

Articles

Disilaselirane and Disilatellurane: Synthesis and Crystal Structures

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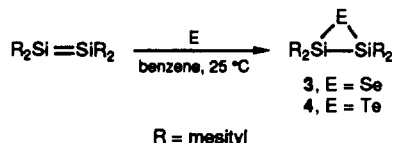
Reaction of elemental selenium and tellurium with 1,1,2,2-tetramesityldisilene produces respectively 1,1,2,2-tetramesityl-1,2-disilaselirane (**3**) and 1,1,2,2-tetramesityl-1,2-disilatellurane (**4**). The structures of **3** and **4** are confirmed by X-ray crystal analysis. Crystals of **3** are monoclinic, space group $P2_1/c$: $a = 11.625$ (4) Å, $b = 8.896$ (4) Å, $c = 31.398$ (10) Å; $\beta = 99.78$ (3)°; $V = 3200$ (2) Å³; $d_{\text{calcd}} = 1.270$ g/mL for $Z = 4$; $R = 5.67\%$; 3236 reflections with $F > 4.0\sigma(F)$. Crystals of **4** are orthorhombic, space group $Pnn2$: $a = 18.516$ (4) Å, $b = 15.954$ (3) Å, $c = 11.917$ (2) Å; $V = 3520.3$ (12) Å³; $d_{\text{calcd}} = 1.329$ g/mL for $Z = 4$; $R = 5.18\%$; 2723 reflections with $F > 4.0\sigma(F)$. The Si-Si bond lengths are 2.303 (3) Å for **3** and 2.337 (4) Å for **4**. Both **3** and **4** have a nearly planar arrangement of C, C, Si atoms around each silicon atom. The spectroscopic and structural properties of **3** and **4** are presented along with those of 1,1,2,2-tetramesityl-1,2-disilaoxirane (**1**) and 1,1,2,2-tetramesityl-1,2-disilathiirane (**2**), the two other chalcogen derivatives with similar constitution.

Introduction

Disilenes have been shown to display a rich and diverse chemistry as a result of addition reactions to the very reactive Si-Si π bond.¹ Cycloaddition reactions of disilenes often provide a convenient route to novel heterocyclic rings containing two silicon atoms.² Among these are two three-membered rings containing a chalcogen atom: 1,1,2,2-tetramesityl-1,2-disilaoxirane (**1**), prepared from tetramesityldisilene and dinitrogen oxide,³ and 1,1,2,2-tetramesityl-1,2-disilathiirane (**2**), synthesized by the reaction of the disilene with elemental sulfur.⁴ In this paper we describe the synthesis of the corresponding selenium- and tellurium-containing rings, **3** and **4**, completing this series of chalcogen compounds. The X-ray crystal structures were determined for **3** and **4**: these appear to be the first structure determinations for three-membered ring compounds containing either selenium or tellurium. The molecular structures of **3** and **4** will be compared with those previously reported for **1** and **2**.

Results and Discussion

Synthesis of 3 and 4. Reaction of elemental selenium with tetramesityldisilene in benzene at room temperature produced exclusively the disilaselirane **3**. Under similar



(1) For reviews of disilenes, see: West, R. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1201-1302. Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, pp 1015-1142.

(2) Piana, H.; Schubert, U. *J. Organomet. Chem.* 1988, 348, C19-C21. Masamune, S.; Murakami, S.; Tobita, H. *J. Am. Chem. Soc.* 1983, 105, 7776-7778. Michalczuk, M. J.; West, R.; Michl, J. *J. Chem. Soc. Chem. Commun.* 1984, 1525-1526. Yokelson, H. B.; Millevolte, A. J.; Haller, K. J.; West, R. *J. Chem. Soc., Chem. Commun.* 1987, 21, 1605-1606.

(3) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* 1987, 109, 6865-6866.

(4) West, R.; DeYoung, D. J.; Haller, K. J. *J. Am. Chem. Soc.* 1985, 107, 4942-4946.

conditions elemental tellurium reacted with the disilene to give disilatellurane **4** as the sole product. Both compounds were isolated as colorless solids and studied by ¹H, ²⁹Si, and ⁷⁷Se or ¹²⁵Te NMR spectroscopy.

