

$J = 1.6$  Hz, 1 H), 8.25 (dd,  $J = 1.6, 8.1$  Hz, 1 H), 7.66 (d,  $J = 8.1$  Hz, 1 H), 5.55 (s, 2 H), 2.19 (s, 3 H), 1.62 (s, 9 H);  $R_f$  (CA), 0.62;  $R_f$  (BPAW), 0.81.

Anal. Calcd for  $C_{14}H_{17}NO_6$  ( $M_r$ , 295.29): C, 56.95; 5.80; N, 4.74. Found: C, 57.07; H, 5.81; N, 4.78.

**tert-Butyl 4-(Hydroxymethyl)-3-nitrobenzoate (8).** The corresponding acetoxyethyl derivative **7** (10.9 g, 37 mmol) was dissolved in  $CHCl_3$  (150 mL), and hydrazine hydrate (4.7 g, 150 mmol) was added dropwise at 25 °C over 0.5 h. After an additional 2-h stirring at 25 °C, ethyl acetate (300 mL) was added and the organic phase was washed with saturated NaCl (3 × 100 mL), dried ( $MgSO_4$ ), and concentrated in vacuo to give a solid which was recrystallized from ethyl acetate-pentane by the method used for **6** and **7**. The title product (8.8 g, 94%) comprised pale orange needles: mp 68–70 °C; NMR ( $CDCl_3$ )  $\delta$  8.63 (d,  $J = 1.6$  Hz, 1 H), 8.26 (dd,  $J = 1.7, 6.3$  Hz, 1 H), 7.86 (d,  $J = 6.3$  Hz), 5.05 (s, 2 H), 1.62 (s, 9 H);  $R_f$  (CA), 0.48;  $R_f$  (BPAW), 0.77.

Anal. Calcd for  $C_{12}H_{15}NO_5$  ( $M_r$ , 253.25): C, 56.91; H, 5.97; N, 5.53. Found: C, 56.79; H, 5.82; N, 5.42.

**Protected Dipeptidyl-Resins (9, 10, and 11) for Experiments on Formation of Diketopiperazine 12 (Scheme II; Table I).** By conventional solid-phase methodologies [deprotection with TFA- $CH_2Cl_2$  (3:7) (2 + 15 min); neutralization with DIEA- $CH_2Cl_2$  (1:19) (2 × 5 min); single coupling with DCC (3 equiv, 90 min)], Boc-leucine as an "internal reference" amino acid was coupled onto an aminomethyl-resin, followed by 4-(bromomethyl)-3-nitrobenzoic acid (**5**) introduced<sup>12b</sup> via its performed symmetrical anhydride. Next, the cesium salt of Boc-L-proline was prepared<sup>32</sup> and coupled (95% yield) onto this resin by reaction in *N,N*-dimethylformamide as the solvent at 50 °C for 14 h. After washings according to the standard procedures, the resultant Boc-Pro-ONb-Leu-resin was divided into three portions, and the appropriate  $N^\alpha$ -protected derivatives of D-valine were each quantitatively incorporated by DCC-mediated couplings. Details on experiments to treat these resins with deblocking agents and study retention of chains on the resin are in the

notes to Table I. The filtrates after treatments of resins **9** and **10** were evaporated to dryness and redissolved for reversed-phase HPLC analysis [ $CH_3OH-H_2O$  (1:4), 1.0 mL/min] to reveal a major peak ( $t_R$  4.4 min) comigrating with an authentic standard of cyclo[D-Val-L-Pro] (**12**).

**Acknowledgment.** We thank Robert L. Walsky for assistance with synthesis of several intermediates, Dr. Stephen Philson of the University of Minnesota for 300-MHz NMR spectra, Dr. Ken Tomer of the University of Nebraska for FABMS spectra, and Dr. E. Giralt and Dr. E. Pedrosa of the University of Barcelona, Spain, for a gift of authentic diketopiperazine **12**. Most especially, we are indebted to Prof. Bruce Merrifield of The Rockefeller University for his longstanding encouragement of and interest in this project, for which the groundwork was laid in earlier joint reports with G. B. (ref 8 and 10).

**Registry No.** **1** (R =  $CH(CH_3)_2$ ), 96965-23-0; **1** (R =  $CH_2CH(CH_3)_2$ ), 70824-58-7; **1** (R =  $CH_2C_6H_5$ ), 64724-53-4; **1** (R = H), 64724-51-2; **1** (R =  $CH_2-p-C_6H_4OC(CH_3)_3$ ), 96998-89-9; **3a**, 96965-24-1; **3b**, 96965-25-2; **3c**, 96965-26-3; **4a**, 96965-27-4; **4b**, 96965-28-5; **4c**, 96965-29-6; **5**, 55715-03-2; **6**, 96965-30-9; **7**, 96965-31-0; **8**, 65276-91-7; **12**, 27483-18-7; Dts-Tyr(*t*-Bu)-Gly-Gly-Phe-Leu-OH, 96998-93-5; Dts-Tyr-Gly-Gly-Phe-Leu-OH, 96998-94-6; H-Tyr(*t*-Bu)-Gly-Gly-Phe-Leu-OH, 66912-84-3; Boc-D-Val-OH, 22838-58-0; Fmoc-D-Val-OH, 84624-17-9; Dts-D-Val-OH, 96965-36-5; leucine-enkephalin, 58822-25-6; Dts-glycylvaline, 70711-37-4; 4-(bromomethyl)benzoic acid, 6232-88-8; Boc-leucine, 13139-15-6; Boc-L-proline cesium salt, 42538-66-9; *p*-toluic acid, 99-94-5.

