Anionic *vs.* radical intermediates in the fragmentation reactions of dendritic polysilanes

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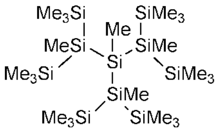
Fragmentation reactions during the formation of highly congested dendritic polysilanes can conceivably occur by either anionic or radical mechanisms. In the specific case of the production of $[(SiMe_3)_2SiMeSiMe_2]_3SiH$ from the reaction of $(ClSiMe_2)_4Si$ with $(Me_3Si)_2MeSiLi$, the two types of mechanisms were tested by trapping reactions. Product formation was found to be independent of the presence of proton sources, contrary to the expectations of the anionic mechanism. Homolytic fragmentation of the initial product $[(SiMe_3)_2SiMeSiMe_2]_4Si$ was supported by the observation of products with the radical trap phenylacetylene. Evidence is presented that the reaction produced, in low yield, this dendritic polysilane, which would be the first such structure with a fourfold-substituted core.

Dendritic polysilanes contain a skeleton based entirely on silicon–silicon connectivity within a dendritic architecture. In the simplest example (**1**), the central or core silicon atom is attached to three wings. For a molecule to qualify as a dendrimer, it must contain a branching point in each wing. In a first generation dendrimer such as **1**, there is only one branching point per wing. In second generation dendrimers, each wing contains two branch points in tandem. Dendrimers also can possess four wings, in which the core silicon would be bonded to four silicon atoms (no such molecules heretofore have been prepared), and there can be spacers between the core and the branch point. We[1] gave molecule **1** the abbreviation **1302**, in which the first number indicates that it is first generation, the second that the core has threefold branching, the third that there are no spacers between the core and the branch point, and the fourth that the branch point is connected to two silicons.



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The synthesis of dendritic polysilanes by three groups[1–3] utilized anionic chemistry, whereby the skeleton was built through nucleophilic displacements by silyl anions on silicon atoms bonded to a good leaving group such as chloride or triflate (as in eqn. (1)). Steric congestion is increased appreciably as each chlorine or triflate is replaced by the large polysilyl group. It is for this reason that no dendritic polysilane previously has been prepared with four wings attached to the core. Derouiche and Lickiss[4] attempted to make such a polysilane by carrying out the reaction of $(Me_3Si)_3SiLi$ with $SiCl_4$ in the manner of eqn. (1). They observed the attachment of only one tris(trimethylsilyl)silyl group to the core silicon. The desired dendrimer would have had the structure $Si[Si(Me_3Si)_3]_4$ (**1403**). We[1] carried out the reaction of a less sterically demanding silyllithium reagent, $(Me_3Si)_2MeSiLi$, with $SiCl_4$ in hopes of obtaining the less sterically congested dendrimer $Si[SiMe(Me_3Si)_2]_4$ (**1402**), still with a fourfold core. Mass spectral evidence indicated that only three wings had been attached to the core.

$$(Me_3Si)_2MeSi\mathbf{:}^- \quad + \quad SiMeCl_3 \quad \longrightarrow \quad \mathbf{1} \qquad (1)$$

In order to reduce steric congestion further within the architecture of a fourfold core, we[1] placed a spacer dimethylsilyl group between the core and the branch point by using $Si(SiMe_2Cl)_4$ in place of $SiCl_4$ in the manner of eqn. (1). Reaction of the smaller silyllithium reagent $(Me_3Si)_2MeSiLi$ with this substrate appeared not to place four groups around the core silicon (the product would have been **1412**). In light of this failure, we did not examine the reaction of the larger reagent $(Me_3Si)_3SiLi$ (to give **1413**).

The major product in the reaction of $Si(SiMe_2Cl)_4$ with $(Me_3Si)_2MeSiLi$ had a completely unexpected structure, $[(Me_3Si)_2MeSiMe_2Si]_3SiH$ (**2**).[1] This molecule is dendritic, as the core silicon is bonded to three silicon groups that lead to a branch point. The unexpected aspect was the presence of hydride on the core silicon. This structure was demonstrated by the presence of the hydridic proton resonance at δ 3.19 and by the crystal structure.[1] There are both anionic and radical pathways to fragmentation product **2**.

