

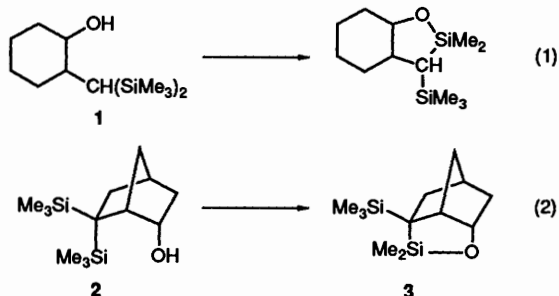
Cleavage of an Si–Me Bond by Intramolecular Alkoxide-ion Attack. Crystal Structure of 6,6-Bis(trimethylsilyl)norbornan-*endo*-2-ol

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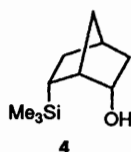
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The crystal structure of the title alcohol, **2**, has been determined in order to throw light on the ease of intramolecular displacement of a Me group to give **3** when **2** is treated with Bu^tOK–Bu^tOH. In **2** (and thus presumably in the alkoxide ion derived from it) the O-atom and the *endo*-SiMe₃ group are held in a very favourable disposition for this displacement, and because of this, and the high rigidity of the substrate molecule, there is little loss of entropy on going to the cyclic transition state.

Cleavages of Si–C bonds by base have been much studied.^{1,2} In mechanistic studies the base is usually alkoxide ion in alcohol, and the Si–R bonds to be cleaved are those in which the carbanion, R[–], is stabilized, *e.g.* PhCH₂[–],³ but the cleavages are known to be much faster in dipolar aprotic media, such as dimethyl sulphoxide,⁴ dimethylformamide or hexamethylphosphoramide (HMPA), and even Si–alkyl bonds in tetraalkylsilanes are cleaved by alkoxides or hydroxides in such media.¹ It is also relevant to the subsequent discussion to note that Si–Me and Si–Ph bonds can be broken fairly readily in intramolecular attack by the incipient carbanion in an organosilicon compound containing a lithio-carbon centre.⁵



There have been two recent examples of ring-closure involving intramolecular base cleavage of Si–Me bonds, as depicted in eqns. (1)⁶ and (2).⁷ The cleavage of compound **1** shown in eqn. (1) is less surprising in that it involves alkoxide ion in THF/HMPA, whereas that of **2** to give **3**, shown in eqn. (2), was found by Kirmse and Söllenhömer to take place with (among other reagents) Bu^tOK in Bu^tOH. An important feature is that the related compound **4**, bearing only one Me₃Si group, does not react under the conditions used; the authors concerned rightly attributed the higher reactivity to the steric compression of the geminal Me₃Si groups,⁷ as we show below where we consider how the effect of this compression is exerted.



For nucleophilic attack on silicon by alkoxide ion centres of equal inherent nucleophilicity, intramolecular attack is (unless stereochemically inhibited) likely to be much faster than that of the corresponding (entropically disfavoured) bimolecular reaction involving an external nucleophile; thus cleavage of the Si–CH₂Ph bond in PhCH₂SiMe₂(CH₂)₃OH by NaOMe–

