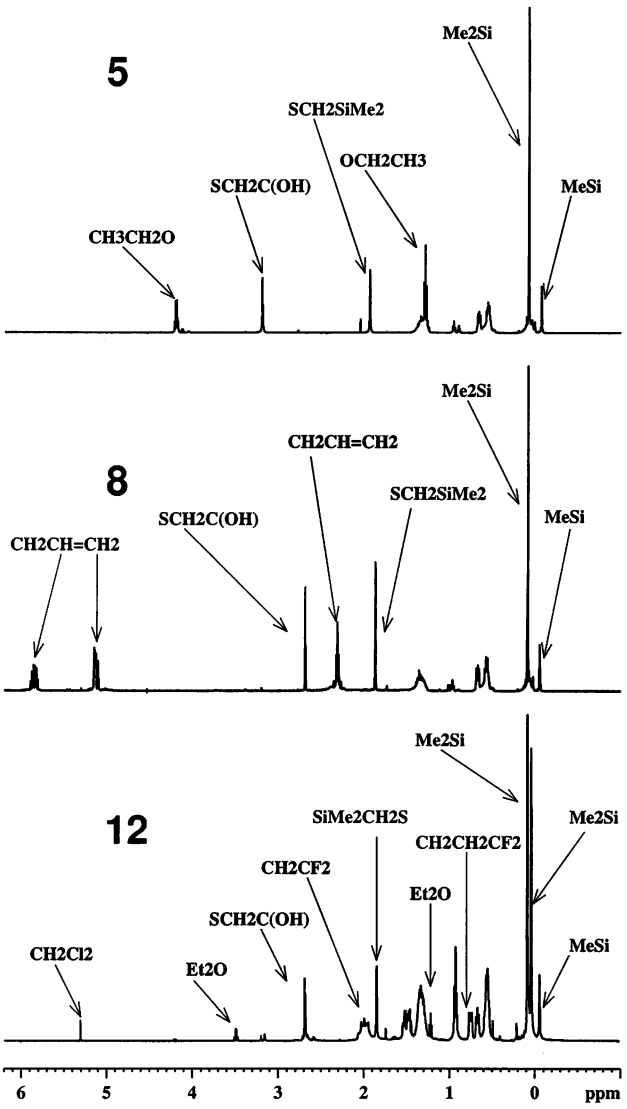


Figure 4. ^{1}H NMR spectra of **5**, **8**, and **12**.

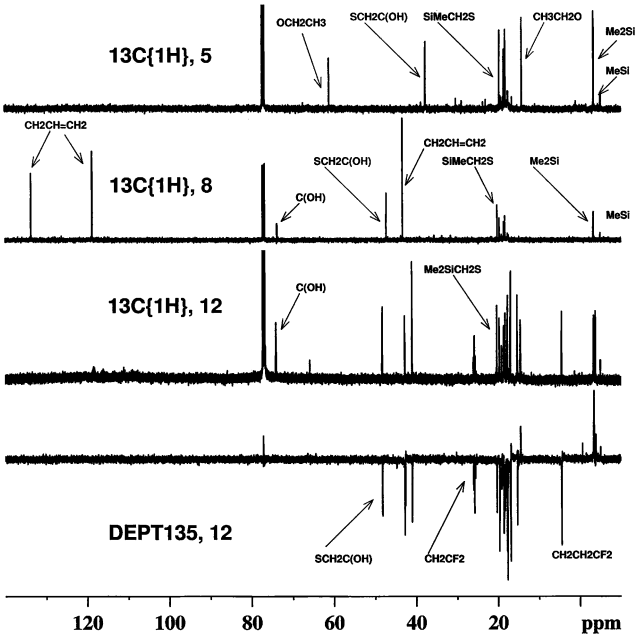


Figure 5. ^{13}C NMR spectra of **5**, **8**, and **12**.

