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1,3-Migration of a phenyl group in the conversion of $(Me_3Si)_2(PhMe_2Si)CSiMePhX$ into $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$ species

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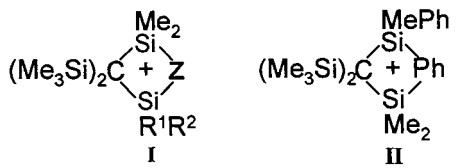
Abstract

The finding that compounds of the type $(Me_3Si)_2(PhMe_2Si)CSiMePhX$ react with electrophiles to give very predominantly rearranged products $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$, which would be expected to be thermodynamically disfavoured, can be rationalized in terms of a mechanism in which the anchimerically-assisted departure of X^- gives the Ph-bridged cation $[(Me_3Si)_2C\overline{SiMe_2(\mu\text{-}Ph)Si}MePh]^+$ which is attacked by the nucleophile at the less hindered centre bearing two Me groups rather than that bearing one Me and one Ph group, with the outcome determined by kinetic rather than thermodynamic factors. Both $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$ and its isomer $(Me_3Si)_2(PhMe_2Si)CSiMePhBr$ react with $AgBF_4$ in CH_2Cl_2 or Et_2O to give $>95\%$ of the fluoride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$. Reaction of the bromide $(Me_3Si)_2(PhMe_2Si)CSiMePhBr$ with AgO_2CCF_3 in Et_2O, and that of the hydride $(Me_3Si)_2(PhMe_2Si)CSiMePhH$ with ICl in CCl_4, likewise give $>95\%$ of the rearranged $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_2CCF_3$ and $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$, respectively. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 1,3-phenyl migration; Organosilanes; Anchimeric assistance; Reaction mechanism

1. Introduction

It is known that appropriate groups Z in compounds of the type $(Me_3Si)_2(ZMe_2Si)CSiR^1R^2X$ can provide anchimeric assistance to the leaving of X^-, usually I^-, in reactions with some electrophiles, including Ag^I salts, ICl, CF_3CO_2H and CF_3CH_2OH [1–7]. For example, Z can be Me [2], Ph [3], CH=CH_2 [4], OMe [5,6], N_3 [7], NCS [7], or OCOMe [8]. The anchimeric assistance is associated with formation of a 1,3-bridged cation of type **I**, which can be attacked by a nucleophile, with ring opening, at either the α- or γ-Si atom; that is, 1,3-migration of Z can occur [1–7]. In general, but by no means always [9], the proportion of attack at the two centres seems to be determined mainly by the relative degrees of steric hindrance at those centres; for example, in reactions of the iodide $(Me_3Si)_3CSiPh_2I$ with silver sa1ts AgY the exclusive or greatly predominant product in each case is the rearranged species $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$ (actually the fluoride from $AgBF_4$), attack at the α-Si atom in an intermediate **I** with $R^1R^2 = Ph_2$ being much more hindered than that at the γ-Si bearing two Me groups.



It was recently shown that in reactions of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$, **1d**, with electrophiles a Ph group provides nucleophilic assistance to the leaving of I^- to give the intermediate cation **II** but that since this is attacked by the nucleophile more readily at the $SiMe_2$

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centre little, if any, migration of a Ph group is observed, the products being exclusively or very predominantly of the unrearranged type $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$ **1** [10]. If the proposed mechanistic picture is correct, the same intermediate should be formed in corresponding reactions of compounds $(Me_3Si)_2(PhMe_2Si)CSiMePhX$, **2**, which should thus also give predominantly the species **1** with X = Y (in this case the rearranged products). However, this would involve going from a compound with the two Ph groups on different Si centres to one with both of them on a single Si centre, which in such a highly crowded system would be expected to be thermodynamically very unfavourable. We show below that compounds of type **2** do, indeed, give wholly or very predominantly products of type **1**, the outcome evidently being determined by kinetic rather than thermodynamic factors. The results serve to confirm the validity of the proposed mechanism.

