

Synthesis and Properties of Ethyl, Propyl, and Butyl Hexa-alkyldisilanes and Tetrakis(tri-alkylsilyl)silanes

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Keywords: Silanes; Synthesis; Atomic layer deposition; Mass spectrometry

Abstract. The preparation of $(R_3Si)_4Si$ (R = ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, and *iso*-butyl) was attempted using the procedure reported for $[(CH_3)_3Si]_4Si$.^[1] The type of alkyl group affected the resulting materials significantly. For R = ethyl, $[(C_2H_5)_3Si]_2$ [hexaethyl-disilane (**1**)] was obtained phase pure if careful fractional distillation (under vacuum) was used, otherwise a mixture of **1**, $[(C_2H_5)_2Si]_4$ (octaethyltetra-cyclo-silane), and other unidentified product(s) was obtained. For R = *n*-propyl a mixture of $[(CH_3CH_2CH)_3Si]_2$ (hexa-*n*-propyldisilane), $[(CH_3CH_2CH_2)_2Si]_4$, (octa-*n*-propyltetra-cyclo-silane), $[(CH_3CH_2CH_2)_3Si]_4Si$ {tetrakis(tri-*n*-propylsilyl)silane} (**2**), and other unidentified product(s) was obtained. From this mixture only **2**, a new

and previously unreported compound, was purified. **2** is the second compound of this type to be reported and is characterized by mass spectrometry (MS), elemental analysis (EA), and thermogravimetry (TG). The crystal structure of **2** is also reported [space group $R\bar{3}$ (no.148), $a = 17.9249(10)$ Å, $c = 12.2752(7)$ Å, at 100 K]. For R = *iso*-propyl pure $[(CH_3)_2CH_2]_3Si]_2$ [hexa-*iso*-propyldisilane (**3**)] was obtained in a good yield. For R = *n*-butyl or *iso*-butyl no phase pure compounds were synthesized. The pure compounds prepared have potential as precursors for the currently problematic atomic layer deposition of silicon, as demonstrated by their complete sublimation under thermal analysis. The sublimation temperature is dependent on the size of the molecule.

1 Introduction

Tetrakis(trimethylsilyl)silane (TTMSS) was first prepared by Gilman et al. from the reaction of $SiCl_4$, $(CH_3)_3SiCl$, and Li in tetrahydrofuran (THF).^[1,2] A slight modification of the procedure of Gilman et al. has also been reported.^[3] TTMSS can also be prepared from decomposition of dodecamethylpentasilane with $AlCl_3$ as catalyst in boiling benzene.^[4] Characterization of TTMSS is widely reported, e.g. 2H , ^{13}C , and ^{29}Si NMR,^[5–11] IR and Raman spectroscopy,^[12–14] thermal analysis,^[15] and crystal structure determination.^[16,17] It has been used as precursor for preparation of other compounds, e.g. hypersilylpotassium,^[18] aryl(tris(trimethylsilyl)silanes),^[19] and Ag nanoparticles^[20] as well as in the production of amorphous hydrogenated silicon-carbon (a-Si:C:H),^[21] and silicon carbide thin films.^[22]

The first method reported for the synthesis of an organodisilanes utilized the reaction between hexaiododisilane and diethylzinc.^[23] The most efficient methods for synthesis of disilanes are Wurtz-type coupling of halotriorganosilanes, mediated by alkali or alkaline earth metals,^[24] e.g. the reaction of chlorotriethylsilane and lithium in 1,3-dimethyl-2-imidazolidinone (DMI),^[25] chlorotriethylsilane, and lithium in THF,^[26] refluxing Et_3SiCl , and Na.^[27] The preparation of hexa-*iso*-propyldisilane has previously been reported^[28] using a reaction

between methylchlorodisilane or hexachlorodisilane and isopropyllithium.

