Novel Cage Polycarbosilanes. Preparation and Characterization of Dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane and Its Derivatives

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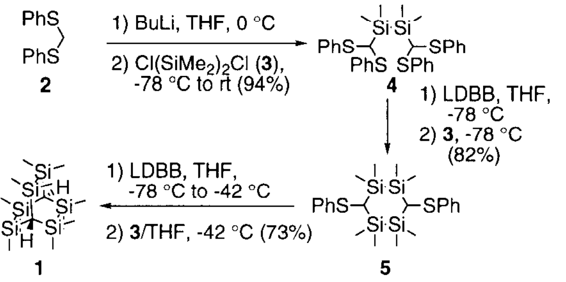
2,2,3,3,5,5,6,6,7,7,8,8-Dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (**1**) was synthesized for the first time via three steps in 56% overall yield through triple silylation with three dichlorodimethyldisilane molecules of two trianionic molecules derived from bis(phenylthio)methane. The molecular structure of **1** was shown to be slightly distorted from an ideal bicyclo[2.2.2]octane skeleton by X-ray analysis. The derivatization of **1** and UV spectra of those compounds are described.

In view of the development of new silicon-based materials, much interest has been focused on organopolysilanes whose backbones consist only of silicons because these compounds show unique electronic and optical properties resulting from delocalization of the Si-Si σ-electrons. This delocalization of σ-electrons is called σ-conjugation and is highly affected by the structural dimensions of the polysilanes.[1] In connection with σ-conjugation of Si-Si bonds, very recently, σ-electrons of *linear* polycarbosilanes consisting of such heterocatenate as -Si-Si-C-[2] and -Si-Si-Si-Si-C-[3] linkage were found to be delocalized along the acyclic skeletons. Therefore, it is intriguing to synthesize and characterize *three-dimensional* polycarbosilanes in the light of the novel possibilities of silicon-containing materials. We report herein the first synthesis, crystal structure and UV spectra of 2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (**1**) and its derivatives.[4]

Deprotonation of bis(phenylthio)methane (**2**) with BuLi in THF at 0 °C followed by silylation with 1,2-dichloro-1,1,2,2-tetramethyldisilane (**3**)[5] at -78 °C gave **4** in 94% yield (Scheme 1). Reductive lithiation of **4** with lithium 4,4'-di-*tert*-butylbiphenylide (LDBB) at -78 °C and subsequent silylation with **3** afforded 1,2,4,5-tetrasilacyclohexane **5** in 82% yield as a diastereomer mixture (*cis* : *trans* = 1 : 1). Finally, again, reduction of **5** with LDBB in THF at -78 °C and silylation with **3** at -42 °C successfully produced cage polycarbosilane **1** as a colorless solid in 73% yield along with 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasilacyclohexane (**6**) in 5% yield. The structure of **1** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and mass spectroscopy, and was confirmed unambiguously by X-ray crystallographic analysis.[6] Single crystals of **1** suitable for X-ray measurement were obtained by recrystallization from cyclohexane as colorless prisms (mp 283-284 °C).

The ORTEP drawing of **1** is shown in Figure 1.[7] The molecule possesses one C_2 axis passing through the midpoints of the C(1)-C(1)* line and the Si(3)-Si(3)* bond. The molecular structure is slightly distorted from an ideal bicyclo[2.2.2]octane geometry and the three Si-Si bond lengths range from 2.369(1)-2.373(2) Å which are slightly longer than that of the normal Si-Si bond (2.34 Å), probably due to the steric repulsion between the methyl groups oriented in a nearly eclipsed position. The angle of deviation from the perfectly eclipsed arrangement of the C(1)-Si(1) and C(1)*-Si(2)* bonds is about 12° which is also observed in other pairs of C(1) or C(1)*-Si bonds.



Scheme 1.

