1,3-Migration of Chloride and Azide Ligands in Reactions of Highly Sterically Hindered Organosilicon Halides

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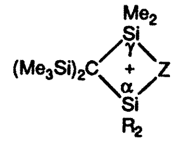
Reaction of $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$, **1**, with $AgBF_4$ in CH_2Cl_2 or Et_2O gives a *ca.* 3:1 mixture of the unrearranged fluoride $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2F)$, **2**, and the rearranged $(Me_3Si)_2C(SiEt_2F)(SiMe_2Cl)$, **3**. The reverse 1,3-migration of Cl takes place when $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2I)$, **4**, is treated similarly in CH_2Cl_2, a *ca.* 2:1 mixture of **2** and **3** being formed. Reaction of $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2Br)$, **5**, with $AgBF_4$ in CH_2Cl_2 likewise gives a *ca.* 3:1 mixture of $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2F)$ and $(Me_3Si)_2C(SiEt_2F)(SiMe_2N_3)$. The preparation of compounds **1**, **4** and **5** and of the following (R = $SiMe_3$) are described: $R_2C(SiMe_2Cl)(SiEt_2H)$, $R_2C(SiEt_2Cl)(SiMe_2H)$ and $R_2C(SiEt_2N_3)(SiMe_2H)$.

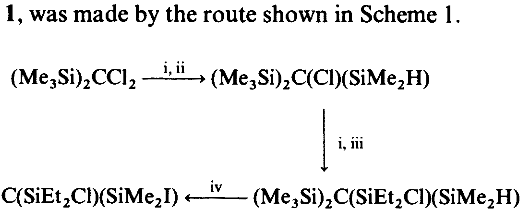
It has been shown previously that in reactions of the compounds of the type $(Me_3Si)_2C(SiMe_2Z)(SiR_2X)$ with silver salts AgY (as in reactions with some other electrophiles) 1,3-migration of the group Z can take place to give the rearranged product $(Me_3Si)_2C(SiMe_2Y)(SiR_2Z)$, either exclusively or, more usually, along with the unrearranged $(Me_3Si)_2C(SiMe_2X)(SiR_2Y)$.[1-3] The reactions are thought to involve formation of the 1,3-bridged cation of type **I** by abstraction of X^-, the departure of the latter being synchronous with, and anchimerically assisted by, the formation of the bridge. The nucleophile Y^- can then attack at either the α- or γ-silicon centre to give the unrearranged or rearranged product, respectively, attack at the less hindered centre usually being favoured. The rearrangements have been shown to take place for Z = Me,[1] $CH{=}CH_2$,[4] Ph[5] and OMe.[6] Following a preliminary report[7] we now present the detailed evidence for the corresponding migrations for Z = Cl or N_3.



I

Results and Discussion

Migration of Cl.—The compound $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$, **1**, was made by the route shown in Scheme 1.



$$\begin{tikzcd}
(Me_3Si)_2CCl_2 \arrow[r, "i, ii"] & (Me_3Si)_2C(Cl)(SiMe_2H) \arrow[d, "i, iii"] \\
(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I) & (Me_3Si)_2C(SiEt_2Cl)(SiMe_2H) \arrow[l, "iv"']
\end{tikzcd}$$

Scheme 1 *Reagents and conditions:* i, BuLi in hexane–THF–Et_2O–pentane at −110 °C; ii, Me_2SiHCl; iii, Et_2SiCl_2; iv, I_2 in CCl_4.

