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Synthesis and properties of fluorosilicon-containing polybutadienes by hydrosilylation of fluorinated hydrogenosilanes. Part 1. Preparation of the silylation agents

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Abstract

The synthesis of new fluorinated hydrogenosilanes $C_nF_{2n+1}(CH_2)_xC_2H_4Si(CH_3)_2H$ with $n=6$ or 8 and $x=0$ or 1 is presented. Such compounds were prepared in 85%–90% yield by the selective reduction of the corresponding fluorine-containing (dimethyl)chlorosilanes. These chlorinated derivatives were produced by the hydrosilylation of (dimethyl)chlorosilane with perfluoroalkylvinyl, $C_nF_{2n+1}CH{=}CH_2$ ($x=0$), or allyl, $C_nF_{2n+1}CH_2CH{=}CH_2$ ($x=1$), olefins, both obtained from perfluoroalkyl iodides in two steps, the latter olefins being more reactive than the former. For all these steps, the influence of the spacer (C_2H_4 or C_3H_6) located between the fluorinated chain and the silicon atom with respect to the reactivity is discussed.

Keywords: Perfluoroalkyl iodide; Fluorinated olefin; Hydrosilylation; Reduction; Chlorofluorosilane; Polyfluoroalkyl(dimethyl)hydrogenosilanes

1. Introduction

Previous work described the synthesis and the properties of fluorinated hydroxy-terminated polybutadienes, achieved by photochemical [1] or radical [2] grafting of fluorinated mercaptans on to the double bonds of polybutadienes (PBd). However, if their physicochemical properties were interesting, their thermal characteristics, especially their thermostability, were not satisfactory because of the weak C–S bond that underwent decomposition from 200 °C. It was thus worth substituting the sulfur atom by another heteroatom that would improve the thermal behaviour of these diols.

Although it is well known that silicones exhibit good properties at low temperatures, recent investigations have shown that fluorosilicones preserve their interesting characteristics at high temperatures [3–6]. This work concerns the first synthesis of fluorine-containing organosilanes with Si–H end-groups which can be added to the double bonds of PBd by hydrosilylation.

Few fluorinated silanes have been prepared from the numerous investigations performed on the synthesis of non-halogenated organosilicon products. Two main methods of obtaining such compounds have been suggested: organometallic and hydrosilylation routes.

The first involves fluorinated lithium and magnesium reactants. For instance, $R_FC_2H_4Li$ [where R_F represents CF_3, $(CF_3)_2CF$ and C_6F_{13}] reacted with chloro- or fluoro-silanes and produced tri- or tetra-(alkyl)silanes [7]. It was shown that the longer and the more hindered the R_F group, the lower the yield. On the other hand, additions of $CF_3C_2H_4MgI$ [8] or $C_3F_7C_2H_4MgBr$ [9] to $SiCl_4$ were successfully reported. Furthermore, Smith and Gilman achieved the synthesis of α,ω-bis(dimethylhydrosilyl)perfluorohexane in good yields, from the in situ reaction of 1,6-dibromoperfluorohexane with magnesium and chloro(dimethyl)hydrosilane [10]. A recent investigation [7] with longer fluorinated chains led to tri-(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)hydrogeno- or -chlorosilanes in good yields.

The second possibility is the hydrosilylation of fluorinated olefins with hydrogenosilanes, mainly studied by Lukevics et al. [11], who showed that such a reaction depends upon the structures of both reactants, the solvent and the catalyst. Several authors report the use of different transition metals [4,12–20] whereas Haszeldine et al. [8] and Kim et al. [14] utilized more simple conditions of initiation, by UV or radical initiators. Recently, the hydrosilylation of $C_6F_{13}(CH_2)_x$–

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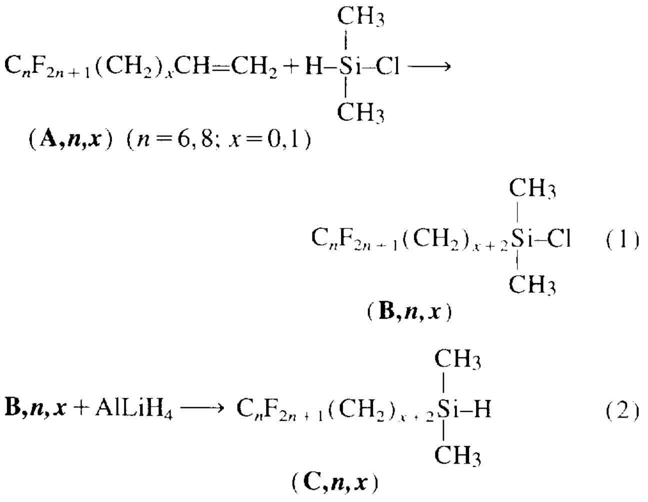
CH=CH$_2$, (where $x=0$ or 1) with tri-(*1H,1H,2H,2H*-polyfluoroalkyl)hydrogenosilane or chlorosilanes showed that the allyl olefin was more reactive [21].

