Synthesis and studies of new tris(trimethylsilyl)silyl derivatives of germanium and tin

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Abstract

The reactions of $(THF)_3LiSi(SiMe_3)_3$ with Me_3GeCl, Ph_3GeCl and $GeCl_4$ give $R_3GeSi(SiMe_3)_3$, R = Me (75%), Ph (79%) and Cl (20%), respectively. The products, colorless, crystalline solids, unreactive toward air except for $Cl_3GeSi(SiMe_3)_3$ which is hygroscopic and rapidly hydrolyzed, were characterized by elemental analyses, GC-MS and their ^1H, ^{13}C and ^{29}Si NMR spectra. An X-ray structure determination established that crystals of $Ph_3GeSi(SiMe_3)_3$ are monoclinic, $C2/c$, with $a = 17.102(6)$, $b = 9.997(3)$, $c = 37.368(9)$ Å, $\beta = 91.61(2)°$, $V = 6386$ Å^3 and $Z = 8$. Examination of the structural parameters revealed the presence of twisting distortions among the phenyl and trimethylsilyl substituents evidently relieving steric strain along the Ge–Si vector. Bond distances and angles predicted from force field calculations closely matched those determined by diffraction for the phenyl derivative. Calculations on $Me_3GeSi(SiMe_3)_3$ and $Cl_3GeSi(SiMe_3)_3$ confirmed the expectation that steric strain is minimal in those molecules. The reactions of $(Me_3Si)_3SiSnCl_3 \cdot THF$ and $((Me_3Si)_3Si)_2SnCl_2$ with $LiAlH_4$ in ether were investigated as a possible means to prepare silyltin(IV) hydrides. Despite use of a variety of conditions following those in published preparations of alkyltin(IV) hydrides, no silyltin hydrides were isolated. MNDO calculations indicated that decomposition of $((Me_3)_3Si)_3SiSnH_3$ to $((Me_3)_3Si)SiH$, Sn and H_2 is thermodynamically favored.

Introduction

Spatially demanding groups such as $-C(SiMe_3)_3$ and $-Si(SiMe_3)_3$ are known to produce steric strain in molecules with a central atom from Group 14. Our recent studies [1, 2] on tin and germanium derivatives containing one or two $Si(SiMe_3)_3$ groups have revealed pronounced structural distortion in $((Me_3Si)_3Si)_2SnCl_2$ attributable to the crowding induced by the two bulky silyl groups. Presumably for the same reason, we have been unable to prepare the corresponding disubstituted germanium compound, $((Me_3Si)_3Si)_2GeCl_2$, isolating instead digermane [2] and tetragermane [3] products which contained only one $Si(SiMe_3)_3$ group per germanium. Other workers have also reported unsuccessful attempts to prepare $((Me_3Si)_3C)_2SiR_2$ and $((Me_3Si)_3Si)_2SiR_2$ derivatives owing, it was believed, to the intensive crowding created by the two bulky groups [4]. Cone angle determinations have been recognized as a means of comparing the steric demands of $(Me_3Si)_3E)$-M arrangements (where E and M are Group 14 elements) [5]. It was of interest to assess the degree of steric strain in related molecules having $Si(SiMe_3)_3$ groups interacting with other substituents of differing steric requirements. We report here the preparation of three new tris(timethylsilyl)silyl-germanium derivatives along with an X-ray structural characterization of $((CH_3)_3Si)_3SiGe(C_6H_5)_3$ and the results of molecular mechanics studies of the new molecules. Attempts to prepare tris(trimethylsilyl)silyltin(IV) hydrides will also be described.

Experimental

Materials

Trimethyl- and triphenylgermanium chlorides were from Strem and were used as obtained. The lithium silyl reagent, $(THF)_3LiSi(SiMe_3)_3$, was prepared by a literature method [6]. Using the lithium silyl, $(Me_3Si)_3SiSnCl_3 \cdot THF$ and $((Me_3Si)_3Si)_2SnCl_2$ were prepared as described elsewhere [1]. Other reactions and manipulations were carried out under argon using Schlenk techniques. All solvents were distilled from $LiAlH_4$ or sodium under flowing nitrogen.

Elemental analyses were performed by Atlantic Microlaboratories. IR spectra were recorded on a Perkin-Elmer model 1330 IR spectrophotometer with Nujol-mulled samples pressed between AgBr windows. ^1H

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and ^{13}C NMR spectra were recorded using a General Electric QE-300 spectrometer. ^{29}Si spectra (56.6 MHz) were obtained using a General Electric (Nicholet) NT-300 widebore NMR instrument fitted with a Libra data station and an array processor.

