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

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Abstract

Treatment of $(Me_3Si)_3SiLi$ with various silicon halides has given a range of compounds of the type $(Me_3Si)_3SiSiR_2X$ (R = Me, X = H; R = Ph, X = Cl etc.). These compounds can be converted into other derivatives by simple substitution reactions at the Si–X centre. Symmetrical pentasilanes $(XMe_2Si)_4Si$ (X = Cl, F, and OAc) have been prepared from $(Me_3Si)_4Si$. The reactivities of these species have been compared with those of analogous carbon-centred compounds eg. $(Me_3Si)_3CSiR_2X$. 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 $(Me_3Si)_3C$ 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 $TsiSiMe_2I$ has a half-life at 50 °C in MeOH of about 13 days [2], and treatment of $TsiSiPh_2I$, with, for example, silver salts AgX (X = OAc, ONO_2, OSO_2CF_3, etc.) affords rearranged products $(Me_3Si)_2C(SiMe_2X)(SiPh_2Me)$ [3] which are formed via bridged silicocationic intermediates. We have prepared a range of analogous silicon-centred compounds $(Me_3Si)_3SiSiR_2X$ 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 $(Me_3Si)_3SiSiRR'X$ (R = Me, R′ = X = F; R = Ph, R′ = Me, X = Cl; R = H, R′ = X = t-Bu etc.) but have reported only their reactions with lithium amides [4,5]. A small number of

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$(Me_3Si)_3Si$ derivatives of Ge [6] and Sn [6,7] have also been prepared but little of their chemistry has been described.

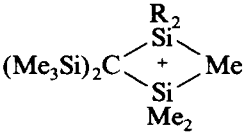
Results and discussion

The reaction between $(Me_3Si)_3SiLi(thf)_3$ and $SiCl_4$ gives $(Me_3Si)_3SiSiCl_3$ but, as in the analogous $(Me_3Si)_3C$ case [8], only one of the bulky groups can be introduced into the molecule. (It should be noted that the reaction of $GeCl_4$ with two equivalents of $(Me_3Si)_3SiLi(thf)_3$ also fails to introduce two $(Me_3Si)_3Si$ groups on to the central metal atom but gives the dimer $[Cl_2GeSi(SiMe_3)_3]_2$ while the analogous reaction with $SnCl_4$ does give $Cl_2Sn[Si(SiMe_3)_3]_2$ presumably due to the greater space available around the large tin atom [6].) Similarly, treatment of $(Me_3Si)_3SiLi(thf)_3$ with Me_2SiHCl and Ph_2SiCl_2 affords $(Me_3Si)_3SiSiMe_2H$ and $(Me_3Si)_3SiSiPh_2Cl$ respectively. All three of these derivatives have a very different reactivity from their $(Me_3Si)_3C$ analogues and react in a manner similar to less-crowded species. For example $(Me_3Si)_3SiSiCl_3$ reacts readily with cold water in less than 1 h to give $(Me_3Si)_3SiSi(OH)_3$ [9] and with a dilute solution of MeOH in refluxing THF to give $(Me_3Si)_3SiSi(OMe)_3$. This is in great contrast to $TsiSiCl_3$, which appears to be indefinitely stable in, for example, H_2O/THF or H_2O/Et_2O [10], and does not react with boiling MeOH during many hours [11]. The inertness of $TsiSiCl_3$ required that a multistep synthesis, via $TsiSiH_3$, be used for the synthesis of the silanetriol $TsiSi(OH)_3$ [12].

