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Synthesis of model organosiloxanes containing perfluoroether side-chains†

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A series of organotrisiloxanes $[(Me_3SiO)_2MeSi(CH_2)_nO(CH_2)_mR_f]$, ($n=3$, $m=1$, $R_f=CF_3$; $n=3$, $m=2$, $R_f=C_4F_9$, C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$, C_7F_{15}; $n=5$, $m=1$, $R_f=CF_3$; $n=10$, $m=0$, $R_f=C_3HF_6$; $n=10$, $m=1$, $R_f=CF_3$) have been prepared by the [Pt(cyclooctadiene)Cl_2] catalysed hydrosilylation reaction between heptamethyltrisiloxane and $CH_2=CH(CH_2)_{n-2}O(CH_2)_mR_f$. Yields are dependent upon the alkene chain length and degree of branching of the R_f group. Isomeric products $[(Me_3SiO)_2MeSi(CH_2)_3OCH_2CF_3]$ and $[(Me_3SiO)_2MeSiCH(Me)CH_2OCH_2CF_3]$ were detected in reactions involving $CH_2=CHCH_2OCH_2CF_3$ only.

Introduction

Organofunctional trisiloxanes of the type $[(Me_3SiO)_2MeSi(CH_2)_nR]$ have for some time been used as models for catalyst supports[1,2] (R = –PPh_2, –SPh, –C_5H_4N, –CN, –$CH=CH_2$, –Ph), and for selective fluid extractants[3,4] (R = –crown ethers, –NMe_2, –OEt). More recently trisiloxanes of this stoichiometry in which R = –polyoxyethylene,[5,6] –$OCH_2CH(OH)CH_2NMe_3^+Cl^-$,[7] and –$NMe_2(CH_2)_2OH^+X^-$,[8] have been shown to be excellent surfactants which promote the rapid spreading of dilute aqueous solutions on surfaces. Considerable attention has now centred on fluoroalkyl modified siloxanes which have been shown to be particularly effective spreading agents for oils.[9,10] Although poly(methyltrifluoropropylsiloxane) has been commercially available for several decades, the fluorine content of this polymer is too low to reveal the full potential of more highly fluorinated siloxanes as low surface tension materials.[11] Consequently in order to accurately evaluate the thermal and surface modifying properties of perfluoroalkyl-functionalised siloxanes containing side-arm substituents with differing loadings of fluorine, high-yielding synthetic procedures capable of wide applicability are required. The three procedures (A), (B) and (C) which are generally used for the preparation of side-arm functionalised trisiloxanes are illustrated below.

Method A

$$2Me_3SiX + MeSi(\{CH_2\}_nR)X_2 \xrightarrow{\text{hydrolysis}} (Me_3SiO)_2MeSi(CH_2)_nR + 4HX\ (X = \text{halide})$$

Method B

$$(Me_3SiO)_2MeSi(CH_2)_nX + R^- \longrightarrow (Me_3SiO)_2MeSi(CH_2)_nR + X^-$$

Method C

$$(Me_3SiO)_2MeSiH + CH_2=CH(CH_2)_{n-2}R \xrightarrow{\text{catalyst}} (Me_3SiO)_2MeSi(CH_2)_nR$$

The extreme reactivity of chlorosiloxanes towards –OH and –NH containing groups in the substituent R, the difficulty of preparing the precursor $MeSi(\{CH_2\}_nR)X_2$, as well as multiple product formation during the hydrolytic process, has limited the application of method (A). Nucleophilic attack on the siloxane backbone as well as at the C–X linkage is a disadvantage of method (B). The ready commercial availability of 1,1,1,3,5,5,5,-heptamethyltrisiloxane, together with an expansion in the range of effective hydrosilylation catalysts available,[12] has resulted in method (C) being more frequently used. The availability of polymeric analogues of heptamethyltrisiloxane, $Me_3SiO(MeSi(H)O)_nSiMe_3$, as well as co-polymers $Me_3SiO(MeSi(H)O)_n(Me_2SiO)_mSiMe_3$ with varying $n:m$ ratios also allows this methodology to be applied to the derivatisation of siloxane polymers. The main disadvantages of hydrosilylation are attributable to catalyst poisoning and the simultaneous formation of both Markownikoff and anti-Markownikoff products.[13] This latter complication has only infrequently been acknowledged in either functional tri- or poly-siloxane synthesis.

This paper describes the synthesis and characterisation of a series of trisiloxanes containing a range of fluorinated side-arm substituents separated in each case from the central silicon atom by an alkenyloxy spacer chain (Fig. 1). NMR has been used to determine the isomeric composition of the products.

Experimental

General

Solvents for reactions, extractions and chromatography were dried and purified using standard procedures: toluene, tetrahydrofuran (sodium–benzophenone); dichloromethane, chloroform (Na_2SO_4–$MgSO_4$). All other chemicals were used as received. Analytical TLC was carried out using Merck Kieselgel 60F plates. Visualisation was accomplished by UV light, iodine, phosphomolybdic acid or potassium permanga-

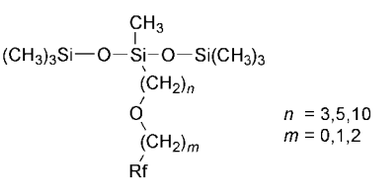

Fig. 1 Perfluoroether substituted trisiloxanes.