Syntheses

Tris(trimethylsilyl)silyl-trimethylgermane, $(Me_3Si)_3SiGeMe_3$ (I)

A solution of Me_3GeCl (1000.0 mg, 6.53 mmol) in ether (30 ml) was added dropwise with vigorous stirring to a cold ether solution (70 ml) of $(THF)_3LiSi(SiMe_3)_3$ (3308.9 mg, 7.025 mmol). The reaction mixture was stirred at −78 °C for 8 h, then was allowed to warm to ambient temperature where stirring was continued another 40 h. The ether was removed, *in vacuo*, and the white solid residue was stirred with pentane (2×30 ml) after which the remaining solid was removed by filtration. Upon concentration and cooling (4 °C for 2 days), the pentane solution afforded **I** as colorless crystals. The crystals were separated, washed with a small quantity of pentane and dried under vacuum (1790 mg, 75%, m.p. 135 °C). The product was unaffected by exposure to air and moisture. *Anal.* Calc. for $C_{12}H_{36}GeSi_4$: C, 39.45; H, 9.93. Found: C, 39.74, H, 10.06%. NMR (C_6D_6): ^{1}H, δ 0.398 (Me_3Ge), 0.251, 0.260 (Me_3Si); ^{13}C, δ 2.33 (Me_3Ge), 2.79, 2.92 (Me_3Si); ^{29}Si, δ +0.25 (Si(SiMe$_3$)$_3$), −118.0 (Si(SiMe$_3$)$_3$). IR (cm^{-1}) 2620m, 1925w, 1865w, 1305m, 1255sh, 1240s, 1225sh, 1080w, 1020w, 830vs, 725sh, 680s, 675sh, 620s, 585s, 560s, 460m.

Tris(trimethylsilyl)silyl-triphenylgermane, $(Me_3Si)_3SiGePh_3$ (II)

Using the procedure described for **I**, Ph_3GeCl (1881.3 mg, 5.54 mmol) was reacted with $(THF)_3LiSi(SiMe_3)_3$ (2611 mg, 5.54 mmol) in diethyl ether. Work up gave colorless, transparent crystals of **II** (2400 mg, 79%, m.p. 265 °C) which were not hygroscopic. *Anal* Calc. for $C_{27}H_{42}GeSi_4$: C, 58.79; H, 7.67. Found: C, 58.56; H, 7.55%. NMR (C_6D_6): ^{1}H, δ 7.09 (m), 7.6 (m) (Ph_3Ge), 0.17 (Me_3Si); ^{13}C, δ 128.4, 136.0, 139.9 (Ph_3Ge), 3.12 (Me_3Si); ^{29}Si, δ −0.20 (Si(SiMe$_3$)$_3$), −113.3 (Si(SiMe$_3$)$_3$). IR (cm^{-1}): 1955w, 1875w, 1810w, 1575m, 1430m, 1300m, 1235vs, 1175w, 1150w, 1080vs, 1060sh, 1015m, 990m, 825vs, 695s, 685s, 620vs, 465vs, 435m, 405sh, 310m.

Tris(trimethylsilyl)silyl-trichlorogermane, $(Me_3Si)_3SiGeCl_3$ (III)