When a solution of **1** in CH_2Cl_2 was treated with $AgBF_4$ for 5 min at room temperature, the product after work-up was shown by ^1H and ^{19}F NMR spectroscopy to be a *ca.* 3:1 mixture of the unrearranged fluoride $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2F)$, **2**, and its rearranged isomer $(Me_3Si)_2C(SiEt_2F)(SiMe_3Cl)$, **3**. Thus the ^{19}F NMR spectrum showed two signals in 3:1 integration ratio, a heptet at δ −143.0 and a quintet at δ −160.2, which were respectively attributed to $SiMe_2F$ in **2** [*cf.* δ −144.7 for $(Me_3Si)_3CSiMe_2F$] and $SiEt_2F$ in **3** [*cf.* δ −160.4 for $(Me_3Si)_3CSiEt_2F$]. The ^1H NMR spectrum showed signals at δ 0.33 (s), 0.49 (d), 0.66 (d) and 0.94–1.18 (m) attributable to the protons in $SiMe_3$, $SiMe_2F$, $SiMe_2Cl$ and ($SiEt_2F$ + $SiEt_2Cl$) groups, respectively, in *ca.* 13:3:1:8 integration ratios, satisfactorily consistent with a 3:1 mixture of **2** and **3**, for which the integration ratios should be 12:3:1:7. Linked GLC-mass spectrometry (GLC–MS) gave only one peak, showing a mass spectrum consistent with either of the fluorides **2** and **3**. When the reaction was carried out in Et_2O instead of CH_2Cl_2 virtually identical results were obtained; this was not necessarily to be expected, as, for example, in the reactions of the compounds $(Me_3Si)_3CSiRHI$ (R = Ph or Me) with $AgBF_4$, the unrearranged fluoride is seemingly formed exclusively in Et_2O but along with a substantial amount of the rearranged fluoride in CH_2Cl_2.[8,*]

$(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$ **1** $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2F)$ **2**

$(Me_3Si)_2C(SiEt_2F)(SiMe_2Cl)$ **3** $(Me_3Si)_2C(SiEt_2I)(SiMe_2Cl)$ **4**

The results show clearly that the Cl atom can take part in 1,3-migration, and readily provide the bridge in a cation of type **I**, Z = Cl, as was predicted by calculations on simple model systems.[9] In all cases, of course, it should be possible to generate cations of type **I** from either $(Me_3Si)_2C(SiMe_2Z)(SiR_2X)$ or $(Me_3Si)_2C(SiR_2Z)(SiMe_2X)$, and if the ions become fully free and exist for a significant time the ratio of rearranged to unrearranged product should be the same from either starting material. We thus thought it of interest to examine also the reaction of the iodide **4**, the relevant isomer of the previously used **1**. Thus **4** was made by the route depicted in Scheme 2.

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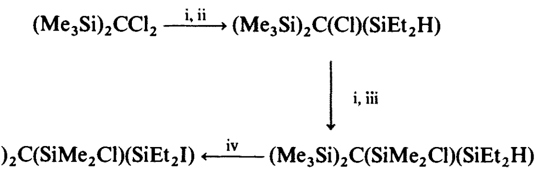
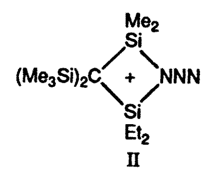
* In reference 8*b* it was mistakenly stated that the ratio of 40:60 for unrearranged to rearranged fluoride in CH_2Cl_2 that was roughly estimated from IR data was confirmed by GLC-MS analysis. In fact GLC–MS examination was carried out only on the separated fluorides, and the approximate ratio based solely on the IR data should be taken to imply only that a substantial amount of the rearranged product was formed.



Scheme 2 *Reagents and conditions:* i, BuLi in hexane–THF–Et_2O–pentane at −110 °C; ii, Et_2SiHCl; iii, Me_2SiCl_2; iv, I_2 in CCl_4.

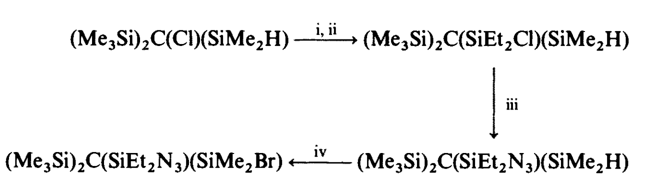
When the iodide **4** was treated with $AgBF_4$ in CH_2Cl_2 the fluorides **2** and **3** were again formed, as expected, but in a *ca.* 2:1 ratio. (In this case, of course, the rearranged product predominates). The observed product ratios are only approximate, but it is probable that they do differ for reactions of **1** and **4**. The direction of the difference is consistent with the possibility that, other things being equal, the fluoride ion shows some preference for attachment to the α-Si, from which the I^- is abstracted, rather than to the more distant γ-Si. For example, some of the anions BF_4^- liberated from an $[Ag^+{\cdot}BF_4^-]$ ion-pair near the α-Si centre upon formation of AgI may be able to transfer a fluoride ion to that centre before diffusing away; this would give less of the rearranged product in both cases than would be expected on simple steric grounds.

