

## Novel bicyclic Si-ring systems

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### Abstract

Two diphenylated bicyclic silanes bi(3-phenyldecamethylcyclohexasilanyl) and bi(4-phenyldecamethylcyclohexasilanyl) were synthesized by action of Na/K alloy on the mixed substituted monocycles 1-chloro-3-phenyl- or 1-chloro-4-phenyldecamethylcyclohexasilane. UV absorption spectra are reported compared with the spectra of (cyclo-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub> and its monophenylated derivatives. Reaction of the di-Grignard reagent BrMg–C<sub>6</sub>H<sub>4</sub>–MgBr with chloroundecamethylcyclohexasilane (cyclo-Si<sub>6</sub>Me<sub>11</sub>)Cl and bromononaphenylcyclopentasilane (cyclo-Si<sub>5</sub>Ph<sub>9</sub>)Br afforded the 1,4-bis(cyclosilanyl) substituted benzene derivatives 1,4-bis(undecamethylcyclohexasilanyl)benzene (cyclo-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and 1,4-bis(nonaphenylcyclopentasilanyl)benzene (cyclo-Si<sub>5</sub>Ph<sub>9</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. Both were investigated by <sup>29</sup>Si CP/MAS NMR. The single crystal structure and the cyclic voltammogram of (cyclo-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> are reported.

**Keywords:** Silicon; Bicyclic silanes; <sup>29</sup>Si CP/MAS NMR

### 1. Introduction

For the last decade our major interest has been the synthesis of polycyclic Si-ring systems and the evaluation and interpretation of their physical properties such as electron delocalization, color shifting, etc. Most of the polycyclic Si-ring systems synthesized so far containing linearly connected cyclohexasilanes [1,2] and cyclopentasilanes [3,4] are permethylated and therefore less appropriate for further chemical reactions.

The connecting Si–Si bonds in these compounds are weak, sensitive to chemical attack, and the force constants are lower than the force constants within the SiSi bonds of the ring systems [5]. The formation of radical anions was found in only one case [6]. The additional electron seems to be localized exclusively in one ring. In all other cases the formation of radical anions was not possible. There the polycyclosilane was cleaved and the result was the formation of a cyclopentasilanyl

radical anion which is known to be the most stable of all monocyclosilanyl radical anions.

Methylated polycyclics, connected directly by Si–Si bonds, are of great interest when functionalized by phenyl groups because they can be used as chemical synthons for further reactions. Action of triflic acid on these compounds yields the corresponding polycyclic silyl triflates, which can be converted into other derivatives by triflate substitution [7]. In contrast, by comparing diphenylated as well as monophenylated derivatives of (cyclo-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub> with the parent compound, information can be obtained about the influence of phenyl substitution on the UV absorption spectra of methylated polycyclosilanes.

As the perturbation of the benzene  $\pi$ -system can be used to determine the electronic influence of substituents, silyl substituted benzene derivatives have been the subject of numerous investigations. For their radical anions ESR data demonstrate a C <sub>$\pi$</sub>   $\rightarrow$  Si electron delocalization into empty silicon orbitals. We have now started an investigation of the influence of cyclosilanyl groups, which are known to possess electron delocalisation potential superior to monosilyl groups. In this paper we wish to report the synthesis of two 1,4-bis(cyclo-

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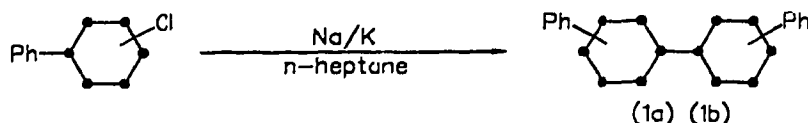


Fig. 1. Synthesis of bi(4-phenyldecamethylcyclohexasilanyl) (**1a**) and bi(3-phenyldecamethylcyclohexasilanyl) (**1b**). ● = SiMe<sub>2-n</sub>, n = 0, 1.

silanyl) substituted benzene derivatives, (*cyclo*-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and (*cyclo*-Si<sub>5</sub>Ph<sub>9</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. These were characterized by means of <sup>29</sup>Si CP/MAS NMR and X-ray structure determination.