Disilanes are precursors of polymeric organosilicon compounds, which are commercially important.^[24,29] Silyl anions, generated from disilanes^[30] are valuable in synthesis and are used in the preparation of a large variety of functionalized organosilicon compounds.^[24]

Volatile silanes are becoming increasingly important as precursors in vapor phase deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). Although the ALD technique is relatively mature, no scalable processes for deposition of silicon containing materials such as Si, SiO_x , SiC, and SiN_x are currently available. These materials are all highly applicable within the fields of photovoltaics and electronics. Numerous attempts have been made to grow SiO_2 by ALD using $SiCl_4$ and water resulting in rather lengthy processes due to low reactivity.^[31] Silanes are surprisingly stable towards reactions with water and oxygen at lower temperatures, which limits their use in ALD processes. The development of new, strained and possibly more reactive volatile molecules is therefore important in order to advance the field of deposition of silicon containing materials. Suitable precursor molecules containing Si–Si bonds are even more desirable due to their potential in maintaining such bonds in the deposited state. Notable efforts to deposit elemental Si by ALD were conducted in the early 1990's, utilizing sequential thermal decomposition of silanes or chlorosilanes^[32] or sequential chemical reactions between silicon chlorides and silanes.^[33] One of the main limitations in achieving suitable growth was the limited thermal stability of the silanes at temperatures

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above 385 °C, combined with low reactivity at lower temperatures.^[34] This means high dosages (200 Torr) and long exposure times (minutes) are required, rendering the process inefficient.

Silicon nitrides are of interest for passivation layers and anti-reflection coatings for photovoltaics, whereas silicon carbide films may open up the possibility of compact high power electronics. CVD of these materials requires rather high deposition temperatures (ca. 500 and 800 °C, respectively),^[35] which currently limits the number of potential applications.

We have attempted the preparation of tetrakis(triethylsilyl)silane, tetrakis(tri-*n*-propylsilyl)silane, tetrakis(tri-*iso*-propylsilyl)silane, tetrakis(tri-*n*-butylsilyl)silane, and tetrakis(tri-*iso*-butylsilyl)silane, using the procedure^[1] reported for the preparation of tetrakis(trimethylsilyl)silane. The resulting products were proved by chemical analysis such as mass spectrometry (MS) and elemental analysis (EA) to be mainly hexa-alkyldisilanes [(R₃Si)₂] mixed (except in the case of compound **3**) with other products such as (R₂Si)₄, (R₃Si)₄Si (as minor phase in some cases) in addition to other un-identified product(s). It appears that alkyl groups larger than methyl destabilize the tetrakis(trialkylsilyl)silane structure.

2 Experimental Section

2.1 Reactants and or Solvents

Chlorotriethylsilane (Aldrich, Wacker, ≥ 99.0%), chlorotri-*n*-propylsilane (VWR, Alfa Aesar, ≥ 98%), Chlorotri-*iso*-propylsilane (VWR, Alfa Aesar, ≥ 97%), Chlorotri-*n*-butylsilane (VWR, Alfa Aesar, ≥ 97%), Chlorotri-*iso*-butylsilane (Aldrich, ≥ 99%), lithium (Aldrich, granular, 99%), and silicone tetrachloride (Aldrich, 99%) were used as reactants without further purification. THF (Merck, ≥ 99.9%) was refluxed over sodium and benzophenone for 1 d, distilled in an argon atmosphere and used directly after distillation.

2.2 Synthesis

All procedures until the hydrolysis were performed in a dry argon atmosphere using a combination of glove box and Schlenk line. The procedures were similar in all experiments and based on the reported preparation of tetrakis(trimethylsilyl)silane:^[1] In a glove box, Li (0.96 mol, 50% excess), chlorotrialkylsilane (0.384 mol, 20% excess), and THF (ca. 120 mL) were added to a round bottomed flask. SiCl₄ (0.08 mol) and THF (70 mL) were added to a special funnel (which can be sealed and used under inert atmosphere). This funnel was connected to the reaction flask, closed and brought out from the glove box. The system was joined to the Schlenk line and exposed to an argon atmosphere. Ca. 8 mL of the mixture of SiCl₄ and THF was added to the reaction mixture of Li and chlorotrialkylsilane and stirred for ca. 4 h. After that, the remaining SiCl₄ in THF was added drop wise to the reaction mixture at room temperature over ca. 4 h. The reaction mixture was stirred at room temperature for ca. 30 h, after which the system was transferred back to the glove box and filtered through glass wool. The filtrate was brought out from the glove box and added to a beaker containing HCl (ca. 180 mL, 15%) and some ice and stirred well to allow hydrolysis. The organic layer was separated from the aqueous layer, washed several times with distilled water, and dried with anhydrous sodium sulfate. In the case of hexaethylsilane, hexa-*n*-propylsilane, hexa-*n*-butylsilane and hexa-*iso*-butyl-

silane, the product was distilled. In the case of hex-*iso*-propylsilane, the final product was a solid, which was filtered off, washed several times with distilled water, dried and purified by sublimation.