$(Me_3Si)_2C(SiEt_2N_3)(SiMe_2Br)$
5
$(Me_3Si)_2C(SiEt_2F)(SiMe_2N_3)$
6
$(Me_3Si)_2C(SiEt_2N_3)(SiMe_2F)$
7



II

For a study of the possible migration of a γ-N_3 group the bromide **5** was made by the route shown in Scheme 3. It was treated with $AgBF_4$ in CH_2Cl_2 for 5 min at room temperature to give a *ca.* 1:3 mixture of the rearranged fluoride **6** and the unrearranged **7**. Again the ^{19}F NMR spectrum showed two signals, one a heptet at δ −143.4 ($SiMe_2F$) and the other a quintet at δ −160.3 ($SiEt_2F$) in *ca.* 3:1 integration ratio. The ^1H NMR spectrum showed doublets at δ 0.289 ($SiMe_3$), 0.293 ($SiMe_3$), 0.45 ($SiMe_2F$) and 0.52 ($SiMe_2N_3$) in a *ca.* 2:6:3:1 integration ratio, along with a complex multiplet at δ 0.88–1.25 from the $SiEt_2$ protons. The 3:1 integration ratio for the $SiMe_2F$ and $SiMe_2N_3$ signals is as expected for a 3:1 mixture of **7** and **6**. Linked GLC–MS again gave only one chromatographic peak, with a mass spectrum consistent with either **6** or **7**. Essentially identical results were obtained when the procedure was repeated with Et_2O as solvent.



Scheme 3 *Reagents and conditions:* i, BuLi in hexane–THF–Et_2O–pentane at −100 °C; ii, Et_2SiCl_2; iii, NaN_3 in MeCN; iv, Br_2 in CCl_4.

We assume that the azide group bridges to give a four-membered ring, as in **II**. We cannot exclude the possibility that the γ-N of the N_3 group attaches to the α-Si to give a 6-membered ring, but the energy needed to distort the linear N–N–N linkage[10] in this way would probably be prohibitive. [The acetoxy group is thought to bridge to give a cation with a six-membered ring in providing powerful anchimeric assistance in the solvolysis of the compound $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$.[11]]

Experimental

Solvents.—All solvents used as reaction media were carefully dried by standard methods.

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

Mass spectra were obtained by electron impact with a Kratos MS25 spectrometer, and for GLC–MS this was linked to a 2 m column of 3% OV-17 on 100–120 mesh Chromasorb Q. Halogen-containing ions showed the expected isotope patterns.

Preparations.—In the preparations of the compounds described below an argon atmosphere was used whenever organolithium reagents were present.