## 2. Syntheses

The synthesis of diphenylated derivatives of (*cyclo*-Si<sub>6</sub>Me<sub>11</sub>)<sub>2</sub> requires mixed disubstituted cyclohexasilanes as starting materials. Recently we published a paper describing a new method of separating 1,3- and 1,4-disubstituted methylcyclohexasilanes by using oxygen-bridged and dihydroxy derivatives [8]. On treating 1,4- or 1,3-diphenyldecamethylcyclohexasilane with one equivalent of triflic acid, one phenyl group is split off selectively to give the monotriflate derivatives. These are easily transformed into the corresponding monohalo- or hydrogenated cyclohexasilanes by action of LiX (X = Cl, Br) or LiAlH<sub>4</sub>.

Reaction of 1-chloro-4-phenyldecamethylcyclohexasilane or 1-chloro-3-phenyldecamethylcyclohexasilane with Na/K alloy in n-heptane afforded the novel diphenylated bicycles **1a** or **1b** (Fig. 1).

Synthesis of **1a** or **1b** by the reaction of 1-hydro-4-phenyldecamethylcyclohexasilane or 1-hydro-3-phenyldecamethylcyclohexasilane with <sup>1</sup>Bu<sub>2</sub>Hg and subsequent UV irradiation of the bicyclic Hg compounds was not successful.

Reaction of the monocycles with <sup>1</sup>Bu<sub>2</sub>Hg in n-heptane always formed a mixture of different isomeric bicyclic Hg compounds. Subsequent UV irradiation yielded the corresponding isomeric SiSi-connected cyclohexasilanes, which could not be separated.

In addition to directly connected cyclohexasilanes, we were also interested in the synthesis of compounds

where the rings are separated by a phenyl group. The "one-pot in situ" Grignard procedure, as reported for the synthesis of 1,4-bis(tris(trimethylsilyl)silyl)benzene from tris(trimethylsilyl)chlorosilane [9], failed in the case of the preparation of 1,4-bis(undecamethylcyclohexasilanyl)benzene (**2**). The reaction of monohalocyclohexasilanes (*cyclo*-Si<sub>6</sub>Me<sub>11</sub>)-X (X = F, Cl, Br) with *p*-dibromobenzene and Mg afforded **2** in very poor yields depending on X. Bi(undecamethylcyclohexasilanyl), the separation of which required chromatographic methods, was formed as the main product by transmetalation of the halosilane (Br > Cl > F).

The reaction of *p*-dibromobenzene with Mg in THF, as a first step, formed a white suspension of the Grignard reagent BrMg-C<sub>6</sub>H<sub>4</sub>-MgBr. By treating chloroundecamethylcyclohexasilane with this suspension in THF under sonication conditions, the formation of **2** was achieved in suitable yields (GC analysis more than 50%) without any transmetalation products (Fig. 2).

From the synthesis of the bicyclic perphenylated cyclopentasilane (*cyclo*-Si<sub>5</sub>Ph<sub>9</sub>)<sub>2</sub>, transmetalation is known to be of only minor importance [10]. This fact encouraged us to employ the one pot synthesis for compound **3** (Fig. 3).

The reaction of bromononaphenylcyclopentasilane with 1,4-dibromobenzene and Mg formed a white solid which was absolutely insoluble. It was therefore almost impossible to characterize its structure. Solid state NMR, however, suggests the formation of compound **3** (see Section 4).

## 3. UV spectra

The ultraviolet spectra of the cyclopolysilanes **1a**, **1b** and **2** are shown in Fig. 4 compared with the spectra of

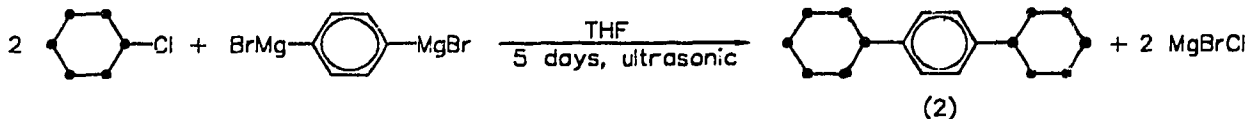


Fig. 2. Synthesis of 1,4-bis(undecamethylcyclohexasilanyl)benzene (**2**). ● = SiMe<sub>2-n</sub>, n = 0, 1.

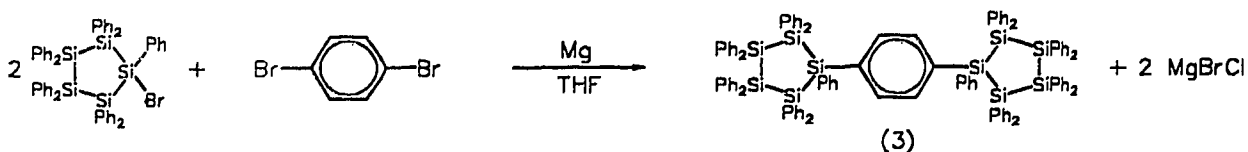


Fig. 3. Synthesis of 1,4-bis(nonaphenylcyclopentasilanyl)benzene (**3**).

