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Anchimeric assistance by the γ-N_3 and γ-NCS groups in solvolysis of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ and $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$ *

Colin Eaborn and M. Novella Romanelli [1]

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

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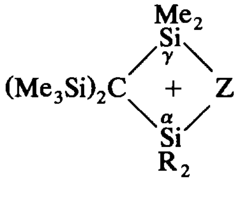
Abstract

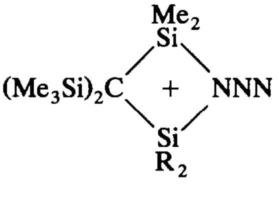
The reaction of the bromide $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (**1**) with MeOH gives the monomethoxy-compound $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OMe)$ in the presence of Et_3N but, as a result of acid-catalysis of the departure of N_3^-, the dimethoxy-compound $(Me_3Si)_2C(SiMe_2OMe)_2$, in its absence. The reaction is much faster than that of $(Me_3Si)_3CSiMe_2Br$, by a factor in the region of 10^5, revealing powerful anchimeric assistance by the γ-N_3 group to the leaving of Br^-. In keeping with this interpretation, the reaction is not accelerated by NaOMe, and the solvolysis is *ca.* 150 times as fast in CF_3CH_2OH as in MeOH. In contrast, in reaction with KSCN in MeCN, which involves direct bimolecular displacement of Br^- by SCN^-, **1** is only *ca.* 16 times as reactive as $(Me_3Si)_3CSiMe_2Br$. The bromide $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$ (**8**) is much less reactive than **1** towards MeOH at 60°C but is still markedly more reactive than $(Me_3Si)_3CSiMe_2Br$, probably by a factor in the region of 250–500; thus the γ-NCS group provides effective anchimeric assistance, but this is considerably weaker than that by γ-N_3. The reaction of **8** with CF_3CH_2OH is, as expected, faster than that with MeOH, though only by a factor of *ca.* 2.5. The chloride $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (**11**) is markedly more reactive than $(Me_3Si)_3CSiMe_2Cl$, but this is to be attributed to the lower steric hindrance in **11** to direct bimolecular attack at the Si–Cl bond, since **11** is unreactive towards CF_3CH_2OH and *ca.* 350 times as reactive as $(Me_3Si)_3CSiMe_2Cl$ towards KSCN in MeCN at 60°C. The sequence of ability of γ-substituents to provide anchimeric assistance in systems of this type appears to be $OCOCH_3 > OMe > OCOCF_3 > N_3 > NCS > Ph > CH{=}CH_2 > Me$, H.

1. Introduction

It has been shown previously that appropriate groups Z in compounds of the type $(Me_3Si)_2C(SiMe_2Z)(SiMe_2X)$ (X = I or Cl), *viz.* Z = Me [1], Ph [2], $CH{=}CH_2$ [3], OMe [4–6], $OCOCH_3$ [6,7], and $OCOCF_3$ [6,8], provide anchimeric assistance to the leaving of X in reactions with alcohols or (for Z = Me, X = I) trifluoroacetic acid (see also ref. 9). The anchimeric assistance is associated with rate-determining formation of a 1,3-bridged cation of type **I**, which can then be attacked by a nucleophile, with ring-opening, at either the α- or γ-Si atom [1–9]. We have now shown that the γ-N_3 and γ-NCS groups in $(Me_3Si)_2C(SiMe_2Z)(SiMe_2Br)$ with Z = N_3 and NCS, respectively, provide effective anchimeric assistance in reactions with MeOH and CF_3CH_2OH but that the γ-H atom in $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ does not. A preliminary report on the reactivity of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ appeared previously [10].



(I)



(II)

2. Results and discussion

2.1. *Effects of the γ-azido ligand*

The azido compound $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (**1**) was made by the route shown in Scheme 1. The

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Correspondence to: Professor C. Eaborn.

* Dedicated to Professor Gian Paolo Chiusoli on the occasion of his 70th birthday in recognition of his outstanding pioneering contributions to organometallic chemistry and its applications to organic synthesis.

[1] Present address: Dipartimento di Scienze Farmaceutiche, Università di Firenze, 50121 Firenze, Italy.