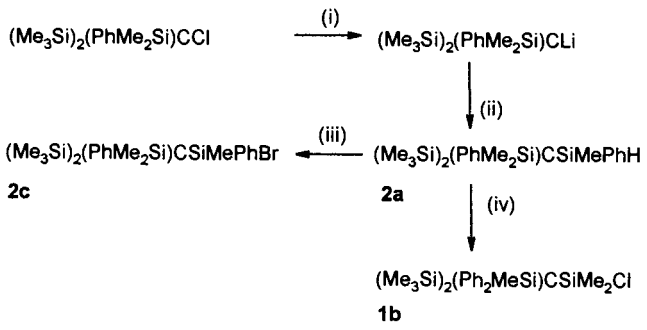
We concentrated primarily on the reactions of the bromides **1c** and **2c** with $AgBF_4$, since the identities and relative proportions of formed fluorides can be established by ^{19}F-NMR spectroscopy; not only can the chemical shifts be compared with those of authentic or related fluorides but furthermore the multiplicity of the signal distinguishes unambiguously between $SiMe_2F$ and SiMePhF groups. To look for possible effects of changing the leaving group X and the electrophilic reagent we also examined the reactions of the bromide **2c** with AgO_2CCF_3 and the hydride **2a** with ICl.

$(Me_3Si)_2(Ph_2MeSi)$-CSiMe$_2$X		$(Me_3Si)_2(PhMe_2Si)$-CSiMePhX	
la	X=H	**2a**	X=H
b	Cl	**b**	Cl
c	Br	**c**	Br
d	I	**d**	I
e	F	**e**	F
f	O_2CCF_3	**f**	O_2CCF_3

2. Results and discussion

The hydride **2a**, bromide **2c**, and chloride **1b** were prepared by the methods outlined in Scheme 1.

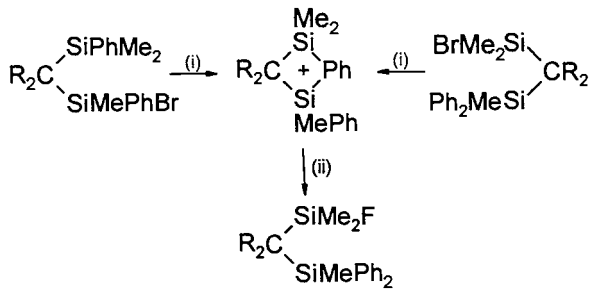
The bromide **2c** was found to react with an excess of $AgBF_4$ in Et_2O at room temperature ca. ten times as fast as $(Me_3Si)_3CSiMe_2Br$ under the same conditions. (For details see Section 3) The rate of reaction of **1c** in Et_2O was roughly similar to that of **2c**, in agreement with observations on the relative reactivities of the iodides **1d** and $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$ towards silver salts [10].) This confirmed that there is anchimeric assistance by the γ-Ph group, consistent with the view that the intermediate cation is formed in the rate-determining step. The product was very predominantly the rearranged fluoride **1e** along with ca. 5% of the unrearranged **2e**. When the reaction was carried out in CH_2Cl_2 the product appeared to be exclusively the rearranged fluoride **1e**, but up to ca. 3% of the unrearranged **2e** could possibly have escaped detection. Under comparable conditions the bromide **1c** gave **1e** and **2e** in a ca. 98/2 ratio in CH_2Cl_2 and apparently exclusively **1e** in Et_2O. Thus there is no significant difference between the outcomes of the reactions of the two bromides, in keeping with Scheme 2. (The apparent formation of a little more **1e** than **2e** from **1c** in Et_2O than in CH_2Cl_2, and correspondingly of a little more **2e** than **1e** from **2c** in CH_2Cl_2 than in Et_2O, may not be real, but it would be consistent with observations that the extent of rearrangement in reactions of this general type tends to be lower in Et_2O than in CH_2Cl_2 [11]).



Scheme 1. Reagents and conditions: (i) BuLi, THF–pentane–Et_2O–hexanes, −110°C. (ii) PhMeSiHCl. (iii) Br_2 in CCl_4. (iv) ICl (two equivalents) in CCl_4.

Reaction of the bromide **2c** with AgO_2CCF_3 occurred in Et_2O at room temperature. The product appeared from the ^{1}H-NMR spectrum to be exclusively the rearranged trifluoroacetate **1f**, and GLC-MS revealed only one product, with the expected mass spectrum. However, the^{19}F-NMR spectrum showed two peaks, one very small and possibly arising from the presence of up to ca. 4% of the unrearranged **2f**.