The ²⁹Si NMR chemical shifts of compounds **1-4** are tabulated in Table I. The upfield shift from -27.2 ppm for **1** to -90.3 ppm for **4** can be explained by electronegativity trends; as the chalcogen atom that is bound to the two silicon atoms becomes more electropositive, the corresponding silicon atoms become more shielded and hence the ²⁹Si chemical shift moves in the upfield direction. The smallest difference in the chemical shifts from one compound to another (5.8 ppm) in this series is found for **2** and **3**, reflecting the small difference in electronegativities between sulfur and selenium ($\Delta\chi = 0.03$). The ¹J(Si-Te) coupling constant for **4** is 166 Hz, 2.1 times the ¹J(Si-Se) coupling constant of 78 Hz for **3**. From calculations and usually in practice, tellurium coupling constants are found to be approximately twice as large as selenium coupling constants in analogous compounds.⁵

The ⁷⁷Se NMR chemical shift of -287.1 ppm (singlet) is substantially upfield from Me₂Se (0 ppm), consistent with other directly bonded silicon-selenium compounds. It is known that, when selenium is bound to an electropositive element such as silicon or tin, there is usually a substantial increase in shielding.⁵ Likewise, the ¹²⁵Te chemical shift of -783.8 ppm in **4** is substantially upfield from the reference standard, Me₂Te (0 ppm). In both ⁷⁷Se and ¹²⁵Te spectra there were marked silicon isotope shift effects, resulting in unsymmetrical silicon satellites about the main selenium or tellurium peaks. The satellites were located 42.4 and 35.6 Hz upfield and downfield of the main peak for **3** and 93 and 73 Hz for **4**, giving ²⁹Si/²⁸Si isotope shifts of 0.036 ppm for **3** and 0.063 ppm for **4**. The isotope shift is understandable, as the heavier ²⁹Si isotope would tend to shield the selenium atom or tellurium atom more than the lighter ²⁸Si isotope;⁶ thus the satellites, which

(5) McFarlane, H. C. E.; McFarlane, W. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 275-299.

Table I. Spectroscopic and Structural Data^a for Compounds 1-4

molecule	Pauling ^b $\chi(E)$	²⁹ Si chem shift, δ	Si-Si bond dist	Si-E bond dist	angle ^c at Si atoms	twist angle ^d	Si-E-Si angle	Si-Si-E angle
1 (E = O) ^e	3.44	-27.2	2.227 (2)	1.732 (3) 1.733 (3)	360.0 (2)	10.0	80.0 (2)	50.0 (1)
2 (E = S) ^f	2.58	-59.0	2.289 (2)	2.161 (2) 2.162 (2)	357.3 (2) 357.5 (2)	12.7	64.0 (1)	58.0 (1)
3 (E = Se)	2.55	-64.8	2.303 (3)	2.303 (2) 2.309 (2)	355.6 (4) 356.0 (3)	10.0	59.9 (1)	59.9 (1) 60.2 (2)
4 (E = Te)	2.10	-90.3	2.337 (4)	2.523 (3) 2.524 (3)	355.3 (6) 355.8 (7)	14.5	55.2 (1)	62.4 (1)

^a Angles are in deg and bond distances in Å. ^b Pauling scale of electronegativity; values from: Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215. ^c Sum of the three angles formed by the arrangement of C, C, Si atoms around each silicon atom. ^d The twist angle is a result of the torsional distortion along the Si-Si bond; this angle is apparent in Figures 2 and 4. ^e From ref 3. ^f From ref 4.

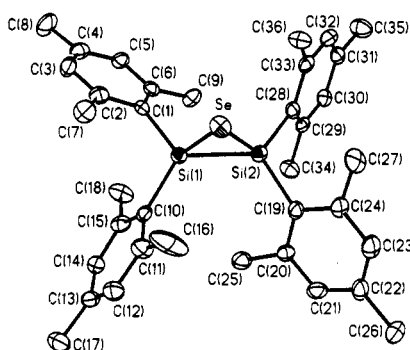


Figure 1. Molecular structure of 3 (hydrogens omitted for clarity).

