Reaction of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ with $AgBF_4$. 1,3-Migration of the Phenyl Group

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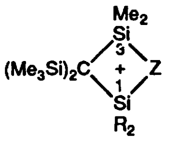
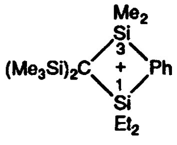
The reaction of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ with $AgBF_4$ in Et_2O has been shown to give a *ca.* 2:3 ratio of the unrearranged $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ and the rearranged $(Me_3Si)_2C(SiEt_2Ph)(SiMe_2F)$. The reaction is thought to proceed *via* a cation, **II**, in which there is a 1,3-phenyl bridge between silicon atoms. Reaction of the organolithium reagent $(Me_3Si)_2C(SiMe_2Ph)Li$, R′Li, with Me_2SiHCl, Et_2SiHCl, Et_2SiF_2 and Et_2SiCl_2 gives the products $R'SiMe_2H$, $R'SiEt_2H$, $R'SiEt_2F$ and $R'SiEt_2Cl$, respectively.

Reactions of compounds of the type $(Me_3Si)_3CSiR_2I$ with various electrophiles, such as Ag^I or Hg^{II} salts, ICl and CF_3CO_2H, are thought to involve rate-determining formation of cations of type **I**, Z = Me, which can be attacked by a nucleophile Y^- at either the Si(1) or Si(3) centre, so that rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$ can be formed exclusively or along with the unrearranged $(Me_3Si)_3CSiR_2Y$.[1,2]



I



II

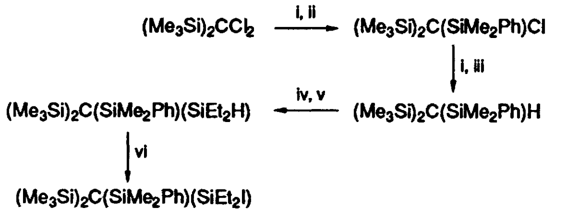
Similar migration of a vinyl group was found to occur in reactions of $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2I)$ with silver salts, apparently *via* the cation **I**, R = Et, Z = $CH{=}CH_2$.[3] The bridging in cations of type **I** bears analogy both to that in the dimers $(AlMe_2Z)_2$[4] and to 1,2-bridging in carbocations.[5] As far as we are aware 1,3-migration of Ph groups between carbon centres in carbocations is, like that of Me groups, unknown, although that of vinyl groups has been observed.[6] However, the phenyl group bridges very effectively in the dimer $(AlMe_2Ph)_2$[4] and readily takes part in 1,2-bridging (and migrations) within carbocations,[5] and so it seemed to us very likely that bridged ions of type **I**, Z = Ph could be formed and the associated rearrangements observed. We thus examined the reaction of the iodide $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$, **1**, with $AgBF_4$, and the results described below show that the expected rearrangements do, in fact, occur, as briefly noted in a preliminary report.[7] Since the appearance of the latter report migration of the Ph group has also been observed in solvolysis of the iodide **1**.[8]

$(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ **1** $\quad$ $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ **2**

$(Me_3Si)_2C(SiEt_2Ph)(SiMe_2F)$ **3**

Results and Discussion

Compound **1** was made by the route depicted in Scheme 1. Attempts by other routes were unsuccessful but gave some results of interest and these are briefly described later. To assist in the analysis of the products, a sample of the fluoride $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$, **2**, was obtained by treatment of $(Me_3Si)_2C(SiMe_2Ph)Li$ with Et_2SiF_2.



Scheme 1 *Reagents and conditions:* i, BuLi in tetrahydrofuran–Et_2O–hexane–pentane at −120 °C; ii, $Me_2PhSiCl$ at −110 °C, then allowed to warm to room temperature; iii, MeOH; iv, MeLi in tetrahydrofuraan under reflux; v, Et_2SiHCl, reflux; vi, I_2 in CCl_4

A mixture of **1** (0.8 mmol) and $AgBF_4$ (1.0 mmol) in Et_2O (20 cm^3) was stirred for 5 min at room temperature and the solvent then evaporated. The residue was extracted with pentane, the extract was filtered and evaporated, and the residue sublimed. Linked GLC–mass spectroscopy (GLC–MS) revealed the presence of two components in *ca.* 3:2 ratio having virtually identical mass spectra consistent with the formulation $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$, **2**, and $(Me_3Si)_2C(SiEt_2Ph)(SiMe_2F)$, **3**. The minor component had a retention time identical with that of the authentic sample of **2**, and so was the unrearranged product. The ^{19}F NMR spectrum of the mixture in CCl_4–$CDCl_3$ showed a quintet at δ_F −156.2, a shift identical to that for authentic **2**, and a heptet at δ_F −138.9 that was assigned to the $SiMe_2F$ groups of **3**. [Compare δ_F −143.0 for $(Me_3Si)_3CSiMe_2F$.] The ^{29}Si NMR spectrum showed the signals from **2** along with those attributable to **3**.

