

## Preparation and X-ray crystal structure of an unusual bicyclic trisilane-tris(disiloxane) \*

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### Abstract

The tetrachloride  $\text{Si}(\text{SiMe}_2\text{Cl})_4$ , when hydrolysed with two equivalents of water, gives an unusual bicyclic product, 1,5-bis(dimethylchlorosilyl)dodecamethyl-3,7,10-trioxa-1,2,4,5,8,9,11-octasilabicyclo[3.3.3]undecane, which contains both trisilane and disiloxane linkages and which appears to be the first compound prepared containing this ring system; its structure has been determined by X-ray diffraction.

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### Introduction

In the last ten years, Eaborn and co-workers have prepared many compounds containing bulky ligands, such as  $\text{C}(\text{SiMe}_3)_3$  attached to functional silicon centres, which have allowed new reaction mechanisms to be observed and novel structures to be stabilised (for reviews, see refs. 1 and 2). We have recently begun to study compounds containing the  $\text{Si}(\text{SiMe}_3)_3$  group, and related compounds, to see whether such ligands would also enable analogous silicon-centred compounds to be prepared. Hydrolysis of the known tetrachloride  $\text{Si}(\text{SiMe}_2\text{Cl})_4$  gave a novel bicyclic compound, the structure of which has been determined by X-ray diffraction.

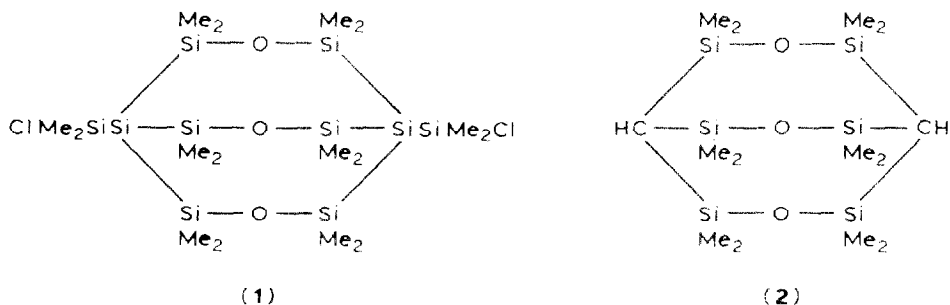
### Results and discussion

The tetrachloride  $\text{Si}(\text{SiMe}_2\text{Cl})_4$  was prepared from  $\text{Si}(\text{SiMe}_3)_4$  using the method of Sakurai et al. [3]. It was found to be readily hydrolysed using a water/diethyl ether/aniline mixture at  $0^\circ\text{C}$  to give a dimeric product (**1**), which appears to have been formed either by dimerization of the trisilanol  $(\text{HOMe}_2\text{Si})_3\text{SiSiMe}_2\text{Cl}$  or by dimerization of mono- or di-silanol intermediates in the hydrolysis, which undergo further hydrolysis with final intramolecular condensation to form Si–O–Si bonds.

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\* Dedicated to Professor Colin Eaborn in recognition of his outstanding contributions to organometallic chemistry, and especially for his valued guidance and friendship to P.D.L.

The formation of a simple dimer, rather than a polymer, is surprising and is probably due to the proximity of the OH groups to each other in the  $[(\text{ClMe}_2\text{Si})(\text{HOME}_2\text{Si})_2\text{SiSiMe}_2]_2\text{O}$  formed initially, which favours further condensation to form siloxane bonds to be intra- rather than inter-molecular. The formation of a similar bicyclo[3.3.3]undecane ring system by condensation of a trisilanol was also observed when  $(\text{HOME}_2\text{Si})_3\text{CH}$  was heated to form **2** [4].



The related tetrachloride  $\text{C}(\text{SiMe}_2\text{Cl})_4$  is generally much more resistant to hydrolysis and solvolysis than its silicon analogue, and can for example be recovered unchanged after boiling in aqueous tetrahydrofuran for several hours [5]. The much greater reactivity of tetrasilylsilane than tetrasilylmethane derivatives is presumably due to the longer bonds around the central atom (ca. 2.35 and 1.9 Å for Si–Si and Si–C, respectively) making the functional silicon centres less hindered and more readily attacked by incoming reagents. In accordance with this, recent work on the related pair of compounds  $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{I}$  and  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$  has shown the former to react with methanol at least  $10^5$  times more rapidly than the latter [6].