**Supplementary Material Available:** Table III (<sup>1</sup>H NMR parameters of leucine-enkephalin and protected derivatives), Table IV (analytical and spectral data for Dts-aminoacyl-*o*-nitrobenzyl ester handle intermediates), and figures showing expanded NMR data (ref 19) and full FABMS spectra (ref 21) (12 pages). Ordering information is given on any current masthead page.

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## Disilathiiranes: Synthesis and Crystal Structure

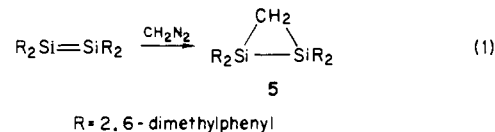
Robert West,\* Douglas J. De Young, and Kenneth J. Haller

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received December 26, 1984

**Abstract:** Reaction of elemental sulfur with disilene **1** or **2** produces respectively disilathiirane 1,1,2,2-tetramesityl-1,2-disilathiirane (**3**) or 1,2-di-*tert*-butyl-1,2-dimesityl-1,2-disilathiirane (**4**). The crystal structure of **3** is reported; this molecule has a short Si-Si distance of 228.9 (2) pm and a nearly planar arrangement of C, C, and Si atoms around each silicon. These results are interpreted in terms of partial  $\pi$  bonding between the silicon atoms. The molecular geometry of **3** is compared with those of other three-membered-ring compounds containing two silicon atoms.

Several kinetically stable disilenes have now been synthesized,<sup>1</sup> and some of their chemical reactions have been investigated.<sup>2</sup> Disilenes readily undergo addition to the Si-Si  $\pi$  bond; for instance, tetramesityldisilene (**1**) reacts with certain alkynes and ketones to give 1,2-disilacyclobutenes and 1,2-disilaoxetones,

respectively. Two addition reactions of disilenes to give three-membered-ring products have been published. Treatment of 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilene with diazomethane yields disilacyclopropane **5**<sup>3</sup> (eq 1), and *trans*-1,2-di-*tert*-butyl-



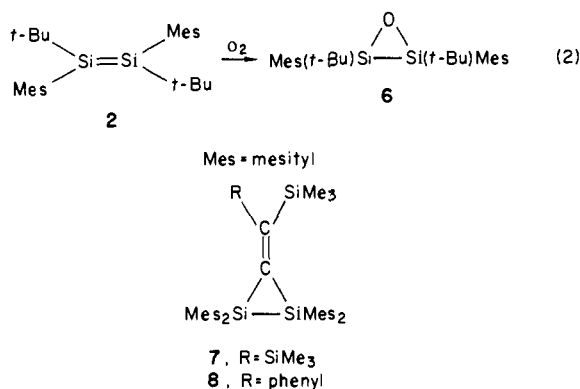
1,2-dimesityldisilene (**2**) reacts with oxygen to give, among other products, disilaoxirane **6**<sup>4</sup> (eq 2). Two other three-membered rings containing two silicon atoms are known, compounds **7** and **8**, synthesized by a different procedure.<sup>5</sup> In this paper we report

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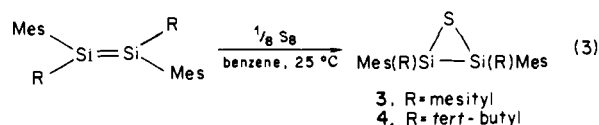
(4) Michalczuk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525.



the synthesis of two disilathiiranes, compounds with similar structure but with a sulfur atom in the three-membered ring.

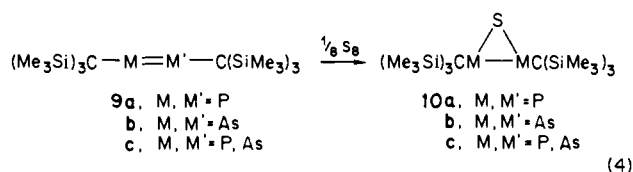
### Results and Discussion

**Addition of Sulfur to 1 and 2.** Reaction of disilenes **1** and **2** with elemental sulfur in benzene solution produced disilathiiranes **3** and **4**, respectively, in high yield (eq 3). The same products



were obtained when a large excess of sulfur was used. Compounds **3** and **4** are colorless crystalline solids, soluble in most organic solvents. The synthesis of **4** is stereoselective, and probably stereospecific; pure *trans*-**2** produces a single isomer of **4**, as is seen from its gas chromatogram and proton NMR spectrum.