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$$\begin{tikzcd}
(Me_3Si)_2C(Cl)(SiMe_2Br) \arrow[r, "(i)"] & (Me_3Si)_2C(Cl)(SiMe_2N_3) \arrow[d, "(ii)"] \\
(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br) & (Me_3Si)_2C(SiMe_2N_3)(SiMe_2H) \arrow[l, "(iii)"']
\end{tikzcd}$$

(1)

Scheme 1. Reagents and conditions: (i) NaN_3 in MeCN under reflux; (ii) BuLi in THF–Et_2O–pentane–hexane at −110°C then Me_2SiHCl at −80°C, and warm to room temperature; (iii) Br_2 in CCl_4.

solvolysis of **1** in MeOH at 35°C was monitored by ^1H NMR spectroscopy, and a good first order plot was obtained for the disappearance of **1**, with $t\frac{1}{2}$ *ca.* 90 min (see Table 1). However, the product was not the expected $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OMe)$ (**2**) but instead the dimethoxy compound, $(Me_3Si)_2C(SiMe_2OMe)_2$ (**3**); compound **2** was observed as an intermediate, but its concentration was never more than *ca.* 12% of the initial concentration of **1**. It was shown previously that **2** is inert to MeOH alone, but when one equivalent of Ph_3SiBr was added to an 0.03 M solution of **2** in order to generate an equivalent of HBr, there was a rapid first order reaction, with $t\frac{1}{2}$ *ca.* 8 min, to give the dimethoxy compound **3** [7]. Thus the formation of **3** during the methanolysis of **1** could be attributed to acid catalysis by the HBr liberated in the reaction, and this was confirmed when the methanolysis of **1** was conducted in the presence of 3 equivalents of Et_3N, compound **2** then being the sole product. The observed value of $t\frac{1}{2}$ was *ca.* 100 min, probably a little higher than that in the absence of Et_3N, when there is electrophilic assistance to the leaving of Br^- by the acid generated. * However, this effect is not large enough to cause a significant departure from first order kinetics in the absence of the amine.

$(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$
(1)
$(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OMe)$
(2)
$(Me_3Si)_2C(SiMe_2OMe)_2$
(3)
$(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OCH_2CF_3)$
(4)
$(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$
(5)

The presence of NaOMe had only a small effect on the rate of methanolysis; the rate was found to be little different in the presence of 0.03 M NaOMe ($t\frac{1}{2}$ 110 min) but apparently to rise slightly on going to 0.06 or 0.12 M NaOMe ($t\frac{1}{2}$ *ca.* 90 min in both cases). The absence of substantial acceleration by base is consistent with the view that the rate-determining step in the solvolysis is the ionization to give the azide-bridged cation **I**, R = Me, Z = N_3. The validity of this interpretation was confirmed by the observation that the solvolysis of **1** was much faster in the markedly less nucleophilic but more strongly electrophilic solvent CF_3CH_2OH. At *ca.* 1 min after dissolution of **1** in CF_3CH_2OH at 35°C the dialkoxy compound $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$ (**5**) and unchanged **1** were present in 3/1 ratio, indicating a value of $t\frac{1}{2}$ of roughly 0.5 min, and implying that the trifluoroethanolysis is > 150 times as fast as the methanolysis. When a 1:4 v/v mixture of dioxane and CF_3CH_2OH was used $t\frac{1}{2}$ was *ca.* 12.5 min; there was no detectable signal from the initial product $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OCH_2CF_3)$ (**4**) which apparently undergoes solvolysis very rapidly as a result of a combination of anchimeric assistance by the OCH_2CF_3 group and electrophilic assistance to the leaving of the N_3^- by the generated HBr, which is more acidic in CF_3CH_2OH than in MeOH.

The bromide **1** is much more reactive in methanolysis than $(Me_3Si)_3CSiMe_2Br$, probably by a factor in the region of 10^5. (Methanolysis of $(Me_3Si)_3CSiMe_2I$ has $t\frac{1}{2}$ *ca.* 13 days at 50°C, and the bromide is likely to react at least 10 times as slowly; $(Me_3Si)_3CSiPhHBr$ undergoes methanolysis *ca.* 14 times as slowly as $(Me_3Si)_3CSiPhHI$ at 35°C [11]). It is, however, markedly less reactive than the corresponding methoxy derivative $(Me_3Si)_2CSi(Me_2OMe)(SiMe_2Br)$, which has $t\frac{1}{2}$ *ca.* 17 min at 35°C in a 9:1 v/v mixture of dioxane at MeOH containing 0.05 M NaOMe, which suppresses acid-catalysis [5]. The anchimeric assistance by the γ-N_3 group is thus markedly weaker than that by the γ-OMe group, but it is considerably stronger than that by a γ-Ph [2] or γ-vinyl [3] group. We assume that in the intermediate cation the azide group bridges to form a four-membered ring, as in **II** (in which canonical forms can be written with the charge on the various nitrogen atoms); the possibility that a six-membered ring, involv-

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* The methanolysis of the related compound $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Br)$ is known to be acid-catalysed [5].

