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Synthesis, structure, and reactivity of the permethylated decasilane $(Me_3Si)_3Si{-}SiMe_2{-}SiMe_2{-}Si(SiMe_3)_3$ [☆]

Stephen M. Whittaker, Mari-Carmen Brun, Francisco Cervantes-Lee, Keith H. Pannell *

Department of Chemistry, The University of Texas at El Paso El Paso, TX 79968-0513, USA

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Abstract

The reaction between $ClMe_2SiSiMe_2Cl$ and two equivalents of $(Me_3Si)_3SiLi \cdot 3THF$ resulted in a 40% yield of $(Me_3Si)_3Si{-}SiMe_2{-}SiMe_2{-}Si(SiMe_3)_3$, **I**. **I** crystallized in space group $P\bar{1}$, $a = 9.229(2)$ Å, $b = 9.312(2)$ Å, $c = 13.709(3)$ Å, $\alpha = 104.15(2)°$, $\beta = 91.35(2)°$, $\gamma = 114.64(2)°$. The internal Si–Si bond lengths ($(Me_3Si)_3Si{-}SiMe_2$) (**B**) and ($Me_2Si{-}SiMe_2$) (**C**) are equivalent at 237.5(1) pm and 237.4(2) pm, respectively, and marginally longer than the terminal $Me_3Si{-}Si$ bonds **A** which are in the range 234.5(1)–236.1(2) pm. The $Me_3Si{-}Si{-}SiMe_2$ angle of 115.3(1)° and $Me_3SiSi{-}SiMe_2{-}SiMe_2$ angle of 117.1(1)° are the major structural deformations that reflect the steric complexity of the molecule. Photochemical irradiation of **I** in CCl_4 leads to predominant cleavage of the central Si–Si bond **C** with minor cleavage of bond **B**; photochemistry in hexane is more indiscriminate, both **B** and **C** were homolytically cleaved but silylene eliminations and secondary reactions also occurred. Treatment with Li or MeLi led to cleavage of Si–Si bonds **B** and **C**. In the case of Li, predominant cleavage of **B** was observed (> 90%), whereas with MeLi cleavage took place at bond **C** (> 90%).

Keywords: Silicon; Decasilane; Photochemistry; X-ray diffraction; Lithium; Methyl lithium

1. Introduction

Tris(trimethylsilyl)silane derivatives of the Group 14 elements of the type $(Me_3Si)_3Si{-}EX_2EX_2{-}Si(SiMe_3)_3$, E = Ge; X = Cl, Me or Ph [1], E = Pb; X = Ph [2], have recently been reported. The synthetic procedures used were not obvious. The germanium products were suggested to result from the thermal decomposition of a target molecule $[(Me_3Si)_3Si]_2GeR_2$, presumably due to steric congestion at the central atom. Examples of the related Sn and Pb compounds $[(Me_3Si)_3Si]_2ER_2$, E = Sn or Pb, where the larger size of the Group 14 metal precludes significant steric congestion, are stable isolable compounds [3]. The mode of formation of the diplumbane $[(Me_3Si)_3SiPbPh_2]_2$ involved a more complex process [2].

The related silicon analog $(Me_3Si)_3Si{-}SiMe_2SiMe_2{-}Si(SiMe_3)_3]$ (**I**) was reported in 1981 by the Kumada group from the $AlCl_3$-catalyzed transformation of the linear decasilane $Me_3Si(SiMe_2)_8SiMe_3$ [4]. This high yield reaction is also a complex route because of the prior synthesis of the linear decasilane. We now report the systematic synthesis of **I** from the readily available reactants $(Me_3Si)_3SiLi$ and $ClSiMe_2SiMe_2Cl$, together with its X-ray structural analysis, photochemistry, and reactivity with Li and MeLi.

2. Experimental details

All solvents were used dry and oxygen-free; 1,2-dichlorotetramethyldisilane was prepared by literature procedures [5]; methyllithium was purchased from Aldrich. NMR spectra were obtained from a Bruker NR 200 or 250 MHz instrument, and GC–MS data were recorded on a Hewlett-Packard 5890/5871 instrument with 70 eV ionizing voltage.

2.1. Preparation of $[(Me_3Si)_3SiSiMe_2]_2$, I

A solution of 28.1 mmol of $(Me_3Si)_3SiLi$ prepared from 9 g (28.1 mmol) of $(Me_3Si)_4Si$ and 20 ml of a 1.4 M methyllithium ether solution in 50 ml of toluene was added dropwise over a period of 30 min to an ice-cooled 40 ml toluene solution of 2.9 g (15.5 mmol) of

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[☆] Dedicated to Prof. Hideki Sakurai on the occasion of his retirement from Tohoku University. Hideki: Happy retirement from Tohoku University and good luck at Science University of Tokyo.