With **1** in hand, we next studied its derivatization by functionalization of the bridgehead positions (Table 1). Treatment of **1** with BuLi under various conditions[8] followed by the addition of Me$_3$SiCl did not afford the silylated products **7a** and **8aa** at all, and **1** was recovered quantitatively. However, deprotonation of **1** with a superbase composed of BuLi and *t*-BuOK[9] followed by silylation with Me$_3$SiCl proceeded smoothly to give the desired mono-silylated product **7a** in nearly quantitative yields (Table 1, run 1-3).[10] It is noteworthy that only mono-silylation occurred without producing bis-silylated product **8aa**, even when excessive base and Me$_3$SiCl were used.[11] In a similar way, mono-silylation with Me$_2$PhSiCl, mono-stannylation, and mono-alkylation with methyl iodide or allyl bromide succeeded, giving rise to **7b-e** in excellent yields, respectively (entry 4-7). The second introduction of a silyl or methyl group into **7a** was performed effectively under the same conditions to afford **8aa** (run 8) and **8ad** (run 9) quantitatively.

The UV absorption spectra of **1**, **6**, **7a**, **7c**, **8aa**, and (Me$_3$Si)$_2$ were measured in cyclohexane (0.0001 M) at room temperature. As shown in Figure 2, λ_{max} and ε of **6** (201 nm, ε = 12500), **1** (206 nm, ε = 16400), **7a** (209 nm, = 19300), **7c**

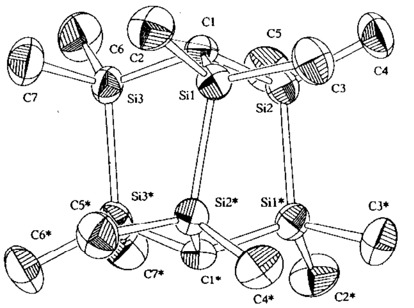
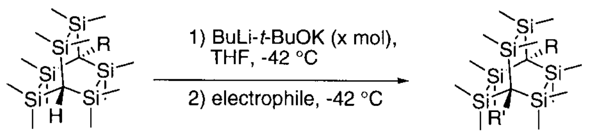


Figure 1. ORTEP drawing of **1** (hydrogen atoms are not shown for clarity).



1 or **7a** → **7** or **8**

Table 1. Derivatization of **1** or **7a** using BuLi-*t*-BuOK

Run		R	x/mol	electrophile		R'	Yield/%
1	**1**	H	2	Me_3SiCl	**7a**	$SiMe_3$	98
2	**1**	H	3	Me_3SiCl	**7a**	$SiMe_3$	96
3	**1**	H	6	Me_3SiCl	**7a**	$SiMe_3$	97
4	**1**	H	2	$Me_2PhSiCl$	**7b**	$SiPhMe_2$	90
5	**1**	H	2	Bu_3SnCl	**7c**	$SnBu_3$	88
6	**1**	H	2	MeI	**7d**	Me	100
7	**1**	H	2	allyl bromide	**7e**	$CH_2CH{=}CH_2$	94
8	**7a**	$SiMe_3$	2	Me_3SiCl	**8aa**	$SiMe_3$	98
9	**7a**	$SiMe_3$	4	MeI	**8ad**	Me	98

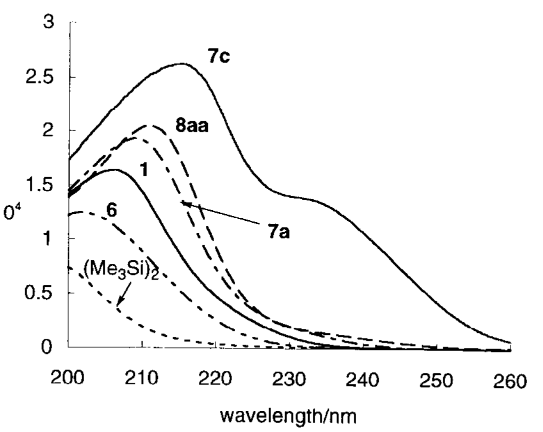


Figure 2. UV absorption spectra of **1**, **6**, **7a**, **7c**, **8aa**, and $(Me_3Si)_2$ in cyclohexane.