In the case of compounds of the type $(Me_3Si)_3CSiR_2X$, reaction of the hydride



Scheme 2. Course of the reaction of $(Me_3Si)_2(PhMe_2Si)CSiMePhBr$, **2c**, and $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$, **1c**, with $AgBF_4$. (i) $AgBF_4$, –AgBr. (ii) BF_4^-, $-BF_3$.

$(Me_3Si)_3CSiR_2H$ with one molar equivalent of ICl usually gives the corresponding iodide $(Me_3Si)_3CSiR_2I$, which with a further molar equivalent of ICl gives the rearranged chloride $(Me_3Si)_2(R_2MeSi)CSiMe_2Cl$, either exclusively (e.g. R = Ph), or (e.g. R = Et) along with unrearranged chloride $(Me_3Si)_3SiR_2Cl$ [2,12]. Thus in order to determine the outcome of the reaction of the iodide **2d** with ICl we treated the hydride **2a** with two molar equivalents of ICl in CCl_4. The product was judged from the ^{1}H-NMR spectrum to be exclusively the expected rearranged chloride **1b**, though perhaps up to 4% of the unrearranged **2b** could have escaped detection. (In contrast, when the hydride **2a** was treated with 2.4 equivalents of ICl_3 a ca. 1:1 mixture of rearranged **1b** and unrearranged **2b** was obtained, the latter presumably being formed by direct chlorination of the hydride, perhaps by some Cl_2 liberated from the ICl_3.)

Having obtained the chloride **1b** as described above, we examined its reactions with $AgBF_4$. As expected, it reacted more slowly than the bromide **1c**, and faster in CH_2Cl_2 than in Et_2O, and the reaction was not taken to completion in the latter. The fluorides **1e** and **2e** were formed in ca. 92/8 ratio in CH_2Cl_2 and ca. 88/12 ratio in Et_2O, these ratios not being significantly different. (There could have been a little **2b** in the initial **1b**, but this would not have an appreciable effect since it would also mainly give **1e**.) There thus may be a small difference between the proportion of rearranged product from the chloride and bromide but it is too little to justify speculative discussion at this stage, and a more detailed study might be appropriate.

The fact that the outcome of the attack of the nucleophile on the cation **II** is determined by the comparative ease of attack at the relevant Si centres rather than by the relative thermodynamic stabilities of the products implies that the transition state for the reaction of the nucleophile with the cation **II** is close to the latter, so that the relative stabilities of the possible products have little influence. It is noteworthy that in the reaction of the iodide $(Me_3Si)_3CSiMePhI$ with AgO_2CMe in $MeCO_2H$, the attack on the closely related intermediate cation I with Z = Me, R^1 = Me, and R^2 = Ph (i.e. differing from **II** only in having bridging Me in place of Ph) is less selective, taking place at the $SiMe_2$ centre only ca. three times as readily as at the SiMePh centre [2]a. This is consistent with expected lower stability, and thus lower selectivity, of an Me-than of a Ph-bridged cation.

3. Experimental

3.1. General

All reactions were carried out under argon with exclusion of moisture. The room temperature was 18–20°C. Solvents were dried by standard methods and stored over molecular sieves or a sodium mirror as appropriate.

The ^{1}H and ^{19}F-NMR spectra were recorded at 200 or 300 MHz on a Bruker AC or MSL spectrometer, respectively. The ^{13}C spectra were recorded at 300 Hz on the MSL instrument; the signals from the quaternary carbons were not observed. The mass spectra were obtained by electron impact at 70 eV unless otherwise indicated. (Except in the case of the M^+ ion, only ions of relative intensity >10 are included. Suggested identities of ions are not meant to indicate fragmentation patterns.) Gas chromatography was carried out with linear programming from 50–250°C at 15 °C min^{-1} on a 25 m capillary column coated with 10% OV-101 unless otherwise indicated.