* Corresponding author.

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$ClMe_2SiSiMe_2Cl$. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. Filtration of the white precipitate and evaporation of the solvent under reduced pressure gave a white solid which was crystallized from hexane to give colorless crystals of **I** (3.75 g, 40%), m.p. 238–240°C; ^1H NMR (δ in $CDCl_3$) 0.21 (s, Me_3Si), 0.35 (s, Me_2Si); ^{13}C NMR (δ in $CDCl_3$) 1.2, 3.6; ^{29}Si NMR (δ in $CDCl_3$) −9.04, −29.5, −119.6; UV (in hexane) λ_{max} 258 nm (ε 24000). Anal. Calc. for $C_{22}H_{66}Si_{10}$: C, 43.20; H, 10.88%; Found C, 43.58; H, 10.90%.

2.2. Photolysis of $[(Me_3Si)_3SiSiMe_2]_2$ in hexane

A 2 ml hexane solution of **I** (150 mg, 0.25 mmol) in a quartz tube, under an atmosphere of dinitrogen, was irradiated with a 450 W low-pressure mercury lamp for 22 h at a distance of 4 cm. After this time > 95% of **I** had been consumed. The resulting mixture was analyzed by GC–MS as being $(Me_3Si)_4Si$, **II**, (8%) MS *m/z* 320 $[M]^+$; $(Me_3Si)_3SiMe$, **III**, (5%) MS *m/z* 262 $[M]^+$; $(Me_3Si)_3SiSiMe_2SiMe_3$, **IV**, (11%) MS *m/z* 378 $[M]^+$; $(Me_3Si)_3SiH$, **V**, (5%) MS *m/z* 248 $[M]^+$; $(Me_3Si)_3SiSiMe_2H$, **VI**, (23%) MS *m/z* 306 $[M]^+$; $(Me_3Si)_3SiSiMe_2SiMe_2H$, **VII**, (9%) MS *m/z* 364 $[M]^+$; $[(Me_3Si)_3Si]_2$, **VIII**, (13%) MS *m/z* 494 $[M]^+$. Photolysis in the presence of 2,3-dimethylbutadiene resulted in the formation of 8% of 1,1-dimethylsila-3,4-dimethylcyclopentene [11].

A similar irradiation for 2 h (when only 66% of the starting material was consumed) led to the following product distribution: **II**, 1.5%; **III**, 0.5%; **IV**, 10%; **V**, 0%; **VI**, 22%, **VII**, 7%; **VIII**, 11%; $(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3$, **IX**, 24%.

2.3. Photolysis of $[(Me_3Si)_3SiSiMe_2]_2$ in the presence of CCl_4

A 5 ml CCl_4 solution of **I** (200 mg, 0.33 mmol) in a quartz tube under an atmosphere of dinitrogen was irradiated as noted above for 9 h. After this time all of **I** had been consumed. The resulting mixture was analyzed by GC–MS as being $(Me_3Si)_3SiSiMe_2SiMe_3$, **IV**, (1.5%) MS *m/z* 378 $[M]^+$; $(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3$, **IX**, (2%) MS *m/z* 436 $[M]^+$; $(Me_3Si)_3SiCl$, **X** (5%) MS *m/z* 282 $[M]^+$; $(Me_3Si)_2SiCl_2$, **XI**, (1%) MS *m/z* 244 $[M]^+$; $(Me_3Si)_3SiSiMe_2SiMe_2Cl$, **XII**, (25%) MS *m/z* 398 $[M]^+$; $Me_{12}Si_6Cl_2$, **XIII**, (1.5%) MS *m/z* 419 $[M]^+$; $(Me_3Si)_3SiSiMe_2Cl$, **XIV**, (45%) MS *m/z* 325 $[M–Me]^+$, ^{29}Si NMR(C_6D_6) −129.2 ($SiSi_4$), −9.7 (Me_3Si), 32.7 ($SiMe_2Cl$) ppm, and $Me_{10}Si_5Cl_2$, **XV**, (5%) MS *m/z* 345 $[M–Me]^+$.