The ^1H NMR spectrum also showed the signals from **2** along with those attributable to **3**, and relevant integration ratios were consistent with a 3:2 ratio of compounds **3** and **2**. An important feature was the integration ratio of *ca.* 2.2:1 for the signals from the protons of Ph groups relative to those from the Me groups of $SiMe_2Ph$, since the ratio would be 5:6 if no migration of Ph groups took place. Expansion of the spectrum showed the ratio of the integrated signals from $Si\mathit{Me}_2Ph$ and $Si\mathit{Me}_2F$ to be *ca.* 1:1.4 reasonably consistent with a 3:2 ratio of **3** to **2**.

The formation of more **3** than **2** was to be expected, since there is less steric hindrance to attack of F^- at Si(3), bearing two Me groups, than at Si(1), bearing two Et groups. In the solvolysis of **1** in CF_3CH_2OH there is an even higher proportion of rearranged product.[8]

Aspects of some Syntheses.—Our first attempt to obtain **1** involved generating $(Me_3Si)_2C(SiMe_2Ph)Li$ by treatment of

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$(Me_3Si)_2C(SiMe_2Ph)Cl$ with BuLi in Et_2O–THF–pentane–hexane at −100 °C, adding Et_2SiCl_2, and allowing the mixture to warm to room temperature. The product after hydrolytic work-up was a 1:1 mixture of $(Me_3Si)_2C(SiMe_2Ph)Bu$ and $(Me_3Si)_2C(SiMe_2Ph)H$. The result can be attributed to the failure of $(Me_3Si)_2C(SiMe_2Ph)Li$ to react with Et_2SiCl_2 under the conditions used; some of it reacts instead with the BuCl formed in the initial cross-metallation, and the remainder is hydrolysed on work-up to give $(Me_3Si)_2C(SiMe_2Ph)H$. In keeping with this, when the less sterically hindered Me_2SiHCl was used in place of Et_2SiCl_2 the expected $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$ was obtained in good yield, showing that $(Me_3Si)_2C(SiMe_2Ph)Li$ had indeed been formed. Later, when $(Me_3Si)_2C(SiMe_2Ph)Li$ generated from $(Me_3Si)_2C(SiMe_2Ph)H$ and MeLi was treated with Et_2SiCl_2 in refluxing THF, the chloride $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2Cl)$ was obtained, but only in 10% yield. Subsequently, $(Me_3Si)_2C(SiMe_2Ph)Li$ generated in this way was found to react readily with Et_2SiHCl and Et_2SiF_2, which are less sterically hindered than Et_2SiCl_2. The low reactivity of $(Me_3Si)_2C(SiMe_2Ph)Li$ towards the latter is consistent with the unreactivity of $(Me_2PhSi)_3CLi$ towards this chloride, which reacts readily with $(Me_3Si)_3CLi$.[9]

The $(Me_3Si)_2C(SiMe_2Ph)H$ used in the reactions described above was initially made by metallation of $(Me_3Si)_2CH_2$ with MeLi to give $(Me_3Si)_2CHLi$ followed by addition of Me_2SiPhF, but the yield based on the amount of $(Me_3Si)_2CH_2$ was only 25% because only *ca.* 27% of the $(Me_3Si)_2CH_2$ had been converted into $(Me_3Si)_2CHLi$. [The inefficiency of the metallation of $(Me_3Si)_2CH_2$ by MeLi was observed some time ago.[10]] A subsequent attempt to make $(Me_3Si)_2C(SiMe_2Ph)H$ by metallation of $(Me_3Si)_2CH_2$ with BuLi·TMEDA followed by treatment of Me_2SiPhF gave a 3:2 mixture of two isomeric products, as indicated by GLC–MS, both giving mass spectra consistent with the formulation $(Me_3Si)_2C(SiMe_2Ph)H$ (see Experimental section), though it is difficult to envisage formation of any isomer of the expected product. The ^1H NMR spectrum of the mixture showed that $(Me_3Si)_2C(SiMe_2Ph)H$ (of which an authentic sample was available) was the major product, and metallation of the mixture with MeLi in THF followed by treatment with Et_2SiF_2 gave the expected $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$.