One of the few simple displacement reactions known to be undergone by $TsiSiCl_3$ is reduction by $LiAlH_4$ to give $TsiSiH_3$ [8], and as expected the analogous reaction occurs for $(Me_3Si)_3SiSiCl_3$ to give $(Me_3Si)_3SiSiH_3$. However, unlike $TsiSiH_3$, which is unreactive towards CCl_4 at room temperature, $(Me_3Si)_3SiSiH_3$ reacts with CCl_4, apparently to give $(Me_3Si)_3SiSiH_2Cl$, $(Me_3Si)_3SiSiHCl_2$, and $(Me_3Si)_3SiSiCl_3$. The silane $TsiSiH_3$ does react slowly in boiling CCl_4 to give $TsiSiH_2Cl$, $TsiSiHCl_2$, and $TsiSiCl_3$. This is a similar type of reaction to that shown by $(Me_3Si)_3SiH$ which reduces a variety of alkyl halides by a radical mechanism [13]. The silane $(Me_3Si)_3SiSiH_3$ reacts with PhLi to give $(Me_3Si)_3SiSiH_2Ph$ in a manner analogous to the reaction of $TsiSiH_3$ with p-MeC_6H_4Li to give $TsiSiH_2C_6H_4Me$-p [14].

Other compounds that have been extensively studied by Eaborn et al. are the derivatives of $TsiSiMe_2H$. Treatment of $(Me_3Si)_3SiLi(thf)_3$ with Me_2SiHCl gave $(Me_3Si)_3SiSiMe_2H$, which when treated with I_2 in CCl_4 surprisingly gave the chloride $(Me_3Si)_3SiSiMe_2Cl$, again presumably via a radical process similar to that mentioned above for $(Me_3Si)_3SiH$. (Recently the reaction between $TsiSiH_3$ and Br_2 in CCl_4 was found to give a mixture of halogenated products $TsiSiBr_3Cl_{3-n}$ ($n = 0$–3 [10].) Reaction between $(Me_3Si)_3SiSiMe_2H$ and I_2 in benzene gave the required $(Me_3Si)_3SiSiMe_2I$, which reacted within 10 min in a mixture of $CH_2Cl_2/MeOH$ (5 : 2 v/v) to give $(Me_3Si)_3SiSiMe_2OMe$ and with a 70 : 1 v/v mixture of CH_2Cl_2/H_2O to give $(Me_3Si)_2SiSiMe_2OH$ in less than 15 min. This reactivity is in great contrast to the remarkable stability of $TsiSiMe_2I$, which can be prepared by treatment of $TsiSiMe_2H$ 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, $(Me_3Si)_3SiSiMe_2H$, is also much more reactive than $TsiSiMe_2H$, reacting readily with MeOH or H_2O whereas $TsiSiMe_2H$ undergoes no reaction during 1.5 h with a $MeOH/H_2O/AgNO_3$ mixture at the reflux temperature [3].

In reactions of $(Me_3Si)_3SiSiMe_2I$ with silver salts AgOAc, AgO_2CCF_3, and $AgBF_4$ simple substitution takes place to give $(Me_3Si)_3SiSiMe_2X$ (X = OAc, O_2CCF_3, and F). This is similar to the reaction of the Trisyl analogue although it is thought that for $TsiSiMe_2I$ 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 $(Me_3Si)_3Si$ silicon derivatives.



(1)

A striking example of anchimeric assistance via a bridged cationic intermediate occurs when $TsiSiMe_2OMe$ is treated with CF_3CO_2H to give $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, with loss of an Me group as MeH [16]. In contrast to this, the reaction between $(Me_3Si)_3SiSiMe_2OMe$ and CF_3CO_2H gives the simple solvolysis product $(Me_3Si)_3SiSiMe_2O_2CCF_3$, suggesting that a bridged silicocation is not involved:

