Synthesis, Structure, and Reactivity of 1,2-(1′,1′,2′,2′-Tetramethyldisilane-1′,2′)carborane

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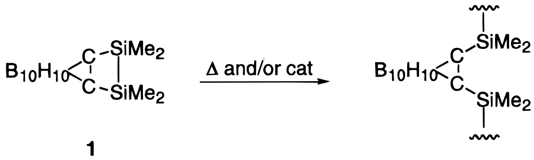
The novel strained compound 1,2-(1′,1′,2′,2′-tetramethyldisilane-1′,2′)carborane (**1**) was synthesized by the reaction of 1,2-dilithiocarborane and dichlorotetramethyldisilane. Compound **1** was characterized by solution methods and its structure determined by single-crystal X-ray diffraction. In contrast to its organic analogue *o*-(disilanyl)phenylene, the reaction of **1** with ethanol leads to cleavage of a Si−C bond rather than a Si−Si bond. Similarly to other cyclic disilanes, exposure of a solution of **1** to oxygen leads to the insertion of an oxygen atom into the Si−Si bond. The structure of the oxygen inserted product was also determined by X-ray crystallography. The general chemistry and attempts at polymerizing **1** are briefly discussed.

Introduction

There exists considerable interest in cyclic molecules containing Si−Si and Si−C bonds because these compounds have been shown to undergo insertion reactions with small molecules,[1] intermolecular ring enlargements,[2] and ring-opening polymerization (ROP) reactions.[3] Concomitantly there has been interest in the incorporation of carboranes into organic and silicon-containing polymers to make advanced thermooxidatively stable materials and ceramic precursors.[4] Interestingly we have seen no reports of poly(carborane−silane) polymers, an intriguing possibility since such a polymer would presumably exhibit combined physical, electronic, and chemical properties of polysilanes[5] and carboranes.[6] One logical route to such a polymer is ROP of an appropriately designed monomer.[3a] With this aim in mind we report herein the synthesis of 1,2-(1′,1′,2′,2′-tetramethyldisilane-1′,2′)carborane (**1**) (Scheme 1) as well as its structure, general chemistry, and ability to form polymers.

Scheme 1



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Experimental Section

All manipulations were performed in a dry He atmosphere in a glovebox or under an argon atmosphere on a vacuum manifold unless otherwise noted. The starting materials were purchased from KatChem (*o*-carborane), TCI America (1,2-dichlorotetramethyldisilane), and Aldrich (*n*-BuLi, 1.6 M in hexane). Solvents were deoxygenated and dried by refluxing under a nitrogen atmosphere over an appropriate drying agent. Low temperatures (below −80 °C) were achieved in the glovebox using a cold well, cooled with liquid nitrogen and filled with sand. The ^{1}H, ^{11}B, and ^{13}C NMR spectra were collected on a Varian 300 MHz NMR instrument. Gas chromatography (GC) was performed on a Hewlett-Packard 5890 Series II Plus gas chromatograph equipped with a 30 m 5% phenyl methyl polysiloxane column. The GC samples were manipulated in air, where the time of exposure was limited as much as possible. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer.

Synthesis of 1,2-(1′,1′,2′,2′-Tetramethyldisilane-1′,2′)carborane (1). A cold well was used to cool a THF (200 mL) solution of *o*-carborane (1.442 g, 10 mmol) to below −50 °C in a 500 mL flask equipped with a stirbar. The flask was then removed from the well, the solution was set to stir, and *n*-BuLi (12.5 mL, 20 mmol) was added. The solution color slowly changed to light yellow and a white precipitate formed over the course of 1 h. The 500 mL flask and a vial containing a