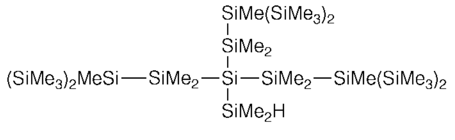
Scheme 1 illustrates the anionic pathway to this product. Three moles of the silyllithium reagent successfully displace chloride to create the three wings of the product, but the fourth displacement is thwarted by steric congestion. Instead of displacement of chloride by the silyllithium reagent at the fourth silicon atom bearing chloride, congestion is considerably reduced by expulsion of the core silicon atom. The product is a new silyllithium reagent (**3**), which would receive a proton during workup to give the product **2**.

Scheme 2 presents the homolytic pathway to **2**. Two groups[5,6] have previously presented evidence in support of homolytic pathways during photochemical irradiation of oligosilanes. Ohshita *et al.*[6] found that homolytic Si–Si bond scission increased with steric congestion. The mechanism of Scheme 2 starts from the unknown dendrimer **1412** (**5**), which would be formed from the reaction of $(ClSiMe_2)_4Si$ with four moles of $(Me_3Si)_2MeSiLi$. Cleavage of bond **a** leads to the previously observed product **2**. Cleavage of bond **b** predicts the formation of an alternative dendrimer **4**.

Results and discussion

Intervention of the anionic intermediate **3** could be supported by trapping experiments. We carried out the reaction of

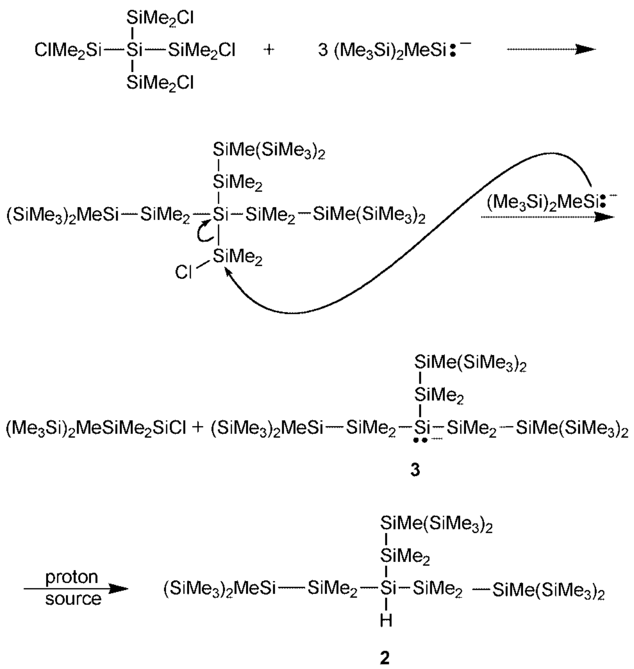
$(ClSiMe_2)_4Si$ with $(Me_3Si)_2MeSiLi$ in tetrahydrofuran (THF), followed by three separate hydrolysis conditions. (1) The conditions used previously[1] involved quenching with acid (1 M HCl). We now have found two products under these conditions. In addition to the previously reported dendrimer **2** (*ca.* 90%) with hydride on the core silicon, we have found a small amount of a second dendrimer, **4** (*ca.* 5%), with the same three wings as **2** but



$$\begin{array}{c} \mathrm{SiMe(SiMe_3)_2} \\ | \\ \mathrm{SiMe_2} \\ | \\ \mathrm{(SiMe_3)_2MeSi{-}SiMe_2{-}Si{-}SiMe_2{-}SiMe(SiMe_3)_2} \\ | \\ \mathrm{SiMe_2H} \end{array}$$

4

instead of hydride as the fourth group on the core silicon there is a dimethylhydridosilyl group, Me_2HSi-. (2) Quenching of the anion **3** with iodomethane should yield the fully methylated dendrimer **1312**, which we previously isolated.[1] Methylation of silyllithium reagents with iodomethane is precedented.[7] No **1312** was formed. Instead, the same pair of dendrimers, **2** and **4**, with an increased proportion of **4**, were obtained. (3) Finally, the reaction was worked up without the addition of acid, *i.e.*, without a proton source. The same results were obtained: compounds **2** and **4**.



