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THE GENERATION OF HEXAMETHYL-1,4-DISILABENZENE AND ITS NOVEL THERMAL CHEMISTRY *

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Summary

Reaction of a mixture of *cis*- and *trans*-1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene (**7**) and dilithioanthracenide yields the 9,10-bridged-anthracene adduct of the disilacyclohexadiene, **2**. Photolysis or thermolysis of **2** yields transient hexamethyl-1,4-disilabenzene (**1**), which is trapped by alkynes to give 1,4-disilabarrelenes **8a**,**8b**, by methanol to give 1-methoxy-4-hydrohexamethyl-1,4-disilacyclohexa-2,5-diene (**9**), and by oxygen to give 1,2,3,4,5,6-hexamethyl-1,4-disila-7-oxa[2.2.1]bicyclohepta-2,5-diene (**14**). Thermolysis of *cis*-1,4-dihydrohexamethyl-1,4-disila-cyclohexa-2,5-diene (**6**) also produces **1**, which rearranges at higher temperatures to 2,3,4,5,6-pentamethyl-1,4-disilabicyclo[2.2.1]hepta-2,5-diene (**10**) and 1,1,3,4-tetramethyl-2,5-dimethylene-1-silacyclopent-3-ene (**11**). Mechanisms are proposed to account for the observed reactions.

Introduction

Recent studies have shown that a silicon atom can replace one of the carbons of a benzene ring, and that aromatic character is at least partly preserved in the resulting silabenzene [2,3]. In the disilabenzene series, hexamethyl-1,4-disilabenzene [4] (**1**) has been obtained as a transient species from pyrolysis or photolysis of the bridged anthracene adduct, **2**. Recently Maier, Schottler and Reisenauer [5] have shown that the parent compound 1,4-disilabenzene (**3**) is produced by thermolysis of 1,4-disilacyclohexa-2,5-diene. Compound **3** was trapped in an argon matrix and identified by UV-VIS and IR spectroscopy.

Two theoretical studies on disilabenzenes have appeared. The relative energies of 1,2- 1,3- and 1,4-disilabenzene were investigated by Baldridge and Gordon [6], who

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* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

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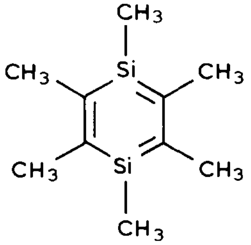
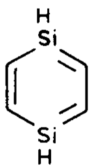


(1)

report that the stability order is 1,3 > 1,4 > 1,2 by both direct energy comparisons and calculations of aromaticity using bond separation reactions. The relative stabilities of the valence isomers of 1,4-disilabenzene were studied by Chandrasekhar and Schleyer [7], who found that the planar benzene **3**, Dewar isomer **4**, and 1,4-disilacyclohexa-2,5-dienylidene (**5**) are surprisingly similar in energy at 0.0, 5.9, and −9.9 kcal/mol, respectively.



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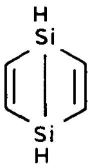

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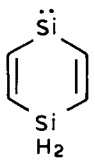

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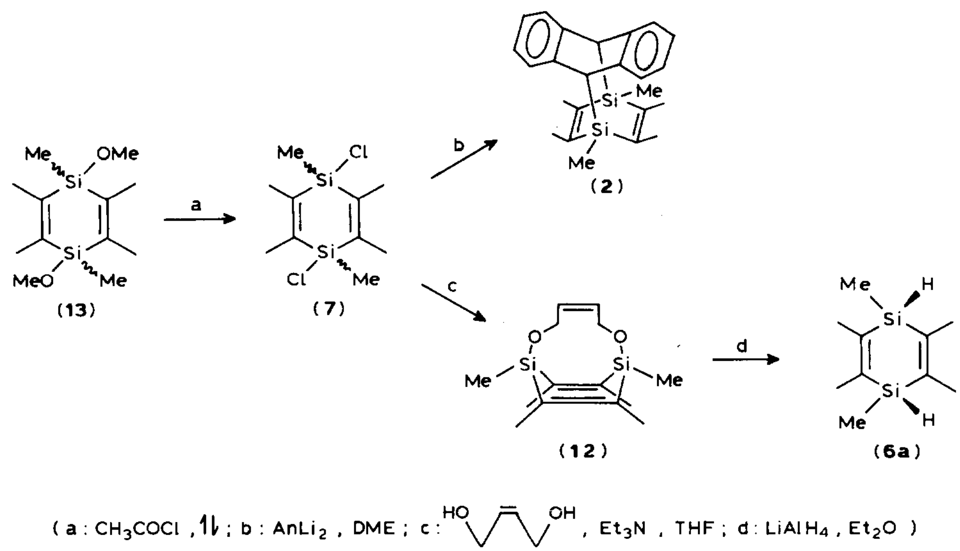
In this paper, we describe our results on the generation of **1** by photolysis and thermolysis of **2**, and report that thermolysis of *cis*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (**6**) leads to the formation of **1** by thermal extrusion of H_2 [8]. We have also found that when **1** is thermally generated in the absence of trapping reagents it rearranges to give a silanorbornadiene, **10**, and a novel silacyclopentene, **11**.