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solution of 1,2-dichlorotetramethyldisilane (1.872 g, 10 mmol) in THF (15 mL) were placed in the cold well for 15 min. The reaction flask was removed from the cold well, set to stir and the dichlorotetramethyldisilane solution was slowly added. The reaction mixture was allowed to stir at room temperature for 3 h during which time the precipitate disappeared, leaving a light yellow solution. The solvents were removed under vacuum leaving a light tan solid. Extraction of the product **1** from the solid was accomplished by adding toluene (100 mL) to the reaction flask and separating by filtration the lithium salts with Celite. The filtrate was concentrated under vacuum to approximately 15 mL leading to the precipitation of the crude product **1**. The product was collected on a fritted funnel and washed with three 5 mL portions of toluene. Analysis by GC showed a single peak, assigned to compound **1**. The average yield of three experiments for **1** was 35% (0.9 g) based on *o*-carborane. ^{1}H NMR (C_6D_6, δ) −0.17 (s, 12 H), 1−4 (several broad peaks, 10 H). ^{11}B NMR (C_6D_6, δ vs $BF_3{\cdot}OEt_2$) −12.70 (d, 187 Hz, 2 B), −10.25, (d, 162 Hz, 4 B), −4.03 (d, 148 Hz, 2 B), 0.26 (d, 148 Hz, 2 B). ^{13}C{^{1}H} NMR (C_6D_6, δ) −3.19, 80.30. Anal. Calcd for $C_6B_{10}H_{22}Si_2$: C, 27.88; H, 8.58. Found: C, 27.83; H, 8.56.

Ethanolysis of 1, Isolation of 1,2-(Ethylenyl-3′,3′,4′,4′-tetramethyl-5′-ethoxydisilanyl-1′)carborane (2). Anhydrous ethanol was added to a well-stirred solution of **1** (0.259 g, 1 mmol) in THF (8 mL). The reaction mixture was allowed to stir for 1 h, and the solvents were removed under vacuum leaving a gold colored oil. Flash chromatography (20 mL silica, 98:2 hexane/ether eluent) of the oil left 0.219 g (71% yield based on **1**) of clear oily product **2**. GC analysis of **2** indicates that it was >99% pure. ^{1}H NMR (C_6D_6, δ) −0.03 (s, 6 H), 0.04 (s, 6 H), 0.91 (t, 6.9 Hz, 3 H), 3.23 (q, 6.9 Hz, 2 H), 3.69 (s, broad, 1 H), 1−4 (several broad peaks, 10 H). ^{11}B NMR (C_6D_6, δ vs $BF_3{\cdot}OEt_2$) −13.80 (d, 159 Hz, 2 B), −12.30, (d, 148 Hz, 2 B), −11.38 (d, 162 Hz, 2 B), −7.10 (d, 152 Hz, 2 B), −1.61 (d, 137 Hz, 1 B), −0.33 (d, 123 Hz, 1 B). ^{13}C NMR (C_6D_6, δ) −2.62 (q, 92 Hz), −0.32 (q, 104 Hz), 18.43 (q, 96 Hz), 59.14 (t, 94 Hz), 61.14 (d, 120 Hz), 66.55 (s). Anal. Calcd for $C_8B_{10}H_{28}Si_2O$; C, 31.55; H, 9.27. Found: C, 31.52; H, 9.21.

Reaction of 1 With O_2, Isolation of 1,2-(1′,1′,3′,3′-Tetramethyldisiloxanyl-1′,3′)carborane (3). Compound **1** (0.259 g, 1 mmol) and 9 mL of toluene were loaded into a 10 mL vial. The white starting material only partially dissolved into the toluene. The mixture was stirred with exposure to air for 24 h, during which time the solution became homogeneous. The solvent was removed under vacuum yielding a white powder. GC analysis showed one major product in 96% yield. The product was crystallized from a saturated solution of ether at −30 °C yielding flat rectangular and needle-shaped crystals. GC of a homogeneous mixture of the crystals showed the product **3** to be >99% pure. The average yield of three experiments was 0.110 g, 40% based on **1**. ^{1}H NMR (C_6D_6, δ) −0.02 (s, 12 H), 1−4 (several broad peaks, 10 H). ^{11}B NMR (C_6D_6, δ vs $BF_3{\cdot}OEt_2$) −13.03 (d, 187 Hz, 2 B), −11.05 (d, 165 Hz, 4 B), −3.73 (d, 148 Hz, 2 B), −0.37 (d, 148 Hz, 2 B). ^{13}C{^{1}H} NMR (C_6D_6, δ) −1.63, 73.70. Anal. Calcd for $C_6B_{10}H_{22}Si_2O$: C, 26.35; H, 8.08. Found: C, 26.15; H, 8.04.