†Details of the fragments in the MS spectrum of $Me_3SiOSiMe(R)OSiMe_3$ are available as supplementary data. For direct electronic access see http://rsc.org/suppdata/jm/b0/b001376p/

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nate. Column chromatography was performed using Merck Silica Gel 60 (0.040–0.063 mm). Kugelrohr distillations were carried out in a Büchi GKR-51 apparatus and the boiling points given correspond to the Kugelrohr oven temperature.

NMR data were recorded on JEOL GX270 (270.05 MHz ^{1}H; 67.8 MHz ^{13}C) and EX400 (399.65 MHz ^{1}H; 100.4 MHz ^{13}C; 376.05 MHz ^{19}F; 79.3 MHz ^{29}Si) instruments. $CFCl_3$ was used as an internal standard for ^{19}F NMR. Residual $CHCl_3$ was used as an internal standard for ^{1}H and ^{13}C NMR samples that contained Si atoms. Tetramethylsilane was used as an internal standard for other compounds. Mass spectral data were obtained using a VG 7070E instrument. Elemental CHN analyses were determined by the Analytical Services Unit, University of Bath.

Syntheses

General procedure (a) for fluorinated alkenes F1–6 and F9. Procedure (a) is based on the method used by Boutevin *et al.*[14] for the preparation of several fluorinated allylic ethers and thioethers.

A solution of the appropriate perfluoro-alcohol, tetrabutylammonium hydrogen sulfate (TBAHS) and 40% sodium hydroxide were stirred at high speed for 20 min in a 100 ml round-bottomed flask fitted with a condenser and an overhead stirrer. A 50% molar excess of bromoalkene was added dropwise, and the mixture heated at 65 °C for 16 hours. The cooled solution was treated with dichloromethane (20 ml), and extracted with water (4 × 20 ml) until the aqueous layer was neutral to litmus paper. The organic layer was dried over sodium sulfate for 24 hours, then filtered and the solvent removed by rotary evaporation to leave the crude product. The product was purified by column chromatography using $CHCl_3$ as eluent. The residue left after removal of chloroform was finally distilled (Kugelrohr 50 °C/10 mmHg).

Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorohexane (F1). 1*H*,1*H*,2*H*,2*H*-Perfluorohexan-1-ol (6.12 g, 23.2 mmol), tetrabutylammonium hydrogen sulfate (0.75 g, 2.2 mmol) and 40% sodium hydroxide solution (25 ml) were reacted with allyl bromide (4.21 g, 34.8 mmol). Product **F1** was isolated as a colourless oil (5.3 g, 76%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.32–2.52 (2H, tt, $J_{H-H}=7.0$ Hz, $J_{H-F}=18.7$ Hz, CF_2CH_2), 3.70–3.76 (2H, t, $J=7.0$ Hz, CH_2-O), 4.00 (2H, d, $J=5.5$ Hz, O-CH_2), 5.20–5.33 (2H, m, CH=CH_2), 5.83–5.97 (1H, m, CH=CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.5–32.0 (t, $J=21.2$ Hz, CF_2-CH_2), 62.0 (-CH_2-O), 72.2 (-O-CH_2), 117.3 (-CH=CH_2), 134.0 (-CH=CH_2). Anal. Calc. for $C_9H_9F_9O$: C, 35.5; H, 2.98. Found: C, 34.8; H, 2.91%.

Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorooctane (F2). 1*H*,1*H*,2*H*,2*H*-Perfluorooctan-1-ol (10.9 g, 29.9 mmol), tetrabutylammonium hydrogen sulfate (1.01 g, 2.91 mmol) and 40% sodium hydroxide solution (25 ml) were reacted with allyl bromide (5.45 g, 4.50 mmol). Product **F2** was obtained as a colourless oil (11.3 g, 87%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.35–2.48 (2H, tt, $J_{H-H}=7.0$ Hz, $J_{H-F}=18.7$ Hz, CF_2CH_2), 3.70–3.74 (2H, t, $J=6.7$ Hz, CH_2-O), 3.99–4.02 (2H, dt, $J=5.7$ Hz, 1.3 Hz, O-CH_2), 5.19–5.32 (2H, m, CH=CH_2), 5.85–5.95 (1H, m, CH=CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.2 (t, $J=22.0$ Hz, CF_2-CH_2), 61.8 (-CH_2-O), 72.2 (-O-CH_2), 117.1 (-CH=CH_2), 134.2 (-CH=CH_2). Anal. Calc. for $C_{11}H_9F_{13}O$: C, 32.7; H, 2.25. Found: C, 32.6; H, 2.39%.

Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorodecane (F3). 1*H*,1*H*,2*H*,2*H*-Perfluorodecan-1-ol (7.05 g, 15.2 mmol), tetrabutylammonium hydrogen sulfate (0.40 g, 1.2 mmol) and 40% sodium hydroxide solution (20 ml) were reacted with allyl bromide (2.76 g, 22.8 mmol). The alkene **F3** was isolated as a colourless oil (6.35 g, 83%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.42 (2H, tt, $J_{H-H}=7.0$ Hz, $J_{H-F}=18.7$ Hz, CF_2CH_2), 3.73 (2H, t, $J=7.0$ Hz, CH_2-O), 4.01 (2H, dt, $J=5.5$ Hz, 1.3 Hz, O-CH_2), 5.16–5.34 (2H, m, CH=CH_2), 5.83–5.99 (1H, m, CH=CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.4–31.9 (t, $J=21.5$ Hz, CF_2-CH_2), 61.9 (-CH_2-O), 72.1 (-O-CH_2), 117.3 (-CH=CH_2), 133.9 (-CH=CH_2). Anal. Calc. for $C_{13}H_9F_{17}O$: C, 31.0; H, 1.80. Found: C, 29.2; H, 1.80%.

Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorododecane (F4). 1*H*,1*H*,2*H*,2*H*-Perfluorododecan-1-ol (4.40 g, 7.80 mmol), tetrabutylammonium hydrogen sulfate (0.26 g, 0.77 mmol), and 40% sodium hydroxide solution (20 ml) were reacted with allyl bromide (1.0 ml, 1.42 g, 11.7 mmol). Product **F4** was isolated as a white solid (3.35 g, 71%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.43 (2H, tt, $J_{H-H}=7.0$ Hz, $J_{H-F}=18.7$ Hz, CF_2CH_2), 3.73 (2H, t, $J=7.0$ Hz, CH_2-O), 4.01 (2H, dt, $J=5.2$ Hz, 1.5 Hz, O-CH_2), 5.19–5.34 (2H, m, CH=CH_2), 5.83–5.98 (1H, m, CH=CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 32.0 (CF_2-CH_2), 61.8 (-CH_2-O), 72.0 (-O-CH_2), 117.3 (-CH=CH_2), 133.8 (-CH=CH_2). Anal. Calc. for $C_{15}H_9F_{21}O$: C, 29.2; H, 1.54. Found: C, 29.8; H, 1.50%.

1,1,1-Trifluoroethoxypropene (F5). Method (a) except where noted. 2,2,2-Trifluoroethanol (10.0 g, 100 mmol), tetrabutylammonium hydrogen sulfate (3.4 g, 10.0 mmol), 40% sodium hydroxide solution (20 ml) and allyl bromide (18.2 g, 7.2 g, 150 mmol) were reacted as above. After reaction, xylene (20 ml) was added to the cooled solution prior to extraction with water (4 × 20 ml) until the aqueous layer was neutral to litmus paper. The organic layer was separated and dried over anhydrous sodium sulfate for 24 h. The product was distilled from the xylene after removal of sodium sulfate. Product **F5** was isolated as a colourless oil (10.4 g, 74%, bp 75 °C/750 mmHg, lit.,[14] 82 °C/720 mmHg). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.80–3.84 (2H, q, $J_{H-F}=8.9$ Hz, CF_3CH_2-), 4.13 (2H, dt, $J=5.8$ Hz, OCH_2), 5.15–5.40 (2H, m, =CH_2), 5.84–5.92 (1H, m, -CH=). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 66.6–67.6 (q, CF_2-CH_2-O-), 73.1 (-O-CH_2), 118.4 (-CH=CH_2), 133.0 (-CH=CH_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −74.79 to −74.76 (t, $J_{H-F}=7.9$ Hz, CF_3-). Anal. Calc. for $C_5H_7F_3O$: C, 42.9; H, 5.04. Found: C, 42.7; H, 5.13%.

3-(2,2,2-Trifluoroethoxy)pentene (F6). 2,2,2-Trifluoroethanol (3.10 g, 31.0 mmol), tetrabutylammonium hydrogen sulfate (1.30 g, 3.83 mmol), 40% sodium hydroxide solution (20 ml) were reacted with bromopentene (6.00 g, 40.3 mmol). After reaction dichloromethane (20 ml) was added to the cooled solution prior to extraction with water (4 × 20 ml) until the aqueous extract was neutral to litmus. The organic layer was separated and dried overnight over anhydrous sodium sulfate. Dichloromethane was first evaporated and the crude product distilled. Product **F6** was isolated as a colourless oil (1.7 g, 34%, bp 117–118 °C/750 mmHg). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.50–2.05 (4H, m, aliphatic -CH_2-), 3.60 (2H, t, $J=6.6$ Hz, OCH_2), 3.72–3.86 (2H, q, $J_{H-F}=8.8$ Hz, CF_3CH_2-), 4.9–5.1 (2H, m, =CH_2), 5.70–5.90 (1H, m, -CH=). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.3 (t, $J=21.4$ Hz, CF_2-CH_2), 61.8 (-CH_2-O), 71.9 (-O-CH_2), 117.0 (-CH=CH_2), 133.7 (-CH=CH_2). Anal. Calc. for $C_7H_{11}F_3O$: C, 50.0; H, 6.60. Found: C, 49.9; H, 6.62%.

Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluoro-9-methyldecane (F9). 1*H*,1*H*,2*H*,2*H*-Perfluoro-9-methyldecan-1-ol (1.0 g, 1.9 mmol), tetrabutylammonium hydrogen sulfate (0.10 g, 0.29 mmol), 40% sodium hydroxide solution (10 ml) were reacted with allyl bromide (0.35 g, 2.9 mmol). Product **F9** was isolated as a colourless oil (0.80 g, 76%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.42 (2H, tt, $J_{H-H}=7.0$ Hz, $J_{H-F}=18.7$ Hz, CF_2CH_2), 3.73 (2H, t, $J=7.0$ Hz, CH_2-O), 4.02 (2H, dt, $J=5.5$ Hz, 1.3 Hz, O-CH_2), 5.19–5.34 (2H, m, CH=CH_2), 5.83–

5.98 (1H, m, C*H*=CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 31.7–32.2 (t, $J=22.0$ Hz, CF_2-*C*H_2), 62.2 (-*C*H_2-O), 72.4 (-O-*C*H_2), 117.6 (-CH=*C*H_2), 134.2 (-*C*H=CH_2). Anal. Calc. for $C_{14}H_9F_{19}O$: C, 30.3; H, 1.64. Found: C, 29.7; H, 1.66%.

General procedure (b) for fluorinated alkenes (F7, F8)

The procedure reported by Falck *et al.*[15] for the preparation of unsymmetrical polyfluoroethers was adapted as noted below for the preparation of **F7** and **F8**.

The appropriate unsaturated alcohol, 1,1′-(azodicarbonyl)-dipiperidine (ADDP), dry toluene and tri-*n*-butylphosphine were reacted in a 500 ml round-bottomed flask at 65 °C for 10 min. Perfluoro-alcohol was then added slowly over a 5 min period, and the reaction mixture was heated for 16 hours. Toluene and other volatiles were removed by rotary evaporation from the cooled solution to leave a pale pink waxy solid. The product was first purified by column chromatography using hexane–ethyl acetate (4 : 1) as eluant. Final traces of contaminants were removed by column chromatography using a dichloromethane solvent system. After solvent removal the residue was distilled (Kugelrohr 120 °C/10 mmHg).

1′,1′,1′-Trifluoroethoxydec-9-ene (F7). Dec-9-en-1-ol (0.77 g, 4.9 mmol), 1,1′-(azodicarbonyl)dipiperidine (2.50 g, 9.90 mmol), dry toluene (150 ml) and tri-*n*-butylphosphine (2.0 g, 9.9 mmol) were reacted with 2,2,2-trifluoroethanol (9.9 g, 99 mmol). Product **F7** was isolated as a colourless oil (0.79 g, 67%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.23–1.43 (8H, m, $4\times$CH_2), 1.45–1.63 (4H, m, $2\times$CH_2), 1.9–2.5 (2H, m, CH_2=CH-CH_2), 3.59 (2H, t, $J=6.6$ Hz, CH_2-O), 3.79 (2H, q, $J_{H-F}=8.8$ Hz, O-CH_2-CF_3), 4.90–5.03 (2H, m, CH_2=), 5.73–5.88 (1H, m, CH_2=C*H*). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 25.6 (-*C*H_2), 29.0–29.4 (m, CF_3-*C*H_2), 33.7 (-*C*H_2), 72.8 (-*C*H_2-O-), 113.9 (-CH=*C*H_2), 138.9 (-*C*H=CH_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −74.7 (3F, t, $J_{H-F}=9.2$ Hz, CH_2CF_3). Anal. Calc. for $C_{12}H_{21}F_3O$: C, 60.5; H, 8.88. Found: C, 60.0; H, 8.82%.

1–(1′,1′,1′,3′,3′,3′-Hexafluoropropoxy)dec-9-ene (F8). Dec-9-en-1-ol (1.56 g, 10.0 mmol), 1,1′-(azodicarbonyl)dipiperidine (5.0 g, 20.0 mmol), dry toluene (200 ml) and tri-*n*-butylphosphine (4.0 g, 20.0 mmol) were reacted with 1,1,1,3,3,3-hexafluoroisopropanol (3.37 g, 20.0 mmol). Product **F8** was isolated as a colourless oil (1.67 g, 54%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.20–1.40 (12H, m, aliphatic $6\times$CH_2), 1.52–1.65 (2H, m, CH_2-CH_2), 3.77–3.86 (2H, t, $J=6.4$ Hz, -CH_2-O), 4.80–4.90 (1H, m, OC*H*-$(CF_3)_2$), 4.90–5.03 (2H, m, CH_2=), 5.73–5.88 (1H, m, CH_2=C*H*). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 28.9–29.5 (m, CF_3-*C*H_2), 33.9 (-*C*H_2), 75.6 (-*C*H_2-O-), 114.0 (-CH=*C*H_2), 139.0 (-*C*H=CH_2). Anal. Calc. for $C_{13}H_{20}F_6O$: C, 51.0; H, 6.58. Found: C, 50.0; H, 6.39%.

General method for trisiloxanes

A solution of 1,1,1,3,5,5,5-heptamethyltrisiloxane (4.40 mmol) in toluene (20 ml) was stirred in a nitrogen atmosphere and treated with the appropriate alkene (4.40–44.0 mmol). A solution of (cycloocta-1,5-diene)platinum dichloride (1.75×10^{-4} mmol) in dichloromethane (0.25 ml) was then added and the solution heated at 82 ± 1 °C for 12 h. A second portion of (cyclooctadiene)platinum dichloride (1.75×10^{-4} mmol) in dichloromethane (0.25 ml) was then added and heating was continued for a further 12 h. The reaction mixture was allowed to cool to ambient temperature and passed through a plug of Celite to remove catalyst residues. Solvent and unreacted volatile precursors were removed by evaporation under reduced pressure. Products **T5** and **T6** were finally distilled at low pressures.

