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Synthesis, properties and characterization of octadecamethylbicyclo[4.4.0]decasilane *

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Abstract

The title compound **1** was obtained by Wurtz-type dehalogenative coupling of *sym*-dichlorotetramethyldisilane and trichloromethylsilane under appropriate conditions. Spectroscopic data for **1** are compared with those for bi(undecamethylcyclopentasilanyl) (**2**), a possible structural isomer. An X-ray structural study and ^{29}Si-INEPT-INADEQUATE-NMR spectroscopy confirmed that only the *trans*-isomer of **1** is formed. Several attempts were made to obtain functional derivatives, but monocyclic and catenated oligosilanes were always obtained owing to breakdown of the bicyclic compound. Chemical and electrolytic reduction towards an anion radical was carried out at various temperatures. The ESR signal at 150 K shows an overlap of two distinct species; along with the spectrum of the well known $Si_5Me_{10}^{-\cdot}$ radical anion that of a hitherto unknown species was observed.

1. Introduction

Although several new methods of forming Si–Si bonds have been introduced in the past decade [1–3], Wurtz-type reductive coupling of functional organosilanes is still the most widely used. Larger oligosilane structures and their functional derivatives are useful for building new types of polysilane high polymers. Recently we described a variety of coupling reactions with mono- and di-silanes leading to new branched ring- and cage-like oligosilanes ($n_{Si} = 7$–10). The UV spectra of these compounds exhibit a strong bathochromic shift due to σ–σ^*-delocalization within the silicon backbone. Our interest was drawn to octadecamethylbicyclo[4.4.0]decasilane, the only bicyclic permethyloligosilane known at present. Twenty years ago, West *et al.* [4] described a compound of the formula $Si_{10}Me_{18}$ but could not assign a definite structure; indeed, there is the possibility of several structural isomers. Ishikawa *et al.* were able to isolate $Si_{10}Me_{18}$ in very poor yield and some spectroscopic data were obtained [5]. However, the ^{29}Si-NMR signals are consistent with at least two isomers **1** and **2**; see Fig. 1.

To determine which isomer was present, a computational molecular model simulation (Tripos-ALCHEMY-II) of **1** was performed. Indications were that the *trans* isomer should have a double chair conformation with the two rings in the same plane and the *cis*-isomer should have a bent bicyclic structure. There is no evidence for significant skew interactions of some axial methyl substituents as reported previously [6]. Nevertheless, the *trans* isomer should be favoured by geometric factors arising from the Si–Si backbone and

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* Dedicated to Professor M.G. Voronkov in recognition of his important contributions to organosilicon chemistry.

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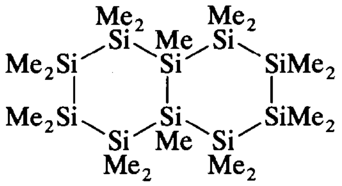
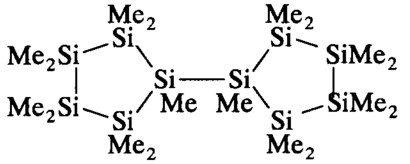


Octadecamethylbicylo[4.4.0]decasilane (**1**)



Bi(nonamethylcyclopentasilanyl) (**2**)

Fig. 1.

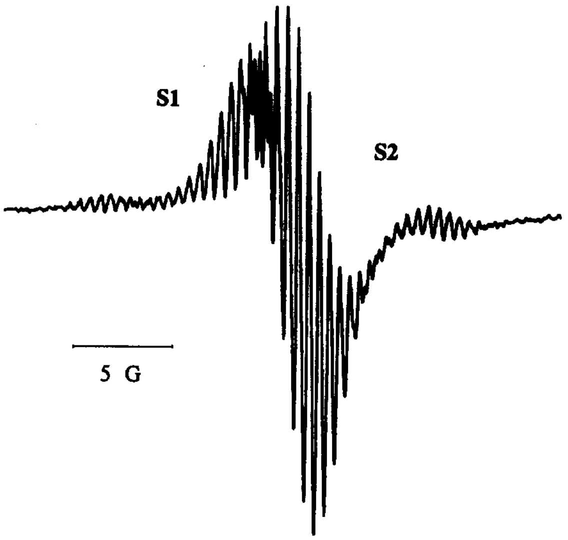


Fig. 2. ESR at 150 K.

this shows up in the calculated intramolecular energies (polarization, orbitals and bond values).