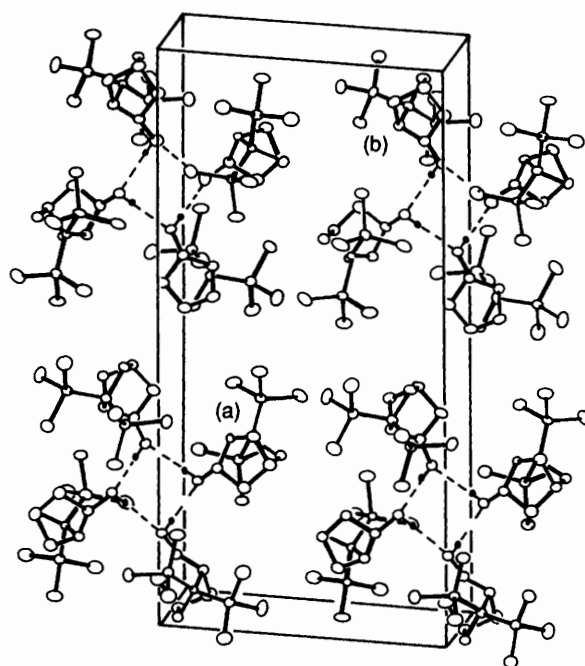


Fig. 1 Unit cell for **2**, showing the independent molecules a and b and with the hydrogen bonds indicated by the dotted lines

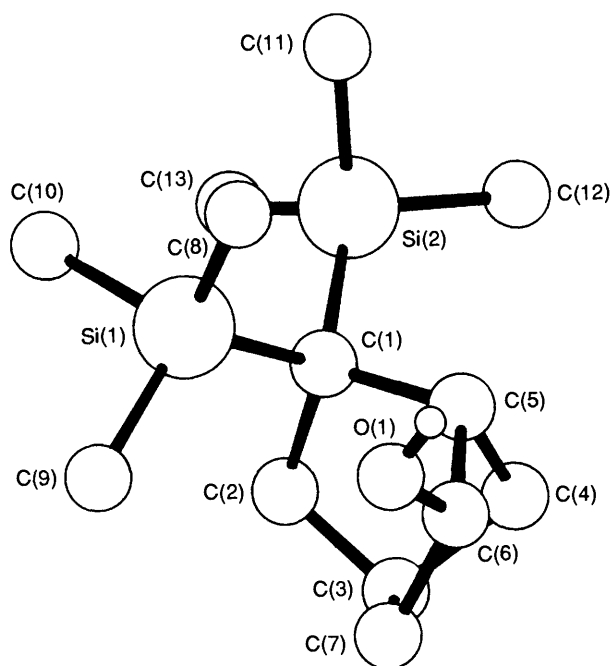
MeOH is *ca.* 93–135 times as fast as that of PhCH₂SiMe₃,⁸ and the true factor between the specific rate constants for intra- and inter-molecular attack is substantially larger than this because only a little of the anion PhCH₂SiMe₂(CH₂)₂CH₂O[–] is present in the methanolic medium. When, in intramolecular attack, the alkoxide ions are held close to the silicon atom under attack the cleavage is likely to be much faster (*cf.* ref. 9), but even so the cleavage of a Si–Me bond by the moderately nucleophilic alkoxide-ion centre in the anion derived from **2**, and the non-occurrence of such cleavage in the case of **4**, seemed rather striking, and we decided to determine the crystal structure of **2** in order to gain information about the relative locations of the OH group and the *endo*-SiMe₃ group and the degree of crowding in the molecule. A sample of **2** was generously provided by Professor Kirmse.

Results and Discussion

In the crystal the molecules of **2** are present as hydrogen-bonded tetramers, as can be seen from the unit cell depicted in Fig. 1. There are two crystallographically independent molecules of **2**, denoted by a and b, but, as can be seen from the lists of bond lengths and angles in Table 1, their geometries are not

Table 1 Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for the two independent molecules