Scheme 1

Formation of **2** thus is independent of the presence of a proton source (the third experiment), and an anionic intermediate **3** is not trapped by iodomethane. Trapping experiments thus do not support an anionic pathway. Moreover, the new product **4** is not predicted by an anionic pathway.

The radical pathway of Scheme 2 on the other hand provides a straightforward means of explaining both products, **2** and **4**. We sought stronger evidence for a radical pathway by carrying out the reaction in the presence of phenylacetylene as a radical trap. Two products were observed, which respectively exhibited highest mass peaks at 858 and 901 within the highest isotopic clusters. The expected products from trapping the larger fragments from cleavage of bonds **b** and **a** in Scheme 2 respectively have structures **6** and **7**, with molecular weights 874.5 and 932.4

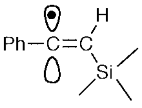
$[(SiMe_3)_2MeSi{-}SiMe_2]_3Si{-}CH{=}CHPh$

6

$[(SiMe_3)_2MeSi{-}SiMe_2]_3Si{-}SiMe_2{-}CH{=}CHPh$

7

(based on elemental atomic weights). The largest molecular ion peaks calculated for the parent isotopic clusters of **6** and **7** respectively are 873.4 and 931.4. The observed peaks could arise from these molecular ions respectively by loss of one and two methyls. Although these results are not definitive, they strongly support the presence of the two silyl radicals shown in Scheme 2. The trapped radicals would have a structure resembling **8**. It is expected that such a radical is stabilized by



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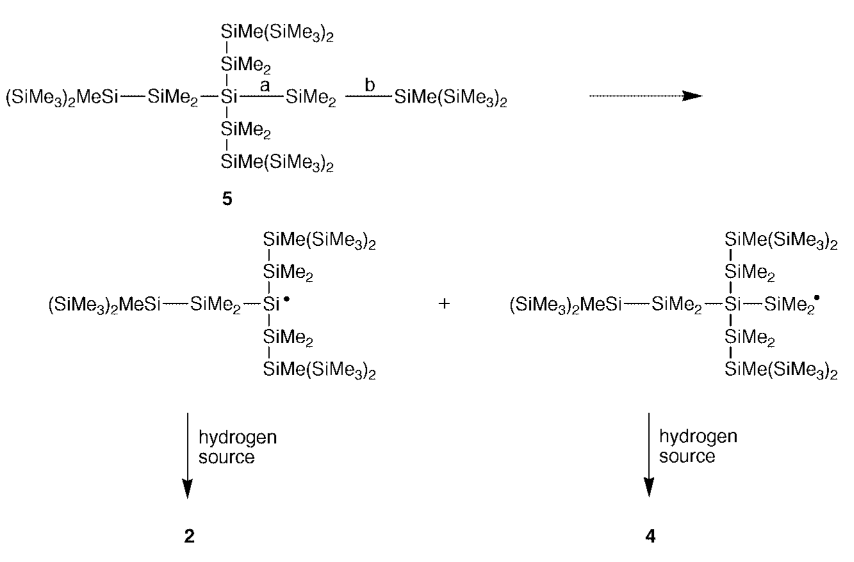
hyperconjugative overlap of the radical with the C–Si bond, by analogy with studies of β-silyl radical cations[8] and β-silyl vinyl cations.[9]

The radical mechanism of Scheme 2 proceeds from the assumption that the fourfold dendrimer **5** (**1412**) is initially formed and decomposes. Consequently, we sought evidence for the formation of this species. Re-examination of the reaction mixture for higher molecular weight materials revealed the



Scheme 2

presence of a small amount of a component exhibiting a highest mass peak at 945 within the highest significant isotopic cluster (**2** has a molecular weight of 772.1 and **4** of 830.2 and the largest peaks within the respective calculated molecular ion clusters are 770.3 and 829.4). The molecular weight of **5** is 1018.7 (based on elemental atomic weights; the largest peak within the calculated molecular ion cluster is 1018.5). Loss of trimethylsilyl would lead to the observed peak at 945. This is the first, albeit tenuous, evidence for the isolation of a polysilane dendrimer with a fourfold core, although the yield was extremely low.