$$(Me_3Si)_3CSiMe_2OMe + CF_3CO_2H \rightarrow (Me_3Si)_2C(SiMe_2O_2CCF_3)_2$$

$$(Me_3Si)_3SiSiMe_2OMe + CF_3CO_2H \rightarrow (Me_3Si)_3SiSiMe_2O_2CCF_3$$

Many of the reactions of the silicon iodide $TsiSiPh_2I$ such as those with silver salts have also been found to give rearranged products of the type $(Me_3Si)_2C(SiPh_2Me)(SiMe_2X)$ and are again thought to involve intermediate silicocationic species of the type **1** (R = Ph) [3]. Unfortunately we have been unable to prepare $(Me_3Si)_3SiSiPh_2I$ intended for analogous studies, but the chloride $(Me_3Si)SiSiPh_2Cl$ was conveniently prepared by treatment of $(Me_3Si)_3SiLi$ with Ph_2SiCl_2. The chloride readily undergoes solvolysis with either MeOH or H_2O but does not react with silver salts AgOAc, $AgBF_4$, or AgO_3SCF_3 during several hours in boiling CH_2Cl_2. The solvolysis reactions are again in great contrast to the Trisyl analogue $TsiSiPh_2Cl$, which does not react with boiling methanol even in the presence of $AgNO_3$ [8]. Although the solvolysis reactions proceed via a different mechanism to those with silver salts it is likely that the more reactive iodide $(Me_3Si)_3SiSiPh_2I$ 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 $(ClMe_2Si)_4M$ (M = C or Si). We have previously reported [17] that $(ClMe_2Si)_4Si$ is readily hydrolysed to give a bicyclic siloxane product whereas $(ClMe_2Si)_4C$ does not react under similar conditions [10]. Treatment of $(ClMe_2Si)_4Si$ with AgOAc or $AgBF_4$ gave $(XMe_2Si)_4Si$ (X = OAc or F) but the Trisyl analogue does not react readily with silver salts [10]. (For other reactions of $(ClMe_2Si)_4C$ 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 $(Me_3Si)_3Si$ group compared with the $(Me_3Si)_3C$ 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 $(Me_3Si)_3Si$ silicon derivatives can be seen as similar to those normally associated with much less hindered systems. It should be noted that although these $(Me_3Si)_3Si$ 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 $(Me_3Si)_3SiLi(thf)_3$ was prepared according to ref. 23, $(ClMe_2Si)_4Si$ according to ref. 24, and $(Me_3Si)_3SiSiCl_3$, and $(Me_3Si)_3SiSiPh_2Cl$ according to ref. 4. The preparation of $(Me_3Si)_3SiSi(OH)_3$ 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 $(Me_3Si)_3Si$ 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.

$(Me_3Si)_3SiSi(OMe)_3$

A solution of $(Me_3Si)_3SiSiCl_3$ (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. δ(H) 0.19 (s, 27H, $SiMe_3$), 3.64 (s, 9H, OMe), ν(Si–OMe) 1195 cm^{-1}, m/z 368 (10%, $[M]^+$), 353 (20, $[M-Me]^+$), 337 (15, $[M-OMe]^+$), 315(35), 295 (45, $[M-SiMe_3]^+$), 278 (15, $[M-Si(OMe)_2]^+$), 264 (35, $[M-Me_3SiOMe]^+$), 258 (15), 247 (10 $[M-Si(OMe)_3]^+$), 232(15, $[(Me_3Si)_2SiSiMe_2]^+$), 217 (40, $[M-2Me-Si(OMe)_3]^+$), 210 (33), 121 (10, $[Si(OMe)_3]^+$), 101 (15), 73 (100, $[SiMe_3]^+$), 59 (45, $[SiMe_2H]^+$).

$(Me_3Si)_3SiSiH_3$

A solution of $(Me_3Si)_3SiSiCl_3$ (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. δ(H) (C_6H_6) 0.23 (s, 27H, $SiMe_3$), 3.43 (s, 3H, SiH_3), δ(Si) (C_6H_6/C_6D_6) −9.43 ($SiMe_3$), −99.53 (q, ^1J(Si–H) 187.6 Hz, SiH_3), −144.0 ($\mathit{Si}SiH_3$), ν(Si–H) 2122 cm^{-1}, m/z 278 (6%, $[M]^+$), 263 (45, $[M-Me]^+$), 232 (20, $[M-Me-SiH_3]^+$), 204 (55, $[M-Me_3SiH]^+$), 189 (15, $[M-2Me-SiMe_3H]^+$), 173 (15), 159 (10, $[M-Me_4Si-SiH_3]^+$), 144 (40), 73 (100, $[Me_3Si]^+$), 59 (20, $[SiMe_2H]^+$).

