Synthesis and characterization of mono-, bis-, tris- and tetrakis(trimethylsilylmethyl)silanes: $(Me_3SiCH_2)_x SiH_{4-x}$ ($x = 1-4$)

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Abstract

The mono-, bis-, tris-, and tetrakis(trimethylsilylmethyl)silanes, $(Me_3SiCH_2)_x SiH_{4-x}$ ($x = 1-4$), have been prepared for use as "models" of the various Si-centered functional units in a complex, highly branched polycarbosilane polymer of the approximate composition, "$(SiH_2CH_2)_n$". These compounds have been characterized by GC, IR, ^1H, ^{13}C, ^{29}Si NMR, MS, and elemental analysis. The IR and NMR data for this series of compounds show distinct trends on increasing substitution, which are related to the structural differences within the series.

Introduction

We are currently investigating the structure of highly branched carbosilane polymers with extensive Si–H substitution as potential precursors to SiC ceramics [1]. Although there is considerable information available on NMR spectral assignments for siloxanes, polysilanes, and alkyl/aryl silanes [2], relatively little data exists on carbosilanes with one or more Si–H groups. Due to the highly branched nature of the polymers we have obtained [1], the ^1H, ^{13}C, and ^{29}Si NMR spectra consist of broad and/or highly complex groups of peaks. In order to more fully understand both the structure and the polymerization process for this system, it is desirable to confirm unambiguously the NMR assignments. For this purpose, we have prepared a series of compounds of the general formula: $(Me_3SiCH_2)_x SiH_{4-x}$ (where $x = 1-4$) for use as "models" for the various functional units present in the polycarbosilane. In the course of the preparation of these compounds certain modifications in existing synthetic methodology were employed that may have general utility in organosilicon chemistry.

$Me_3SiCH_2SiH_3$, was previously isolated by Fritz, et al. [3–6], and more recently has been investigated as a CVD precursor for silicon carbide films [7]. Daniels et al. [8] employed Me_3SiCH_2Br and $HSiCl_3$ to prepare the dichloro derivative, $Me_3SiCH_2SiHCl_2$. Sommer et al. [9] have prepared $Me_3SiCH_2SiCl_3$ by substituting

$SiCl_4$ for $HSiCl_3$. Neither of these compounds were reduced to $Me_3SiCH_2SiH_3$. The second compound of the series, $(Me_3SiCH_2)_2SiH_2$, does not appear to have been previously prepared, although the derivatives, $(Me_3SiCH_2)_2SiHCl$ [8] and $(Me_3SiCH_2)_2SiCl_2$ [9], and several related compounds have been reported [3–6]. One of these compounds, $Me_3SiCH_2SiH_2SiHMe_2$, is sufficiently similar that the relevant ^{1}H NMR assignments are comparable [3]. The remaining compounds of the series, $(Me_3SiCH_2)_3SiH$ and $(Me_3SiCH_2)_4Si$, have been previously reported in conjunction with studies on the properties of silicon compounds bearing bulky substituents [8–10].

The three previously known compounds of this series were prepared 30–40 years ago, before the advent of modern spectroscopic methods, and in general, they have not been re-investigated. For most of these compounds, IR, MS, and ^{1}H NMR data do not exist; in addition, there have been no ^{13}C or ^{29}Si NMR studies. The availability of the complete series now permits a detailed analysis of the effect of structural variations on the NMR and IR spectra.