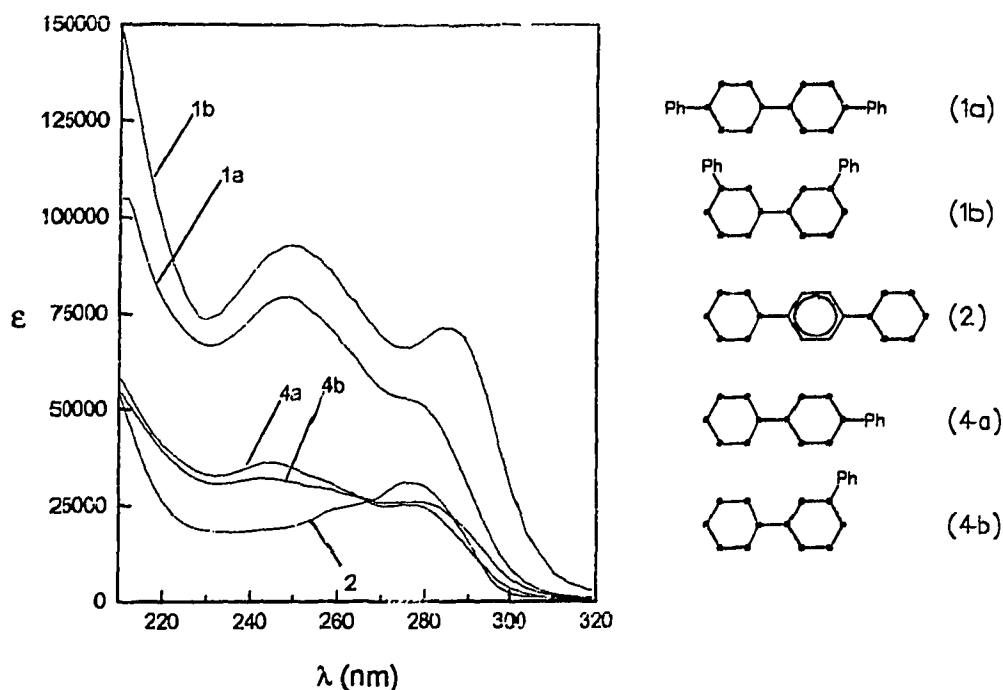


Fig. 4. UV spectra of phenyl substituted bicyclic methylcyclohexasilanes.

the monophenylated compounds 1-phenyl-4- (4a) and 1-phenyl-3-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (4b). The absorption maxima are listed in Table 1. All of the compounds studied have absorptions in the near ultraviolet region attributable to their silicon framework. Phenyl substituents are expected to have electronic as well as steric effects on the spectra of the permethylated system bi(undecamethylcyclohexasilanyl) (5), leading to bathochromic shifts and marked intensification of absorption bands. Similar

Table 1  
Ultraviolet spectral data for phenyl substituted bicyclic polysilanes

Compound	$\lambda_{\max}$ (nm) ( $\epsilon$ (l mol <sup>-1</sup> cm <sup>-1</sup> ))
1a	248.1 (79300) 278.3 (51900) sh
1b	249.6 (92800) 284.8 (71200)
2	260.4 (24400) sh 276.1 (31000)
4a	244.7 (36200) 276.7 (25200)
4b	242.4 (32200) 277.6 (25900)
5	237 (4700) 276 (3500)

Table 2  
<sup>29</sup>Si chemical shifts of compounds 2 (solution and CP/MAS) and 3 (CP/MAS)

Solution (ppm)	CP/MAS (ppm)	
2	2	3
-40.862	-36.366	-23.759
-41.780	-40.276	-38.919
-41.815	-40.905	-54.217
-42.258	-41.626	