X-ray Structure Determination for 1. Rectangular, plate-shaped, clear crystals of **1** were grown from toluene by cooling a saturated solution to −30 °C for several days. A single crystal was mounted on a glass fiber using silicon grease and placed under a liquid nitrogen cold stream on a Siemens P4/CCD diffractometer. The lattice was determined using 40 reflections. A hemisphere of data was collected using a combination of φ and ω scans with 30 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART software.[7] Frame integration and final cell parameter calculation were carried out using SAINT software.[7] The final cell parameters were determined using a least-squares fit to 2745 reflections. Data collection parameters are given in Table 1.

The structure was solved in space group *P*2/*n* using direct methods and difference Fourier techniques. This solution yielded all non-hydrogen atom positions. The molecule occupies a 2-fold axis. Subsequent Fourier synthesis revealed all hydrogen atoms bound to boron. These hydrogen atom positions were refined with isotropic temperature factors set to 0.08 Å^2. The methyl hydrogens were idealized with C−H distances set at 0.96 Å and their isotropic temperature factors set to 1.5 times the isotropic *U* of the carbon atom to which they were bonded. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0369 and wR2 = 0.1102.[8]

X-ray Structure Determination for 3. Needle-shaped clear crystals of **3** were obtained as outlined previously. A single crystal of **3** was mounted on a glass fiber using silicon grease and placed under a liquid nitrogen cold stream on a Siemens P4/PC diffractometer. The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.86° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS.[7] All data reduction, including Lorentz and polarization corrections, structure solution and graphics were performed using SHELEXTLPC software.[7] The structure refinements was performed using SHELX 93 software[7] The data were not corrected for absorption due to the low absorption coefficient. Data collection parameters are given in Table 1.

The structure was solved in space group *Pnma* using direct methods and difference Fourier techniques. This solution yielded all non-hydrogen atom positions. All hydrogen positions were found in the subsequent Fourier map and refined with isotropic temperature factors fixed at 0.08 Å. The final refinement included anisotropic temperature factors on all non-hydrogen atoms and converged to R1 = 0.0448 and wR2 = 0.1054.[8]

Results and Discussion

Compound **1** was prepared in moderate yield through the two step reaction shown in Scheme 2. A similar method has been reported by Kira[9] for generating [2.2]paracyclophanes. The 1,2-dilithiated carborane was generated by the reaction of *n*-BuLi with *o*-carborane[6,10] which was subsequently reacted in situ with dichlorotetramethyldisilane. Low temperature and high dilution were important factors in the second step of this reaction. At higher concentrations the ^{1}H NMR and GC analyses showed evidence of oligomerization and resulted in lower yields of the desired product. Partial oligomerization still occurs which

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(7) SMART 7.210, SAINT 4.05, XSCANS 2.01, and SHELXTL PC 4.2/360 are products of Bruker Analytical X-ray Systems, Inc., 6300 Enterprise Lane, Madison, WI 53719. SHELX93 and SADABS were written by G. M. Sheldrick, University of Göttingen Germany.

(8) $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $a = 0.0581$ for **1** and $a = 0.057$ for **3**.

(9) Kira, M.; Tokura, S. *Organometallics* **1997**, *16*, 1100.

