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Anchimeric assistance by γ-substituents Z, Z = MeO, PhO, MeS or PhS, in reactions of the bromides $(Me_3Si)_2(ZMe_2Si)CSiMe_2Br$ with $AgBF_4$

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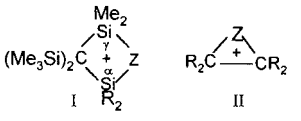
Abstract

The new organosilicon bromides $(Me_3Si)_2(ZMe_2Si)CSiMe_2Br$ with Z = PhO or MeS have been prepared and new spectroscopic data obtained for the previously reported compounds with Z = H, F, Br, Me, Ph, MeO or PhS. Competitions between pairs of bromides for a deficiency of $AgBF_4$ in Et_2O, with the determination of the ratio of the fluoride products by ^{19}F-NMR spectroscopy, have led to the following approximate relative reactivities of the bromides and so to the relative abilities of the γ-Z groups to provide anchimeric assistance to the leaving of Br^- in this reaction: Me, 1; Ph, 40; PhO, 3400; PhS, 5000; MeS, 7000; MeO, 54 000. In methanolysis in CH_2Cl_2, $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ has been found to be roughly 120 times as reactive as $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$. Combination of the results with previously available information suggests the following approximate order of ability of γ-groups Z to provide anchimeric assistance in reactions at the Si–X bonds in compounds $(Me_3Si)_2(ZMe_2Si)CSiMe_2X$: $OCOMe > OMe > OCOCF_3 > MeS > PhS$, $PhO > N_3$, $Cl > NCS > Ph > CH{=}CH_2 > Me$. © 2001 Published by Elsevier Science B.V.

Keywords: Silicon; Trisyl; Mechanism; Anchimeric assistance

1. Introduction

It is known that appropriate groups Z in compounds of the type $(Me_3Si)_2(ZMe_2Si)CSiR_2X$ can provide anchimeric assistance to the leaving of X^- in reactions with electrophiles, including Ag(I) and Hg(II) salts [1], ICl [2], CF_3CO_2H [1] and CF_3CH_2OH [3–5]. For example, Z can be Me [1], Ph [4,6], $CH_2{=}CH$ [5], MeO [7–9], N_3 [9], SCN [9b] or MeC(O)O [10,11]. Usually X is I, but with Z groups that supply especially powerful assistance, such as MeO or MeC(O)O, it can be Br, Cl or even H [3], and where there is such activation even MeOH can serve as the electrophile. Thus $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ reacts readily with MeOH, at least 10^6 times as rapidly as $(Me_3Si)_3CSiMe_2Cl$ [7], and $(Me_3Si)_2\{MeC(O)OMe_2Si)\}CSiMe_2Cl$ is even more reactive [11b]. The anchimeric assistance is associated with the formation of a 1,3-bridged cation of the type I, which can then be attacked by a nucleophile at either the α- (the original point of attachment of X) or the γ-Si atom. When R = Me, as in the compounds considered below, the same product is formed in both cases.



The aim of the present work was to obtain information on the relative abilities of the groups MeO, PhO, MeS and PhS to provide anchimeric assistance, a comparison given added interest by the fact that in anchimeric assistance to ionisation of organic compounds involving 1,2-bridging in ions of the type II, to which the assistance to reactions of the silicon compounds shows some analogy, RS groups are known to be substantially more effective than RO groups [12].

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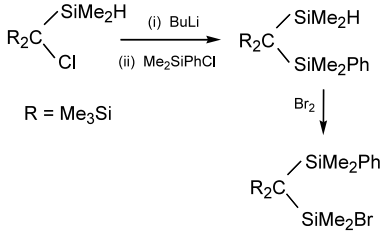
Throughout the account below R denotes Me_3Si.

2. Results and discussion

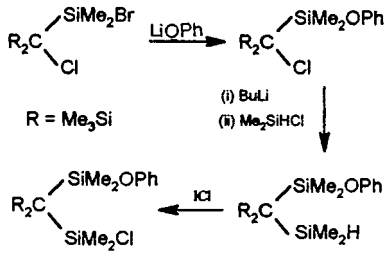
2.1. Syntheses

For comparison the bromides $R_2(ZMe_2Si)CSiMe_2Br$ with R = Me_3Si and Z = Me, Ph, MeO, PhO, MeS, or PhS were mainly used. Those with Z = Me [13] or MeO [14] were prepared as described previously and the others were obtained by the routes shown in Schemes 1–3. Comments on some aspects of the preparations are given below:

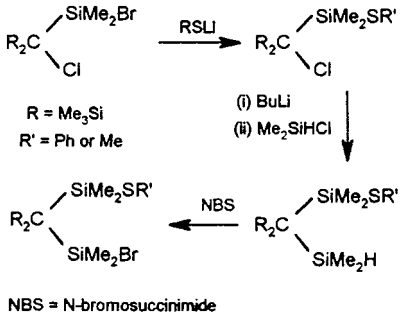
1. The compound $R_2(PhMe_2Si)CSiMe_2Br$ (Scheme 1) was prepared previously by a different route [15].
2. In the sequence shown in Scheme 2 the organolithium reagent $R_2(PhOMe_2Si)CLi$ was generated and this could no doubt be used to attach the ligand $R_2(PhOMe_2Si)C$ to a range of metals, including those to which the PhO group could be expected to coordinate. It is also noteworthy that the use of a one molar proportion of ICl in the reaction with the hydride $R_2(PhOMe_2Si)CSiMe_2H$ led to the formation of a chloride $R_2(PhOMe_2Si)CSiMe_2Cl$ rather than an iodide which is the most usual outcome of this type of reaction [2]. Similar behaviour was observed previously for the reaction of $R_2(MeOMe_2Si)CSiMe_2H$ [3].
3. In Scheme 3 the use of *N*-bromosuccinimide, NBS, to convert an Si–H into an Si–Br bond is noteworthy. When the usual reagent, bromine, was used in a one molar proportion the organosilicon product from $R_2(PhSMe_2Si)CSiMe_2H$ was almost exclusively the dibromide $R_2C(SiMe_2Br)_2$ with a substantial amount of PhSSPh as a by product. It seems likely that the initial reaction is to give the monobromide $R_2(PhSMe_2Si)CSiMe_2Br$ and HBr, with the latter then cleaving the Si–SPh bond. The hydride $R_2(MeSMe_2Si)CSiMe_2H$ likewise gave very predominantly the dibromide when treated with one equivalent of Br_2 but the required $R_2(MeSMe_2Si)$-$CSiMe_2Br$ when NBS was used (Scheme 3). Use of NBS in the place of Br_2 also gave a slightly better yield of the monobromide $R_2(HMe_2Si)CSiMe_2Br$ from the dihydride $R_2C(SiMe_2H)_2$.