Table 3  
Crystallographic data and some experimental details for 2

<i>Crystal data</i>	
Empirical formula	C <sub>28</sub> H <sub>70</sub> Si <sub>12</sub>
Formula weight	743.9
Crystal system	triclinic
Space group	P1
<i>a</i> (Å)	10.088(12)
<i>b</i> (Å)	10.216(10)
<i>c</i> (Å)	41.51(5)
$\alpha$ (°)	83.48(9)
$\beta$ (°)	86.77(8)
$\gamma$ (°)	61.28(7)
Volume (Å <sup>3</sup> )	3727(8)
<i>Z</i>	3
Density (calc.) (g cm <sup>-3</sup> )	0.994
Absorption coeff. (mm <sup>-1</sup> )	0.329
<i>F</i> (000)	1218
<i>Data collection</i>	
2 $\theta$ range (°)	5.7–46
Index ranges	-11/ <i>h</i> /11 -11/ <i>k</i> /11 -17/ <i>l</i> /45
Reflections collected	13082
Independent reflections	10658 ( $R_f = 0.1274$ )
Observed reflections	7678 ( $I > 2\sigma(I)$ )
<i>Solutions and refinement</i>	
Number of parameters refined	1147
Restraints	411
Weighting scheme	$1/\sigma^2(F^2) + (0.0799P)^2$ $+ 0.1104P$ $P = (F_o^2 + 2F_c^2)/3$
Final <i>R</i> indices	$R_1 = 0.0649$ , $wR_2 = 0.1463$
<i>R</i> indices (all data)	$R_1 = 0.1004$ , $wR_2 = 0.1918$
Goodness-of-fit on $F^2$	1.113
Largest diff. peak/hole (e Å <sup>-3</sup> )	0.43/-0.32

spectral changes were observed upon phenyl substitution in monocyclic silanes and attributed to mixing between the  $\pi^*$  orbitals of the benzene rings and the cyclosilane ( $\sigma^*$ ) excited state orbitals [11].

#### 4. $^{29}\text{Si}$ CP/MAS NMR spectra of **2** and **3**

$^{29}\text{Si}$  CP/MAS NMR spectra were recorded with a Bruker MSL 300 spectrometer having the following parameters: spectrometer frequency for  $^{29}\text{Si}$  59.627 MHz; rotation frequency 3 kHz; CP-MAS pulse length 3  $\mu\text{s}$ , contact time 5 ms, repetition time 5 s.

Comparison of compounds **2** and **3** shows a wide spread of the chemical shifts of the phenylated analogue **3** in the solid state spectrum, whereas the methylated one exhibits a narrow distribution of resonance lines in the same region as the chemical shifts of the solution spectrum (Table 2).

The solution spectrum of the insoluble **3** is not expected to have as wide a chemical shift spread as that observed in the solid state.

The reason for this phenomenon could be found in the deformation of sterically stressed ring systems – as is the phenylated one (**3**) – in a crystal lattice.

#### 5. Structure analysis of **2**

A single crystal suitable for X-ray diffraction analysis was crystallized in diethylether. The structure of **2** was determined at room temperature using a modified STOE four-circle diffractometer and graphite monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The crystal was glued onto a glass fiber with a two component adhesive. Owing to the large cell dimensions a very narrow slit diaphragm had to be used for the detector. After careful consideration we had to exclude space groups with higher symmetry. This, along with other reasons, is because of the lack of a symmetry element in the molecule itself. Therefore space group *P1* was chosen and later confirmed by a successful structure solution. Transformation into a monoclinic *c*-centered cell is possible, but only in rough approximation do  $\alpha$  and  $\gamma$  represent a  $90^\circ$  angle, and the symmetry of the diffraction pattern matches a monoclinic system very poorly with  $R(f) = 0.223$ . The structure was solved by direct methods using XS [12] and refined by full-matrix least-squares with SHELXL-93 [13] minimizing the residuals for  $F^2$ . Hydrogen atoms were included in the model at their calculated positions. An additional torsion angle was refined for each methyl-