Molecule	a	b	a	b
(a) Bonds				
Si(1)–C(1)	1.919(3)	1.917(4)	Si(1)–C(8)	1.873(5)
Si(1)–C(9)	1.880(4)	1.861(4)	Si(1)–C(10)	1.883(5)
Si(2)–C(1)	1.924(3)	1.921(4)	Si(2)–C(11)	1.873(5)
Si(2)–C(12)	1.870(4)	1.874(5)	Si(2)–C(13)	1.873(5)
O(1)–C(6)	1.431(4)	1.429(4)	O(1)–H(01)	0.74(4)
C(1)–C(2)	1.587(5)	1.589(5)	C(1)–C(5)	1.567(5)
C(2)–C(3)	1.526(6)	1.529(6)	C(3)–C(4)	1.528(6)
C(3)–C(7)	1.543(5)	1.538(6)	C(4)–C(5)	1.539(5)
C(5)–C(6)	1.525(5)	1.528(5)	C(6)–C(7)	1.546(6)
(b) Angles				
C(1)–Si(1)–C(8)	112.9(2)	114.8(2)	C(1)–Si(1)–C(9)	115.8(2)
C(1)–Si(1)–C(10)	108.4(2)	110.0(2)	C(8)–Si(1)–C(9)	109.0(2)
C(8)–Si(1)–C(10)	109.1(2)	106.0(2)	C(9)–Si(1)–C(10)	101.0(2)
C(1)–Si(2)–C(11)	112.2(2)	111.5(2)	C(1)–Si(2)–C(12)	114.3(2)
C(1)–Si(2)–C(13)	111.5(2)	112.0(2)	C(11)–Si(2)–C(12)	102.7(2)
C(11)–Si(2)–C(13)	109.8(2)	110.5(2)	C(12)–Si(2)–C(13)	105.8(2)
C(6)–O(1)–H(01)	106(3)	109(3)	Si(1)–C(1)–Si(2)	108.3(2)
Si(1)–C(1)–C(2)	108.8(2)	109.5(2)	Si(1)–C(1)–C(5)	119.4(2)
Si(2)–C(1)–C(2)	111.4(2)	111.0(2)	Si(2)–C(1)–C(5)	108.0(2)
C(2)–C(1)–C(5)	100.6(3)	100.9(3)	C(1)–C(2)–C(3)	103.3(3)
C(2)–C(3)–C(4)	101.0(3)	101.1(3)	C(2)–C(3)–C(7)	109.9(3)
C(4)–C(3)–C(7)	103.1(3)	101.7(3)	C(3)–C(4)–C(5)	93.4(3)
C(1)–C(5)–C(6)	103.0(3)	102.6(3)	C(1)–C(5)–C(6)	114.1(3)
C(4)–C(5)–C(6)	97.4(3)	96.7(3)	O(1)–C(6)–C(5)	115.8(3)
O(1)–C(6)–C(7)	112.9(3)	112.2(3)	C(5)–C(6)–C(7)	103.4(3)
C(3)–C(7)–C(6)	101.5(3)	102.4(3)		
Hydrogen bonds				
O(1a)–H...O(1b) ⁱ : O(1a)–H 0.74(4); H...O(1b) 2.19(4); O(1a)–H...O(1b) 163(4)				
O(1b)–H...O(1a) ⁱⁱ : O(1b)–H 0.75(4); H...O(1a) 2.14(4); O(1b)–H...O(1a) 162(4)				
Symmetry element: I; 1 + x, \bar{y} , $\frac{1}{2} + z$; II; 1 – x, \bar{y} , 1 – z.				

**Fig. 2** The molecular structure of **2** with atom numbering

significantly different, and for simplicity only molecule **a** is considered in the subsequent discussion.

The molecular structure, with atom numbering, is shown in Fig. 2, and the bond lengths and angles are listed in Table 1. The distortions arising from the severe steric compression are considered later, and it is sufficient to note here that even

though the Si(1)–C(1)–C(5) angle is widened to 119.4(2)°, the intra-ring C(1)–C(5)–C(6) angle to 114.1(3)° (from a 'normal' value in the region of 109°), and the C(5)–C(6)–O(1) angle to 115.8(3)°, and the C(1)–C(5) bond is lengthened to 1.567(5) Å (from a 'normal' value of *ca.* 1.53 Å), all effects that serve to increase the distance between Si(1) and O(1), this distance, of 3.038(3) Å, is still substantially below the sum (3.60 Å) of the relevant van der Waals radii. Furthermore the O(1)···Si(1)–C(10) angle is 174.8°, *i.e.* close to the value of 180° for the preferred apical-apical arrangement of the incoming and leaving group in the transition state (see later). If the structure of the alkoxide ion in solution is similar to that of the alcohol **2** in the solid, then, apart from some movement of the other three ligands on silicon towards equatorial positions, very little change in atom positions is involved in going to the ideal five-coordinate transition state, and so there will be little increase in the compression and so in the enthalpy. There will also be very little increase in the rigidity of this system, and so only a very small unfavourable entropy change, and this is probably the dominant reason for the ready cleavage of the Si–Me bond in **2**.