Results and discussion

Photolysis of anthracene adduct. Addition of dilithioanthracenide, ($AnLi_2$), to 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene (**7**) in THF produced the bridged-anthracene adduct **2** in approximately 25% yield (Scheme 1). Photolysis of **2** at 254 nm in THF gave anthracene as the only volatile product (Scheme 2). When **2** was irradiated in the presence of hexafluoro-2-butyne, anthracene was again isolated, and the 1,4-disilabarrelene derivative **8a** was also formed in 88% yield. This compound can be assumed to be formed by a Diels–Alder type addition of the acetylene to hexamethyl-1,4-disilabenzene. Photolysis of **2** in THF in the presence of methanol gave a 1/1 mixture of the *cis*- and *trans*-isomers of 1-methoxy-4-hydrohexamethyl-1,4-disilacyclohexa-2,5-diene (**9**) as a result of the 1,4-addition of methanol to **1**. The identity of **9** was confirmed by independent synthesis. If **2** is photolysed in THF saturated with oxygen, **14** is obtained. This product arises from the addition of an oxygen atom to **1**.


Me
OMe
Si
Si
MeO
Me
(13)
a
Me
Cl
Si
Si
Cl
Me
(7)
b
Si
Me
Si
Me
(2)
c
O
O
Me
Si
Si
Me
(12)
d
Me
H
Si
Si
Me
H
(6a)
(a : CH3COCl , 1l ; b : AnLi2 , DME ; c : HO OH , Et3N , THF ; d : LiAlH4 , Et2O)

SCHEME 1

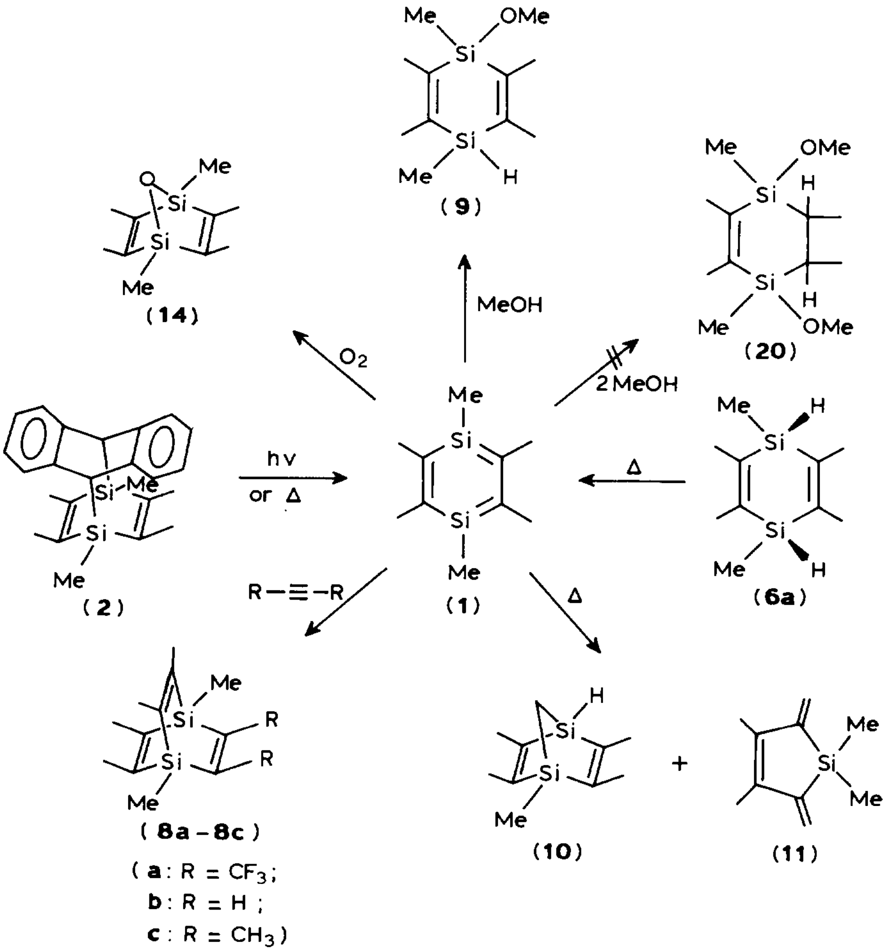
Thermolysis of anthracene adduct. The 1,4-disilabenzene precursor **2** can be decomposed thermally either in a flow system using nitrogen as a carrier gas at 600 ° C or in a low pressure thermolysis (10^{-5} to 10^{-3} torr) at temperatures ranging from 700 to 800 ° C. In flow thermolyses with acetylene as a trap (1/4 acetylene/nitrogen) the 1,4-disilabarrelene **8b** was obtained in low yield. Anthracene was also isolated. Thermolyses carried out using methanol as a trap yielded a 1 : 1 mixture of *cis*- and *trans*-**9** in 38% yield.

