

Preparation and reactions of tris(trimethylsilyl)silyl silicon derivatives and related tetrasilylsilanes

Youcef Derouiche and Paul D. Lickiss ^{*,*}

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9Q1 (UK)

(Received September 26th, 1990)

Abstract

Treatment of $(\text{Me}_3\text{Si})_3\text{SiLi}$ with various silicon halides has given a range of compounds of the type $(\text{Me}_3\text{Si})_3\text{SiSiR}_2\text{X}$ ($\text{R} = \text{Me}$, $\text{X} = \text{H}$; $\text{R} = \text{Ph}$, $\text{X} = \text{Cl}$ etc.). These compounds can be converted into other derivatives by simple substitution reactions at the Si–X centre. Symmetrical pentasilanes $(\text{XMe}_2\text{Si})_4\text{Si}$ ($\text{X} = \text{Cl}$, F , and OAc) have been prepared from $(\text{Me}_3\text{Si})_4\text{Si}$. The reactivities of these species have been compared with those of analogous carbon-centred compounds eg. $(\text{Me}_3\text{Si})_3\text{CSiR}_2\text{X}$. Substitution reactions in the silicon-centred compounds are much more rapid than those in the carbon analogues, presumably reflecting the increase in bond lengths around the central atom which makes the functionalized silicon centre less sterically hindered and more susceptible to attack.

Introduction

During the last ten years Eaborn and co-workers have prepared a large number of silicon compounds containing the bulky $(\text{Me}_3\text{Si})_3\text{C}$ group (often known as the “trisyl” group and denoted by Tsi; for reviews of some of this work see ref. 1). Due to the very great steric hindrance provided by the bulky group when attached to a potentially reactive silicon centre the reactions that were to be expected at such centres were either much slower or forced to take a completely different course. For example, the silicon iodide $\text{TsiSiMe}_2\text{I}$ has a half-life at 50°C in MeOH of about 13 days [2], and treatment of $\text{TsiSiPh}_2\text{I}$, with, for example, silver salts AgX ($\text{X} = \text{OAc}$, ONO_2 , OSO_2CF_3 , etc.) affords rearranged products $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{X})(\text{SiPh}_2\text{Me})$ [3] which are formed via bridged silicocationic intermediates. We have prepared a range of analogous silicon-centred compounds $(\text{Me}_3\text{Si})_3\text{SiSiR}_2\text{X}$ in order to see whether this related ligand can give derivatives of similar, unusual reactivity. Haase and Klingebiel have prepared a similar range of compounds $(\text{Me}_3\text{Si})_3\text{SiSiRR}'\text{X}$ ($\text{R} = \text{Me}$, $\text{R}' = \text{X} = \text{F}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$, $\text{X} = \text{Cl}$; $\text{R} = \text{H}$, $\text{R}' = \text{X} = \text{t-Bu}$ etc.) but have reported only their reactions with lithium amides [4,5]. A small number of

* Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK.

(Me₃Si)₃Si derivatives of Ge [6] and Sn [6,7] have also been prepared but little of their chemistry has been described.

Results and discussion

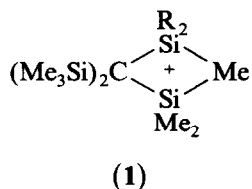
The reaction between (Me₃Si)₃SiLi(thf)₃ and SiCl₄ gives (Me₃Si)₃SiSiCl₃ but, as in the analogous (Me₃Si)₃C case [8], only one of the bulky groups can be introduced into the molecule. (It should be noted that the reaction of GeCl₄ with two equivalents of (Me₃Si)₃SiLi(thf)₃ also fails to introduce two (Me₃Si)₃Si groups on to the central metal atom but gives the dimer [Cl₂GeSi(SiMe₃)₃]₂ while the analogous reaction with SnCl₄ does give Cl₂Sn[Si(SiMe₃)₃]₂ presumably due to the greater space available around the large tin atom [6].) Similarly, treatment of (Me₃Si)₃SiLi(thf)₃ with Me₂SiHCl and Ph₂SiCl₂ affords (Me₃Si)₃SiSiMe₂H and (Me₃Si)₃SiSiPh₂Cl respectively. All three of these derivatives have a very different reactivity from their (Me₃Si)₃C analogues and react in a manner similar to less-crowded species. For example (Me₃Si)₃SiSiCl₃ reacts readily with cold water in less than 1 h to give (Me₃Si)₃SiSi(OH)₃ [9] and with a dilute solution of MeOH in refluxing THF to give (Me₃Si)₃SiSi(OMe)₃. This is in great contrast to TsiSiCl₃, which appears to be indefinitely stable in, for example, H₂O/THF or H₂O/Et₂O [10], and does not react with boiling MeOH during many hours [11]. The inertness of TsiSiCl₃ required that a multistep synthesis, via TsiSiH₃, be used for the synthesis of the silanetriol TsiSi(OH)₃ [12].