Experimental section

Solvents were distilled from appropriate drying agents [11] immediately before use whenever air, or moisture-sensitive, materials were involved. Air-sensitive materials were manipulated using oven dried glassware and standard inert atmosphere techniques [12]. Reagents were typically > 97% pure, and were used as received unless otherwise specified. Boiling points are uncorrected. Infrared spectra were taken as films between NaCl plates on a Perkin–Elmer 298 spectrometer using medium slit and 12 min. scan time. Gas chromatograms were run on a Shimadzu GC9-A equipped with a CR3-A recorder-integrator unit. Unless otherwise specified, components separated satisfactorily using the following parameters: column, SE-30 X 6Ft; INJ, TCD, 300°C; oven, 100–250°C @ 15°C/min; carrier gas, He @ 45 cc/min. NMR spectra were obtained on a Varian XL-200 using C_6D_6 as solvent. The sample concentration was approximately 20%. ^{1}H and ^{13}C NMR spectra were referenced to residual protons in the solvent, as TMS tended to interfere with the Me-Si peaks in the samples. ^{29}Si NMR spectra were referenced by running a sample of TMS and setting the peak to 0 ppm immediately prior to running the actual sample. Any slight drifting of this setting is relatively insignificant compared to the [29]Si peak widths. Gated decoupling was employed except when coupled [29]Si spectra were desired. The mass spectrum of $Me_3SiCH_2SiH_3$ was studied using a Hiden Analytical Ltd. model HAL 201 mass spectrometer (EI, 77 eV) with a modified sample introduction system due to its volatility. In the case of EI – MS only the major and/or molecular ion peaks are listed. Mass spectra of the other compounds were obtained using a Hewlett–Packard 5987A GC/MS system in the direct insertion mode under CI conditions (isobutane or methane at 70 eV). Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratory or Galbraith laboratories.

Preparation of Me₃SiCH₂MgCl

Me_3SiCH_2MgCl was prepared essentially as in reference 8, by the reaction of Me_3SiCH_2Cl with #50 mesh Mg powder in ether under nitrogen.

Preparation of mono-, bis-, and tris(trimethylsilylmethyl)silanes

The compounds $Me_3SiCH_2SiH_3$, $(Me_3SiCH_2)_2SiH_2$, and $(Me_3SiCH_2)_3SiH$ were prepared by slowly adding an ether solution of 0.437 mole of Me_3SiCH_2MgCl (based on the amount of Me_3SiCH_2Cl used) to a stirred solution containing 15 g (0.111 mol) of trichlorosilane in 100 mL of ether, and allowing it to boil under reflux overnight [13*]. The resulting solution was found by GC to contain a mixture of the di-, and tri-substituted compounds, as well as a large amount of unreacted Grignard reagent. Addition of excess trichlorosilane (25 mL) and further refluxing, produced a mixture of $Me_3SiCH_2SiHCl_2$, $(Me_3SiCH_2)_2SiHCl$, and $(Me_3SiCH_2)_3$-SiH, in approximately equal quantities by GC. The crude mixture was separated from $MgCl_2$ by cannula transfer, then stripped of solvent and excess $HSiCl_3$. The resulting mixture was redissolved in ether and reduced with 1.4 g (0.037 mole 50% excess) $LiAlH_4$ suspended in ether. After workup with approximately 4 *M* HCl (about 750 mL), the ether layer was separated and the most of the solvent removed under vacuum. $Me_3SiCH_2SiH_3$ was distilled from this mixture under nitrogen at ambient pressure. $(Me_3SiCH_2)_2SiH_2$, and $(Me_3SiCH_2)_3SiH$ were isolated by vacuum distillation. $Me_3SiCH_2SiH_3$; purity: 98.4% (by GC), b.p. 81–84°C @ 1 ATM. (Lit. 90–91°C [7]), MS (EI, 77 eV); 118 [M^+], 117, 103, 73 [Me_3Si^+], 59, 45 [$CH_2SiH_3^+$], 43 [$MeSi^+$, or CH_2SiH^+]. Elemental analysis [14*]: Found: C, 40.76; H, 11.66. $C_4H_{14}Si_2$ calc.: C, 40.68; H, 11.86%. IR (cm^{-1}): 2950s, 2895m, 2140vs, 1410w, 1350w, 1250s, 1045vs, 965w, sh, 940vs, 840vs, 785m, 755m, 695m, 675m. $(Me_3SiCH_2)_2SiH_2$; purity: 94.6% (by GC), B.p. 40–46°C @ 0.5 mmHg, MS [DIP, CI, (isobutane)] 204 [M], 202 [$M - 2$], 188 [$M - 16$]. Elemental analysis: Found: C, 47.02; H, 11.83. $C_8H_{24}Si_3$ calc.: C,47.06; H, 11.77%. IR (cm^{-1}): 2950s, 2895m, 2120s, 1415w, 1350w, 1245s, 1040s, 995w, 955s, 880m,sh, 835vs, 765s, 690m, 660m. $(Me_3SiCH_2)_3SiH$; purity: 91.3% (by GC), b.p. 78–84°C @ 0.5 mmHg, (Lit. 110–12°C @ 10 mmHg). MS [DIP, CI, (isobutane)]: 290 [M], 274 [$M - 16$]. Elemental analysis: Found: C, 48.36; H, 11.53. $C_{12}H_{34}Si_4$ calc.: C, 49.65; H, 11.72%. IR (cm^{-1}): 2950vs, 2895m, 2090m, 1405w, 1350w, 1245vs, 1040vs, 995w, 955vw, 860sh, 830vs, 770vs, 685m, 660m.