The low pressure thermolysis of **2** in the absence of trapping reagents gave two new volatile products, **10** and **11**. Both are stable and and have been characterized spectroscopically. The yields are low, and an appreciable amount of nonvolatile polymeric material is obtained.

These experiments have demonstrated that both the photolysis and thermolysis of **2** lead to hexamethyl-1,4-disilabenzene as a transient intermediate which can be trapped. Several points of interest arise in connection with the reaction of **1** with methanol to give **9**. First, the product is exclusively that of 1,4-addition to the two silicon atoms of **1**. Compound **20**, which could arise from two successive 1,2-addition reactions, is not observed.

The product **9**, and also the disilabarrelenes **8a**,**8b** could be formed directly from **1** or could arise from the Dewar-isomer, **15**. Hexamethyl-1,2-disilacyclobut-3-ene [9] is known to add alcohols across its strained Si–Si bond and to oxidize rapidly when exposed to air. It has also been shown to react with dienophiles, presumably via a 1,4-disilabuta-1,3-diene intermediate [10]. The Dewar-isomer **15** should exhibit similar reactivity to disilacyclobutenes and its trapping products would be indistinguishable from those of **1**. We have no evidence that will allow us to rule out its intermediacy.

Why are both the *cis*- and *trans*-isomers of **9** formed? If the product comes from a concerted 1,4-addition of methanol to disilabenzene or a 1,2-addition across the strained Si–Si bond in the Dewar-isomer one would expect to see only the



SCHEME 2

cis-isomer. However, alkoxysilanes are known to racemize in the presence of alcohols [11]. This could explain the observation of both products even though only one may have been formed initially. Alternatively the addition may occur in a stepwise fashion through the intermediacy of a zwitterionic species, which could lead to the formation of both stereoisomers.

Thermolysis of cis-dihydride (6a). 1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (**6**) was obtained by the reduction of the 1,4-dichloride **7** with lithium aluminum hydride giving a mixture of *cis*- and *trans*-isomers. Nitrogen flow pyrolyses (600–700 ° C) and low pressure thermolyses (750–850 ° C/0.01 Torr) were performed on **6** (1/4 *cis*/*trans*). In each case the *cis*-isomer was completely destroyed while the *trans*-isomer remained unreacted. Flow thermolysis of **6** in the presence of 2-butyne gave, in 20% yield, octamethyl-1,4-disilabicyclo[2.2.2]octa-2,5,7-triene (**8c**). This is the product of the addition of 2-butyne to **1** in a Diels–Alder fashion.

Recently Maier [3b] has shown that silabenzene can be generated by the thermal extrusion of molecular hydrogen from 1-silacyclohexa-2,5-diene, but not by thermolysis of the isomeric 1-silacyclohexa-2,4-diene. He interpreted this as evidence that the extrusion of H_2 was a concerted process and could only occur in a 1,4 manner. If the thermal extrusion of molecular hydrogen from **6** is indeed a concerted process, it is reasonable that only the *cis*-isomer **6a** should eliminate H_2 to provide **1**.

Since the *cis*- and *trans*-isomers of **6** were not separable by recrystallization or chromatographic techniques, **6a** was synthesized by a stereospecific route [12]. The 1,4-dichloride **7** was treated, at high dilution, with *cis*-2-butene-1,4-diol in the presence of triethylamine to give the adduct **12**, which was easily purified using column chromatography. Reduction of silyl ethers with lithium aluminum hydride is known to proceed with retention of configuration. Reaction with **12** gave **6a** as the pure *cis*-isomer [13].

Thermolysis of **6a** in the presence of 2-butyne gave **8c** in high yield. Flow thermolyses performed with acetylene as the trapping reagent produced **8b**. As in the case of **2**, when the thermolyses were performed in the absence of trapping reagents the only volatile products obtained were **10** and **11** and a third product, which was formed in minute quantities and could only be analysed by GC-MS. On the basis of its molecular weight and fragmentation pattern this third product was found to be **14**, which most likely results from the oxidation of **1** by residual air in the thermolysis apparatus.