One of the few simple displacement reactions known to be undergone by TsiSiCl₃ is reduction by LiAlH₄ to give TsiSiH₃ [8], and as expected the analogous reaction occurs for (Me₃Si)₃SiSiCl₃ to give (Me₃Si)₃SiSiH₃. However, unlike TsiSiH₃, which is unreactive towards CCl₄ at room temperature, (Me₃Si)₃SiSiH₃ reacts with CCl₄, apparently to give (Me₃Si)₃SiSiH₂Cl, (Me₃Si)₃SiSiHCl₂, and (Me₃Si)₃SiSiCl₃. The silane TsiSiH₃ does react slowly in boiling CCl₄ to give TsiSiH₂Cl, TsiSiHCl₂, and TsiSiCl₃. This is a similar type of reaction to that shown by (Me₃Si)₃SiH which reduces a variety of alkyl halides by a radical mechanism [13]. The silane (Me₃Si)₃SiSiH₃ reacts with PhLi to give (Me₃Si)₃SiSiH₂Ph in a manner analogous to the reaction of TsiSiH₃ with *p*-MeC₆H₄Li to give TsiSiH₂C₆H₄Me-*p* [14].

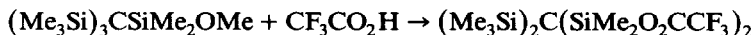
Other compounds that have been extensively studied by Eaborn et al. are the derivatives of TsiSiMe₂H. Treatment of (Me₃Si)₃SiLi(thf)₃ with Me₂SiHCl gave (Me₃Si)₃SiSiMe₂H, which when treated with I₂ in CCl₄ surprisingly gave the chloride (Me₃Si)₃SiSiMe₂Cl, again presumably via a radical process similar to that mentioned above for (Me₃Si)₃SiH. (Recently the reaction between TsiSiH₃ and Br₂ in CCl₄ was found to give a mixture of halogenated products TsiSiBr₃Cl_{3-n} (*n* = 0–3 [10].) Reaction between (Me₃Si)₃SiSiMe₂H and I₂ in benzene gave the required (Me₃Si)₃SiSiMe₂I, which reacted within 10 min in a mixture of CH₂Cl₂/MeOH (5:2 v/v) to give (Me₃Si)₃SiSiMe₂OMe and with a 70:1 v/v mixture of CH₂Cl₂/H₂O to give (Me₃Si)₂SiSiMe₂OH in less than 15 min. This reactivity is in great contrast to the remarkable stability of TsiSiMe₂I, which can be prepared by treatment of TsiSiMe₂H with iodine monochloride in methanol solution [15] and has a half life in MeOH at 50 °C of 13 days [2], and which is not hydrolysed under the conditions described above. The hydride itself, (Me₃Si)₃SiSiMe₂H, is also much more reactive than TsiSiMe₂H, reacting readily

with MeOH or H₂O whereas TsiSiMe₂H undergoes no reaction during 1.5 h with a MeOH/H₂O/AgNO₃ mixture at the reflux temperature [3].

In reactions of (Me₃Si)₃SiSiMe₂I with silver salts AgOAc, AgO₂CCF₃, and AgBF₄ simple substitution takes place to give (Me₃Si)₃SiSiMe₂X (X = OAc, O₂CCF₃, and F). This is similar to the reaction of the Trisyl analogue although it is thought that for TsiSiMe₂I the reactions proceed via a bridged silicocationic intermediate of type 1 (R = Me) [3]. Such cationic intermediates containing a variety of bridging groups have been shown to be important in reactions of Tsi silicon derivatives and related species [1] and attempts were made in the present work to see if such reactions might also occur with (Me₃Si)₃Si silicon derivatives.



A striking example of anchimeric assistance via a bridged cationic intermediate occurs when TsiSiMe₂OMe is treated with CF₃CO₂H to give (Me₃Si)₂C(SiMe₂O₂-CCF₃)₂, with loss of an Me group as MeH [16]. In contrast to this, the reaction between (Me₃Si)₃SiSiMe₂OMe and CF₃CO₂H gives the simple solvolysis product (Me₃Si)₃SiSiMe₂O₂CCF₃, suggesting that a bridged silicocation is not involved:



Many of the reactions of the silicon iodide TsiSiPh₂I such as those with silver salts have also been found to give rearranged products of the type (Me₃Si)₂C(SiPh₂Me)(SiMe₂X) and are again thought to involve intermediate silicocationic species of the type 1 (R = Ph) [3]. Unfortunately we have been unable to prepare (Me₃Si)₃SiSiPh₂I intended for analogous studies, but the chloride (Me₃Si)₃SiSiPh₂Cl was conveniently prepared by treatment of (Me₃Si)₃SiLi with Ph₂SiCl₂. The chloride readily undergoes solvolysis with either MeOH or H₂O but does not react with silver salts AgOAc, AgBF₄, or AgO₃SCF₃ during several hours in boiling CH₂Cl₂. The solvolysis reactions are again in great contrast to the Trisyl analogue TsiSiPh₂Cl, which does not react with boiling methanol even in the presence of AgNO₃ [8]. Although the solvolysis reactions proceed via a different mechanism to those with silver salts it is likely that the more reactive iodide (Me₃Si)₃SiSiPh₂I would also undergo simple substitution reactions with silver salts.