Preparation of tris(trimethylsilylmethyl)silane [(Me₃SiCH₂)₃SiH] using CuCN catalyst

$HSiCl_3$ (0.25 mole) was added, dropwise, to 1 mole of Me_3SiCH_2MgCl in 500 mL of ether with rapid stirring and cool water bath. After the addition was complete, the mixture was allowed to reflux for 2 days during which much $MgCl_2$ precipitated. The crude product was separated from the $MgCl_2$ and found by GC to consist of a 2:1 ratio of $(Me_3SiCH_2)_2SiHCl$ and $(Me_3SiCH_2)_3SiH$, respectively, and unreacted Grignard reagent. Addition of Me_3SiCH_2MgCl (0.25 mol), and refluxing for 1 day, resulted in a 1:1 product ratio (by GC). CuCN catalyst [15] (0.3 g) was added, the color changed from pale yellow to black in a few minutes, and reflux was continued overnight. GC of the crude product showed almost quantitative conversion to $(Me_3SiCH_2)_3SiH$. Subsequent aqueous workup (as previously described) and vacuum distillation, gave the desired product $(Me_3CH_2)_3SiH$, in 65% yield (91.3% purity by GC). IR and ^1H NMR spectra of this compound matched those of $(Me_3SiCH_2)_3SiH$ produced without use of CuCN.

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* Reference number with asterisk indicates a note in the list of references.

Preparation of tris[trimethylsilylmethyl]bromosilane [(Me₃SiCH₂)₃SiBr]

Preparation of tris[trimethylsilylmethyl]bromosilane [(Me$_3$SiCH$_2$)$_3$SiBr]

Preparation of (Me$_3$SiCH$_2$)$_3$SiBr, involved a variation on the procedure used by Daniels and Post [8]. A 100 mL single-neck flask with nitrogen inlet was charged with 0.16 mole (Me$_3$SiCH$_2$)$_3$SiH and 50 mL of dry benzene. The temperature was maintained at approximately 10°C with a cool water bath. Bromine (0.18 mole, 1.1 eq.) was added, dropwise, over about 2 h, with stirring. The bromine was immediately decolorized until approximately 90% had been added. An oil bubbler allowed the by-product, HBr, to escape. After stirring overnight at 20°C, the contents were purged with nitrogen to drive out HBr, excess Br$_2$, and most of the benzene. The product, (Me$_3$SiCH$_2$)$_3$SiBr, was isolated in 73.2% yield (93.2% pure by GC) by vacuum distillation. B.p. 89–94°C @ 0.5 mmHg (Lit. 110°C @ 1.8 mmHg [8]). IR (cm^{-1}) 2950s, 2895m, 1400w, 1350w, 1245vs, 1060vs, 1000w, 835vs, 775vs, 690m, 665w.
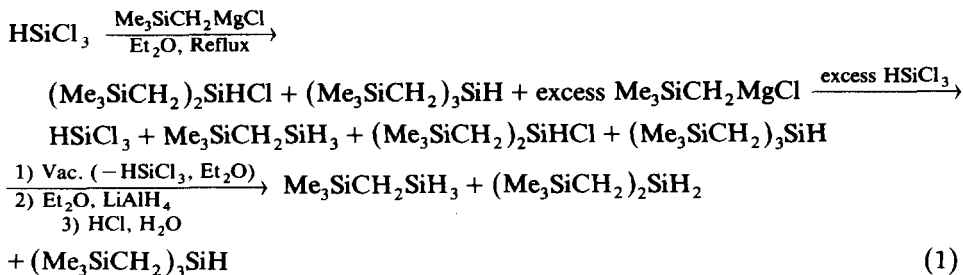
Conversion of (Me$_3$SiCH$_2$)$_3$SiBr to (Me$_3$SiCH$_2$)$_4$Si

