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Study of the alkylation of chlorosilanes. Part II. Synthesis of (fluoroalkyl)chlorosilanes and tetra(fluoroalkyl)silanes via hydrosilylation

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Abstract

The hydrosilylation of various fluorinated olefins and of a diene with different chlorosilanes and with a tri(fluoroalkyl)silane, in the presence of a peroxide or a Pt catalyst, is reported. The reactivity is influenced considerably by the structure of the silane and of the fluorinated olefin. The following (fluoroalkyl)chlorosilanes and (fluoroalkyl)-α,ω-chlorodisilanes are described; $C_6F_{13}(CH_2)_nSiR^1R^2Cl$ where $n=2$ or 3 and $(ClR^1R^2SiC_2H_4C_3F_6)_2$ with $R^1=R^2=Cl$, $R^1=Cl$ and $R^2=CH_3$ or $C_2H_4CF_3$, $R^1=R^2=CH_3$ and $R^1=CH_3$ and $R^2=C_6H_5$. Three new tetra(fluoroalkyl)silanes have also been synthesized. All the products were characterized by ^1H, ^{19}F and ^{29}Si NMR spectroscopy.

Introduction

It is well known that the introduction of a fluoroalkyl chain into a silane may be achieved via two main routes, one using an organometallic reagent and the other being the hydrosilylation of a fluorinated olefin. In work described in a previous paper, we mainly used the first route to synthesize tetra(fluoroalkyl)silanes [1].

This present study describes the hydrosilylation of fluorinated olefins leading to new tetra(fluoroalkyl)silanes and to (fluoroalkyl)chlorosilanes, which are potential precursors of fluorinated siloxanes and polysiloxanes.

Fluorinated polysiloxanes or silicones are expected to show interesting properties in terms of chemical and thermal stability, and interesting surface properties. They have generated increasing interest in various fields of application: coatings, water-repellent and oil-resistant sealants and joints, defoaming agents, wide temperature range lubricants and rubbers [2].

Many different cases involving the hydrosilylation reaction have been studied. Lukevics *et al.* [3a, b] reported that the reaction depends on the structures of the silane and the olefin, as well as on the solvent and catalyst, and Speier [3c] studied a variety of different transition metals as catalysts. The hydrosilylation of fluorinated olefins has also been reported by different authors using, for example, UV irradiation [4], radical initiation with peroxides [5] or various metal catalysts containing Pt, Ru, Rh or Pd [6–11].

In this work, we have explored the influence of the nature of the silane $HSiR^1R^2Cl$, the catalyst (peroxide or Pt catalyst) and the reaction conditions on the hydrosilylation of various fluorinated olefins $R_F(CH_2)_n$-$CH=CH_2$, where $n=0$ or 1, and $R_F=C_mF_{2m+1}$. We first studied the hydrosilylation of tridecafluoro-octene (**1**), followed by tridecafluorononene (**4**) and finally perfluoro-3,4,5,6,7,8-decadi-1,8-ene (**6**) with different chlorosilanes. The hydrosilylation of olefin **4**, diene **6** and heptadecafluorodecene (**11**) with tris(tridecafluoro-octyl)hydrogenosilane (**8**) was employed to prepare the corresponding tetra(fluoroalkyl)silanes.

Results and discussion

Synthesis of $C_6F_{13}(CH_2)_nSiClR^1R^2$

When n = 2

Several attempts were carried out at hydrosilylating tridecafluoro-1*H*,1*H*, 2*H*-octene (**1**) with different chlorosilanes of the general structure $HSiClR^1R^2$ (**2**) (Scheme 1).

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$$\underset{(1)}{C_6F_{13}CH{=}CH_2} + \underset{(2)}{HSiClR^1R^2} \longrightarrow \underset{(3)}{C_6F_{13}(CH_2)_2SiClR^1R^2}$$

(a) $R^1 = R^2 = Cl$
(b) $R^1 = Cl, R^2 = CH_3$
(c) $R^1 = R^2 = CH_3$
(d) $R^1 = CH_3, R^2 = C_6H_5$
(e) $R^1 = Cl, R^2 = C_2H_4CF_3$

Scheme 1.