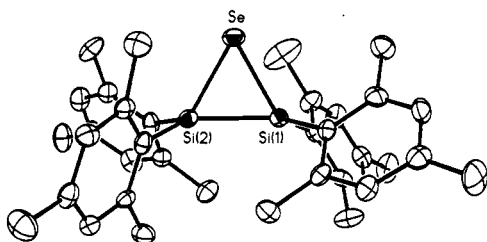


Figure 2. Molecular structure of 3 showing the nearly planar arrangement of the C, C, Si atoms around each silicon atom and the torsional distortion about the silicon-silicon axis.

result from the active ²⁹Si nuclei, are shifted upfield about the main singlet peak. The larger isotope shift effect in 4 is not surprising, since nuclei with larger chemical shift ranges tend to exhibit greater isotope shift effects.⁶

Seleniranes are well-known to be unstable compounds,^{7,8} decomposing rapidly at room temperature to selenium metal and olefins. Unlike seleniranes, 3 does not decompose even on heating to its melting point of 272-274 °C. It decomposes slowly, however, if left dissolved in an organic solvent, liberating a reddish precipitate of elemental selenium. To the best of our knowledge, telluriranes have never been observed. The disilatellurirane 4 is thus surprisingly stable; it is inert in air and when heated decomposes only at its melting point of 184 °C. In solution 4 decomposes slowly, liberating a fine black precipitate of tellurium.

(6) Webb, G. A. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 1, p 93.

(7) Tyerman, W. J. R.; O'Callaghan, W. B.; Kebarle, P.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 4277-4278. Tyerman, W. J. R.; Callear, A. B. *Trans. Faraday Soc.* **1966**, *62*, 2760-2767. Chan, T. H.; Finkenbine, J. R. *Tetrahedron Lett.* **1974**, *24*, 2091-2094. Behan, J. M.; Johnstone, R. A. W.; Wright, M. J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1216. Caló, V.; Lopez, L.; Mincuzzi, A.; Pesce, G. *Synthesis* **1976**, 200-201. Lakshminantham, M. V.; Cava, M. P. *J. Org. Chem.* **1976**, *41*(5), 879-881. Krief, A.; Van Ende, D. *Tetrahedron Lett.* **1975**, *31*, 2709-2712.

(8) The first report of a stable selenirane derivative was published recently: Ando, W.; Kumamoto, Y.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*(25), 2867-2870.

Table II. Bond Lengths (Å) for 3

Se-Si(1)	2.303 (2)	Se-Si(2)	2.309 (2)
Si(1)-Si(2)	2.303 (3)	Si(1)-C(1)	1.885 (6)
Si(1)-C(10)	1.913 (6)	Si(2)-C(19)	1.904 (6)
Si(2)-C(28)	1.906 (6)	C(1)-C(2)	1.422 (9)
C(1)-C(6)	1.398 (8)	C(2)-C(3)	1.389 (9)
C(2)-C(7)	1.510 (9)	C(3)-C(4)	1.384 (10)
C(4)-C(5)	1.363 (9)	C(4)-C(8)	1.515 (10)
C(5)-C(6)	1.412 (9)	C(6)-C(9)	1.493 (9)
C(10)-C(11)	1.412 (8)	C(10)-C(15)	1.407 (8)
C(11)-C(12)	1.400 (9)	C(11)-C(16)	1.497 (10)
C(12)-C(13)	1.361 (9)	C(13)-C(14)	1.394 (9)
C(13)-C(17)	1.483 (9)	C(14)-C(15)	1.396 (8)
C(15)-C(18)	1.506 (9)	C(19)-C(20)	1.404 (8)
C(19)-C(24)	1.416 (8)	C(20)-C(21)	1.386 (9)
C(20)-C(25)	1.544 (9)	C(21)-C(22)	1.375 (9)
C(22)-C(23)	1.399 (9)	C(22)-C(26)	1.499 (10)
C(23)-C(24)	1.362 (9)	C(24)-C(27)	1.510 (9)
C(28)-C(29)	1.392 (8)	C(28)-C(33)	1.424 (7)
C(29)-C(30)	1.393 (8)	C(29)-C(34)	1.511 (8)
C(30)-C(31)	1.377 (7)	C(31)-C(32)	1.393 (9)
C(31)-C(35)	1.514 (9)	C(32)-C(33)	1.413 (8)
C(33)-C(36)	1.484 (9)		