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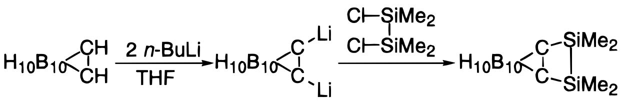
Table 1. Crystal Data and Structure Refinement for **1** and **3**

	1	**3**
empirical formula	$C_6H_{22}B_{10}Si_2$	$C_6H_{22}B_{10}OSi_2$
fw	258.52	274.52
temperature	20 °C	−75 °C
wavelength	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	orthorhombic
space group	$P2/n$	$Pnma$
unit cell dimensions	$a = 6.9126(6)$ Å	$a = 13.126(1)$ Å
	$b = 8.8029(7)$ Å	$b = 14.355(5)$ Å
	$c = 12.7727(10)$ Å	$c = 8.472(1)$ Å
	$\beta = 93.736(2)°$	
volume	775.9(1) $Å^3$	1596.3(6) $Å^3$
Z	2	4
density (calculated)	1.107 mg/m^3	1.142 mg/m^3
absorption coefficient	0.091 98 cm^{-1}	0.0201 cm^{-1}
F(000)	272	576
cryst size	0.05 × 0.18 × 0.30 mm	0.14 × 0.18 × 0.54 mm
theta range for data collection	2.31−26.42°	2.79−27.50°
index ranges	$-8 \leq h \leq 8, 0 \leq k \leq 11, 0 \leq l \leq 15$	$-1 \leq h \leq 17, -1 \leq k \leq 18, -1 \leq l \leq 11$
no. of reflcns collcd	1581	2509
no. of indep reflcns	1581 [R(int) = 0.0000]	1908 [R(int) = 0.0295]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	1581/0/97	1908/0/129
goodness-of-fit on F^2	1.375	1.162
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0369, wR2 = 0.1062	R1 = 0.0448, wR2 = 0.1054
R indices[a] (all data)	R1 = 0.0449, wR2 = 0.1102	R1 = 0.0731, wR2 = 0.1181
largest diff. peak and hole	0.301/−0.231 e $Å^{-3}$	0.361/−0.231 e $Å^{-3}$

Scheme 2



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explains the moderate yields in this reaction. Even higher dilution did not significantly increase our yields and became impractical.

Compound **1** is highly soluble in THF and methylene chloride, somewhat less soluble in ether and toluene and has low solubility in hexanes. The white solid sublimes at 221 °C (1 atm). The material is less air and moisture sensitive compared with other similar disilacyclobutanes.[1c,3d] Thus the powder or a solution of the material can be handled in air for several minutes without significant decomposition. The ^1H, ^{13}C, and ^{11}B NMR are consistent with a highly symmetrical structure.

An ORTEP picture of **1** is shown in Figure 1. The C(1)−C(1a) bond length [1.706(3) Å] is typical for *o*-carboranes [1.63−1.72 Å].[11] The C(1)−Si(1) bond length [1.931(2) Å] is slightly longer than a typical Si(sp^3)−C(sp^3) bond length [1.88−1.91 Å].[3c,12] Finally the Si−Si bond length [2.3640(9) Å] is unexceptional for Si(sp^3)−Si(sp^3) bond lengths [2.33−2.34 Å].[3c,12b,13] The Si(1)−C(1)−C(1a) bond angle [99.0(3)°] is greater than 20° more acute than the ideal angle of 121.7°.[14] Thus the structure determination confirmed the solution data and our expectations that **1** is a symmetric and strained molecule.