The initial attempts were carried out in hexane at 70 °C using hexachloroplatinic acid (H_2PtCl_6) as catalyst, as previously reported for other fluorinated olefins [8]. The results were not satisfactory, and reactions were attempted at a higher temperature, in sealed tubes, without any solvent and with H_2PtCl_6 as catalyst, or in some cases, with t-butyl peroxide ($(^tBuO)_2$) [5]. The results obtained are summarized in Table 1.

These results show the influence of the silane structure. When the electron density on the Si atom of the silane decreases, hydrosilylation would be expected to occur more readily, i.e. more readily for $HSiCl_3$ and $HSiCl_2R$ than for $HSiClR^1R^2$. Indeed, although no reaction occurred with dimethylchlorosilane (**2c**) and phenylmethylchlorosilane (**2d**), the reaction with dichlorosilanes **2b** and **2e** or with trichlorosilane **2a** led to the expected addition products in good yield.

For methyldichlorosilane (**2b**), the results obtained under various reaction conditions indicate the sensitivity of the reaction to temperature as well as to the catalyst. The product of inverse addition was never observed in any noticeable quantity.

The structures of the chlorosilanes **3a**, **3b** and **3e** have been determined by ^1H, ^{19}F and ^{29}Si NMR spectroscopy and confirmed by their conversion to the corresponding fluorosilanes **3a'**, **3b'**, and **3e'**, using HF/EtOH, for which the ^{19}F and ^{29}Si NMR spectra exhibited characteristic signals (Scheme 2).

$$\mathbf{3a} \longrightarrow \underset{(\mathbf{3a'})}{C_6F_{13}C_2H_4SiF_3}$$

$$\mathbf{3b} \xrightarrow{HF/EtOH} \underset{(\mathbf{3b'})}{C_6F_{13}C_2H_4Si(CH_3)F_2}$$

$$\mathbf{3e} \longrightarrow \underset{(\mathbf{3e'})}{C_6F_{13}C_2H_4Si(C_2H_4CF_3)F_2}$$

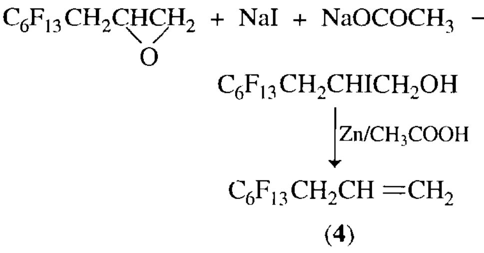
Scheme 2.

The NMR data obtained are summarized in Table 2 and are consistent with the values given in the literature for this type of compound [12].

Since the best results were obtained with reactions carried out in sealed tubes at 100 °C and with H_2PtCl_6 as catalyst, these conditions were maintained in the reactions described below.

When n = *3*

Tridecafluoro-1*H*,1*H*,2*H*,3*H*,3*H*-nonene (**4**) was synthesized via the intermediate hydroxyiodide followed by reduction with Zn according to Cornforth *et al.* [13] (Scheme 3).



$$C_6F_{13}CH_2\underset{O}{CHCH_2} + NaI + NaOCOCH_3 \longrightarrow C_6F_{13}CH_2CHICH_2OH \xrightarrow{Zn/CH_3COOH} \underset{(4)}{C_6F_{13}CH_2CH{=}CH_2}$$

Scheme 3.

Olefin **4**, which was obtained in 35% yield, was identified via its ^1H NMR spectrum [14].

Hydrosilylation was undertaken for 18 h at 100 °C in a sealed tube, in the presence of H_2PtCl_6 (10^{-3} Pt/olefin) (Scheme 4).

$$\underset{(4)}{C_6F_{13}CH_2CH{=}CH_2} + \underset{\substack{(2)\\(\mathbf{a, b, c, d})}}{HSiR^1R^2Cl} \longrightarrow \underset{\substack{(5)\\(\mathbf{a, b, c, d})}}{C_6F_{13}(CH_2)_3SiR^1R^2Cl}$$

Scheme 4.