Table III. Significant Bond Angles (deg) for 3

Si(1)-Se-Si(2)	59.9 (1)	Se-Si(1)-Si(2)	60.2 (1)
Se-Si(1)-C(1)	109.9 (2)	Si(2)-Si(1)-C(1)	124.0 (2)
Se-Si(1)-C(10)	120.8 (2)	Si(2)-Si(1)-C(10)	122.2 (2)
C(1)-Si(1)-C(10)	109.8 (2)	Se-Si(2)-Si(1)	59.9 (1)
Se-Si(2)-C(19)	113.2 (2)	Si(1)-Si(2)-C(19)	121.4 (2)
Se-Si(2)-C(28)	118.2 (2)	Si(1)-Si(2)-C(28)	124.3 (2)
C(19)-Si(2)-C(28)	109.9 (3)	Si(1)-C(1)-C(2)	117.3 (4)
Si(1)-C(1)-C(6)	123.7 (5)	Si(1)-C(10)-C(11)	124.5 (4)
Si(1)-C(10)-C(15)	117.3 (4)	Si(2)-C(19)-C(20)	124.8 (4)
Si(2)-C(19)-C(24)	118.0 (4)	Si(2)-C(28)-C(29)	115.9 (4)
Si(2)-C(28)-C(33)	125.0 (4)		

Crystal Structure of Disilaseliran 3. Thermal ellipsoid plots of 3 are shown in Figures 1 and 2. The molecule has an approximate C₂ rotational axis passing through the selenium atom and the midpoint of the Si-Si bond.⁹ As in 1 and 2, the four aryl substituents are twisted about the Si-C_{Ar} bond in the same direction, forming a four-bladed propeller. In this orientation, the ortho methyls of the aryl rings are spaced in such a way as to minimize steric hindrance.

Torsional distortion about the silicon-silicon axis results in a twist angle of 10.0°, apparent in Figure 2. The twist angle is taken as the average of the angles subtended by the C(1)-Si(1)-Si(2) and C(28)-Si(2)-Si(1) planes (10.6°) and the C(10)-Si(1)-Si(2) and C(19)-Si(2)-Si(1) planes (9.4°). The Si-Si bond length is 2.303 (3) Å, about 0.05 Å shorter than the typical Si-Si single bond (e.g., the dihydro derivative Mes₂HSiSiHMe₂ has two independent

(9) The torsional angles Si(2)-Si(1)-C(10)-C(11) and Si(1)-Si(2)-C(28)-C(33) are 66.7 (0.6) and 84.8 (0.5)°, respectively, and the angles Si(1)-Si(2)-C(19)-C(24) and Si(2)-Si(1)-C(1)-C(2) are -138.5 (0.4) and -141.5 (0.4)°, respectively.

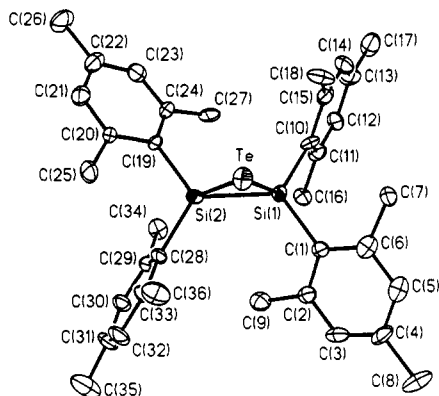


Figure 3. Molecular structure of **4** (hydrogens omitted for clarity).