TABLE 1. Solvolysis of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (1), $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$ (8), and $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (11) in ROH

Substrate [a]	R	Temp/°C	Additive	Product(s)	$t\frac{1}{2}$
1	Me	35	none	3 [b]	90 min
			Et_3N, 0.03 M	2	100 min
			NaOMe, 0.03 M	2	115 min
			0.06 M	2	90 min
			0.12 M	2	90 min
	CF_3CH_2		none	5	*ca.* 0.5 min
			dioxane [c]	5	12.5 min
8	Me	60	none	3 [d]	77 h
	CF_3CH_2		none	3 [e]	30 h
11	Me		none	12, 3	130 h
	CF_3CH_2		none	[f]	[f]

[a] Concn. 0.025 M. [b] Compound **2** grows and disappears. [c] 20% by volume. [d] Compound **9** grows and disappears. [e] Compound **10** grows and disappears. [f] No reaction in 10 days.

ing all three nitrogen atoms, is formed cannot be ruled out, but seems unlikely in view of the linearity of the N_3 ligand in silicon azides [12].

To obtain information on the effect of the γ-N_3 group in a reaction thought to involve direct bimolecular displacement of bromide, we examined the reactivity of **1** towards KSCN in MeCN. A solution of **1** (2.5×10^{-5} mol) in MeCN (10 cm^3) containing an excess of KSCN (5×10^{-4} mol) was kept at 35°C for 30 min, after which **1** and the product $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCS)$ were present in a *ca.* 50/50 ratio, *i.e.* $t\frac{1}{2} =$ *ca.* 30 min. With $(Me_3Si)_3CSiMe_2Br$ under the same conditions, after 4 h the ratio of $(Me_3Si)_3CSiMe_2Br$ to $(Me_3Si)_2CSiMeNCS$ was *ca.* 75/25, implying a half life of *ca.* 8 h. Thus **1** is *ca.* 16 times as reactive as $(Me_3Si)_3CSiMe_2Br$. (A similar ratio was observed between $(Me_3Si_2C(SiMe_2OMe)(SiMe_2Cl)$ and $(Me_3Si)_3CSiMe_2Cl$ in reaction with KSCN in MeCN [5].) The higher reactivity of **1** can be attributed to the electron-withdrawing inductive effect of the N_3 group.

$(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCS)$

(**6**)

$(Me_3Si)_2C(SiMe_2NCS)_2$

(**7**)

It is noteworthy that when the reaction of **1** with the same solution of KSCN in MeCN was carried out under reflux for 60 min a three-component mixture was obtained, and analysis by GLC-MS showed that $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCS)$ (**6**) $(Me_3Si)_2C(SiMe_2NCS)_2$ (**7**) and the diazido compound $(Me_3Si)_2C(SiMe_2N_3)_2$ were present in *ca.* 50:20:30 ratio. Apparently the SCN^- ion can reversibly displace N_3^- from silicon. Other things being equal the equilibrium $R_3SiN_3 + SCN^- \rightleftharpoons R_3SiNCS + N_3^-$ would be expected to lie well over to the left, but in the system under consideration there is a 20-fold excess of SCN^-, and the effective excess may be even greater since it is possible that not all of the NaN_3 that could theoretically be formed would be soluble in the MeCN.

The bromide **1** was also much less reactive than $(Me_3Si)_3CSiMe_2Br$ towards KOCN in MeCN, the rate factor between them being *ca.* 17. (For details see the Experimental section.) Again, when the reaction of **1** with KOCN in MeCN under reflux was prolonged the product was the diisocyanato derivative $(Me_3Si)_2C(SiMe_2NCO)_2$.

Authentic samples of $(Me_3Si)_2C(SiMe_2NCS)_2$ and $(Me_3Si)_2C(SiMe_2NCO)_2$ were obtained by reaction of the dibromide $(Me_3Si)_2C(SiMe_2Br)_2$ with KSCN and KOCN, respectively, in MeCN.

2.2. *Effects of the γ-NCS ligand*

The bromide $(Me_3Si)C(SiMe_2NCS)(SiMe_2Br)$ (**8**) was made by the route shown in Scheme 2.

$$\begin{tikzcd}
(Me_3Si)_2C(Cl)(SiMe_2H) \arrow[r, "(i)"] & (Me_3Si)_2C(SiMe_2H)(SiMe_2Cl) \arrow[d, "(ii)"] \\
(Me_3Si)_2(SiMe_2NCS)(SiMe_2Br) & (Me_3Si)_2C(SiMe_2H)(SiMe_2NCS) \arrow[l, "(iii)"']
\end{tikzcd}$$

(**8**)

Scheme 2. Reagents and conditions: (i) BuLi in THF–Et_2O–pentane–hexane at −120°C, then Me_2SiCl_2 at −80°C and warm to room temperature; (ii) KSCN in MeCN under reflux; (iii) Br_2 in CCl_4.