By searching for optimal conditions we succeeded in developing an efficient synthesis of the bicyclic compound, among other oligomers. Purification on a preparative scale was performed by reversed phase HPLC. A purity of > 99% was confirmed by GLC. Compound **2**, which was synthesized as previously described [6], and **1** were investigated by ^{29}Si-NMR spectroscopy and the INEPT-INADEQUATE technique [6]. By use of ^{1}J and ^{2}J coupling constants exact assignment of single Si atoms and an evaluation of the structures were achieved. No additional ^{2}J(Si1–Si2′) couplings, which would indicate the presence of *cis / trans* isomers, were found for **2** at given resolution (see Experimental section). Thus only one stereoisomer must be present in benzene-d_6 solution. Compound **1** was recrystallized from benzene to give triclinic crystals and a crystal structure determination was carried out. This showed that the *trans* conformation is the only structure present in the solid state, as predicted by computational simulation.

2. Electron spin resonance studies

Cyclosilanes [7] and bicyclic or cage oligosilanes [5] can be reduced to anion radicals. These radicals are stable only at low temperatures (< 200 K) and give colours from yellow ($Si_6Me_{12}^{-}$), green ($Si_nEt_{2n}^{-}$) to dark blue ($Si_5Me_{10}^{-}$) on a macroscopic scale. Numerous anion radials of monocyclic oligosilanes have been observed [8], but no systematic study of the existence and nature of electron transfer to bicyclic silanes has been published so far. Since the orbital geometry and electronic structure of the cyclosilanes are still under discussion, reduction of bicyclic compounds may improve understanding.

Chemical reduction of $Si_{10}Me_{18}$ with Na/K in a 3 : 1 mixture of diethyl ether/glyme was carried out at 130 K. ESR monitoring was carried out every 10 K starting from 150 K. Immediately after preparation the yellow solution gives a signal at 150 K (Fig. 2), which shows an overlap of two distinct spectra. One of them (S1) remains unchanged up to 210 K, and is in agreement with all the essential ESR parameters published for $Si_5Me_{10}^{-\cdot}$ (g factor: 2.0032; centre line intensities are in good agreement) [9]. Over the range 155–170 K the signal from the second species (S2) progressively decreases (Fig. 3) and the colour changes from yellow to greenish blue. The only known cyclosilane radical to give yellow colour in solution is $Si_6Me_{12}^{-\cdot}$.

The relative line intensities of S2 correspond to a 24 proton system which is significantly different from the 36 proton system of the six membered ring $Si_6Me_{12}^{-\cdot}$.

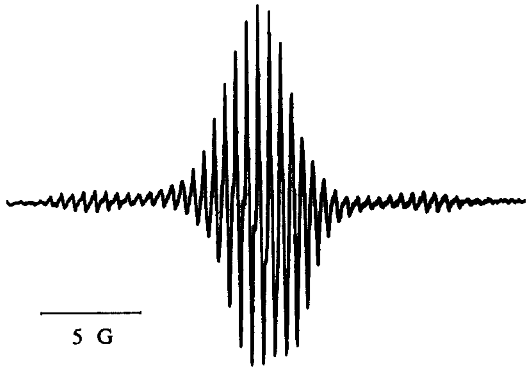


Fig. 3. ESR at 165 K.

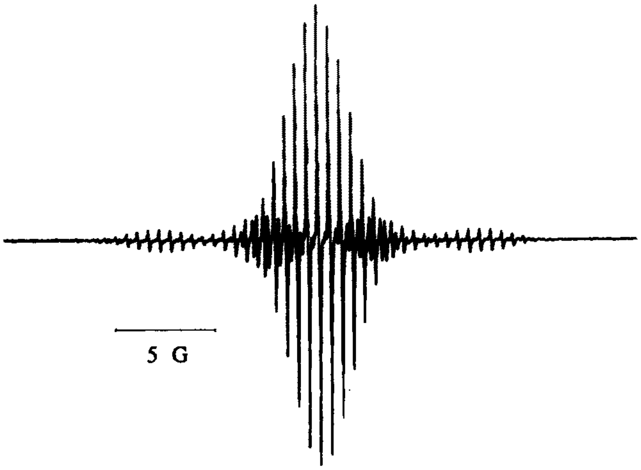


Fig. 4. ESR at 180 K.

The g factor was found to be 2.0019 ± 0.0001 ($Si_6Me_{12}^{-\cdot}$, 2.0028) and the hyperfine ^1H coupling constant was 0.52 ± 0.03 Gauss and we conclude that S2 does not come from the $Si_6Me_{12}^{-\cdot}$ species. The presence of a 24 proton hfs splitting in S2 relates to a concentration of the radical electron wave function around four equivalent Si atoms, each attached to two methyl groups. $Si_4Me_8^{-\cdot}$ would have this number of methyl groups, but gives an entirely different g factor of 2.0037 and exists in the reduced state as a blue solution. Since no further splitting from other protons is observable in S2, we assume that there is no essential distribution of the wave function outside the system of the equivalent Si atoms. Ring interconversion, which is required for electron delocalization, is not possible for $Si_{10}Me_{18}^{-\cdot}$. Thus the observed ESR spectrum S2 can be ascribed to a bicyclic anionic structure. The ^{29}Si and ^{13}C coupling constants could not be derived from the present spectra due to the overlap with S1. The fully resolved spectrum of $Si_5Me_{10}^{-\cdot}$ was observed at temperatures above 190 K (Fig. 4).