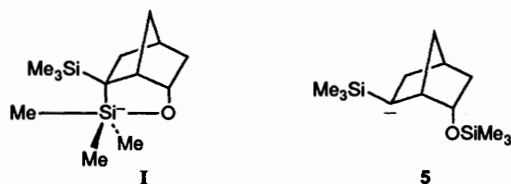
In the case of the monosilylated alcohol **4** there is markedly greater freedom of internal motion, so that there would be a correspondingly greater unfavourable entropy change. Furthermore, as an aspect of this greater freedom in **4**, the *endo*-SiMe₃ group is not forced to lie so close to the oxygen atom and in a disposition approximating to that of an early stage in the reaction coordinate on the way to the five-coordinate transition state. [In **2** the *endo*-SiMe₃ group cannot move away from the oxygen without encountering the *exo*-SiMe₃ group, which is itself buttressed in place by contact with the C(4) atom of the bridge.] We had hoped to determine the crystal structure of **4**, but could not obtain suitable crystals.

Table 2 Some selected bond lengths (Å) and angles (°) in compounds **2** and **6–9**^a

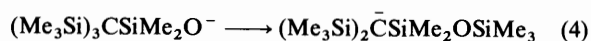
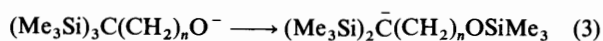
	2	6	7	8	9
Bond length					
C(1)–C(2)	1.587(5)	1.543(4)	1.556(4)	1.545(8)	1.531(5)
C(1)–C(5)	1.567(5)	1.523(4)	1.516(4)	1.529(6)	1.539(4)
C(2)–C(3)	1.526(6)	1.537(4)	1.540(5)	1.528(6)	1.537(4)
Bond angle					
C(1)–C(5)–C(6)	114.1(3)	107.0(3)	107.2(2)	108.9(3)	108.3(2)
C(2)–C(3)–C(7)	109.9(3)	106.7(3)	107.6(3)	106.9(4)	109.1(2)
C(2)–C(1)–C(5)	100.6(3)	103.3(2)	103.3(2)	103.2(4)	103.9(3)
C(1)–C(5)–C(4)	103.0(3)	102.4(3)	103.1(2)	102.0(4)	100.8(3)
C(6)–C(5)–C(4)	97.4(3)	101.6(3)	101.6(2)	101.4(3)	100.6(3)
C(5)–C(6)–O	115.8(3)	110.4(3)			
C(5)–C(1)–Si(1)	119.4(2)				

^a For each of **2** and **6** data for only one of the two crystallographically independent molecules are shown. For **9** data for only one of the two norbornyl groups are shown.

It should be noted that the markedly greater ease of cleavage of an Si–Me bond in **2** than in **4** can be regarded as another example of the *gem*-dialkyl (Thorpe–Ingold) effect, whereby the presence in a chain of a carbon atom bearing two alkyl groups, the bulkier the better, facilitates ring closure.¹⁰ Various factors have been suggested to contribute to this effect, but the main one is probably that the presence of steric constraints in the substrate lowers the unfavourable entropy change on going to the transition state, as discussed above. Normally the two alkyl substituents are removed from the reaction centre, but there is no reason why one of them should not be involved in the ring-closure, as it is in the reaction of **2**.