$(Me_3Si)_2C(SiMe_2Cl)(SiEt_2H)$. A 1.5 mol dm^{-3} solution of BuLi in hexane (30 cm^3, 0.045 mol), cooled to −80 °C, was added dropwise to a stirred solution of $(Me_3Si)_2CCl_2$ (10 g, 0.044 mol) in a mixture of tetrahydrofuran (THF) (100 cm^3), Et_2O (10 cm^3), and pentane (10 cm^3) kept at −110 °C. The mixture was stirred at −110 °C for a further 2 h and Et_2SiHCl (5.72 g, 0.047 mol), cooled to −80 °C, was added dropwise. The stirred mixture was allowed to warm to room temperature and the solvent removed under vacuum. The residue was extracted with pentane, the extract filtered, and the solvent and unchanged $(Me_3Si)_2CCl_2$ distilled off under vacuum to leave an oil (9.0 g), the ^1H NMR spectrum of which showed it to be very predominantly $(Me_3Si)_2C(Cl)(SiEt_2H)$, δ_H 0.23 (18 H, s, $SiMe_3$), 0.68–1.28 (10 H, m, $SiEt_2$) and 3.91 (1 H, m, SiH), along with some impurities. Analysis by GLC–MS gave five peaks, the main one (87% by peak area) having a mass spectrum consistent with its being $(Me_3Si)_2C(Cl)(SiEt_2H)$ [*m/z* 265 (5%, M–Me), 251 (10, M–Et), 191 (5), 143 (40), 73 (100) and 59 (50)]. The oil was dissolved in a mixture of THF (80 cm^3), Et_2O (10 cm^3) and pentane (10 cm^3), the solution cooled to −110 °C, and a 2.5 mol dm^{-3} solution of BuLi (13 cm^3, 0.033 mol), cooled to −80 °C, added dropwise with stirring. The mixture was allowed to warm to −80 °C and Me_2SiCl_2 (4.16 g, 0.033 mol) was added dropwise with stirring. The mixture was then allowed to warm to room temperature and the solvent removed under vacuum. The residue was extracted with pentane, the extract filtered and evaporated, and the residue recrystallized from MeOH and then sublimed at 100 °C at 0.2 torr to give (chlorodimethylsilyl)(diethylsilyl)bis(trimethylsilyl)methane (7.0 g, 65% based on Me_2SiCl_2 taken), m.p. 240 °C (Found: C, 45.9; H, 10.6. $C_{13}H_{35}ClSi_4$ requires: C, 46.15; H, 10.4%); δ_H 0.28 (18 H, s, $SiMe_3$), 0.60 (6 H, s, $SiMe_2$), 0.80–1.20 ($SiEt_2$), and 3.85 (1 H, m, SiH); ν/cm^{-1} 2065 (Si–H); *m/z* 323 (45%, M − Me), 309 (90, M − Et), 221 (40), 201 (30), 157 (10), 87 (10), 73 (100) and 59 (55).

$(Me_3Si)_2C(SiMe_2Cl)(SiEt_2I)$. A mixture of $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2H)$ (0.50 g, 1.48 mmol) and iodine (0.40 g, 1.58 mmol) in CCl_4 (20 cm^3) was stirred at room temperature for 8 h (probably longer than necessary) washed with aqueous $NaHSO_3$, and dried ($MgSO_4$). Removal of the solvent left a solid, which was sublimed at 100 °C at 0.2 torr to give (chlorodimethylsilyl)(diethyliodosilyl)bis(trimethylsilyl)methane (0.47 g, 68%), m.p. > 300 °C (Found: C, 33.0; H, 7.15. $C_{13}H_{34}ClISi_4$ requires: C, 33.6; H, 7.3%); δ_H 0.48 (18 H, s, $SiMe_3$), 0.84 (6 H, s, $SiMe_2$) and 0.97–1.47 (10 H, m, $SiEt_2$); *m/z* 449 (10% M − Me), 435 (5, M − Et), 337 (80, M − I), 201 (20), 185 (10), 73 (100) and 59 (55).

$(Me_3Si)_2C(SiEt_2Cl)(SiMe_2H)$. A 2.5 mol dm^{-3} solution of BuLi in hexane (12 cm^3, 0.030 mol) was added dropwise to a stirred solution of $(Me_3Si)_2C(Cl)(SiMe_2H)$ (6.0 g, 0.024 mol) (made as described previously[12]) in a mixture of THF (80 cm^3), Et_2O (10 cm^3), and pentane (10 cm^3) maintained at -100 °C. The stirred mixture was kept at -100 °C for a further 40 min then allowed to warm to -80 °C, and Et_2SiCl_2 (5.72 g, 0.036 mol) was added dropwise. The mixture was allowed to warm to room temperature with stirring and then added cautiously to ice-cold saturated aqueous NH_4Cl (200 cm^3). The organic layer was separated, washed and dried ($MgSO_4$) and the solvent then removed under vacuum. The residual solid was recrystallized from MeOH and then sublimed, at 100 °C at 0.2 torr, to give (chlorodiethylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane (6.60 g, 82%), m.p. 245 °C (Found: C, 46.05; H, 10.1. $C_{13}H_{35}ClSi_4$ requires: C, 46.15; H, 10.4%); δ_H 0.32 (18 H, s, $SiMe_3$), 0.41 (6 H, d, $SiMe_2$), 0.90–1.40 (10 H, m, $SiEt_2$) and 4.20 (1 H, m, SiH); ν/cm^{-1} 2090 (Si–H); m/z 323 (100%, M − Me), 309 (75, M − Et), 221 (20), 201 (33), 129 (25), 73 (98) and 59 (55).