Alkenes do not react with sulfur under these conditions, but several compounds containing double bonds between phosphorus and arsenic atoms do combine with sulfur to give three-membered rings. For example, diphosphene **9a**,<sup>6a</sup> diarsene **9b**,<sup>6b</sup> and the mixed phosphorus-arsenic compound **9c**<sup>6c</sup> react with sulfur to form thiiranes **10a-c**, respectively (eq 4).<sup>7</sup>



The <sup>29</sup>Si NMR chemical shifts of -59.03 ppm for **3** and -36.05 ppm for **4** fall considerably upfield from that of the analogous disilaoxirane, **6**, -8.0 ppm.<sup>4</sup> Possibly the increased shielding of the silicon nuclei in **4** compared with that in **6** reflects greater electron-donating ability of sulfur than oxygen in these three-membered-ring compounds.<sup>8</sup>

**Crystal Structure of 3.** ORTEP drawings of **3** in the crystal are shown in Figures 1 and 2, and the numbering scheme for the molecule is given in Figure 3. The molecule possesses no rotation axis. The four aryl substituents are each twisted about the C<sub>Ar</sub>-Si bond in the same direction, forming a four-bladed propeller in

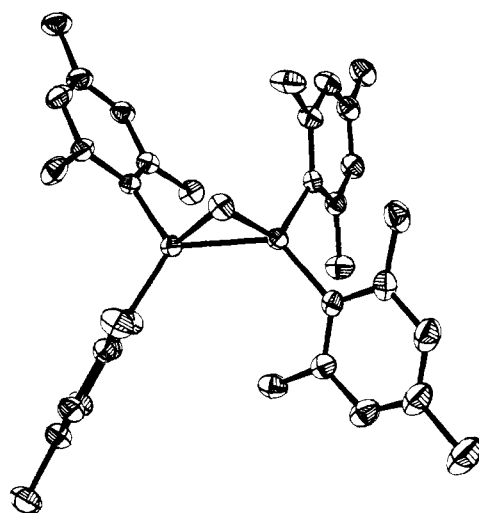


Figure 1. ORTEP drawing of tetramesityldisilathiirane, **3**.

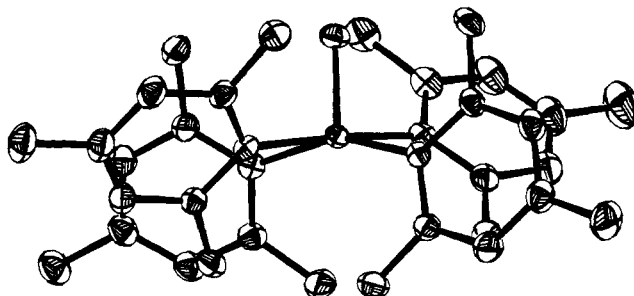


Figure 2. ORTEP drawing of **3** along the silicon-silicon axis.

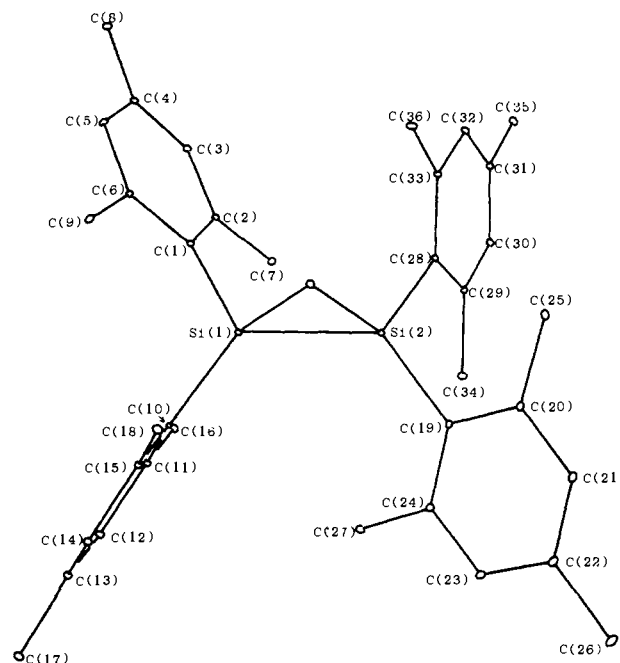


Figure 3. Numbering scheme for non-hydrogen atoms in **3**.

which the plane of each aromatic ring is rotated from the central three-membered ring by 60–70°.

Torsional distortion along the silicon-silicon axis results in a twist angle of 12.7 (3)°,<sup>9</sup> apparent in Figure 2. The C(1)-Si(1)-Si(2) and C(19)-Si(2)-Si(1) planes form a dihedral angle of only 6.3 (2)°. Each of the mesityl rings forms a different angle with its C<sub>Ar</sub>-Si-Si plane. The dihedral angle between ring A and

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(8) Few pairs of Si-O and Si-S compounds are known in which <sup>29</sup>Si chemical shifts have been determined for both species. For the six-membered rings (Me<sub>2</sub>SiO)<sub>3</sub> and (Me<sub>2</sub>SiS)<sub>3</sub> the <sup>29</sup>Si resonances appear at -9.2 and +21.1 ppm, respectively; the silicon in the oxygen-containing compound is the more shielded. From: Schraml, J.; Bellama, J. M. "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Randall, E. W., Eds.; Academic Press: New York, 1976; Vol. 6, p 203. See also: Wojnowski, W.; Pkies, J. *Z. Anorg. Allg. Chem.* **1984**, *501*, 201.