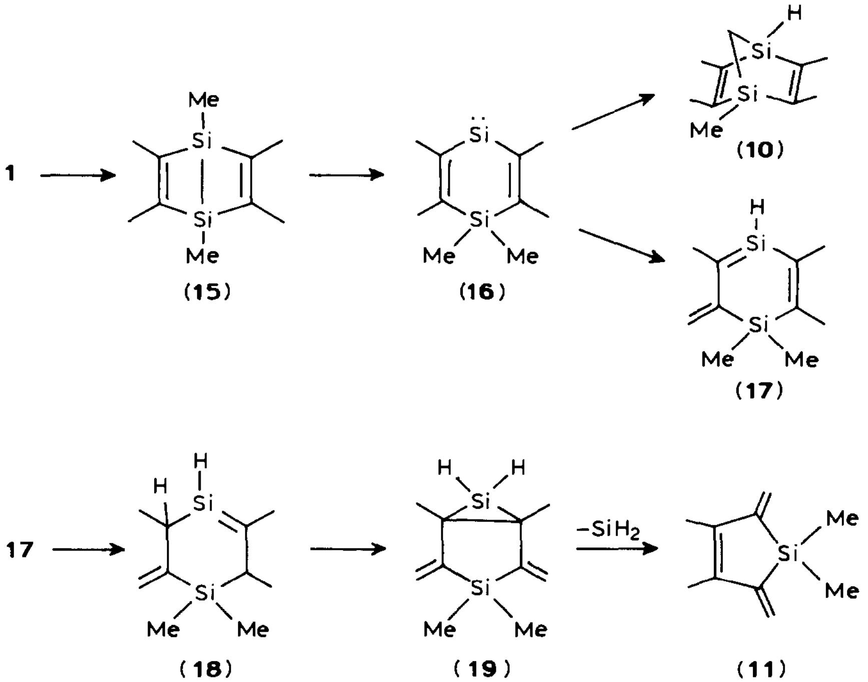
Flow thermolysis of **6a** in the presence of methanol gave two volatile products, the monomethoxide **9** and the corresponding dimethoxide. Thermolysis of **6a** with MeOD however did not lead to deuterated **9**. This indicated that, rather than thermal elimination of H_2, **6a** was undergoing a nucleophilic displacement of hydride at silicon by methoxide.

To demonstrate that molecular hydrogen is indeed extruded from the 1 and 4 positions of **6a**, *cis*-1,4-dideuteriohexamethyl-1,4-disilacyclohexa-2,5-diene (**6a**-d_2) was prepared by treating **12** with lithium aluminum deuteride. Thermolysis of **6a**-d_2 in a flow system in the presence of 2-butyne gave, as expected, **8c**. Mass spectral analysis indicated no deuterium incorporation in the product. Likewise, in the low pressure thermolysis of **6a**-d_2, in the absence of trapping reagents, both **10** and **11** were obtained, neither of which contained deuterium.

As further confirmation that only the *cis*-isomer **6a** undergoes elimination of H_2 to give **1** we prepared *trans*-isomer **6b**. Careful recrystallization of a *cis* and *trans* mixture of **9** gave the pure *trans*-isomer, which was then reduced with $LiAlH_4$ to **6b**. Under the same conditions which converted **6a** into **1**, **6b** was unchanged.

Matrix isolation experiments were attempted by use of a low pressure thermolysis oven attached directly to the deposition port of a cryostat. The *cis*-dihydride **6a** was premixed with argon gas and deposited through a hot tube onto a CsI window cooled to 12 K. No products that could be identified as hexamethyl-1,4-disilabenzene or its Dewar isomer were found. Instead, only **11** was observed, indicating that **1** is thermally unstable. This is confirmed by flow pyrolysis experiments in which the trapping reagents were added downstream from the hot zone. In these experiments only **10**, **11** and **14** were observed.

A possible mechanism by which **1** might decompose to **10** and **11** is outlined in Scheme 3. Disilabenzene **1** could close to give its corresponding Dewar isomer **15**,



SCHEME 3

which might then undergo a 1,2-methyl shift to cleave the strained Si–Si bond, giving 1,1,2,3,5,6-hexamethyl-1,4-disilacyclohexa-2,5-dienylidene (**16**). The silylene could then insert in an intramolecular fashion into a C–H bond of the silyl-methyl to give **10**. Silylene **16** could alternatively undergo three successive hydrogen shifts to give **17**, **18** and **19** which could then extrude H_2Si: to give the observed product, 1,1,3,4-tetramethyl-2,5-dimethylene-1-silacyclopent-3-ene (**11**).