A 500 mL 3-neck flask fitted with reflux condenser and nitrogen atmosphere was charged with 31.9 g of (Me$_3$SiCH$_2$)$_3$SiBr (0.086 mole), 0.25 mole of Me$_3$SiCH$_2$MgCl in 300 mL of ether, and 0.3 g of CuCN as catalyst. After 4 days reflux, the "aqueous workup" was performed as described above. The crude product was a mixture of tetrakis(trimethylsilylmethyl)silane [(Me$_3$SiCH$_2$)$_4$Si] and tris(trimethylsilylmethyl) silanol [from hydrolysis of unreacted (Me$_3$SiCH$_2$)$_3$SiBr], in an approximately 2:1 ratio, respectively (by GC). Repeated vacuum distillation failed to give complete separation. A 60/37% mixture (by GC) of (Me$_3$SiCH$_2$)$_4$Si and (Me$_3$SiCH$_2$)$_3$SiOH was treated with excess LiAlH$_4$ and subjected to aqueous workup. Resulting in a mixture of (Me$_3$SiCH$_2$)$_3$SiH and (Me$_3$SiCH$_2$)$_4$Si. This mixture was separable by vacuum distillation, giving the desired compound (Me$_3$SiCH$_2$)$_4$Si in 94.7% purity (by GC). B.p. 96–97°C @ 0.5 mmHg. MS (CI methane DIP): M, $M-14$, $M-86$, $M-174$, Me$_3$Si (73). Elemental analysis: Found: C, 47.90; H, 11.30. C$_{16}$H$_{44}$Si$_5$ calc.: C, 51.06; H, 11.70%. IR (cm^{-1}): 2950s, 2895m, 1405w, 1350w, 1250s, 1055s, 990w, 835vs, 780s, 690m, 670w.
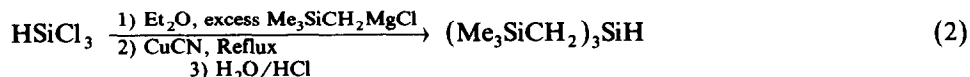
Results and discussion

Syntheses

The purpose of this study was to more fully characterize the series of compounds represented by the general formula [Me$_3$SiCH$_2$]$_x$SiH$_{4-x}$ ($x = 1$–4), particularly with respect to their NMR and IR spectra. Although large quantities were not needed, samples of each member of the series were required. It was found that a modification to the procedure of Daniels and Post [8] produces the first three compounds of the series in one preparation (eq. 1).

$$HSiCl_3 \xrightarrow[Et_2O, \ Reflux]{Me_3SiCH_2MgCl}$$

$$(Me_3SiCH_2)_2SiHCl + (Me_3SiCH_2)_3SiH + excess \ Me_3SiCH_2MgCl \xrightarrow{excess \ HSiCl_3}$$

$$HSiCl_3 + Me_3SiCH_2SiH_3 + (Me_3SiCH_2)_2SiHCl + (Me_3SiCH_2)_3SiH$$

$$\xrightarrow[\substack{2) \ Et_2O, \ LiAlH_4 \\ 3) \ HCl, \ H_2O}]{1) \ Vac. \ (-HSiCl_3, \ Et_2O)} Me_3SiCH_2SiH_3 + (Me_3SiCH_2)_2SiH_2$$