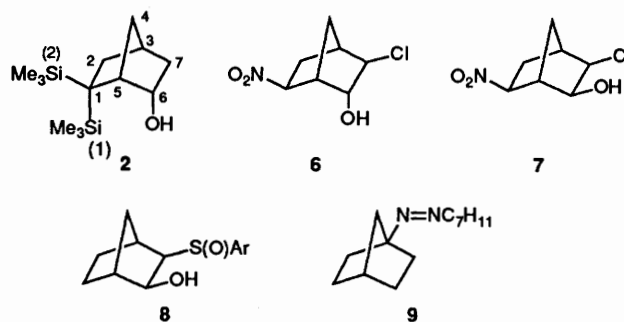
Although the unusually ready loss of an Me group from **2** can be satisfactorily accounted for, it is instructive to consider why it is not the bond between C(1) and the *endo*-SiMe₃ group that is cleaved, since this would involve a markedly greater relief of steric strain. It is convenient to consider the competition between these alternatives in terms of the (possibly hypothetical) intermediate (**I**), since the rate-determining transition state is likely to be not far removed from this species. Cleavage of the C(1)–SiMe₃ bond to give the carbanion **5** would be favoured by the greater relief of strain (and in a synchronous process breaking of the bond would be favoured by this effect as the Si–O bond was formed), but against this, departure of the group in the apical position would be favoured over that in the equatorial position. However, the dominant factor is that the carbanion Me[–] can be expected to be more stable than the tertiary carbanion **5**. (The order of solution acidity is MeH > EtH > Pr[–]H > Bu[–]H,¹¹ and the carbanion-stabilizing effect of the α -Me₃Si group, although approaching that of an α -Ph,¹² is unlikely to render Me₃SiCMe₂H as acidic as Me). However, when the forming carbanion is stabilized by two or three α -Me₃Si groups cleavage of a C–SiMe₃ is favoured over that of an Si–Me in the intramolecular processes shown in eqns. (3) ($n = 2^{13}$ or 4^{14}) and (4).¹⁵



It is instructive to consider in the light of the foregoing discussion the usual assumption^{6,13–15} that reactions such as those shown in eqs. (3) and (4) are facilitated by the relief of steric compression on going to the products, with the implication that there will be some such relief in the transition state and so a lowering of the activation energy. In fact in such processes there must an *increase* in compression as the silicon centre under attack becomes five-coordinate in the transition state, but because there is so much crowding in the substrate molecule the additional increase in enthalpy on going to the transition state is smaller than that for initially less crowded species (*cf.* ref. 16). But probably more important is the entropy effect considered above for the reaction of **2**.

Finally we note that detailed studies of cleavage by NaOMe–MeOH of Me₃Si–R bonds in which R is derived from a carbon acid RH at least as acidic as toluene have indicated that the carbanion R[–] is generated,¹⁷ whereas in the corresponding cleavages of Me₃Sn–R bonds there is concerted proton transfer from the solvent to the separating carbon centre unless R[–] is highly stabilized.¹⁸ It would not be surprising if such concerted proton transfer were required in cleavage of Me₃Si–R bonds which would otherwise generate highly unstable carbanions such as Me[–], and we hope to investigate this possibility. If such proton transfer is needed, then the hindrance of approach of the bulky Bu[–]OH molecule to the very congested C(1) carbon in the cleavage of **2** would also favour loss of an Me rather than the SiMe₃ group.

Structure of the Alcohol 2.—To allow assessment of the extent of distortion of the norbornane system in **2** some relevant bond lengths and angles are listed in Table 2 along with the corresponding data for: (a) the alcohol **6**,¹⁹ apparently the only norbornan-*endo*-2-ol derivative that has been satisfactorily structurally characterized; (b) the isomeric alcohol **7**,¹⁹ (c) the unsubstituted *exo*-2-ol **8** (Ar = C₆H₄Me-*p*);²⁰ and (d) *cis*-azonorbornane **9** (C₇H₁₁ = 1-norbornyl),²¹ in which there is the least distortion of the norbornane skeleton.