Experimental

General data. All reactions unless otherwise noted were carried out under dry nitrogen or argon. Solvents were dried by standard techniques. Methanol was freshly distilled from magnesium turnings and I_2. Cyclohexane was washed repeatedly with sulfuric acid, dried over sodium sulfate, and distilled from fresh lithium aluminum hydride. All glassware was thoroughly dried in an oven at 110–120 °C prior to use. Methods for the preparation of *sym*-dimethyltetramethoxydisilane [14], 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene (**13**) [15], and 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene (**7**) [16] have been previously described. ^1H NMR spectra were recorded on a Bruker WP-270 (270 MHz) spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-200 (200 MHz) spectrometer. All NMR spectra were recorded at ambient temperature and chemical shifts are reported relative to an internal standard of TMS.

Mass spectra and exact mass determinations were performed on a Kratos MS-80 mass spectrometer operating at an ionizing voltage of 30 eV. A Kratos MS-25 equipped with a Carlo–Erba gas chromatograph was employed for GC-MS. The gas chromatograph was fitted with a 30 m × 0.36 mm i.d. fused silica capillary column coated with 5% phenylmethylsilicone.

A Hewlett–Packard 5890 gas chromatograph with a FID and a 10 m × 0.56 mm i.d. megabore column coated with 5% phenylmethylsilicone was used for analytical gas chromatography. Preparative gas chromatography was performed on a Gow Mac Model 550P gas chromatograph using a thermal conductivity detector and helium as the carrier gas. Normally, a 6′ × 0.25″ column packed with 5% SE-30 adsorbed on Chromosorb-W was used. Elemental analyses were performed by Galbraith Laboratories Inc.

Solution photolyses. Photochemical experiments were conducted using a Rayonet Model RPR-100 photochemical reactor equipped with low pressure mercury lamps. The sample was dissolved in the appropriate solvent and the solution was placed in a quartz tube equipped with a Schlenk-type side arm to permit evacuation. The total volume of this photolysis cell was approximately 10 ml. Prior to irradiation the cell and its contents were freeze-pump-thaw degassed (5 cycles, 5×10^{-5} Torr). Unless otherwise noted the photolyses were performed at ambient temperatures.

Flow thermolyses. A vertical quartz tube (50 cm × 15 mm i.d.) with standard taper joints at either end packed with quartz chips was placed in a Lindberg tube furnace. The top of the tube was fitted with a 10 ml addition funnel and an inlet for the carrier gas, the flow of which was maintained at approximately 20 ml/min. The bottom of the tube was fitted with a trap which was immersed in a cold bath of dry ice/isopropyl alcohol. The trap was vented to allow escape of the carrier gas. The temperature of the hot zone was monitored with a built-in thermocouple. The sample was dissolved in cyclohexane and the solution was added to the hot zone via the addition funnel at a rate of 1 ml/10 min. The residence time of the sample in the hot zone was between 2 and 3 s.

Flash vacuum thermolyses. The apparatus used for low pressure pyrolysis is the same as that described above except that it was assembled horizontally, no carrier gas inlet was provided and the additional funnel was replaced with an introduction flask which could be heated by placement in a kugelrohr oven. The system was evacuated through the vent on the cold trap which was now immersed in liquid nitrogen. The outlet of the tube could be wrapped with heating tape to prevent premature condensation of the pyrolysate.

Matrix-isolation spectroscopy. Argon matrices were prepared on CsI windows attached to the cold tip of an Air Products CS-202 Displex closed-cycle helium cryostat with indium gaskets. Standard vapor mixing techniques were used. Deposition rates were about 0.5 mmol/min through a custom pyrolysis oven with a 5 cm × 0.5 cm i.d. quartz tube heated with an insulated nichrome wire. The temperature of the oven was monitored with an iron-constantan thermocouple and digital thermometer (Omega). The argon deposition temperature was maintained at 12–14 K. All UV-VIS spectra were recorded on a Cary 17 spectrophotometer interfaced to a PDP-11/23 computer and the IR spectra were recorded on a Nicolet 6000 series Fourier-transform spectrometer.