3.2. Preparations of compounds *1a–c*, *2a* and *2c*

3.2.1. Hydride *2a*

A solution of $(Me_3Si)_2(PhMe_2Si)CCl$ [13] (10.05 g, 0.031 mol) in a mixture of THF (90 cm^3), pentane (10 cm^3) and Et_2O (20 cm^3) was treated with stirring at −110°C with a 2.5 mol dm^{-3} solution of BuLi in hexanes (13 cm^3, 0.0325 mol of BuLi) precooled to −78°C. The stirred mixture was kept at −110°C for 2 h and PhMeSiHCl (5.5 cm^3, 0.035 mol) was added. The mixture was stirred for 1 h at −110°C then allowed to warm to room temperature. The solvents were removed under reduced pressure and the residue was extracted with pentane (50 cm^3). The extract was filtered, the solvent evaporated, and the residue recrystallized from MeOH to give the hydride **2a** (5.0 g, 40%); m.p. 73°C. Ana1. Found: C, 64.2; H, 8.9. $C_{22}H_{38}Si_4$ Calc.: C, 63.7; H, 9.2%. ^{1}H-NMR (C_6D_6): δ 0.14 (9H, s, $SiMe_3$), 0.30 (9H, s, $SiMe_3$), 0.44 (3H, d, J = 3.9 Hz, SiMePhH), 0.57 (3H, s, $SiMe_2Ph$), 0.58 (3H, s, $SiMe_2Ph$), 5.1 (^{1}H, q J = 3.9 Hz, SiH) and 7.2–7.8 (m 10H, Ph). ^{13}C-NMR (C_6D_6): δ 2.5 (Si*Me*PhH), 4.41 (Si*Me*$_2$Ph), 4.61 (Si*Me*$_2$Ph), 5.9 ($SiMe_3$). 6.5 ($SiMe_3$), 128.2, 128.4, 129.9, 130.2, 137.1, 137.5 (all Ph). ^{29}Si-NMR (C_6D_6): δ −0.69 ($SiMe_3$), −0.84 ($SiMe_3$), −7.08 ($SiMe_2Ph$), −12.51 (SiMePhH). MS: m/z 414 (2%, M^+), 399 (20, M–Me), 355 (40, M–$SiMe_2H$), 321 (100, M–Me–PhH), 135 (5, $SiMe_2Ph$).

3.2.2. Bromide *2c*

A 2.1 mol dm^{-3} solution of Br_2 in CCl_4 (0.42 cm^3) was added with stirring to a solution of the hydride **2a** (0.37 g, 0.90 mmol) in CCl_4 (2.5 cm^3). The mixture was stirred for 0.5 h at room temperature and the solvent was then removed under vacuum to leave the bromide **2c** (0.44 g, 99%), which was recrystallized from light petroleum to give a solid of m.p. 142°C. Anal. Found: C, 53.0; H, 7.4. $C_{22}H_{37}BrSi_4$ Calc.: C, 53.5; H, 7.6%. ^{1}H-NMR (C_6D_6); δ 0.33 (9H, s, $SiMe_3$), 0.35 (9H, s,

$SiMe_3$), 0.64 (3H, s, Si*Me*$_2$Ph), 0.68 (3H, s, Si*Me*$_2$Ph), 1.04 (3H, s, Si*Me*PhBr), 7.0–7.6 (10H, m, Ph); ^{13}C-NMR (C_6D_6): δ 5.8 (Si*Me*$_2$Ph), 7.21 ($SiMe_3$), 7.29 ($SiMe_3$), 10.5 (Si*Me*PhBr), 128.2, 129.9, 130.5, 137.1, 137.6 (all Ph). ^{29}Si-NMR (C_6D_6): δ −6.71 ($SiMe_2$Ph), −0.17 ($SiMe_3$), 0.13 ($SiMe_3$), 13.5 (SiMePhBr). MS: m/z 492 (2%, M^+), 477 (47%, M–Me), 278 (100, M–Me–SiMePhBr), 135 (22), 73 (10).