Scheme 1. Preparation of $R_2(PhMe_2Si)CSiMe_2Br$



Scheme 2. Preparation of $R_2(PhOMe_2Si)CSiMe_2Cl$



Scheme 3. Preparation of $R_2(R'SMe_2Si)CSiMe_2Br$

2.2. Reactivity comparisons

For the reactivity comparisons the two substrates in an 1:1 molar ratio were dissolved in anhydrous Et_2O and one molar proportion or less of $AgBF_4$ was added, After an appropriate time the solvent was evaporated off under vacuum and the residue extracted with pentane. The solution was filtered and evaporated to dryness. The mixture was analysed by NMR spectroscopy, with the identities of the products confirmed by GLC–mass spectrometry. The ^{19}F-NMR spectrum was used to determine the ratio of the fluorides formed but this does not correspond with the actual reactivity ratio. This is because in a competition between initially equimolar amounts of substrates A and B for a deficiency of C to give AC and BC, as the reaction proceeds the ratio of the concentration of the more reactive substrate A relative to that of the less reactive B falls off and so does the instant rate ratio. Thus the final ratio of AC/BC will not be equal to the ratio of the two rate constants. The correction needed for the latter is especially important when the reactivity ratio is high and is also larger when the molar proportion of the silver salt is higher. To calculate the course of the reaction requires the use of two coupled non-linear differential equations that cannot be obtained in a closed analytic form. The equations were thus integrated numerically (by implementation of Gear's method in the Nag Library [16]) for selected values of the initial molar proportion of C. From these calculation graphs, we obtained the values of the correction

Table 1
Ratio R of products $(Me_3Si)_2(ZMe_2Si)CSiMe_2F$ and $(Me_3Si)_2(Z'Me_2Si)CSiMe_2F$ from $(Me_3Si)_2(ZMe_2Si)CSiMe_2Br$ and $(Me_3Si)_2(Z'Me_2Si)CSiMe_2Br$ in 1:1 molar ratio with $AgBF_4$

Z	Z′	$AgBF_4$ [a]	R	R (corr) [b]
Ph	Me	1.0	18	38
PhS	Ph	1.0	68	130
MeO	PhS	0.33	10	12
MeO	MeS	0.65	5.7	8
MeS	PhO	0.34	2.0	2.0

[a] Molar proportion.
[b] Reactivity ratio after correction as described in text.

factor against the final AC/BC ratio for initial molar proportions of C of 0.1, 0.5, and 1.0. These were used to derive approximate correction factors for the final ratios of the fluorides from the various $R_2(ZMe_2Si)CSiMe_2Br$ and $R_2(Z'Me_2Si)CSiMe_2Br$ pairs to give the results shown in Table 1.

The procedure used provides only an approximate measure of the relative reactivities and thus of the ability of the groups Z to provide anchimeric assistance in this type of reaction. It is clear, however, that the R′O and R′S (R′ = Me or Ph) groups provide much greater assistance than the Ph group, but that there is relatively little difference between the effects of the R′O and R′S groups. For the range of Z groups the following rough ratios of activating effects can be derived: Me, 1; Ph, 40; PhO, 3400; PhS, 5000; MeS, 7000; MeO, 54 000. (The possible cumulative errors are such that this last number can be regarded as correct only within an order of magnitude.) As expected, for the PhO group the delocalisation of the lone pair of electrons on the oxygen atom into the phenyl ring substantially lowers the ability to provide the anchimeric assistance in comparison with that of the MeO group, and to an extent that renders the group somewhat less effective than the PhS and MeS groups. The difference between PhS and MeS is smaller, in keeping with the less effective delocalisation of the lone pair of electron on sulphur, but even so it seems surprisingly small. (Direct comparison of these groups was not possible because the ^{19}F-NMR shifts were the same for the two fluorides.) However, we can conclude that while for the ligands $R_2(ZMe_2Si)C$ attached to metals such as Al or Yb the PhO group would probably be significantly less strongly coordinated than the MeO group, there should be little difference between the PhS and MeS groups.

To provide a more direct indication of the effects of MeO and PhO groups we made an approximate comparison of the reactivities of the chlorides $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ and $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$ towards MeOH in CH_2Cl_2, a type of reaction known to involve powerful anchimeric assistance by the MeO group [8]. In a refluxing solution under conditions in which the methoxy compound underwent 70% of methanolysis, only ca. 4% of the phenoxy compound reacted. (Essentially identical results were obtained when an equimolar amount of Et_3N was present to inhibit possible catalysis by formed acid.) If pseudo-first order kinetics is assumed the results indicate that the methoxy compound is roughly 120 times more reactive. This figure should be regarded as only a rough estimate, but it is clear that the PhO group does provide markedly less anchimeric assistance than the MeO group. The fact that the difference in reactivity should be much larger in the methanolysis than in the reactions with silver salts is not surprising, since whereas the driving force in the latter reaction is provided mainly by the attack of the silver ion on the Cl atom of the substrate, with secondary assistance from the R′O group, in the methanolysis it is provided mainly by the intramolecular nucleophilic attack of the R′O group on silicon, with concerted solvation of the leaving chloride ion.

Combination of the new data with those previously available gives rise to the following approximate order of increasing ability of γ-groups Z to provide anchimeric assistance in reactions of compounds $R_2(ZMe_2Si)CSiMe_2X$: OCOMe [10,11] > OMe [3,7–9] > $OCOCF_3$ [3] > MeS > PhS, PhO > N_3, Cl [9] > NCS [9b] > Ph [3,4,6] > $CH{=}CH_2$ [6] > Me.

3. Experimental

3.1. General

All reactions were carried out under Ar with exclusion of moisture. Solvents were dried by standard methods and stored over a Na mirror or molecular sieves.