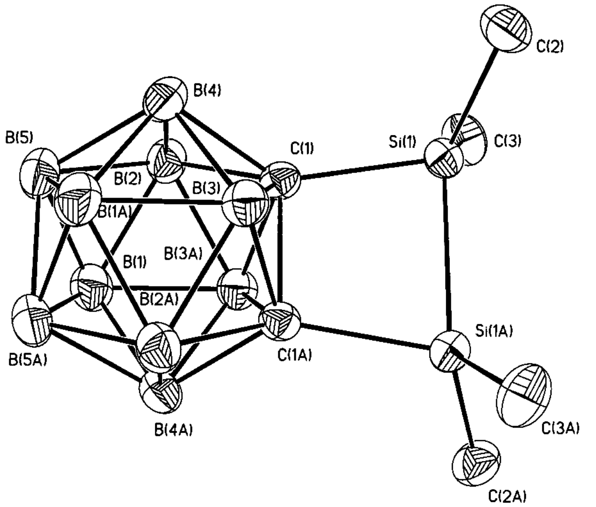

Figure 1. ORTEP (50% probability ellipsoids) of **1**. Bond distances and angles: Si(1)−Si(1a), 2.3640(9) Å; C(1)−C(1a), 1.706(3) Å; Si(1)−C(1), 1.930(2) Å; Si(1)−C(1)−C(1a), 99.81(5)°.

In contrast to the analogous *o*-(disilanylene)phenylene, **1** does not dimerize in the presence of $(Ph_3P)_4Pd$[2b] nor does it polymerize spontaneously at room temperature or in the presence of $AlCl_3$.[3d] The reactivity of (disilanylene)phenylene has been attributed to the *o*-quinonedisilane resonance contribution in the electronic structure.[15] *o*-Carborane has been described as "superaromatic" due to the delocalized nature of the bonding in the framework.[6,10,16] In the case of thermal stability and electrophilic substitution reactions, *o*-carborane acts similarly to arenes. There are also examples of fused aryl-*o*-carborane compounds where there is evidence that the electrons are delocalized throughout the structure.[17] However, the poor overlap between the delocalized MO of the carborane framework

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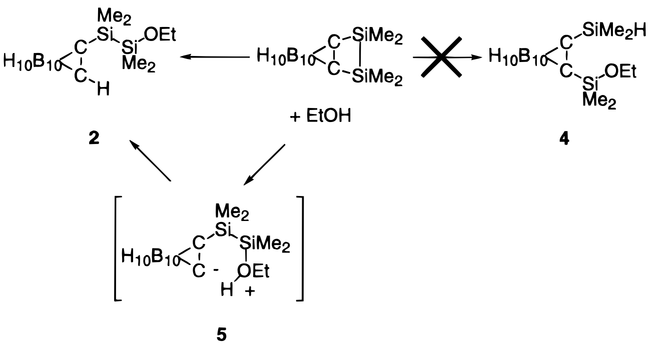
Scheme 3



and the “p-like” orbitals needed from the sp^2 silicon must inhibit any significant resonance contribution of an *o*-quinonedisilane-type for **1**.

Attempts were made to polymerize **1** using previously described Pd, Ni, and Pt catalysts that are known to perform the ROP of cyclic silicon- and carbon-containing molecules.[3] Our results were inconclusive since under our conditions either no reaction occurred or the reactions lead to several products from which we were unable to deconvolute the NMR spectra. Reactions with nucleophiles such as MeLi and sodium *tert*-butyloxide likewise led to many products. Under high-temperature, sealed-tube conditions (>250 °C), a liquid material formed which solidified to a glassy intractable and pale yellow material at room temperature. It is likely that this intractable material is a polymer and modification of **1** may lead to a more easily characterized material.

The compound **1** was shown to react with ethanol to give one major product which was purified by chromatography on silica. Two reasonable products include **2** where a Si−C bond is cleaved and **4** where the Si−Si bond is broken (Scheme 3). Since the product is an oil at room temperature, we determined its connectivity exclusively by solution characterization methods and elemental analysis. In the ^{1}H NMR spectrum of the product, the broad singlet at 3.69 ppm in C_6D_6 is characteristic of a proton attached to the carborane carbon.[18] This carbon in the proton-coupled ^{13}C NMR spectra appears as a doublet (120 Hz). These features are consistent with **2** rather than **4**. This reactivity contrasts with most other cyclic disilanes where Si−Si bond cleavage is seen in nucleophilic reactions. We propose that this is due to the formation of **5** as a stable anionic intermediate in the formation of **2**.

