

Crystal Structure of the 1,3-Disilacyclobutane Derivative $(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{C}(\text{SiMe}_3)_2\text{SiMe}_2^\dagger$

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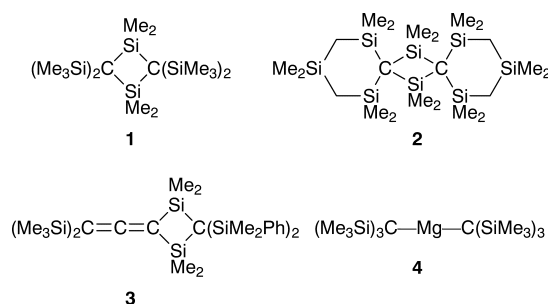
The disilacyclobutane ring in the title compound is planar but not quite square [C–Si–C 93.84(10), Si–C–Si 86.16(13)°]; unusual features are attributed to cross-ring steric interactions between Me groups.

Following a preparation of the compound $\text{CH}_2\text{SiMe}_2(\text{SiMe}_3)_2\text{CSn}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2 \cdot \text{tmen}$ (tmen = *N,N,N',N'*-tetramethylethylenediamine) from SnCl_2 and $[\text{Li}(\text{tmen})_2][\text{CH}_2\text{SiMe}_2(\text{SiMe}_3)_2\text{CLi}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2]$ as previously described,¹ the red mother-liquor left after crystallization of the product from light petroleum was exposed for a short time to laboratory light at room temperature. The solution was then filtered and the filtrate kept at -10°C to deposit a colourless crystalline solid. This gave a ^1H NMR spectrum which suggested the presence of Me_3Si and Me_2Si groups in 2:1 ratio, and chemical shifts which suggested that it could be 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane **1**.^{2,3} We decided to determine its crystal structure because (i) this would provide confirmation of its identity, (ii) there is some similarity in the steric interactions between its $(\text{Me}_3\text{Si})_2\text{C}$ systems and those of the $(\text{Me}_3\text{Si})_3\text{C}$ systems in molecules of the type $\text{M}\{\text{C}(\text{SiMe}_3)_3\}_2$, and (iii) it would provide information relevant to discussion elsewhere of the structures of heterocyclic compounds of the type $(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{XML}_n$ with, for example, X = OMe or NMe₂ and M = Li, Mg or Al.⁴

Compound **1** was first obtained by Seyferth and Lefferts² from the reaction between $(\text{Me}_3\text{Si})_2\text{C}(\text{Br})\text{Li}$ and Me_2SiCl_2 , probably *via* the intermediate $(\text{Me}_3\text{Si})_2\text{C}(\text{Li})\text{SiMe}_2\text{Cl}$. It was later obtained by Wiberg *et al.*³ by thermal elimination of LiBr from $(\text{Me}_3\text{Si})_2\text{C}(\text{Li})\text{SiMe}_2\text{Br}$ to give the silaalkene $(\text{Me}_3\text{Si})_2\text{C}=\text{SiMe}_2$, which readily dimerized. [The same silaalkene was shown by them to be formed analogously from a range of compounds $(\text{Me}_3\text{Si})_2\text{C}(\text{Li})\text{SiMe}_2\text{X}$, and in each case would no doubt have given **1** in the absence of a trapping agent.] The compound was not structurally characterized in either study. We do not know how, or at what stage, it was formed during our procedure, but it probably arose by dimerization of $(\text{Me}_3\text{Si})_2\text{C}=\text{SiMe}_2$ generated in the photolysis.

Structures have been established previously for the related species **2**⁵ and **3**,⁶ but only partial information was given for

3. (For information on the structures of other 1,3-disilacyclobutanes see refs 7 and 8.)