Other compounds in which there is a great difference in reactivity between silicon and carbon centred species are those of the type (ClMe₂Si)₄M (M = C or Si). We have previously reported [17] that (ClMe₂Si)₄Si is readily hydrolysed to give a bicyclic siloxane product whereas (ClMe₂Si)₄C does not react under similar conditions [10]. Treatment of (ClMe₂Si)₄Si with AgOAc or AgBF₄ gave (XMe₂Si)₄Si (X = OAc or F) but the Trisyl analogue does not react readily with silver salts [10]. (For other reactions of (ClMe₂Si)₄C see ref. 18.)

The great difference in reactivity between many of the silicon- and carbon-centred compounds discussed above is most likely to be due to the lower degree of steric hindrance afforded by the (Me₃Si)₃Si group compared with the (Me₃Si)₃C group.

This is attributable to the longer bonds to the central Si (ca. 2.35 Å) compared with those to C (ca. 1.89 Å). Thus many of the reactions of $(\text{Me}_3\text{Si})_3\text{Si}$ silicon derivatives can be seen as similar to those normally associated with much less hindered systems. It should be noted that although these $(\text{Me}_3\text{Si})_3\text{Si}$ silicon derivatives do not have particularly unusual chemistry the ligand has found much use in transition metal chemistry, forming interesting derivatives of, for example, Sc [19], Pt [20], Cr, Mn, Fe [21], and Zr and Hf [22].

Experimental

Solvents were dried by standard methods. The silyllithium reagent $(\text{Me}_3\text{Si})_3\text{SiLi}(\text{thf})_3$ was prepared according to ref. 23, $(\text{ClMe}_2\text{Si})_4\text{Si}$ according to ref. 24, and $(\text{Me}_3\text{Si})_3\text{SiSiCl}_3$, and $(\text{Me}_3\text{Si})_3\text{SiSiPh}_2\text{Cl}$ according to ref. 4. The preparation of $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{OH})_3$ has been reported previously [9]. The ^1H NMR spectra were recorded at 80 or 90 MHz using either CCl_4 solutions, containing CH_2Cl_2 as lock, or CDCl_3 solutions. The ^{13}C and ^{29}Si NMR spectra were recorded at 90.5 and 71.5 MHz respectively using CDCl_3 solutions. Satisfactory carbon analysis for compounds containing the $(\text{Me}_3\text{Si})_3\text{Si}$ group were difficult to obtain. This problem has been noted by other workers and has been attributed to the formation of SiC which is incompletely burnt during the combustion analysis [21,25]. Mass spectra were obtained by electron impact (70 eV); where relevant the m/z values refer to ions containing ^{35}Cl . Only the more significant peaks are given.

$(\text{Me}_3\text{Si})_3\text{SiSi}(\text{OMe})_3$

A solution of $(\text{Me}_3\text{Si})_3\text{SiSiCl}_3$ (1 g, 2.62 mmol) in dry THF (15 cm^3) containing MeOH (0.1 cm^3) was heated under reflux for 2 h. After cooling, removal of the solvent under vacuum left a white solid, which was sublimed (120°C, 0.05 mmHg) to give (trimethoxysilyl)tris(trimethylsilyl)silane as a white solid (0.92 g, 96%), m.p. 165–167°C. $\delta(\text{H})$ 0.19 (s, 27H, SiMe_3), 3.64 (s, 9H, OMe), $\nu(\text{Si}-\text{OMe})$ 1195 cm^{-1} , m/z 368 (10%, $[\text{M}]^+$), 353 (20, $[\text{M}-\text{Me}]^+$), 337 (15, $[\text{M}-\text{OMe}]^+$), 315 (35), 295 (45, $[\text{M}-\text{SiMe}_3]^+$), 278 (15, $[\text{M}-\text{Si}(\text{OMe})_2]^+$), 264 (35, $[\text{M}-\text{Me}_3\text{SiOMe}]^+$), 258 (15), 247 (10 $[\text{M}-\text{Si}(\text{OMe})_3]^+$), 232 (15, $[(\text{Me}_3\text{Si})_2\text{SiSiMe}_2]^+$), 217 (40, $[\text{M}-2\text{Me}-\text{Si}(\text{OMe})_3]^+$), 210 (33), 121 (10, $[\text{Si}(\text{OMe})_3]^+$), 101 (15), 73 (100, $[\text{SiMe}_3]^+$), 59 (45, $[\text{SiMe}_2\text{H}]^+$).