A hexane solution (200 ml) of $(THF)_3LiSi(SiMe_3)_3$ (5431 mg, 11.53 mmol) was added with stirring to a solution (100 ml) of $GeCl_4$ (2472 mg, 11.53 mmol) at −78 °C over 1 h. The reaction mixture was stirred 8 h at −78 °C, then permitted to warm to ambient temperature with continuous agitation for an additional 14 h. Hexane was removed under vacuum, about 100 ml of pentane was added and the mixture was stirred for 1 h. The mixture was then filtered, concentrated and held at 4 °C overnight. The clear solution was separated via cannula from a deposit of yellow oil which had formed in the bottom of the flask. Cooling the solution to −78 °C afforded transparent, very hygroscopic crystals of **III**. The crystals were taken up in pentane and crystallized twice more at −78 °C to obtain a purified product (1000 mg; 20%; m.p. 44 °C) according to its NMR spectrum (NMR (C_6D_6): ^{1}H, δ 0.219; ^{13}C, δ −0.622). IR (neat, cm^{-1}): 3765vw, 3575vw, 3215sh, 3085sh, (2985, 2935 doublet)vs, 2645w, 2505vw, 2125vw, 1925w, 1860w, 1655w, 1500sh, 1430s, sh, 1395vs, 1305m, 1245vs, 1055m, 1005vw, 935w, 830br, s, 740m, 685s, 615vs, 480vs, 440w, 385m, 360w, 315m. The GC-mass spectrum of a sample of the product in pentane solution contained four minor bands accompanying the major component. The identity of the product (major component) as $((CH_3)_3Si)_3SiGeCl_3$ was confirmed by the appearance of the parent ion (envelope) at $m/z = 427$ $(p+H)^+$. Other significant ions seen were m/z 369 (50.8%), $((CH_3)_3Si)_2Si(CH_3)GeCl_3^+$; 281 (28.1%), $(CH_3)_3SiSiGeCl_3^+$; 265 (17.1%), $(CH_3)_2SiGeCl_3\text{-}H^+$; 221 (6.7%), $CH_3SiGeCl_3\text{-}H^+$; 207 (14.9%), $SiGeCl_3^+$; 205 (17.9%), $(CH_3)_3Si(CH_3)_2SiGe^+$; 174 (4.8%), $((CH_3)_3Si)_2Si^+$; 147 (100%), $(CH_3)_3SiGe^+$; 131 (28.4%), Si_2Ge^+; 117 (12.4%), CH_3SiGe^+. One of the minor components was identified as $(Me_3Si)_4Ge$ and the others were believed to represent hydrolysis products originating from the brief exposure of the solution to air necessitated during GC-MS analysis.

Structure determination of II

A clear, colorless multifaceted block having approximate dimensions 0.45×0.45×0.40 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown to be either Cc or $C2/c$. Intensities were measured using the ω-scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant change. During data reduction Lorentz and polarization corrections were applied, as well as an empirical absorption correction based on psi scans of ten reflections having χ values between 70 and 90°.

TABLE 1. Data collection and processing parameters

Space group	$C2/c$ (monoclinic)
Cell constants	
a (Å)	17.102(6)
b (Å)	9.997(3)
c (Å)	37.368(9)
β (°)	91.61(2)°
V (Å^3)	6386
Molecular formula	$C_{27}H_{42}Si_4Ge$
Formula weight	551.64
Formula units per cell, Z	8
Density, ρ (g cm^{-3})	1.15
Absorption coefficient, μ (cm^{-1})	11.05
Radiation (Mo Kα), (Å)	0.71073
Collection range (°)	$4 \leqslant 2\theta \leqslant 45$
Scan width	$\Delta\theta = 1.30 + (K\alpha_2 - K\alpha_1)$
Scan speed range (° min^{-1})	2.0–15.0
Total data collected ($h+k=2n$)	4175
Independent data, $I > 3\sigma(I)$	3177
Total variables	319
$R = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$	0.035
$R_w = [Sw(\lvert F_o \rvert - \lvert F_c \rvert)^2 / Sw \lvert F_o \rvert^2]^{1/2}$	0.026
Weights	$w = \sigma(F)^{-2}$
Extinction coefficient	$x = 0.00044$

Since the unitary structure factors displayed centric statistics, space group $C2/c$ was assumed from the outset. The structure was solved by use of the Patterson technique, which revealed the position of the Ge atom. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for the phenyl hydrogens and a separate variable for the methyl hydrogens. Since examination of the Fourier difference map indicated that some of the methyl groups were not quite in ideal orientations, all nine of them were allowed to rotate freely as individual rigid bodies. The sample crystal was of extremely high quality and the diffraction data showed the classic symptoms of extinction, so an empirical isotropic extinction parameter similar to that used by Larson [7], except omitting polarization factors, was also refined in the final cycles of least-squares. Inclusion of this parameter alone dropped the R value from 6.5 to 3.5%. After all shift/e.s.d. ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.3 e/Å^3. All calculations were made using Nicholet's SHELXTL PLUS (1987) series of crystallographic programs.