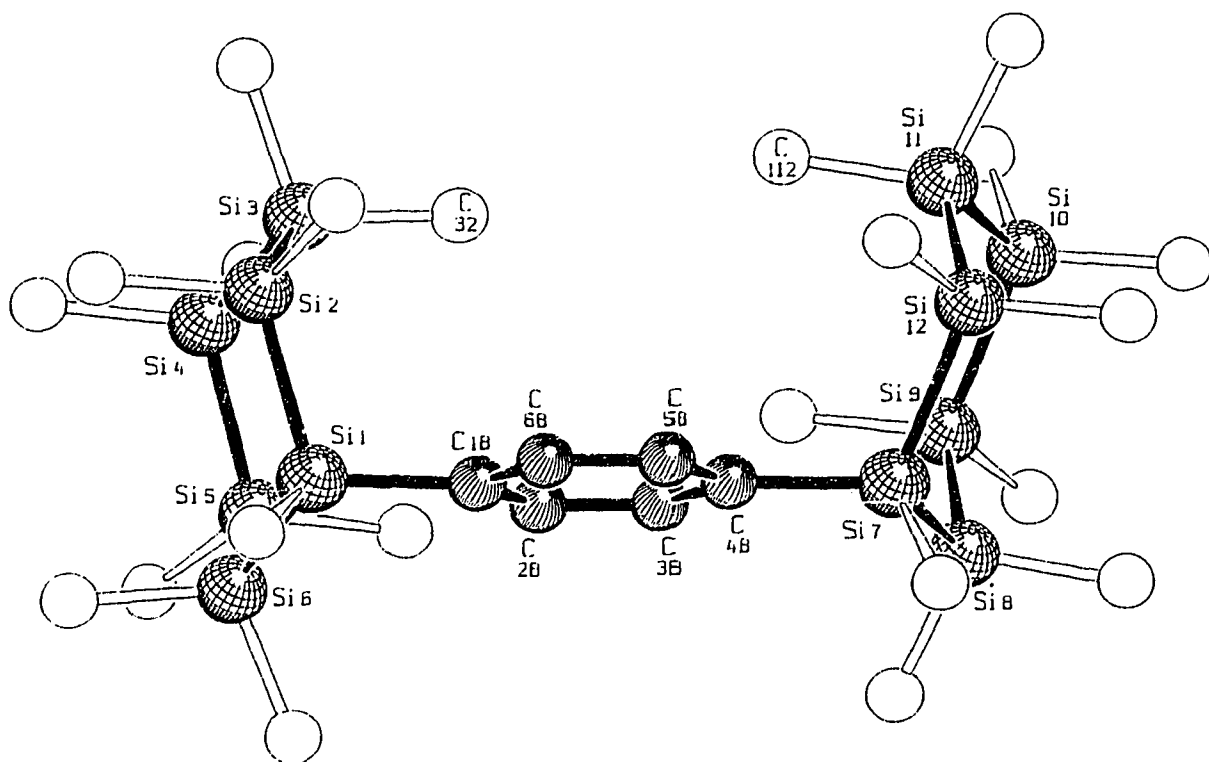


Fig. 5. X-ray structure and atom labeling of **2** (C(32) means the second C bonded to Si(3)).

group maintaining an idealized geometry. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, isotropic displacement parameters were used for hydrogen atoms (1.5 times the equivalent isotropic displacement parameter of the respective heavy atom).

Further crystallographic details are given in Table 3.

The molecules exhibit a surprising degree of rigidity. By superimposing two of these three non-symmetry related molecules of the unit cell, it can be shown that the RMS deviation is 0.0978 Å (1–2), 0.0663 Å (1–3) and 0.1246 Å (2–3) respectively.

In the molecule itself the benzene ring is somewhat stretched. It shows *ipso* angles of only  $116^\circ$ . This stretching of the benzene ring along the substituent axis widens correspondingly all other ring angles to about  $122^\circ$ . The closest non-bonded distance between two methyl-carbons, bonded to different Si-rings of the same molecule, amounts to only 3.82 Å. The bonding Si–Me distances of about 1.88 Å are in the normal range. Si–Si distances exhibit rather usual values between 2.35 and 2.33 Å.

The structure is shown in Fig. 5.

Selected intramolecular angles and distances with estimated standard deviations for compound **2** are given in Table 4, fractional coordinates and equivalent isotropic thermal parameters for one molecule in Table 5.

Lists of the fractional atomic coordinates, displacement parameters, bond distances, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre as supplementary material. All estimated standard deviations in these and subsequent tables are given in parentheses.

## 6. Cyclic voltammetry of **2**

Cyclic voltammetric measurements of **2** in 0.1 M tetrabutylammoniumperchlorate (TBAP)/CH<sub>2</sub>Cl<sub>2</sub> exhibited one irreversible oxidation wave at +1.39 V vs. SCE ( $\nu = 0.1 \text{ V cm}^{-1}$ ). The silane did not undergo any reduction in 0.1 M TBAP/THF down to  $-3 \text{ V}$  vs. SCE.

Probably, by oxidation of the cyclosilane a radical cation is obtained and SiSi bond cleavage takes place. These results are in accordance with electrochemical investigations of a series of polycyclosilanes [14,15].

## 7. Experimental section

### 7.1. General data

All manipulations involving air-sensitive materials and all electrochemical measurements were performed under nitrogen employing standard Schlenk techniques.