3. UV-spectra

The isomers **1** and **2** show significant differences concerning the spectra in the UV region (Fig. 5). Compound **2** exhibits a strong bathochromic shift (three absorption maxima), whereas the two absorption maxima of **1** are comparable with those of other bicyclic species [10] that consist of exocyclic bonded six membered rings (Table 1).

This phenomenon is in agreement with the stronger affinity of Si_5Me_{10} to absorb lone electrons, which is reflected by the relative stability of $Si_5Me_{10}^{-}$ compared to $Si_6Me_{12}^{-}$.

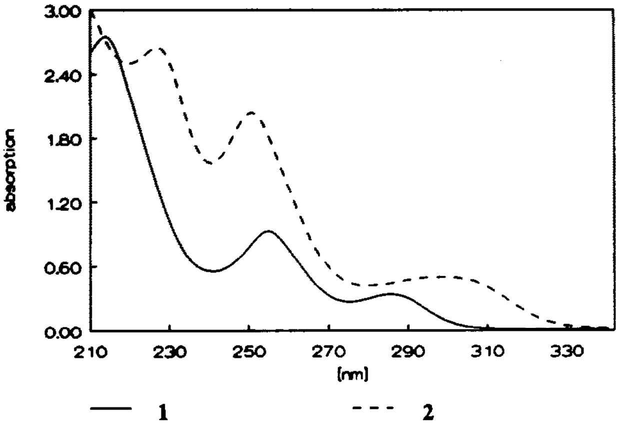


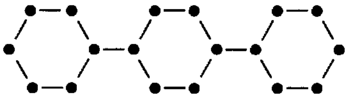
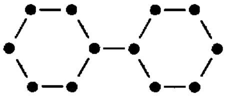
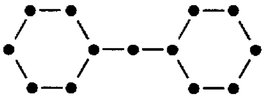
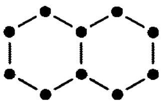
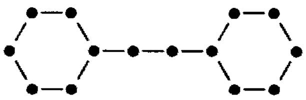
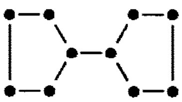
Fig. 5. UV spectra of **1** and **2**.

A comparison of the UV spectra reveals the influence of ring size on geometric overlap of silicon $\nu^*(3d)$ orbitals. The more planar five membered rings (**2**) exhibit a more bathochromic shift in comparison to the fused bicyclic structure of **1**.

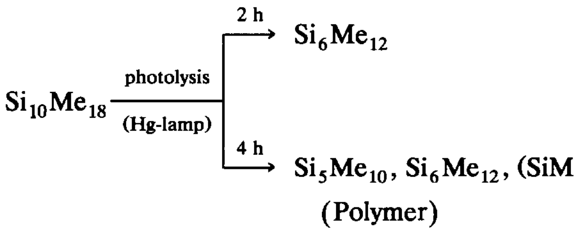
4. Reactions of $Si_{10}Me_{18}$

Photolysis with a low pressure mercury lamp at 254 nm proceeded slowly and gave small amounts of Si_6Me_{12} within 2 h. After a longer period the pen-

TABLE 1. UV-spectra of several bi- and tricyclic permethylated oligosilanes

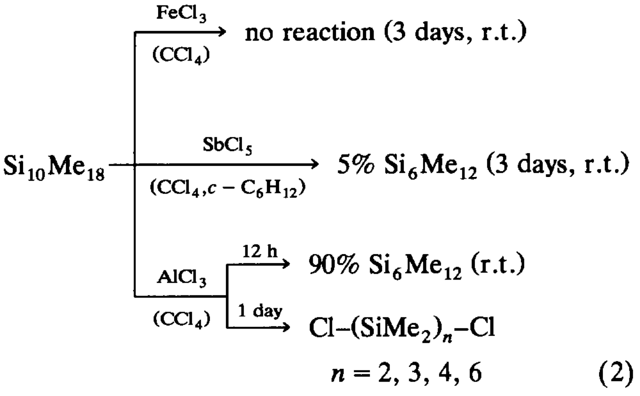
Compound	Maximum (nm)
	270, 233
	276, 257, 237
	279, 250
	284, 253
	296, 260
	298, 249

tameric ring and some (methylpolysilane)polymer is formed (eqn. (1)). Presumably Si_5Me_{10} is formed from the Si_6Me_{12} initially produced by extrusion of an $SiMe_2$: unit, which is well known to occur upon irradiation.