3-(Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T1) from alkene (F1). Product **T1** was isolated as a colourless oil (2.36 g, 85%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.42–0.49 (2H, m, Si-CH_2), 1.54–1.65 (2H, m, Si-CH_2-CH_2), 2.33–2.47 (2H, m, CF_2-CH_2), 3.30 (2H, t, $J=7.0$ Hz, $R_fCH_2CH_2$-O), 3.65 (2H, t, $J=7.0$ Hz, O-CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 1.78 (Si-*C*H_3), 13.5 (Si-*C*H_2), 23.2 (Si-CH_2-*C*H_2), 31.5 (-CF_2-*C*H_2), 62.4 (-*C*H_2-O), 73.9 (-O-*C*H_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −81.7 (3F, t, $J_{F-F}=9.2$ Hz, CF_2CF_3), −113.2 to −114.3 (2F, br, CF_2CF_3), −125.2 (2F, s, $CF_2CF_2CF_3$), −126.6 (2F, t, $J_{F-H}=12.1$ Hz, CH_2CF_2). ^{29}Si-NMR (79.3 MHz, $CDCl_3$) δ 7.38 ($(CH_3)_3$-*Si*-O), −21.7 (O-*Si*$(CH_3)(CH_2)$-O). Anal. Calc. for $C_{16}H_{31}F_9O_3Si_3$: C, 36.5; H, 5.95. Found, C, 36.5; H, 6.13%.

3-(Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T2) from alkene (F2). Product **T2** was isolated as a colourless oil (2.80 g, 99%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.42–0.49 (2H, m, Si-CH_2), 1.53–1.65 (2H, m, Si-CH_2-CH_2), 2.33–2.40 (2H, m, CF_2-CH_2), 3.40 (2H, t, $J=7.0$ Hz, $R_fCH_2CH_2$-O), 3.70 (2H, t, $J=7.0$ Hz, O-CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 1.76 (Si-*C*H_3), 13.5 (Si-*C*H_2), 23.2 (Si-CH_2-*C*H_2), 31.6–31.9 (t, $J=22.0$ Hz, CF_2-*C*H_2), 62.4 (-*C*H_2-O), 73.9 (-O-*C*H_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −81.43 (3F, t, $J_{F-F}=9.3$ Hz, CF_2CF_3), −114.0 (2F, br, CF_2CF_3), −122.5 (2F, s, $CF_2CF_2CF_3$), −123.5 (2F, s, $CF_2CF_2CF_2CF_3$), −124.3 (2F, s, $CF_2(CF_2)_3CF_3$), −126.7 (2F, s, CH_2CF_2). ^{29}Si-NMR (79.3 MHz, $CDCl_3$) δ 7.38 ($(CH_3)_3$-*Si*-O), −21.7 (O-*Si*$(CH_3)(CH_2)$-O). Anal. Calc. for $C_{18}H_{31}F_{13}O_3Si_3$: C, 34.5; H, 5.00. Found: C, 35.4; H, 5.10%.

3-(Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T3) from alkene (F3). Product **T3** was isolated as a colourless oil (18.8 g, 81%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.44 (2H, m, Si-CH_2), 1.53–1.64 (2H, m, Si-CH_2-CH_2), 2.32–2.39 (2H, m, CF_2-CH_2), 3.40 (2H, t, $J=7.0$ Hz, $R_fCH_2CH_2$-O), 3.70 (2H, t, $J=7.0$ Hz, O-CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 1.75 (Si-*C*H_3), 13.5 (Si-*C*H_2), 23.2 (Si-CH_2-*C*H_2), 31.6 (t, $J=22.0$ Hz, CF_2-*C*H_2), 62.4 (-*C*H_2-O), 73.9 (-O-*C*H_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −81.41 (3F, s, CF_2CF_3), −114.0 (2F, s, CF_2CF_3), −122.3 (2F, s, $CF_2CF_2CF_3$), −122.5 (4F, s, $(CF_2)_2(CF_2)_2CF_3$), −123.3 (2F, s, $CF_2(CF_2)_4CF_3$), −124.2 (2F, s, $CF_2(CF_2)_5CF_3$), −126.7 (2F, s, CH_2CF_2). ^{29}Si-NMR (79.3 MHz, $CDCl_3$) δ 7.42 ($(CH_3)_3$-*Si*-O), −21.71 (O-*Si*$(CH_3)(CH_2)$-O). Anal. Calc. for $C_{20}H_{31}F_{17}O_3Si_3$: C, 33.1; H, 4.31. Found: C, 33.5; H, 4.61%.