The ^{1}H-, ^{13}C-, ^{19}F-, ^{31}P- and ^{29}Si-NMR spectra were recorded in C_6D_6 solutions with a Brüker MSL 300 or Brüker DRX spectrometer. The mass spectra were obtained by electron impact at 70 eV with a Finnigan MAT95 spectrometer; m/z values for bromine-containing ions refer to ^{79}Br; assignments of some frequently observed ions are: 201 ($Me_2Si{=}C(SiMe_3)_2SiMe_2$); 187 ($Me_2Si{=}C(SiMe_2H)_2SiMe_2$) or an isomer; 135 ($SiMe_2Ph$); 73 ($SiMe_3$). Suggested identities of ions are not intended to indicate fragmentation routes. A Carlo Erba CHNS-O EA 1108 elemental analyser was used for microanalyses (C, H), and for GLC analysis a Hewlett–Packard GC 5890A apparatus with capillary columns HP17 or HP50 and linear programming at 50–260 °C min^{-1} was used.

3.2. Syntheses

In the case of previously reported compounds information is presented only when a different synthesis was used or new spectroscopic data were obtained.

3.2.1. $(Me_3Si)_3CSiMe_2Br$

This compound was prepared as described previously [12] and obtained in 92% yield after sublimation at 60 °C/1 mmHg, m.p. 255 °C. Anal. Found: C, 39.2; H, 9.2. Calc. for $C_{12}H_{33}BrSi_4$: C, 39.0; H, 9.0%. ^{1}H-NMR: δ 0.30 (s, 27H, $SiMe_3$), 0.73 (s, 6H, $SiMe_2$); ^{13}C-NMR: δ 5.97 ($SiMe_3$), 10.9 ($SiMe_2$); ^{29}Si-NMR: δ −21.6 ($SiMe_3$), 22.75 ($SiMe_2Br$). MS; m/z: 353 (100%, [M − Me]), 265 (5, [M − Me − $SiMe_4$]), 201 (40), 73 (5).

3.2.2. $(Me_3Si)_2C(SiMe_2H)_2$ (cf. Ref. [17])

A stirred solution of $(Me_3Si)_2(HMe_2Si)CCl$ (12.8 g, 51 mmol) in a mixture of THF (90 cm^3), Et_2O (40 cm^3) and pentane (20 cm^3) was maintained at −110 °C as a 2.5 mol dm^{-3} solution of *n*-BuLi in hexane (22 cm^3, 55 mmol) cooled to −78 °C was added dropwise. The mixture was stirred at −110 °C for a further 2 h and then Me_2HSiCl (10 cm^3, 90 mmol) was added dropwise. This mixture was stirred at −110 °C for 2 h and then allowed to warm to room temperature (r.t.). The solvents were removed under reduced pressure and the residue was extracted with pentane. The extract was filtered, the solvent removed, and the residue recrystallised from MeOH to give $(Me_3Si)_2C(SiMe_2H)_2$ (9.71 g, 69%). ^{1}H-NMR: δ 0.23 (s, 18H, $SiMe_3$), 0.29 (d, 12H, $J = 3.7$ Hz, $SiMe_2H$), 4.34 (sept, 2H, $J = 3.7$ Hz, SiH). ^{13}C-NMR: δ 1.35 ($SiMe_3$), 4.31 ($SiMe_2H$). ^{29}Si-NMR: δ −0.67 ($SiMe_3$), −16.5 ($SiMe_2H$). MS; m/z: 261 (100%, [M − Me]), 187 (20, [M]).

3.2.3. $(Me_3Si)_2(BrMe_2Si)CSiMe_2H$ (cf. Ref. [17])

NBS (1.74 g, 9.8 mmol) was added to a solution of $(Me_3Si)_2C(SiMe_2H)_2$ (2.69 g, 9.8 mmol) in hexane (10 cm^3) and the mixture was stirred for 24 h at r.t. with monitoring by GLC–MS. Filtration of the solution followed by removal of the solvent gave a mixture that was shown by GLC–MS analysis to consist of the starting material (10%), $(Me_3Si)_2(HMe_2Si)CSiMe_2Br$ (80%) and $(Me_3Si)_2C(SiMe_2Br)_2$ (10%). Sublimation at 10 °C/0.05 mmHg gave $(Me_3Si)_2(BrMe_2Si)CSiMe_2Br$ (3.0 g). ^{1}H-NMR: δ 0.28 (s, 18H, $SiMe_3$), 0.34 (d, 6H, $J = 3.7$ Hz, $SiMe_2H$), 0.69 (s, 6H, $SiMe_2Br$), 4.28 (sept, 1H, $J = 3.7$ Hz, SiH). ^{13}C-NMR: δ 2.02 ($SiMe_2H$), 4.94 ($SiMe_3$), 9.88 ($SiMe_2Br$). ^{29}Si-NMR: δ −6.8 ($SiMe_2H$), −0.77 ($SiMe_3$), 22.5 ($SiMe_2Br$). MS; m/z: 339 (100%, [M − Me]), 187 (20).

3.2.4. $(Me_3Si)_3CSiMe_2H$ (cf. Ref. [18])

The procedure described for $(Me_3Si)_2C(SiMe_2H)_2$ was used but starting from $(Me_3Si)_2(HMe_2Si)CCl$ (4.15 g, 16.4 mmol) in a mixture of THF (50 cm^3), Et_2O (20 cm^3) and pentane (10 cm^3) and a 2.5 mol dm^{-3} solution of *n*-BuLi in hexane (2 cm^3, 19 mmol) and subsequent treatment with Me_3SiCl (2.6 cm^3, 20 mmol). Yield 3.0 g, 63%. ^{1}H-NMR: δ 0.25 (s, 27H, $SiMe_3$), 0.30 (d, 6H, $J = 3.7$ Hz, $SiMe_2H$), 4.33 (sept, 1H, $J = 3.7$ Hz, SiH). ^{13}C-NMR: δ 2.33 ($SiMe_2H$), 5.2 ($SiMe_3$). ^{29}Si-NMR: δ −1.2 ($SiMe_3$), −16.8 ($SiMe_2H$). MS; m/z: 275 (100%, [M − Me]), 201 (20), 187 (5), 73 (5).