(1)

Additionally, we carried out some reactions with metal halides of different Lewis acidity. Previous results were obtained by treating a CCl_4 solution of Si_5Me_{10} [11]. Depending on Lewis acidity of the salts *mono*chlorination of the ring can be achieved by $FeCl_3$ at room temperature but ring opening and formation of α,ω-dichlorosilanes occurs with $SbCl_5$ and $AlCl_3$. Si_6Me_{12} does not react with $FeCl_3$ but readily undergoes mono-, di- and trisubstitution with $SbCl_5$. 1 does not react with $FeCl_3$ and only 5% (GLC/FID) rearranges to give Si_6Me_{12} by treatment with $SbCl_5$. Upon reaction with $AlCl_3$ a 90% conversion results after 12 h. Usually Si_6Me_{12} undergoes ring contraction to give trimethylsilylnonamethylcyclopentasilane but, interestingly, after 24 h α,ω-dichlorosilanes can be detected as the only products. No other intermediate could be detected on monitoring by GLC/FID and GC/MS (eqn. 2).



(2)

5. Crystal structure of octadecamethylbicyclo[4.4.0]decasilane

Only few structural analyses have been carried out with permethylated cyclic polysilanes. Among the monocyclic rings Si_nMe_{2n} structures of the following homologues have been determined: $n = 4$, 6, 7, 8, 13, 16 [12–16]. One fused bicyclic species, hexadecamethylbicyclo[3.3.1]nonasilane, has been determined [17] and two exocyclic bonded bicyclic compounds were measured by our group [18].

5.1. Crystal structure determination

Crystals (colourless) were grown from benzene. A considerable number of crystal specimens of dimensions 0.1 × 0.15 × 0.5 mm was investigated, all of them either twinned or cracked, judging from the splitting of reflection profiles. The specimen eventually chosen for further investigations showed profile-splitting of up to 1.0°, which adversely affected the quality of the structure analysis.

Diffraction data were collected at low temperature (99(1) K) on a modified STOE diffractometer using graphite monochromated Mo K radiation ($\lambda = 0.71069$ Å). Unit cell parameters were obtained by least squares refinement against the setting angles of 23 reflections with $9° \leqslant 2\theta \leqslant 15°$. Crystals are triclinic, space group $P\bar{1}$, with 2 formula units ($Si_{10}C_{18}H_{54}$, formula weight 551.48) in the unit cell: $a = 10.471$ (12) Å, $b = 13.480$ (20) Å, $c = 14.264$ (13) Å, $\alpha = 102.32$ (8)°, $\beta = 90.17$ (6)°, $\gamma = 112.77$ (10)°, V 1805.5 (1.2) $Å^3$, $d_{calc} = 1.014$ g/cm^3 (calculated from the 99 K unit cell dimensions, $F(000) = 604$ e).

Intensity data (ω-scan, $\Delta\omega = 2.5°$) were collected for four octants of reciprocal space ($-14 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 20$, $< 5.5 \leqslant 2\theta \leqslant 60°$), yielding 8827 observed, 8629 unique and 4275 significant ($F_{abs} > 4\sigma(F)$) structure factors. Lp correction and a semiempirical absorption correction (DIFABS) were applied to the data.

The structure was solved with direct methods (SHELXS) and refined by the least squares method (SHELX76), including anisotropic atomic displacement parameters (ad) for all non-hydrogen atoms. H atoms were included at calculated positions, with only one isotropic ad refined for each of them. $R = 0.1124$, $R_w = 0.1023$ ($w_i = 1/(\sigma^2(F) + aF^2$, $a = 0.001$) for 308 parameters and 4275 observations. A final difference electron density map showed features up to 1.0 e $Å^{-3}$. Computer programs are listed [20]. Relevant data are given in Tables 2 and 3.

The crystal structure confirms the *trans* geometry of the fused cyclohexasilane rings, which adopt a regular chair conformation (Fig. 6). The unit cell contains two crystallographically non-equivalent molecules (A and B) (Fig. 7), which are both located on a crystallographic centre of symmetry. Thus, the asymmetric unit consists of two non-equivalent molecule halves. Although not related by a crystallographic symmetry operation, the two molecules are identical within experimental limits; a superposition of the nonhydrogen atoms of the two molecules shows an rms deviation between corresponding atoms of 0.03 Å. The observed average Si–Si bond

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\times 10^4$, U in Å^2) for the non-hydrogen atoms of octadecamethylbicyclo[4.4.0]decasilane. The equivalent isotropic displacement coefficient was obtained as one third of the trace of the orthogonalized U_{ij}-tensor. E.s.d.'s are given in parentheses. The isotropic temperature factor has the form $T = \exp[-8\pi^2 U \sin^2 \Theta/\lambda^2]$