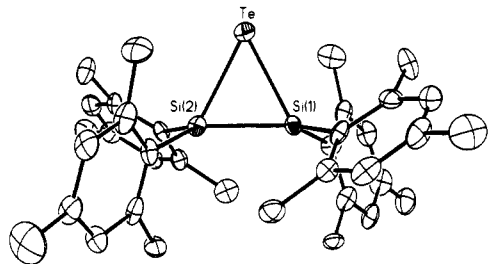


Figure 4. Molecular structure of **4** showing the nearly planar arrangement of the C, C, Si atoms around each silicon atom and the torsional distortion about the silicon-silicon axis.

Si-Si bond distances of 2.350 and 2.363 Å¹⁰). This short Si-Si bond length will be discussed further below.

The silicon-selenium bond lengths are almost equal at 2.303 (2) and 2.309 (2) Å. These values are slightly longer than the average Si-Se bond length (2.27) (2) Å in crystalline H₃Si-Se-SiH₃¹¹ or in selenosilicates. For example, in Tl₄SiSe₄ the average Se-Si bond length is 2.272 (8) Å¹² and in Ba₂SiSe₄ the average bond distance is 2.264 Å.¹³

The internal Si-Se-Si angle is 59.9 (1)°, the Se-Si(1)-Si(2) angle is 60.2 (2)°, and the Se-Si(2)-Si(1) angle is 59.9 (1)°. The independent Si-C bond lengths are 1.885 (6), 1.913 (6), 1.906 (6), and 1.904 (6) Å. The C-C bond lengths and angles in the mesityl groups are normal; the endocyclic distances range from 1.361 (9) to 1.422 (9) Å, and the exocyclic distances range from 1.483 (9) to 1.544 (9) Å. Other bond lengths and angles for **3** are listed in Tables II and III.

Crystal Structure of Disilatellurirane 4. Thermal ellipsoid plots of **4** are shown in Figures 3 and 4. Compound **4** possesses a 2-fold rotational axis passing through the tellurium atom and the midpoint of the Si-Si bond.¹⁴ As in **3**, the four aryl substituents twist in the same direction about the Si-C_{Ar} bonds. The torsional distortion about the silicon-silicon axis in **4** results in a twist angle of 14.5°, as illustrated in Figure 4. The Si-Si bond length is 2.337 (4) Å, only about 0.01 Å shorter than the typical Si-Si bond length. This will be discussed further below.

The Si-Te bond lengths are identical, 2.524 (3) and 2.523 (3) Å, and are about the same as the Si-Te bond length

Table IV. Bond Lengths (Å) for **4**

Te-Si(1)	2.524 (3)	Te-Si(2)	2.523 (3)
Si(1)-Si(2)	2.337 (4)	Si(1)-C(1)	1.891 (10)
Si(1)-C(10)	1.889 (11)	Si(2)-C(19)	1.894 (10)
Si(2)-C(28)	1.892 (11)	C(1)-C(2)	1.419 (15)
C(1)-C(6)	1.397 (14)	C(2)-C(3)	1.376 (15)
C(2)-C(9)	1.522 (16)	C(3)-C(4)	1.361 (16)
C(4)-C(5)	1.390 (18)	C(4)-C(8)	1.522 (17)
C(5)-C(6)	1.391 (17)	C(6)-C(7)	1.536 (19)
C(10)-C(11)	1.413 (16)	C(10)-C(15)	1.438 (15)
C(11)-C(12)	1.366 (15)	C(11)-C(16)	1.514 (16)
C(12)-C(13)	1.419 (18)	C(13)-C(14)	1.365 (19)
C(13)-C(17)	1.526 (21)	C(14)-C(15)	1.379 (16)
C(15)-C(18)	1.485 (16)	C(19)-C(20)	1.415 (13)
C(19)-C(24)	1.400 (15)	C(20)-C(21)	1.366 (15)
C(20)-C(25)	1.503 (15)	C(21)-C(22)	1.421 (17)
C(22)-C(23)	1.376 (15)	C(22)-C(26)	1.495 (17)
C(23)-C(24)	1.379 (14)	C(24)-C(27)	1.500 (15)
C(28)-C(29)	1.388 (16)	C(28)-C(33)	1.424 (16)
C(29)-C(30)	1.374 (16)	C(29)-C(34)	1.525 (16)
C(30)-C(31)	1.403 (16)	C(31)-C(32)	1.417 (16)
C(31)-C(35)	1.469 (18)	C(32)-C(33)	1.370 (16)
C(33)-C(36)	1.523 (17)		