Pure [(C₂H₅)₃Si]₂ (**1**) was prepared by careful fractional distillation of the dried organic layer obtained with chlorotriethylsilane as starting material. The colorless liquid was proved (EA and MS) to be pure **1** (Table 1 and Table 2).

Table 1. Analytically determined and theoretically calculated (printed in italics) composition (in wt%) for [(C₂H₅)₃Si]₂ (**1**), (CH₃CH₂CH₂)₃Si]₄Si (**2**), and [(*iso*-propyl)₃Si]₂ (**3**) complexes (elemental analysis).

Complex	C	H
1	62.30	13.09
	<i>62.52</i>	<i>13.12</i>
2	65.60	12.82
	<i>65.76</i>	<i>12.88</i>
3	68.55	13.55
	<i>68.70</i>	<i>13.45</i>

Table 2. Mass spectroscopic (MS) data for [(C₂H₅)₃Si]₂ (**1**).

Ions	<i>m/z</i>		Relative intensity /%
	obsd.	calcd ^{a)}	
C ₁₂ H ₃₀ Si ₂ ⁺	230.1	230.19	54.44
C ₁₀ H ₂₅ Si ₂ ⁺	201.1	201.15	40.28
C ₁₀ H ₂₅ Si ⁺	173.1	173.17	29.6
C ₈ H ₂₁ Si ⁺	145.0	145.14	20.46
C ₆ H ₁₅ Si ⁺	115.1	115.09	100
C ₆ H ₁₅ ⁺	87.0	87.12	79.94

a) Calculated value according to the isotope with highest abundance.

Complex **2** was obtained from the reaction described above using chloro-*tri-n*-propylsilane. After hydrolysis and separation of the aqueous layer, the organic layer was left to stand overnight, after which it separated into three layers: a clear orange layer on the top, a thick orange layer in the middle, and a thicker brighter orange layer on the bottom. The last layer was dissolved in ether or hexane, filtered off and the yellowish solution was left for slow evaporation at room temp., open to air. Afterwards, the yellowish solid was re-crystallized from hot ethanol or alternatively it can be washed carefully with cold ethanol to obtain a white solid, which proved to be pure tetrakis(tri-*n*-propylsilyl)silane (**2**), melting point (m.p.) = 262–267 °C. Single crystals suitable for single-crystal X-ray structure determination were obtained by re-crystallization of the white solid from a mixture of acetonitrile and toluene at boiling point (Table 1 and Table 3).

For R = *iso*-propyl, a quantitative amount of a solid precipitated directly on hydrolysis. The mixture was stirred well, filtered off, and washed with distilled water several times, dried at 60 °C and sublimed at 100 °C under vacuum. The white solid proved (EA and MS) to be pure complex **3**, m.p. 207–210 °C (yield ca. 50%) (Table 1 and Table 4).

2.3 Elemental Analysis

Elemental analyses were performed by the standard combustion technique at Mikroanalytisches Labor Pascher (Germany) or Birmingham University (UK).

Table 3. Mass spectroscopic (MS) data for [(*n*-C₃H₇)₃Si]₄Si (**2**).

Ions	<i>m/z</i>		Relative intensity /%
	obsd.	calcd ^{a)}	
C ₃₆ H ₈₄ Si ₅ ⁺	656.5	656.54	1.09
C ₃₃ H ₇₇ Si ₅ ⁺	613.4	613.49	3.21
C ₃₀ H ₇₁ Si ₅ ⁺	571.4	571.44	2.84
C ₂₄ H ₅₆ Si ₄ ⁺	456.3	456.35	100
C ₂₁ H ₅₀ Si ₄ ⁺	414.2	414.3	39.17
C ₁₈ H ₄₄ Si ₄ ⁺	372.2	372.25	11.72
C ₁₅ H ₃₉ Si ₄ ⁺	331.2	331.21	5.28
C ₁₂ H ₃₃ Si ₄ ⁺	289.1	289.16	6.50
C ₉ H ₂₇ Si ₄ ⁺	247.1	247.12	7.07
C ₆ H ₂₁ Si ₄ ⁺	205.0	205.07	5.08
C ₉ H ₂₁ Si ⁺	157.1	157.14	87.24
C ₆ H ₁₅ Si ⁺	115.0	115.09	39.87
C ₆ H ₁₅ ⁺	87.0	87.12	8.58

a) Calculated value according to the isotope with highest abundance.