(215 nm, ε = 26200; 233 nm, ε = 13700) and **8aa** (211 nm, ε = 20500) exhibited a bathochromic shift when the dimensions of the molecular structure increased and a trimethylsilyl or tributylstannyl group was introduced at a bridgehead carbon.[12]

In summary, the synthesis of dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane **1** was accomplished efficiently *via* three steps starting from bis(phenylthio)methane (**2**) by triple silylation with dichlorodisilane **3** in 56% overall yield. In addition, silylation and alkylation at the bridgehead of **1** was established in excellent yields using BuLi-*t*-BuOK reagent as a base, and the functionalization allowed us to briefly desymmetrize **1**. The molecular structure of **1** by X-ray analysis was shown to be slightly distorted from an ideal bicyclo[2.2.2]octane skeleton. Further study on cage polycarbosilanes is in progress.

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4 Tetradecamethylbicyclo[2.2.2]octasilane whose skeleton was made up entirely of silicon was reportedly prepared in 3-5% yields by Na/K or Li condensation of trichloromethylsilane and dichlorodimethylsilane. a) R. West and A. Indriksons, *J. Am. Chem. Soc.*, **94**, 6110 (1972). b) M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, and M. Kumada, *Organometallics,* **1**, 317 (1982). Cage compounds $E(Me_2SiSiMe_2)_3E$ (E = P, As, Sb, Bi) also were synthesized to examine through-bond interactions of heteroatoms. c) K. Hassler, *J. Organomet. Chem.*, **246**, C31 (1983). d) K. Hassler and S. Seidl, *J. Organomet. Chem.*, **347**, 27 (1988). e) U. Winkler, M. Schieck, H. Pritzkow, M. Driess, I. Hyla-Kryspin, H. Lange, and R. Gleiter, *Chem. Eur. J.*, **3**, 874 (1997).

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6 Spectral data for **1**: ^1H NMR (200 MHz, $CDCl_3$): δ -0.12 (s, 2H), 0.19 (s, 36H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 3.3, 4.2; ^{29}Si NMR (79.3 MHz, $CDCl_3$): δ -22.1; IR (KBr): 2980, 2943, 2893, 2831, 1396, 1255, 974, 820, 709, 679, 665 cm^{-1}; MS *m/z* 377 (M^++3, 4), 376 (M^++2, 9), 375 (M^++1, 24), 374 (M^+, 40), 301 (35), 286 (11), 187 (3), 157 (8), 129 (24), 73 (100); HRMS calcd for $C_{14}H_{38}Si_6$ 374.1589; Found 374.1611.

7 Crystal data for **1**: $C_{14}H_{38}Si_6$, M = 374.97, monoclinic, space group C2/c (#15), a = 16.360(2), b = 9.422(3), c = 15.613(3) Å, β = 108.23(1)°, V = 2286.0(7) $Å^3$, Z = 4, ρcalcd = 1.089 g cm^{-3}, $F(000)$ = 824.00, $2\theta max$ = 55.0°, MoKα (λ = 0.71069 Å), μ(MoKα) = 3.57 cm^{-1}, T = 296 K; Of the 2894 reflections which were collected, 2795 were unique (R*int* = 0.021). The final cycle of full-matrix least-squares refinement was based on 1796 observed reflections {I > 3.00σ(I)} and 92 variable parameters and converged with unweighted and weighted agreement factors of R = 0.044 and Rw = 0.049.

8 The conditions attempted with BuLi were as follows: THF, -42 °C, 0 °C; hexane/TMEDA, 0 °C; cyclohexane, rt, 60 °C, cyclohexane/TMEDA, rt, 60 °C. All attempts treating **1** with MeLi (THF, reflux), *s*-BuLi (THF, -42 °C), or *t*-BuLi (THF , -42 °C) followed by quenching with D_2O turned out futile.

9 Reviews of superbase: a) M. Schlosser, *Pure & Appl. Chem.*, **60**, 1627 (1988). b) F. Mongin, R. Maggi, and M. Schlosser, *Chimia*, **50**, 650 (1996).

10 Deprotonation did not occur when only *t*-BuOK was used as the base at 0 °C.

11 A possible reasoning for the fact that a bridgehead dianion is prevented may be attributed to an electrostatic repulsion via through-space or through-bond interaction.

12 Further studies about the interpretation of UV absorbtion spectra are required. The details will be reported in due course.