3-(Propenyloxy-1*H*,1*H*,2*H*,2*H*-perfluorododecyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T4) from alkene (F4). Product **T4** was isolated as a white solid (0.83 g, 93%). ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.46 (2H, m, Si-CH_2), 1.56–1.62 (2H, m, Si-CH_2-CH_2), 2.4 (2H, m, CF_2-CH_2), 3.41 (2H, t, $J=6.8$ Hz, $R_fCH_2CH_2$-O), 3.71 (2H, t, $J=7.0$ Hz, O-CH_2). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 1.77 (Si-*C*H_3), 13.51 (Si-*C*H_2), 23.21 (Si-CH_2-*C*H_2), 31.6 (t, $J=22.0$ Hz, CF_2-*C*H_2), 62.4 (-*C*H_2-O), 73.9 (-O-*C*H_2). ^{19}F-NMR (376 MHz, $CDCl_3$) δ −81.4 (3F, t, $J_{F-F}=9.0$ Hz, CF_2CF_3), −114.0 (2F, s, CF_2CF_3), −122.3 (10F, br, $(CF_2)_5CF_2CF_3$), −123.3 (2F, s, $CF_2(CF_2)_6CF_3$), −124.2 (2F, s, $CH_2CF_2CF_2$), −127.2 (2F, s, CH_2CF_2). ^{29}Si-NMR (79.3 MHz, $CDCl_3$) δ 7.38 ($(CH_3)_3$-*Si*-O), −21.7 (O-*Si*$(CH_3)(CH_2)$-O). Anal. Calc. for $C_{22}H_{31}F_{21}O_3Si_3$: C, 32.0; H, 3.78. Found: C, 32.2; H, 4.06%.

3-(1′,1′,1′-Trifluoroethoxypropyl)-1,1,1,3,5,5,5-heptamethyl)-trisiloxane (T5) from alkene (F5). Product **T5** was isolated as a colourless oil (4.84 g, 94%). Anal. Calc. for $C_{12}H_{29}F_3O_3Si_3$: C, 39.7; H, 8.06. Found: C, 39.6; H, 8.18%.

Major isomer. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.43–0.49 (2H, m, Si-CH_2), 1.60–1.66 (2H, m, Si-CH_2-CH_2), 3.53–3.58

(2H, t, $J=6.8$ Hz, -CH_2-O-), 3.75–3.85 (2H, q, $J_{H-F}=8.8$ Hz, -CH_2CF$_3$). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 1.9–2.5 (Si-*C*H$_3$), 13.2–13.8 (Si-*C*H$_2$), 23.4–-23.8 (-*C*H$_2$), 67.9–-69.2 (CF$_3$-*C*H$_2$), 75.4–76.0 (-*C*H$_2$-O-). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −74.76 to −74.80 (3F, t, $J=8.1$ Hz, C*F*$_3$-). ^{29}Si-NMR (79.3 MHz, CDCl$_3$) δ 7.49 ((CH$_3$)$_3$-*Si*-O), −21.9 (O-*Si*(CH$_3$)(CH$_2$)-O).

Minor isomer. ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.43–0.49 (1H, m, Si-C*H*), 0.9–1.0 (3H, m, Si-CH-CH_3), 3.53–3.58 (2H, t, $J=6.8$ Hz, -CH_2-O-), 3.75–3.85 (2H, q, $J_{H-F}=8.8$ Hz, -CH_2CF$_3$). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 1.9–2.5 (Si-*C*H$_3$), 11.6 (CH-*C*H$_3$), 23.8 (Si-*C*H), 67.9–69.2 (CF$_3$-*C*H$_2$), 75.4–76.0 (-*C*H$_2$-O-). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −74.56 to −74.62 (3F, t, $J=8.1$ Hz, CF$_3$-). ^{29}Si-NMR (79.3 MHz, CDCl$_3$) δ 9.71 ((CH$_3$)$_3$-*Si*-O), −24.0 (O-*Si*(CH$_3$)(CH)-O).

3-(1′,1′,1′-Trifluoroethoxypentyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T6) from alkene (F6). Product **T6** was isolated as a colourless oil (0.63 g, 54%). ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.08–0.13 (21H, m, 7 × Si-CH_3), 0.44–0.49 (2H, m, Si-CH_2), 1.33–1.38 (2 × 2H, m, -CH_2-CH_2-), 1.57–1.63 (2H, m, Si-CH$_2$-CH_2), 3.58–3.61 (2H, t, $J=6.6$ Hz, -CH_2-O-), 3.77–3.83 (2H, q, $J_{H-F}=9.0$ Hz, -CH$_2$CF$_3$). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 0.12–2.2 (Si-*C*H$_3$), 17.9 (Si-*C*H$_2$), 23.3 (-*C*H$_2$), 29.6–29.7 (-*C*H$_2$), 73.2 (-*C*H$_2$-O). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −74.76 to −75.71 (3F, t, $J=9.2$ Hz, C*F*$_3$-). Anal. Calc. for C$_{14}$H$_{33}$F$_3$O$_3$Si$_3$: C, 43.1; H, 8.51. Found: C, 42.6; H, 8.53%.