2.4. Reaction of $[(Me_3Si)_3SiSiMe_2]_2$ with Li

To a solution of **I** (0.65 g, 1.06 mmol) in 10 ml of THF was added 20 mg of naphthalene and 74 mg (10.7 mmol) of Li metal and the mixture was stirred overnight. A 1-ml aliquot of the resulting red–orange solution was then quenched with MeI. After removal of the solvent under reduced pressure, the residue was extracted with 5 ml hexane and the LiI removed by filtration. Subsequent removal of the solvent under reduced pressure produced a white solid which was shown by GC–MS analysis to be a mixture of $(Me_3Si)_3SiMe$, **III**, (63%); $(Me_3Si)_3SiSiMe_2SiMe_3$, **IV**; (29%) and $(Me_3Si)_2SiMeSiMe_2SiMe_2Si(SiMe_3)_3$, **XVI**, (6.5%) MS *m/z* 537 $[M–Me]^+$. Further 1-ml aliquots were taken and quenched with MeI over the next 5 d as the color of the solution slowly faded. Examination of the aliquots by GC–MS showed a gradual change in product distribution. Thus, after 20 h reaction time the ratio of products was, **III** (59%), **IV** (33%) and **XVI** (4%), and the product distributions after varying time periods are recorded below.

66 h: $(Me_3Si)_4Si$, **II**, (12%); **III**, (59%); **IV**, (11%); $(Me_3Si)_3SiH$, **V**, (8%).

90 h: **II** (57.5%); **III** (36%); **IV** (2%); **V** (4%).

120 h: **II** (93%); **III** (3.5%); **V** (3%).

2.5. Reaction of $[(Me_3Si)_3SiSiMe_2]_2$ with MeLi

To a solution of **I** (1 g, 1.64 mmol) in 10 ml of THF was added 1.3 ml (1.82 mmol) of a 1.4 M methyllithium ether solution and the mixture was stirred overnight. The resulting lemon-yellow solution was then quenched with MeI. After removal of the solvent under reduced pressure, the residue was extracted with 15 ml hexane and the LiI was removed by filtration. Removal of the solvent under reduced pressure gave a white solid which was shown by GC–MS analysis to be a mixture of $(Me_3Si)_4Si$, **II** (92%) MS *m/z* 320 $[M]^+$; $(Me_3Si)_3SiMe$, **III** (7%) MS *m/z* 262 $[M]^+$; and $(Me_3Si)_3SiSiMe_2SiMe_3$, **IV** (1%) MS *m/z* 378 $[M]^+$.

2.6. Structural determination of I

A colorless fragment of approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre for X-ray examination and data collection. All data were collected at room temperature on a Siemens R3m/v single-crystal diffractometer with graphite-monochromated Mo Kα radiation; λ (Mo Kα) = 0.71073 Å. Unit cell parameters and standard deviations were obtained by least-squares fit of 25 randomly selected reflections in the 2θ range of 15–30°. Intensity data were collected in the ω-scan mode with a scan range of 1.2° in ω and a variable speed of 3–15 deg min^{-1}. Background counts were taken with a stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored every 97 reflections and showed no significant decay. The data were corrected for Lorentz and polarization effects and a semi-empirical absorption correction with min./max. transmission = 0.926/0.960 was also applied.

TABLE 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Si(1)	1956(1)	1535(1)	2162(1)	38(1)
Si(2)	4221(1)	3676(1)	1856(1)	50(1)
Si(3)	2910(2)	165(1)	3061(1)	56(1)
Si(4)	549(1)	2669(1)	3267(1)	52(1)
Si(5)	235(1)	−478(1)	687(1)	44(1)
C(1)	5269(5)	2862(6)	880(3)	74(3)
C(2)	5731(5)	4872(5)	3033(3)	80(2)
C(3)	3619(6)	5146(5)	1448(3)	77(3)
C(4)	1288(6)	−1846(5)	3098(3)	77(3)
C(5)	4569(6)	−215(6)	2478(4)	90(3)
C(6)	3741(6)	1429(6)	4409(3)	88(3)
C(7)	−778(6)	1170(6)	3913(3)	89(3)
C(8)	−748(5)	3313(6)	2599(3)	74(3)
C(9)	1983(6)	4532(5)	4272(3)	83(3)
C(10)	−1731(5)	−1596(5)	1134(3)	71(2)
C(11)	1091(6)	−1983(5)	218(3)	71(2)

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

The space group was found to be $P\bar{1}$. The structure was solved by direct methods and refined by full-matrix least-squares using the VMS version of the SHELXTL-PLUS software package minimizing $\Sigma w(Fo - Fc)^2$. All non-hydrogen atoms were placed at calculated positions with C–H bond distances of 0.96 Å and average isotropic thermal parameters of 0.08. The weighting scheme has the form $w^{-1} = \sigma^2(F) + gF^2$ with $g = 0.0003$ and the final R factors the form $R = \Sigma | Fo - Fc | / \Sigma Fo$ and $Rw = [w | Fo - Fc |^2 / \Sigma Fo^2]^{1/2}$ with the corresponding values of 0.043 and 0.042.