TABLE 1. Results of the hydrosilylation of $C_6F_{13}CH{=}CH_2$ with chlorosilanes **2**

Chlorosilane	Reaction conditions		
	70 °C, hexane, 18 h, $H_2PtCl_6/^iPrOH$	100 °C, sealed tube, 18 h, $H_2PtCl_6/^iPrOH$	100 °C, sealed tube, 18 h, $(^tBuO)_2$
2a	**3a** (65%)	**3a** (79%)	–
2b	no reaction	**3b** (85%)	no reaction
2c	no reaction	no reaction	no reaction
2d	–	no reaction	–
2e [1]	–	**3e** (85%)	–

TABLE 2. ^{1}H, ^{19}F and ^{29}Si NMR chemical shifts for compounds **3**

	^{1}H (TMS) δ (ppm)						^{19}F (CFCl$_3$) δ (ppm)				^{29}Si (TMS) δ (ppm)	^{1}J(Si–F) (Hz)
							CF$_3$C$_2$H$_4$	*CF*$_3$C$_5$F$_{10}$ [a]	SiF$_3$	SiF$_2$		
3a	C$_6$F$_{13}$	CH$_2$	CH$_2$	SiCl$_3$				−81.9 (3F)			+11.53	
		2.35	1.65								(s)	
		(m)	(m)									
3b	C$_6$F$_{13}$	CH$_2$	CH$_2$	Si(CH$_3$)Cl$_2$				−81.9 (3F)			+31.4	
		2.25	1.35	0.88							(s)	
		(m)	(m)	(s)								
3e	C$_6$F$_{13}$	CH$_2$	CH$_2$	Si(CH$_2$	CH$_2$	CF$_3$)Cl$_2$	−69.5 (3F)	−81.9 (3F)			+31.5	
		2.3	1.4	2.3	1.4		(t)				(s)	
		(m)	(m)	(m)	(m)							
3a′	C$_6$F$_{13}$	CH$_2$	CH$_2$	SiF$_3$				−81.9 (3F)	−138.2 (3F)		−60.4	278
		2.26	1.27								(q)	
		(m)	(m)									
3b′	C$_6$F$_{13}$	CH$_2$	CH$_2$	Si(CH$_3$)F$_2$				−81.9 (3F)		−136 (2F)	+1.7	295
		2.2	1.08	0.45							(t)	
		(m)	(m)	(t)								
3e′	C$_6$F$_{13}$	CH$_2$	CH$_2$	Si(CH$_2$CH$_2$CF$_3$)F$_2$			−69.5 (3F)	−81.9 (3F)		−135 (2F)	+1.5	295
											(t)	

[a] The C$_6$F$_{13}$ chain resonated for all products as follows:

CF$_3$	CF$_2$	CF$_2$	CF$_2$	CF$_2$	CF$_2$	CF$_2$	CH$_2$
−81.9	−127	−124.2	−123.6	−122.5	−117.5		

The expected silane **5** was obtained in quantitative yield in all cases, whereas for olefin **1** under the same conditions no reaction occurred with hydrogenosilanes **2c** and **2d** and the reactions with **2a** and **2b** gave lower yields.

Silanes **5a**, **5b**, **5c** and **5d** were characterized by ^{1}H and ^{29}Si NMR spectroscopy (see Table 3).

TABLE 3. NMR chemical shifts for compounds **5**[a]

	^{1}H (TMS) δ (ppm)						^{29}Si (TMS) δ (ppm)
5a	C$_6$F$_{13}$	CH$_2$	CH$_2$	CH$_2$	SiCl$_3$		+11.6
		2.18	1.80	1.44			(s)
		(m)	(m)	(m)			
5b	C$_6$F$_{13}$	CH$_2$	CH$_2$	CH$_2$	Si(CH$_3$)	Cl$_2$	+31.65
		2.12	1.70	1.17	0.81		(s)
		(m)	(m)	(m)	(s)		
5c	C$_6$F$_{13}$	CH$_2$	CH$_2$	CH$_2$	Si(CH$_3$)$_2$	Cl	+31.2
		2.10	1.5	0.95	0.8		(s)
		(m)	(m)	(m)	(s)		
5d	C$_6$F$_{13}$	CH$_2$	CH$_2$	CH$_2$	Si(CH$_3$)	(C$_6$H$_5$)Cl	+20.3
		2.12	1.8	1.15	0.7	7.35–7.77	(s)
		(m)	(m)	(m)	(s)		

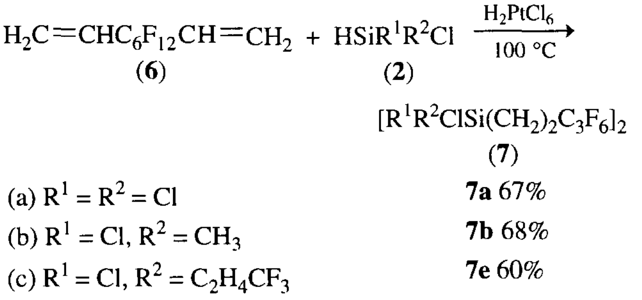
[a] All the products exhibit the signals for the C$_6$F$_{13}$ chain in ^{19}F NMR spectra (see Table 2).