However, the influence of the reaction parameters such as the time, temperature, initial reactant molar ratios and the vessel material on the yield was not optimized, and this is the first objective of this paper. Then, the following step deals with the selective reduction of the chlorofluorosilanes to hydrogenofluorosilanes.

2. Results and discussion

The synthesis of fluorinated silanes, $R_F(CH_2)_xC_2H_4$–Si(CH$_3$)$_2$H, was performed by the hydrosilylation of (dimethyl)chlorosilane with fluorinated olefins in the presence of a Speier catalyst, followed by the reduction of the chlorosilanes into hydrogenosilanes, according to the following scheme:



$$C_nF_{2n+1}(CH_2)_xCH{=}CH_2 + H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}Cl \longrightarrow$$

(**A,*n*,*x***) ($n=6,8$; $x=0,1$)

$$C_nF_{2n+1}(CH_2)_{x+2}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}Cl \qquad (1)$$

(**B,*n*,*x***)

$$\mathbf{B,}n,x + AlLiH_4 \longrightarrow C_nF_{2n+1}(CH_2)_{x+2}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}H \qquad (2)$$

(**C,*n*,*x***)

Each step is detailed below and first of all the preparation of the fluorinated olefins is presented.

2.1. Synthesis of fluorinated vinyl or allyl olefins

The preparation of vinyl or allyl olefins [22] or non-conjugated dienes [23] that contain a perfluorinated chain was recently reviewed and the optimal preparation of these derivatives were produced via two-step processes from perfluoroalkyl iodides as follows:

For vinyl olefins:

$$C_nF_{2n+1}I + H_2C{=}CH_2 \xrightarrow{CuI} C_nF_{2n+1}C_2H_4I$$

($n=6,8$) (**1,*n***)

$$\mathbf{1,}n + KOH \longrightarrow C_nF_{2n+1}CH{=}CH_2$$

(**A,*n*,0**)

For allyl olefins:

$$C_nF_{2n+1}I + H_2C{=}CHCH_2OCOCH_3 \xrightarrow{\text{radical}} C_nF_{2n+1}CH_2CHICH_2OCOCH_3$$

(**2,*n***)

$$\mathbf{2,}n + Zn \longrightarrow C_nF_{2n+1}CH_2CH{=}CH_2$$

(**A,*n*,1**)

Under these conditions, both vinyl alkenes were obtained in 91%–94% yield from the corresponding 1-iodo-*1H,1H,2H,2H*-perfluoroalkanes.

The iodoacetates **2,6** and **2,8** were produced quantitatively and did not require purification for the second step. The allyl olefins **A,6,1** and **A,8,1** were isolated after distillation with yields higher than 60% based on the starting $C_nF_{2n+1}I$. The synthesis of **A,8,1** was scaled-up and gave about 250 g in 67% yield from $C_8F_{17}I$.

Thus, it is observed that the synthesis of fluorinated allyl alkenes is more easily achieved than that of vinyl derivatives since both their steps are performed at atmospheric pressure and also because the iodoacetate produced selectively does not require to be distilled for the subsequent step. For both the fluorinated olefins, it seems that the longer the fluorinated chain, the higher the yield.

2.2. Synthesis of (fluoroalkyl)(dimethyl)chlorosilanes

Various catalysts have been involved in hydrosilylation [4,12–20] and in this study a solution of hexachloroplatinic acid in 2-propanol was chosen. A previous study investigated the hydrosilylation of fluorinated vinyl or allyl olefins with different hydrogenosilanes in the presence of such a catalyst [21]. The experiments were carried out in sealed Carius tubes with hexane as solvent. The results showed that the allyl monomers were more reactive than the vinyl since at 100 °C the conversion of the allyl olefin was quantitative whereas the vinyl one did not react.

It was thus interesting to optimize such reactions, taking into account parameters such as the material of the vessel, the time, the temperature and the initial [chlorosilane]$_0$/[olefin]$_0$ and [catalyst]$_0$/[olefin]$_0$ molar ratios.

2.2.1. Hydrosilylation of (dimethyl)chlorosilane with fluorinated vinyl olefins

Such a reaction was performed under various experimental conditions in a steel autoclave without any solvent, from alkenes that contain two different fluorinated olefins. The results are summarized in Table 1 and they show the efficient reactivity of the vinyl olefins with the (dimethyl)-chlorosilane, even if this latter compounds is less reactive than the trichlorosilane or the methyldichlorosilane [21]. In fact, such a reaction performed in a steel autoclave is successful contrary to similar experiments carried out either in a Hastelloy autoclave that might poison the catalyst [24] or in a glass sealed tube in which possible moisture could hydrolyze the silane into siloxanes [21].