Table 4. Mass spectroscopic (MS) data for [(*iso*-C₃H₇)₃Si]₂ (**3**).

Ions	<i>m/z</i>		Relative intensity /%
	obsd.	calcd ^{a)}	
C ₁₈ H ₄₂ Si ₂ ⁺	314.3	314.28	7.33
C ₁₅ H ₃₅ Si ₂ ⁺	271.2	271.23	31.77
C ₁₂ H ₂₉ Si ₂ ⁺	229.2	229.18	24.22
C ₉ H ₂₃ Si ₂ ⁺	187.1	187.13	25.59
C ₉ H ₂₁ Si ⁺	157.1	157.14	100
C ₆ H ₁₅ Si ⁺	115.1	115.09	62.98
C ₃ H ₇ Si ⁺	71.0	71.03	10.44
C ₃ H ₇ ⁺	43.0	43.05	11.38

a) Calculated value according to the isotope with highest abundance.

2.4 Thermogravimetric Analysis

Thermogravimetric (TG) analysis was performed with a Perkin-Elmer TGA7 system in a nitrogen atmosphere. Silica-glass containers were used as sample holders. The heating rate was 5 °C·min⁻¹ over a temperature range of 30–700 °C. The sample masses were in the range 15–30 mg.

2.5 Mass Spectrometry

Mass spectra were recorded with a Fisons Prospec (EBE) mass spectrometer. The electron energy for ionization was 70 eV, ion acceleration voltage was 8 kV, and the source temperature was 250 or 350 °C.

2.6 X-ray Diffraction

SXD data for **2** were collected at 100 K (Bruker D8 Venture diffractometer; Mo-*K*_α radiation from an IncoTec microfocus source). The crystal was mounted on a Kapton loop using Pareto oil. The data were integrated with SAINT and corrected for absorption using SADABS.^[36] During space group determination with XPREP^[36] observe/reverse twinning of the rhombohedral structure was detected and corrections were applied for this (structure refined as an inversion twin). The structure was solved using SHELXS 2012 (intrinsic phasing methods) and refined using full-matrix least-squares against |*F*|² with SHELXL 2012^[37] as implemented in WinGX.^[38] Publication checks were made with Platon^[39] using Farrugia's Platon for Windows toolbar.^[40] Details of the data collection and refinement are given in Table 6.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1006295 (for **2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

3 Results and Discussion

In most cases the products of the reactions were liquids, which were difficult to purify sufficiently by distillation. Only the original [(CH₃)₃Si]₄Si,^[1] **2**, and **3** are solid products and can be conveniently purified by sublimation under vacuum conditions (ca. 0.3 mbar) or by re-crystallization.

For *R* = Et, MS data indicate that the product is a mixture of (Et₃Si)₂ (as a major phase), (Et₂Si)₄, and other un-identified very minor product(s). Careful fractional distillation gave a colorless liquid, which proved (EA, and MS, see Table 1 and Table 2) to be pure (Et₃Si)₂ (**1**). TG analysis shows that **1** loses weight in just one step (onset at ca. 50 °C, completed at ca. 150 °C, total weight loss 99.4 %) and MS showed the molecular ion C₁₂H₃₀Si₂⁺ (*m/z* = 230.1), in addition to other lighter ions generated from its fragmentation in the MS tube (Table 2). When not fully purified **1** appears as the major phase in a mixture with higher molecular species such as (Et₂Si)₄ (a fragment, C₁₆H₄₀Si₄⁺, with *m/z* = 344.1, which has not been obtained as a pure phase). Other higher mass ion fragments, probably formed in the ion chamber of the MS, can be seen in some of the mass spectra. For example, a sample of [(C₂H₅)₃Si]₂, was shown by EA to be single phase [EA for C₁₂H₃₀Si₂: C 62.51 (calcd. 62.52), H 13.08 (calcd. 13.12)%], whereas its mass spectrum showed some higher mass ions (Table 5). This is an unusual observation but it cannot be ignored.^[41]

Table 5. Mass spectroscopic (MS) data for [(C₂H₅)₃Si]₂ (**3**), which proved (EA) to be [(C₂H₅)₃Si]₂, but its MS showed higher molecular ions than the parent molecular ion.