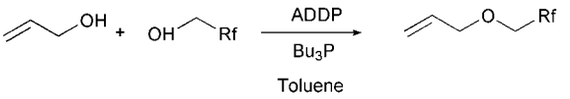
3-(1′,1′,1′-Trifluoroethoxydecyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T7) from alkene (F7). Product **T7** was isolated as a colourless oil (0.40 g, 52%). ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.10 (21H, m, 7 × Si-CH_3), 0.43 (2H, m, Si-CH_2-), 1.30–1.40 (4H, m, Si-CH$_2$CH_2CH_2), 1.45–1.90 (12H, m, 6 × aliphatic CH_2), 3.55 (2H, t, $J=6.6$ Hz, -CH_2-O-), 3.75 (2H, q, $J_{H-F}=8.8$ Hz, -CH_2CF$_3$). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 2.1 (Si-*C*H$_3$), 17.9 (Si-*C*H$_2$), 23.3 (-*C*H$_2$), 26.0 (-*C*H$_2$), 29.5–29.8 (-*C*H$_2$), 33.4 (-*C*H$_2$), 76.9 (-*C*H$_2$-O-). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −74.78 to −75.83 (3F, t, $J=9.1$ Hz, C*F*$_3$-). ^{29}Si-NMR (79.3 MHz, CDCl$_3$) δ 6.88 ((CH$_3$)$_3$-*Si*-O), −21.1 (O-*Si*(CH$_3$)(CH$_2$)-O). Anal. Calc. for C$_{19}$H$_{43}$F$_3$O$_3$Si$_3$: C, 49.5; H, 9.41. Found: C, 50.3; H, 9.38%.

3-(1′,1′,1′,3′,3′,3′-Hexafluoropropoxydecyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T8) from alkene (F8). Product **T8** was isolated as a colourless oil (0.49 g, 57%). ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.10 (21H, m, 7 × Si-CH_3), 0.40–0.45 (2H, m, Si-CH_2), 1.20–1.40 (14H, m, 7 × aliphatic CH_2), 1.52–1.65 (2H, m, Si-CH$_2$-CH_2), 3.77–3.86 (2H, t, $J=6.4$ Hz, -CH_2-O), 4.88–4.95 (1H, m, OC*H*-(CF$_3$)$_2$). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 2.12 (Si-*C*H$_3$), 17.9 (Si-*C*H$_2$), 23.3–23.7 (-*C*H$_2$), 29.2–29.7 (-*C*H$_2$), 75.8–76.8 (-*C*H$_2$-O). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −74.7 to −74.8 (6F, d, $J=5.7$ Hz, 2 × C*F*$_3$-). Anal. Calc. for C$_{12}$H$_{29}$F$_3$O$_3$Si$_3$: C, 45.4; H, 8.01. Found: C, 44.7; H, 7.83%.

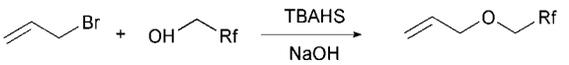
3-(Propoxy-1*H*,1*H*,2*H*,2*H*-perfluoro-9-methyldecyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (T9) from alkene (F9). Product **T9** was isolated as a colourless oil (0.55 g, 47%). ^{1}H-NMR (270 MHz, CDCl$_3$) δ 0.08–0.12 (21H, m, 7 × Si-CH_3), 0.42–0.52 (2H, m, Si-CH_2-), 1.64 (2H, m, SiCH$_2$CH_2-), 2.35 (2H, m, -CF$_2$CH_2-), 3.40 (2H, t, -CF$_2$CH$_2$CH_2-O), 3.80 (2H, t, -CH_2O). ^{13}C-NMR (67.8 MHz, CDCl$_3$) δ 0.0 (Si-*C*H$_3$), 13.9 (Si-*C*H$_2$), 23.5 (Si-CH$_2$-*C*H$_2$), 31.9 (-CF$_2$-*C*H$_2$), 62.7 (-*C*H$_2$-O), 74.1 (-O-*C*H$_2$). ^{19}F-NMR (376 MHz, CDCl$_3$) δ −72.4 to −72.6 (6F, m, CF(C*F*$_3$)$_2$), −113.7 (2F, s, C*F*$_2$CF), −115.4 (2F, s, C*F*$_2$CF$_2$CF), −121.1 (2F, m, C*F*$_2$(CF$_2$)$_2$CF), −121.8 (2F, s, C*F*$_2$(CF$_2$)$_3$CF), −122.0 (2F, s, C*F*$_2$(CF$_2$)$_4$CF), −124.0 (2F, s, CH$_2$C*F*$_2$(CF$_2$)$_5$CF), −186.0 (1F, CF). Anal. Calc. for C$_{12}$H$_{29}$F$_3$O$_3$Si$_3$: C, 32.4; H, 4.27. Found: C, 33.3; H, 4.56%.

Discussion

As the preparation of several of the perfluoroalkyl allyl ethers required for the target heptamethyltrisiloxanes had not been published previously, the fluorinated alkenes **F1**–**9** were first synthesised either by the phase-transfer catalysed reaction of a 1-bromoalkene with a fluorinated alcohol,[14] (Scheme 1) or in the case of **F7** and **F8**, by a variant of the Mitsunobu condensation[15] (Scheme 2) in which the fluoroalcohol acts as the proton donor/nucleophile.



Scheme 2 Ether formation *via* ADDP initiator.



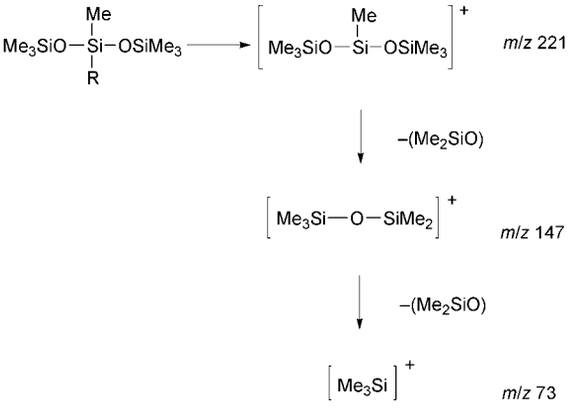
Scheme 1 Ether formation *via* phase transfer.