(9) The twist angle is taken as half the difference of the angles subtended by the C(1)-Si(1)-Si(2) and C(28)-Si(2)-Si(1) planes (12.2 (3)°) and the C(19)-Si(2)-Si(1) and C(10)-Si(1)-Si(2) planes (13.2 (3)°).

**Table I.** List of Bond Lengths (Å) in **3** (esd's in Parentheses)

Si(1)–Si(2)	2.289 (2)	C(13)–C(17)	1.507 (8)
Si(1)–S	2.161 (2)	C(14)–C(15)	1.396 (7)
Si(1)–C(1)	1.878 (5)	C(15)–C(18)	1.494 (7)
Si(1)–C(10)	1.882 (4)	C(19)–C(20)	1.417 (7)
Si(2)–S	2.162 (2)	C(19)–C(24)	1.405 (7)
Si(2)–C(19)	1.886 (5)	C(20)–C(21)	1.399 (7)
Si(2)–C(28)	1.898 (5)	C(20)–C(25)	1.492 (8)
C(1)–C(2)	1.409 (6)	C(21)–C(22)	1.351 (9)
C(1)–C(6)	1.422 (7)	C(22)–C(23)	1.400 (8)
C(2)–C(3)	1.408 (7)	C(22)–C(26)	1.515 (8)
C(2)–C(7)	1.513 (7)	C(23)–C(24)	1.392 (7)
C(3)–C(4)	1.367 (7)	C(24)–C(27)	1.509 (7)
C(4)–C(5)	1.395 (7)	C(28)–C(29)	1.412 (7)
C(4)–C(6)	1.520 (8)	C(28)–C(33)	1.412 (7)
C(5)–C(6)	1.389 (7)	C(29)–C(30)	1.386 (6)
C(6)–C(9)	1.517 (7)	C(29)–C(34)	1.517 (7)
C(10)–C(11)	1.412 (6)	C(30)–C(31)	1.367 (8)
C(10)–C(15)	1.415 (7)	C(31)–C(32)	1.385 (7)
C(11)–C(12)	1.401 (7)	C(31)–C(35)	1.513 (7)
C(11)–C(16)	1.515 (7)	C(32)–C(33)	1.410 (7)
C(12)–C(13)	1.378 (8)	C(33)–C(36)	1.499 (7)
C(13)–C(14)	1.395 (7)		

**Table II.** Significant Bond Angles (deg) in **3** (esd's in Parentheses)

Si(2)–Si(1)–S	58.0 (1)	C(19)–Si(2)–C(28)	115.0 (2)
Si(2)–Si(1)–C(1)	116.4 (1)	Si(1)–S–Si(2)	64.0 (1)
Si(2)–Si(1)–C(10)	125.8 (1)	Si(1)–C(1)–C(2)	124.2 (3)
S–Si(1)–C(1)	108.4 (2)	Si(1)–C(1)–C(6)	118.4 (3)
S–Si(1)–C(10)	118.0 (1)	Si(1)–C(10)–C(11)	126.0 (4)
C(1)–Si(1)–C(10)	115.1 (2)	Si(1)–C(10)–C(15)	115.5 (3)
Si(1)–Si(2)–S	58.0 (1)	Si(2)–C(19)–C(20)	116.3 (4)
Si(1)–Si(2)–C(19)	123.4 (1)	Si(2)–C(19)–C(24)	124.3 (3)
Si(1)–Si(2)–C(28)	119.1 (1)	Si(2)–C(28)–C(29)	117.1 (3)
S–Si(2)–C(19)	107.2 (2)	Si(2)–C(28)–C(33)	124.8 (3)
S–Si(2)–C(28)	119.3 (2)		

the C(1)–Si(1)–Si(2) plane is 52°; rings B, C, and D form dihedral angles of 85°, 47°, and 73° with their respective C<sub>ar</sub>–Si–Si planes.

The short silicon–silicon bond length of 228.9 (2) pm in this molecule will be discussed further below. The silicon–sulfur bond lengths are equal at 216.1 (2) and 216.2 (2) pm. This value is approximately normal, being only ~1 pm shorter than the Si–S bond length in tetramethylcyclodisilathiane.<sup>10</sup> The internal Si–Si–S and Si–S–Si angles are 58.0 (1)° and 64.0 (1)°, respectively. The independent silicon–carbon bond lengths are 187.9 (5), 188.2 (4), 188.5 (5), and 189.8 (5) pm. The carbon–carbon bond lengths and angles in the mesityl groups are normal; the endocyclic distances range from 136.6 (7) to 142.1 (7) pm, and the exocyclic distances span the range 149.3 (7)–152.0 (7) pm. Other bond lengths and angles for **3** are listed in Tables I and II.