Ions	<i>m/z</i>	
	obsd.	calcd ^{a)}
C ₂₀ H ₅₀ Si ₃	374.2	374.32
C ₁₈ H ₄₅ Si ₃	345.1	345.28
C ₁₂ H ₃₀ Si ₃	258.1	258.17
C ₁₂ H ₃₀ Si ₂	230.1	230.19
C ₁₀ H ₂₅ Si ₂	201.1	201.15
C ₁₀ H ₂₅ Si	173.1	173.17
C ₆ H ₁₅ Si	115.1	115.09
C ₆ H ₁₅	87.0	87.12
C ₃ H ₇ ⁺	43.05	11.38

a) Calculated value according to the isotope with highest abundance.

For *R* = *n*-propyl a mixture of [(CH₃CH₂CH)₃Si]₂, [(CH₃CH₂CH₂)₂Si]₄, [(CH₃CH₂CH₂)₃Si]₄Si (**2**), and other un-identified product(s) was obtained. Complex **2** was separated (see above) as colorless crystals in low yield (ca. 5 %). TG showed that **2** losses weight in a single step (onset at ca. 165 °C, completed at ca. 330 °C, total weight loss). Its purity was also confirmed by EA and MS (Table 1 and Table 3); and its X-ray structure was determined (see below). Its melting point was found to be 262–267 °C.

From MS, the parent molecular ion $C_{36}H_{84}Si_5^+$ ($m/z = 656,5$) was also observed but in a very low intensity, which may reflect its instability under the experimental conditions. This may also be the reason for its low yield. The highest (100%) peak observed was $C_{24}H_{56}Si_4^+$ ($m/z = 456,3$), which might be octa-*n*-propyltetracyclosilane formed under the MS experimental conditions (see Table 3).

The crystal structure of complex **2** is disordered with two possible orientations of the entire asymmetric unit related by inversion, which can be expressed in the space group $R\bar{3}$. The R factors for refinement in this space group are, however, poor and it is better to represent the structure in the lower symmetry space group $R3$ (Table 6). In this space group the two orientations of the central Si_5 tetrahedron are found to exist in a ratio of 65:35 with the exact positions of the isopropyl groups connected to the less abundant orientation (Si2A and Si3A) being impossible to locate from the data. The structure of the molecule and asymmetric unit are shown in Figure 1. It is possible to connect the *iso*-propyl groups described in the structural model to the less abundant form of the silicon tetrahedron with slightly extended Si–C bonds [Si2A–C1 = 2.25(2) Å; Si3A–C7 = 2.24(3) Å], thus describing all the atoms for the less abundant form in an approximate manner. All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in idealized positions and refined with isotropic displacement parameters proportional to those of the atoms to which they are attached (riding model). Bond lengths and angles are given in Table 7. The C–C bond lengths in the *iso*propyl groups were restrained to a value of around 1.37 Å based on other refinements of compounds with C–C single bonds. A DELU similarity restraint was also used

to control the thermal displacement parameters of the isopropyl carbons. The Si–Si bond lengths obtained from the structure are typical for Si–Si single bonds, however the Si–C bond lengths are somewhat longer than the expected 1.85 Å. This is probably due to the disordered nature of the structure. Restraining the Si–C bond lengths results in a set of bond lengths, which fit better with the literature values, but significantly worsens the R -factor. The angles are much as expected for a tetrahedral structure with the high estimated standard deviations on the bond angles involving only carbon indicating some disorder which is not accounted for in the model due to the absence of separate *isopropyl* groups for the lower abundance inverted form of the molecule. Despite the high R -factor for the refinement we believe this to be a good representation of the structure of complex **2**, a compound which, typically for an ALD precursor, exists at the limits of the crystalline state with high disorder. The crystal packing of **2** is shown in Figure 2. The Flack parameter of 0.7(7) for the non-centrosymmetric structure is inconclusive regarding the absolute structure. This is not surprising considering the inversion disorder in the asymmetric unit.