3.2.5. $(Me_3Si)_2(PhMe_2Si)CSiMe_2H$ (cf. Ref. [18])

The procedure described for $(Me_3Si)_2C(SiMe_2H)_2$ was used but starting from a solution of $(Me_3Si)_2(HMe_2Si)CCl$ (5.0 g, 20 mmol) in a mixture of THF (40 cm^3), Et_2O (40 cm^3) and pentane (10 cm^3) and a 2.5 mol dm^{-3} solution of *n*-BuLi in hexane (12 cm^3, 30 mmol) with subsequent addition of $PhMe_2SiCl$ (9 cm^3, 42 mmol). Work up gave $(Me_3Si)_2(PhMe_2Si)CSiMe_2H$ (4.5 g, 64%). ^{1}H-NMR: δ 0.17 (d, 6H, $J = 3.7$ Hz, $SiMe_2H$), 0.20 (s, 12H, $SiMe_3$), 0.53 (s, 6H, Si*Me*$_2$Ph), 2.24 (sept, 1H, SiH), 7.2–7.8 (m, 5H, Ph). ^{13}C-NMR: δ 2.24 ($SiMe_2H$), 3.85 (Si*Me*$_2$Ph), 5.67 ($SiMe_3$), 128.2–136.9 (Ph). ^{29}Si-NMR: δ −17.1 ($SiMe_2H$), −7.6 ($SiMe_2Ph$), −0.98 ($SiMe_3$). MS; m/z: 352 (6%, [M$^+$]), 337 (70, [M − Me]), 335 (100%, [M − MeH − H]), 274 ([M − PhH]), 201 (20), 135 (20) 73 (20).

3.2.6. $(Me_3Si)_2(PhMe_2Si)CSiMe_2Br$

A solution of $(Me_3Si)_2(PhMe_2Si)C(SiMe_2H)$ [9] (2.33 g, 6.6 mmol) in CCl_4 (20 cm^3) was stirred at 20 °C as Br_2 (6.6 mmol) in CCl_4 (6.6 cm^3) was added dropwise. After 20 min the solvent was removed in vacuum and the residue was recrystallised from pentane at −78 °C to give $(Me_3Si)_2(PhMe_2Si)C(SiMe_2Br)$ (2.65 g, 93%), m.p. 176 °C. Anal. Found: C, 47.2; H, 8.1. Calc. for $C_{17}H_{35}BrSi_4$: C, 473; H, 8.2%. ^{1}H-NMR: δ 0.31 (s, 18H, $SiMe_3$), 0.62 (s, 6H, Si*Me*$_2$Ph), 0.68 (s, 6H, $SiMe_2Br$), 7.2–7.8 (m, 5H, Ph). ^{13}C-NMR: δ 5.16 (Si*Me*$_2$Ph), 6.76 ($SiMe_3$), 11.33 ($SiMe_2Br$), 128.3–140.5 (Ph). ^{29}Si-NMR: δ −6.73 ($SiMe_2Ph$), −0.91 ($SiMe_3$), 22.9 ($SiMe_2Br$). MS; m/z: 415 (75%, [M − Me]), 335 (100, [M − MeH − Br]), 216 (54, [M − $SiMe_2Ph$ − Br]), 201 (45), 135 (30), 73(30).

3.2.7. $(Me_3Si)_2(MeOMe_2Si)CSiMe_2H$

This compound was prepared as described previously [14]. ^{1}H-NMR: δ 0.29 (s, 6H, $SiMe_2O$), 0.31 (s, 8H, $SiMe_3$), 0.35 (d, 6H, $J = 3.7$ Hz, Si*Me*$_2$H), 3.14 (sept, 1H, $J = 3.7$ Hz, SiH). ^{13}C-NMR: δ 2.18 (Si*Me*$_2$H), 3.15 ($SiMe_2O$), 4.99 ($SiMe_3$), 50.0 (OMe). ^{29}Si-NMR: δ −17.2 ($SiMe_2H$), −1.7 ($SiMe_3$), 14.2 ($SiMe_2OMe$). MS; m/z: 305 (30%, [M − H]), (100, [M − Me]), 217 (20, [M − $SiMe_2OMe$]).

3.2.8. $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Br$

This compound was prepared as described previously [14]. ^{1}H-NMR: δ 0.29 (s, 6H, $SiMe_2O$), 0.37 (s, 12H, $SiMe_3$), 0.80 (s, 6H, $SiMe_2Br$), 3.04 (3H, OMe). MS: m/z; 369 (2%, [M − Me]), 325 (100, [M − $SiMe_2H$]), 305 (5, [M − Br]), 217 (10, [M − Me − $SiMe_2Br$]), 201 (10, [M − $SiMe_3OMe$ − Br]), 305 [M − Br]), 217 (10, [M − Me − $SiMe_3Br$]), 201 (10), 73 (5).

3.2.9. $(Me_3Si)_2(PhOMe_2Si)CCl$

A solution of $(Me_3Si)_2(BrMe_2Si)CCl$ [9] (3.14 g, 9.5 mmol) in toluene (20 cm^3) was added dropwise at 0 °C to a stirred dispersion of lithium phenolate made by adding *n*-BuLi (3.8 cm^3 of 2.5 mol dm^{-3} solution in hexanes) to a solution of phenol (1.69 g, 21 mmol) in toluene (50 cm^3). The mixture was stirred at 115 °C for 56 h, the solvent was then removed in vacuum, and the solid residue extracted with *n*-pentane. The extract was filtered and the solvent evaporated to give a white solid, which was recrystallised from MeOH to yield 1.12 g (32%) of $(Me_3Si)_2(PhOMe_2Si)CCl$, Anal. Found: C, 52.0; H, 8.60. Calc. for $C_{15}H_{29}OClSi_3$: C, 52.2; H, 8.47%. ^{1}H-NMR: δ 0.28 (s, 18H, $SiMe_3$), 0.36 (s, 6H, $SiMe_2OPh$), 6.9–7.1 (m, 5H, Ph). MS; *m*/*z*; 344 (2%, $[M^+]$), 329 (25, $[M-Me]$), 221 (10, $[M-Me-SiMe_3Cl]$), 85 (100, $SiPhMe_2H$), 73 (78).