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Si1	3970(3)	4839(2)	396(1)	120(15)	Si6	871(3)	4839(2)	5397(2)	123(14)
C11	4319(11)	4834(9)	1707(1)	201(58)	C61	525(10)	4845(9)	6708(5)	185(55)
Si2	2238(3)	3106(2)	−323(2)	163(15)	Si7	869(3)	3104(2)	4675(2)	154(15)
C21	1717(13)	2993(10)	−1652(6)	321(78)	C71	1305(12)	3020(9)	3378(6)	250(64)
C22	626(11)	2856(11)	387(7)	319(72)	C72	2215(11)	2859(10)	5378(7)	300(71)
Si3	3021(3)	1711(3)	−258(2)	187(16)	Si8	1315(3)	8300(3)	5261(2)	182(16)
C31	1608(13)	339(10)	−910(8)	318(72)	C81	1634(12)	8344(10)	3956(7)	306(70)
C32	3238(14)	1653(10)	1062(7)	331(83)	C82	1272(12)	9655(10)	5906(7)	312(76)
Si4	4908(3)	8001(3)	1029(2)	182(16)	Si9	3097(3)	7999(2)	6023(2)	177(15)
C41	5296(12)	8205(9)	2384(6)	259(64)	C91	2883(12)	8198(10)	7385(6)	279(71)
C42	4121(12)	9019(10)	880(8)	315(75)	C92	4901(11)	9059(10)	5867(8)	309(68)
Si5	3180(3)	6247(2)	394(2)	138(15)	Si10	3064(3)	6245(2)	5394(2)	134(15)
C51	2545(12)	6208(9)	−870(6)	236(64)	C101	3661(10)	6210(10)	4122(6)	253(64)
C52	1670(10)	6091(10)	1196(6)	236(63)	C102	4422(10)	6096(9)	6195(7)	241(63)

TABLE 3. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $Si_{10}Me_{18}$. Estimated standard deviations are given in parentheses

Si1–Si2	2.3416(53)	Si1–Si5	2.3469(54)	Si1–C11	1.9062(87)
Si1–Si1B	2.3697(53)	Si2–Si3	2.3420(57)	Si2–C21	1.9294(95)
Si2–C22	1.9244(128)	Si3–Si4	2.3677(57)	Si3–C31	1.9012(129)
Si3–C32	1.9180(101)	Si4–C41	1.9137(92)	Si4–C42	1.8996(140)
Si4–Si5B	2.3334(54)	Si5–C51	1.9020(98)	Si5–C52	1.9265(117)
Si6–Si7	2.3456(53)	Si6–Si10	2.3452(54)	Si6–C61	1.9055(84)
Si6–Si6A	2.3673(53)	Si7–Si8	2.3544(56)	Si7–C71	1.8976(97)
Si7–C72	1.8964(125)	Si8–Si9	2.3637(56)	Si8–C81	1.9018(97)
Si8–C82	1.8791(129)	Si9–C91	1.9301(90)	Ci9–C92	1.9260(130)
Si9–Si10A	2.3294(54)	Si10–C101	1.9185(96)	Si10–C102	1.9173(114)
Si2–Si1–Si5	110.64(81)	Si2–Si1–C11	106.90(87)	Si2–Si1–Si1B	110.95(81)
Si5–Si1–C11	107.47(88)	Si5–Si1–Si1B	110.47(81)	C11–Si1–Si1B	110.29(89)
Si1–Si2–Si3	109.93(82)	Si1–Si2–C21	112.07(90)	Si1–Si2–C22	109.14(88)
Si3–Si2–C21	108.56(90)	Si3–Si2–C22	107.67(90)	C21–Si2–C22	109.36(97)
Si2–Si3–Si4	110.63(82)	Si2–Si3–C31	107.70(91)	Si2–Si3–C32	108.84(91)
Si4–Si3–C31	109.28(90)	Si4–Si3–C32	112.83(93)	C31–Si3–C32	107.38(96)
Si3–Si4–C41	109.79(90)	Si3–Si4–C42	112.34(90)	Si3–Si4–Si5B	111.99(81)
C41–Si4–C42	106.71(96)	C41–Si4–Si5B	110.09(89)	C42–Si4–Si5B	105.71(90)
Si1–Si5–C51	111.71(88)	Si1–Si5–C52	109.84(89)	Si1–Si5–Si4B	112.03(82)
C51–Si5–C52	108.49(95)	C51–Si5–Si4B	108.20(88)	C52–Si5–Si4B	106.36(87)
Si7–Si6–Si10	110.57(81)	Si7–Si6–C61	107.39(87)	Si7–Si6–Si6A	110.78(81)
Si10–Si6–C61	107.38(87)	Si10–Si6–Si6A	110.50(81)	C61–Si6–Si6A	110.11(88)
Si6–Si7–Si8	110.00(82)	Si6–Si7–C71	111.56(89)	Si6–Si7–C72	108.96(88)
Si8–Si7–C71	109.92(88)	Si8–Si7–C72	107.60(90)	C71–Si7–C72	108.70(96)
Si7–Si8–Si9	110.38(82)	Si7–Si8–C81	109.78(89)	Si7–Si8–C82	107.67(91)
Si9–Si8–C81	110.60(91)	Si9–Si8–C82	109.71(90)	C81–Si8–C82	108.65(95)
Si8–Si9–C91	108.59(91)	Si8–Si9–C92	110.75(89)	Si8–Si9–Si10A	112.41(81)
C91–Si9–C92	107.78(95)	C91–Si9–Si10A	109.99(89)	C92–Si9–Si10A	107.23(89)
Si6–Si10–C101	111.95(89)	Si6–Si10–C102	110.11(88)	Si6–Si10–Si9A	112.18(82)
C101–Si10–C102	108.41(93)	C101–Si10–Si9A	107.79(90)	C102–Si10–Si9A	106.17(87)