$(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$. A mixture of $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2H)$ (0.50 g, 1.48 mmol) and I_2 (0.51 g, 2.0 mmol) in CCl_4 was stirred at room temperature for 1 h. The solution was shaken with saturated aqueous $NaHSO_3$ then separated and dried ($MgSO_4$). Removal of the solvent left a solid, which was sublimed at 110 °C at 0.2 torr to give (chlorodiethylsilyl)(iododimethylsilyl)bis(trimethylsilylmethane) (0.60 g, 87%), m.p. > 300 °C (Found: C, 34.1; H, 7.4. $C_{13}H_{34}ClISi_4$ requires: C, 33.6; H, 7.3%); δ_H 0.46 (18 H, s, $SiMe_3$), 1.18 (6 H, s, $SiMe_2I$) and 1.0–1.40 (10 H, m, Et_2); m/z 449 (15%, M − Me), 435 (5, M − Et), 337 (70, M − I), 201 (20), 185 (10), 73 (100, $SiMe_3$) and 59 (45).

$(Me_3Si)_2C(SiEt_2N_3)(SiMe_2H)$. A mixture of $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2H)$ (0.20 g, 0.60 mmol), NaN_3 (0.40 g, 6.20 mmol) and MeCN (25 cm^3) was heated under reflux for 1.5 h. The solvent was then removed under reduced pressure and the residue extracted with pentane. The extract was filtered and the solvent evaporated to leave a solid, which was sublimed at 90 °C at 0.2 torr to give $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2H)$, m.p. 230 °C (Found: C, 45.5; H, 10.0. $C_{13}H_{35}N_3Si_4$ requires: C, 45.2; H, 10.15%); δ_H 0.27 (18 H, s, $SiMe_3$), 0.36 (6 H, d, $SiMe_2H$), 0.81–1.30 (10 H, m, $SiEt_2$) and 4.15 (1 H, m, SiH); ν/cm^{-1} 2110 (N_3); m/z 330 (25%, M − Me), 316 (40, M − Et), 303 (100, M − N_3), 228 (65), 129 (60), 73 (85) and 59 (40).

$(Me_3Si)_2C(SiEt_2N_3)(SiMe_2Br)$. A 1.0 mol dm^{-3} solution of Br_2 in CCl_4 (0.58 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2H)$ (0.20 g, 0.58 mmol) in CCl_4 (5 cm^3) at room temperature. The solvent was removed and the solid residue sublimed at 110 °C at 0.2 torr to give (azidodiethylsilyl)(bromodimethylsilyl)bis(trimethylsilyl)methane, (0.21 g, 81%), m.p. 276 °C (Found: C, 37.1; H, 8.1. $C_{13}H_{34}BrN_3Si_4$ requires: C, 36.8; H, 8.0%); δ_H 0.39 (18 H, s, $SiMe_3$), 0.87 (6 H, s, $SiMe_2$) and 1.0–1.30 (10 H, m, $SiEt_2$); m/z 410 and 408 (10%, M − Me), 396 and 394 (10, M − Et), 383 and 381 (10, M − N_3), 324 (10), 297 and 295 (20), 214 (70), 139 and 137 (25), 73 (100) and 59 (80).