Table 1
Hydrosilylation of chlorodimethyl silane with $C_nF_{2n+1}CH{=}CH_2$ in a stainless steel autoclave in the presence of H_2PtCl_6/2-propanol as the catalyst [a]

n of $C_nF_{2n+1}CH{=}CH_2$	R_0	C_0 (%)	Temp. (°C)	Time (h)	Yield after distillation (%)
6	1.5	0.2	130	16	58
	1.7	0.2	130	16	63
	1.7	0.2	100	6	60
	2.0	0.2	70	16	56
	2.0	0.2	70	6	50
8	1.0	0.3	130	15	61
	1.5	0.2	130	15	62
	2.0	0.4	130	15	66

[a] R_0 = [chlorosilane]$_0$/[olefin]$_0$; C_0 = [catalyst]$_0$/[olefin]$_0$.

Table 2
Hydrosilylation of chlorodimethylsilane with $C_nF_{2n+1}CH_2CH{=}CH_2$ in a stainless steel autoclave in the presence of H_2PtCl_6/2-propanol as the catalyst

n of $C_nF_{2n+1}CH_2CH{=}CH_2$	R_0	C_0 (%)	Temp. (°C)	Time (h)	Yield after distillation (%)
6	1.0	0.2	70	16	50
	1.0	0.3	100	18	55
8	1.6	0.3	100	18	70

Table 1 shows that the higher the R_0 value, the higher the yield. A similar increase was observed for greater catalyst amounts (i.e. C_0) and for higher temperatures. Furthermore, it is noted that under the same conditions, the unsaturated compound with the C_8F_{17} end-group was slightly more reactive than that bearing the C_6F_{13} group.

Both these fluorinated chlorosilanes were characterized by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy and by IR spectroscopy. Their ^{1}H NMR spectra show the absence of the ethylenic protons at about 5.8 ppm and the presence of multiplets centred at 2.1 and 1.05 ppm assigned to the characteristic methylene groups adjacent to the fluorinated chain and the silicon atom, respectively. Moreover, the singlet at 0.65 ppm corresponds to both methyl groups. Interestingly, no reverse or β-addition occurred leading to $R_FCH(CH_3)SiCl(CH_3)_2$, since an absence of a doublet in the 1–2 ppm range was noted.

Their ^{19}F NMR spectra are identical to those of the corresponding fluorinated olefins with a slightly high-field-shifted signal to −116.5 ppm assigned to the difluoromethylene group adjacent to the CH_2. Both the ^{29}Si NMR spectra exhibit a unique singlet at 31.4 ppm characteristic of a chlorodimethylsilyl group [10,21,25].

The FT-IR spectra show absorptions in the 800–900 cm^{-1} range which correspond to Si–C and Si–Cl frequencies, whereas strong bands between 1100–1300 cm^{-1} are assigned to C–F vibrations. These spectra also exhibit the absence of ethylenic carbon since no band is present in the 3000–3200 cm^{-1}.

2.2.2. Hydrosilylation of (dimethyl)chlorosilane with fluorinated allyl olefins

Similar experimental conditions as above were used and the results are summarized in Table 2. They show the efficient reactivity of these allyl olefins (better than the vinyl ones) in hydrosilylation and that the yield depends upon R_0, C_0 and the temperature, as in the vinyl series. The yields are satisfactory at moderate temperatures. Furthermore, the longer the fluorinated chain length, the higher the yield.

Both fluorinated chlorosilanes were characterized by NMR spectroscopy. The ^{1}H and ^{29}Si NMR spectra are very similar to those described above. However the presence of a complex signal centred at 1.55 ppm is assigned to the methylene group in the β-position to the fluorinated chain and the signal corresponding to the CH_2 group adjacent to the silicon atom is slightly high-field-shifted above that of the previous fluorinated chlorosilane.

2.3. Synthesis of (fluoroalkyl)(dimethyl)hydrogenosilanes

The selective reduction of the fluorinated chlorosilane $R_F(CH_2)_{x+2}Si(CH_3)_2Cl$ into $R_F(CH_2)_{x+2}Si(CH_3)_2H$ was performed according to Gilman's method [26] in the presence of lithium aluminium hydride at reflux in anhydrous diethyl ether. The yields obtained are listed in Table 3.

These four reductions led to yields higher than 80% and around 90%–95% for the synthesis of $C_nF_{2n+1}C_2H_4Si(CH_3)_2H$. It seems that the spacer between the fluorinated

Table 3
Yields arising from the reduction of $R_F(CH_2)_{x+2}Si(CH_3)_2Cl$ into $R_F(CH_2)_{x+2}Si(CH_3)_2H$

$C_nF_{2n+1}(CH_2)_{x+2}Si(CH_3)_2Cl$		Yield of $C_nF_{2n+1}(CH_2)_{x+2}Si(CH_3)_2H$ after distillation (%)
x	n	
0	6	90
0	8	93
1	6	82
1	8	80

chain and the silicon atom play a significant role since the shorter the spacer length, the higher the yield of such a reaction. Thus, the proximity of the electron-withdrawing group improves the yield. However, the chain length of the fluorinated group does not have a drastic influence on the yield.

Interestingly, this reduction performed in mild conditions is quite selective for the chlorine atom only, since the ^{19}F NMR spectra of the precursors and of the products are almost identical.