$(\text{Me}_3\text{Si})_3\text{SiSiH}_3$

A solution of $(\text{Me}_3\text{Si})_3\text{SiSiCl}_3$ (3 g, 7.86 mmol) and LiAlH_4 (0.9 g, 23.6 mmol) in dry diethyl ether (30 cm^3) was heated under reflux for 3 h. After cooling to room temperature solids were removed by filtration and the solvent was removed from the filtrate under reduced pressure to leave a white solid, which was washed with n-pentane (5 cm^3). Evaporation of solvent from the pentane washings left a white solid, (silyl)tris(trimethylsilyl)silane (1 g, 87%), m.p. 125–127°C. $\delta(\text{H})$ (C_6H_6) 0.23 (s, 27H, SiMe_3), 3.43 (s, 3H, SiH_3), $\delta(\text{Si})$ ($\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$) -9.43 (SiMe_3), -99.53 (q, $^1J(\text{Si}-\text{H})$ 187.6 Hz, SiH_3), -144.0 (SiSiH_3), $\nu(\text{Si}-\text{H})$ 2122 cm^{-1} , m/z 278 (6%, $[\text{M}]^+$), 263 (45, $[\text{M}-\text{Me}]^+$), 232 (20, $[\text{M}-\text{Me}-\text{SiH}_3]^+$), 204 (55, $[\text{M}-\text{Me}_3\text{SiH}]^+$), 189 (15, $[\text{M}-2\text{Me}-\text{SiMe}_3\text{H}]^+$), 173 (15), 159 (10, $[\text{M}-\text{Me}_4\text{Si}-\text{SiH}_3]^+$), 144 (40), 73 (100, $[\text{Me}_3\text{Si}]^+$), 59 (20, $[\text{SiMe}_2\text{H}]^+$).

Reaction of $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ with CCl_4

A sample of $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ (ca. 20 mg) was dissolved in CCl_4 in an NMR tube. After 10 min at room temperature the ^1H NMR spectrum showed that only $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ was present, but after 6 h the spectrum showed that most of the starting material had disappeared and new Me_3Si signals at δ 0.21, 0.26, and 0.34 had appeared, and these can be attributed to the formation of $(\text{Me}_3\text{Si})_3\text{SiSiClH}_2$, $(\text{Me}_3\text{Si})_3\text{SiSiCl}_2\text{H}$, and (the known) $(\text{Me}_3\text{Si})_3\text{SiSiCl}_3$.

Reaction of $(\text{Me}_3\text{Si})_3\text{CSiH}_3$ with CCl_4

A solution of $(\text{Me}_3\text{Si})_3\text{CSiH}_3$ (20 mg) in CCl_4 (0.5 cm^3) in an NMR tube was set aside at room temperature for 24 h after which the ^1H NMR spectrum showed only starting material to be present.

A solution of $(\text{Me}_3\text{Si})_3\text{CSiH}_3$ (0.45 g) in CCl_4 (10 cm^3) was heated under reflux and the reaction progress was monitored by ^1H NMR spectroscopy. After 24 h the NMR spectrum showed the presence of $(\text{Me}_3\text{Si})_3\text{CSiH}_3$, $(\text{Me}_3\text{Si})_3\text{CSiH}_2\text{Cl}$, and $(\text{Me}_3\text{Si})_3\text{CSiHCl}_2$ in an approximate 4.7:4.5:1 ratio respectively together with some CHCl_3 . After 50 h the spectrum indicated the presence of $(\text{Me}_3\text{Si})_3\text{CSiH}_3$ [$\delta(\text{H})$ 0.16 (SiMe₃), 3.63 (SiH₃, $^1J(\text{Si-H})$ 198 Hz)], $(\text{Me}_3\text{Si})_3\text{CSiH}_2\text{Cl}$ [δ 0.24 (SiMe₃), 4.86 (SiH₂Cl, $^1J(\text{Si-H})$ 234 Hz)], $(\text{Me}_3\text{Si})_3\text{CSiHCl}_2$ [δ 0.31 (SiMe₃), 5.51 (SiHCl₂, $^1J(\text{Si-H})$ 281 Hz)], and $(\text{Me}_3\text{Si})_3\text{CSiCl}_3$ (δ 0.38) in an approximate 1:6.9:6.3:1.1 ratio respectively as well as CHCl_3 .

Reaction of $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ with PhLi

To a solution of $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ (1.7 g, 2.51 mmol) in dry ether (10 cm^3) was added a 2.4 M solution of PhLi (1.05 cm^3 , 2.51 mmol) in cyclohexane and the mixture was stirred at room temperature for 3 h. Filtration and removal of the solvent from the filtrate left a pale pink solid from which was sublimed (95°C/0.01 mmHg) a white solid, that appeared to be (phenylsilyl)tris(trimethylsilyl)silane (0.4 g, 50%), $\delta(\text{H})$ (CH_2Cl_2) 0.25 (s, 27H, SiMe₃), 3.40 (s, 2H, SiH), 7.40–7.49 (m, 5H, Ph), $\nu(\text{Si-H})$ 2080 cm^{-1} .