Table 4  
Selected intramolecular angles ( $^\circ$ ) and distances (Å) with estimated standard deviations for compound **2**

Atoms	Distance	Bond	Angle
Si(1)–Si(2)	2.333(06)	Si(2)–Si(1)–Si(6)	111.6(2)
Si(2)–Si(3)	2.328(06)	Si(1)–Si(2)–Si(3)	113.0(2)
Si(3)–Si(4)	2.336(06)	Si(2)–Si(3)–Si(4)	110.5(2)
Si(4)–Si(5)	2.333(06)	Si(3)–Si(4)–Si(5)	112.2(2)
Si(5)–Si(6)	2.354(06)	Si(4)–Si(5)–Si(6)	112.9(2)
Si(6)–Si(1)	2.338(06)	Si(5)–Si(6)–Si(1)	114.4(2)
Si(1)–C(1B)	1.884(10)	C(1B)–Si(1)–Si(2)	107.0(4)
C(1B)–C(2B)	1.354(14)	C(2B)–C(1B)–C(6B)	116.0(9)
C(2B)–C(3B)	1.382(14)	C(1B)–C(2B)–C(3B)	123.4(9)
C(3B)–C(4B)	1.407(14)	C(2B)–C(3B)–C(4B)	121.3(9)
C(4B)–C(5B)	1.381(14)	C(3B)–C(4B)–C(5B)	115.3(9)
C(5B)–C(6B)	1.378(14)	C(4B)–C(5B)–C(6B)	122.9(9)
C(6B)–C(1B)	1.409(14)	C(5B)–C(6B)–C(1B)	121.2(9)
C(4B)–Si(7)	1.882(10)	C(4B)–Si(7)–Si(12)	110.7(4)
Si(7)–Si(8)	2.331(06)	Si(8)–Si(7)–Si(12)	110.9(2)
Si(8)–Si(9)	2.341(06)	Si(7)–Si(8)–Si(9)	115.2(2)
Si(9)–Si(10)	2.342(05)	Si(8)–Si(9)–Si(10)	111.1(2)
Si(10)–Si(11)	2.333(06)	Si(9)–Si(10)–Si(11)	110.7(2)
Si(11)–Si(12)	2.336(06)	Si(10)–Si(11)–Si(12)	113.0(2)
Si(12)–Si(7)	2.348(05)	Si(11)–Si(12)–Si(7)	111.6(2)
Si(1)–Si(7)	6.624(13)	C(1B)–Si(1)–Si(2)–Si(3)	69.8(4)
Si(3)–Si(11)	7.388(14)	C(4B)–Si(7)–Si(12)–Si(11)	–72.9(4)
C(32)–C(112)	3.821(14)	Si(2)–Si(1)–Si(7)–Si(12)	17.2(4)

Table 5

Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$  for compound 2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Si(1)	2344(04)	3943(04)	7987(1)	54(1)
Si(2)	1464(04)	2655(04)	8362(1)	65(1)
Si(3)	2905(04)	60(04)	8372(1)	62(1)
Si(4)	5433(04)	-706(04)	8482(1)	69(1)
Si(5)	6434(04)	501(04)	8116(1)	69(1)
Si(6)	4916(04)	3126(04)	8058(1)	61(1)
C(11)	1263(15)	5995(12)	8043(3)	72(4)
C(21)	-557(13)	3262(17)	8259(5)	119(8)
C(22)	1485(20)	3239(19)	8777(3)	118(7)
C(31)	2156(18)	-856(18)	8695(4)	106(6)
C(32)	2773(18)	-574(18)	7973(4)	100(6)
C(41)	6589(17)	-2797(15)	8448(5)	128(8)
C(42)	5633(20)	-374(20)	8912(3)	112(6)
C(51)	8320(13)	80(16)	8285(4)	94(5)
C(52)	6817(18)	-348(17)	7720(4)	110(6)
C(61)	5640(18)	4014(19)	7720(4)	110(6)
C(62)	5103(18)	3818(16)	8443(3)	95(5)
C(1B)	1947(12)	3641(14)	7571(2)	60(3)
C(2B)	3018(13)	2560(14)	7400(3)	67(3)
C(3B)	2751(13)	2254(14)	7102(3)	69(3)
C(4B)	1328(12)	3089(13)	6952(2)	57(3)
C(5B)	242(13)	4204(14)	7124(3)	77(4)
C(6B)	517(13)	4487(14)	7423(3)	76(4)
Si(7)	924(03)	2750(04)	6541(1)	51(1)
Si(8)	3135(04)	1080(04)	6292(1)	57(1)
Si(9)	4155(04)	-1426(04)	6510(1)	63(1)
Si(10)	2330(04)	-2230(04)	6541(1)	66(1)
Si(11)	179(04)	-594(04)	6814(1)	65(1)
Si(12)	-861(04)	1886(04)	6580(1)	57(1)
C(71)	128(16)	4630(14)	6291(3)	86(5)
C(81)	4607(15)	1727(17)	6283(4)	94(5)
C(82)	2654(18)	1161(16)	5856(3)	92(5)
C(91)	5697(18)	-2565(17)	6220(4)	113(7)
C(92)	5037(17)	-1809(17)	6920(3)	100(6)
C(101)	3139(18)	-4169(15)	6761(5)	126(8)
C(102)	1811(20)	-2334(20)	6118(4)	121(7)
C(111)	-1281(16)	-1239(18)	6811(4)	102(6)
C(112)	660(20)	-643(20)	7245(3)	119(7)
C(121)	-2467(15)	3071(18)	6842(4)	110(6)
C(122)	-1605(16)	2065(18)	6162(3)	92(5)