**Structure of **3** and Related Molecules.** A remarkable structural feature of **3** is the silicon–silicon bond length of 228.9 (2) pm, 6 pm shorter than the typical silicon–silicon bond distance of 235 pm.<sup>11</sup> The silicon–silicon distance in **5** is even shorter (227.2 pm),<sup>3</sup> and the corresponding bond length for **8** (232.7 pm)<sup>5</sup> is also slightly shorter than the normal value. The short Si–Si distances are not characteristic of silicon in all three-membered rings, since hexakis(2,6-dimethylphenyl)cyclotrisilane has a longer-than-normal bond distance between silicons, 240.7 pm.<sup>12</sup>

Compounds **3**, **5**, and **8** share another surprising structural similarity: in all three compounds, *the arrangement of the bonded carbon and silicon atoms around each silicon is nearly planar.* In **3**, the sum of the bond angles C–Si–Si, C'–Si–Si, and C–Si–C'

around the two silicon atoms is 357.4 (4)°. Similar values are 357.4 (2)° and 357.7 (1)° for **5**, and 356.6° for **8**.<sup>13</sup> The latter structural features suggest that in all three compounds, the hybridization at silicon may be better represented as sp<sup>2</sup>–p rather than sp<sup>3</sup>. According to this model, the sulfur and carbon bridging groups would be bonded mainly to 3p orbitals from the silicon. In addition, with the short Si–Si distances, some overlap of 3p orbitals on adjacent silicon atoms may take place, leading to partial  $\pi$  bonding between silicons and hence to a bond order greater than one.

Similar, although smaller, distortions are found for the analogous carbon compounds oxirane and thiirane; these have likewise been interpreted in terms of partial  $\pi$  bonding between the carbon atoms.<sup>14,15</sup> The bonding in **3**, **5**, and **8** may also be compared with the familiar Dewar–Chatt–Duncanson model for coordination of olefins to transition metals.<sup>16</sup> Here the bonding is viewed in terms of donation from the  $\pi$  orbitals of the olefin into a vacant orbital on the metal, accompanied by back-donation from metal d orbitals into the  $\pi^*$  orbitals of the olefin. In this process, the olefin is more or less distorted from planarity and the C–C bond length becomes intermediate between that for a single and a double bond. In the disilathirane, and likewise in ethylene oxide and related molecules, such back-donation to  $\pi^*$ -like orbitals could take place from a filled orbital on the sulfur or oxygen atom.

The only calculations done on these systems have been on disilacyclopropane and 3-methylene-1,2-disilacyclopropane.<sup>5</sup> In disilacyclopropane the Si–Si bond length was calculated to be 231.4 pm, shorter than the normal Si–Si distance but longer than that in **5**.

The arrangement of the aryl groups around the three-membered ring in **3** is similar to that in other known disilicon three-membered-ring systems. The C(1)–Si(1)–C(10) and C(19)–Si(2)–C(28) planes are twisted in opposite directions relative to the normal to the plane of the Si–Si–S three-membered ring whereas in **5** the corresponding planes are twisted in the same direction. The C(10)–Si(1)–C(10) plane is –1.8° twisted from the normal, and the C(19)–Si(2)–C(28) plane is twisted by –19.4°.

**Intra- and Intermolecular Interactions.** Several close contacts between carbon atoms occur in **3**, which may also have an influence on the molecular geometry. The four ortho methyl groups C(7), C(18), C(27), and C(34) directed away from the sulfur atom are grouped closely together, with an average C–C distance of 371.9 pm. This is about 30 pm less than the sum of the van der Waals' radii for two methyl groups, 400 pm. Other close carbon–carbon interactions are found between methyl and ring carbons on different mesityl rings: C(7)–C(28), 336 pm; C(7)–C(29), 343 pm; C(10)–C(27), 364 pm; C(15)–C(26), 358 pm; and C(15)–C(27), 367 pm. These distances are 20–50 pm less than the 385-pm value estimated for the sum of the van der Waals radii of a methyl and an aromatic carbon. Such interactions would tend to move the mesityl rings apart, and may contribute to the planarization seen at the two silicon centers.

There are also a few close intermolecular carbon–carbon contacts. The shortest are those between C(7) and C(7) (365.5 pm), C(17) and C(23) (372.9 pm), and C(22) and C(35) (365.5 pm), which range from 10 to 35 pm less than the sum of the van der Waals radii of the carbon atoms involved. Therefore, crystal packing forces may also have some influence on the molecular geometry of **3**.