Attempts to prepare $((Me_3Si)_3Si)_2SnH_2$

The reaction of $((Me_3Si)_3Si)_2SnCl_2$ with $LiAlH_4$ was initially carried out according to the published procedure [8] for the preparation of di-n-butyltin(IV) hydride from di-n-butyltin(IV) chloride. In a typical reaction, a solution of $((Me_3Si)_3Si)_2SnCl_2$ (200 mg, 0.29 mmol) in ethyl ether (25 ml) was slowly added to a stirred solution of $LiAlH_4$ (22 mg, 0.58 mmol) in ethyl ether (15 ml) at room temperature. The reaction was stirred for 3 h until ^1H NMR showed that the starting material had been consumed, then it was cooled in an ice bath and water was added dropwise until the hydrolysis reaction subsided, then a 2–3 ml excess was added. A solution of sodium potassium tartrate (1.0 g) in water (15 ml) was added and stirring continued for 10 min. The ether layer was separated and the aqueous layer was washed with another portion of ether (15 ml). The ether solutions were combined, dried and then the ether was removed under reduced pressure leaving a viscous oil. NMR showed that a mixture of compounds bearing $-SiMe_3$ groups was present in the oily residue. Column chromatography of the mixture in hexane placed on grade 62 silica gel (60–200 mesh) and eluted with hexane/ethyl acetate (9:1) separated the mixture into three fractions but ^1H NMR showed each fraction still contained more than one component. *Anal.* of the major fraction: Found C, 44.39; H, 10.00. Calc. for $(((CH_3)_3Si)_3Si)_2SnH_2$: C, 35.09, H, 8.52%. GC-MS analysis of solutions of the fractions in pentane, hexane and dichloromethane failed to detect any tin-containing species. Several variations on the procedure were carried out including omission of the tartrate, omission of the hydrolysis step, conducting the reaction at a lower temperature (10–15 °C) and reversal of the order of addition but the results were qualitatively the same in each.

Attempts to prepare $((CH_3)_3Si)_3SiSnH_3$

In a representative reaction aimed at preparing tris(trimethylsilyl)silyltin(IV) hydride, a solution of $LiAlH_4$ (156.0 mg, 4.126 mmol) in 60 ml of ethyl ether was slowly added with stirring to $(Me_3Si)_3SiSnCl_3 \cdot THF$ (50.0 mg, 1.38 mmol) [1] in 75 ml of ethyl ether held at 10–12 °C in an ice-water bath. The progress of the reaction was monitored using thin layer chromatography (silica gel plates). Stirring was continued until the spot representing the starting material was no longer visible. Cold water (about 10 ml) was added dropwise until the hydrolysis reaction subsided, then an additional 20 ml of water was added while stirring was maintained. After 10 min, the ether layer was separated and washed four times with 10 ml portions of water. The aqueous layer was washed with two 10 ml portions of ether and the combined ether solutions were dried. Removal of the solvent under reduced pressure left a colorless oil which was filtered to remove some suspended solid. Both ^{1}H NMR (SiMe$_3$ region: δ 0.130(s), 0.151(s), 0.170(s), 0.177(s), 0.183(s), 0.203(s), 0.212(s)) and TLC indicated that the oil consisted of a mixture of products. Column chromatography of the mixture in hexane placed on grade 62 silica gel (60–200 mesh) and eluted with hexane/ethyl acetate (9:1) was ineffective in separating the components. *Anal.* of the major fraction: Found C, 36.67; H 9.36%, indicating that incorporation of tin into the product was deficient. Calc. for $((CH_3)_3Si)_3SiSnH_3$: C, 29.3; H, 8.19%. GC-MS analysis of a pentane solution of the oil mixture with temperature programming to 250 °C detected only $(Me_3Si)_4Si$ ($m/e = 320.8$; Calc. C, 44.92; H, 11.31%; ^{1}H NMR: δ 0.20(s)) and $(Me_3Si)_3SiH$ ($m/e = 248.7$; Calc. C, 43.47; H, 11.35%; ^{1}H NMR (C_6D_6): δ 0.203–0.206, *Me*$_3$Si).