Reaction did not occur between **7**−**9** and hexamethyldisilazane to produce the respective trimethylsilyl ethers. Also, when the mixture of **7**, **8**, or **9** and $C_6F_{13}CH_2CH_2SiMe_2H$ in THF was stirred at reflux for 24 h, NMR spectral evidence showed that no reaction had occurred. Although not unexpected for teriary alkoxides, the results indicated that the dendrimers **7**−**9** are poor nucleophiles.

The chloroplatinic acid (CPA)-catalyzed hydrosilylation reaction of **7** and **8** with $C_6F_{13}CH_2CH_2SiMe_2H$ proceeded in THF over 18 h and gave **11** and **12**, respectively. Free radical conditions did not trigger the conversion of tertiary alcohols to silyl ethers in similar reactions.[25] The volatile materials were removed in vacuo, leaving a residue of crude **11** and **12** that were purified by column chromatographic elution with pentane, dichloromethane, and diethyl ether. The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were useful for the characterization of both compounds.

Several NMR experiments have been used to determine the structure of the dendrimers. While it does not confirm the molecular weight, NMR has become a strong tool for establishing bonds and linkages in new types of dendrimers. Mass spectrometry (MALDI-TOF, electrospray, APcI, etc.) and GPC combined with light scattering (SANSor SAXS) still remain invaluable techniques for the determination of molecular weights and sizes of dendrimers.[13,15,17,26,27]

Many possible complex combinations of reactions can occur during the synthesis of carbosilane dendrimers, ranging from a mixture of α/β-addition during hydrosilylation reactions, to C−C and other bond cleavage, to incomplete derivation of the terminal reactive sites, and to folding inward of terminal groups or chains.[15,28] These phenomena are more prevalent in the higher (third and fourth) generation carbosilane dendrimers. Hence, even when MS and combustion analysis confirm their composition, NMR spectra of the dendrimers can be used to evaluate the structural defects that may have occurred during their syntheses.[28a,29]

Available literature on detailed NMR studies of organometallic dendrimers have been limited to the hydrides, i.e., those terminating in $-SiH_3$, $-SiMeH_2$, $-SiMe_2H$, and $-SnH_3$ groups in the zeroth-, first-, and second-generation dendrimers.[30,31] Although third- and fourth-generation dendrimers are known,[11a,26] there are no detailed NMR studies of their structures. This is, perhaps, because of the increasing complexity in the spectra obtained.

We undertook a detailed NMR spectral study of **12** (Scheme 2), a second-generation dendrimer with a multifunctional periphery. This involved the 1D ^{1}H, ^{13}C, and ^{13}C 135-DEPT spectra, as well as 2D ^{1}H/^{1}H, 2D ^{1}H/^{13}C, heteronuclear multiple quantum (HMQC), and heteronuclear multiple bond (HMBC) correlation experiments.[29] Comparisons of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **5**, **8**, and **12** are shown in Figures 4−6, respectively.

Despite chromatographic purification, the ^{13}C NMR spectrum of **12** showed that the combination of α- and β-addition reactions occurred during CPA-catalyzed reaction of **8** with $C_6F_{13}CH_2CH_2SiMe_2H$. Two quaternary carbon signals were seen at δ 74.8 and 74.9 ppm, which indicated that there were two types of neighbors to the carbon atom in the *C*OH groups in **12**. The related signal in the ^{13}C spectrum of **8** was a singlet. Separation of the isomers by column chromatography was not