### Experimental Section

Proton NMR spectra were recorded on a Bruker WP-200 FT spectrometer; <sup>29</sup>Si NMR spectra were recorded on a JEOL FX-200 spectrometer. Mass spectral analyses were obtained with a KRATOS MS-80 mass spectrometer. All reactions were carried out under an atmosphere of argon, and the solvents used were dried and distilled prior to use. Syringe and Schlenk techniques were used where appropriate. The sulfur

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Table III. Summary of Crystal Data and Intensity Collection

empirical formula	Si <sub>2</sub> SC <sub>36</sub> H <sub>44</sub>
formula weight	565.0
crystal dimensions, mm	0.15 × 0.40 × 0.40
temp, K	138 ± 2
cell parameters	
<i>a</i> , Å	11.746 (5)
<i>b</i> , Å	17.837 (7)
<i>c</i> , Å	8.767 (3)
α, deg	92.85 (2)
β, deg	111.45 (5)
γ, deg	73.82 (2)
space group	<i>P</i> <sub>1</sub>
<i>Z</i>	2
density, calcd, g/cm <sup>3</sup>	1.14
absorption coeff, μ, cm <sup>-1</sup>	1.56
scan range	
deg below 2θ <sub>Kα1</sub>	0.7
deg above 2θ <sub>Kα2</sub>	0.7
scan speed, deg/min	2.0–24.0
scan type	θ–2θ
2θ limits, deg	3.5–54.9
(sin θ)/λ <sub>max</sub> , Å <sup>-1</sup>	0.649
unique data	
theor	7493
<i>F</i> <sub>o</sub> > 3σ( <i>F</i> <sub>o</sub> )	4744
discrepancy indices	
<i>R</i> <sub>1</sub>	0.069
<i>R</i> <sub>2</sub>	0.090
goodness of fit	2.41

was obtained from Aldrich Chemical Co. and sublimed prior to use. Degassing of the solutions and mixtures was achieved by bubbling argon through them for 20 min. Melting points are uncorrected.

The disilenes **1** and **2** were prepared as previously reported<sup>11</sup> with the following exceptions: (1) no sidearm attachment was used on the photolysis tube; (2) after the photolysis was complete the solvent was removed in vacuo and 50 mL of degassed benzene was added, making the standard solution of **1** or **2**.

**Addition of Sulfur to 1.** A mixture of 19.2 mg (0.6 mmol) of sulfur (sublimed) in 25 mL of benzene was placed in a 100-mL sidearm flask and degassed. A standard solution of **1** (0.6 mmol) in benzene was added. The mixture decolorized immediately to pale yellow. Evaporation of the solvent in vacuo followed by recrystallization from hexane gave a white crystalline solid identified as **3** in 38% isolated yield. The yield based on the proton NMR of **3** before recrystallization is 56%: mp 172–174 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.02 (s, 12 H, *p*-CH<sub>3</sub>), 2.55 (s, 24 H, *o*-CH<sub>3</sub>), 6.62 (s, 8 H, Ar H); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ -59.03; MS (30 eV), *m/e* (relative intensity) 564 (M<sup>+</sup>, 3.8), 445 (M - Mes, 85.4), 326 (M - 2(Mes), 20.1); exact mass calcd. for C<sub>36</sub>H<sub>44</sub>Si<sub>2</sub>S 564.2691, found 564.2704.

**Addition of Sulfur to 2.** A mixture of 21.7 mg (0.68 mmol) of sulfur in 25 mL of benzene was placed in a 100-mL sidearm flask and degassed. A standard solution of **2** (0.68 mmol) in benzene was added to the sulfur mixture by cannulation under argon. The mixture decolorized immediately. Evaporation of the solvent in vacuo followed by recrystallization from hexane gave an off-white powdery solid identified as **4**. Prior to stabilization the isolated solid was 82% **4** by proton MMR: mp 204–205.5 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.00 (s, 18 H, *t*-Bu H), 2.08 (s, 6 H, *p*-CH<sub>3</sub>), 2.76 (s, 6 H, *o*-CH<sub>3</sub>), 2.82 (s, 6 H, *o*-CH<sub>3</sub>), 6.76 (s, 2 H, Ar H), 6.78 (s, 2 H, Ar H); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ -36.046; MS (30 eV), *m/e* (relative intensity) 440 (M<sup>+</sup>, 46.0), 383 (M - *t*-Bu, 100), 263 (M - (MesH + *t*-Bu), 25.6); exact mass calcd. for C<sub>26</sub>H<sub>40</sub>Si<sub>2</sub>S 440.2379, found 440.2392.

A single crystal of Si<sub>2</sub>SC<sub>36</sub>H<sub>44</sub> obtained by slow cooling of a saturated toluene solution was mounted in a thin-walled glass capillary for the X-ray study. Preliminary examination of the crystal and collection of the diffraction data were carried out on a Syntex-Nicolet *P*<sub>1</sub> diffractometer equipped with a graphite-monochromated Mo Kα X-radiation source (λ = 0.71073 Å) and a modified L7-1 low-temperature device. Unit cell dimensions were determined from 30 accurately centered high-angle reflections (28° < 2θ < 38°), each collected at plus and minus 2θ. The unit cell was found to be triclinic. Delouny cell reduction did not reveal any cell of higher symmetry. Intensity data were collected and structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously.<sup>17</sup> Four standard reflections were monitored periodically during the data