Results and discussion

The syntheses of $((CH_3)_3Si)_3SiGe(CH_3)_3$ (**I**), $((CH_3)_3Si)_3SiGe(C_6H_5)_3$ (**II**) and $(Me_3Si)_3SiGeCl_3$ (**III**) in yields of 75, 79 and 20%, respectively, were achieved by the action of $(THF)_3LiSi(Si(CH_3)_3)_3$ on the appropriate Ge(IV) chloride in diethyl ether according to eqn. (1).

$$R_3GeCl + (THF)_3LiSi(Si(CH_3)_3)_3 \longrightarrow ((CH_3)_3Si)_3SiGeR_3 + LiCl \quad (1)$$

$R = CH_3,\ C_6H_5,\ Cl$

^{1}H, ^{13}C and ^{29}Si NMR spectra were consistent with the proposed formulation of the products. The ^{1}H and ^{13}C signals of the Me$_3$Si groups in the spectrum of **I** appeared as two closely spaced lines perhaps due to conformational effects; no splitting of the ^{29}Si resonance was observed and the elemental analytical results were very close to the expected values. Products **I** and **II** are stable towards air and moisture but **III** is rapidly hydrolyzed upon exposure to air. The trimethylgermane derivative sublimed readily at 135 °C but the crystals obtained were not suitable for structure determination. The triphenyl derivative is stable up to its melting point of 265 °C. The tris(trimethylsilyl)silyl-organogermanium derivatives appear to have thermal stabilities comparable to corresponding tris(trimethylsilyl)methyl compounds, $(Me_3Si)_3CGeMe_3$ and $(Me_3Si)_3CGePh_3$, (melting points >360 and 263 °C, respectively [9–11]. Our cone angle determinations indicated that the angle of the cone with its apex at germanium and touching the outer van der Waals surfaces of the trimethylsilyl groups is greater for $(Me_3Si)_3C$–Ge than for $(Me_3Si)_3Si$–Ge, owing to the smaller radius of carbon [5]. The magnitude of the cone angles for these substituents suggest that there may be appreciable steric crowding in derivatives such as **II** where there are other large groups on germanium. In order to gauge the magnitude of these anticipated interactions, we carried out an X-ray structure determination on **II**. Figure 1 shows the molecular structure of **II**.

Table 1 lists data collection and unit cell parameters for **II**, Table 2 gives heavy atom coordinates and Table 3 lists selected bond lengths and angles found in the molecule. The Si–Ge bond length, 2.416 Å, is slightly larger than the sum of the covalent radii (2.40 Å) [12]; it exceeds the length of the Ge–Si bonds in $Me_3SiGePh_3$ (2.384 Å) [13] and $Ph_3SiGeMe_3$ (2.394) [13]. The coordination around the Ge–Si vector is somewhat distorted from tetrahedral, with the three Si–Si–Si angles being smaller (av. 108.3°) and the three Ge–Si–Si angles being larger (av. 110.7°), consistent with the presence of steric interactions between the phenyl and SiMe$_3$ groups. The relative magnitudes of the Si–Si–Si and M–Si–Si bond angles have been used as a qualitative indication of the degree of steric crowding in $R_nMSi(SiMe_3)_3$ compounds [14]. In $(\eta^5\text{-}C_5Me_5)Cl_2HfSi(SiMe_3)_3$ [14] and $(CO)_5MSi(SiMe_3)_3$ (M = Mn [15], Re [16]), the av. M–Si–Si angles exceed the av. Si–Si–Si angles leading to the conclusion that there is a greater steric interaction between the substituents on M and the SiMe$_3$ groups than among the three SiMe$_3$ groups. This circumstance is normally accompanied by a lengthened M–Si bond. Both of these conditions are observed in **II**, however an examination of intramolecular approaches found no contacts shorter than the sums of van der Waal radii of the atoms so we conclude that the degree of steric conflict between the phenyl and trimethylsilyl substituents is not pronounced in this molecule.

The Me$_3$Si groups are not oriented in the usual lowest overlap configuration where the three torsional angles of the type Ge–Si1–Si2–C21 equal 180°. Instead, the average of these angles is 160°, indicating a significant tilt which appears to be induced by interaction with

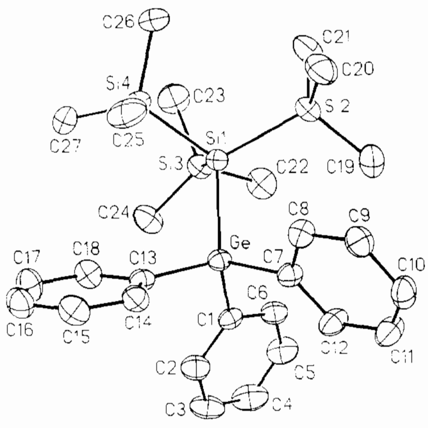

Fig. 1. Molecular structure of $Ph_3GeSi(SiMe_3)_3$ (**II**).