Experimental

General.—Diethyl ether and pentane were dried over sodium wire. Tetrahydrofuran was heated under reflux with $LiAlH_4$, then distilled, and stored over sodium wire. Solutions of BuLi and MeLi in hexane were obtained from Aldrich. Where indicated MeLi in ether was made from MeBr and Li. All reactions involving organolithium reagents were conducted under nitrogen.

Instrumentation.—The ^1H NMR spectra were recorded with a Perkin-Elmer R32 spectrometer at 90 MHz or, where indicated, a Bruker WM360 at 360 MHz. Unless otherwise indicated solutions were in CCl_4 containing CH_2Cl_2 as lock and internal reference. *J* Values are in Hz. The ^{19}F NMR spectra were recorded on a Bruker WP80SY instrument at 75.4 MHz with solutions in CCl_4–$CDCl_3$; shifts are in ppm relative to external $CFCl_3$ in $CDCl_3$. The ^{29}Si NMR spectra were recorded on a Bruker WM360 instrument at 71.5 MHz with solutions in $CDCl_3$.

For GLC–MS a 2 m column of 3% or OV-17 on Gaschrome Q (150–250 °C at 8 °C min^{-1}) linked to a Kratos MS25 spectrometer was used. Mass spectra were obtained by electron impact at 70 eV unless otherwise indicated.

Preparation of $(Me_3Si)_2C(SiMe_2Ph)Cl$.—A solution of $(Me_3Si)_2CCl_2$ (9.0 g, 0.040 mol) in a mixture of THF (60 cm^3), pentane (4 cm^3) and Et_2O (10 cm^3) was stirred at −120 °C and a 2.5 mol dm^{-3} solution of BuLi in hexane (15.7 cm^3) cooled to −78 °C was added dropwise. The mixture was stirred for 3 h at −110 °C and neat $Me_2PhSiCl$ (6.7 g, 0.040 mol) was added. The mixture was allowed to warm to room temperature, the solvents were removed under reduced pressure, and pentane (30 cm^3) was added to the residue. The pentane solution was filtered, volatile materials were distilled off, and the residue was recrystallized from MeOH to give chloro(dimethylphenylsilyl)bis(trimethylsilyl)methane (6.5 g, 50%), m.p. 57 °C (Found: C, 55.05; H, 9.3. $C_{15}H_{29}ClSi_4$ requires: C, 54.8; H, 8.9%); δ_H 0.10 (18 H, s, $SiMe_3$), 0.55 (6 H, s, $SiMe_2$) and 7.2–7.7 (5 H, m, Ph); *m/z* 313 (10%, M − Me), 240 (10), 220 (35), 135 (100, $SiMe_2Ph$), 73 (85, $SiMe_3$) and 59 (20, $SiMe_2H$). (All chlorine-containing ions gave the expected isotope pattern.)

Preparation of $(Me_3Si)_2C(SiMe_2Ph)H$ *from* $(Me_3Si)_2C(SiMe_2Ph)Cl$.—A solution of $(Me_3Si)_2C(SiMe_2Ph)Cl$ (9.8 g, 0.030 mol) in a mixture of THF (60 cm^3), pentane (5 cm^3) and Et_2O (10 cm^3) was stirred at −120 °C and a 2.5 mol dm^{-3} solution of BuLi in hexane (32 cm^3, 0.080 mol) cooled to −78 °C was added dropwise. The mixture was stirred at −110 °C for a further 1 h and MeOH (3.2 g, 0.10 mol) was added dropwise with stirring. The mixture was allowed to warm to room temperature, solvents were taken off under reduced pressure, and the residue was distilled under vacuum. The fraction of b.p. 100–120 °C at 0.2 torr was crystallized from MeOH to give (dimethylphenylsilyl)bis(trimethylsilyl)methane (6.3 g, 70%) as a low-melting solid; δ_H 0.10 (18 H, s), 0.51 (6 H, s) and 7.2–7.7 (5 H, m); *m/z* 279 (100%, M − Me), 263 (15), 135 (45), 75 (55) and 59 (10).

Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2H)$.—An 0.80 mol dm^{-3} solution of MeLi (prepared from MeBr and Li) in Et_2O (50 cm^3, 0.040 mol) was added to a stirred solution of $(Me_3Si)_2C(SiMe_2Ph)H$ (10 g, 0.034 mol) in THF (100 cm^3). The Et_2O was distilled off, the solution refluxed for 6 h, and Et_2SiHCl (5.0 g, 0.040 mol) added. The mixture was refluxed for 10 min then cooled and added to saturated aqueous ammonium chloride. The organic layer was separated and dried ($MgSO_4$) and volatile materials were removed under reduced pressure. The solid residue was recrystallized to give (diethylsilyl)(dimethylphenylsilyl)bis(trimethylsilyl)methane (7.0 g, 54%), m.p. 102 °C (Found: C, 59.8; H, 10.7. $C_{19}H_{40}Si_4$ requires: C, 60.0; H, 10.5%); δ_H 0.25 (18 H, s), 0.60 (6 H, s), 0.80–1.20 (10 H, m, Et), 4.10–4.22 (1 H, m, SiH) and 7.20–7.8 (5 H, m); 2090 ν/cm^{-1} (Si–H); *m/z* 365 (30%, M − Me), 349 (75), 321 (15), 201 (10), 135 (45), 73 (100) and 59 (55).

Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$.—A solution of $(Me_4Si)_2C(SiMe_2Ph)(SiEt_2H)$ (1.0 g, 2.65 mmol), $PhSiMe_3$ (4 g; to take up HI) and iodine (0.75 g, 0.30 mmol) in CCl_4 (100 cm^3) was stirred for 24 h at room temperature then washed with saturated aqueous $Na_2S_2O_3$ and dried ($MgSO_4$). Removal of the solvent left a solid, which was sublimed (130 °C at 0.2 torr) to give (diethyliodosilyl)(dimethylphenylsilyl)bis(trimethylsilyl)methane (1.0 g, 74%), m.p. 232–234 °C (Found: C, 44.8; H, 7.5. $C_{14}H_{39}ISi_4$ requires: C, 45.1; H, 7.7%); δ_H 0.40 (18 H, s), 0.72 (6 H, s), 0.95–1.25 (10 H, m) and 7.20–7.8 (5 H, m); *m/z* (CI, NH_3) 491 (15%, M − Me), 477 (10, M − Et), 429 (10, M − Ph), 379 (100, M − I), 335 (30), 261 (20), 135 (50), 73 (70) and 59 (35).

Reaction of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$, **1**, *with* $AgBF_4$.—A mixture of **1** (0.40 g, 0.78 mmol) and $AgBF_4$ (0.20 g, 1.0 mmol) in Et_2O (20 cm^3) was stirred at room temperature for 5 min. The solid residue was extracted with pentane and the extract filtered and evaporated to dryness. The residue was sublimed (100 °C at 0.2 torr). Analysis by GLC–MS gave two peaks in 3:2 area ratio; the second component had a retention time identical to that of an authentic sample of unrearranged fluoride **2**, and both components gave mass spectra virtually identical to that of the latter. The ^{19}F NMR spectrum showed the expected quintet at δ_F −156.2 (*J* 10.1) for **2**, and a heptet at δ_F −138.9 (*J* 7.8) that was assigned to the rearranged fluoride **3**; the signals gave an integration ratio of *ca.* 2:3. The ^{29}Si NMR spectrum showed the expected signals from **2** [δ −2.63 (d, *J* 4.2, $SiMe_3$), −6.71 (d, *J* 4.1, $SiMe_2Ph$), 26.77 (d, *J* 294.5, $SiEt_2F$)] along with those from **3** [δ −2.69 (d, *J* 4.2, $SiMe_3$), −0.55 (d, *J* 2.5, $SiEt_2Ph$) and 27.37 (d, *J* 284.5, $SiMe_2F$)]; slightly different δ values were obtained in an earlier experiment.[7] The ^1H NMR spectrum (at 360 MHz) showed the following signals (with approximate integration ratios and assignments in parenthesis): δ 0.20 (d, *J* 7.7) (1.7, $SiMe_2F$), 0.26 (s) (6.9, $SiMe_3$), 0.58 (s) (1.0, $Si\mathit{Me}_2Ph$); 0.60–1.44 (m) (5.2, $SiEt_2$) and 7.32–7.78 (m) (2.2, Ph). (The signals assigned to **2** were effectively identical to those from the authentic sample.) Expansion of the spectrum showed the actual ratio of integrated signals from $Si\mathit{Me}_2Ph$ and $SiMe_2F$ to be 1:1.4, and that of the integrated signals from $SiMe_2$ and $SiMe_3$ protons to be 1:2.9, compared with the theoretical 1:3.