Table IV. Fractional Atomic Coordinates for **3**<sup>a</sup>

atom	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.77661 (12)	0.27744 (7)	0.10155 (17)
Si(2)	0.63309 (12)	0.21684 (7)	0.11826 (17)
S	0.71151 (12)	0.29199 (7)	0.30504 (16)
C(1)	0.9482 (4)	0.21804 (26)	0.1793 (6)
C(2)	0.9915 (4)	0.14036 (26)	0.1396 (6)
C(3)	1.1181 (5)	0.09567 (28)	0.2235 (7)
C(4)	1.2027 (5)	0.12530 (30)	0.3460 (7)
C(5)	1.1624 (5)	0.2024 (3)	0.3858 (7)
C(6)	1.0390 (4)	0.24868 (28)	0.3029 (6)
C(7)	0.9080 (5)	0.10058 (27)	0.0062 (6)
C(8)	1.3370 (5)	0.0742 (3)	0.4388 (7)
C(9)	1.0036 (5)	0.33261 (29)	0.3505 (7)
C(10)	0.7380 (4)	0.36633 (24)	-0.0354 (6)
C(11)	0.6929 (4)	0.44486 (25)	-0.0007 (6)
C(12)	0.6609 (5)	0.50472 (27)	-0.1196 (7)
C(13)	0.6731 (5)	0.49030 (28)	-0.2698 (7)
C(14)	0.7167 (5)	0.41265 (29)	-0.3044 (7)
C(15)	0.7497 (4)	0.35104 (26)	-0.1899 (6)
C(16)	0.6754 (5)	0.46961 (27)	0.1592 (7)
C(17)	0.6345 (6)	0.5547 (3)	-0.3994 (8)
C(18)	0.7974 (5)	0.26973 (27)	-0.2360 (7)
C(19)	0.4551 (4)	0.26172 (24)	0.0283 (6)
C(20)	0.3882 (5)	0.26111 (28)	0.1338 (7)
C(21)	0.2575 (5)	0.2989 (3)	0.0774 (8)
C(22)	0.1929 (5)	0.3375 (3)	-0.0719 (8)
C(23)	0.2587 (5)	0.33762 (29)	-0.1767 (7)
C(24)	0.3886 (5)	0.30065 (26)	-0.1281 (6)
C(25)	0.4520 (5)	0.2218 (3)	0.3023 (7)
C(26)	0.0523 (6)	0.3805 (4)	-0.1277 (9)
C(27)	0.4521 (5)	0.3041 (3)	-0.2484 (7)
C(28)	0.6862 (4)	0.10707 (25)	0.1664 (6)
C(29)	0.6472 (4)	0.05970 (26)	0.0339 (6)
C(30)	0.6963 (5)	-0.02100 (27)	0.0537 (7)
C(31)	0.7848 (5)	-0.05870 (27)	0.1987 (7)
C(32)	0.8209 (5)	-0.01295 (28)	0.3309 (7)
C(33)	0.7729 (5)	0.06927 (27)	0.3196 (6)
C(34)	0.5561 (5)	0.09443 (29)	-0.1364 (7)
C(35)	0.8407 (5)	-0.14663 (28)	0.2126 (8)
C(36)	0.8178 (6)	0.1105 (3)	0.4747 (7)

<sup>a</sup> Estimated standard deviations for the least significant digits are given in parentheses.

collection. Their intensities did not show any systematic variations. ψ curve data showed intensity variations of less than 10%; absorption corrections were not applied. Crystal data and details of the intensity data collection are given in Table III.

The structure was solved by direct methods using the MULTAN78 package and the 410 highest normalized structure factors. The *E* map revealed positions for all 39 non-hydrogen atoms. After isotropic refinement on the non-hydrogen atoms had converged, a difference electron density map was calculated and examined for hydrogen positions. About 80% of the hydrogen atoms could be located. All hydrogen atoms were included in the model in idealized positions. The methyl hydrogens were included, putting in rigid CH<sub>3</sub> groups (3-fold symmetry maintained by use of equal change instructions; *d*[C-H] = 0.95 Å) with origins on the carbon atoms. Full matrix least-squares refinement was carried out with the program RAELS.<sup>18</sup> Standard values for the atomic scattering factors, including corrections for anomalous dispersion, were employed throughout the analysis.<sup>19</sup> Each mesityl group was assumed to possess a single reorientable thermal libration axial system (TL model)<sup>20</sup> centered on the silicon atom to which the group is attached.

Least-squares refinement of this model converged with discrepancy indices *R*<sub>1</sub> = Σ||*F*<sub>o</sub> - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>| = 0.069 and *R*<sub>2</sub> = [Σw(|*F*<sub>o</sub> - |*F*<sub>c</sub>||)<sup>2</sup>/Σw(*F*<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup> = 0.090. The conventional *R* factor for the data with (sin θ)/λ < 0.1 was 0.034, indicating model completeness. The estimated error in an observation of unit weight was 2.41 and the final data/variable ratio was 15:1. There were no significant peaks on the final electron

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density difference map. Atomic coordinates for the non-hydrogen atoms are given in Table IV. Additional bond angles, anisotropic thermal parameters, positional parameters for the hydrogen atoms, and a listing of  $10|F_o|$  and  $10|F_c|$  are available as supplementary material.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, hydrogen atomic and triclinic coordinates, additional bond angles, and a listing of  $10|F_o|$  and  $10|F_c|$  (21 pages). Ordering information is given on any current masthead page.