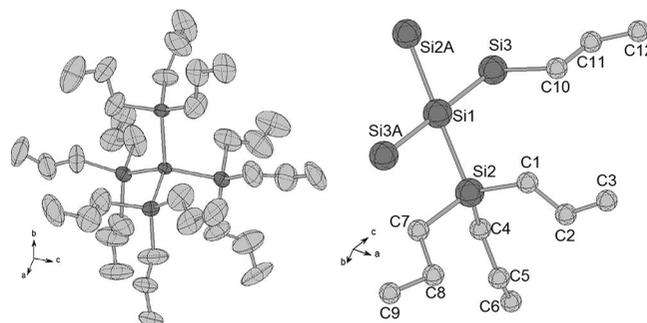


Figure 1. Molecule (left) and asymmetric unit (right) views of the crystal structure of complex **2**. Thermal ellipsoids are drawn at 50% probability in the molecule view. The inverted tetrahedron formed with Si2A and Si3A is omitted from the molecule view for clarity. Hydrogen atoms are also omitted.

Table 6. Crystal data for complex **2**.

Formula	$Si_5(C_3H_7)_{12}$
Formula weight	657.48
Crystal system	trigonal (hexagonal axes)
Space group	$R3$ (No.146)
a, c / Å	17.9249(10), 12.2752(7)
V / Å ³	3415.6(5)
Z	3
Density (calc) / g·cm ⁻³	0.959
μ (Mo- $K\alpha$) / mm ⁻¹	0.177
$F(000)$	1110
Crystal size / mm	0.31 × 0.35 × 0.39
Data collection	
Temperature / K	100
Radiation / Å	Mo- $K\alpha$, 0.71073
Theta min-max / °	3.1, 26.3
Dataset	–22: 11; 0: 22, –15: 15
Tot., uniq. data, R (int)	17549, 3077, 0.043
Observed data [$I > 2.0$ sigma(I)]	2198
Refinement	
Number of reflections, parameters, restraints	3077, 128, 42
R, wR_2, S	0.1528, 0.4388, 1.83
Max. and av. shift/error	0.06, 0.01
Flack x	0.7(7)
Min. and Max. residual density. / e·Å ⁻³	–0.77, 0.88

Table 7. Selected bond lengths / Å and angles / ° for complex **2**.

Si1–Si2	2.368(5)	Si2–Si1–Si2	108.8(2)
Si1–Si2A	2.360(10)	Si1–Si2–C1	107.3(7)
Si1–Si3	2.353(9)	Si1–Si2–C4	109.0(8)
Si1–Si3A	2.286(16)	Si1–Si2–C7	108.5(8)
Si2–C1	2.00(2)	Si1–Si3–C10	102.2(7)
Si2–C4	1.96(2)	Si2–C1–C2	123.6(19)
Si2–C7	1.99(2)	Si2–C4–C5	117.6(18)
Si3–C10	2.10(3)	Si2–C7–C8	117.1(18)
C1–C2	1.36(4)	Si3–C10–C11	109(2)
C2–C3	1.36(4)	C1–Si2–C4	117.4(11)
C4–C5	1.42(3)	C1–Si2–C7	109.1(11)
C5–C6	1.38(2)	C4–Si2–C7	105.3(10)
C7–C8	1.41(4)	C10–Si3–C10	115.6(11)
C8–C9	1.38(4)	C1–C2–C3	119(2)
C10–C11	1.33(3)	C4–C5–C6	117(2)
C11–C12	1.38(4)	C7–C8–C9	103(3)
		C10–C11–C12	129(3)

For $R = iso$ -propyl, $[(C_3H_7)_3Si]_2$ (**3**) was obtained as a solid product and purified by sublimation under vacuum conditions. TG analysis in a nitrogen atmosphere shows a one-step weight