3.2.3. Chloride **1b**

A 0.82 mol dm^{-3} solution of ICl (5.4 mmol) in CCl_4 (6.7 cm^3) was added to a solution of hydride **2a** (1.06 g, 2.6 mmol) in CCl. (3 cm^3). After 1 h at room temperature the solvent and traces of ICl were removed under vacuum and the residue was recrystallized from pentane to give the chloride **1b** (86%), m.p. 151°C (lit. 156°C [2]b). Anal. Found C, 58.2; H, 8.5. $C_{22}H_{37}ClSi_4$ Calc. C, 58.8; H, 8.3%. ^{1}H-NMR (C_6D_6); δ 0.35 (18H, s, $SiMe_3$), 0.58 (6H, s, $SiMe_2Cl$), 0.99 (3H, s, Si*Me*Ph$_2$), 7.2–8.1 (10H, m, Ph); ^{13}C-NMR (C_6D_6): δ 4.9 (Si*Me*Ph$_2$), 7.3 ($SiMe_3$), 10.7 ($SiMe_2Cl$), 129.0, 129.2, 130.0, 137.8 (all Ph). ^{29}Si-NMR (C_6D_6): δ −12.21 (Si*Me*Ph$_2$), −0.77 ($SiMe_3$), 26.3 ($SiMe_2Cl$).(The presence of up to ca. 4% of **2b** could have escaped detection.) Examination by GLC-MS revealed only peak, giving m/z 433 (13%, M–Me], 398 (10, M–Me–Cl),), 356 (38, M–Me–Ph), 236 (20, M–Me–$SiMePh_2$), 216 (100, M–Me–$SiPh_2Cl$), 197 (33, $SiMePh_2$

3.2.4. Hydride **1a**

A mixture of the chloride **1b** (0.18 g, 0.40 mmol) and $LiAlH_4$ (0.25 g, 6.6 mmol) in THF (50 cm^3) was refluxed for 8 h and then allowed to cool to room temperature before being added to wet hexane (40 cm^3). The mixture was then added to saturated aqueous NH_4Cl and the organic layer was separated, dried ($MgSO_4$), and evaporated. The residue was recrystallized from MeOH to give **1a** (0.083 g, 50%), m.p. 96°C (lit. 121°C [10]). Anal. Found: 63.1; H, 9.0. $C_{22}H_{38}Si_4$. Calc. 63.7: H, 9.2%. ^{1}H-NMR (C_6D_6); δ 0.18 (6H, d, $J_{HH} = 3.7$ Hz, $SiMe_2$), 0.21 (18H, s, $SiMe_3$), 0.91 (3H, s, $SiMePh_2$), 7.5–8.0 (10H, m, Ph), 5.1 (^{1}H, inept., SiH) (the data are in agreement with those for a sample obtained earlier by a different method [10]). MS: m/z 414 (1%, M^+), 399 (14, M–Me), 321 (100, M–Me–PhH), 247 (31), 197 (45, $SiMePh_2$), 135 (42, $SiMe_2Ph$), 73 (30, $SiMe_3$).

3.2.5. Bromide **1c**

A 1.83 mol dm^{-3} solution (0.070 cm^3) of Br_2 (0.131 mmol) in CCl_4 was added to a stirred solution of the hydride **1a** (0.048 g, 0.121 mmol) in CCl_4. After 30 min solvent and traces of Br_2 were removed under vacuum to leave bromide **1c** (0.056 g, 98%), m.p. 164°C. Anal. Found: C, 54.1; H, 7.2. $C_{22}H_{37}BrSi_4$ Calc.: C, 53.5; H, 7.6%. δ ^{1}H-NMR (C_6D_6); δ 0.27 (18H, s, $SiMe_3$), 0.67 (6H, s, $SiMe_2$), 0.93 (3H, s, Si*Me*Ph$_2$), 7.2–8.1 (10H, m, Ph). ^{13}C-NMR (C_6D_6): δ 5.0 ($SiMePh_2$), 7.5 ($SiMe_3$), 12.1 ($SiMe_2Br$), 128.2, 129.0, 130.1 and 137.9 (all Ph). MS: m/z 492 (1%, M), 477 (35, M–Me), 413 (10, M–Br), 280 (40, M–Me–$SiMePh_2$), 216 (100, M–Me–$SiPh_2Br$), 73 (10).