Attempted Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2Cl)$ *from* $(Me_3Si)_2C(SiMe_2Ph)Cl$.—A solution of $(Me_3Si)C(SiMe_2Ph)Cl$ (2.0 g, 6.10 mmol) in a mixture of THF (40 cm^3), Et_2O (5 cm^3) and pentane (5 cm^3) was stirred at −100 °C and a 1.5 mol dm^{-3} solution of BuLi in hexane (4.2 cm^3, 6.3 mmol) was added dropwise. When addition was complete the mixture was stirred at −100 °C for 1 h then allowed to warm to −78 °C and Et_2SiCl_2 (1.04 cm^3, 6.8 mmol) was added. The mixture was allowed to warm slowly to room temperature and the solvent and excess of Et_2SiCl_2 were removed under reduced pressure. The solid residue was extracted with pentane and the extract filtered and evaporated, to leave an oil that was shown by GLC–MS to be a *ca.* 1:1 mixture of $(Me_3Si)_2C(SiMe_2Ph)Bu$ [*m*/*z* 335 (10%, M − Me), 200 (40), 135 (100, $SiMe_2Ph$), 73 (45) and 59 (10)] and $(Me_3Si)_2C(SiMe_2Ph)H$ [*m*/*z* 279 (100%, M − Me), 135 (25), 73 (20) and 59 (5)].

Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2H)$ *from* $(Me_3Si)_2C(SiMe_2Ph)Cl$.—The procedure described in the preceding experiment was used but starting from $(Me_3Si)_2C(SiMe_2Ph)Cl$ (6.0 g, 18.0 mmol), THF (50 cm^3), Et_2O (5 cm^3), pentane (5 cm^3), BuLi (13.3 cm^3 of 1.5 mol dm^{-3} solution in hexane; 20 mmol), and Me_2SiHCl (2.4 cm^3, 22 mmol). Work-up as before gave a solid, which was recrystallized from MeOH and then sublimed (100 °C at 0.3 torr) to give (dimethylphenylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane (4.0 g, 62%), m.p. 84 °C (Found: C, 58.3; H, 10.1. $C_{17}H_{36}Si_4$ requires: C, 57.95; H, 10.2%); δ_H 0.20 (6 H, d, *J* 3.8, $Si\mathit{Me}_2H$), 0.23 (18 H, s, $SiMe_3$), 0.59 (6 H, s, $SiMe_2Ph$), 4.47 (1 H, s, SiH) and 7.24–7.82 (5 H, m, Ph); *m*/*z* 337 (55%, M − Me), 274 (10), 201 (20), 135 (70), 73 (100) and 59 (10).

Preparation of $(Me_3Si)_2C(SiMe_2Ph)H$ *from* $(Me_3Si)_2CH_2$.—A 1.5 mol dm^{-3} solution of MeLi in Et_2O (67 cm^3, 0.10 mol; prepared from MeBr and Li) was added to a stirred solution of $(Me_3Si)_2CH_2$ (15 g, 0.094 mol) in THF (100 cm^3). The Et_2O was distilled off and the remaining solution was refluxed for 22 h. A sample (1 cm^3) of the (pale red) solution was withdrawn and added to Me_3SiCl (1 cm^3), and after a few minutes the solvent and excess of Me_3SiCl were removed under reduced pressure. The residue was extracted with pentane, the extract was filtered, and the solvent was removed. The residue was dissolved in CCl_4 containing 5% of CH_2Cl_2 and the ^1H NMR spectrum recorded, and from the relative heights of the signal from the Me_3Si protons of $(Me_3Si)_2CH_2$ at δ 0.12 and that from the corresponding protons of $(Me_3Si)_3CH$ at δ 0.15 it was concluded that *ca.* 27% of the $(Me_3Si)_2CH_2$ had been converted into $(Me_3Si)_2CHLi$. To the bulk of the solution containing the latter was added Me_2SiPhF (4.6 g, 0.030 mol), and the mixture was stirred at room temperature for 4 h then added cautiously to cold saturated aqueous NH_4Cl. The solvent and remaining $(Me_3Si)_2CH_2$ were distilled off and the residue distilled at 122 °C at 0.3 torr to give, as a colourless liquid, (dimethylphenylsilyl)bis(trimethylsilyl)methane [7.2 g, *ca.* 97% based on the $(Me_3Si)_2CHLi$ generated]; δ_H 0.11 (18 H, s), 0.61 (6 H, s) and 7.26–7.61 (5 H, m); *m*/*z* 279 (100%, M − Me), 263 (15), 249 (5), 135 (45), 73 (55) and 59 (10).

Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2Cl)$ *from* $(Me_3Si)_2C(SiMe_2Ph)H$.—A 1.5 mol dm^{-3} solution of MeLi (14 cm^3, 0.021 mol) (prepared from MeBr and Li in Et_2O) was added to a stirred solution of $(Me_3Si)_2C(SiMe_2Ph)H$ (6.0 g, 0.020 mol) in THF (100 cm^3). The Et_2O was distilled off and the remaining solution refluxed for 6 h and Et_2SiCl_2 (3.5 g, 0.22 mol) then added. The mixture was refluxed for 24 h and then added to cold saturated aqueous ammonium chloride. The organic layer was separated and dried ($MgSO_4$). Volatile materials were removed by distillation under reduced pressure and the residue was recrystallized from MeOH to give a solid, which was sublimed at 125 °C at 0.2 torr to give (chlorodiethylsilyl)(dimethylphenylsilyl)bis(trimethylsilyl)methane (0.80 g, 9.5%), m.p. 166–167 °C (Found: C, 55.0; H, 9.4. $C_{19}H_{39}ClSi_4$ requires: C, 55.1; H, 9.4%); δ_H 0.34 (18 H, s, $SiMe_3$), 0.65 (6 H, s, $SiMe_2$), 0.75–1.15 (10 H, m, Et) and 7.15–7.90 (10 H, m, Ph); *m*/*z* 399 (100%, M − Me), 385 (45, M − Et), 337, 135 (100), 121 (20) and 73 (100).

Preparation of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$.—Neat $(Me_3Si)_2CH_2$ (17.6 g, 0.11 mol) was added to an ice cold solution of BuLi·TMEDA (0.10 mol) in hexane (40 cm^3). The mixture was allowed to warm to room temperature overnight then Me_2SiPhF (15.4 g, 0.10 mol) was added dropwise with stirring, and stirring was continued for a further 6 h. The mixture was then added cautiously to an excess of ice-cold dilute hydrochloric acid, the organic layer was separated, dried ($MgSO_4$), and distilled at 95–100 °C at 0.2 torr to give a liquid, which was found to be a mixture of the expected $(Me_3Si)_2C(SiMe_2Ph)H$ (δ_H 0.11 and 0.61, identical with values for an authentic sample) with a second component (δ_H 0.10 and 0.57) that appeared from its mass spectrum to be an isomer of the main product. Examination by GLC–MS (OV-17 on GasChrom Q at 178 °C) gave two peaks in *ca.* 3:2 area ratio, both components giving the same main ions in the mass spectrum [*m*/*z* 279 (M − Me), 263, 207, 191, 135, 73 and 59] but with different relative intensities. Nevertheless, a solution of the product mixture in THF (100 cm^3) was treated dropwise with stirring with a 1.62 mol dm^{-3} solution of MeLi (30 cm^3, 0.50 mol) (prepared from MeBr and Li) in Et_2O. The Et_2O was distilled off, the solution was refluxed for 6 h, and Et_2SiF_2 (6.2 g, 0.050 mol) was added. The mixture was refluxed for 24 h then added cautiously to cold saturated aqueous ammonium chloride. The aqueous layer was separated and dried ($MgSO_4$) and volatile materials were distilled off under reduced pressure. The solid residue was recrystallized from MeOH and sublimed at 100 °C at 0.2 torr to give (diethylfluorosilyl)(dimethylphenylsilyl)bis(trimethylsilyl)methane (6.0 g, 30% based on Et_2SiF_2 taken), m.p. 95 °C (Found: C, 57.5; H, 9.5. $C_{19}H_{39}FSi_4$ requires: C, 57.3; 9.8%); δ_H 0.27 (18 H, s, $SiMe_3$), 0.59 (6 H, s, $SiMe_2$), 0.60–1.04 (10 H, m, $SiEt_2$) and 7.20–7.80 (5 H, m, Ph); δ_F −156.11 (m, *J* 11.5); δ_{Si} − 6.67 (d, 4.1, $SiMe_2Ph$), −2.65 (d, *J* 4.2, $SiMe_3$) and 26.79 (d, *J* 295, $SiEt_2F$); *m*/*z* 383 (70%, M −Me), 369 (80, M − Et), 277 (10), 263 (10), 215 (40), 135 (75), 73 (100) and 59 (65).

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