The molecular structure of **1**, with the atom numbering scheme, is shown in Fig. 1. The molecule is disordered about a site of 222 symmetry, with one two-fold axis through Si(1) and Si(1)', and another through O(2) and the mid-point of the

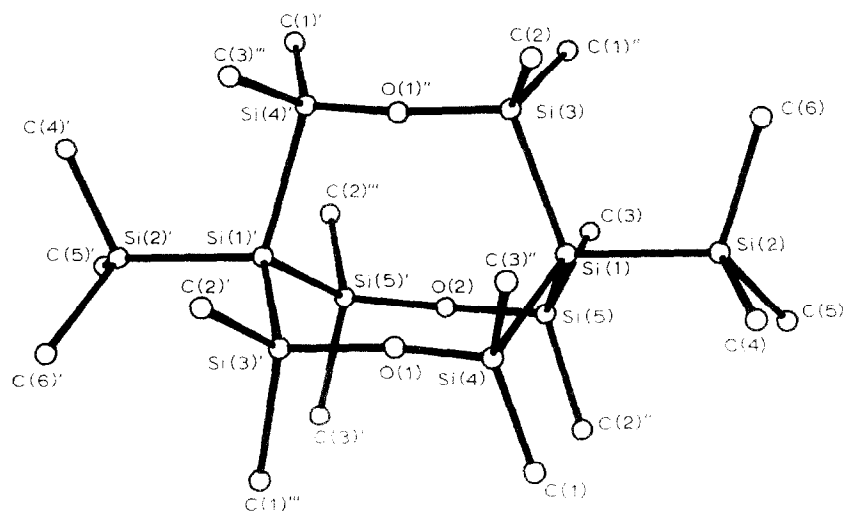


Fig. 1. An ORTEP [7] drawing of the molecular structure of **1**, and the atom numbering scheme.

Table 1

Intramolecular distances (Å) and angles (°) for **1**, with estimated standard deviations in parentheses

<i>(a) Bonds</i>			
Si(1)–Si(2)	2.311(7)	Si(1)–Si(3)	2.314(10)
Si(1)–Si(4)	2.421(13)	Si(1)–Si(5)	2.339(9)
Si(2)–C(4)	1.84(2)	Si(2)–C(5)	1.93(2)
Si(2)–C(6)	2.08(3)	Si(3)–C(2)	1.86(3)
Si(3)–O(1)''	1.72(3)	Si(3)–C(1)''	2.20(2)
Si(4)–O(1)	1.46(3)	Si(4)–C(1)	1.78(2)
Si(4)–C(3)''	2.10(2)	Si(5)–O(2)	1.66(4)
Si(5)–C(3)	1.99(4)	Si(5)–C(2)''	1.93(3)
<i>(b) Angles</i>			
Si(2)–Si(1)–Si(3)	109.2(3)	Si(2)–Si(1)–Si(4)	108.8(4)
Si(2)–Si(1)–Si(5)	107.3(3)	Si(3)–Si(1)–Si(4)	110.2(4)
Si(3)–Si(1)–Si(5)	114.8(6)	Si(4)–Si(1)–Si(5)	106.4(7)
Si(1)–Si(2)–C(4)	111.7(7)	Si(1)–Si(2)–C(5)	117.0(8)
Si(1)–Si(2)–C(6)	108.0(8)	C(4)–Si(2)–C(5)	94(1)
C(4)–Si(2)–C(6)	112(1)	C(5)–Si(2)–C(6)	114(1)
Si(1)–Si(3)–C(2)	110.4(8)	Si(1)–Si(3)–C(1)''	101.9(6)
Si(1)–Si(3)–O(1)''	108.7(8)	O(1)''–Si(3)–C(1)''	104(1)
O(1)''–Si(3)–C(2)	110(1)	C(1)''–Si(3)–C(2)	121(1)
Si(1)–Si(4)–O(1)	104(1)	Si(1)–Si(4)–C(1)	112(1)
Si(1)–Si(4)–C(3)''	100.0(9)	O(1)–Si(4)–C(1)	114(1)
O(1)–Si(4)–C(3)''	103(1)	C(1)–Si(4)–C(3)''	122(1)
Si(1)–Si(5)–O(2)	109(1)	Si(1)–Si(5)–C(3)	106(1)
Si(1)–Si(5)–C(2)''	107(1)	O(2)–Si(5)–C(3)	98(1)
O(2)–Si(5)–C(2)''	111(1)	C(2)''–Si(5)–C(3)	124(1)
Si(4)–O(1)–Si(3)'	174(2)	Si(5)–O(2)–Si(5)'	175(3)
Symmetry elements: ' $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$			
'' $-\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} - z$			
''' $-x, 1 - y, z$			