The main relevant features are as follows: (i) The C(1)–C(2) and C(1)–C(5) bonds in **2** are lengthened to 1.587(5) and 1.567(5) Å from values in the region of 1.53–1.54 Å. (ii) The angle C(1)–C(5)–C(6) is opened to 114.1(3)° from values in the region of 107–109°. [It is significant that the corresponding C(2)–C(3)–C(7) angle is only 109.9(3)°]. (iii) The C(5)–C(6)–O angle is 115.8(3)°, compared with that of 110.4(3)° in **6**. (iv) The C(5)–C(1)–Si(1) angle, 119.4(2)°, is exceptionally large.

Further indications of the effects of crowding in **2** can be seen in the data (Table 1) for the (Me₃Si)₂C system. One of the most significant features is that the Si(1)–C(1)–Si(2) angle is only 108.3(2)°. When they are able to, *gem*-SiMe₃ groups move apart, and in (Me₃Si)₂CH₂, for example, the corresponding angle is 123.2(9)°,²² and that in (Me₃Si)₃CH is 117.2(4)°.²³ In a compound in which the angle between the other two bonds to the central carbon is small, as in **2** [100.6(3)°], significant opening of the Me₃Si–C–SiMe₃ angle would be expected but it is prevented in this case by contact of the *exo*-SiMe₃ group with

Table 3 Fractional atomic coordinates ($\times 10^4$)

Atom	Molecule a			Molecule b		
	x	y	z	x	y	z
Si(1)	7328.4(9)	1018.9(12)	7098.4(4)	735.0(9)	5069.8(11)	1240.6(4)
Si(2)	6476.3(9)	508.1(12)	5979.6(4)	2839.2(9)	4501.6(13)	777.2(4)
O(1)	8500(2)	-1747(3)	7340(1)	272(2)	2196(3)	1737(1)
C(1)	6736(2)	-390(4)	6635(1)	1527(3)	3672(3)	898(1)
C(2)	5709(3)	-979(5)	6853(1)	932(3)	3223(4)	376(1)
C(3)	5912(3)	-2589(5)	6913(2)	792(3)	1598(4)	432(1)
C(4)	6447(3)	-2910(4)	6424(2)	1826(3)	1172(4)	688(2)
C(5)	7322(3)	-1836(4)	6552(1)	1726(3)	2154(4)	1151(1)
C(6)	7742(3)	-2548(4)	7044(1)	765(3)	1448(4)	1344(1)
C(7)	6767(3)	-2847(4)	7335(2)	60(3)	1278(4)	856(1)
C(8)	8713(4)	1387(5)	6996(2)	1086(4)	5270(5)	1934(2)
C(9)	7185(4)	654(5)	7795(1)	-681(3)	4839(5)	1148(2)
C(10)	6576(5)	2739(5)	7011(2)	910(4)	6910(4)	950(2)
C(11)	7538(4)	1754(5)	5817(2)	3413(4)	5425(5)	1360(2)
C(12)	6409(4)	-775(5)	5430(2)	3863(3)	3180(6)	627(2)
C(13)	5224(4)	1499(6)	5942(2)	2765(4)	5763(6)	221(2)
H(01)	8955(26)	-1692(38)	7183(13)	631(28)	2254(42)	1967(14)