The reaction of **8** with MeOH at 60°C gave a good first order plot for the disappearance of the starting material, with $t\frac{1}{2}$ *ca*. 76 h (see Table 1). The expected monomethoxide $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2OMe)$ (**9**) was formed but then disappeared as the reaction progressed, and the final product was the dimethoxy derivative **3**. The value of $t\frac{1}{2}$ of *ca*. 76 h at 60°C is to be compared with that of *ca*. 1.5 h for **1** at 35°C, implying that **8** is *ca*. 250–500 times less reactive than **1**, and that the anchimeric assistance by the γ-NCS group is markedly weaker than that by the γ-N_3 group. It is nevertheless stronger than that by a γ-Ph group, since the bromide **8** undergoes methanolysis approximately twice as readily as the *iodide* $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ [2]. As with the azide, we assume that the bridging in the cation involves a four-membered ring, formation of a six-membered ring by attachment of the sulphur atom to the α-Si atom being unlikely in view of the linearity of the NCS ligand in silicon isothiocyanates [12].

$(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$

(8)

$(Me_3Si)_2C(SiMe_2NCS)(SiMe_2OMe)$

(9)

$(Me_3Si)_2C(SiMe_2NCS)(SiMe_2OCH_2CF_3)$

(10)

As expected for an anchimerically-assisted reaction proceeding *via* a bridged cation (**I**, Z = NCS), compound **8** reacted more quickly with CF_3CH_2OH than with MeOH (Table 1). However the factor between the two rates, of *ca*. 2.5, is unusually small, and it is possible that relatively strong hydrogen bonding between the NCS group and the CF_3CH_2OH reduces the ability of the group to provide nucleophilic assistance. In the solvolysis in CF_3CH_2OH the initial product $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2OCH_2CF_3)$ (**10**) reacts further to give the dialkoxy compound $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$ (**5**); examination by GLC-MS of the reaction mixture before reaction was complete confirmed the presence of both products.

2.3. *Effects of a γ-H substituent*

The compound $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (**11**) was made by treatment of $(Me_3Si)_2C(Li)(SiMe_2H)$ with Me_2SiCl_2 at low temperature.

$(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$

(11)

$(Me_3Si)_2C(SiMe_2H)(SiMe_2OMe)$

(12)

Reaction with MeOH gave a good first order plot for disappearance of **11**, with $t\frac{1}{2}$ *ca*. 130 h (see Table 1). Both $(Me_3Si)_2C(SiMe_2H)(SiMe_2OMe)$ and $(Me_3Si)_2C(SiMe_2OMe)_2$ were formed, the latter no doubt as a result of acid catalysis by formed HCl. (When the reaction was conducted in the presence of an excess of Et_3N none of the dimethoxy derivative was formed, but the hydroxide $(Me_3Si)_2C(SiMe_2H)(SiMe_2OH)$ was produced alongside the monomethoxide, indicating that there must have been small amounts of water in the 'dried' MeOH and/or the Et_3N.)

The observed rate of methanolysis is comparable with that of the *iodide* $(Me_3Si)_3CSiMe_2I$, and thus substantially higher than that of the chloride $(Me_3Si)_2CSiMe_2Cl$, but it is very unlikely that this is due to anchimeric assistance by γ-H since **11** underwent no detectable reaction with CF_3CH_2OH in 10 days at 60°C. Instead it can be attributed to a significant reduction in steric hindrance to approach of a nucleophile to the silicon atom of the $SiMe_2Cl$ group, as confirmed by the finding that **11** was much more reactive than $(Me_3Si)_2CSiMe_2Cl$ towards KSCN in MeCN, as described below.

In the reaction of **11** (3.2×10^{-5} mol) with KSCN (64×10^{-5} mol) in MeCN (10 cm^3) at 60°C, after 10 min compound **11** and $(Me_3Si)_2C(SiMe_2H)(SiMe_2NCS)$ were present in a ratio of *ca*. 10:90, corresponding to a value of $t\frac{1}{2}$ of roughly 3 min. Under similar conditions but with $(Me_3Si)_3CSiMe_2Cl$ the reaction was *ca*. 55% complete after 20 h, corresponding to a rough value for $t\frac{1}{2}$ for 17 h. Thus **11** is roughly 350 times as reactive as $(Me_3Si)_3CSiMe_2Cl$ in direct bimolecular substitution. In similar reaction with KOCN in MeCN at 60°C **1** was roughly 340 times as reactive as $(Me_3Si)_3CSiMe_2Cl$ (for details see the Experimental section.) These factors give an indication of the considerable reduction in steric hindrance when even only one of the Me groups of the $(Me_3Si)_3C$ ligand is replaced by H.

The absence of anchimeric assistance in the solvolysis of **11** does not necessarily mean that γ-H is incapable of providing such assistance under suitable conditions. It must be remembered that the methanolysis of $(Me_3Si)_3CSiMe_2I$ does not proceed *via* a cationic intermediate [13], and so is not anchimerically assisted, but nevertheless 1,3-methyl-bridged cations are involved in reactions of this and related iodides with a range of electrophiles, including CF_3CO_2H, implying anchimeric assistance to the leaving of I^- [1]. We examined the reaction of CF_3CO_2H with **11** with this in mind, but found that the initial reaction took place at the Si–H bond (presumably with anchimeric assistance by the γ-Cl substituent) to give $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2O_2CCF_3)$.