Crystal Structure

The structure of compound **1** is shown in Fig. 1, and selected bond lengths and angles in Table 1. The molecule lies on a crystallographic twofold rotation axis through C1 and C2. The four-membered ring is planar, the sum of the internal angles being 360° , but not quite square, the C–Si–C angles being $93.84(10)^\circ$ and the mean Si–C–Si angle $86.16(13)^\circ$. These parameters are the same, within the uncertainty limits, as those for **2**,⁵ and perhaps also as those for **3**, for which the corresponding angles were simply stated all to be close to 90° .⁶ The lengths of the Si–C bonds within the ring, 1.916(2) and 1.918(2) Å, are not significantly different from those of the external Me_3Si –C bonds, mean 1.907(2), both sets being essentially identical to those in **2**, and long relative to most alkyl–Si bonds.⁹ [Endocyclic Si–C bond lengths of up to 1.972(9) Å have been observed in more crowded 1,3-disilacyclobutanes.⁸] The Si–Me bonds in **1** are markedly shorter, mean 1.881(2) Å, and within the fairly narrow range observed for numerous $(\text{Me}_3\text{Si})_3\text{CX}$ compounds.¹⁰

A difference between compounds **1** and **2** is that whereas in the latter the plane defined by the two Si–C bonds to

Table 1 Selected bond lengths (Å) and angles (°) in compound **1**^a

Si1–C1	1.916(2)	Si2–C2	1.908(2)
Si1–C2	1.918(2)	Si3–C1	1.907(2)
		Si–Me (mean)	1.881(2)
C1–Si1–C2	93.84(10)	Si2–C2–Si2'	106.0(2)
Si1–C1–Si1'	86.19(13)	Si3–C1–Si3'	106.0(2)
Si1'–C1–Si3	112.81(3)	C1–Si3–C8	118.06(11)
Si1–C1–Si3	119.41(4)	C2–Si2–C5	117.48(11)
Si1–C2–Si2	112.95(4)	C1,2–Si–Me (mean) ^c	112.2(6)
Si1'–C2–Si2	119.29(4)	C3–Si1–C4	100.70(11)
		Me–Si2,3–Me	104.6 ^b

^aSymmetry transformations: ' – *x*, *y* – *z* + $\frac{1}{2}$. ^bValues range from 101.6(1) to 108.0(1)°. ^cExcluding C8 and C5.

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the spiro centre is perpendicular to that of the four-membered ring, in **1** the Si2–C2–Si2' plane (and likewise the Si3–C1–Si3' plane) lies at an angle of 85° to the plane of the ring. The Me_3Si –C–SiMe₃ angles, both $106.0(2)^\circ$

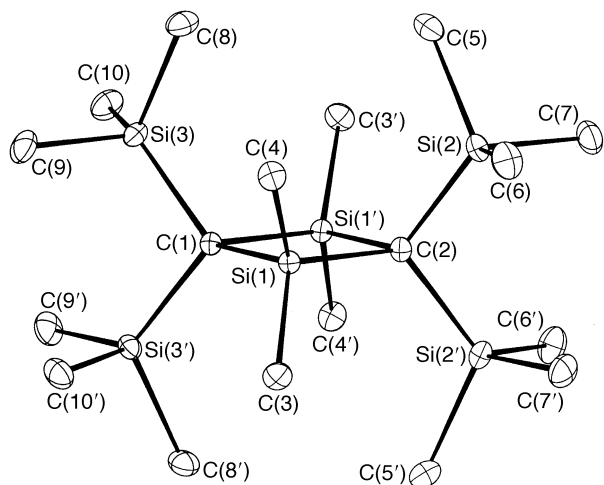


Fig. 1 Structure of compound 1

(closely similar to the corresponding angles in **2**), are notably small (see below), as is the C3–Si1–C4 angle, $100.70(11)^\circ$, which is itself very close to the corresponding angle in **2**.