The presence of the Si–H group is clearly seen from the FT-IR spectra that exhibit a band at 2126 cm^{-1} and from the ^{29}Si NMR spectra that show doublets from the coupling of the silicon and the hydrogen atoms, with a characteristic coupling constant of 185 Hz and high-field-shifted to -11.5 ppm compared with the chemical shifts of the chlorinated precursors. When the proton was irradiated, one singlet only was observed. Furthermore, the ^1H signal was identified by ^1H NMR spectroscopy as a hextuplet centred at 3.9 ppm ($J=3.6$ Hz). The ^1H NMR spectra show the high-field shifts of both the CH_2Si group from 1.05 (chlorosilane) to 0.85 ppm, and the methyls from 0.65 to 0.15 ppm. These latter groups are doublets owing to the coupling with the terminal proton ($J=3.6$ Hz).

In conclusion, the yields of each step in both separate reaction schemes, (i) addition of ethylene or allyl acetate on perfluoroalkyl iodides (R_FI); (ii) dehydroiodination or deiodoacetalization; (iii) hydrosilylation of (dimethyl)-chlorosilane and (iv) reduction into fluorinated (dimethyl)-hydrogenosilane, are 65%, 94%, 66% and 92%, and 100%, 70%, 70% and 85%, using vinyl or allyl routes, respectively. Thus, the minimum overall yields of $R_F(CH_2)_{x+2}SiH(CH_3)_2$ from R_FI were 37% and 42% for $x=0$ and 1, respectively, with a quantitative conversion of R_FI in both cases.

3. Experimental details

3.1. Starting materials

Perfluoroalkyl iodides were kindly given by Elf-Atochem and the other reactants were supplied by Aldrich and did not require further purification prior to use. Diethyl ether was freshly distilled over sodium under nitrogen prior to use.

Hydrosilylations were conducted in a 250 ml stainless steel autoclave stirred with a magnet bar.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE-30 column, 1 m × 1/8 in (i.d.). The nitrogen pressure at the entrance to the column was held at 0.6 bar and the detector and injector temperatures were 260 °C and 255 °C, respectively. The temperature programme started from 50 °C and attained 250 °C at a heating rate of 15 °C min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

Gas chromatography/mass spectrometry analyses were performed with a Hewlett Packard apparatus composed of a chromatograph type 5972 coupled to a mass detector type with quadrupole scanning at 90 eV. The BPX5 column was 25 m long and 0.19 mm in inner diameter. The oven temperature was raised from 100 °C to 230 °C with a heating rate of 5 °C min^{-1}. Helium was the eluent at 0.12 ml min^{-1} and the injection temperature was 220 °C.

Fourier-transform infrared (FT-IR) spectra were obtained with a Nicolet-510P spectrometer. The frequencies of the bands was given with an error of ± 2.0 cm^{-1} and the letters vs, s, m or w indicate very strong, strong, medium or weak intensity, respectively.

The products were analyzed by microanalysis at the Laboratory for Microanalysis (CNRS) at the ENSCM.

The products were characterized by ^1H and ^{19}F NMR spectroscopy, all recorded at room temperature. The ^{19}F and ^1H NMR spectra were recorded on Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform as the solvent. TMS and $CFCl_3$ were the respective internal references. The letters s, d, t, h and m designate singlet, doublet, triplet, heptuplet and multiplet, respectively.

3.2. Synthesis of fluorinated olefins

3.2.1. Preparation of vinyl derivatives

Synthesis of 1H,1H,2H-tridecafluorooctene ***(A,6,0)***

The experimental procedure was similar to that described in Ref. [21]. To 500 ml two-necked round-bottom flask equipped with a condenser and containing $C_6F_{13}C_2H_4I$ (300 g, 0.63 mol) and 100 ml of methanol was added dropwise at room temperature a solution composed of potassium hydroxide (53 g, 0.94 mol) dissolved in 200 ml of methanol. The mixture was then refluxed for 6 h. After cooling and washing with water, the olefin was distilled under reduced pressure as a colourless liquid, b.p. 33–35 °C/25 mmHg. The yield was 91%. ^1H NMR ($CDCl_3$) δ: 5.8 (m, 3H) ppm. ^{19}F NMR ($CDCl_3$) δ: -81.16 (t, $J=9.5$ Hz, CF_3, 3F); -114.28 (m, CF_2CH, 2F); -122.05 (m, CF_2CF_2CH, 2F); -123.96 (m, $CF_2C_2F_4CH$, 2F); -124.04 (m, $C_2F_5CF_2$, 2F); -126.52 (m, CF_3CF_2, 2F) ppm.

Synthesis of 1H,1H,2H-heptadecafluorodecene ***(A,8,0)***

A similar experimental procedure as above was conducted using $C_8F_{17}C_2H_4I$ (100 g, 0.174 mol) dissolved in 60 ml of Freon-113, dropped into KOH (29 g, 0.52 mol) dissolved in 100 ml of methanol. The olefin was distilled as a colourless liquid, b.p. 49–50 °C/24 mmHg. The yield was 94%. ^{1}H NMR ($CDCl_3$) δ: 5.8 (m, 3H) ppm. ^{19}F NMR ($CDCl_3$) δ: − 81.24 (t, J = 9.8 Hz, CF_3, 3F); − 114.30 (m, CF_2CH, 2F); − 114.34 (m, CF_2CF_2CH, 2F); − 122.35 (m, $CF_2CF_2CF_2CH$, 4F); − 123.12 (m, $C_3F_7CF_2$, 2F); − 124.02 (m, $C_2F_5CF_2$, 2F); − 126.51 (m, CF_3CF_2, 2F) ppm.