3. Experimental section

3.1. General

Solvents were dried by standard methods. In particular, the MeOH and CF_3CH_2OH used for the kinetic studies were dried as described previously [5].

All reactions involving organolithium reagents were carried out under argon.

3.2. Instrumentation

The ^1H NMR spectra were recorded at 90 MHz with solutions in CCl_4 unless otherwise stated.

Mass spectra were obtained by electron impact at 70 eV with a Kratos MS25 spectrometer. For GLC-MS, a 2 m column of 3% OV-101 on Chromasorb Q was used.

3.3. Preparations

3.3.1. $(Me_3Si)_2C(Cl)(SiMe_2N_3)$

A solution of $(Me_3Si)_2C(Cl)(SiMe_2Br)$ (0.65 g, 2.0 mmol) (made as described in ref. 14) in MeCN (50 cm^3) containing NaN_3 (1.3 g, 20 mmol) was heated under reflux for 1 h. The solvent was removed, the residue extracted with boiling pentane, and the extract filtered and evaporated. The residue was sublimed at 80°C at 0.2 torr to give $(Me_3Si)_2C(Cl)SiMe_2N_3$ (0.44 g, 75%), m.p. 114°C (Found: C, 36.5; H, 8.1. $C_9H_{24}N_3Si_4$ calc.: C, 36.9; H, 8.2%); δ(H) 0.26 (18H, s, $SiMe_3$), and 0.47 (6H, s, $SiMe_2$); $\nu(N_3)$ 2150 cm^{-1}.

3.3.2. $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2H)$

(i) A solution of $(Me_3Si)_2C(Cl)(SiMe_2N_3)$ (0.60 g, 2.0 mmol) in a mixture of THF (100 cm^3), Et_2O (10 cm^3), and pentane (10 cm^3) was cooled to −110°C and a 1.6 M solution of BuLi in hexane (1.4 cm^3, 2.2 mmol), cooled to −80°C, was added dropwise with stirring. The mixture was kept at −110°C for a further 1 h then allowed to warm to −80°C and Me_2SiHCl (0.25 g, 2.7 mmol) was added with stirring. The stirred mixture was allowed to warm to room temperature and the solvent then removed. The residue was extracted with boiling pentane, the extract filtered and evaporated, and the residual solid recrystallized from MeOH to give $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2H)$ (0.30 g, 40%), m.p. 291°C (Found: C, 41.9; H, 9.8. $C_{11}H_{31}N_3Si_4$ calc.: C, 41.6; H, 9.8%); δ(H) 0.24 (18H, s, $SiMe_3$); 0.32 (6H, d, Me_2SiH), 0.47 (6H, s, Me_2SiN_3), and 4.12 (1H, m, SiH); $\nu(N_3)$ 2100 cm^{-1}; m/z 302 (10%, M − Me), 275 (35, M − N_3), 274 (40, M − N_3H), 258 (20), 244 (15), 214 (70), 200 (85), 186 (80), 130 (80), 100 (73, $SiMe_2N_3$), and 73 (100, $SiMe_3$).

(ii) A solution of $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2H)$ (0.02 g) (see below) in MeOH (5 cm^3) containing NaN_3 (0.08 g, excess) was heated under reflux for 0.5 h. The solvent was removed under reduced pressure, the residue extracted with pentane, and the extract filtered and evaporated to leave a solid that had properties identical with those given under (i).

3.3.3. $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (1)

A 1.0 M solution of Br_2 in CCl_4 (1.0 cm^3, 1.0 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2H)$ (0.20 g, 6.3 mmol) in CCl_4 (5 cm^3). The solvent was removed and the residue recrystallized from hexane to give **1** (0.15 g, 60%), m.p. 314°C (Found: C, 33.9; H, 7.7. $C_{11}H_{30}BrN_3Si_4$ calc.: C, 33.3; H, 7.6%); δ(H) 0.35 (18H, s, $SiMe_3$), 0.59 (6H, s, $SiMe_2N_3$), and 0.83 (6H, s, $SiMe_2Br$); m/z 382 and 380 (30, M − Me), 355 and 353 (20, M − N_3), 280 and 278 (35), 214 (70), and 200 (100%).

3.3.4. $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OCH_2CF_3)$

A solution of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (0.050 g, 0.12 mmol) in a mixture of CCl_4 (2 cm^3), CF_3CH_2OH (8 cm^3), and Et_3N (2 cm^3) was stirred for 1 h at room temperature. Volatile materials were then evaporated under reduced pressure and the residue extracted with boiling pentane. The extract was filtered and the solvent evaporated to leave a solid, which was shown from its spectra to be the expected $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2OCH_2CF_3)$ (**4**); δ(H) 0.28 (18H, s, $SiMe_3$), 0.38 (6H, s, $SiMe_2O$), 0.50 (6H, s, $SiMe_2N_3$), and 3.84 (2H, m, CH_2); m/z 400 (40, M − Me), 373 (25, M − N_3), 292 (35), 218 (50), 214 (30), 205 (35), 200 (65), 130 (15), and 73 (100, Me_3Si); $\nu(N_3)$ 2120 cm^{-1}.