Unit cell dimensions determined were $a = 9.229(2)$ Å, $b = 9.312(2)$ Å, $c = 13.709(3)$ Å, $\alpha = 104.15(2)°$, $\beta = 91.35(2)°$, $\gamma = 114.64(2)°$. Atomic coordinates are recorded in Table 1, and bond lengths and angles in Table 2.

3. Results and discussion

Compound I was prepared in moderate (40%) yield by addition of 2 equivalents of $(Me_3Si)_3SiLi$ to $ClMe_2SiSiMe_2Cl$ (Eq. 1).

$$(Me_3Si)_3SiLi + ClMe_2SiSiMe_2Cl \rightarrow (Me_3Si)_3Si\text{–}SiMe_2SiMe_2\text{–}Si(SiMe_3)_3 \quad (1)$$

This represents a systematic salt-elimination reaction, and differs from the mode of formation of the other Group 14 analogs, $(Me_3Si)_3SiER_2ER_2Si(SiMe_3)_3$, E = Ge, Pb, and the original report of **I**. The published report for the synthesis of the Ge analog from the reaction between $(Me_3Si)_3SiLi$ and Me_2GeCl_2 suggested the initial step to be the formation of the di-substituted compound $[(Me_3Si)_3Si]_2GeR_2$. The instability of this species, due to severe steric interactions, resulted in cleavage of the Ge–Si bond with loss of a tris(trimethylsilyl)silyl radical to produce the monosilyl-substituted germyl radical $[(Me_3Si)_3SiGeR_2]^{\cdot}$ which dimerized to the observed product (Eq. 2) [1].

$$(Me_3Si)_3SiLi + Me_2GeCl_2 \rightarrow [((Me_3Si)_3Si)_2GeMe_2] \rightarrow [(Me_3Si)_3SiGeMe_2]^{\cdot} \quad (2a)$$

$$2[(Me_3Si)_3SiGeMe_2]^{\cdot} \rightarrow (Me_3Si)_3Si\text{–}GeMe_2GeMe_2\text{–}Si(SiMe_3)_3 \quad (2b)$$

For the Pb analog, $EX_2 = PbPh_2$, from a similar reaction between $(Me_3Si)_3SiLi$ and Ph_2PbCl_2, a more complex reaction was suggested since the disubstituted lead compound $[(Me_3Si)_3Si]_2PbPh_2$ was isolable and did not decompose to the diplumbane [2]. The initial formation of a monosilyl-substituted plumbane, $(Me_3Si)_3SiPbPh_2Cl$, was suggested, that subsequently reacted with a second equivalent of the silyllithium to produce $[(Me_3Si)_3Si]_2$ and the monosilyl-substituted plumbyl radical which then dimerized to the observed product (Eq. 3).

$$(Me_3Si)_3SiLi + Ph_2PbCl_2 \rightarrow [(Me_3Si)_3SiPbPh_2Cl] \quad (3a)$$

$$[(Me_3Si)_3SiPbPh_2Cl] \xrightarrow{(Me_3Si)_3SiLi} [(Me_3Si)_3Si]_2 + [(Me_3Si)_3SiPbPh_2]^{\cdot} \quad (3b)$$

$$2[(Me_3Si)_3SiPbPh_2] \rightarrow (Me_3Si)_3Si\text{–}PbPh_2PbPh_2\text{–}Si(SiMe_3)_3 \quad (3c)$$

While the arguments outlined above for the formation of the digermane and diplumbane molecules are

TABLE 2
Bond lengths (Å) and angles (°)