3.2.2. Preparation of allyl olefins

*Synthesis of 1H,1H,2H,3H,3H-tridecafluorononene (**A,6,1**)*

The experimental procedure was identical to that for α,ω-diallyl non-conjugated dienes [23]. In a 500 ml three-necked round-bottom flask equipped with a condenser and a thermometer, a mixture composed of perfluorohexyl iodide (100 g, 0.22 mol) and allyl acetate (24 g, 0.24 mol) was stirred and heated. When the temperature reached 85–90 °C, dibenzoyl peroxide (1.0 g, 0.04 mol) was introduced in small fractions of 0.1 g every 10 min. Suddenly, an exotherm occurred up to 160–170 °C in 2 s, turning the solution colourless. Then the whole became dark red. The yield of iodoacetate was higher than 96% without distillation. The whole 124 g was added dropwise at 65 °C in a slurry of 24 g of activated zinc in 100 ml of methanol with vigorous stirring. The mixture was left stirring for 2 h. After reaction, the zinc complex was filtered off, the filtrate washed with an acid solution and the organic layer dried over magnesium sulfate. Finally, 49.3 g of the allyl olefin were distilled under reduced pressure as a colourless liquid, b.p. 49–51 °C/24 mmHg. The yield was 62% based on $C_6F_{13}I$. Analysis: Found: C, 30.81; H, 1.48; F, 67.48%. $C_9H_5F_{13}$ requires: C, 30.02; H, 1.39; F, 68.58; M, 360.1. ^{1}H NMR ($CDCl_3$) δ: 2.9 (td, $^{3}J_{HF}$ = 18.3 Hz, $^{3}J_{HH}$ = 6.86 Hz, R_FCH_2, 2H); 5.2 (m, 2H); 5.8 (ddt, $^{3}J_{HH}$ = 16.5 Hz (*trans*), $^{3}J_{HH}$ = 10.8 Hz (*cis*), $^{4}J_{HH}$ = 3.6 Hz, CH, 1H) ppm. ^{19}F NMR ($CDCl_3$) δ: − 81.18 (t, J = 9.5 Hz, CF_3, 3F); − 113.70 (m, CF_2CH_2, 2F); − 122.42 (m, $CF_2CF_2CF_2CH$, 4F); − 123.49 (m, $C_2F_5CF_2$, 2F); − 126.59 (m, CF_3CF_2, 2F) ppm.

*Synthesis of 1H,1H,2H,3H,3H-heptadecafluoroundecene (**A,8,1**)*

As previously, perfluorooctyl iodide (437 g, 0.8 mol) and allyl acetate (80 g, 0.80 mol) were stirred at 85–90 °C and dibenzoyl peroxide was introduced. An exotherm up to 180 °C also occurred. The iodoacetate was produced in 98.3% yield. This gross product was added dropwise at 65 °C on to 96 g of activated zinc in 300 ml of methanol. After refluxing for 3 h, the same work-up was performed as previously, leaving 246.6 g of a colourless liquid which were distilled, b.p. 55–60 °C/24 mmHg. The yield based on $C_8F_{17}I$ was 67%. Analysis: Found: C, 28.35; H, 1.20; F, 71,48%. $C_{11}H_5F_{17}$ requires: C, 28.71; H, 1.09; F, 70.19; M, 460.1. ^{1}H NMR ($CDCl_3$) δ: 2.9 (td, $^{3}J_{HF}$ = 18.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, R_FCH_2, 2H); 5.2 (m, 2H); 5.8 (ddt, $^{3}J_{HH_t}$ = 16.5 Hz, $^{3}J_{HH_c}$ = 10.8 Hz, $^{4}J_{HH}$ = 3.5 Hz, CH, 1H) ppm. ^{19}F NMR ($CDCl_3$) δ: − 81.10 (t, J = 9.5 Hz, CF_3, 3F); − 113.57 (m, CF_2CH_2, 2F); − 122.24 (m, $CF_2CF_2CF_2CF_2CH_2$, 6F); − 123.07 (m, $C_3F_7CF_2$, 2F); − 123.43 (m, $C_2F_5CF_2$, 2F); − 126.46 (m, CF_3CF_2, 2F) ppm.