3.3.5. $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (11)

A stirred solution of $(Me_3Si)_2C(SiMe_2H)Cl$ (0.70 g, 2.8 mmol) (made as described in ref. 14) in a mixture of THF (100 cm^3), Et_2O (10 cm^3), and pentane (10 cm^3) was kept at −120°C as a 1.2 M solution of BuLi in hexane (2.5 cm^3, 3.0 mmol) was added dropwise. The mixture was stirred at −120°C for a further 0.5 h and then allowed to warm to −80°C and Me_2SiCl_2 (1.0 cm^3, 8.0 mmol) was added. The mixture was allowed to warm to room temperature, the solvent was evaporated, and the residue extracted with pentane. The extract was filtered and the solvent evaporated to leave a solid, which was recrystallized from MeOH then sublimed at 100°C at 0.2 torr to give a solid, m.p. 252°C, that was shown from its spectra to be $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (0.65 g, 75%); δ(H) 0.24 (18H, s, $SiMe_3$), 0.32 (6H, d, $Si\mathit{Me}_2H$), 0.57 (6H, s, $SiMe_2Cl$), and 4.12 (1H, m, SiH); ν(SiH) 2080 cm^{-1}; m/z 309 (5%, M − H), 295 (100, M − Me), 221 (35), 207 (15), 201 (15), 187 (70), 129 (30), 73 (65, $SiMe_3$), and 59 (70, $SiMe_2H$).

3.3.6. $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2H)$

A solution of $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (0.31 g, 1.0 mmol) in MeCN (40 cm^3) containing KSCN (2.0 g, 20 mmol) was heated under reflux for 0.5 h. The solvent was evaporated off under reduced pressure, the residue was extracted with boiling pentane, the extract filtered, and the solvent evaporated. The residual solid was sublimed at 110°C at 0.3 torr to give $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2H)$ (0.30 g, 91%), m.p. 277°C (Found: C, 43.1; H, 9.4; N, 4.5. $C_{12}H_{31}NSSi_4$ calc.: C, 43.2; H, 9.3; N, 4.2%); δ(H) 0.25 (18H, s, $SiMe_3$), 0.34 (6H, d, $Si\mathit{Me}_2H$), 0.48 (6H, s, $SiMe_2NCS$), and 4.12 (1H, m, SiH); ν(NCS) 2080, ν(SiH) 2040 cm^{-1}; *m/z* 332 (5%, M – H), 318 (100, M – Me), 244 (20), 201 (20), 187 (45), 129 (20), and 73 (40).

3.3.7. $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$ (8)

A 1.0 M solution of Br_2 in CCl_4 (1.0 cm^3, 1.0 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2H)$ (0.30 g, 0.90 mmol) in CCl_4 (10 cm^3). The solvent was removed and the residue recrystallized from pentane and shown to be $(Me_3Si)_2C(SiMe_2NCS)(SiMe_2Br)$ (0.25 g, 67%), m.p. 284°C (Found: C, 34.5; H, 7.4; N, 3.1. $C_{12}H_{30}BrNSSi_4$ calc.: 34.95; H, 7.3; N, 3.4%); δ(H) 0.37 (18H, s, Me_3Si), 0.64 (6H, s, $SiMe_2NCS$), and 0.85 (6H, s, $SiMe_2Br$); *m/z* 398 and 396 (100%, M – Me), 355 and 353 (5, M – NCS), 332 (5, M – Br), 267 and 265 (25), 244 (30), 201 (5), and 73 (15).

3.3.8. $(Me_3Si)_2C(SiMe_2H)(SiMe_2OH)$

A solution of $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (0.050 g, 0.16 mmol) in a mixture of MeOH (20 cm^3), H_2O (1 cm^3) and Et_3N (1 cm^3) was refluxed for 5 h. The solvents were taken off under reduced pressure, the residue extracted with pentane, the extract filtered, and the solvent evaporated to leave a solid, which was sublimed at 85°C at 0.2 torr to give a solid (0.030 g, 65%), m.p. 295°C, which was shown from its spectra to be $(Me_3Si)_2C(SiMe_2H)(SiMe_2OH)$; δ(H) 0.21 (18H, s, $SiMe_3$), 0.29 (6H, s, $Si\mathit{Me}_2OH$), 0.30 6H, d, $Si\mathit{Me}_2H$), 1.40 (1H, br s, SiOH), and 4.12 (1H, m, SiH); ν(SiOH) 3710, ν(SiH) 2070 cm^{-1}; *m/z* 277 (75%, M – Me), 275 (100, M – OH), 261 (25), 203 (15), 187 (40), 129 (25), and 73 (80).