the C(3)–C(4)–C(5) bridge system and of the *endo*-SiMe₃ group with the OH group. To relieve the strain, the C(1)–Si(1) and C(1)–Si(2) bonds are substantially lengthened, to 1.919(3) and 1.924(3) Å, respectively, some C(1)–Si–Me angles substantially widened [e.g. C(1)–Si(1)–C(8), 112.9(2); C(1)–Si(1)–C(9), 115.8(2); C(1)–Si(2)–C(11), 112.2(2); C(1)–Si(2)–C(12) 114.3(2)°], and some Me–Si–Me angles substantially narrowed [e.g. C(9)–Si(1)–C(10), 101.0(2); C(11)–Si(2)–C(12), 102.7(2)°]. Similar distortions are observed in very crowded molecules such as (Me₃Si)₃CSiMe₂Ph²⁴ and (Me₃Si)₂C(SiMe₂OMe)–(SiPh₂Cl).²⁵ The strain is also relieved by the rotation of the Si(1)–C(1)–Si(2) plane by *ca.* 5° with respect to the C(2)–C(1)–C(5) plane, so that while the Si(1)–C(1)–C(2), Si(2)–C(1)–C(5) and Si(1)–C(1)–Si(2) angles remain close to tetrahedral [108.8(2), 108.0(2) and 108.3(2)°, respectively] the Si(1)–C(1)–C(5) and Si(2)–C(1)–C(2) angles are opened to 119.4(2) and 111.4(2)°.

Experimental

Suitable crystals of **2** were obtained by recrystallization from pentane.

Crystal Data.—C₁₃H₂₈OSi₂, *M* = 256.5, monoclinic, space group *P2₁/c* (No. 13), *a* = 13.046(4), *b* = 9.294(2), *c* = 26.261(3) Å, β = 93.38(2)°, *U* = 3178.6 Å³, *Z* = 8, *D_c* = 1.07 g cm⁻³, *F*(000) = 1136. Monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 2.0 cm⁻¹.

Data were collected from a crystal of *ca.* 0.3 × 0.3 × 0.2 mm on an Enraf–Nonius CAD4 diffractometer in the θ–2θ mode with Δθ = (0.8 + 0.35 tanθ)° and a maximum scan time of one min. A total of 5945 unique reflections were measured for 2 < θ < 25° and +*h* + *k* ± *l*, and 2922 reflections with |*F*²| > 3σ(*F*²) where σ(*F*²) = {σ²(*I*) + (0.041)²}^{1/2}/Lp, were used in the refinement. There was no correction for absorption.

The structure was solved by using the direct method routines of SHELXS-86.²⁶ Non-hydrogen atoms were refined anisotropically by full matrix least squares using the programs from the Enraf–Nonius SDP-Plus package. Hydrogen atoms were located on a difference map and their positions refined freely.

* A full list of hydrogen-atom co-ordinates and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

The hydrogen isotropic thermal parameters were refined for the hydroxyl hydrogens, but otherwise fixed at 1.3 × *U*_{iso} for the atom to which they are bonded. With a weighting scheme of *w* = 1/σ²(*F*) the final residuals were *R* = 0.044, *R*' = 0.056. The atomic coordinates are listed in Table 3.*

The crystals contain two crystallographically independent molecules, a and b (see Fig. 1), which have essentially the same geometry. The shortest intramolecular O...Si contact for a, O(1a)...Si(1a), is 3.038(3) and that for b, O(1b)...Si(1b), is 3.048(3) Å. In the crystal four molecules (two of a and two of b) are associated in hydrogen-bonded tetramers lying on the crystallographic two-fold rotation axes.

Acknowledgements

We are very grateful to Professor W. Kirmse for supplying samples of **2** and **4**, and for his interest in this investigation. We thank Mr. A. Habtemariam for obtaining suitable crystals of **2**, SERC for supporting this work and Mr. R. W. Bott for helpful comments.