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Ge	6183(1)	5959(1)	914(1)	43(1)
Si(1)	6568(1)	5669(1)	1536(1)	45(1)
Si(2)	6342(1)	7616(2)	1877(1)	63(1)
Si(3)	5847(1)	3902(2)	1789(1)	60(1)
Si(4)	7913(1)	5118(2)	1584(1)	62(1)
C(1)	5182(3)	5125(4)	780(1)	48(2)
C(2)	5098(3)	4334(5)	475(1)	64(2)
C(3)	4369(3)	3834(6)	372(1)	84(3)
C(4)	3730(3)	4100(7)	573(2)	92(3)
C(5)	3804(3)	4879(6)	875(2)	80(3)
C(6)	4524(3)	5388(5)	975(1)	61(2)
C(7)	6043(3)	7850(5)	787(1)	47(2)
C(8)	6645(3)	8767(4)	868(1)	53(2)
C(9)	6536(3)	10124(5)	792(1)	60(2)
C(10)	5835(3)	10564(5)	642(1)	66(2)
C(11)	5249(3)	9678(6)	561(1)	73(2)
C(12)	5355(3)	8325(5)	630(1)	63(2)
C(13)	6970(2)	5196(4)	606(1)	44(2)
C(14)	7381(3)	5927(5)	359(1)	53(2)
C(15)	7964(3)	5373(5)	160(1)	64(2)
C(16)	8152(3)	4051(6)	199(1)	68(2)
C(17)	7752(3)	3288(5)	439(1)	70(2)
C(18)	7171(3)	3857(5)	639(1)	60(2)
C(19)	5375(3)	8381(6)	1740(2)	96(3)
C(20)	7128(3)	8913(5)	1833(1)	85(2)
C(21)	6307(3)	7127(6)	2363(1)	89(3)
C(22)	4839(3)	4413(6)	1921(1)	86(2)
C(23)	6387(3)	3281(6)	2207(1)	93(3)
C(24)	5749(3)	2481(5)	1466(1)	84(2)
C(25)	8503(3)	6106(7)	1267(1)	93(3)
C(26)	8276(3)	5520(6)	2051(1)	85(2)
C(27)	8095(3)	3288(5)	1504(2)	88(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Heavy atom bond lengths (Å) and bond angles (°)