Reaction of $(Me_3Si)_3SiSiH_3$ with CCl_4

A sample of $(Me_3Si)_3SiSiH_3$ (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 $(Me_3Si)_3SiSiH_3$ 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 $(Me_3Si)_3SiSiClH_2$, $(Me_3Si)_3SiSiCl_2H$, and (the known) $(Me_3Si)_3SiSiCl_3$.

Reaction of $(Me_3Si)_3CSiH_3$ with CCl_4

A solution of $(Me_3Si)_3CSiH_3$ (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 $(Me_3Si)_3CSiH_3$ (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 $(Me_3Si)_3CSiH_3$, $(Me_3Si)_3CSiH_2Cl$, and $(Me_3Si)_3CSiHCl_2$ in an approximate 4.7 : 4.5 : 1 ratio respectively together with some $CHCl_3$. After 50 h the spectrum indicated the presence of $(Me_3Si)_3CSiH_3$ [δ(H) 0.16 ($SiMe_3$), 3.63 (SiH_3, ^1J(Si–H) 198 Hz)], $(Me_3Si)_3CSiH_2Cl$ [δ 0.24 ($SiMe_3$), 4.86 (SiH_2Cl, ^1J(Si–H) 234 Hz)], $(Me_3Si)_3CSiHCl_2$ [δ 0.31 ($SiMe_3$), 5.51 ($SiHCl_2$, ^1J(Si–H) 281 Hz], and $(Me_3Si)_3CSiCl_3$ (δ 0.38) in an approximate 1 : 6.9 : 6.3 : 1.1 ratio respectively as well as $CHCl_3$.

Reaction of $(Me_3Si)_3SiSiH_3$ with PhLi

To a solution of $(Me_3Si)_3SiSiH_3$ (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%), δ(H) (CH_2Cl_2) 0.25 (s, 27H, $SiMe_3$), 3.40 (s, 2H, SiH), 7.40–7.49 (m, 5H, Ph), ν(Si–H) 2080 cm^{-1}.

$(Me_3Si)_3SiSiMe_2H$

A solution of $(Me_3Si)_3SiLi(thf)_3$ [prepared from $(Me_3Si)_4Si$ (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, δ(H) 0.20 (s, $SiMe_3$), 0.27 (d, ^3J = 4.4 Hz, $SiMe_2$), 4.02 (m, 1H, SiH), δ(C) 2.79 (s, $SiMe_3$), 2.98 (s, $SiMe_2$), ν(Si–H) 2088 cm^{-1}, *m/z* 232 (65%, $[M - H - Me_3Si]^+$), 217 (25, $[M - Me - H - Me_3Si]^+$), 173 (15, $[M - Me_3Si - Me_2SiH]^+$), 158 (15, $[M - Me_4Si - Me_3SiH]^+$), 129 (15), 73 (100, $[Me_3Si]^+$), 59 (22, $[Me_2SiH]^+$).

$(Me_3Si)_3SiSiMe_2I$

A mixture of $(Me_3Si)_3SiSiMe_2H$ (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, δ(H) (C_6H_6) 0.27 (s, 27H, $SiMe_3$), 0.93 (s, 6H, $SiMe_2I$), m/z 432 (5%, $[M]^+$), 417 (15, $[M - Me]^+$), 359 (20, $[M - Me_3Si]^+$), 305 (10, $[M - I]^+$), 232 (75, $[M - I - SiMe_3]^+$), 173 (20, $[M - Me_4Si - Me_2SiH]^+$), 158 (45, $[M - Me_4Si - Me_2SiHI]^+$), 131 (25, $[Me_3SiSiMe_2]^+$), 73 (100, $[Me_3Si]^+$), 59 (15, $Me_2SiH]^+$).

Reaction between $(Me_3Si)_3SiSiMe_2H$ and I_2 in CCl_4

A solution of $(Me_3Si)_3SiSiMe_2H$ (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, δ(H) 0.25 (s, 27H, $SiMe_3$), 0.58 (s, 6H, $SiMe_2Cl$), m/z 340 (4%, $[M]^+$), 325 (50, $[M - Me]^+$), 305 (35, $[M - Cl]^+$), 291 (10), 252 (7, $[M - Me_3SiCl]^+$), 232 (75, $[(Me_3Si)_2Si\text{-}SiMe_2]^+$), 173 (30), 158 (30), 143 (25), 131 (25, $[Me_3SiSiMe_2]^+$), 115 (25), 93 (35, $[Me_2ClSi]^+$), 73 (100 $[Me_3Si]^+$), 59 (50, $[Me_2HSi]^+$).