## Meso Substitution of Chlorophyll Derivatives: Direct Route for Transformation of Bacteriopheophorbides *d* into Bacteriopheophorbides *c*

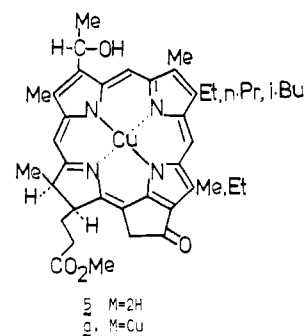
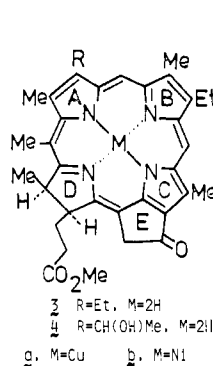
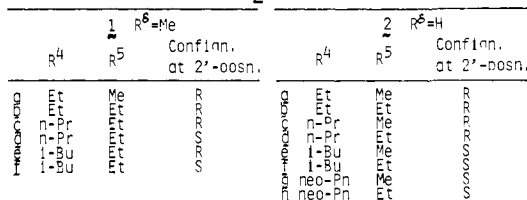
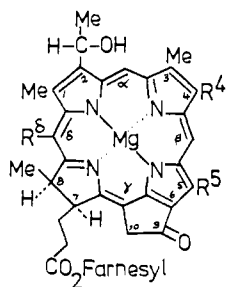
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**Abstract:** In order to develop a procedure for direct methylation of methyl bacteriopheophorbides *d* (Bmph-*d*) to afford methyl bacteriopheophorbides *c* (Bmph-*c*), several reactions involving *meso* substitution of chlorophyll derivatives were investigated. Treatment of zinc(II) methyl mesopyropheophorbide *a* (**7b**) with bromine in chloroform accomplished oxidation, presumably via the  $\pi$ -cation radical, to the corresponding porphyrin, phylloerythrin methyl ester (**16**); *meso* bromination (to give **17**) resulted when metal-free methyl mesopyropheophorbide *a* (**7**) was treated with bromine in chloroform. Friedel-Crafts cyanation (cyanogen bromide/aluminum chloride) of copper(II) methyl mesopyropheophorbide *a* (**7a**) gave 40–50% yields of the *meso*-cyanochlorin **18** after demetalation, but attempts to transform the cyano group into methyl were unsuccessful. Oxidation reactions of **7** using thallium(III) trinitrate resulted in formation of the corresponding *meso*-nitrochlorins **20**. Treatment of copper(II) methyl mesopyropheophorbide *a* (**7a**) with chloromethyl methyl sulfide and titanium tetrachloride afforded the *meso*-methylthiomethyl derivative **19a** (74–77% yields); use of the nickel(II) complex **7d** likewise gave 80–84% yields of **19b**. With Raney nickel, both **19a** and **19b** gave good yields of the required *meso*-methyl metallochlorins **3a** and **3b**, respectively, the former being readily demetalated with HCl gas in dichloromethane to give the *meso*-methylchlorin **3**. Thus, the Bmph-*d* to Bmph-*c* transformation was accomplished by initially protecting the vinyl group in methyl pyropheophorbide *a* (**9**) as the corresponding 2-chloroethyl group; the copper(II) complex **25a** was then methylthiomethylated, treated with Raney nickel (to give **26a**), and finally demetalated with HCl gas to give **27**. Compound **27** has previously been converted into Bmph-*c* [Et, Me] (**4**) by treatment with base (to give the 2-vinyl derivative) followed by hydration of the vinyl with HBr in acetic acid.

Bacteriochlorophylls *c* (**1**) and *-d* (**2**) (Bchls-*c*, *-d*) are found in various strains of green sulfur bacteria such as *Prosthecochloris aestuarii* (Bchl-*c*) and *Chlorobium vibrioforme* (Bchl-*d*). The pigments produced by such organisms occur as a mixture of homologues (**1a–f**; **2a–h**), and recent work has established the major structural features of these homologues in both the Bchl-*c*<sup>1</sup> and Bchl-*d*<sup>2</sup> series. The major structural difference between the

Bchls-*c* and *-d* is the  $\delta$ -*meso*-methyl substituent found in the former. In our previous synthesis<sup>3</sup> of methyl mesobacteriopheophorbide *c* [Et, Me] (**3**) and methyl bacteriopheophorbide *c* (Bmph-*c*) [Et, Me] (**4**) from copper(II) chlorin *e*<sub>6</sub> trimethyl ester derivatives, the key *meso*-methyl group was introduced by Vilsmeier formylation and one-step reduction of the resulting *meso*-formyl group. The success of this approach depended on



the previously demonstrated fact that aromatic electrophilic substitution occurs adjacent to the reduced D ring in chlorins.<sup>4,5</sup>

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