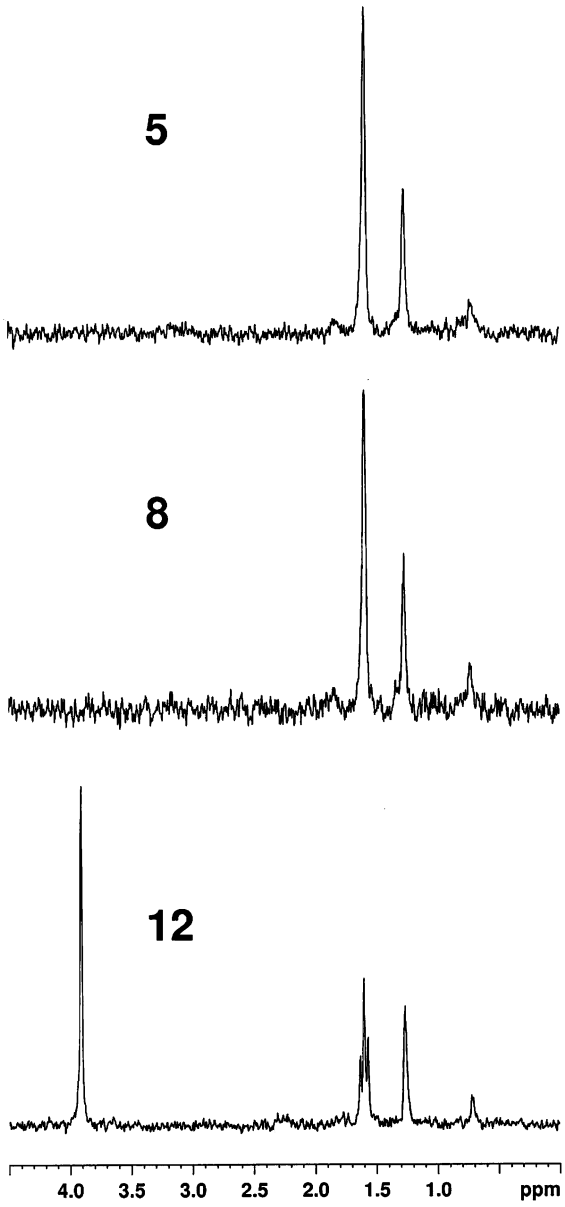


Figure 6. ^{29}Si NMR spectra of **5**, **8**, and **12**.

achieved. Further evidence for the α-addition was obtained on the basis of the two CH signals in the ^{13}C DEPT at δ 15.4 and 15.5 ppm.

There was only one set of $-CH_2SiMe_2C^aH_2C^bH_2C_6F_{13}$ signals at 5.3 (C^a) and 26.7 (t, $J_{C-F} = 23$ Hz) (C^b), and no evidence for the formation of silyl ether, i.e., $-OSiMe_2C^aH_2C^bH_2C_6F_{13}$. The C^a and C^b signals are very sensitive to the substituent X in $XSiMe_2C^aH_2C^bH_2C_6F_{13}$. The three types of *Me*Si in **12** were seen in the ^{1}H and ^{13}C/^{13}C DEPT spectra. The integration of the corresponding signals in the ^{1}H NMR spectrum indicated a ratio of 1:4:8 for Si*Me*, SiMe_2CH_2S, and SiMe_2-$CH_2CH_2C_6F_{13}$. These indicate that the dendritic architecture was as expected for **12**. Supporting evidence for this was found in the ^{29}Si NMR spectral signals at δ 0.72, 1.26, 1.60, and 3.90 ppm. The first three signals were seen in the spectra of the precursors **5** and **8**. However, the fourth resulted from hydrosilylation of terminal olefins in **8** by $HSiMe_2CH_2CH_2C_6F_{13}$ [with δ(*Si*H) at −11.0 ppm]. The eight silicon atoms responsible for the signal at δ 1.60 ppm were no more symmetric in the ^{29}Si NMR spectrum of **12**, and resulted in three signals with very close chemical shifts. No other signal was seen in the ^{29}Si NMR spectrum of **12**.

The new bond formed by the hydrosilylation of the olefins in **8** and $C_6F_{13}CH_2CH_2Si-H$ also resulted in new signals in the region between δ 15 ppm and δ 21 ppm in the ^{13}C NMR spectrum of **12**. Thirteen CH_2 signals were found in the ^{13}C 135-DEPT spectrum. It is the most complex section of the ^{13}C spectrum. The types of addition expected to produce the multiple signals are illustrated in Scheme 4.

The two different methylene groups of the $(-CH_2)_2$-COH moiety in **12** were seen in the ^{13}C NMR spectrum as signals at δ 41.9 and 43.7 ppm. These possibilities resulted in a rather large number of signals between δ 16 ppm and δ 20 ppm in the ^{13}C spectrum of **12**.