3.3. Synthesis of fluorinated (dimethyl)chlorosilanes

*3.3.1. Preparation of $C_nF_{2n+1}(CH_2)_2Si(CH_3)_2Cl$ (**B,n,0**)*

*Synthesis of (1H,1H,2H,2H-tridecafluorooctyl)(dimethyl)chlorosilane (**B,6,0**)*

In a stainless steel autoclave were introduced 200 μl of a solution of 10% hexachloroplatinic acid in isopropanol, vinyl olefin **A,6,0** (60 g, 0.17 mol) and chlorodimethylsilane (33 g, 0.34 mol). The autoclave was closed and the mixture was heated at 130 °C for 14 h with stirring. After cooling, the catalyst was filtered off and the black filtrate was distilled as a colourless liquid (46.8 g) in 63% yield, b.p. 76–80 °C/25 mmHg. Analysis: Found: C, 27.02; H, 2.39; F, 57.59; Cl, 7.63%. $C_{10}H_{10}F_{13}SiCl$ requires: C, 27.25; H, 2.28; F, 56.04; Cl, 8.04%; M, 440.7). IR (KBr) (cm^{-1}): 2971 (m, CH); 1362 (s, CF); 1318 (s, CF); 1260–1150 (broad) (vs, CF); 1050 (s, CF); 895 [s, $Si(CH_3)_2$]; 805–860 (broad) [s, $Si(CH_3)_2$]. ^{1}H NMR ($CDCl_3$) δ: 0.60 (s, CH_3, 6H); 1.08 (m, CH_2Si, 2H); 2.10 (m, R_FCH_2, 2H) ppm. ^{19}F NMR ($CDCl_3$) δ: − 81.18 (t, J = 9.4 Hz, CF_3, 3F); − 116.5 (m, CF_2CH_2, 2F); − 122.3 (m, $CF_2CF_2CH_2$, 2F); − 123.3 (m, $CH_2C_2F_4CF_2$, 2F); − 123.7 (m, $C_2F_5CF_2$, 2F); − 126.5 (m, CF_3CF_2, 2F) ppm. ^{29}Si NMR ($CDCl_3$) δ: + 31.45 (s, SiCl) ppm.

*Synthesis of (1H,1H,2H,2H-heptadecafluorodecyl)-(dimethyl)chlorosilane (**B,8,0**)*

A similar procedure was performed from a two-fold excess of (dimethyl)chlorosilane with respect to the vinyl olefin **A,8,0**. After distillation, a colourless liquid was obtained in 66% yield, b.p. 106–108 °C/25 mmHg. Analysis: Found: C, 25.79; H, 1.52; F, 61.15; Cl, 6.97%. $C_{12}H_{10}F_{17}SiCl$ requires: C, 26.65; H, 1.86; F, 59.73; Cl, 6.55%. The IR spectrum was similar to that of **B,6,0**. ^{1}H NMR ($CDCl_3$): similar to that of **B,6,0**. ^{19}F NMR ($CDCl_3$) δ: − 81.18 (t, J = 9.5 Hz, CF_3, 3F); − 116.3 (m, CF_2CH_2, 2F); − 122.3 (m, $CH_2CF_2CF_2CF_2CF_2$, 6F); 123.1 (m, $C_3F_7CF_2$, 2F); − 123.7 (m, $C_2F_5CF_2$, 2F); − 126.5 (m, CF_3CF_2, 2F) ppm. ^{29}Si NMR ($CDCl_3$) δ: + 31.48 (s, SiCl) ppm. MS *m/z*: 69/18 $(CF_3)^{+\bullet}$; 73/6 $[Si(CH_3)_3]^{+\bullet}$; 77/17 $[FSi(CH_3)_2]^{+\bullet}$; 109/15 $[CF_2Si(CH_3)_2H]^{+\bullet}$; 151/100 $(C_3F_6H)^{+\bullet}$; 155/42 $[CF_2C_2H_4Si(CH_3)_2F]^{+\bullet}$; 219/1 $(C_4F_9)^{+\bullet}$; 231/2 $(C_5F_9)^{+\bullet}$; 339/10 $(C_8F_{10}SiH)^{+\bullet}$; 409/5 $(C_7F_{14}CH_2\text{-}CHSi)^{+\bullet}$; 483/2 $[M-Si(CH_3)_2]^{+\bullet}$; 537/0 $(M-3H)^{+\bullet}$.

*3.3.2. Preparation of $C_nF_{2n+1}(CH_2)_3SiCl(CH_3)_2$ (**B,n,1**)*

*Synthesis of (1H,1H,2H,2H,3H,3H-tridecafluorononyl)-(dimethyl)chlorosilane (**B,6,1**)*

Hydrosilylation of a two-fold excess of (dimethyl)chlorosilane with the allyl olefin **A,6,1** was carried out similarly. After working-up, the fluorinated (dimethyl)chlorosilane **B,6,1** was distilled as a colourless liquid in 62% yield, b.p. 91–95 °C/25 mmHg. Analysis: Found: C, 28.76; H, 3.08; F, 55.26; Cl, 7.06%. $C_{11}H_{12}F_{13}SiCl$ requires: C, 29.05; H, 2.65; F, 54.31; Cl, 7.79%; M, 454.7. ^{1}H NMR ($CDCl_3$) δ: 0.70 (s, CH_3, 6H); 0.90 (m, CH_2Si, 2H); 1.55 (m, CH_2CH_2Si, 2H); 2.15 (m, R_FCH_2, 2H) ppm. ^{19}F NMR