$$+ (Me_3SiCH_2)_3SiH \tag{1}$$

After the initial reflux, the crude mixture contained approximately equal quantities of the di- and tri-substituted compounds due to the rather sluggish formation of $(Me_3SiCH_2)_3SiH$. Addition of excess trichlorosilane to the reaction mixture at this stage not only formed the desired mono-substituted compound, but served to eliminate any remaining Grignard reagent prior to the $LiAlH_4$ reduction. Unreacted trichlorosilane was stripped off before the reduction of the crude products to avoid the formation of pyrophoric silane gas. Due to large boiling point differences, the components were easily separated after the final workup.
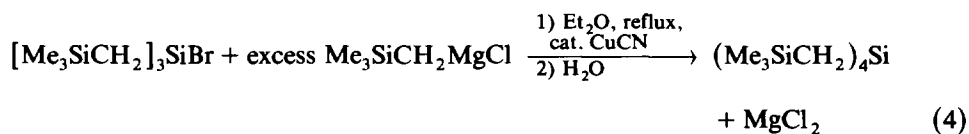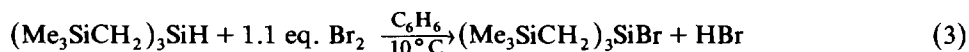
Using an alternative approach, $(Me_3SiCH_2)_3SiH$ was prepared in high yield by the use of CuCN [15] as catalyst, as shown in eq. 2.

$$HSiCl_3 \xrightarrow[\substack{2)\ CuCN,\ Reflux \\ 3)\ H_2O/HCl}]{1)\ Et_2O,\ excess\ Me_3SiCH_2MgCl} (Me_3SiCH_2)_3SiH \qquad (2)$$

In this case, the CuCN was not added until the $HSiCl_3$ had already been partially reacted, as the initial substitution is highly vigorous and exothermic. Even with only a single extraction (to isolate the crude products from $MgCl_2$) before CuCN addition, yields of 65% were achieved. These results were comparable to those obtained by employing the more active lithium reagent Me_3SiCH_2Li (71%), and much better than the uncatalysed Grignard reaction (18.6%) [8].

The exact nature of the catalytic effect is not completely understood, but CuCN has been reported to greatly increase the yield of reactions involving bulky Grignard reagents with chlorosilanes [15]. The use of Si–H-containing chlorosilanes as substrates for this catalytic process does not appear to have been previously reported. Our results suggest that the scope of the CuCN-catalysed reactions can be extended to include sterically hindered, Si–H bearing compounds.

The compound $(Me_3SiCH_2)_3SiH$ was found to be a convenient intermediate in the preparation of $(Me_3SiCH_2)_4Si$. The procedure is outlined in equations 3 and 4.

$$(Me_3SiCH_2)_3SiH + 1.1\ eq.\ Br_2 \xrightarrow[10°C]{C_6H_6} (Me_3SiCH_2)_3SiBr + HBr \qquad (3)$$

$$[Me_3SiCH_2]_3SiBr + excess\ Me_3SiCH_2MgCl \xrightarrow[2)\ H_2O]{\substack{1)\ Et_2O,\ reflux, \\ cat.\ CuCN}} (Me_3SiCH_2)_4Si$$

$$+ MgCl_2 \qquad (4)$$

The bromination of $(Me_3SiCH_2)_3SiH$, in CCl_4 followed by aqueous ammonium hydroxide workup, has been previously reported [8], however yields of only about 20% were obtained. Presumably, a large portion of the product was hydrolysed. It was found in this study that using benzene as solvent and omitting the aqueous workup enabled, after purification, a yield of 73.2% to be achieved. Difficulties were encountered with the final substitution step as, despite the use of excess Grignard reagent, CuCN and an extended reflux period, the reaction did not go to completion. Subsequent aqueous workup formed $(Me_3SiCH_2)_3SiOH$ from the unreacted $(Me_3SiCH_2)_3SiBr$. Direct separation of this mixture by distillation was not successful, however, after treatment of the crude mixture with $LiAlH_4$ the silanol was quantitatively converted to $(Me_3SiCH_2)_3SiH$. The boiling points of the resulting mixture were now sufficiently different to give good separation of the desired compound: $(Me_3SiCH_2)_4Si$.