The ^{29}Si NMR chemical shifts observed are consistent with the literature values [12], and no evidence was found for the isomeric addition products.

These results show that olefin **4** is much more reactive than olefin **1**, in good agreement with previously observed effects of the structure of the olefin [3]. Because of the strong electron-withdrawing effect of the R$_F$ group directly linked to the double bond in olefin **1**, the electron density on this double bond is strongly decreased and consequently so is the reactivity.

Synthesis of $R^1R^2ClSi(CH_2)_2C_6F_{12}(CH_2)_2SiClR^1R^2$

On the basis of the results obtained with tridecafluoro-1*H*,1*H*,2*H*-octene (**1**), hydrosilylation of the fluorinated diene **6** with trichlorosilane **2a** and dichlorosilanes **2b** and **2e** was undertaken (Scheme 5).



$$\underset{(\mathbf{6})}{H_2C{=}CHC_6F_{12}CH{=}CH_2} + \underset{(\mathbf{2})}{HSiR^1R^2Cl} \xrightarrow[100\ ^\circ C]{H_2PtCl_6} \underset{(\mathbf{7})}{[R^1R^2ClSi(CH_2)_2C_3F_6]_2}$$

(a) $R^1 = R^2 = Cl$ **7a** 67%

(b) $R^1 = Cl$, $R^2 = CH_3$ **7b** 68%

(c) $R^1 = Cl$, $R^2 = C_2H_4CF_3$ **7e** 60%

Scheme 5.

The products **7** were characterized by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy (see Table 4).

TABLE 4. NMR chemical shifts for compounds 7[a]

	^1H (TMS) δ (ppm)	^{29}Si (TMS) δ (ppm)
7a	$[Cl_3Si\ CH_2\ CH_2\ CF_2\ CF_2\ CF_2]_2$ 1.60 2.34 (m) (m)	+12 (s)
7b	$[Cl_2(CH_3)\ Si\ CH_2\ CH_2\ CF_2\ CF_2\ CF_2]_2$ 0.87 1.36 2.25 (s) (m) (m)	+31.8 (s)
7e	$[Cl_2(CF_3CH_2\ CH_2)\ Si\ CH_2\ CH_2\ CF_2\ CF_2\ CF_2]_2$ 2.20 1.10 1.10 2.20 (m) (m) (m) (m)	+31.5 (s)
7b'	$[F_2(CH_3)\ Si\ CH_2\ CH_2\ CF_2\ CF_2\ CF_2]_2$ 0.45 1.08 2.2 (t) (m) (m)	+1.5 (t) ^1J(Si–F) =294 Hz

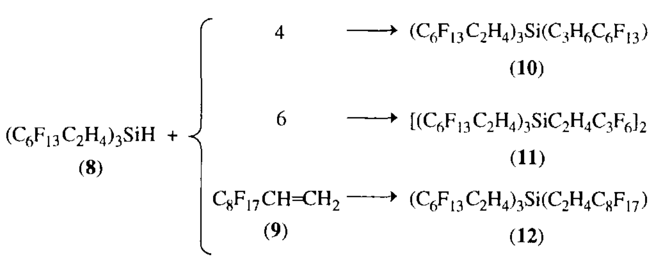
[a] For all compounds, the ^{19}F NMR chemical shifts in ppm (relative to $CFCl_3$) were as follows:
$-CH_2\ CH_2\ CF_2\ \ CF_2\ \ [CF_2]_2$ with **7b'** showing a signal at −136 ppm for SiF_2.
−123.5 −122.3 −117

Compound **7b** was converted to the corresponding bis-difluorosilane $[F_2(CH_3)SiC_2H_4C_3F_6]_2$ (**7b'**) by means of HF/EtOH, and the ^{19}F and ^{29}Si NMR spectra of **7b'** confirmed its structure.