*U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>*i j*</sub> tensor.

THF, *n*-heptane and dichloromethane were dried by refluxing over Na/K alloy or P<sub>4</sub>O<sub>10</sub> respectively under nitrogen and distilled prior to use. TBAP (Fluka "puriss.") was dried under vacuo at 80 °C for two days.

Chloroundecamethylcyclohexasilane [16], bromononaphenylcyclopentasilane [17], 1-chloro-4-phenyldecamethylcyclohexasilane and 1-chloro-3-phenyldecamethylcyclohexasilane [7] were prepared according to published procedures.

All NMR spectra were recorded with a Bruker MSL 300 spectrometer (<sup>1</sup>H 300.13 MHz, <sup>29</sup>Si 59.627 MHz, <sup>13</sup>C 75.47 MHz). All samples were dissolved in CDCl<sub>3</sub>.

UV spectra were recorded with a Philips PU-8740 spectrometer. C, H analyses were performed on a Her-

aeus-Mikro-K1 apparatus. GC analyses were carried out on a HP 5890 Series II (capillary column DB-1HT, 15 m × 0.251 mm, 0.10 μm, FID detection). Mass spectra were recorded with a Kratos profile spectrometer. All voltammograms were obtained with a Werking POS 73 potentiostat and an NGI Servogor 790 recorder. The three-electrode system consisted of a platinum working and counter electrode and a double junction reference electrode (0.001 M AgClO<sub>4</sub> (0.1 M TBAP) in CH<sub>2</sub>Cl<sub>2</sub> or THF respectively | Ag wire) with a potential of 0.780 V vs. SCE.

The electrochemical measurements were performed in a 0.1 M solution of TBAP in CH<sub>2</sub>Cl<sub>2</sub> or THF respectively. The concentration of the silane was 1 × 10<sup>-3</sup> M.

### 7.2. Bi(4-phenyldecamethylcyclohexasilanyl) (1a)

A flask containing 0.2 ml Na/K alloy (1:3) in 10 ml *n*-heptane was placed in an ultrasonic bath. A solution of 0.5 g (1.15 mmol) 1-chloro-4-phenyldecamethylcyclohexasilane in 5 ml *n*-heptane was added slowly. After 12 h no more starting material could be detected by GC analysis. The dark blue precipitate was filtered off and washed with *n*-heptane. After removing the solvent the white solid residue was purified by recrystallization from ethyl acetate/methanol to give 0.35 g (76%) **1a**, m.p. 200–202 °C.

<sup>29</sup>Si NMR (ppm/TMS): -35.84, -38.91, -42.08, -68.61. <sup>1</sup>H NMR (ppm/TMS): 7.36 (m, 10H), 0.46 (6H), 0.36 (6H), 0.35 (12H), 0.32 (12H), 0.27 (12H), 0.15 (12H). <sup>13</sup>C NMR (ppm/TMS): 137.89, 133.80, 128.93, 126.84; -4.87 m. UV (nm/ε): 248.1 (79 300), 278.3 sh (51 900). MS (*m/e*): 790 (M<sup>+</sup>) (54.0%), 395 (-Si<sub>6</sub>Me<sub>10</sub>Ph) (60.5%). Anal. Found: C, 48.30; H, 8.94. C<sub>32</sub>H<sub>70</sub>Si<sub>12</sub> Calc.: C, 48.53; H, 8.91%.