Characterization and properties

The series of compounds, $(Me_3SiCH_2)_xSiH_{4-x}$ (where $x = 1-4$), are clear, watery liquids. Even the first member of the series, $Me_3SiCH_2SiH_3$, is sufficiently stable to be briefly handled in air without any evidence of decomposition or fuming [14].

The only compound of this series for which infrared spectral data has been previously reported is tris(trimethylsilylmethyl)silane [8]. The IR spectra for this series of compounds are found to be quite similar, as they are dominated by the Me_3SiCH_2-based bands. The most notable change is a decrease in the relative intensity of the Si–H stretch vs C–H stretch as the number of Me_3SiCH_2- groups increases from 1 to 3, due to the considerable change in the ratio of Si–H to C–H for the series. This increased substitution is also associated with a shift of the Si–H stretch from 2140 to 2090 cm^{-1}. The SiH stretching and bending modes observed for this series of compounds are very similar to published IR data for the series Ph_xSiH_{4-x} (where $x = 1-3$) [16c].

Prior NMR studies of these compounds are rather limited. No ^{13}C or ^{29}Si spectra have been reported and ^{1}H NMR data are incomplete, although related silicon compounds have been investigated [3–6]. The proton NMR spectrum of the compound $Me_3SiCH_2SiH_3$ has been previously reported by others, however, there are disagreements regarding the chemical shift values. The SiH_3 group has been assigned values of 4.47 [4], 4.15 [7] and 3.53 [3] ppm. None of the values agreed well with our result of 3.7 ppm obtained using a ca 20% solution in C_6D_6. Differences in the chemical shifts for the methyl and methylene protons were also significant. A solvent or concentration effect was suspected as multiplicities and coupling constants were in agreement. Attempts to confirm concentration effects were made by increasing the portion of $Me_3SiCH_2SiH_3$ in C_6D_6 from ca 3 to 25%. The results showed only minor changes in the chemical shifts [$(SiCH_2Si)$ -0.44 to -0.40, $(SiMe_3)$ -0.12 to -0.005, (SiH_3) 3.72 to 3.69, respectively]. The magnitude of the concentration effect appears to be too small to to explain the wide variation in chemical shifts reported for the SiH_3 group. In addition, minimal differences in chemical shift data for the compound $H_2C(SiH_3)_2$ (neat vs CCl_4) and for the compound $(Me_3SiCH_2)_3SiH$ (C_6D_6 vs CCl_4) (Table 1) suggest that solvent effects are not very important.

The proton NMR spectrum of $(Me_3SiCH_2)_2SiH_2$ has not been reported; however, the compound, $Me_3SiCH_2SiH_2CH_2SiHMe_2$, isolated in small amounts from the pyrolysis products of trimethylsilane, gave very similar chemical shifts [4]. Published ^{1}H NMR chemical shifts for $(Me_3SiCH_2)_3SiH$ [10] agree with our results within 0.1 ppm for all peaks, but the coupling constants were not given. No prior NMR data for $(Me_3SiCH_2)_4Si$ has been reported.

The NMR chemical shift and coupling constant data for these compounds are collected in Table 1 and 2, respectively. Examination of the NMR data (Table 1) shows that the central silicon, the Si–H, and the methylene groups (both carbons and hydrogens) in the series of compounds, $[Me_3SiCH_2]_nSiH_{4-n}$, all have significant, progressive, downfield shifts corresponding to the number of Me_3SiCH_2- groups. The chemical shifts in the ^{29}Si NMR spectra of the series $(Me_3SiCH_2)_xSiH_{4-x}$ are comparable to those of the corresponding methyl series [2a–d] Me_xSiH_{4-x} (which lack the steric crowding of the Me_3Si- functionalities). The silicon chemical shifts in these compounds move progressively downfield as Si–H is replaced with Me_3SiCH_2 (or Me), presumably due to the higher electro-

Table 1

^{1}H, ^{13}C, and ^{29}Si NMR chemical shift values for the series $(Me_3SiCH_2)_xSiH_{4-x}$ $(x=1-4)$ and some related compounds ^{a}