Si(1)–Si(2)	2.345(1)	Si(1)–Si(3)	2.361(2)
Si(1)–Si(4)	2.355(2)	Si(1)–Si(5)	2.375(1)
Si(2)–C(1)	1.864(5)	Si(2)–C(2)	1.873(4)
Si(2)–C(3)	1.868(6)	Si(3)–C(4)	1.862(4)
Si(3)–C(5)	1.865(6)	Si(3)–C(6)	1.873(4)
Si(4)–C(7)	1.862(5)	Si(4)–C(8)	1.856(6)
Si(4)–C(9)	1.868(4)	Si(5)–C(10)	1.882(4)
Si(5)–C(11)	1.873(6)	Si(5)–Si(5A)	2.374(2)
Si(2)–Si(1)–Si(3)	107.0(1)	Si(2)–Si(1)–Si(4)	109.0(1)
Si(3)–Si(1)–Si(4)	106.1(1)	Si(2)–Si(1)–Si(5)	115.3(1)
Si(3)–Si(1)–Si(5)	106.9(1)	Si(4)–Si(1)–Si(5)	111.9(1)
Si(1)–Si(2)–C(1)	111.2(1)	Si(1)–Si(2)–C(2)	111.2(1)
C(1)–Si(2)–C(2)	106.6(2)	Si(1)–Si(2)–C(3)	110.1(2)
C(1)–Si(2)–C(3)	110.5(2)	C(2)–Si(2)–C(3)	107.2(2)
Si(1)–Si(3)–C(4)	112.0(2)	Si(1)–Si(3)–C(5)	111.2(2)
C(4)–Si(3)–C(5)	108.3(2)	Si(1)–Si(3)–C(6)	111.0(2)
C(4)–Si(3)–C(6)	107.2(2)	C(5)–Si(3)–C(6)	107.0(2)
Si(1)–Si(4)–C(7)	111.4(2)	Si(1)–Si(4)–C(8)	112.6(1)
C(7)–Si(4)–C(8)	107.1(2)	Si(1)–Si(4)–C(9)	110.7(2)
C(7)–Si(4)–C(9)	107.7(2)	C(8)–Si(4)–C(9)	107.1(2)
Si(1)–Si(5)–C(10)	105.4(1)	Si(1)–Si(5)–C(11)	108.2(1)
C(10)–Si(5)–C(11)	107.8(2)	Si(1)–Si(5)–Si(5A)	117.1(1)
C(10)–Si(5)–Si(5A)	109.6(2)	C(11)–Si(5)–Si(5A)	108.4(2)

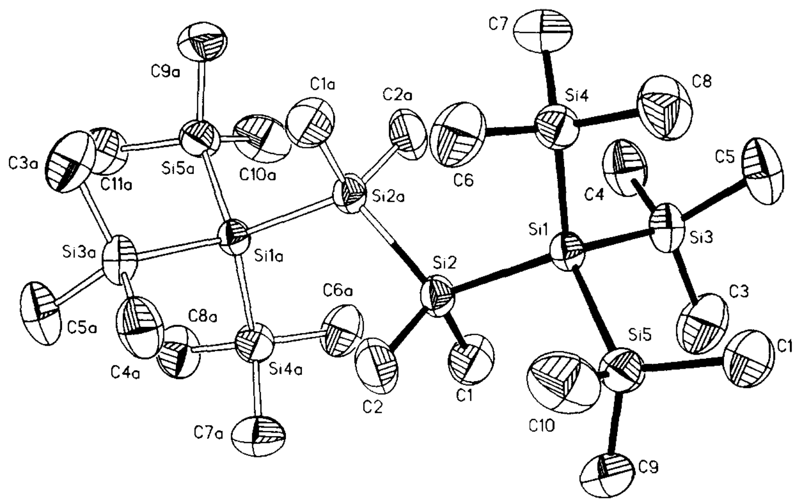
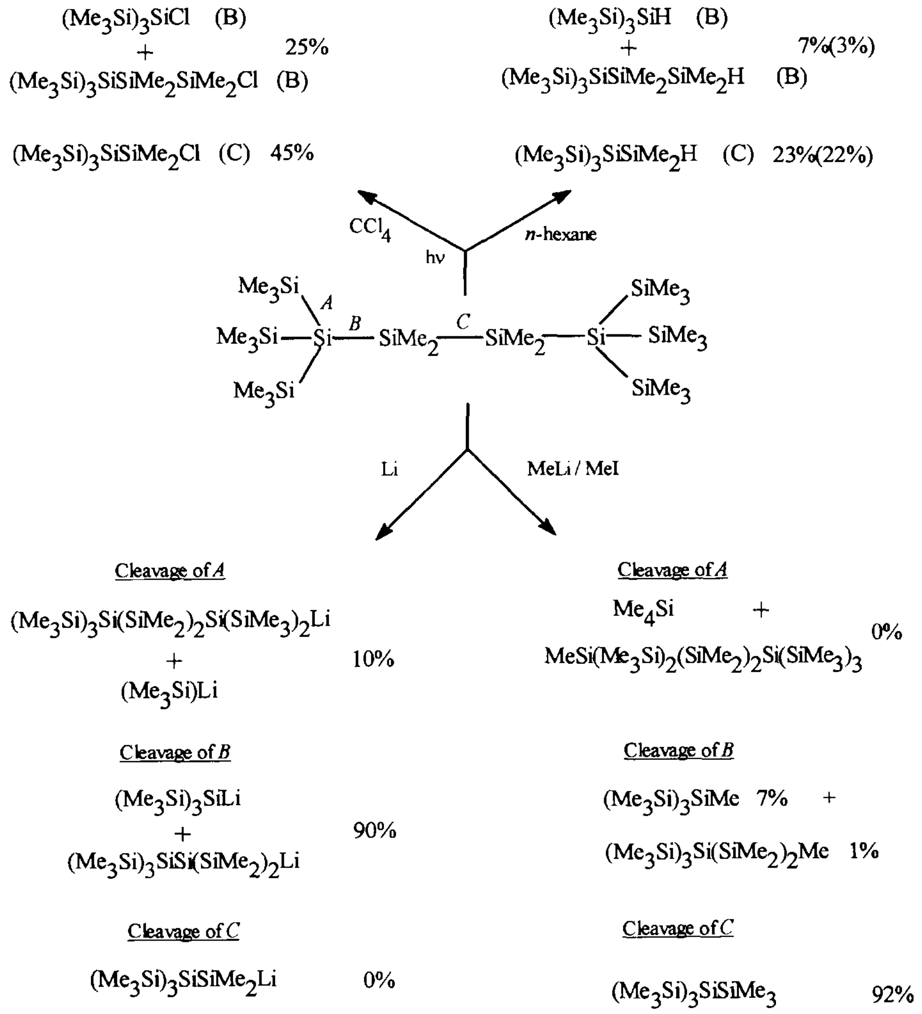