Another manifestation of the strained nature of **1** is its reaction with O_2. A 0.259 g solution of **1** with toluene (9 mL) is only partially soluble in an inert atmosphere. Exposure of this heterogeneous mixture to atmospheric oxygen leads, over several hours, to a homogeneous colorless solution. Analysis of this solution by GC over time showed one major product (**3**) increasing at the expense of **1**. Compound **3** crystallizes cleanly from ether, often as large flat rectangular crystals. The largest crystal was measured as 1 × 0.5 × 0.2 cm. The ^{1}H, ^{11}B, and ^{13}C NMR spectra of **3** are similar to **1** and suggestive of a compound with similar high symmetry. On the basis of the solution data and elemental analyses, we propose that an oxygen atom inserts between the Si−Si bond of **1**. Similar and usually more vigorous reactivity is seen with *o*-(disilanylene)phenylene and other strained disilanes.[1c,3d] Compound **3** has been made previously by reacting H_2O with 1,2-bis(chlorodimethylsilyl)-carborane.[19]

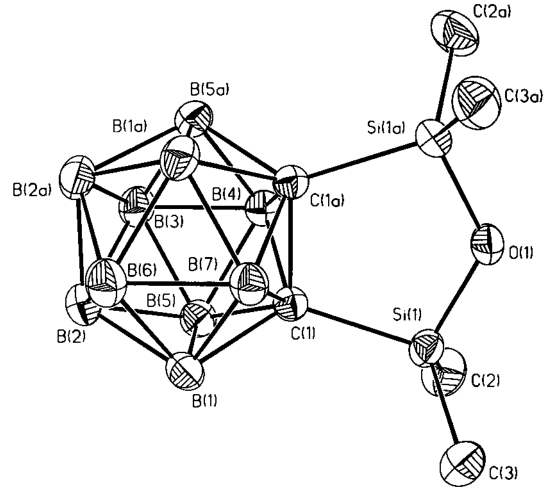


Figure 2. ORTEP (50% probability ellipsoids) of **3**. Bond distances and angles: C(1)−C(1a), 1.691(4) Å; Si(1)−C(1), 1.914(2) Å; Si(1)−O, 1.642(1) Å; Si(1)−C(1)−C(1a), 108.97(6)°.

The single-crystal structure for **3** confirmed our assignment based on the solution data and is shown as an ORTEP picture in Figure 2. The C(1)−C(1a) [1.691(4) Å] and Si(1)−C(1) [1.914(2)] bond lengths are not significantly different from the corresponding bond lengths in **1**. As expected, the Si(1)−C(1)−C(1a) bond angle of **3** [108.97(6)°] is more obtuse than the same bond angle in **1**.

In conclusion we have shown a convenient synthesis of **1**, a novel strained disilacyclobutane. The structure of this new compound was determined by single-crystal X-ray diffraction. Compound **1** was shown in its reaction with ethanol to form **2** by cleavage of a Si−C bond. The contrast in reactivity between *o*-(disilanylene)phenylene and **1** is presumably due to a lack of significant electron delocalization between the Si atoms and the carborane cage within **1**. Dioxygen also reacts cleanly with **1** giving **3** where an oxygen atom inserts between the Si−Si bond. The crystal structure of **3** shows a relaxation in the bond angles as compared to the strained bond angles in **1**.

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Supporting Information Available: Tables of atomic coordinates, bond angles, hydrogen atomic coordinates, and anisotropic displacement parameters are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) ^{1}H NMR for *o*-carborane ($CDCl_3$, *δ*): 3.55 (s, 2 H), 3.0−1.5 (several broad peaks, 10 H).

(19) No NMR data or X-ray structure was reported in this early report: Papetti, S.; Heying, T. L. *Inorg. Chem.* **1963**, *2*, 1105.