3.3.9. $(Me_3Si)_2C(SiMe_2NCS)_2$ (7)

A solution of $(Me_3Si)_2C(SiMe_2Br)_2$ (40 mg, 0.09 mmol) in the MeCN containing KSCN (0.20 g, 2 mmol) was heated under reflux for 1 h. The solvent was removed under reduced pressure, the residue extracted with boiling pentane, and the extract filtered and evaporated. The residue was recrystallized from pentane to give $(Me_3Si)_2C(SiMe_2NCS)_2$ (20 mg, 50%), m.p. 250°C; δ(H) 0.32 (18H, s, $SiMe_3$) and 0.56 (12H, s, $SiMe_2$); ν(NCS) 2045 cm^{-1}; *m/z* 375 (100%, M – Me), 332 (20, M – NCS), 244 (35), 201 (10), 116 (5, $SiMe_2NCS$), and 73 (60).

3.3.10. $(Me_3Si)_2C(SiMe_2NCO)_2$

A solution of $(Me_3Si)_2C(SiMe_2Br)_2$ (30 mg, 0.07 mmol) in MeCN (30 cm^3) containing KOCN (0.20 g, 2.4 mmol) was refluxed for 3 h. The solvent was removed under reduced pressure, the residue extracted with hot CCl_4, and the extract filtered and evaporated, to leave a solid, which was recrystallized from pentane to give $(Me_3Si)_2C(SiMe_2NCO)_2$ (20 mg, 80%), m.p. > 330°C; δ(H) 0.32 (18H, s, $SiMe_3$) and 0.51 (12H, s, $SiMe_2$); ν(NCO) 2280 cm^{-1}; *m/z* 343 (100%, M – Me), 225 (5), 228 (30), 201 (5), 100 (10, $SiMe_2NCO$), and 73.

3.4. Rates of solvolysis

Reactions were carried out in NMR tubes. For runs at 35°C the tubes were firmly capped and kept in the probe of the spectrometer; for those at 60°C the tubes were sealed and kept in a thermostat bath with occasional transfer to the spectrometer for rapid recording of the spectrum. For runs in MeOH at 35°C the substrate was dissolved in a drop (*ca.* 0.01 cm^3) of CCl_4 before addition of the MeOH. The extent of disappearance of the substrate at any time was given by the ratio of the height of the peak from the $SiMe_2X$ protons (X = Cl in **11** and Br in **1** and **8**) to (a) that of the peak from the $Si\mathit{Me}_2OR$ (R = Me or CH_2CF_3) protons in the initial monoalkoxy product, or (b) to the combined heights of the peaks for the $SiMe_2OR$ protons in the mono- and di-alkoxy products, with allowance for the presence of two $SiMe_2OR$ groups in the latter. Good first order plots were obtained in all cases. Rate constants (and thus values of $t_{\frac{1}{2}}$) were reproducible to within *ca.* ±6%, and the absolute values are probably accurate to within *ca.* ±10%. However, *relative* rates for a given reaction under slightly different conditions (*e.g.* for methanolysis in the absence and presence of Et_3N) are probably somewhat more accurate than that. In some cases the results were checked by use of $SiMe_4$ as an internal standard against which the extent of disappearance of the substrate could be assessed, and the results agreed satisfactorily with those obtained by the usual method.

As an illustration, for the methanolysis of **1**, a 5 mg sample (giving a *ca.* 0.025 M solution) in an NMR tube was dissolved in a small drop (*ca.* 0.01 cm^3) of CCl_4 and MeOH (0.5 cm^3), prewarmed to 35°C, was added. The tube was closed, shaken briefly, and placed in the spectrometer, and recording of the spectra was begun. In the absence of added Et_3N or NaOMe, in the early stages of the reaction both the monomethoxy product **2** and the dimethoxy product **3** were present, the concentration of **2** building up to a maximum of *ca.* 12% of that of the initial concentration of **1** and then falling towards zero. A good first-order plot, giving a value of the first order rate constant of 1.3×10^{-4} s^{-1} ($t\frac{1}{2}$ *ca.* 90 min), was obtained. When Et_3N or NaOMe were present only the monoethoxy product **2** was formed.

Relevant details for individual runs were as follows.

(a) In the reaction of **1** with CF_3CH_2OH at 35°C the first spectrum recorded, *ca.* 1 min after the mixing of the reactants, showed that **1** and the dialkoxy compound **5** were present in *ca.* 25/75 ratio. When a 1:4 v/v mixture of dioxane–CF_3CH_2OH was used a satisfactory first order plot, giving $k = 9.2 \times 10^{-4}$ s^{-1}, was obtained. The product was the di-alkoxy compound **5**, and there was no detectable trace of the monoalkoxy compound at any stage.