Conclusions

Reaction of methylbis(trimethylsilyl)silyllithium with tetrakis(chlorodimethylsilyl)silane appears to give the dendrimer **1412** (**5**) with a fourfold core in small amounts, as well as the dendrimers **1312-H** (**2**) and **1312-SiMeH** (**4**). Molecule **2** can be imagined as forming either by reaction of the silyllithium reagent with a monochlorinated threefold core by the anionic reaction of Scheme 1 or by decomposition of the fourfold dendrimer **1412** to a silyl radical that abstracts hydrogen according to Scheme 2. Iodomethane, however, failed to trap the proposed anionic intermediate of Scheme 1, but phenylacetylene did appear to trap the radical intermediate of Scheme 2. The anionic mechanism also does not explain the second product **4**. Consequently, we conclude that the dendritic hydridosilanes **2** and **4** arose from a radical pathway from the fourfold dendrimer **1412**.

Experimental

Attempted preparation of tetrakis[1,1,2,3,3,3-hexamethyl-2-(trimethylsilyl)trisilyl]silane (1412, 5)[1]

Methylbis(trimethylsilyl)silyllithium was prepared in a 250 ml, three-necked flask from methyltris(trimethylsilyl)silane (6.8 g, 0.026 mol) in tetrahydrofuran (THF, 120 ml). Freshly sublimed tetrakis(chlorodimethylsilyl)silane (2.0 g, 4.9 ml) in 25 ml of THF was added over a 20 min period to the cooled (0 °C) lithium reagent. The mixture was stirred overnight at room temperature and then at 35–40 °C again overnight. The workup then followed one of the following three procedures.

Quenching with HCl

The reaction mixture was poured onto 120 ml of 1 M HCl. The layers were separated, and the water layer was extracted twice with ether. The combined organic layers were washed with sat. aqueous $NaHCO_3$ and dried over $MgSO_4$. After rotary evaporation, the oily residue was found by GC/MS (70 eV electron impact) to contain 91% of **2**, and about 5% of **4**. For **2**: ^1H NMR ($CDCl_3$) δ 0.13, 0.16, 0.18; ^{13}C NMR ($CDCl_3$) δ 0.3, 0.9, 1.5; MS 770 (M^+), 669, 595, 522, 421. For **4**: MS 828 (M^+), 770, 669, 595, 522. Molecule **5**, if present, did not survive the GC conditions. However, direct insertion of the sample indicated the presence of a component of higher molecular weight: MS 974, 958, 945.

Quenching with CH_3I

A molar equivalent of CH_3I was added, and the mixture was stirred for one day. Rotary evaporation yielded a semi-solid, containing, by GC/MS, 16% of **2** and 34% of **4**. No other component was >10% of the integrated intensity.

No quenching

The reaction mixture was stirred at room temperature for 2 days. Rotary evaporation gave a milky residue containing, by GC/MS, 18% of **2** and 45% of **4**. No other component was >10% of the integrated intensity.

Quenching with phenylacetylene

A 25 ml Schlenk-valved flask was charged with 3.82 mmol of methylbis(trimethylsilyl)silyllithium and 10 ml of anhydrous THF. To this solution, 0.46 g (1.14 mmol) of tetrakis(chlorodimethylsilyl)silane in 2.0 ml of THF was added. The mixture was stirred for 4 h, and 4.5 mmol of phenylacetylene was added. The mixture was concentrated by rotary evaporation and the residue analyzed by GC/MS. There was evidence for three main components, one corresponding to **2** (M^+ 772), one with the highest main peak at 901 (most intense member of isotopic multiplet), and one with the highest main peak at 858.

Acknowledgements

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