Compound/ref.	^{1}H			^{13}C		^{29}Si	
	SiCH$_2$Si	Si–Me	Si–H	SiCH$_2$Si	Si–Me	Si–H	Si–Me
Me$_3$SiCH$_2$SiH$_3$							
This study	−0.40	0.02	3.70	−8.86	−0.235	−65.1	1.81
3 (CCl$_4$)	^{b}	^{b}	4.47	^{b}	^{b}	^{b}	^{b}
4 (CCl$_4$?)	^{b}	0.09	3.53	^{b}	^{b}	^{b}	^{b}
7 (C$_6$D$_6$)	−0.05	0.15	4.15	^{b}	^{b}	^{b}	^{b}
H$_2$C(SiH$_3$)$_2$							
7 (neat, −20 °C)	−0.10	^{b}	3.69	−21.03	^{b}	^{b}	^{b}
6 (CCl$_4$, 20%)	−0.08	^{b}	3.63	^{b}	^{b}	^{b}	^{b}
H$_2$Si[CH_2SiH$_3$]$_2$							
6 (CCl$_4$, 20%)	−0.03	^{b}	3.65	^{b}	^{b}	−69.04 ^{c}	^{b}
(Me$_3$SiCH$_2$)$_2$SiH$_2$							
This study	−0.26	0.076	4.05	−1.25	0.906	−38.7	1.13
Me_3SiCH_2SiH_2CH$_2$SiHMe$_2$							
4 (CCl$_4$?)	−0.17	0.09	3.88	^{b}	^{b}	^{b}	^{b}
H$_2$Si(CH_2SiH$_3$)$_2$							
6 (CCl$_4$, 20%)	−0.03	^{b}	3.95	^{b}	^{b}	−30.44 ^{c}	^{b}
(Me$_3$SiCH$_2$)$_3$SiH							
This study	−0.19	0.10	4.29	3.39	1.15	−17.3	0.66
10 (CCl$_4$)	−0.10	0.02	4.20	^{b}	^{b}	^{b}	^{b}
(Me$_3$SiCH$_2$)$_4$Si							
This study	−0.11	0.14	^{b}	8.58	1.65	14.5	−0.54

^{a} For this study, NMR spectra were run in benzene-d_6 (ca 20%), expected peak multiplicities and integration values were seen in all cases. Conditions for spectra of compounds done by others are given when known. Nuclei of interest when not obvious are indicated in italics. ^{b} Not applicable, or not reported in reference. ^{c} Si chemical shifts for H$_2$Si(CH$_2$SiH$_3$)$_2$ are from ref. 2a, presumably run in a deuterated solvent.

negativity of carbon vs hydrogen. The nearly identical values observed for the two series of compounds, suggest that neither steric factors, not the Me$_3$Si– functionalities, are very important in determining the ^{29}Si chemical shifts for these compounds. Chemical shifts for the –SiMe$_3$ groups, which are more remote from the central silicon, show only moderate downfield shifts for ^{1}H, and ^{13}C, and slight upfield shifts for ^{29}Si.

Coupling constants obtained from the ^{1}H, ^{13}C, and ^{29}Si NMR of these, and some related compounds are collected in Table 2. The new values obtained appear to be consistent with the published values for the related compounds. The sequential replacement of Si–H by Me$_3$SiCH$_2$– groups causes definite trends in the coupling constants of this series of compounds. The ^1J(SiH) value decreases from 194.7 to 181.1 Hz as the number of Me$_3$SiCH$_2$– groups increases from 1 to 3. The coupling constants for the trimethylsilyl groups [^1J(CH) and ^1J(SiC)] show only small decreases in value progressing from Me$_3$SiCH$_2$SiH$_3$ to (Me$_3$SiCH$_2$)$_4$Si. This is consistent with the chemical shift data for these groups (Table 1) that show relatively small, but systematic, changes with increasing substitution of Me$_3$SiCH$_2$– on Si, suggesting that the trimethylsilyl groups are only slightly affected by steric crowding. The ^1J(CH) coupling constants for the methylene units show a more