3.2.10. $(Me_3Si)_2(PhOMe_2Si)CSiMe_2H$

To a stirred solution of $(Me_3Si)_2(PhOMe_2Si)CCl$ (1.04 g, 3 mmol) in a mixture of THF (25 cm^3), Et_2O (5 cm^3) and pentane (2 cm^3) maintained at −120 °C a 2.5 mol dm^{-3} solution of *n*-BuLi in hexane (2.5 cm^3, 6.2 mmol) cooled to −78 °C was added dropwise. The mixture was stirred at −110 °C for a further 2 h and Me_2SiHCl (1.0 cm^3, 9 mmol) was added dropwise. This mixture was stirred at −110 °C for 2 h and then allowed to warm to r.t. The solvents were removed under reduced pressure and the residue extracted with *n*-pentane (5 cm^3). The extract was filtered and the solvent removed. The residue was taken up in hot MeOH, the solution allowed to cool, and the MeOH decanted off. The viscous material obtained could not be crystallised but was kept under vacuum to give a viscous material that appeared to be essentially pure $(Me_3Si)_2(PhOMe_2Si)CSiMe_2H$ (0.52 g, 47%). Anal. Found: C, 55.5; H, 9.75. Calc. for $C_{17}H_{36}OSi_4$: C, 55.4; H, 9.8%. ^{1}H-NMR: δ 0.33 (s, 18H, $SiMe_3$), 0.37 (s, 6H, $SiMe_2O$), 0.38 (d, 6H, $J=3.7$ Hz, $SiMe_2H$), 4.42 (septet, 1H, $J=3.7$ Hz, SiH), 6.9–7.1 (m, 5H, OPh). ^{13}C-NMR: δ 3.91 ($SiMe_2H$), 4.67 ($SiMe_2O$), 4.98 ($SiMe_3$), 121.4–130.5 (Ph). ^{29}Si-NMR: δ −4.5 ($SiMe_2O$), −1.36 ($SiMe_3$), −17.0 ($SiMe_2H$. MS; *m*/*z*; 368 (35%, $[M^+]$), 353 (100, $[M-Me]$).

3.2.11. $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$

A solution (2.0 cm^3) of a 0.51 mol dm^{-3} solution of ICl in CCl_4 added dropwise to a stirred solution of $(Me_3Si)_2(PhOMe_2Si)C(SiMe_2H)$ (0.28 g, 0.76 mmol) in CCl_4 (10 cm^3). The mixture was stirred for a further 30 min and the solvent was then removed under vacuum. The residue was recrystallised from pentane at −78 °C to give $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$ (0.14 g, 46%), m.p. 157 °C. Anal. Found: C, 50.4; H, 8.6. Calc. for $C_{17}H_{35}OClSi_4$: C, 50.6; H, 8.7%. ^{1}H-NMR: δ 0.39 (s, 18H, $SiMe_3$), 0.44 (s, 6H, $SiMe_2O$), 0.68 (s, 6H, $SiMe_2Cl$), 6.9–7.1 (m, 5H, OPh). MS; *m*/*z*: 402 (3%, $[M^+]$), 387 (100, $[M-Me]$), 309 (10, $[M-SiMe_2Cl]$).

3.2.12. $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Br$

A 1.0 mol dm^{-3} solution of Br_2 in CCl_4 (0.35 cm^3, 0.35 mmol of Br_2) was added dropwise to a stirred solution of $(Me_3Si)_2(PhOSMe_2Si)CSiMe_2H$ (0.13 g, 0.35 mmol) in CCl_4 (10 cm^3). After 30 min the solvent was removed under reduced pressure and the residue sublimed at 110 °C/1 mmHg to give $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Br$ (0.11 g, 70%), m.p. 132 °C. Anal. Found: C, 45.6; H, 7.7. Calc. for $C_{17}H_{35}OBrSi_4$: C, 45.6; H, 7.9%. ^{1}H-NMR: δ 0.40 (s, 18H, $SiMe_3$), 0.45 (s, 6H, $SiMe_2O$), 0.84 (s, 6H, $SiMe_2Br$), 6.9–7.1 (m, 5H, Ph). ^{13}C-NMR: δ 5.24 ($SiMe_2OPh$), 5.71 ($SiMe_3$), 10.57 ($SiMe_2Br$), 121.3–130.6 (Ph). MS; *m*/*z*: 446 (4%, $[M^+]$), 431 (100, $[M-Me]$), 353 (25, $[M-OPh]$), 280 (10, $[M-Me_3SiOPh]$), 265 (5, $[M-Me-Me_3SiOPh]$), 201 (10), 73 (15).

3.2.13. $(Me_3Si)_2(PhOMe_2Si)CSiMe_2F$

A mixture of $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$ (0.020 g, 0.050 mmol) and $AgBF_4$ (0.12 g, 0.051 mmol) in CH_2Cl_2 (2 cm^3) was stirred for 15 h at r.t. The solvent was removed and the residue extracted with pentane. The extract was filtered and the pentane evaporated to leave exclusively $(Me_3Si)_2(PhOMe_2Si)CSiMe_2F$. ^{1}H-NMR: δ 0.36 (s, 18H, $SiMe_3$), 0.40 (s, 6H, $SiMe_2O$), 0.46 (d, 6H, $J=7.5$ Hz, $SiMe_2F$), 6.8–7.2 (m, 5H, OPh). ^{19}F-NMR: δ −144.2 (sept, $J=7.5$ Hz). MS; *m*/*z*: 386 (3%, $[M^+]$), 371 (100, $[M-Me]$), 279 (5, $[M-Me-Me_3SiF]$).