$(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$

A solution of $(\text{Me}_3\text{Si})_3\text{SiLi}(\text{thf})_3$ [prepared from $(\text{Me}_3\text{Si})_4\text{Si}$ (6g, 0.018 mol)] in dry toluene (30 cm^3) was added dropwise to a solution of Me_2SiClH (3.54 g, 0.037 mol) in dry toluene (3 cm^3) and the resulting mixture was stirred at room temperature for 7 h. Filtration and removal of the volatiles from the filtrate under reduced pressure gave a sticky white solid from which was sublimed (dimethylsilyl)tris(trimethylsilyl)silane as a white solid (3.2 g, 58%), m.p. 207–210°C, $\delta(\text{H})$ 0.20 (s, SiMe₃), 0.27 (d, $^3J = 4.4$ Hz, SiMe₂), 4.02 (m, 1H, SiH), $\delta(\text{C})$ 2.79 (s, SiMe₃), 2.98 (s, SiMe₂), $\nu(\text{Si-H})$ 2088 cm^{-1} , m/z 232 (65%, [$M - \text{H} - \text{Me}_3\text{Si}$]⁺), 217 (25, [$M - \text{Me} - \text{H} - \text{Me}_3\text{Si}$]⁺), 173 (15, [$M - \text{Me}_3\text{Si} - \text{Me}_2\text{SiH}$]⁺), 158 (15, [$M - \text{Me}_4\text{Si} - \text{Me}_3\text{SiH}$]⁺), 129 (15), 73 (100, [Me_3Si]⁺), 59 (22, [Me_2SiH]⁺).

$(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{I}$

A mixture of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ (1.5 g, 4.9 mmol) and I_2 (2.48 g, 9.8 mmol) in dry benzene (25 cm^3) was stirred at room temperature for 30 min. Solvent and most of excess iodine were then removed under reduced pressure to leave a brown solid which was rinsed several times with a little CH_2Cl_2 to leave a pale brown solid from

which was sublimed (70 °C/0.02 mmHg) (iododimethylsilyl)tris(trimethylsilyl)silane (1.85 g, 88%), m.p. 234–236 °C, $\delta(\text{H})$ (C_6H_6) 0.27 (s, 27H, SiMe_3), 0.93 (s, 6H, SiMe_2I), m/z 432 (5%, $[\text{M}]^+$), 417 (15, $[\text{M} - \text{Me}]^+$), 359 (20, $[\text{M} - \text{Me}_3\text{Si}]^+$), 305 (10, $[\text{M} - \text{I}]^+$), 232 (75, $[\text{M} - \text{I} - \text{SiMe}_3]^+$), 173 (20, $[\text{M} - \text{Me}_4\text{Si} - \text{Me}_2\text{SiH}]^+$), 158 (45, $[\text{M} - \text{Me}_4\text{Si} - \text{Me}_2\text{SiHI}]^+$), 131 (25, $[\text{Me}_3\text{SiSiMe}_2]^+$), 73 (100, $[\text{Me}_3\text{Si}]^+$), 59 (15, $[\text{Me}_2\text{SiH}]^+$).

Reaction between $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ and I_2 in CCl_4

A solution of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ (0.5 g, 1.63 mmol) and I_2 (0.45 g, 1.77 mmol) in dry CCl_4 (15 cm^3) was stirred for 1.5 h at room temperature. The solvent was then removed and the resulting residue was rinsed several times with small amounts of CCl_4 to remove most of the remaining I_2 . This left a pale brown solid from which was sublimed (75 °C/0.02 mmHg) to give (chlorodimethylsilyl)tris(trimethylsilyl)silane (0.39 g, 71%) as a white solid, m.p. 175–177 °C, $\delta(\text{H})$ 0.25 (s, 27H, SiMe_3), 0.58 (s, 6H, SiMe_2Cl), m/z 340 (4%, $[\text{M}]^+$), 325 (50, $[\text{M} - \text{Me}]^+$), 305 (35, $[\text{M} - \text{Cl}]^+$), 291 (10), 252 (7, $[\text{M} - \text{Me}_3\text{SiCl}]^+$), 232 (75, $[(\text{Me}_3\text{Si})_2\text{Si} - \text{SiMe}_2]^+$), 173 (30), 158 (30), 143 (25), 131 (25, $[\text{Me}_3\text{SiSiMe}_2]^+$), 115 (25), 93 (35, $[\text{Me}_2\text{ClSi}]^+$), 73 (100 $[\text{Me}_3\text{Si}]^+$), 59 (50, $[\text{Me}_2\text{HSi}]^+$).