Reaction of $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$, (**1**), *with* $AgBF_4$. (a) In CH_2Cl_2: a mixture of **1** (0.20 g, 0.43 mmol) and $AgBF_4$ (0.090 g, 0.46 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 5 min at room temperature, the solvent was removed under reduced pressure, and the residue extracted with pentane. The extract was filtered and the solvent evaporated to leave a solid, the ^{19}F NMR spectrum of which showed two signals (with J values given in Hz), at δ −143.19 (heptet, J 7.35) and δ −160.29 (quintet, J 11.30) in 3:1 integration ratio, attributed to $SiMe_2F$ in the fluoride **2** [*cf.* δ −144.7 (heptet, J 7.57) for $(Me_3Si)_3SiMe_2F$] and $SiEt_2F$ in the fluoride **3** [*cf.* δ −160.4 (quintet, J 11.23) for $(Me_3Si)_3SiEt_2F$]. The ^1H NMR spectrum was consistent with a *ca.* 3:1 mixture of **2** and **3**, showing signals at 0.333 (s, $SiMe_3$), 0.488 (d, J 7.5, $SiMe_2F$), 0.658 (d, J 0.6, $SiMe_2Cl$) and 0.95–1.18 (m, $SiEt_2$) in *ca.* 13:3:1:8 integration ratio. Examination by GLC–MS gave only one chromatographic peak, giving rise to a mass spectrum consistent with both **2** and **3**, *i.e.* m/z 341 (50%, M − Me), 327 (35, M − Et), 235 (25), 219 (25), 73 (100) and 59 (60). (b) in Et_2O: the procedure described in (a) was repeated but with Et_2O as solvent. The ^{19}F and ^1H NMR spectra of the product mixture were essentially identical with those reported under (a).

Reaction of $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2I)$, (**4**) *with* $AgBF_4$ *in* CH_2Cl_2. The procedure described under (a) in the previous experiment was repeated but with **4** in place of **1**. The ^{19}F NMR signals at δ −143.14 ($SiMe_2F$) and δ −160.26 ($SiEt_2F$) were in this case in *ca.* 2:1 ratio. The integration ratios of the ^1H NMR signals at δ 0.335, 0.488, 0.660 and 0.95–1.20 were *ca.* 9:2:1:5, reasonably consistent with a 2:1 mixture of **2** and **3**.

Reaction of $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2Br)$, (**5**) *with* $AgBF_4$. (a) In CH_2Cl_2. A mixture of **5** (0.10 g, 0.24 mmol) and $AgBF_4$ (0.046 g, 0.24 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 5 min and the solvent then taken off under reduced pressure. The residue was extracted with pentane, and the extract filtered and evaporated to leave a solid, the ^{19}F NMR spectrum of which showed two signals, at δ −143.31 (quintet, J 7.3, $SiMe_2F$) and δ −160.20 (heptet, 10.3, $SiEt_2F$) in *ca.* 3:1 ratio, consistent with a 3:1 ratio of the fluorides **7** and **6**. The ^1H NMR spectrum (360 MHz) showed peaks at δ 0.289 (d, 0.5, $SiMe_3$), 0.293 (d, 0.4, $SiMe_3$), 0.451 (d, J 7.4, $SiMe_2F$), and 0.516 (d, 0.5, $SiMe_2N_3$), in *ca.* 2:6:3:1 integration ratio, along wih a complex multiplet at δ 0.88–1.25 from $SiEt_2$ protons. The ratio of the integrals from $SiMe_2F$ and $SiMe_2N_3$ is consistent with a 2:1 ratio of **7** and **6**. Analysis by GLC–MS gave only one chromatographic peak, which gave a mass spectrum consistent with both **6** and **7**; *i.e.* m/z 348 (50%, M − Me), 334 (65, M − Et), 321 (20, M − N_3), 292 (30), 200 (30), 77 (10), 73 (100) and 59 (50). (b) In Et_2O. The procedure described in (a) above was repeated but with Et_2O as solvent. Essentially identical results were obtained.

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