References

- C. Eaborn and R. W. Bott in *Organometallic Compounds of the Group IV Elements*, ed. A. G. MacDiarmid, Dekker, New York, vol. 1, part 1, 1968, pp. 359–407 and 431–435.
- I. Fleming in *Comprehensive Organic Chemistry*, eds. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 3, part 13; E. W. Colvin in *The Chemistry of the Metal–Carbon Bond*, ed. F. R. Hartley, Wiley–Interscience, Chichester, 1987, vol. 4, ch. 6.
- See, for example, C. Eaborn, G. Pirazzini, G. Seconi and A. Ricci, *J. Organomet. Chem.*, 1980, **192**, 339; C. Eaborn and G. Seconi, *J. Chem. Soc., Perkin Trans. 2*, 1979, 203 and references therein.
- See, for example, C. Eaborn, J. R. Jones and G. Seconi, *J. Organomet. Chem.*, 1976, **116**, 83.
- Ref. 1, pp. 359–407; D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, 1958, **80**, 2677.
- C. Rücker, *Tetrahedron Lett.*, 1984, **25**, 4349.
- W. Kirmse and F. Söllenhömer, *J. Chem. Soc., Chem. Commun.*, 1989, 774.
- C. Eaborn and F. M. S. Mahmoud, *J. Organomet. Chem.*, 1981, **209**, 13.
- F. M. Menger, *Acc. Chem. Res.*, 1985, **18**, 128.
- E. L. Eliel, *Stereochemistry of Carbon Compounds*, McGraw Hill, New York, 1962, pp. 197–202; N. S. Isaacs, *Physical Organic Chemistry*, Longman, Harlow, 1987, pp. 611–613.
- R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen and T. Chivers, *J. Am. Chem. Soc.*, 1966, **88**, 460; R. B. Bates and C. A. Ogle, *Carbanion Chemistry*, Springer–Verlag, Berlin, 1983, p. 19; O. A.

- Reutov, I. P. Beletskaya and K. P. Butin, *CH-Acids*, Pergamon, Oxford, 1978, p. 105.
- 12 C. Eaborn, R. Eidenschink, P. M. Jackson and D. R. M. Walton, *J. Organomet. Chem.*, 1975, **101**, C40.
- 13 I. Fleming and C. D. Floyd, *J. Chem. Soc., Perkin Trans. 1*, 1981, 969.
- 14 C. Eaborn, M. N. El-Kheli, N. Retta and J. D. Smith, *J. Organomet. Chem.*, 1983, **249**, 23.
- 15 R. Damrauer, C. Eaborn, D. A. R. Happer and A. I. Mansour, *J. Chem. Soc., Chem. Commun.*, 1983, 348; A. I. Al-Mansour, M. I. Al-Gurashi, C. Eaborn, F. A. Fattah and P. D. Lickiss, *J. Organomet. Chem.*, 1990, **393**, 27.
- 16 A. E. Dorigi and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3698.
- 17 C. Eaborn, D. R. M. Walton and G. Seconi, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1857; D. Macciantelli, G. Seconi and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1978, 834; P. Dembech, C. Eaborn and G. Seconi, *J. Chem. Soc., Chem. Commun.*, 1985, 1289.
- 18 C. Eaborn and G. Seconi, *J. Chem. Soc., Perkin Trans. 2*, 1979, 203.
- 19 J. C. A. Boeyens, L. Denner and J. O. Michael, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1569.
- 20 A. L. J. Beckwith, J. R. Rodgers and R. D. Wagner, *Aust. J. Chem.*, 1982, **35**, 989.
- 21 M. Schmittl, A. Schulz, C. Rüchardt and E. Hädicke, *Chem. Ber.*, 1981, **114**, 3533.
- 22 T. Fjeldberg, R. Seip, M. F. Lappert and A. J. Thorne, *J. Mol. Struct.*, 1983, **99**, 295.
- 23 B. Beagley, R. G. Pritchard, C. Eaborn and S. S. Washburne, *J. Chem. Soc., Chem. Commun.*, 1981, 710.
- 24 C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1981, **221**, 13.
- 25 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and S. T. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1987, 891.
- 26 G. M. Sheldrick in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, pp. 175–189.

Paper 1/00493J

Received 4th February 1991

Accepted 21st March 1991