The "fingerprint signals", i.e, $-SiMe_2C^aH_2SC^bH_2C$-(OH)−, were observed in the spectrum of **12**. The respective carbon signals appeared as well-resolved singlets at δ 21.2 (a) and 49.1 (b) ppm [cf. δ 20.3 and 47.3 ppm, respectively, in the ^{13}C spectrum of **8**]. This evidence confirms that the dendritic architecture of the core has remained intact. When compared to those of **5** and **8**, the different reactions that occurred for the transformation of **8** to **12** did not alter the chemical shifts of the carbon atoms in this link. The assignments of signals in the ^{1}H NMR spectra was achieved by combining ^{13}C 135-DEPT spectra with 2D ^{1}H/^{13}C correlation, 2D ^{1}H/^{1}H correlation, HMBC, and HMQC.

Molecular weight data were obtained from mass spectral characterizations of some of the dendrimers by either FAB+, electrospray, APcI, and MALDI-TOF mass spectrometry or a combination of more than one of them, and the results of these are summarized in the Experimental Section.

Thermal Studies. A summary of the data obtained from DSC and the TGA thermograms of the amphiphilic carbosilane dendrimers is reported in Table 1.

The results in the TGA columns show that the thermal stability increased with generation number [**7** (zeroth) < **8** (first) < **9** (second)], and that polyfluorination increased the thermal stability [**10** and **11** derived from **7**, and **12** from **8**]. Although, **7**−**12** were liquids, none showed a phase transition between −80 and +100 °C. However, they lose a significant percentage of weight between 100 and 200 °C.

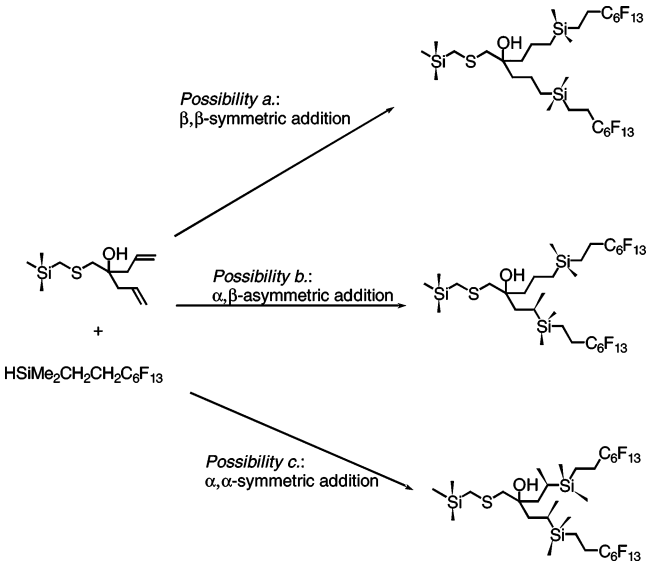
According to the DSC thermograms, only **11** of **7**−**12** has a glass transition temperature that is observed at −40.8 °C. Some phase transitions occurred in the 100−300 °C range. However, when the temperatures for phase transitions are compared to weight loss patterns in the TGA columns, it appears that some of the phase transitions are a result of fusion, rather than structural rearrangement. Loss of water, oxidation of sulfur, and loss of SO_2, as well as cleavage of the perfluoroalkyl chains, are assumed to be the main products of the degradation process. Hence, the utility of these compounds is limited to temperatures below 100 °C, where no phase transitions occur.