($CDCl_3$) δ: −81.20 (t, J = 10.0 Hz, CF_3, 3F); −114.90 (m, CF_2CH_2, 2F); −122.4 (m, $CH_2CF_2CF_2$, 2F); −123.3 (m, $CH_2C_2F_4CF_2$, 2F); −124.1 (m, $C_2F_5CF_2$, 2F); −126.6 (m, CF_3CF_2, 2F) ppm. ^{29}Si NMR ($CDCl_3$) δ: +31.05 (s, SiCl) ppm. MS m/z: 69/8 $(CF_3)^{+\bullet}$; 73/13 $[Si(CH_3)_3]^{+\bullet}$; 77/26 $[Si(CH_3)_2F]^{+\bullet}$; 119/3 $(C_2F_5)^{+\bullet}$; 121/3, 123/1 $[[C_2H_4Si(CH_3)_2Cl]^{+\bullet}$; 151/100 $(C_3F_6H)^{+\bullet}$; 155/37 $[CF_2CH_2CH_2Si(CH_3)_2F]^{+\bullet}$; 169/2 $(C_3F_7)^{+\bullet}$; 219/1 $(C_4F_9)^{+\bullet}$; 361/2 $[M-Si(CH_3)_2Cl]^{+\bullet}$; 399/5 $(M-FCl)^{+\bullet}$; 421/2 $(M-FCH_3)^{+\bullet}$.

*Synthesis of (1H,1H,2H,2H,3H,3H-heptadecafluoroundecyl)(dimethyl)chlorosilane (**B,8,1**)*

In a similar manner, a two-fold excess of (dimethyl)chlorosilane was reacted with the allyl olefin **A,8,1**. After working up, the fluorinated dimethylchlorosilane **B,8,1** was distilled as white crystals. The yield was 70%, b.p. 118–122 °C/23 mmHg, m.p. 55 °C. Analysis: Found: C, 27.34; H, 2.61; F, 59.80; Cl, 5.89%. $C_{13}H_{12}F_{17}SiCl$ requires: C, 28.15; H, 2.18; F, 58.22; Cl, 6.40%; M, 554.8. ^1H NMR ($CDCl_3$): similar to that of **B,6,1**. ^{19}F NMR ($CDCl_3$) δ: −81.10 (t, J = 9.7 Hz, CF_3, 3F); −114.8 (m, CH_2CF_2, 2F); −122.3 (m, $CH_2CF_2C_3F_6$, 6F); −123.1 (m, $C_3F_7CF_2$, 2F); −124.0 (m, $C_2F_5CF_2$, 2F); −126.5 (m, CF_3CF_2, 2F) ppm. ^{29}Si NMR ($CDCl_3$) δ: +31.00 (s, SiCl) ppm.

3.4. Synthesis of fluorinated (dimethyl)hydrogenosilanes

3.4.1. Preparation of fluorinated silanes C,n,0

*Synthesis of (1H,1H,2H,2H-tridecafluorooctyl)(dimethyl)-hydrogenosilane (**C,6,0**)*

In a 500 ml two-necked round-bottom flask equipped with a condenser flushed with a nitrogen flow, **B,6,0** (50 g, 0.113 mol) dissolved in 30 ml of anhydrous diethyl ether was added dropwise into $AlLiH_4$ (2.15 g, 0.05 mol) in 8 ml of anhydrous diethyl ether at 20 °C. After addition, the solution was heated at 35 °C for 2 h. After cooling, it was carefully worked-up with aqueous acid (10% HCl). The organic phase was dried with $MgSO_4$ and distilled having 41 g of colourless liquid. The yield was 88%, b.p. 60–62 °C/25 mmHg. Analysis: Found: C, 28.96; H, 2.25; F, 62.08%. $C_{10}H_{11}F_{13}Si$ requires: C, 29.56; H, 2.73; F, 60.79%; M, 406.3. IR (KBr): similar to that of **B,6,0** with a characteristic band at 2125 cm^{-1} assigned to the Si–H function. ^1H NMR ($CDCl_3$) δ: 0.15 (d, J = 3.7 Hz, CH_3, 6H); 0.85 (m, CH_2Si, 2H); 2.1 (m, R_FCH_2, 2H); 3.95 (h, J = 3.7 Hz, SiH, 1H) ppm. ^{19}F NMR ($CDCl_3$): similar to that of **B,6,0**. ^{29}Si NMR ($CDCl_3$) δ: −11.26 (d, J_{SiH} = 179 Hz, SiH) ppm; with H irradiation: −11.26 (s, SiH) ppm. MS m/z: 62/40 $(SiFCH_3)^{+\bullet}$; 69/51 $(CF_3)^{+\bullet}$; 77/100 $[FSi(CH_3)_2]^{+\bullet}$; 90/10 $[CFSi(CH_3)_2H]^{+\bullet}$; 109/65 $[CF_2Si(CH_3)_2H]^{+\bullet}$; 119/15 $(CF_3CF_2)^{+\bullet}$; 131/13 $(C_3F_5)^{+\bullet}$; 150/3 $(C_3F_6)^{+\bullet}$; 169/8 $(C_3F_7)^{+\bullet}$; 181/6 $(C_4F_7)^{+\bullet}$; 219/4 $(C_4F_9)^{+\bullet}$; 238/19 $(C_4F_{10})^{+\bullet}$; 245/18 $(C_6F_9H_2)^{+\bullet}$; 263/10 $(C_5F_{10}CH)^{+\bullet}$; 269/3 $(C_5F_{11})^{+\bullet}$; 289/7 $(C_8F_{10}H_3)^{+\bullet}$; 309/6 $(C_6F_{11}C_2H_4)^{+\bullet}$; 328/1 $(C_6F_{12}CH_2CH_2)^{+\bullet}$.