It should be noted that, as for mono-olefins, the reactivity of the α,ω-diolefin towards the three hydrogenosilanes was very similar, but in the case of hydrosilane **2e** steric hindrance of $C_2H_4CF_3$ led to a slight decrease in the reactivity compared with **2b**.

Synthesis of tetra(fluoroalkyl)silanes

In order to obtain new tetra(fluoroalkyl)silanes, the hydrosilylation reaction of olefin **4**, diene **6** and a new olefin, heptadecafluorodecene (**9**) was carried out with tris(tridecafluoro-octyl)silane (**8**) [1] (Scheme 6).



$$(C_6F_{13}C_2H_4)_3SiH\ (\mathbf{8}) + \begin{cases} 4 \longrightarrow (C_6F_{13}C_2H_4)_3Si(C_3H_6C_6F_{13})\ (\mathbf{10}) \\ 6 \longrightarrow [(C_6F_{13}C_2H_4)_3SiC_2H_4C_3F_6]_2\ (\mathbf{11}) \\ C_8F_{17}CH{=}CH_2\ (\mathbf{9}) \longrightarrow (C_6F_{13}C_2H_4)_3Si(C_2H_4C_8F_{17})\ (\mathbf{12}) \end{cases}$$

Scheme 6.

Reactions were carried out in sealed tubes in the presence of H_2PtCl_6, and after 18 h at 100 °C the expected tetra(fluoroalkyl)silane **10** was obtained in quantitative yield (98%) from olefin **4**. For diene **6** and olefin **9**, reactions were carried out for 18 h at 120 °C and 110 °C, respectively, giving the expected products **11** and **12** in good yield (80%). It should be noted that olefin **4**, which has an additional CH_2 group between the R_F chain and the double bond, was again more reactive compared to diene **6** and olefin **9**.

Compounds **10**, **11** and **12** were characterized by ^1H, ^{19}F and ^{29}Si NMR spectroscopy (see Table 5).

Experimental

NMR spectra were recorded on a Bruker WP 200 or WH 250 spectrometer with TMS as reference for ^1H and ^{29}Si NMR and $CFCl_3$ as reference for ^{19}F NMR. Chemical shifts are downfield from TMS and upfield (negative in value) for $CFCl_3$ being reported in ppm and denoted as follows: s = singlet, d = doublet, t = triplet, q = quadruplet and m = multiplet. All spectra were recorded in $CDCl_3$ solutions, the data obtained being reported in Tables 2–5.

General procedure for hydrosilylation reactions

(a) In a flask fitted with a condenser

A solution consisting of 1.2 mol of silane in 20 ml hexane, 1 mol of the fluorinated olefin in 20 ml hexane and 200 ppm of H_2PtCl_6 relative to the amount of olefin (10% solution of $H_2PtCl_6\cdot 6H_2O$ in 2-propanol) was placed in a two-necked flask equipped with a condenser and a magnetic stirrer. The mixture was heated overnight (18 h) at 70 °C. The resulting black mixture was filtered, hexane evaporated and the product distilled.

TABLE 5. NMR chemical shifts for tetra(fluoroalkyl)silanes[a]

	^{1}H (THS) δ (ppm)									^{29}Si (TMS) δ (ppm)
10	(C_6F_{13}	CH_2	$CH_2)_3$	Si	(CH_2	CH_2	CH_2	C_6F_{13})		+6.84
		1.6–1.8	0.7–1.05		0.7–1.05	1.6–1.8	1.9–2.35			
		(m)	(m)		(m)	(m)	(m)			
11	[(C_6F_{13}	CH_2	$CH_2)_3$	Si	CH_2	CH_2	$C_3F_6]_2$			+8.06
		2.10	0.95		0.95	2.10				
		(m)	(m)		(m)	(m)				
12	(C_6F_{13}	CH_2	$CH_2)_3$	Si	(CH_2	CH_2	C_8F_{17})			+8.05
		2.1	1.0		1.0	2.1				
		(m)	(m)		(m)	(m)				

[a] In the ^{19}F NMR spectra, all products exhibited signals for the C_6F_{13} chain (see Table 2) and in compound **12** two additional CF_2 groups of the C_8F_{17} chain resonated at −122.5 ppm.