Fig. 1. The crystal structure of **I**.

reasonable, there remains a question as to the stability of the $(Me_3Si)_3Si$ derivatives of the group 14 element system, $[(Me_3Si)_3Si]_2ER_2$. The Pb and Sn compounds are stable materials, whilst that of Ge was suggested to be an unstable intermediate en route to the formaton of the digermane. This trend suggests that the silane ana-



Scheme 1. Product distributions from cleavage of bonds A, B, and C in I via photolysis and treatment with Li and MeLi.

log, $[(Me_3Si)_3Si]_2SiMe_2$, should also be unstable since the bulk of the $(Me_3Si)_3Si$ group at Si should be the most disadvantageous. However, this molecule is reported in the literature; hence the dichotomy. Possibly the route of formation may play a key role in such considerations, since the reported synthesis of $[(Me_3Si)_3Si]_2SiMe_2$ involved an $AlCl_3$-catalyzed intramolecular rearrangement from a preformed linear nonasilane [4].

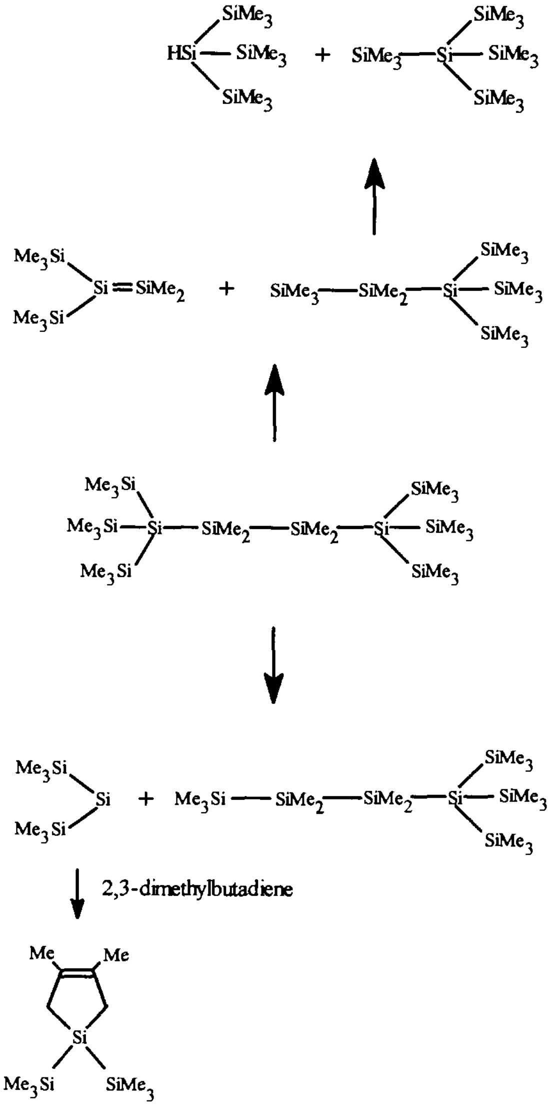
3.1. Structural analysis of I

The single crystal X-ray determined structure of **I** is illustrated in Fig. 1, and the atomic coordinates and geometric parameters are listed in Tables 1 and 2, respectively. The primary feature of the structure is that any structural deformations created by the steric bulk of the two $(Me_3Si)_3Si$ groups is manifested primarily in angular distortions and not as bond length extensions. Thus, the central Si–Si bond, $Me_2Si–SiMe_2$, **C**, has a length of 237.4(2) pm which is shorter than the central Si–Si bond in hexakis(trimethylsilyl)disilane, $[(Me_3Si)_3Si]_2$, (240.3(2) pm), a much more crowded molecule [6]. The other internal Si–Si bond, $(Me_3Si)_3Si–SiMe_2$, **B**, has an internuclear distance of 237.5(1) pm while the terminal Me_3Si–Si bonds, **A**, are in the normal range for permethylated Si–Si bonds, 234.5(1)–237.5(1) pm [7]. The terminal Me_3Si Si–C bond distances range from 185.6(6)–188.2(4) pm which is similar to the range observed for the Si–C distances in hexakis(trimethylsilyl)disilane, 185.5(4)–187.6(3) pm, but significantly different to the larger range observed for $[(Me_3Si)_3SiPbPh_2]_2$, 184.4(12)–191.0(10) [2]. Although most of the skeletal bond angles fall within 2° of the expected tetrahedral values, both the Si(1)–Si(5)–Si(5a) angle, 117.1(1)° and Si(2)–Si(1)–Si(5) angle, 115.3(1)° are significantly larger. It is via such deformations that the steric bulk of the molecule is accommodated. The relief of steric strain by distortion of certain bond angles has been observed previously in the related compounds $[(Me_3Si)_3CSiH_2]_2$, with a C–Si–Si angle of 120.1(1)° [8]; $(Bu^t_3SiSiH_2)_2$, Si–Si–Si angle $\approx 120°$ [9]; and $Me_3CSiMe_2GeMe_2SnPh_3$ [10], with C_{methyl}–Si–C_{methyl} and C–Ge–C bond angles reduced to 107.9° and 106.3°, respectively, and the chain angles C–Si–Ge and Si–Ge–C enlarged to 112.5° and 116°, respectively.