Solubility and Solubilization Properties. In view of future applications for these amphiphilic carbosilane dendrimers, an evaluation of their solubility and surfactant properties was explored. Compounds **7**−**12** were generally soluble in most organic solvents, including nonpolar hydrocarbons and more polar ones, such as diethyl ether, dichloromethane, acetonitrile, methanol, etc., but not in water. However, hydrocarbons did not elute from a silica gel column. Diethyl ether was a good

Table 1. Summary of Data from DSC and TGA Thermograms for the Carbosilane Dendrimers

	DSC			TGA			
				total percent loss at various temperatures			
compd	T_m	T_g	onset of decomposition (°C)	120 °C	200 °C	300°C	500 °C
7	149, 205		210	7	19	45	>90
8			220	2	13	27	>93
9	101, 168, 174		240	<1	2	29	>82
10	113		180	5	23	45	>90
11	133	−40.8	190	4	26	40	>90
12	242, 333		220	<1	7	63	>89

Scheme 4

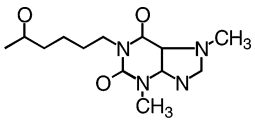


eluent for all of them in silica gel column chromatography. The OH groups in these compounds can be expected to form hydrogen-bonding interactions and weakly associate with water and with many organic compounds.[30,31]

The nonfluorinated dendrimers **7**−**9** were soluble in hexafluorobenzene (C_6F_6), but not in perfluorooctyl bromide ($C_8F_{17}Br$) and perfluorodecalin ($C_{10}F_{18}$). The polyfluorinated dendrimer **12** was soluble in hexafluorobenzene and formed stable emulsions with perfluorooctyl bromide ($C_8F_{17}Br$) and perfluorodecalin ($C_{10}F_{18}$). Therefore, we evaluated the dendrimers as surfactants for solubilizing a nonfluorinated antibiotic, pentoxyfylline (Figure 7), in these solvents.

Pentoxyfylline was found to be soluble in hexafluorobenzene and in perfluorodecalin, but not in perfluorooctyl bromide. Evidence for this was obtained from the IR spectrum of the residue from the perfluoro solvent phase on a KBr plate. Infrared spectra showed that there was no transfer to any of the perfluoro solvents when shaken with a 1 M aqueous solution of the antibiotic.

However, when a 5% solution or emulsion of dendrimer **7**−**9** in perfluoro solvent (hexafluorobenzene, perfluorodecalin, or perfluorooctyl bromide) was shaken with the 1 M aqueous solution of pentoxyfylline, some



Pentoxyfylline

Figure 7.

of the antibiotic did transfer to hexafluorobenzene. Compound **12** facilitated a similar transfer into hexafluorobenzene and perfluorodecalin, but not into perfluorooctyl bromide. The transfer is likely facilitated by hydrogen-bonding interactions.

Conclusion

Using very stable dendrimer cores, we have synthesized polyfluorinated hydroxy-functional carbosilane dendrimers. Our work introduces a new category of amphiphilic carbosilane dendrimers with multifunctional terminal groups. Property modification by polyfluoroalkyl substituents affords this new class of dendrimers unique potential for application in surfactant science, catalysis, surface-supported synthesis, and remediation studies in environmental chemistry, and as models in drug delivery research. Most of the known amphiphilic dendrimers have organic cores, but their application is not entirely universal. For example, the potential reactivity of such functional groups does limit their applications in catalysis. Our new carbosilane dendrimers combine an inert core with a amphiphilic exterior, and many analogues can be synthesized to reflect potential target applications. We expect our results to lead us as well as others to synthesize other interesting analogues.

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(21) This compound was synthesized according to the procedure described for the syntheses of **1**−**3** in this work. The spectral data follow. NMR ($CDCl_3$) (ppm): ^{1}H, δ 0.04 (s, 24H, Si*Me*), 0.10 (s, 24H, SiMe_2), 0.56 and 0.71 [dt, 160H, Si($CH_2CH_2CH_2$-Si)], 1.37 [m 80H, Si($CH_2CH_2CH_2$Si)], 2.79 [s, 48H, SiMe_2CH_2-Cl]; ^{13}C, δ −4.3, 17.8, 18.5, 19.3, 30.4 (J_{Si-C} = 13 Hz); ^{29}Si, δ 0.58, 1.29, 3.22. MS: *m*/*z* calcd ($C_{84}H_{192}Si_{17}Cl_{12}$) 2105.31, found (MALDI-TOF) 2178.

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