(b) In a sealed tube

A solution consisting of 1.2 mol of silane, 1 mol of fluorinated olefin and 200 ppm of H_2PtCl_6 relative to the amount of olefin was placed in a glass tube which was sealed and heated overnight at 100 °C. After cooling and opening the tube, the black reaction mixture was filtered and distilled.

General procedure for converting chlorosilanes to fluorosilanes [15]

An ethereal solution of the chlorosilane was added to an equal volume of ethanol or acetone and treated with an excess of 40% HF at 0 °C. The resulting mixture was stirred at room temperature for a few hours (1–4 h), then poured into a large excess of water and extracted with ether. The ether solution was dried over Na_2SO_4, concentrated and the product distilled.

(1H, 1H, 2H, 2H-Tridecafluoro-octyl)trichlorosilane (3a)

Method a

Following general procedure (a) above for hydrosilylation, the trichlorosilane **3a** was obtained in 65% yield from tridecafluoro-octene, $C_6F_{13}CH{=}CH_2$ (**1**), and trichlorosilane $HSiCl_3$ (**2a**); b.p. 85 °C/20 mmHg [1].

Method b

The same product was obtained in 79% yield from the same reactants following general procedure (b) above for hydrosilylation.

(1H, 1H, 2H, 2H-Tridecafluoro-octyl)(methyl)-dichlorosilane (3b)

Method a

Following general procedure (a) above for hydrosilylation, no dichlorosilane **3b** was formed from olefin **1** and dichlorosilane $HSi(CH_3)Cl_2$ (**2b**), which were recovered unchanged.

Method b

Following general procedure (b) above for hydrosilylation, dichlorosilane **3b** was formed in 85% yield from **1** and **2b**; b.p. 90 °C/20 mmHg.

(1H, 1H, 2H, 2H-Tridecafluoro-octyl)(3,3,3-trifluoropropyl)dichlorosilane (3e)

Following general procedure (b) above for hydrosilylation, dichlorosilane **3e** was obtained in 85% yield from **1** and dichlorosilane $HSi(C_2H_4CF_3)Cl_2$ (**2e**); b.p. 112 °C/20 mmHg.

Conversion to fluorosilanes

(1H, 1H, 2H, 2H-Tridecafluoro-octyl)trifluorosilane (3a′)

Following the general procedure for converting chlorosilanes to fluorosilanes described above trichlorosilane **3a** gave trifluorosilane **3a′** in quantitative yield; b.p. 39 °C/20 mmHg.

(1H, 1H, 2H, 2-Tridecafluoro-octyl)(methyl)-difluorosilane (3b′)

From 17 g (0.037 mol) of dichlorosilane **3b** 14.3 g of difluorosilane **3b′** were obtained; yield 90%, b.p. 63 °C/20 mmHg.

(1H, 1H, 2H, 2H-tridecafluoro-octyl)(3,3,3-trifluoropropyl)difluorosilane (3e′)

From 20 g (0.037 mol) of dichlorosilane **3e**, 16.3 g of difluorosilane **3e′** were obtained; yield 87%, b.p. 86 °C/20 mmHg.

1H, 1H, 2H, 3H, 3H-Tridecafluorononene (4)

Sodium iodide (13.65 g 0.091 mol) and 4.51 g (0.055 mol) of sodium acetate were placed in a two-necked flask equipped with a condenser, a dropping funnel and a magnetic stirrer. Acetic acid (28.56 g, 0.476 mol) and 1.94 g (0.108 mol) of water were added. The mixture was kept at 0 °C, then 13.62 g (0.2080 mol) of zinc powder was added and 20 g (0.0532 mol) of 1*H*,1*H*,2*H*,3*H*,3*H*-perfluoro-1,2-epoxynonane added dropwise. The reaction mixture was left for 2 h at room temperature, the mixture then filtered and separated. The organic layer was dried over Na_2SO_4 and distilled to give 5.84 g of olefin **4**; yield 35%, b.p. 31 °C/20 mmHg.