3.2.14. $(Me_3Si)_2(PhSMe_2Si)CSiMe_2H$

To a solution of $(Me_3Si)_2(PhSMe_2Si)CCl$ [19] (3.0 g, 8 mmol) in THF (75 cm^3), Et_2O (12 cm^3) and pentane (6 cm^3) maintained at −110 °C a 2.5 mol dm^{-3} solution of *n*-BuLi in hexanes (36 cm^3, 90 mmol) cooled to −78 °C was added dropwise. The mixture was stirred for 2 h at −110 °C then Me_2HSiCl (13 g, 120 mmol) was added dropwise. This mixture was stirred at −110 °C for 1.5 h then allowed to warm to r.t. The solvents were removed under reduced pressure and the residue was extracted with *n*-pentane. The extract was filtered, the solvent evaporated, and the residue recrystallised from MeOH to give $(Me_3Si)_2(PhSMe_2Si)CSiMe_2H$ (1.4 g, 43%), m.p. 61 °C. Anal. Found: C, 52.9; H, 9.3. Calc. for $C_{17}H_{36}SSi_4$: C, 53.0; H, 9.4%. ^{1}H-NMR: δ 0.380 (s, 6H, $SiMe_2S$), 0.384 (s, 18H, $SiMe_3$), 0.43 (d, 6H, $J=3.7$ Hz, $SiMe_2H$), 4.44 (septet, 1H, $J=3.7$ Hz, $SiMe_2H$), 7.0–7.45 (m, 5H, Ph). ^{13}C-NMR: δ 2.60 ($SiMe_2H$), 5.47 ($SiMe_2S$), 5.48 ($SiMe_3$), 127.9–137.1 (Ph). ^{29}Si-NMR: δ −16.3 ($SiMe_2H$), −0.37 ($SiMe_3$), 15.5 ($SiMe_2SPh$). MS; *m*/*z*: 369 (10%, $[M-Me]$), 275 (100, $[M-SPh]$).

3.2.15. $(Me_3Si)_2(PhSMe_2Si)CSiMe_2Br$

A solution of $(Me_3Si)_2(PhSMe_2Si)CSiMe_2H$ (0.23 g, 0.60 mmol) and NBS (0.11 g, 0.62 mmol) in heptane (5 cm^3) was stirred at r.t. for 18 h. Analysis by GLC–MS revealed the presence of unchanged hydride (2%), the monobromide $(Me_3Si)_2(PhSMe_2Si)CSiMe_2Br$ (92%), and the dibromide $(Me_3Si)_2C(SiMe_2Br)_2$ (6%). The solution was filtered and was removed and the residue was sublimed (50–90 °C/0.1 mmHg) to give $(Me_3Si)_2(PhSMe_2Si)CSiMe_2Br$ (0.26 g). Anal. Found: C, 43.9; H, 7.55. Calc. for $C_{17}H_{35}SBrSi_4$: C, 44.0; H, 7.6%. ^{1}H-NMR: δ 0.46 (s, 24H, $SiMe_3 + SiMe_2S$), 0.92 (s, 6H, $SiMe_2Br$), 6.9–7.4 (m, 5H, Ph). ^{13}C-NMR: δ 6.13 ($SiMe_2S$), 6.40 ($SiMe_3$), 11.38 ($SiMe_2Br$), 128.2–137.2 (Ph). MS; m/z: 447 (8%, [M − Me]), 353 (100, [M − SPh]), 310 (8, [M − Me_3SiBr]), 201 (19), 73 (5).

When the bromination was carried out with Br_2 in CCl_4, as described for the preparation of $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Br$, analysis of the product mixture by GLC–MS showed it to consist of only 3% of the monobromide along with $(Me_3Si)_2C(SiMe_2Br)_2$ (65%) and PhSSPh (32%).

3.2.16. $(Me_3Si)_2(PhSMe_2Si)CSiMe_2F$

This compound was not isolated in a pure state but its NMR spectra were unambiguously obtained. A solution of $AgBF_4$ (0.040 g, 0.21 mmol) and $(Me_3Si)_2(PhSMe_2Si)CSiMe_2Br$ [0.096 g, 0.21 mmol, but containing ca. 6% of $(Me_3Si)_2C(SiMe_2Br)_2$] was stirred at r.t. for 24 h. Work-up as described for $(Me_3Si)_2(PhOMe_2Si)CSiMe_2F$ gave a product that from its ^{1}H-NMR spectrum and GLC–MS analysis appeared to be exclusively $(Me_3Si)_2(PhSMe_2Si)CSiMe_2F$ but the ^{19}F-NMR spectrum showed it to contain ca. 6% of $(Me_3Si)_2C(SiMe_2F)_2$. For the monofluoride: ^{1}H-NMR: δ 0.39 (s, 6H, $SiMe_2S$), 0.41 (s, 18H, $SiMe_3$), 0.53 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$), 6.9–7.8 (m, 5H, SPh). ^{19}F-NMR: δ −143.3 (sept, $J = 7.5$ Hz). MS; m/z: 387 (10%, [M − Me]), 293 (100, [M − SPh]), 201 (30).

3.2.17. $(Me_3Si)_2(MeSMe_2Si)CCl$

A solution of BuLi (25 mmol) in a mixture of hexanes (10 cm^3) and Et_2O (10 cm^3) cooled to 0 °C was added dropwise to a solution of MeSH (1.4 g, 29 mmol) in Et_2O (50 cm^3) maintained at 0 °C. The mixture was stirred for 30 min to give a white suspension of MeSLi. To this a solution of $(Me_3Si)_2(BrMe_2Si)CCl$ [9] (6.51 g, 19.6 mmol) in Et_2O (10 cm^3) cooled to 0 °C was added slowly with stirring. The mixture was then stirred for 30 min at 0 °C and 38 h at r.t. The solution was filtered. The solvents were removed, and the residue was recrystallised from MeOH to give $(Me_3Si)_2(MeSMe_2Si)CCl$ (5.5 g, 88%), m.p. 124 °C. Anal. Found: C, 39.8; H, 9.2. Calc. for $C_{10}H_{27}ClSSi_3$: C, 40.2; H, 9.05%. ^{1}H-NMR: δ 0.30 (s, 18H, $SiMe_3$), 0.43 (s, 6H, $SiMe_2S$), 1.77 (s, 3H, SMe). ^{13}C-NMR: δ 1.98 ($SiMe_2SMe$), 2.14 ($SiMe_3$), 10.2 (SMe). ^{29}Si-NMR: δ 5.8 ($SiMe_3$), 16.6 ($SiMe_2SMe$). MS; m/z: 298 (30%, [M^+]), 283 (100, [M − Me]), 263 (10, [M − Cl]]), 210 (15, [M − $SiMe_4$]), 190 (100, [M − Me_3SiCl]), 175 (99, [M − Cl − $SiMe_4$]), 73 (83).