### 7.3. Bi(3-phenyldecamethylcyclohexasilanyl) (1b)

Treatment of 0.5 g (1.15 mmol) 1-chloro-3-phenyldecamethylcyclohexasilane in the way described for **1a** gave 0.31 g (67%) white crystals of **1b**, m.p. 180 °C.

<sup>29</sup>Si NMR (ppm/TMS): -36.37, -36.50, -39.26, -39.81, -41.86, -67.94. <sup>1</sup>H NMR (ppm/TMS): 7.34 (m, 10H), 0.47–0.14 (m, 60H). <sup>13</sup>C NMR (ppm/TMS): 138.07, 134.83, 127.90, 127.78, -4.26 m. UV (nm/ε): 249.6 (92 800), 284.8 sh (71 200). MS (*m/e*): 790 (M<sup>+</sup>) (48.0%), 395 (-Si<sub>6</sub>Me<sub>10</sub>Ph) (62.3%). Anal. Found: C, 48.09; H, 8.92. C<sub>32</sub>H<sub>70</sub>Si<sub>12</sub> Calc.: C, 48.53; H, 8.91%.

### 7.4. 1,4 Bis(undecamethylcyclohexasilanyl)benzene (2)

Magnesium shavings (0.658 g, 27 mmol) were dispersed in 30 ml dry THF and a solution of 1.597 g (6.77 mmol) *p*-dibromobenzene in 20 ml dry THF was

added slowly. After addition the mixture was stirred under reflux for 12 h, during which time a white solid precipitated. When no more *p*-dibromobenzene or bromobenzene could be detected by GC analysis, the cooled white suspension of the Grignard reagent was added dropwise to a solution of 5.0 g (13.54 mmol) chloroundecamethylcyclohexasilane in 20 ml dry THF at 0°C. After stirring the mixture for 12 h at room temperature the flask was placed in an ultrasonic bath. Sonication of the suspension over a period of five days resulted in a clear yellow solution, the GC analysis of which showed about 55% **2**. After extraction of the solution with 1 M HCl the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent left a yellow oily residue, which was purified by vacuum sublimation (10<sup>-2</sup> mm, 120°C). Recrystallization of the solid sublimation residue from ethyl acetate/methanol gave 1.91 g (38%) of white crystals, m.p. 292°C.

<sup>29</sup>Si NMR (ppm/TMS): -40.86, -41.78, -41.81, -42.26. <sup>1</sup>H NMR (ppm/TMS): 7.35 (4H), 0.44 (6H), 0.21 (12H), 0.19 (18H), 0.17 (6H), 0.15 (24H). <sup>13</sup>C NMR (ppm/TMS): 137.43, 134.16, -4.67, -5.42, -6.31, -6.88. UV (nm/ε): 260.4 (24 400) sh, 276.1 (31 000). MS (*m/e*): 743 (M<sup>+</sup>) (25.3%), 410 (-Si<sub>6</sub>Me<sub>11</sub>) (8.9%), 333 (-Ph) (6.1%). Anal. Found: C, 45.36; H, 9.52. C<sub>28</sub>H<sub>70</sub>Si<sub>12</sub> Calc.: C, 45.21; H, 9.48%.

### 7.5. 1,4-Bis(nonaphenylcyclopentasilanyl)benzene (**3**)

Magnesium shavings (0.12 g, 4.92 mmol) were dispersed in 5 ml dry THF and a solution of 3.0 g (3.28 mmol) bromononaphenylcyclopentasilane in 20 ml dry THF was added. A solution of 0.39 g (1.64 mmol) *p*-dibromobenzene in 5 ml dry THF was added slowly. On addition the solution turned green and a white solid precipitated. After the addition the mixture was stirred for 48 h at reflux temperature. The white suspension was decanted from excessive magnesium, the white solid was filtered off and extracted with toluene in a Soxhlet extractor for five days to leave 2.3 g (80%) of a solid residue. The recorded <sup>29</sup>Si NMR spectrum of the solution showed only decaphenylcyclopentasilane. The white solid was investigated by <sup>29</sup>Si solid state NMR (see Section 3).

M.p. 342°C (decomp.). Anal. Found: C, 78.52; H, 5.41. C<sub>114</sub>H<sub>94</sub>Si<sub>10</sub> Calc.: C, 78.47; H, 5.43%.

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