3.3. Reactions with silver salts

(i) A mixture of the bromide **2c** (0.142 g, 0.30 mmol) and $AgBF_4$ (0.086 g, 0.44 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 16 h at room temperature. The solution was then filtered and the solvent removed under vacuum, to leave the fluoride **1e** (0.127 g, 98%), m.p. 130°C. Anal. Found: C, 61.3; H, 8.9. $C_{22}H_{37}FSi_4$ Calc.: C, 61.0; H, 8.6%. ^{1}H-NMR (C_6D_6); δ 0.22 (6H, d, $J = 7.8$, $SiMe_2F$), 0.23 (18H, s, $SiMe_3$) 0.96 (3H, s, Si*Me*Ph$_2$) and 7.1–8.1 (10H, m, Ph): ^{19}F-NMR (C_6D_6): δ −134.5 ppm (heptet $J_{FH} = 7.5$ Hz). MS: m/z 432 (2%, M^+), 417 (18, M–Me), 339 (68), 220 (34), 216 (100, M–$SiMePh_2F$), 197 (30, $SiMePh_2$).

(ii) A mixture of the bromide **2c** (0.085 g, 0.173 mmol) and $AgBF_4$ (0.203 g, 1.04 mmol) in Et_2O (40 cm^3) was stirred for 80 min at room temperature, after which analysis by GLC (on OV-17) indicated that only ca. 62% of the substrate had been consumed (indicating a half life of roughly 60 min). After 180 min no detectable **2c** remained; the solvent was removed and the residue taken up in C_6D_6 and shown by ^{19}F-NMR spectroscopy to contain **1e** and **2e** in 95:5 ratio, as indicated by the integrals of the heptet at −134.5 and quartet at −147 ppm. The presence of the minor component was not evident from the ^{1}H or mass spectra, which were as in (i).

Reaction of $(Me_3Si)_3CSiMe_2Br$ under the same conditions was *ca.* 18% complete after 3 h and 74% after 22 h (as indicated by GLC), pointing to a half-life of roughly 10.5 h. The half life for **1c** was less accurately indicated because only a very small amount of the substrate was available, but it was comparable with that of **2c**.

(iii) A mixture of the bromide **1c** (0.0056 g, 0.010 mmol) and $AgBF_4$ (0.023 g, 0.11 mmol) in CH_2Cl_2 (2 cm^3) was stirred for 24 h at room temperature. The solution was then filtered and the solvent removed under vacuum, and the residue was extracted with C_6D_6 to give a solution whose ^{19}F spectrum showed the heptet at −134.5 and quartet at −147 ppm in ca. 98:2 ratio. The ^{1}H-NMR and mass spectra were as in (i).

(iv) A mixture of the bromide **1c** (0.0043 g, 0.0090 mmol) and $AgBF_4$ (0.0102 g, 0.050 mmol) in Et_2O (2 cm^3) was stirred for 24 h at room temperature. The solution was then filtered, the solvent removed under vacuum, and the residue extracted with C_6D_6 to give a solution whose ^{19}F spectrum showed only the heptet at −134.5 ppm. The ^{1}H-NMR and mass spectra were as in (i).

(v) A mixture of $AgBF_4$ (0.0055 g, 0.028 mmol) and chloride **1b** (0.0078 g, 0.017 mmol) in CH_2Cl_2 (3 cm^3) was stirred at room temperature for 48 h. Filtration of the solution, removal of the solvent, and extraction of the residue with C_6D_6 gave a solution showing in its ^{19}F spectrum the heptet at −134.5 and quartet at −147 ppm in 92/8 ratio. The presence of the minor component was not detected in the ^1H spectrum, which was as in (i).

(vi) A mixture of $AgBF_4$ (0.041 g, 0.21 mmol) and chloride **1b** (0.0197 g, 0.044 mmol) in Et_2O (4 cm^3) was stirred at room temperature (ca. 18°C) for 168 h. Work up as in (iv) gave a C_6D_6 solution showing in its ^{19}F-NMR spectrum the heptet at −134.5 and quartet at −147 ppm in 88/12 integration ratio. The ^1H-NMR spectrum revealed that ca. 24% of unchanged **1b** was present.