3.2.18. $(Me_3Si)_2(MeSMe_2Si)CSiMe_2H$

The procedure described for the preparation of $(Me_3Si)_2(PhSMe_2Si)CSiMe_2H$ was used but starting from a solution of $(Me_3Si)_2(MeSMe_2Si)CCl$ [19] (5.0 g, 17 mmol) in THF (70 cm^3), Et_2O (25 cm^3) and pentane (15 cm^3) and a solution of *n*-BuLi (2.5 mmol) in hexane (10 cm^3, 25 mmol), with subsequent addition of Me_2HSiCl (36 mmol). The recrystallisation from MeOH gave $(Me_3Si)_2(MeSMe_2Si)CSiMe_2H$ (1.7 g, 31%), m.p. 210 °C. Anal. Found: C, 44.5; H, 10.8. Calc. for $C_{12}H_{34}SSi_4$: C, 44.65; H, 10.6%. ^{1}H-NMR: δ 0.35 (s, 18H, $SiMe_3$), 0.40 (d, 6H, $J = 3.7$ Hz, $SiMe_2H$), 0.44 (s, 6H, $SiMe_2S$), 1.72 (s, 3H, SMe), 4.37 (septet, 1H, $J = 3.7$ Hz, $SiMe_2H$). ^{13}C-NMR: δ 2.58 ($SiMe_2H$), 4.54 ($SiMe_2S$), 5.47 ($SiMe_3$), 10.05 (SMe). ^{29}Si-NMR: δ −16.4 ($SiMe_2H$), −0.53 ($SiMe_3$), 15.0 ($SiMe_2SMe$). MS; m/z: 307 (60%, [M − Me]), 291 (10, [M − Me − MeH]), 275 (75, [M − SMe]), 233 (10, [M − Me − Me_3SiH]), 201 (60, [M − SMe − Me_3SiH]), 187 (20, [M − Me − Me_3SiSMe]), 129 (20, [M − $SiMe_3$ − Me_3SiSMe]), 73 (100), 59 (20, $SiMe_2H$).

3.2.19. $(Me_3Si)_2(MeSMe_2Si)CSiMe_2Br$

The procedure described for the preparation of $(Me_3Si)_2(PhSMe_2Si)CSiMe_2Br$ was used but starting from $(Me_3Si)_2(MeSMe_2Si)C(SiMe_2H)$ (0.17 g (0.44 mmol) and NBS (0.08 g, 0.44 mmol) in heptane (5 cm^3) and with a reaction time of only 1 h. Sublimation at 50–90 °C/1 mmHg gave $(Me_3Si)_2(MeSMe_2Si)CSiMe_2Br$ (0.14 g, 76%). Anal. Found: C, 35.5; H, 8.2. Calc. for $C_{12}H_{33}SBrSi_4$: C, 35.9; H 8.3%. ^{1}H-NMR: δ 0.42 (s, 18H, $SiMe_3$), 0.52 (s, 6H, $SiMe_2S$), 0.88 (s, 6H, $SiMe_2Br$), 1.66 (s, 3H, SMe). ^{13}C-NMR: δ 5.2 ($SiMe_2S$), 6.3 ($SiMe_3$), 10.2 (SMe), 11.3 ($SiMe_2Br$). MS; m/z: 385 (30%, [M − Me]), 353 (85, M − SMe), 265 (5, M − SMe − $SiMe_4$), 233 (10, M − Me − Me_3SiBr), 201(25, M − SMe − Me_3SiBr), 73 (10, $SiMe_3$).

When Br_2–CCl_4 was used for the bromination a mixture of $(Me_3Si)_2(MeSMe_2Si)CSiMe_2Br$ (27%) and $(Me_3Si)_2C(SiMe_2Br)_2$ (73%) was obtained.

3.3. Preparation of fluorides for recording of their ^{19}F-NMR spectra

Samples of the various fluorides $(Me_3Si)_2(ZMe_2Si)CSiMe_2F$ (except for Z = PhO) were prepared in small amounts by reaction of the corresponding bromides with $AgBF_4$ in Et_2O for the times shown below. The solvent was then removed and the residue extracted

with pentane. The extract was filtered and the solvent removed. In each case the identity of the product was confirmed by GLC–MS analysis. (These reactions were also used to indicate what times should be used in the competition experiments. Most of the fluorides had been made previously in the same way but from the iodides, much shorter reaction times then being required.) The fluoride $(Me_3Si)_2(PhOMe_2Si)CSiMe_2F$ was made from the corresponding chloride in CH_2Cl_2.

Relevant data were as follows:

3.3.1. Z = H (cf. Ref. [16])

Bromide 0.069 mmol; $AgBF_4$ 0.058 mmol, Et_2O, 3 cm^3; 22 h. ^{1}H-NMR: δ 0.25 (s, 18H, $SiMe_3$), 0.30 (d 6H, $J = 3.7$ Hz, $SiMe_2H$), 0.34 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$). ^{19}F-NMR: δ −144.6 (hept, $J = 7.5$ Hz). MS; m/z: 279 (100%, [M − Me]), 205 (15, [M − Me − Me_3SiH]), 187 (25), 3 (10, $SiMe_3$).

3.3.2. Z = Br

Bromide $[(Me_3Si)_2C(SiMe_2Br)_2]$ 1.85 mmol; $AgBF_4$ 0.077 mmol; Et_2O 3 cm^3; 24 h. ^{1}H-NMR: δ 0.27 (s, 18H, $SiMe_3$), 0.37 (d, 12H, $J = 7.5$ Hz, $SiMe_2F$). ^{19}F-NMR: δ −143.9 (heptet, $J = 7.5$ Hz).

3.3.3. Z = F

Bromide $[(Me_3Si)_2C(SiMe_2Br)_2]$ 1.20 mmol; $AgBF_4$ 3.1 mmol; Et_2O 20 cm^3, 24 h. ^{1}H-NMR: δ 0.27 (s, 18H, $SiMe_3$), 0.37 (d, 12H, $J = 7.5$ Hz, $SiMe_2F$). ^{19}F-NMR: δ −44.7 (sept, $J = 7.5$ Hz). MS; m/z: 297 (100%, [M − Me]), 205 (25, [M − Me − Me_3SiF]), 73 (20).