$(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{OMe}$

A solution of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{I}$ (0.1 g, 0.23 mmol) in a mixture of CH_2Cl_2 (5 cm^3) and MeOH (2 cm^3) was stirred at room temperature for 10 min. Removal of the volatiles under reduced pressure gave a white solid from which was sublimed (95 °C/0.01 mmHg) (methoxydimethylsilyl)tris(trimethylsilyl)silane (70 mg, 90%) as a white solid m.p. 178–180 °C, $\delta(\text{H})$ 0.15 (s, 27H, Me_3Si), 0.25 (s, 6H, SiMe_2), 3.33 (s, 3H, OMe), m/z 336 (5%, $[\text{M}]^+$), 321 (15, $[\text{M} - \text{Me}]^+$), 232 (74, $[(\text{Me}_3\text{Si})_2\text{Si} = \text{SiMe}_2]^+$), 189 (10), 173 (20), 158 (25, $[\text{M} - \text{Me}_4\text{Si} - \text{Me}_3\text{SiH}]^+$), 131 (25, $[\text{Me}_3\text{SiSiMe}_2]^+$), 117 (10), 89 (15, $[\text{Me}_2\text{SiOMe}]^+$), 73 (100, $[\text{Me}_3\text{Si}]^+$), 59 (25, $[\text{Me}_2\text{HSi}]^+$).

$(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{OH}$

The procedure described above for $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{OMe}$ was repeated using a mixture of CH_2Cl_2 (7 cm^3) and water (0.1 cm^3) to give (hydroxydimethylsilyl)tris(trimethylsilyl)silane (70 mg, 95%) as a white solid m.p. 172–175 °C, $\delta(\text{H})$ 0.13 (s, 27H, Me_3Si), 0.19 (s, 6H, SiMe_2), 3.19 (s, 1H, OH), $\nu(\text{Si}-\text{OH})$ 3690 cm^{-1} , m/z 307 (16%, $[\text{M} - \text{Me}]^+$), 291 (7, $[\text{M} - \text{MeOH}]^+$), 232 (90, $[\text{M} - \text{Me}_2\text{SiH} - \text{MeOH}]^+$), 189 (15), 173 (25), 147 (50, $[\text{Me}_3\text{SiOSiMe}_2]^+$), 131 (35), 115 (20), 73 (100), $[\text{Me}_3\text{Si}]^+$, 59 (50, $[\text{Me}_2\text{HSi}]^+$).

Reaction of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ with H_2O

A solution of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ (0.1 g, 0.32 mmol) in THF (15 cm^3) containing a little water was stirred at room temperature for 5 h. Removal of solvent left a solid from which was sublimed $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{OH}$ (0.09 g, 90%) with properties as described above.

Reaction of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ with MeOH

A procedure similar to that described for the reaction of $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$ with H_2O but using 0.15 g $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{H}$, 10 cm^3 THF, 3 cm^3 MeOH and 3 h reflux gave $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{OMe}$ (0.13 g, 80%) with properties as described above.

(Me₃Si)₃SiSiMe₂OAc

A mixture of (Me₃Si)₃SiSiMe₂I (0.5 g, 1.15 mmol), CH₂Cl₂ (15 cm³), and AgOAc (0.58 g, 3.45 mmol) was stirred at room temperature for 2 h. Solids were then removed by filtration and solvents were removed from the filtrate under reduced pressure to give a pale yellow oil. The oil was dissolved in pentane, the solution subsequently yielding crystalline (acetoxymethylsilyl)tris(trimethylsilyl)silane (0.15 g, 38%) m.p. 234–236 °C, δ (H) 0.20 (s, 27H, SiMe₃), 0.47 (s, 6H, SiMe₂), 1.98 (s, 3H, OAc), m/z 349 (20%, [$M - Me$]⁺), 291 (100, [$M - Me_3Si$]⁺), 232 (33, [$M - Me_3SiOAc$]⁺), 214 (15), 175 (10), 147 (15, Me₃SiOSiMe₂]⁺), 117 (30, [SiMe₂OAc]⁺), 73 (65, [Me₃Si]⁺), 59 (10, [Me₂HSi]⁺).

(Me₃Si)₃SiSiMe₂O₂CCF₃

A procedure similar to that described above for (Me₃Si)₃SiSiMe₂OAc, but with AgO₂CCF₃ in place of AgOAc and culminating in sublimation of the product instead of crystallization, gave (trifluoroacetoxymethylsilyl)tris(trimethylsilyl)silane (0.35 g, 73%), m.p. 126–128 °C, δ (H) 0.17 (s, 27H, SiMe₃), 0.54 (s, 6H, SiMe₂), δ (F) –76.4 (CF₃), m/z 403 (8%, [$M - Me$]⁺), 345 (45, [$M - Me_3Si$]⁺), 251 (15), 232 (10, [$M - Me_3SiO_2CCF_3$]⁺), 173 (10), 73 (100, [Me₃Si]⁺), 59 (10, [Me₂HSi]⁺).