(vii) A mixture of the bromide **2c** (0.036 g, 0.073 mmol) and AgO_2CCF_3 (0.0205 g, 0.093 mmol) in Et_2O (7 cm^3) was stirred at room temperature. After 3 days analysis by GLC showed that only 77% of the substrate had disappeared and so further AgO_2CCF_3 (0.045 g, 0.20 mmol) was added and stirring was continued for 24 h, after which reaction was complete. The solution was filtered and the solvent removed under vacuum to leave a solid (0.037 g, 96%) which appeared from its ^1H-NMR spectrum in C_6D_6 to be virtually pure **1f**, m.p. 91°C (lit. 94°C [10,14]); ^1H-NMR: δ 0.24 (18H, s, $SiMe_3$), 0.45 (6H, s, $SiMe_2O_2CCF_3$) and 0.87 (3H, s, $SiMePh_2$), but along with the expected ^{19}F peak (in C_6D_6) at −75.6 ppm there was a small peak at −75.4 ppm that could have come from ca. 5% of **2f.** Examination by GLC-MS revealed only one product, with m/z 526 (7%, M^+), 511 (19, M–Me), 461 (15), 314 (16, M–Me–$SiMePh_2$), 216 (100, M–Me–$SiPh_2O_2CCF_3$), 197 (35, $SiMePh_2$) and 185 (17).

(viii) A mixture of the bromide **2c** (0.11 g, 0.22 mmol) and AgO_2CCF_3 (0.048 g, 0.22 mmol) in CH_2Cl_2 (4 cm^3) was stirred for 60 h at 25 °C. The solution was filtered and the solvent removed to leave **1f** with a ^1H-NMR spectrum in C_6D_6 identical with that reported in (vii) above, and showing only one peak in the ^{19}F-NMR spectrum, at −75.6 ppm. Anal. Found: C, 55.3; H, 7.8. $C_{24}H_{37}F_3O_2Si_4$ Calc.: C, 54.7; H, 7.1%.

3.4. Reaction of the hydride *2a* with ICl and with ICl_3

(i) A mixture of **2a** (0.33 g, 0.80 mmol) and ICl (0.26 g, 1.6 mmol) in CCl_4 (15 cm^3) was stirred at room temperature for 1 h. The solvent was then removed under vacuum and the residual solid (0.34 g, 95%) was judged to be virtually pure chloride **1b**; ^1H-NMR (C_6D_6); δ 0.33 (18H, s, $SiMe_3$), 0.55 (6H, s, $SiMe_2Cl$), 0.98 (3H, s, $SiMePh_2$), 7.0–7.8 (10H, m, Ph). Examination by GLC-MS revealed only one product, with m/z (15 eV) 433 (13%, M–Me], 397 (9), 355 (33, M–$SiMe_2Cl$), 236 (20, M–Me–$SiMePh_2$), 216 (100, M–Me–$SiPh_2Cl$), 201 (10), 197 (33, $SiMePh_2$).

(ii) A solution of **2a** (0.23 g, 0.55 mmol) in CCl_4 (5 cm^3) was treated with a solution of ICl_3 (1.30 mmol) in CCl_4 (5 cm^3) and the mixture was stirred at room temperature for 30 min. The solvent was then removed under vacuum and the residual solid (0.24 g, 98%), m.p. ca. 124°C, was shown by GLC-MS analysis to be an ca. 1:1 mixture of the chlorides **1b** and **2b**. For **1b**: ^1H-NMR (C_6D_6): δ 0.33 (18H, s, $SiMe_3$), 0.55 (6H, s, $SiMe_2Cl$), 0.98 (3H, s, $SiMePh_2$) and 7.0–8.1 (10H, m, Ph); m/z 448 (1%, M^+), 433 (50%, M–Me), 397 (25), 355 (62, M–$SiMe_2Cl$)), 236 (37), 197 (54, $SiMePh_2$), 135 (2), 73 (4). For **2b**: ^1H-NMR (C_6D_6): δ 0.31 (9H, s, $SiMe_3$), 0.34 (9H, s, $SiMe_3$), 0.63 (3H, s, $SiMe_2Ph$), 0.66 (3H, s, $SiMe_2Ph$), 0.85 (3H, s, $SiMePhCl$) and 7.1–7.5 (10H, m, Ph). ^{13}C-NMR δ 5.71 ($SiMe_2Ph$), 7.06 ($SiMe_3$), 9.66 ($SiMePhCl$), 129–140 (Ph). MS m/z 448 (2%), 433 (50), 397 (25), 355 (100), 135 (15).

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