Anthracene adduct, 2. Anthracene (Aldrich, gold label, 4.34 g, 24 mmol) and lithium wire (0.20 g, 24 mmol) was added to a mixture of THF (50 ml) and DME (50 ml). This mixture was stirred at room temperature for 4 h during which the characteristic deep blue color of anthracene dianion appeared. The solution was cooled to 0 °C and **7** (3.0 g, 12 mmol) in THF (10 ml) was added dropwise. After the addition was completed the solution was stirred at 0 °C for 30 min and then warmed to room temperature during 1 h. The resulting milky solution was poured into 10% aqueous HCl and extracted with ethyl ether. The organic layer was removed and washed several times with water. An insoluble suspension was filtered off. The filtrate was dried over sodium sulfate and the ether removed in vacuo. The excess of anthracene was removed by careful sublimation at 60 °C/0.1 Torr and **2** was purified by successive recrystallizations from THF/MeOH yield 1.13 g (25%). M.p. 246–247.5 °C; ^{1}H NMR ($CDCl_3$): δ 6.8–6.9 (m, 8H), 3.5 (s,2H), 1.4 (s, 12H), 0.4 (s, 6H) ppm; ^{13}C NMR (C_6D_6): δ 149.3, 141.1, 125.0, 124.6, 46.1, 16.7, −4.3 ppm; mass spectrum: m/e (%) 372 (8.2), 194 (100), 179 (18).

1-Methoxyhexamethyl-1,4-disilacyclohexa-2,5-diene (9). A mixture of *cis-* and *trans*-isomers of **13** (1.0 g, 3.9 mmol) was dissolved in THF (25 ml). Small aliquots of lithium aluminum hydride were then added and the reaction was monitored by GC. When the product ratio of 1,4-dihydride to 1-hydro-4-methoxide to starting material reached 1/2/1 (**9** was present as two isomers in a 4/1 ratio) the reaction was stopped. Hexane (20 ml) was added and the solution was carefully decanted away from the lithium salts. Removal of the solvent in vacuo and separation by preparative GC gave the major isomer of **9**. ^{1}H NMR (C_6D_6): δ 4.2–4.3 (m, 1H), 3.25 (s, 3H), 1.7–1.9 (m, 12H), 0.27 (s, 3H), 0.22 ppm (d, J 3 Hz, 3H); mass spectrum: m/e (%), 226 (20), 211 (100), 157 (84).

Photolysis of anthracene adduct 2. A solution of **2** (30 mg) in dry deolefinated cyclohexane (5 ml) was placed in a quartz photolysis tube, degassed several times at high vacuum, and closed under an atmosphere of nitrogen. The solution was irradiated for 5 minute intervals in a Rayonet photoreactor at 254 nm. The course of the photolysis was monitored by GC. The adduct **2** was completely destroyed and the only volatile product observed was anthracene.

Photolysis of 2 in presence of hexafluoro-2-butyne. Hexafluoro-2-butyne (approximately 1 g) was vacuum transferred to a quartz photolysis vessel to which was added, via syringe, a solution of **2** (50 mg, 0.134 mmol) in degassed cyclohexane (5 ml). The mixture was irradiated for 30 min at 254 nm in a Rayonet photoreactor. Following completion of the photolysis, the solvent was removed in vacuo leaving a white solid. The volatile materials were separated from the mixture by sublimation (90 °C/0.1 torr). The hexafluoro-2-butyne adduct was then isolated by preparative GC (6′ × 3/8″ 20% SE-30 on Chromosorb W 60/80) and identified as 1,2-bis(trifluoromethyl)-3,4,5,6,7,8-hexamethyl-2,6-disila[2.2.2]bicycloocta-1,4,7-triene (**8a**), a white solid, yield 41 mg (88%). ^{1}H NMR (C_6D_6): δ 1.65 (s, 12H), 0.55 (br s, 6H) ppm; exact mass determination: calculated for $C_{14}H_{18}Si_2F_6$ 356.0851, measured 356.0850.

Photolysis of 2 in the presence of methanol. A sample of **2** (30 mg, 0.081 mmol) was placed in a solution of THF (5 ml) and MeOH (0.5 ml). The mixture was placed in a quartz photolysis vessel and freeze-thaw degassed several times before being closed under an atmosphere of dry nitrogen. The tube and its contents were irradiated at 254 nm for 2 min and the product mixture was analyzed by GC. The only volatile product formed, aside from anthracene, was shown to be identical to the authentic sample of *cis-* and *trans*-1-hydro-4-methoxydisilacyclohexadiene (**9**), prepared above.

Photolysis of 2 in presence of oxygen. A solution of the bridged-anthracene adduct **2** (20 mg) in THF (5 ml) was saturated with oxygen and irradiated for 20 min. 1,2,3,4,5,6-Hexamethyl-7-oxa-1,4-disila[2.2.1]bicyclohepta-2,5-diene (**14**) was obtained in 28% yield based on the amount of **2** consumed. Mass spectrum: *m/e* (%), 210 (15), 195 (48), 173 (100).