molecule. The two alternative orientations of the molecule share the same Si(1), Si(2) and C(1), C(2), C(3) atom sites, but have alternative Si(3), Si(4), C(4), C(5), C(6) and O atom sites. The Cl atom is randomly disordered between the three terminal sites on Si(2). The data in Table 1 is not good enough for detailed analysis of the structure or comparison of bond angles and lengths with other compounds, due to the disorder in the crystal. Compound **1** appears to be the first prepared containing the 3,7,10-trioxa-1,2,4,5,8,9,11-octasilabicyclo[3.3.3]undecane ring system, and also the first tetrasilylsilane derivative to have its structure determined by X-ray crystallography. The structure of Si(SiMe<sub>3</sub>)<sub>4</sub> has been determined in the gas phase by electron diffraction [8], where the Si–Si bond lengths were found to average 2.361(3) Å, compared with 2.346(45) Å for the bonds to Si(1) in **1**. The siloxane bonds in **1** are nearly linear (cf. 145.2(1)° in **2** [4]), which is presumably due to the longer bonds to the bridgehead atoms, causing less strain in the rings.

## Experimental

### General

The NMR spectra were recorded in CCl<sub>4</sub>/CDCl<sub>3</sub> solutions at 90 MHz for <sup>1</sup>H and 71.5 MHz for <sup>29</sup>Si; all chemical shifts are in ppm relative to SiMe<sub>4</sub>. Mass

spectra were recorded at 70 eV.  $m/e$  values for chlorine-containing ions refer to the  $^{35}\text{Cl}$  isotope. The  $\text{Si}(\text{SiMe}_2\text{Cl})_4$  was prepared according to ref. 3.

*$\text{ClMe}_2\text{SiSi}(\text{SiMe}_2\text{OSiMe}_2)_3\text{SiSiMe}_2\text{Cl}$  (I)*

A solution of  $\text{Si}(\text{SiMe}_2\text{Cl})_4$  (0.50 g, 1.20 mmol) in dry diethyl ether (15  $\text{cm}^3$ ) was added dropwise under nitrogen to a cool ( $0^\circ\text{C}$ ) vigorously stirred solution of aniline (0.23 g, 2.40 mmol) and water (0.043 g, 2.40 mmol) in diethyl ether (5  $\text{cm}^3$ ). After the addition, the mixture was stirred at  $0^\circ\text{C}$  for a further hour. The solid was then collected by filtration, and the filtrate was evaporated under reduced pressure to leave a white solid which was sublimed ( $150^\circ\text{C}$ , 0.05 mmHg) to give  $\text{ClMe}_2\text{SiSi}(\text{SiMe}_2\text{OSiMe}_2)_3\text{SiSiMe}_2\text{Cl}$  (0.21 g, 41%), m.p.  $236\text{--}238^\circ\text{C}$ ; Found: C, 29.05; H, 7.53.  $\text{C}_{16}\text{H}_{48}\text{Cl}_2\text{O}_3\text{Si}_{10}$  calcd.: C, 28.69; H, 7.1%.  $^1\text{H}$  NMR:  $\delta$  0.40 (s, 36H,  $\text{SiMe}_2\text{O}$ ), 0.52 (s, 12H,  $\text{SiMe}_2\text{Cl}$ );  $^{29}\text{Si}$  NMR:  $\delta$  23.25 ( $\text{SiMe}_2\text{Cl}$ ), 5.47 ( $\text{SiMe}_2\text{O}$ ),  $-136.38$  ( $\text{SiSiMe}_2\text{Cl}$ ); mass spectrum;  $m/e$  638(10% [ $M$ ] $^+$ ), 545(5 [ $M - \text{SiMe}_2\text{Cl}$ ] $^+$ ), 241(5), 207(13), 189(6), 167(12 [ $\text{Me}_3\text{SiOSiMe}_2\text{Cl}$ ] $^+$ ), 147(17 [ $\text{Me}_3\text{SiOSiMe}_2$ ] $^+$ ), 131(13), 117(10), 93(14), 73(100 [ $\text{Me}_3\text{Si}$ ] $^+$ ).