Bond lengths			
Ge–Si(1)	2.416(1)	Ge–C(1)	1.957(4)
Ge–C(7)	1.962(4)	Gc–C(13)	1.950(4)
Si(1)–Si(2)	2.364(2)	Si(1)–Si(3)	2.366(2)
Si(1)–Si(4)	2.368(2)	Si(2)–C(19)	1.878(5)
Si(2)–C(20)	1.878(5)	Si(2)–C(21)	1.884(5)
Si(3)–C(22)	1.878(5)	Si(3)–C(23)	1.897(5)
Si(3)–C(24)	1.869(5)	Si(4)–C(25)	1.860(6)
Si(4)–C(26)	1.879(5)	Si(4)–C(27)	1.880(5)
C(1)–C(2)	1.393(6)	C(1)–C(6)	1.381(6)
C(2)–C(3)	1.386(7)	C(3)–C(4)	1.370(8)
C(4)–C(5)	1.372(8)	C(5)–C(6)	1.375(7)
C(7)–C(8)	1.405(6)	C(7)–C(12)	1.383(6)
C(8)–C(9)	1.396(6)	C(9)–C(10)	1.382(7)
C(10)–C(11)	1.365(7)	C(11)–C(12)	1.388(7)
C(13)–C(14)	1.384(6)	C(13)–C(18)	1.386(7)
C(14)–C(15)	1.378(7)	C(15)–C(16)	1.367(8)
C(16)–C(17)	1.375(7)	C(17)–C(18)	1.382(7)
Bond angles			
Si(1)–Ge–C(1)	114.0(1)	Si(1)–Ge–C(7)	112.1(1)
C(1)–Ge–C(7)	104.4(2)	Si(1)–Ge–C(13)	110.3(1)
C(1)–Ge–C(13)	107.3(2)	C(7)–Ge–C(13)	108.5(2)
Ge–Si(1)–Si(2)	112.1(1)	Ge–Si(1)–Si(3)	110.1(1)
Si(3)–Si(1)–Si(2)	107.7(1)	Ge–Si(1)–Si(4)	109.8(1)
Si(2)–Si(1)–Si(4)	108.9(1)	Si(3)–Si(1)–Si(4)	108.2(1)
Si(1)–Si(2)–C(19)	110.2(2)	Si(1)–Si(2)–C(20)	113.2(2)
C(19)–Si(2)–C(20)	108.8(2)	Si(1)–Si(2)–C(21)	108.4(2)
C(19)–Si(2)–C(21)	108.4(3)	C(20)–Si(2)–C(21)	107.7(2)
Si(1)–Si(3)–C(22)	113.2(2)	Si(1)–Si(3)–C(23)	109.1(2)
C(22)–Si(3)–C(23)	107.5(2)	Si(1)–Si(3)–C(24)	110.4(2)
C(22)–Si(3)–C(24)	108.1(2)	C(23)–Si(3)–C(24)	108.5(2)
Si(1)–Si(4)–C(25)	111.9(2)	Si(1)–Si(4)–C(26)	108.4(2)
C(25)–Si(4)–C(26)	107.8(2)	Si(1)–Si(4)–C(27)	112.3(2)
C(25)–Si(4)–C(27)	108.7(3)	C(26)–Si(4)–C(27)	107.7(3)
Ge–C(1)–C(2)	121.4(3)	Ge–C(1)–C(6)	120.3(3)
C(2)–C(1)–C(6)	118.2(4)	C(1)–C(2)–C(3)	20.2(4)
C(2)–C(3)–C(4)	120.2(5)	C(3)–C(4)–C(5)	120.3(5)
C(4)–C(5)–C(6)	119.5(5)	C(1)–C(6)–C(5)	121.6(5)
Ge–C(7)–C(8)	119.6(3)	Ge–C(7)–C(12)	122.0(3)
C(8)–C(7)–C(12)	118.4(4)	C(7)–C(8)–C(9)	119.9(4)
C(8)–C(9)–C(10)	120.0(4)	C(9)–C(10)–C(11)	120.4(5)
C(10)–C(11)–C(12)	120.0(5)	C(7)–C(12)–C(11)	121.2(4)
Ge–C(13)–C(14)	123.9(3)	Ge–C(13)–C(18)	120.0(3)
C(14)–C(13)–C(18)	116.1(4)	C(13)–C(14)–C(15)	122.5(5)
C(14)–C(15)–C(16)	120.1(5)	C(15)–C(16)–C(17)	119.1(5)
C(16)–C(17)–C(18)	120.2(5)	C(13)–C(18)–C(17)	122.0(4)

the *ortho* hydrogen of the neighboring phenyl ring (Fig. 2). The fact that the phenyl rings are canted with an average torsional twist of 54° with respect to the Ge–Si axis is another indication of the presence of a steric interaction between these substituents. These observations suggest that the strain resulting from some crowding around Ge is mostly accommodated by twisting distortions.

Our previous studies of some trimethylsilane-Group 14 derivatives suggest that bond length and bond angle values from minimum energy structures derived from molecular mechanics calculations closely match those determined by X-ray diffraction [3,17]. These studies were extended here by determining the energy-minimized structures for the new derivatives using the MMX force field (Table 4). Again, heavy atom bond distances and angles of the minimized structure of **II** agree well with those determined by diffraction. MMX predicts slightly shorter Ge–Si and average Si–Si bond lengths for **I** and **III** than found for **II** consistent with less steric crowding between the R_3Ge (R = Me, Cl) and $Si(SiMe_3)_3$ groups. This indication is confirmed by the findings that the average Si–Si–Si angle exceeds the average Ge–Si–Si angle and that the angles around Ge are closer to the tetrahedral value. It is interesting that these angles differ minimally between **I** and **III** suggesting that, insofar as the MMX force field reflects them, the different inductive effects of the methyl and chlorine substituents have little influence on the geometry around Ge.

Our attempts to prepare the silyltin hydrides $(Me_3Si)_3SiSnH_3$ and $((Me_3Si)_3Si)_2SnH_2$ via the reaction

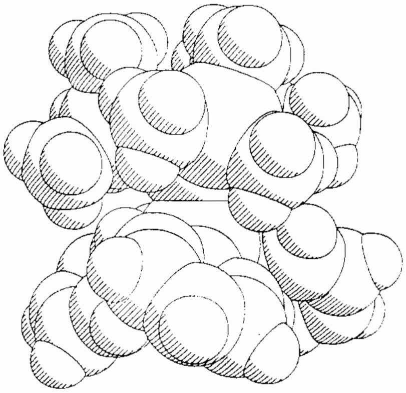

Fig. 2. Space filling rendering of **II** showing a side view.