(Me₃Si)₃SiSiMe₂F

A procedure similar to that described above for (Me₃Si)₃SiSiMe₂O₂CCF₃ but with AgBF₄ in place of AgO₂CCF₃ gave (fluorodimethylsilyl)tris(trimethylsilyl)silane (0.31 g, 76%) as a white solid m.p. 237–239 °C, δ (H) 0.17 (s, 27H, Me₃Si), 0.32 (d, ³ J (H–F) = 8.6 Hz, 6H, SiMe₂F), δ (C) 2.71 (SiMe₃), 5.70 (d, ² J (C–F) = 12.1 Hz, SiMe₂F), δ (F) –160.17 (septet, SiMe₂F), m/z 324 (15%, [$M - Me$]⁺), 305 (35, [$M - F$]⁺), 247 (30, [$M - SiMe_2F$]⁺), 232 (65, [$M - Me_3SiF$]⁺), 228 (30), 217 (25, [$M - Me - Me_3SiF$]⁺), 210 (15), 198 (10), 101 (20), 77 (65, [SiMe₂F]⁺), 73 (70, [Me₃Si]⁺), 59 (20, [Me₂HSi]⁺).

Reaction of (Me₃Si)₃SiSiMe₂OMe with CF₃CO₂H

A solution of (Me₃Si)₃SiSiMe₂OMe (0.5 g, 1.48 mmol) in a mixture of CCl₄ (10 cm³) and CF₃CO₂H (3 cm³) was stirred at room temperature for 1 h. Removal of the solvents under reduced pressure left a white solid which from its ¹H and ¹⁹F NMR spectra (see above) was judged to be pure (Me₃Si)₃SiSiMe₂O₂CCF₃.

(Me₃Si)₃SiSiPh₂OMe

A solution of (Me₃Si)₃SiSiPh₂Cl (0.2 g, 0.43 mmol) in a mixture of dry THF (10 cm³) and dry MeOH (3 cm³) was stirred under reflux for 2 h. Removal of the solvent under vacuum left a white solid from which was sublimed (95 °C/0.05 mmHg) (methoxydiphenylsilyl)tris(trimethylsilyl)silane m.p. 210–213 °C, δ (H) 0.14 (s, 27H, Me₃Si), 3.59 (s, 3H, OMe), 7.29–7.79 (m, 10H, Ph), m/z 225 (20%, [$M - Me$]⁺), 356 (75, [$M - Me_3SiOMe$]⁺), 282 (72, [$M - Me_3SiOMe - Me_3SiH$]⁺), 232 (50, [(Me₃Si)₂Si=SiMe₂]⁺), 197 (15, [SiPh₂Me]⁺), 135 (75, [Me₂PhSi]⁺), 73 (100, [Me₃Si]⁺), 59 (30, [SiMe₂H]⁺).

(Me₃Si)₃SiSiPh₂OH

A solution of (Me₃Si)₃SiSiPh₂Cl (0.1 g, 0.21 mmol) in THF (15 cm³) containing water (0.5 cm³) was stirred under reflux for 1 h. Removal of the solvent under

reduced pressure gave a white solid from which was sublimed (75 °C/0.05 mmHg) to give (hydroxydiphenylsilyl)tris(trimethylsilyl)silane (78 mg, 83%), m.p. 89–92 °C, $\delta(\text{H})$ 0.18 (s, 27H, Me_3Si), 1.74 (br. s. Si–OH), 7.34–7.43 (m, 10H, Ph), $\nu(\text{SiO–H})$ 3650 cm^{-1} , m/z 431 (3%, [$M - \text{Me}$]⁺), 356 (20, [$M - \text{Me}_3\text{SiOH}$]⁺), 282 (30), 267 (10), 253 (10), 232 (15, [$(\text{Me}_3\text{Si})_2\text{Si} = \text{SiMe}_2$]⁺), 220 (35), 199 (35, [SiPh_2OH]⁺), 177 (10), 135 (50, [SiMe_2Ph]⁺), 121 (10), 73 (100, [Me_3Si]⁺), 59 (30, [HMe_2Si]⁺).

Treatment of $(\text{Me}_3\text{Si})_3\text{SiSiPh}_2\text{Cl}$ with silver salts

A mixture of $(\text{Me}_3\text{Si})_3\text{SiSiPh}_2\text{Cl}$ and the silver salt (AgOAc , AgBF_4 , or AgO_3SCF_3) in a 1:2 mole ratio in CH_2Cl_2 was heated under reflux for 5 h. Filtration and removal of the solvent under reduced pressure gave a white solid which was judged by ¹H NMR spectroscopy to be unreacted starting material.

$(\text{FMe}_2\text{Si})_4\text{Si}$

Silver tetrafluoroborate (0.39 g, 2 mmol) was added to a solution of $(\text{ClMe}_2\text{Si})_4\text{Si}$ (0.2 g, 0.5 mmol) in dry CCl_4 (35 cm^3), and the mixture was heated under reflux for 2 h. The solids were then filtered off and the solvent removed under vacuum to give a sticky white solid, which was rinsed twice with small amounts of pentane and dried to give tetrakis[(fluoro)-dimethylsilyl]silane (0.12 g, 71%), m.p. 94–96 °C, $\delta(\text{H})$ 0.63 (d, $J(\text{H–F}) = 8.3$ Hz), $\delta(\text{F}) -159.7$, m/z 321 (15%, [$M - \text{Me}$]⁺), 240 (50, [$M - \text{Me}_2\text{SiF}_2$]⁺), 193 (10), 174 (65), 151 (20), 131 (25), 116 (20), 101 (15), 77 (100, [FMe_2Si]⁺), 60 (15).