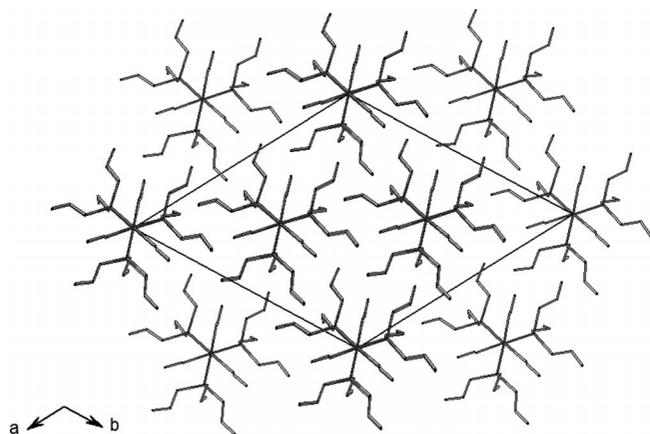


Figure 2. Crystal packing of complex **2** viewed along the *c* axis.

loss with onset at ca. 120 °C, completed at ca. 260 °C (total weight loss). The sublimed species of **3** [parent molecular ion, (*m/z* = 314.3)] is also detected in the mass spectrum, but the component with the highest abundance in the mass spectrum is the monosilane (C₃H₇)₃Si (*m/z* = 157.1), which is formed by cleaving the Si–Si bond (see Table 4).

For *R* = *n*- or *iso*-butyl no pure products were obtained even after fractional distillation. The final products were mixtures of hexa-*n*-butyldisilane or hexa-*iso*-butyldisilane, octa-*n*-butyl-tetracyclosilane or octa-*iso*-butyltetracyclosilane and other unidentified product(s).

The MS findings give useful information on the fragmentation of disilanes, e.g. generally the fragment with the highest abundance in the mass spectrum seems to be a monosilane and accordingly we suggest (in most cases) that the fragmentation begins with cleavage of the Si–Si bond: $R_3SiSiR_3 \rightarrow 2R_3Si$.

Thermal analysis was also carried out on tetrakis(trimethylsilyl)silane in order to compare the thermal properties of all the pure compound in the series. As for **1–3** a single step mass loss of nearly 100% was observed (onset ca. 110 °C, complete ca. 220 °C), indicating that the compound probably sublimates and is therefore well suited for testing as an ALD precursor. The TGA curves of all four compounds investigated are plotted in Figure 3 and we see that the onset temperature of sublimation increases with the size of the complex from the small (Et₃Si)₂ to the very bulky tetrakis(tri-*iso*-propylsilyl)silane.

4 Conclusions

We have applied the synthesis method used to produce [(CH₃)₃Si]₄Si to prepare silanes with a range of alkyl groups up to butyl. Only one analogue of [(CH₃)₃Si]₄Si was obtained as a pure phase while several disilanes were obtained. The separation and purification of the products is difficult. We therefore conclude that the tetrakis-trialkyl-pentasilanes are better synthesized by a different route. However, the thermal properties of the disilane and tetrakis-trialkyl-pentasilane compounds prepared suggest that they may be well suited to use as precursors for atomic layer deposition of silicon containing materials.

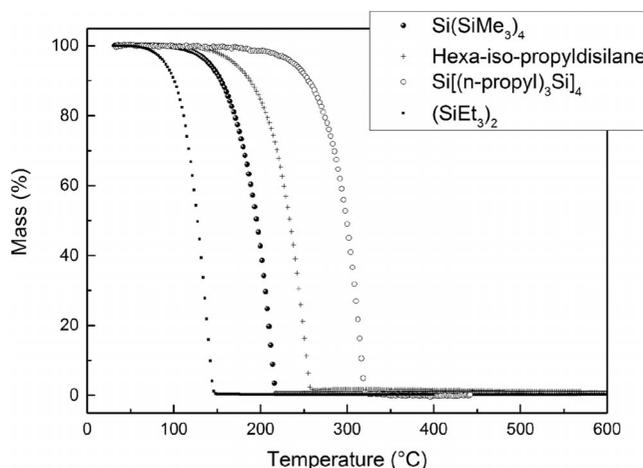


Figure 3. TGA data for compounds **1–3** and tetrakis(trimethylsilyl)silane showing the increase in sublimation temperature with size.

Acknowledgements

The authors are grateful to the Norwegian research council (NFR) for financial support (SiALD 143408) and Mr. *O. Sekiguchi* for performing the mass spectroscopic measurement.

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Received: June 3, 2014
Published Online: October 8, 2014