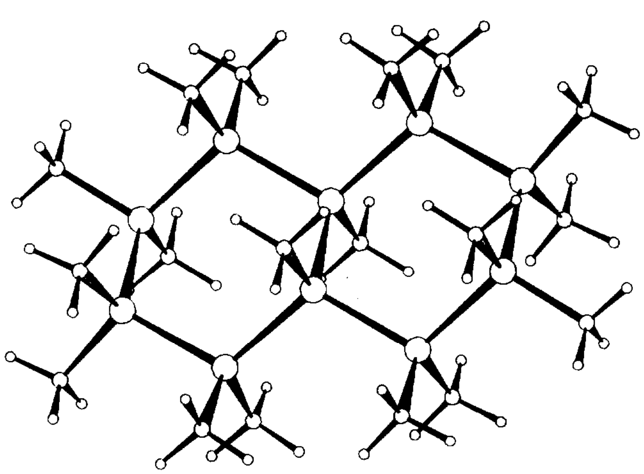


Fig. 6. Projection of one molecule of $Si_{10}Me_{18}$ from the crystal structure. Note that the molecule contains a crystallographic centre of symmetry bisecting the central Si–Si bond. The second molecule of the asymmetric unit is virtually identical to the one shown.

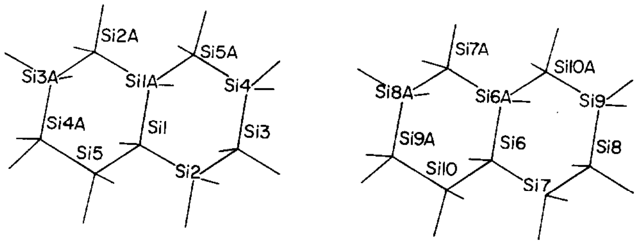


Fig. 7. Numbering of silicon atoms in the two crystallographically non-equivalent molecules in the crystal structure of $Si_{10}Me_{18}$.

length (2.351(14) Å) is as expected for a covalent Si–Si bond (2.34 Å). The Si–Si bond common to the two rings is significantly longer in both molecules (2.369 Å). The two molecules appear to be completely unstrained, with Si–Si–Si angles of 111.0(0.8)°, compared to 111.6° in dodecamethylcyclohexasilane.

Supplementary data are available from the authors.

6. Experimental details

6.1. Syntheses

Decamethylcyclopentasilane [11], dodecamethylcyclohexasilane [19] and bi(undecamethylcyclopentasilanyl) [5] were prepared according to the literature.

6.1.1. Octadecamethylbicyclo[4.4.0]decasilane

All glassware was thoroughly dried and the entire system was kept under argon (N 4.5) during the course of the reaction. Into a 1000 ml three-necked round-bottom flask was placed 7.4 g (1060 mmol) of lithium powder.

Tetrahydrofuran (THF) (400 ml), freshly distilled from potassium, was added and the suspension heated until reflux commenced. Into an addition funnel were then syringed 44.6 ml (240 mmol) of *sym*-$Si_2Me_4Cl_2$ and 18.8 ml (160 mmol) of $SiMeCl_3$ in 100 ml of THF; this solution was added dropwise to the lithium suspension. Near the completion of the reaction (3 h) the mixture turned reddish-brown. After the reaction was found to be complete, the solution was cooled in an ice-bath and HCl (6 M) was slowly added to remove the excess alkali metal. The oligosilanes in solution were extracted with petroleum ether. The bright yellow organic phase, which contained no unsoluble polysilanes, was separated and reduced in volume on a rotary evaporator to a thick viscous syrup. This mixture was directly separated by HPLC and LPLC methods.