$(Me_3Si)_3SiSiMe_2OMe$

A solution of $(Me_3Si)_3SiSiMe_2I$ (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, δ(H) 0.15 (s, 27H, Me_3Si), 0.25 (s, 6H, $SiMe_2$), 3.33 (s, 3H, OMe), m/z 336 (5%, $[M]^+$), 321 (15, $[M - Me]^+$), 232 (74, $[(Me_3Si)_2Si = SiMe_2]^+$), 189 (10), 173 (20), 158 (25, $[M - Me_4Si - Me_3SiH]^+$), 131 (25, $[Me_3SiSiMe_2]^+$), 117 (10), 89 (15, $[Me_2SiOMe]^+$), 73 (100, $[Me_3Si]^+$), 59 (25, $[Me_2HSi]^+$).

$(Me_3Si)_3SiSiMe_2OH$

The procedure described above for $(Me_3Si)_3SiSiMe_2OMe$ 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, δ(H) 0.13 (s, 27H, Me_3Si), 0.19 (s, 6H, $SiMe_2$), 3.19 (s, 1H, OH), ν(Si–OH) 3690 cm^{-1}, m/z 307 (16%, $[M - Me]^+$), 291 (7, $[M - MeOH]^+$), 232 (90, $[M - Me_2SiH - MeOH]^+$), 189 (15), 173 (25) 147 (50, $[Me_3SiOSiMe_2]^+$), 131 (35) 115 (20), 73 (100), $[Me_3Si]^+$), 59 (50, $[Me_2HSi]^+$).

Reaction of $(Me_3Si)_3SiSiMe_2H$ with H_2O

A solution of $(Me_3Si)_3SiSiMe_2H$ (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 $(Me_3Si)_3SiSiMe_2OH$ (0.09 g, 90%) with properties as described above.

Reaction of $(Me_3Si)_3SiSiMe_2H$ with MeOH

A procedure similar to that described for the reaction of $(Me_3Si)_3SiSiMe_2H$ with H_2O but using 0.15 g $(Me_3Si)_3SiSiMe_2H$, 10 cm^3 THF, 3 cm^3 MeOH and 3 h reflux gave $(Me_3Si)_3SiSiMe_2OMe$ (0.13 g, 80%) with properties as described above.

$(Me_3Si)_3SiSiMe_2OAc$

A mixture of $(Me_3Si)_3SiSiMe_2I$ (0.5 g, 1.15 mmol), CH_2Cl_2 (15 cm^3), 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 (acetoxydimethylsilyl)tris(trimethylsilyl)silane (0.15 g, 38%) m.p. 234–236 °C, δ(H) 0.20 (s, 27H, $SiMe_3$), 0.47 (s, 6H, $SiMe_2$), 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, $Me_3SiOSiMe_2]^+$), 117 (30, $[SiMe_2OAc]^+$), 73 (65, $[Me_3Si]^+$), 59 (10, $[Me_2HSi]^+$).

$(Me_3Si)_3SiSiMe_2O_2CCF_3$

A procedure similar to that described above for $(Me_3Si)_3SiSiMe_2OAc$, but with AgO_2CCF_3 in place of AgOAc and culminating in sublimation of the product instead of crystallization, gave (trifluoroacetoxydimethylsilyl)tris(trimethylsilyl) silane (0.35 g, 73%), m.p. 126–128 °C, δ(H) 0.17 (s, 27H, $SiMe_3$), 0.54 (s, 6H, $SiMe_2$), δ(F) -76.4 (CF_3), m/z 403 (8%, $[M-Me]^+$), 345 (45, $[M-Me_3Si]^+$), 251 (15), 232 (10, $[M-Me_3SiO_2CCF_3]^+$), 173 (10), 73 (100, $[Me_3Si]^+$), 59 (10, $[Me_2HSi]^+$).