3.2. Photochemistry of I

We performed a photochemical investigation of **I** under two different environments; in CCl_4 and in hexane. In the former case any radicals produced would be quenched with Cl, while in the second environment H abstraction would be the preferred route. The results from the irradiation of **I** in CCl_4 are outlined in Scheme 1. There are essentially two modes of photochemical reaction in CCl_4, cleavage of the Si–Si bonds **B** and **C** to produce the products $[(Me_3Si)_3SiCl$ (**X**) + $(Me_3Si)_3SiSiMe_2SiMe_2Cl$ (**XII**)] from cleavage of bond **B**, and $(Me_3Si)_3SiSiMe_2Cl$ (**XIV**) from cleavage of bond **C**. Secondary chlorinations occurred upon prolonged irradiation that involve methyl–silicon bond cleavage, but the primary photochemistry is the former Si–Si bond cleavage reactions. The relative amounts of the two sets of products indicate that the central Si–Si bond, **C**, is the more susceptible to cleavage under these conditions.

Photochemical irradiation of **I** in hexane led to a more complex set of products. Again cleavage of the Si–Si bonds **B** and **C** was significant, (with the cleavage of the central bond **C** being favored) leading to formation of $(Me_3Si)_3SiH$ (**V**), $(Me_3Si)_3SiSiMe_2SiMe_2$-H (**VII**) and $(Me_3Si)_3SiSiMe_2H$ (**VI**), respectively (Scheme 1). These Si–Si homolysis products accounted for 35% of the total product formation. Such chemistry is similar to that recently reported by Oshita et al. from



Scheme 2. Product distribution from photochemistry of I in hexane via nonradical pathways.

studies on the photochemistry of some branched penta- and hexasilanes [11]. As the degree of steric congestion in their compounds increased, the degree of Si–Si bond scission increased. Thus, whereas photolysis of $(Me_3Si)_2SiMe–SiMe_2SiMe_3$ did not result in Si–Si bond homolysis, photolysis of $(Me_3Si)_3Si–SiMe_2SiMe_3$ exhibited such cleavage to produce $(Me_3Si)_3Si$ (and thence $(Me_3Si)_3SiH$), and photolysis of $[(Me_3Si)_3Si]_2$ produced significantly more of the same product. From this trend, it is to be expected that I should exhibit a significant amount of Si–Si bond homolysis as noted.