It is of interest to compare the structure of compound **1** (and by implication that of **2**) with that of $\text{Mg}\{\text{C}(\text{SiMe}_3)_3\}_2$ **4**,¹¹ which is typical of the structures of a range of neutral $\text{M}\{\text{C}(\text{SiMe}_3)_3\}_2$ species. As in the latter, in **1** one of the Si–Me bonds within each Me_3Si group, those for C5(5') and C8(8'), points inwards. The C1–Si3–C8 and C2–Si2–C5 angles, $118.1(1)$ and $117.5(1)^\circ$, are markedly larger than the other C1,2–Si–Me angles, mean $112.2(6)^\circ$. In the absence of other bulky groups two Me_3Si groups on the same carbon atom tend to lie well apart [e.g. the Si–C–Si angle in $(\text{Me}_3\text{Si})_2\text{CH}_2$ is 123.2°].¹² Since the endocyclic Si–C–Si angles in **1** are forced to be ca. 86° , the angles between the Me_3Si –C bonds in **1** might have been expected to open up to be substantially wider than those in **4**, viz. 112.6° , whereas, at $106.0(2)^\circ$, they are much narrower. One seemingly obvious reason for this is that the central carbon atoms on each side of the molecule are markedly closer, at 2.84 \AA , than are those in **4**, at 4.23 \AA . In **4** the plane defined by the carbon atoms of the inward-pointing Me groups on one side of the molecule lies 2.97 \AA from the corresponding plane on the other side, i.e. much closer than the 3.6 \AA given by twice the sum of the van der Waals radius of an Me group, but the SiMe_3 groups are twisted about the Si–C bonds in such a way that no cross-ring $\text{Me}\cdots\text{Me}$ distance is below 4.0 \AA . In **1** the preference for the endocyclic Si–C–Si plane to lie at right angles to the corresponding exocyclic plane (as in **2**) means that the inward-pointing Me groups on the two sides are constrained to be almost opposed, which would bring them impossibly close together if all Me_3Si –C– SiMe_3 angles were ca. 112.6° as in **4**, and so these angles narrow to 106° and the C5 and C8 groups are forced outwards to give Me–Si–C1,2 angles, mean $117.8(1)^\circ$, distinctly larger than the other Me–Si–C1,2 angles, mean $112.2(6)^\circ$. These effects would in themselves increase the cross-ring $\text{Me}\cdots\text{Me}$ distances to $3.595(3) \text{ \AA}$, but in addition the angles between the endo- and exo-cyclic CSi_2 planes are reduced slightly to 85° , to raise the distance between the opposed groups to $3.609(3) \text{ \AA}$. This is not, however, the complete picture, because there are even closer contacts between C8 and C4 (and C8' and C4') of 3.436 \AA , and between C5 and C3' (and C5' and C3) of 3.407 \AA , indicating that the repulsions between SiMe_2 and SiMe_3 groups are also very important in determining the overall geometry. (The same factors operate in **2**, but in this case the require-

ments of the six-membered ring system would in themselves serve to keep the relevant Si–C–Si angle well below those in **4**.) It would be of interest to compare parameters for **1** with those for **3** but the relevant data for **3** were not given.⁶

There are other short contacts in compound **1**, viz. C4Si3 3.648 , C4–C5 3.695 , C4–Si2 3.525 , C3'–C5 3.407 , C3'–C8 3.688 , C3'–Si2 3.636 and C3'–Si3 3.504 \AA . The Me–Si–Me angles within the Me_3Si groups in **1** range from $101.6(1)$ to $108.0(1)^\circ$, with an average of 104.6° , values not much different from the spread from $102.9(2)$ to $107.7(1)^\circ$, and an average of 105.4° , for the corresponding angles in **4**. The Me–Si–Me angles at the ring silicon atoms, $100.7(1)^\circ$, are only slightly narrower than the smallest such angle within the Me_3Si groups.

Experimental

Crystal Data for Compound 1.— $M = 433.1$; monoclinic, space group $C2/c$ (no. 15); $a = 15.014(5)$, $b = 11.352(3)$, $c = 16.815(4) \text{ \AA}$, $\beta = 110.69(2)^\circ$, $U = 2681.1(13) \text{ \AA}^3$, $D_c = 1.07 \text{ Mg m}^{-3}$, $Z = 4$, $F(000) = 960$, Mo–K α radiation, $\lambda = 0.71073 \text{ \AA}$, crystal size $0.3 \times 0.3 \times 0.3 \text{ mm}$, $\mu(\text{Mo-K}\alpha) = 0.31 \text{ mm}^{-1}$, $T = 173(2) \text{ K}$. CAD4 diffractometer, θ – 2θ scan mode, $2 < \theta < 25^\circ$, 2349 independent reflections. Structure solution by direct methods (SHELXS 86) on F^2 and full matrix least-squares refinement (SHELXL 93) with all non-hydrogen atoms anisotropic and H atoms in riding mode with $U_{\text{iso}} = 1.5 U_{\text{eq}}(\text{C})$. Final $R1$ 0.038, for 2119 reflections with $I > 2\sigma(I)$, $wR2$ 0.113 (all data). Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/9.

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