$(Me_3Si)_3SiSiMe_2F$

A procedure similar to that described above for $(Me_3Si)_3SiSiMe_2O_2CCF_3$ but with $AgBF_4$ in place of AgO_2CCF_3 gave (fluorodimethylsilyl)tris(trimethylsilyl)silane (0.31 g, 76%) as a white solid m.p. 237–239 °C, δ(H) 0.17 (s, 27H, Me_3Si), 0.32 (d, ^3J(H–F) = 8.6 Hz, 6H, $SiMe_2F$), δ(C) 2.71 ($SiMe_3$), 5.70 (d, ^2J(C–F) = 12.1 Hz, $SiMe_2F$), δ(F) -160.17 (septet, $SiMe_2F$), 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, $[SiMe_2F]^+$), 73 (70, $[Me_3Si]^+$), 59 (20, $[Me_2HSi]^+$).

Reaction of $(Me_3Si)_3SiSiMe_2OMe$ with CF_3CO_2H

A solution of $(Me_3Si)_3SiSiMe_2OMe$ (0.5 g, 1.48 mmol) in a mixture of CCl_4 (10 cm^3) and CF_3CO_2H (3 cm^3) was stirred at room temperature for 1 h. Removal of the solvents under reduced pressure left a white solid which from its ^1H and ^{19}F NMR spectra (see above) was judged to be pure $(Me_3Si)_3SiSiMe_2O_2CCF_3$.

$(Me_3Si)_3SiSiPh_2OMe$

A solution of $(Me_3Si)_3SiSiPh_2Cl$ (0.2 g, 0.43 mmol) in a mixture of dry THF (10 cm^3) and dry MeOH (3 cm^3) 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, Me_3Si), 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, $[(Me_3Si)_2Si{=}SiMe_2]^+$), 197 (15, $[SiPh_2Me]^+$), 135 (75, $[Me_2PhSi]^+$), 73 (100, $[Me_3Si]^+$), 59 (30, $[SiMe_2H]^+$).

$(Me_3Si)_3SiSiPh_2OH$

A solution of $(Me_3Si)_3SiSiPh_2Cl$ (0.1 g, 0.21 mmol) in THF (15 cm^3) containing water (0.5 cm^3) 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, δ(H) 0.18 (s, 27H, Me_3Si), 1.74 (br. s. Si–OH), 7.34–7.43 (m, 10H, Ph), ν(SiO–H) 3650 cm^{-1}, m/z 431 (3%, $[M-Me]^+$), 356 (20, $[M-Me_3SiOH]^+$), 282 (30), 267 (10), 253 (10), 232 (15, $[(Me_3Si)_2Si=SiMe_2]^+$), 220 (35), 199 (35, $[SiPh_2OH]^+$), 177 (10), 135 (50, $[SiMe_2Ph]^+$), 121 (10), 73 (100, $[Me_3Si]^+$), 59 (30, $[HMe_2Si]^+$).

Treatment of $(Me_3Si)_3SiSiPh_2Cl$ with silver salts

A mixture of $(Me_3Si)_3SiSiPh_2Cl$ 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.

$(FMe_2Si)_4Si$

Silver tetrafluoroborate (0.39 g, 2 mmol) was added to a solution of $(ClMe_2Si)_4Si$ (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, δ(H) 0.63 (d, ^3J(H–F) = 8.3 Hz), δ(F) −159.7, m/z 321 (15%, $[M-Me]^+$), 240 (50, $[M-Me_2SiF_2]^+$), 193 (10), 174 (65), 151 (20), 131 (25), 116 (20), 101 (15), 77 (100, $[FMe_2Si]^+$), 60 (15).

$(Me_2AcOSi)_4Si$

A procedure similar to that described above for the preparation of $(FMe_2Si)_4Si$ but with AgOAc in place of $AgBF_4$ gave a sticky white solid showing a $\nu(C=O)$ 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 $(Me_2OAcSi)_4Si$.

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