$(\text{Me}_2\text{AcOSi})_4\text{Si}$

A procedure similar to that described above for the preparation of $(\text{FMe}_2\text{Si})_4\text{Si}$ but with AgOAc in place of AgBF_4 gave a sticky white solid showing a $\nu(\text{C} = \text{O})$ band at 1740 cm^{-1} and an ¹H NMR spectrum consisting of two singlets at 0.52 and 2.01 ppm in a 2:1 ratio, consistent with the formation of $(\text{Me}_2\text{OAcSi})_4\text{Si}$.

Acknowledgements

We thank the Royal Society for a University Research Fellowship (to P.D.L.), the Government of Algeria for a Fellowship (to Y.D.), Professor C. Eaborn for helpful discussions, and Mr S.M. Whittaker for some practical assistance.

References

- 1 C. Eaborn, *J. Organomet. Chem.*, 239 (1982) 93; C. Eaborn in H. Sakumi (Ed.), *Organosilicon and Bioorganosilicon Chemistry*, Ellis Horwood, Chichester, 1985, p. 123–130; A.R. Bassindale and P.G. Taylor in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, p. 839–892.
- 2 S.A.I. Al-Shali, C. Eaborn and F.M.S. Mahmoud, *J. Organomet. Chem.*, 232 (1982) 215.
- 3 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, *J. Organomet. Chem.*, 188 (1980) 179.
- 4 M. Haase and U. Klingebiel, *Z. Anorg. Allg. Chem.*, 524 (1985) 106.
- 5 M. Haase and U. Klingebiel, *Z. Naturforsch. B*, 41 (1986) 697.
- 6 S.P. Mallela and R.A. Geanangel, *Inorg. Chem.*, 29 (1990) 3525.
- 7 A.M. Arif, A.H. Cowley and T.M. Elkins, *J. Organomet. Chem.*, 325 (1987) C11.
- 8 S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa and D.R.M. Walton, *J. Organomet. Chem.*, 178 (1979) 75.

- 9 S.S. Al-Juaid, N.H. Buttrus, R.I. Damja, Y. Derouiche, C. Eaborn, P. B. Hitchcock and P.D. Lickiss, *J. Organomet. Chem.*, 371 (1989) 287.
- 10 P.D. Lickiss, unpublished observations.
- 11 C. Eaborn, D.A.R. Happer and K.D. Safa, *J. Organomet. Chem.*, 191 (1980) 355.
- 12 R.I. Damja and C. Eaborn, *J. Organomet. Chem.*, 290 (1985) 267.
- 13 See e.g. H. Bürger, W. Kilian and K. Burczyk, *J. Organomet. Chem.*, 21 (1970) 291; C. Chatgililoglu, D. Griller and M. Lesage, *J. Org. Chem.*, 53 (1988) 3641; M. Lesage, C. Chatgililoglu and D. Griller, *Tetrahedron Lett.*, 30 (1989) 2733.
- 14 D.B. Azarian, C. Eaborn and P.D. Lickiss, *J. Organomet. Chem.*, 330 (1987) 1.
- 15 C. Eaborn and A.I. Mansour, *J. Organomet. Chem.*, 254, (1983), 273.
- 16 C. Eaborn, P.D. Lickiss and N.A. Ramadan, *J. Chem. Soc., Perkin Trans. II*, (1984) 267.
- 17 S.S. Al-Juaid, Y. Derouiche, P.B. Hitchcock and P.D. Lickiss, *J. Organomet. Chem.*, 341 (1988) 241.
- 18 C. Eaborn and P.D. Lickiss, *J. Organomet. Chem.*, 294 (1985) 305.
- 19 B.K. Campion, R.H. Heyn and T.D. Tilley, *J. Am. Chem. Soc.*, 112 (1990) 2011.
- 20 L.S. Chang, M.P. Johnson and M.J. Fink, *Organometallics*, 8 (1989) 1369.
- 21 D.M. Roddick, T.D. Tilley, A.L. Rheingold and S.J. Geib, *J. Am. Chem. Soc.*, 109 (1987) 945.
- 22 B.K. Campion, J. Falk and T.D. Tilley, *J. Am. Chem. Soc.*, 109 (1987) 2049.
- 23 G. Gutekunst and A.G. Brook, *J. Organomet. Chem.*, 225 (1982) 1.
- 24 H. Sakurai, T. Watanabe and M. Kumada, *J. Organomet. Chem.*, 9 (1967) 11.
- 25 D.B. Chambers, G.E. Coates, F. Glockling and M. Weston, *J. Chem. Soc. A*, (1969) 1712; M.L. Sierra, V.J. de Mel and J.P. Oliver, *Organometallics*, 8 (1989) 2312.