*Determination of structure of I*

*Crystal data:*  $\text{C}_{16}\text{H}_{48}\text{Cl}_2\text{O}_3\text{Si}_{10}$ ,  $M = 640.33$ , tetragonal,  $a$  11.554(2),  $c$  14.486(2) Å,  $U$  1933.9 Å $^3$ ,  $Z = 2$ ,  $D_c$  1.1  $\text{g cm}^{-3}$ ,  $F(000) = 684$ . Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$  4.9  $\text{cm}^{-1}$ . Space group  $P4n2$ .

Data were measured on an Enraf Nonius CAD4 diffractometer using a crystal of size ca.  $0.4 \times 0.4 \times 0.4$  mm, obtained by sublimation. Intensities for  $+h+k+l$  reflections with  $2 < \theta < 25^\circ$  were measured by a  $\theta/2\theta$  scan with a scan width of  $(0.8 + 0.35\tan\theta)^\circ$  and a maximum scan time of 1 min. Every 30 min. two standard reflections were monitored and showed no significant variation. After correction for Lorentz and polarisation effects, but not for absorption, equivalent reflections were averaged and 524 reflections with  $|F|^2 > \sigma(F^2)$  were used for the structure analysis. The values of  $\sigma(F^2)$  were calculated as  $[\sigma^2(I) + (0.04I)^3]^{1/2}/\text{Lp}$ .

The diffraction data had  $4/mmm$  symmetry with systematic absences of  $0kl$  for  $(k+l)$  odd.

There are three possible space groups consistent with these conditions:  $P4_2nm$ ,  $P4n2$  and  $P4_2/mmm$ . Direct methods (MULTAN) [9] were performed on each of the three space groups, which in each case gave a disordered arrangement of the silicon atoms, and in no case could the remaining atoms be located on an electron density map. Refinement of the disordered silicon atoms gave a very distorted tetrahedral geometry in space groups  $P4_2nm$  and  $P4_2/mmm$ , but a rather better geometry in  $P4n2$ .

The structure determination was continued in  $P4n2$ , and oxygen and carbon atoms were placed at calculated positions. The Cl atom was assumed to be disordered equally between the positions C(4), C(5) and C(6), which were given scattering factors corresponding to  $\frac{2}{3}\text{C} + \frac{1}{3}\text{Cl}$ .

Full-matrix least-squares refinement converged adequately for all atoms isotropically, except that O(2) had a very high  $U_{\text{iso}}$  value. The calculation of structure factors without O(2), followed by a difference map, did not produce a better position. All non-hydrogen atoms were then refined anisotropically, except for O(2). Hydrogen atoms were omitted. Refinement converged at  $R = 0.109$ ,  $R' = 0.102$  with

Table 2

Fractional atomic coordinates ( $\times 10^4$ ) for **1** with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	1440(4)	6440	2500
Si(2)	2854(8)	7854	2500
Si(3)	1668(7)	5286(7)	3792(7)
Si(4)	1638(13)	5293(12)	1111(9)
Si(5)	-354(7)	7373(8)	2395(19)
O(1)	763(19)	4390(23)	1217(14)
O(2)	-1409(50)	6409	2500
C(1)	1461(19)	6143(24)	94(10)
C(2)	3124(22)	4599(16)	3790(16)
C(3)	-580(14)	8191(11)	3592(20)
C(4)	3860(14)	7684(22)	1527(15)
C(5)	2380(20)	9396(13)	2152(26)
C(6)	3716(29)	7781(19)	3761(20)

the weighting scheme  $w = 1/\sigma^2(F)$ . A final difference map had peaks of up to  $2 \text{ e}\text{\AA}^{-3}$  near Si(2).

The structure solution and refinement were done on a PDP 11/34 computer using the Enraf Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 10. Bond lengths and angles are listed in Table 1 and final atom coordinates are listed in Table 2. Tables of temperature factors and final structure factors are available from the authors.

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