*Flow thermolysis of **2** in presence of methanol.* The anthracene adduct **2** (50 mg, 0.134 mmol) was dissolved in benzene (2 ml) to which dry MeOH (0.5 ml) was added. The solution was pyrolyzed by dropwise addition through a nitrogen flow pyrolysis apparatus. A nitrogen flow rate between 20 and 30 ml/min was maintained with the heated zone at 600 ° C. The product mixture was trapped at 77 K. After the entire solution was pyrolyzed, the trapping flask was warmed to room temperature and the pale orange product mixture was analyzed by GC. 1-Hydro-4-methoxyhexamethyl-1,4-disilacyclohexa-2,5-diene (**9**) was formed in 38% yield as a 1/1 mixture of *cis* and *trans*-isomers.

*Flow thermolysis of **2** in the presence of acetylene.* A sample of 50 mg (0.134 mmol) of **2** was dissolved in 3 ml of cyclohexane. The solution was thoroughly degassed and flow pyrolyzed in a dropwise fashion at 600 ° C in a 4/1 mixture of nitrogen and acetylene which had been passed through a trap immersed in dry ice and a $CaSO_4$ drying train. The major product (aside from anthracene) was isolated by preparative GC and identified as hexamethyldisilabarrelene (**8b**) by its mass spectrum: *m/e* (%), 220 (100), 205 (52.4), 191 (4.8), 151 (34.8), 125 (9.1), 97 (21.4).

*Flash vacuum thermolysis of **2**.* A sample of **2** (50 mg) was placed in a roundbottom introduction flask and was sublimed at 200 ° C into the hot zone which was maintained at 700 ° C. The outlet was wrapped with heating tape (100 ° C) to prevent the condensation of the pyrolysate before reaching the cold trap, which was immersed in liquid nitrogen. The product mixture contained anthracene and two new products in 8 and 21% yield respectively, based on recovered starting material. The products were isolated by preparative VPC. The minor product was identified as 1,2,3,5,6-pentamethyl-1,4-disila[2.2.1]bicyclohepta-2,5-diene (**10**). Yield: 2.0 mg (8%), ^1H NMR (C_6D_6): δ 4.83 (s, 1H), 1.91 (q, J 0.01 Hz, 3H), 1.78 (q, J 0.01 Hz, 3H), 0.43 (s, 2H), 0.40 (s, 3H) ppm; mass spectrum: *m/e* (%), 194 (100), 179 (18), 140 (82), 125 (55); exact mass determination: calculated for $C_{10}H_{18}Si_2$ 194.0947, measured 194.0941. The major product was identified as 1,1,3,4-tetramethyl-2,5-dimethylene-1-silacyclopent-3-ene (**11**). Yield: 4.6 mg (21%), ^1H NMR (C_6D_6): δ 5.64 (d, J 2 Hz, 2H), 5.29 (d, J 2 Hz, 2H), 1.78 (s, 6H), 0.21 (s, 6H) ppm; mass spectrum: *m/e* (%), 164 (92), 149 (100), 123 (28); exact mass determination: calculated for $C_{10}H_{16}Si$ 164.1017, measured 164.1010.

cis-2-Butene-1,4-diol adduct of disilacyclohexadiene (12). A solution of 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene, **7**, as a 1/1 mixture of *cis*- and *trans*-isomers (1.04 g, 3.9 mmol) in diethyl ether (225 ml) and a solution of *cis*-2-butene-1,4-diol (0.35 g, 3.9 mmol) in diethyl ether (225 ml) were added with rapid stirring in a slow simultaneous manner to a flask containing a solution of triethylamine (10 ml) in diethyl ether (250 ml). After an initial induction period of approximately 10 min a white precipitate (Et_3NHCl) began to form. After the addition, which required 3 h, was complete the slurry was stirred at room temperature overnight. The ammonium salts were removed by filtration and the solvent and amine were stripped by rotary evaporation. Hexane (200 ml) was added and the insoluble material was removed by filtration. The solution was then treated with activated charcoal. Removal of the hexane gave 0.67 g (61%) of **12** as a clear, colorless liquid; ^1H NMR

(270 MHz, C_6D_6): δ 5.42 (t, 2H), 4.09 (d, 4H), 1.80 (s, 1H), 0.31 (s, 6H) ppm; ^{13}C NMR (200 MHz, C_6D_6): δ 149.8, 129.0, 58.4, 16.2, −3.6 ppm; mass spectrum: *m/e* (%) 280 (7), 265 (26), 211 (52); exact mass determination: calculated for $C_{14}H_{24}O_2Si_2$ 280.1315, measured 280.1312.