*(1H, 1H, 2H, 2H, 3H, 3H-Tridecafluorononyl)-trichlorosilane (5a), (1H, 1H, 2H, 2H, 3H, 3H-tridecafluorononyl)(methyl)dichlorosilane (5b), (1H, 1H, 2H, 2H, 3H, 3H-*tridecafluorononyl)-(dimethyl)chlorosilane *(5c) and (1H, 1H, 2H, 2H, 3H, 3H-tridecafluorononyl)(phenyl)(methyl)chlorosilane (***5d***)*

Using general procedure (b) above for hydrosilylation, and after distillation of excess silane, these chlorosilanes were prepared quantitatively from olefin **4** and trichlorosilane, $HSiCl_3$, (methyl)dichlorosilane, $HSi(CH_3)Cl_2$, (dimethyl)chlorosilane, $HSi(CH_3)_2Cl$ and (phenyl)(methyl)chlorosilane, $HSi(CH_3)(C_6H_5)Cl$, respectively.

*α, ω-Di(trichlorosilyl)-1H, 1H, 2H, 2H, 9H, 9H, 10H, 10H-perfluorodecane (7a), α, ω-di(methyldichlorosilyl)-1H, 1H, 2H, 2H, 9H, 9H, 10H, 10H-perfluorodecane (***7b***) and α, ω-di(3, 3, 3-trifluoropropyl dichlorosilyl)-1H, 1H, 2H, 2H, 9H, 9H, 10H, 10H-perfluorodecane (7e)*

As above, these chlorosilanes were prepared from diene **6** and $HSiCl_3$, $HSi(CH_3)Cl_2$ and 3,3,3-trifluoropropyl dichlorosilane, $HSi(C_2H_4CF_3)Cl_2$, respectively. Compound **7a**: yield 67%, b.p. 110–115 °C/0.5 mmHg; compound **7b**: yield 68%, b.p. 120 °C/0.7 mmHg; and compound **7e**: yield 60%, b.p. 150 °C/0.4 mmHg.

*α, ω-Di(methyldifluorosilyl)-1H, 1H, 2H, 2H, 9H, 9H, 10H, 10H-perfluorodecane (***7b'***)*

Following the general procedure for converting chlorosilanes to fluorosilanes, product **7b'** was obtained in quantitative yield from **7b**.

Tris(1H, 1H, 2H, 2H-tridecafluoro-octyl)-1H, 1H, 2H, 2H, 3H, 3H-tridecafluorononyl silane (10)

Tris(tridecafluoro-octyl)silane, $(C_6F_{13}C_2H_4)_3SiH$, 6.42 g, 6×10^{-3} mol) was reacted for 19 h at 100 °C in a flask under nitrogen with 2.16 g (6×10^{-3} mol) of olefin **4** in the presence of $H_2PtCl_6/^iPrOH$. After filtration and distillation, 8.4 g of silane **10** were obtained; yield 98%, b.p. 170 °C/10^{-3} mmHg.

α, ω-Di[tris(1H, 1H, 2H, 2H-tridecafluoro-octyl)]silyl-1H, 1H, 2H, 2H, 9H, 9H, 10H, 10H-perfluorodecane (11)

$(C_6F_{13}C_2H_4)_3SiH$ (8.56 g, 0.008 mol) and 1.45 g (0.0041 mol) of diene **6** were reacted for 19 h at 120 °C in a flask under nitrogen in the presence of $H_2PtCl_6/^iPrOH$. After filtration and elimination of excess diene, 7.5 g of disilane **11** were obtained; yield 80%.

Tris(1H, 1H, 2H, 2H-tridecafluoro-octyl)-1H, 1H, 2H, 2H-heptadecafluorodecyl silane (12)

$(C_6F_{13}C_2H_4)_3SiH$ (4 g 0.0037 mol) and 1.79 g (0.0040 mol) of 1*H*,1*H*,2*H*-perfluorodecene, $C_8F_{17}CH{=}CH_2$, were reacted for 19 h at 110 °C in a flask under nitrogen in the presence of $H_2PtCl_6/^iPrOH$. After filtration and elimination of excess diene, 4.48 g of silane **12** were obtained; yield 80%.

Conclusions

Hydrosilylation of tridecafluoro-octene (**1**) is sensitive both to the structure of the silane and to the reaction conditions. Hydrosilylation of tridecafluorononene (**4**), which was effective with any silane, shows that the hydrosilylation also depends on the structure of the fluorinated olefin. Hydrosilylations of the fluorinated diolefin **6** led to results which were comparable to those obtained with the mono-olefin **4**.

Finally, hydrosilylations with tri(fluoroalkyl)silane (**8**) enabled new tetra(fluoroalkyl)silanes to be obtained and confirmed the influence of the fluorinated olefin, as observed previously.

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