TABLE 4. Comparison of bond distances and angles from X-ray structure determination and from molecular mechanics[a,b] calculations

$(C_6H_5)_3Si(Si(CH_3)_3)_3$	X-ray results	Mol. mech. results[a]	Mol. mech. results[b]
Bond distances (Å)			
Ge–Si(1)	2.416(1)	2.428	2.4
Si–Si(av.)	2.366	2.382	2.4
Bond angles (°)			
Ge–Si–Si (av.)	110.7	110.9	111.2
Si–Si–Si (av.)	108.3	108.0	107.7
Si(1)–Ge–C (av.)	112.1	109.7	106.9

	$(CH_3)_3GeSi(Si(CH_3)_3)_3$	$Cl_3GeSi(Si(CH_3)_3)_3$
Mol. mech. results[a]		
Bond distances (Å)		
Ge–Si(1)	2.420	2.415
Si–Si (av.)	2.368	2.365
Bond angles (°)		
Ge–Si–Si (av.)	108.7	108.4
Si–Si–Si (av.)	110.2	110.5
Si(1)–Ge–C (av.)	109.7	109.5

[a]Obtained using PCModel's implementation of the MMX force field, Serena Software, Bloomington, IN. [b]Obtained using Alchemy II incorporating the TRIPOS force field, Tripos Associates, St. Louis, MO. Added Si–C and Si–Si bond distances of 1.860 and 2.332 Å, and stretching constants of 503 and 266 kcal/mol^{-1} Å^{-2}, respectively, to minbnd.tab table.

of silyltin halides with $LiAlH_4$ in etheral solution, following known synthetic methods for analogous organotin(IV) hydrides [18], were unsuccessful. Although IR bands in the region 1820–1880 cm^{-1}, the range reported as characteristic of Sn–H groups in R_2SnH_2 and $RSnH_3$ species [19], were observed for the colorless oil products of the reactions, the bands were weak to very weak in intensity instead of the intense, sharp peaks reported for the alkyltin hydrides. The absence of ^1H NMR signals in the range of δ 4.2 to 5.2, reported for the Sn–H protons of alkyltin(IV) hydrides [20], also indicated that silyltin(IV) hydrides, if formed, did not persist in the reaction mixture. Both ^1H and TLC showed the products to be mixtures. Our attempts to separate the mixtures using column chromatography gave incomplete separations. Elemental analysis of the major fraction gave %C and %H results too high for the expected formulas of any silyltin hydride or hydride chloride suggesting that tin was either not present or deficient in the product(s). Investigation of the fractions using temperature programmed capillary column GC-MS revealed the presence of $((CH_3)_3Si)_3SiH$ and traces of $((CH_3)_3Si)_4Si$ (which is the precursor of $LiSi(Si(CH_3)_3)_3$); no tin-containing species were detected. The fact that the title compounds were not obtained by the reactions carried out in this study may mean that the methods chosen simply do not produce them or that the compounds, if formed, are thermally unstable at room temperature. Since the starting materials are consumed in every reaction and chloride is found in the aqueous washings, we favor the latter explanation.

In order to assess the thermal stability of $(Me_3Si)_3SiSnH_3$, we conducted MNDO calculations (using the MNDO module from MOPAC Version 2.14), on the molecule and on $(Me_3Si)_3SiH$. Full structural optimization was carried out on each molecule. The ΔH_f values thus computed were -64.9 kcal mol^{-1} for $(Me_3Si)_3SiSnH_3$ and -89.2 kcal mol^{-1} for $(Me_3Si)_3SiH$. Using these values, the ΔH of reaction for the decomposition shown in eqn. (2) is -48.6 kcal mol^{-1}. Since ΔS should be positive for the reaction, the free

$$2((CH_3)_3Si)_3SiSnH_3 \longrightarrow 2((CH_3)_3Si)_3SiH + 2Sn + 3H_2 \qquad (2)$$

energy change will be negative, indicating that the reaction should be spontaneous. Thus eqn. (2) represents a likely decomposition route for the silyltin hydride although other pathways are also possible.

Supplementary material

The following tables of Supplementary Material are available from author. R.A.G: S1, anisotropic displacement parameters for **II**; S2, H-atom coordinates and isotropic displacement parameters for **II**; S3, torsion angles for **II**; S4, observed and calculated structure factors for **II**.

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