All alkenyloxy-perfluoroalkenes with the exception of **F4** (white solid) were isolated in good yields as colourless oils either by distillation under reduced pressure or by column chromatography. As the starting material for **F4**, 1*H*,1*H*,2*H*,2*H*-perfluorododecan-1-ol, is a solid (mp 95 °C), the reaction was carried out at 97 °C to ensure the homogeneity of the reaction mixture. Attempts to carry out the reaction at lower temperatures in ethyl acetate afforded much lower yields. NMR and analytical data on the new complexes **F6**–**9**, together with more complete characterisation of compounds **F1**–**5** than is provided in the literature, are given in the Experimental section.

The trisiloxane derivatives **T1**–**9** were readily synthesised by [Pt(cyclooctadiene)Cl$_2$] catalysed addition reactions of alkenes **F1**–**7** to heptamethyltrisiloxane under strictly anhydrous conditions. Only **T5** and **6** were sufficiently volatile to be distilled, but the remainder were shown to be analytically pure following removal of catalyst residues and then unreacted starting materials, all of which are volatile at reduced pressure. Yields of only *ca.* 50% were achieved for **T6**–**9**, all of which contain either a long methylene spacer group ($n \geqslant 5$) or a branched R$_f$ substituent.

Mass spectral studies of a selection of these trisiloxanes revealed that they exhibit similar fragmentation patterns (Scheme 3). All show the loss of a Me residue from a Si atom to form the $(M-15)^+$ ion, whilst loss of the complete organofunctional group from the parent ion produces an intense fragment ion, *m*/*z* 221.

The ^{1}H, ^{13}C and ^{29}Si spectroscopic data for these trisiloxanes are in keeping with those of other organofunctional analo-



Scheme 3 Trisiloxane fragmentation pattern.

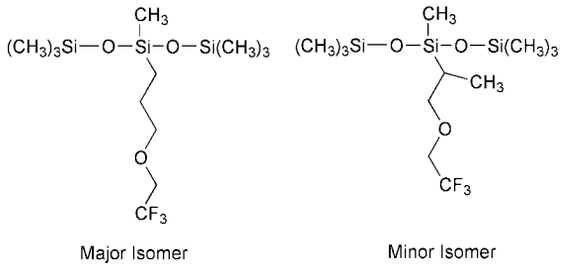


Fig. 2 Isomers of **T5**.

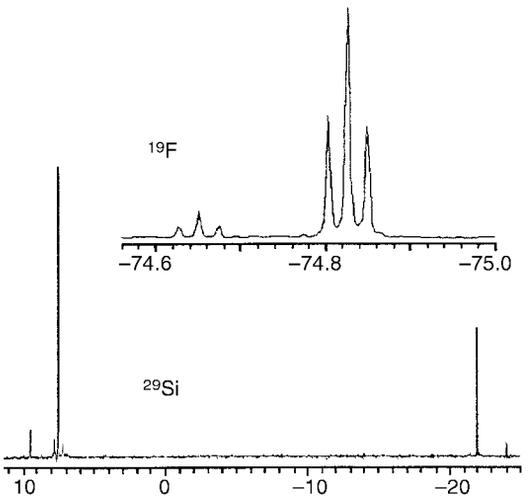


Fig. 3 ^{19}F and ^{29}Si NMR spectra of **T5**.

gues.[1,3,16] However **5** alone exhibited a second set of resonances assignable to a minor product which could not be separated by fractional distillation. As has been shown in earlier studies, both Markownikoff and anti-Markownikoff addition can occur in hydrosilylation reactions,[13,17] and the spectra of **T5** were fully consistent with the presence of both isomeric species (Fig. 2). In particular the major isomer showed only methylene absorptions in the 0.4–1.6 ppm region of the proton NMR spectrum, whereas methine and methyl signals occurred for the minor component. Integrations in this region indicated a 9 : 1 ratio.

The ^{19}F and ^{29}Si NMR spectra of **T5** are illustrated in Fig. 3. Both show separate resonances, triplet and singlet respectively, for the two components. The chemical shift differences in either case are unlikely to be sufficient for the diagnosis of Markownikoff and anti-Markownikoff addition in polymeric perfluorinated siloxanes, whereas proton NMR spectroscopy can be very conveniently used as a probe for this effect.

Conclusions

Hydrosilylation of fluorinated alkenes catalysed by [Pt(cyclooctadiene)Cl_2] in toluene as a solvent provides a facile and high-yielding method for the preparation of pure organofunctional trisiloxanes containing the $-(CH_2)_3O(CH_2)R_f$ substituent, provided the R_f group is not branched. Analogues containing either a long alkyl spacer chain or a branched R_f group were formed in much lower yields under identical experimental conditions. NMR examination revealed that isomeric products resulting from Markownikoff as well as anti-Markownikoff addition occurred in product **T5** only.

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