The course of the reaction was monitored by GLC. Samples were prepared as follows: 20 μl of the reaction mixture was syringed into a 5 ml glass tube containing 1 ml of dry n-heptane; the solution was hydrolyzed and 1 μl of the organic phase injected. Recovery rate after the separation process was found to be high (HPLC: 94% of weight; LPLC: 89% of weight). A total proportion of 24% of $Si_{10}Me_{18}$ was isolated and recrystallized from benzene. Remaining products were Si_6Me_{12} (48%) and the bicyclic compounds Si_8Me_{14} (16%) and Si_9Me_{16} (6%).

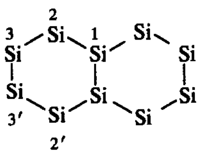
6.2. Chemical reduction

An ESR tube ($\phi = 2$ mm) was thoroughly dried, evacuated (1.10^{-4} bar) and kept under nitrogen. About 10 μl of sodium/potassium alloy (1:3) was syringed into the tube and about 0.3 ml of a freshly distilled 3:1 mixture of diethylether and dimethoxyethane was added. About 0.02 mmol of the cyclosilane was dissolved, the tube sealed and placed in an ultrasonic bath for 30 min. 1-Methylbutane was cooled to −120°C ($Si_{10}Me_{18}$), −100°C (Si_6Me_{12}) or −80°C (Si_5Me_{10}) by stepwise addition of liquid nitrogen and the tube immediately transferred into the cooling bath. After about 5 min the colour specific to the compound appeared. The reduction process is reversible for a long time, even after tenfold repetition of dispersion and cooling of the system. In order to compare and verify reductions of several cyclosilanes, Si_5Me_{10}, Si_6Me_{12}, **1** and **2** were investigated.

6.2.1. Si_5Me_{10}.

The dark blue colour of $Si_5Me_{10}^{\cdot-}$ was present up to −50°C; this changed to orange at room temperature and the solution immediately turned colourless upon contact with air. GLC analysis revealed the main product to be Si_6Me_{12} (Table 4); this phenomenon has been explained to occur as a result of insertion of dimethylsilylene, $SiMe_2$: (West *et al.* [19]).

Octadecamethylbicyclo[4.4.0]decasilane (**1**)



$Si_{10}C_{18}H_{54}$

Mol. wt.: 551.48

Mp. (°C):	164–166 (colourless crystals).
^{29}Si (δ):	**1**: −77.04; **2**: −34.17; **3**: −39.61. ^1J(Si1–Si2) = 49.2 Hz, ^1J(Si2–Si3) = 59.5 Hz, ^2J(Si1–Si3) = 6.4 Hz, ^2J(Si2–Si3′) = 8.6 Hz, ^2J(Si1–Si2′) = 3.4 Hz.
^{13}C (δ):	**1**: −5.78, −8.19; **2**: −3.86, −4.28; **3**: −2.09, −6.56
^{1}H (δ):	0.24 (4 Me), 0.26 (4 Me), 0.33 (2 Me), 0.37 (8 Me)
MS:	550 (100%/M^+), 477 (8%/Si_9Me_{15}), 403 (20%/Si_8Me_{12}), 73 (82%/$SiMe_3$).
CH (%):	calc. Si, 50.93; C, 39.20; H, 9.87. found: (Si, 50.57) C, 39.67; H, 9.76.
IR (cm^{-1}):	1240vs, 835s, 824s, 793vs, 771s, 769s, 726s, 722s, 679s, 645s, 624m, 435w, 425w, 418w, 382m, 369m, 308m, 303m, 290m, 279m.
UV:	212 (73800), 253 (25000), 284 (9200).

Fig. 8.

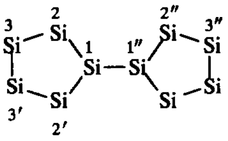
6.2.2. $Si_6Me_{12}^-$

$Si_6Me_{12}^-$ was a lemon yellow colour at −100°C. Upon warming to room temperature the solution appeared slightly yellow. In contrast to what happens with Si_5Me_{10}, repetition of this process only leads to the formation of Si_5Me_{10}.

For **2**, results were in agreement with those of the reduction of Si_5Me_{10}. For **1**, upon warming the dispersed Na/K-suspension to −120°C, the colour turns from yellow to greenish-yellow. Results after warm-up to room temperature were the same as described above.

The colour of the cyclosilane solutions at room temperature may be ascribed to intermediate silyl–alkali species. The colour faded rapidly when cyclopentadiene was added as a trapping agent. As a consequence the mixture turns dark brown on air, when the corresponding cyclopentadienyl/alkali-metal anion is formed.