3.3.4. Z = Me

Bromide 0.103 mmol; $AgBF_4$ 0.061 mmol; Et_2O 24 cm^3; 48 h. ^{1}H-NMR: δ 0.27 (s, 18H, $SiMe_3$), 0.36 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$). ^{13}C-NMR: δ 5.54 ($SiMe_3$), 5.96 ($SiMe_2F$). ^{29}Si-NMR: δ −2.2 ($SiMe_3$), 26.9 (d, J(SiF) = 1431 Hz, $SiMe_2F$). ^{19}F-NMR: δ −144.2 (sept, $J = 7.5$ Hz). MS; m/z: 293 (100%, [M − Me]), 201 (50), 73 (15).

3.3.5. Z = Ph

Bromide 0.67 mmol; $AgBF_4$ 0.67 mmol; Et_2O 5 cm^3; 24 h. ^{1}H-NMR: δ 0.23 (d, 6H, $J = SiMe_2F$), 0.23 (s, 18H, $SiMe_3$), 0.57 (s, $SiMe_2Ph$), 7.1–7.8 (5H, Ph). ^{13}C-NMR: δ 4.51 ($SiMe_2Ph$), 5.72 ($SiMe_2F$), 5.9 ($SiMe_3$), 128–137.1 (Ph). ^{29}Si-NMR:δ −6.67 (d, ^3J(SiF) = 16.5 Hz), $SiMe_2Ph$), −25 (d, ^3J(SiF) = 18.5 $SiMe_3$), 27.4 (d, J(SiF) = 1431 Hz, $SiMe_2F$). ^{19}F-NMR: δ −143.9 (sept, $J = 7.5$ Hz). MS; m/z: 355 (100%, [M − Me]), 263 (10, [M − Me − MePh]), 216 (25, [M − $SiMe_2F$ − Ph]), 201(30), 135 (10), 73 (10).

3.3.6. Z = OMe (cf. Ref. [14])

Bromide 0.25 mmol; $AgBF_4$ 0. 25; mmol; Et_2O 4 cm^3; 24 h. (Reaction was only 80% complete.) ^{1}H-NMR: δ 0.26 (s, $SiMe_2OMe$), 0.31 (s, 18H, $SiMe_3$), 0.41 (d, 6H, $J = 7.4$ Hz, $SiMe_2F$), 3.12 (s, 3H, OMe). ^{19}F-NMR: δ −144.5 (sept, $J = 7.4$ Hz). MS; m/z: 309 (20%, [M − Me]), 305 (5, [M − F]), 291 (100, [M − Me − HF]), 217 (10 [M − Me $SiMe_3F$]), 201(15), 187 (10) 129 (5), 73 (30), 59 (10, $SiMe_2H$).

3.3.7. Z = PhS

Bromide 0.21 mmol; $AgBF_4$ 0.21 mmol; Et_2O 15 cm^3; 24 h. ^{1}H-NMR: δ 0.39 (s, 6H, $SiMe_2S$), 0.41 (s, 18H, $SiMe_3$), 0.53 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$), 6.9–7.8 (m, 5H, Ph). ^{19}F-NMR: δ −143.3 (heptet, $J = 7.5$ Hz). MS; m/z: 387 (10, [M − Me]), 293 (100, [M − SPh]), 201 (30).

3.3.8. Z = MeS

Bromide 0.029 mmol; $AgBF_4$ 0.12 mmol; Et_2O 2 cm^3; 0.5 h. ^{1}H-NMR: δ 0.38 (s, 18H, $SiMe_3$), 0.46 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$), 1.69 (SMe). ^{19}F-NMR: δ −143.31 (sept, $J = 7.5$ Hz). MS; m/z: 325 (30%, [M − Me]), 293 (100, [M − SMe]), 233 (10, [M − Me − $SiMe_3F$]), 201 (19).

3.3.9. Z = PhO

Chloride 0.050 mmol; $AgBF_4$ 0.51 mmol; CH_2Cl_2 2 cm^3; 15 h. ^{1}H-NMR: δ 0.36 (s, 18H, $SiMe_3$), 0.40 (s, 6H, $SiMe_2O$), 0.46 (d, 6H, $J = 7.5$ Hz, $SiMe_2F$), 6.8–7.2 (m, 5H, Ph). ^{19}F-NMR: δ −144.2 (sept, $J = 7.5$ Hz).

3.4. Competition studies

In a typical procedure, a solution of $(Me_3Si)_2(MeSMe_2Si)CSiMe_2Br$ (3.25 mmol), $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Br$ (3.25 mmol) and $AgBF_4$ (2.2 mmol) in Et_2O (3.0 cm^3) was stirred at r.t. under Ar for 2 h. The solvent was then rapidly removed under vacuum and the residue extracted with pentane (3 cm^3). The extract was filtered and the pentane removed. The ^{19}F spectrum of the product mixture in C_6D_6 showed peaks at −144.5 ppm [from $(Me_3Si)_2(MeOMe_2Si)CSiMe_2F$] and −143.3 ppm [from $(Me_3Si)_2(MeSMe_2Si)CSiMe_2F$] in a 85:15 ratio. Analysis by GLC–MS confirmed the identities of the products.

In some of the experiments small amounts of $(Me_3Si)_2C(SiMe_2F)_2$ were detected in the product mixture.

3.5. Methanolysis of $(Me_3Si)_2(R'OMe_2Si)CSiMe_2Cl$ R = Me or Ph

A solution of $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ (1.25×10^{-2} mol dm^{-3}) and MeOH (10.3 mol dm^{-3}) in CH_2Cl_2 (0.70 cm^3) was kept at the reflux temperature for 16 h. Analysis by GLC showed that 70% of the chloride had been converted into $(Me_3Si)_2(CSiMe_2OMe)_2$. When the same procedure was used

with $(Me_3Si)_2(PhOMe_2Si)CSiMe_2Cl$, only ca. 4% underwent conversion into $(Me_3Si)_2(PhOMe_2Si)CSiMe_2OMe$. Repetition of the reactions with the Et_3N (1.25×10^{-2} mol dm^{-3}) present gave essentially identical results.

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