*Synthesis of (1H,1H,2H,2H-heptadecafluorodecyl)(dimethyl)hydrogenosilane (**C,8,0**)*

Similarly, the fluorinated chlorosilane **B,8,0** gave the corresponding silane in 92% yield, b.p. 85–90 °C/25 mmHg. Analysis: Found: C, 27.98; H, 1.88; F, 65.14%. $C_{12}H_{11}F_{17}Si$ requires: C, 28.47; H, 2.19; F, 63.79%; M. 506.28. The IR and ^1H NMR spectra were similar to those of **C,6,0**. The ^{19}F NMR spectrum is similar to that of **B,8,0**. ^{29}Si NMR ($CDCl_3$) δ: −11.30 (d, J_{SiH} = 182 Hz, SiH) ppm; with H irradiation: −11.30 (S, SiH) ppm.

3.4.2. Preparation of fluorinated silanes C,n,1

*Synthesis of (1H,1H,2H,2H,3H,3H-tridecafluorononyl)-(dimethyl)hydrogenosilane (**C,6,1**)*

A similar procedure was used from the corresponding fluorinated chlorosilane **B,6,1**, and after reaction, working-up and distillation, a colourless liquid was obtained in 80% yield, b.p. 91–95 °C/25 mmHg. Analysis: Found: C, 30.77; H, 2.81; F, 60.09%. $C_{11}H_{13}F_{13}Si$ requires: C, 31.43; H, 3.12; F, 58.76%; M, 420.29. The IR spectrum was similar to that of **C,6,0**. ^1H NMR ($CDCl_3$) δ: 0.15 (d, J = 3.6 Hz, CH_3, 6H); 0.70 (m, CH_2Si, 2H); 1.7 (m, CH_2CH_2Si, 2H); 2.10 (m, R_FCH_2, 2H); 3.95 (h, J = 3.7 Hz, Si–H, 1H) ppm. ^{19}F NMR ($CDCl_3$): similar to that of **B,6,1**. ^{29}Si NMR ($CDCl_3$) δ: −11.27 (d, J_{SiH} = 185 Hz, SiH) ppm; with H irradiation: only a singlet at −11.27 ppm.

*Synthesis of (1H,1H,2H,2H,3H,3H-heptadecafluoroundecyl)(dimethyl)hydrogenosilane (**C,8,1**)*

The reduction of the fluorinated chlorosilane **B,8,1** was carried out using similar conditions to those used in the above examples. After reaction, working-up and distillation, a colourless liquid was obtained. The yield was 82%, b.p. 111–116 °C/23 mmHg. Analysis: Found: C, 29.20; H, 1.90; F, 63.65%. $C_{13}H_{13}F_{17}Si$ requires: C, 30.01; H, 2.51; F, 62.07%; M, 520.30. The IR and ^1H NMR spectra were similar to those for **C,6,1**. The ^{19}F NMR spectrum was similar to that of **B,8,1**. ^{29}Si NMR ($CDCl_3$) δ: −11.30 (d, J_{SiH} = 183 Hz, SiH) ppm; with H irradiation: only one singlet at −11.30 (s, SiH) ppm.

4. Conclusions

Four new fluorinated hydrogenosilanes with different fluorinated chains R_F and spacers between R_F and SiH were synthesized by selective reduction of the corresponding fluorinated chlorosilanes that were obtained by hydrosilylation of (dimethyl)chlorosilane (DMC) with fluorinated vinyl or allyl olefins. Such a latter reaction was optimized and for both series the yields depended on the time, temperature and the initial $[DMC]_0/[olefin]_0$ and $[catalyst]_0/[olefin]_0$ molar ratios. Each step gave satisfactory yields.

The allyl olefins showed a higher reactivity in hydrosilylation than the vinyl. The former were prepared from perfluoroalkyl iodides (R_FI) under milder conditions and with higher yields than those obtained for the synthesis of the vinyl ones. The compounds $R_FC_3H_6Si(CH_3)_2H$ and

$R_FC_2H_4Si(CH_3)_2H$ were produced from R_FI in overall yields of 42% and 37%, respectively.

Such fluorinated ω-SiH derivatives are interesting reactants for future hydrosilylations on to double bonds that are under investigation.

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