cis-1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (6a). A solution of **12** (0.50 g, 1.78 mmol) in diethyl ether (25 ml) was added to a solution of lithium aluminum hydride (0.27 g, 7 mmol) also in diethyl ether (25 ml). After stirring at room temperature for 4 h the mixture was placed in an ice bath and the excess $LiAlH_4$ was destroyed by the careful addition of a saturated solution of ammonium chloride. Hexane (150 ml) was added and the solution was worked up in the usual manner. The solvent was stripped and the residue was passed through a 5 cm column of activated silica gel using hexane as eluent giving **6a** in greater than 95% isomeric purity (0.25 g, 72%). ^1H NMR (270 MHz, $CDCl_3$): δ 4.08 (q, *J* 3.2 Hz, 2H), 1.82 (s, 12H), 0.20 (d, *J* 3.2 Hz, 6H) ppm; mass spectrum: *m/e* (%), 196 (34), 181 (100).

cis-1,4-Dideuteriohexamethyl-1,4-disilacyclohexa-2,5-diene (6a-d_2). The preparation of *cis*-**6**-d_2 is the same as that for the dihydride described above. Reduction of **12** (0.50 g, 1.78 mmol) with lithium aluminum deuteride (Aldrich) (0.29 g, 7 mmol) provided 0.24 g (68%) of the dideuteride. ^1H NMR ($CDCl_3$): δ 1.85 (s, 12H), 0.2 (br s, 6H) ppm; exact mass determination: calculated for $C_{10}H_{18}Si_2D_2$ 198.1229, measured 198.1228.

trans-1,4-Dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (6b). 1,4-Dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene [5] (2.50 g) as a 1/4 mixture of *cis*- and *trans*-isomers was dissolved in a minimal amount of refluxing chloroform (approximately 5 ml). The solution was slowly cooled (so as to prevent oiling out) to room temperature and then chilled to −10 °C. The dimethoxide was allowed to crystallize at this temperature for several hours, providing 95% pure *trans*-**13** (1.10 g, 44%) as clear, colorless crystals; m.p. 84.5–87.0 °C (the mixture of isomers had a melting range of 68–76 °C); ^1H NMR ($CDCl_3$): δ 3.31 (s, 6H), 1.85 (s, 12H), 0.14 (s, 6H) ppm. In a manner similar to that for the preparation of **6a** *trans*-**13** (0.50 g, 1.95 mmol) was treated with $LiAlH_4$ (0.10 g, 2.6 mmol) to give **6b**, 0.24 g (63%); ^1H-NMR ($CDCl_3$): δ 3.96 (q, *J* 3.2 Hz, 2H), 1.72 (s, 12H), 0.09 (d, *J* 3.2 Hz, 6H) ppm.

Flash vacuum thermolysis of 6a. The *cis*-dihydride **6a** (100 mg) was distilled from the introduction flask at 65 °C into the thermolysis tube which was heated to 820 °C at 5×10^{-3} Torr. The isolated pyrolysate consisted of three products: **10**, **11** and a new product which had not been observed previously. It was identified on the basis of its mass spectrum as 1,2,3,4,5,6-hexamethyl-1,4-disila-7-oxa[2.2.1]bicyclohepta-2,5-diene (**14**). Mass spectrum: *m/e* (%), 210 (15), 195 (48), 173 (100).

Cothermolysis of 6a and methanol. Fifty mg of **6a** were dissolved in a mixture of benzene (5 ml) and methanol (1 ml). The solution was introduced to the hot zone which was maintained at 620 °C. The pyrolysate was collected and analyzed by GC. The starting material was completely consumed and one new product obtained, a mixture of the *cis*- and *trans*-isomers of 1-methoxy-4-hydrohexamethyl-1,4-disilacyclohexa-2,5-diene (**9**). When the experiment was repeated with MeOD, the same product was obtained. Analysis by mass spectroscopy indicated no incorporation of deuterium. Methanolysis of the Si–H bond was occurring more rapidly than thermal extrusion of H_2.

*Cothermolysis of **6a** and 2-butyne.* A sample of **6a** (100 mg) was dissolved in cyclohexane (5 ml) containing 2-butyne (3 ml). The solution was introduced to the hot zone of the pyrolysis tube and collected in a cold trap. Approximately 45% of the starting material was depleted and three new products were observed by analytical GC. Two were identified as 2-butyne pyrolysis products; the third was found to be octamethyl-1,4-disila[2.2.2]bicycloocta-2,5,7-triene (**8c**). ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 18H), 0.32 (s, 6H) ppm; exact mass determination : calculated for $C_{14}H_{24}Si_2$ 248.1410 measured 248.1415.

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