Table 2

Coupling constants for the series, $[Me_3SiCH_2]_xSiH_{4-x}$ $(x = 1-4)$ and some related compounds [a]

Compound/ref.	$^1J(SiH)$	$^1J(H_3C)$	$^1J(H_2C)$	$^1J(H_3CSi)$	$^1J(H_2CSi)$	$^2J(H_2CSi)$	$^3J(HCSiH)$
$Me_3SiCH_2SiH_3$							
This study	194.7	118.5	113.5	51.25	42.75	9.7	4.6
3	*b*	*b*	*b*	*b*	*b*	*b*	4.4
4	*b*	*b*	*b*	*b*	*b*	*b*	4.5
7	*b*	*b*	*b*	*b*	*b*	*b*	4.3
$HC_2(SiH_3)_2$							
2c	195.4	*b*	118.6	*b*	43.94	*b*	4.7
$H_2Si(CH_2SiH_3)_2$							
2c (SiH_3)	199.0	*b*	*b*	*b*	*b*	(H_3SiCH_2)	4.5
(SiH_2)	196.5	*b*	*b*	*b*	*b*	(H_2SiCH_2)	4.2
$(Me_3SiCH_2)_2SiH_2$							
This study	187.7	117.6	112.5	50.80	43.35	8.9	4.4
$(Me_3SiCH_2)_3SiH$							
This study	181.1	117.0	105.0	50.75	43.95	8.6	3.8
$(Me_3SiCH_2)_4Si$							
This study	*b*	117.0	108	50.60	43.30	8.0	–

[a] Coupling constants were obtained from the appropriate NMR spectra as follows; $^3J(HSiCH)$, ^1H; $^1J(HC)$, ^{13}C; $^1J(CSi)$, $^{13}C\{^1\}$; $^1J(HSi)$, and $^2j(HCSi)$, ^{29}Si. [b] Not applicable, or not reported in original reference.

pronounced dependence, decreasing from 113.5 to 105.0 Hz as the number of Me_3SiCH_2 groups increases from 1 to 3. The corresponding $^1J(SiC)$ couplings undergo a slight increase from 42.75 to 43.95 Hz. The compound $(Me_3SiCH_2)_4Si$ shows slightly anomalous behavior, with values of $^1J(CH)$ of 108 and $^1J(SiC)$ of 43.30 Hz respectively. Values for the $^2J(HCSi)$ coupling ranged from 9.7 to 8.0 Hz as the number of Me_3SiCH_2- groups increased from 1 to 4. Typical values for this coupling range from about 6 to 9 Hz [2c]. The values for the $^3J(HSiCH)$ couplings of the series of compounds, $(Me_3SiCH_2)_xSiH_{4-x}$, decreased from 4.6 to 3.8 Hz on increasing substitution. These values are found to be consistent with literature data for related systems.

Existing mass spectral data [5,10] (EI) and results from this study (EI and CI) suggests that for this series of compounds the parent molecular ion becomes less stable as the number of Me_3SiCH_2- groups increases. One possible explanation may be that the additional crowding resulting from the increase in the number of Me_3SiCH_2- groups facilitates fragmentation of the molecule. Alternatively, the larger molecules may absorb energy more efficiently in the mass spectrometer. Significant peaks at m/e $M - 86$, $M - 87$ are seen in most cases (CI), suggesting the loss of $Me_2Si(CH_2-)_2^+$, or $Me_3SiCH_2-^+$. For $(Me_3SiCH_2)_2SiH_2$, a fragment at m/e $M - 2$ is observed, consistent with facile loss of the SiH_2 hydrogens. Compounds with several Si–H bonds have been found to give complex groups of peaks in the mass spectra by this mechanism [5].

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14 *CAUTION*. During an attempt to obtain a C, H analysis, the compound $Me_3SiCH_2SiH_3$ exploded with sufficient violence to burst the combustion tube of the analyzer. It is suggested that any experiments involving the heating to decomposition of large quantities of this, (or related) compounds in the presence of air or oxygen be approached with caution.
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