The other products obtained by the hexane photolysis of **I** stem from rearrangements and/or silylene eliminations, presumably nonradical processes, i.e. $(Me_3Si)_3SiMe$ (**III**), $(Me_3Si)_3SiSiMe_2SiMe_3$ (**IV**), $(Me_3Si)_4Si$ (**II**), and $[(Me_3Si)_3Si]_2$ (**VIII**) (Scheme 2). We suggest that product **IV** stems from expulsion of $(Me_3Si)_2Si{=}SiMe_2$, and **II** from loss of Me_2Si from **IV** as noted in the literature, although we have been unable to trap these intermediates [11]. As with the Oshita study, we also observed a significant amount of $(Me_3Si)_3SiMe$, and presume that this stems, in part, from the elimination of the silylene $(Me_3Si)_3SiSiMe_2SiMe$ from **I**. Irradiation for a shorter time period, 2 h, when only 66% of **I** was consumed, resulted in a different product distribution. Considerably less $(Me_3Si)_3SiH$ ($\ll 1\%$) and $(Me_3Si)_4Si$ ($< 1\%$) were formed, whereas there was still a significant amount of $(Me_3Si)_3SiSiMe_2H$, 22%. This observation suggests that it is bond **C** that is most prone to photochemical cleavage, and that $(Me_3Si)_3SiH$ and $(Me_3Si)_4Si$ observed from prolonged irradiation (6% and 8%, respectively) are produced by secondary reactions of **IV** and **VIII**, as noted by Oshita et al. [11]. The short irradiation also produced a significant amount of $(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3$, resulting from the elimination of $(Me_3Si)_2Si$, that was not observed upon prolonged irradiation due to its subsequent further reactivity. Using 2,3-dimethylbutadiene we were able to trap this silylene as the appropriate 1,1-dimethylsila-3,4-dimethylcyclopentene. Overall, the photochemistry of **I** in an inert solvent is complex owing to the various possible reaction pathways of the molecule itself, and the variety of secondary reactions.

3.3. Treatment of I with Li and MeLi

As with the photochemistry, treatment of **I** with Li and MeLi may be expected to result in predominant cleavage of the Si–Si bonds. There is much precedent in the literature for the cleavage of Si–Si bonds by both lithium and organolithium reagents as convenient routes to the formation of silyllithium reagents [12].

The reaction of lithium metal with **I** was complete after 14 h, and resulted in the cleavage of Si–Si bonds **A** and **B**, (Scheme 1). Of these bonds, it was predominantly bond **B** that reacted, > 90%; there was no significant cleavage of the central bond **C** by lithium. If the reaction mixture of **I** and Li was permitted to stir unquenched for a long period of time the ultimate product was $(Me_3Si)_4Si$ along with $(Me_3Si)_3SiH$. There are several examples in the literature that illustrate the tendency of $(Me_3Si)_3SiLi$ to react with permethylated silanes to yield $(Me_3Si)_4Si$ (**II**) [13]; furthermore, we permitted a solution of $(Me_3Si)_3SiLi$ to sit for two weeks in solution and observed the predominant formation of **II**.

The reactions of **I** with MeLi resulted in the predominant cleavage of the central bond **C**, to form $(Me_3Si)_3SiSiMe_3$ and $(Me_3Si)_3SiSiMe_2Li$, a reaction in contrast to that noted above for Li. It is thus possible to use such distinctions for synthetic utility by preferential silyllithium formation, i.e. either $[(Me_3Si)_3SiSiMe_2]^-$ from MeLi or $[(Me_3Si)_3Si]^-$ and $[(Me_3Si)_3SiSiMe_2SiMe_2]^-$ from Li. The small amount of **IV** formed cf. **III**, suggests that the latter may primarily occur via a secondary reaction between the initially formed $(Me_3Si)_3SiMe_3$ and MeLi, thus emphasizing the cleavage of the central bond **C**.

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