(b) In the reactions of **8** with MeOH both the mono- and di-alkoxy products, **9** and **3**, were present during much of the reaction, as were **10** and **5** in the reaction with CF_3CH_2OH, but the final products were **3** and **5**, respectively. In the reaction with CF_3CH_2OH the identities of the products were confirmed by GLC-MS analysis of an incomplete reaction mixture; the two product components gave mass spectra as follows: **10**, *m/z* 416 (100, M – Me), 373 (20, M – NCS), 357 (40), 336 (85), 332 (85), 297 (25), 244 (25); **5**, *m/z* 457 (15%, M – Me), 358 (10), and 73 (100). (Authentic samples were available.)

(c) In the methanolysis of $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (**11**) both the mono- and di-alkoxy products were present throughout the extent of reaction studied. When the MeOH contained 0.075 M Et_3N the spectrum indicated that $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2H)$ and $(Me_3Si)_2C(SiMe_2OH)(SiMe_2H)$ were formed in *ca.* 30:70 ratio.

3.5. Reactivities towards alkali metal salts

3.5.1. Reactions of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (1) and $(Me_3Si)_3CSiMe_2Br$

(a) A solution of **1** (10 mg, 0.025 mmol) in MeCN (10 cm^3) containing KSCN (50 mg, 0.50 mmol) was refluxed for 60 min then cooled. The solvent was taken off quickly at low pressure, the residue extracted with CCl_4, and the extract filtered. The ^1H NMR spectrum of the extract indicated that three products were present, and GLC-MS showed that these were $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCS)$ (*m/z* 359 (M – Me)), $(Me_3Si)_2C(SiMe_2N_3)_2$ (*m/z* 343 (M – Me)), and $(Me_3Si)_2C(SiMe_2NCS)_2$ (*m/z* 375 (M – Me)), in 50/30/20 ratio. (Authentic samples of the last two products were available for comparison of retention times and mass spectra).

(b) A similar reaction mixture was kept at 35°C and the ^1H NMR spectrum recorded at intervals. The solid product was $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCS)$. (Its spectrum showed singlets at δ 0.51 and 0.30 ($SiMe_3$) in 2/3 integration ratio, the signals from the $SiMe_2N_3$ and $SiMe_2NCS$ protons having the same chemical shift. The identity was confirmed by GLC-MS.) After 30 min **1** and the product were present in *ca.* 50/50 ratio.

When $(Me_3Si)_3CSiMe_2Br$ was subjected to the same conditions, after 240 min the starting bromide and the product $(Me_3Si)_3CSiMe_2NCS$ were present in *ca.* 75/25 ratio.

(c) A solution of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$ (**1**) (10 mg, 0.025 mmol) in MeCN (10 cm^3) containing KOCN (0.040 g, 0.5 mmol) was refluxed for 3 h. Work-up as under (a) above gave a CCl_4 extract whose ^1H NMR spectrum indicated that it was $(Me_3Si)_2C(SiMe_2NCO)_2$, an authentic sample of which was available.

When a similar mixture was kept for 90 min at 60°C and then worked up as before, the ^1H NMR spectrum showed that **1** and $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2NCO)$ were present in *ca.* 65/35 ratio; *i.e.* $t\frac{1}{2}$ is roughly 2.4 h. When $(Me_3Si)_3CSiMe_2Br$ was subjected to the same conditions, after 17 h the ratio of starting material to $(Me_3Si)_3CSiMe_2NCO$ was *ca.* 75/25; *i.e.* $t\frac{1}{2}$ is roughly 40 h.

(d) A solution of $(Me_3Si)_2C(SiMe_2H)(SiMe_2Cl)$ (**11**) (3.2×10^{-5} mol) in MeCN (10 cm^3) containing KSCN (64×10^{-5} mol) was kept at 60°C for 10 min. Work-up as under (a) above gave an extract whose ^1H NMR spectrum showed it to contain **11** and $(Me_3Si)_2C(SiMe_2H)(SiMe_2NCS)$ in *ca.* 10/90 ratio; *i.e.* $t\frac{1}{2}$ is roughly 3 min.

Under similar conditions, reaction of $(Me_3Si)_3CSiMe_2Cl$ gave the starting material and $(Me_3Si)_3CSiMe_2NCS$ in *ca.* 45/55 ratio after 20 h; *i.e.* $t\frac{1}{2}$ is roughly 17 h.

(e) When KOCN was used in place of KSCN in the procedure described under (d): (i) with **11**, after 10 min the starting material and $(Me_3Si)_2C(SiMe_2H)(SiMe_2NCO)$ were present in *ca.* 75/25 ratio; *i.e.* $t\frac{1}{2}$ is roughly 24 min; (ii) with $(Me_3Si)_3CSiMe_2Cl$, after 64 h the chloride and $(Me_3Si)_3CSiMe_2NCO$ were present in *ca.* 72/28 ratio; *i.e.* $t\frac{1}{2}$ is roughly 135 h.

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