Bi(undecamethylcyclopentasilanyl) (**2**)



$Si_{10}C_{18}H_{54}$

Mol. wt.: 551.48

Mp. (°C):	117–118 (colourless crystals).
Bg.p. (°C):	133 ($9\cdot10^{-5}$ Torr).
^{29}Si (δ):	**1**: −75.78; **2**: −34.30; **3**: −40.98. ^1J(Si1–Si2) = 50.5 Hz, ^1J(Si2–Si3) = 59.5 Hz, ^2J(Si1–Si3) = 8.4 Hz, ^2J(Si2–Si3′) = 12.3 Hz, ^3J(Si1–Si3′) = 3.9 Hz, ^2J(Si1–Si2″) and ^2J(Si1–Si3′) could not be determined due to limits of experimental resolution (±0.3 Hz).
^{1}H (δ):	0.24 (12 Me), 0.34 (4 Me), 0.33 (2 Me).
MS:	550 (100%/M^+), 477 (12%/Si_9Me_{15}), 403 (21%/Si_8Me_{12}), 345 (10%/Si_7Me_{10}), 260 (32%/Si_5Me_8), 201 (22%/Si_4Me_6), 73 (86%/$SiMe_3$).
CH (%):	calc.: Si, 50.93; C, 39.20; H, 9.87. found: (Si, 50.57) C, 39.67; H, 9.76.
IR (cm^{-1}):	1246s, 838m, 801s, 790sh, 764m, 730s, 688m, 651m, 638sh, 411m, 358m, 279w, 248w
UV:	225 (41100), 249 (31700), 298 (7800).

Fig. 9.

The ESR-measurements were done using N_2-cooling and compensating thermostate heating in the cavity. Alkali metals may destroy larger cyclic systems, as several attempts to product anionic species from exocyclic bound bicyclic oligosilanes (Table 1) failed. No reaction of the solvents with alkali metals during dispersion in the ultrasonic bath and change of temperature could be monitored (GLC/MS) and there was no change of colour.

6.3. *Instrumentation*

NMR-spectra were recorded on a Bruker MSL 300 in C_6D_6 solution. IR and UV spectra were measured with Perkin-Elmer 883 (CsBr plates) and Philips PU-8740 instruments respectively.

TABLE 4

Compound (purity; GLC)	Anion radical		% of all products detected by GLC(FID) upon warming to room temperature			
	$T_{stab.}$ (°C)	colour	Si_5Me_{10}	Si_6Me_{12}	Si_7Me_{14}	$Si_{10}Me_{18}$
Si_5Me_{10} (98%)	−80 to −50	dark blue	10	80	1.4	
Si_6Me_{12} (> 99%)	−100 to −50	lemon yellow	13	84	1.7	
Si_6Me_{12} (upon repetition)		dark blue	8	88	1.9	
1 (> 99%)	–	greenish blue	12	28	1.6	54
1 (upon repetition)		dark blue	16	76	1.7	
2 (> 99%)	–	dark blue	14	79	1.5	

GLC-monitoring was carried out on an HP 5890-II (12 m HPI, ϕ 0.53 mm, det.: FID(He)), linked to an HP 3365 Chemstation. GLC/MS analyses were obtained on an HP5971 MSD linked to an HP5890-II (25 m HP1, ϕ 0.2 mm). Mass spectra (solid-probe inlet) were obtained on a Finnigan-MAT-212 (120 eV).

ESR measurements were carried out on a Bruker ER 200 D X-band spectrometer. Operating conditions were as follows. Microwave frequency 9-46 GHz, modulator/receiver frequency 100 KHz and field modulation intensity 0.1 G_{pp}. Field intensity mid range 3358 G and scan range 50 G.

Liquid chromatography procedures were as follows. HPLC: Waters model 240 UV absorbance detector (254 nm) and 6000A chromatography pump (also used for LPLC; Siemens programmable fraction collector and automatic injection system; HP 3396 integration unit.

Chromatographic separations were done by the following columns. HPLC precolumn: LiChroCART 4-4 (Merck, filled with LiChrospher 100 RP-18 (251 m)); semipreparative column: LiChroCART 250-10 (Merck, with LiChrospher 100 RP-18 (101 m)). Sample: 0.1 g dissolved in 150 ml of n-heptane; eluent methanol.

LPLC column Lobar "A" (240–10) or "B" (310–25); (Merck, with LiChroprep (40–631 m)). Sample: 1 g dissolved in 2 ml of n-heptane; eluent methanol.

Irradiations were performed in a quartz-tube (i.d. 20 mm) with a Philips HPK short-wave UV lamp (125 W).

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