Table V. Significant Bond Angles (deg) for **4**

Si(1)-Te-Si(2)	55.2 (1)	Te-Si(1)-Si(2)	62.4 (1)
Te-Si(1)-C(1)	109.2 (3)	Si(2)-Si(1)-C(1)	123.9 (4)
Te-Si(1)-C(10)	120.1 (3)	Si(2)-Si(1)-C(10)	122.1 (3)
C(1)-Si(1)-C(10)	109.8 (5)	Te-Si(2)-Si(1)	62.4 (1)
Te-Si(2)-C(19)	109.1 (3)	Si(1)-Si(2)-C(19)	122.4 (3)
Te-Si(2)-C(28)	120.9 (3)	Si(1)-Si(2)-C(28)	122.8 (3)
C(19)-Si(2)-C(28)	110.1 (4)	Si(1)-C(1)-C(2)	124.6 (8)
Si(1)-C(1)-C(6)	118.5 (9)	Si(1)-C(10)-C(11)	115.6 (8)
Si(1)-C(10)-C(15)	126.8 (8)	Si(2)-C(19)-C(20)	117.1 (7)
Si(2)-C(19)-C(24)	124.9 (7)	Si(2)-C(28)-C(29)	115.9 (8)
Si(2)-C(28)-C(33)	127.0 (9)		

Table VI. Crystal Data and Experimental Details for Structure Determination of **3** and **4**

	3	4
empirical formula	C ₃₆ H ₄₄ Si ₂ Se	C ₃₆ H ₄₄ Si ₂ Te·0.606n-C ₅ H ₁₂
fw	611.9	704.2
cryst dimens, mm	0.25 × 0.35 × 0.4	0.1 × 0.2 × 0.5
cryst syst	monoclinic	orthorhombic
space group	P2 ₁ /c	Pnn2
cell params		
a, Å	11.625 (4)	18.516 (4)
b, Å	8.896 (4)	15.954 (3)
c, Å	31.398 (10)	11.917 (2)
β, deg	99.78 (3)	
V, Å ³	3200 (2)	3520.3 (12)
Z	4	4
density (calcd), g/mL	1.270	1.329
abs coeff, mm ⁻¹	1.154	0.937
F(000)	1288	1461.8080
temp, K	173 (2)	111 (2)
2θ range, deg	3.0-45.0	3.0-50.0
scan type	Wyckoff	Wyckoff
scan speed (in ω), deg/min	variable; 2.0-20.0	variable; 2.0-12.0
scan range	0.60	0.50
no. of obsd reflns (F > 4.0σ(F))	3236	2723
data-to-param ratio	9.2:1	7.4:1
largest diff peak, ^a e Å ⁻³	0.54	1.09
largest diff hole, e Å ⁻³	-0.58	-0.73
R	5.67	5.18
R _w	8.14	6.22
goodness of fit	1.58	1.23

^a For **3**, the largest peaks in the difference map were located around methyl carbons; for **4**, all large (>0.55 e Å⁻³) difference peaks were near the tellurium atom site.

(2.529 Å) of the only other reported X-ray structure of a neutral silicon-tellurium heterocycle.¹⁵ These values,

(10) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* 1980, 36, 605-616.

(11) Barrow, M. J.; Ebsworth, E. A. V. *J. Chem. Soc., Dalton Trans.* 1982, 211-216.

(12) Eulenberger, G. *Acta Crystallogr.* 1986, C42, 528-534.

(13) Brinkmann, C.; Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* 1985, 524, 83-89.

(14) The torsional angles Si(1)-Si(2)-C(28)-C(33) and Si(2)-Si(1)-C(10)-C(15) are 87.5 (1.0) and 85.5 (0.9)°, respectively, and the angles Si(2)-Si(1)-C(1)-C(6) and Si(1)-Si(2)-C(19)-C(20) are -141.3 (0.8) and -144.3 (0.6)°, respectively.

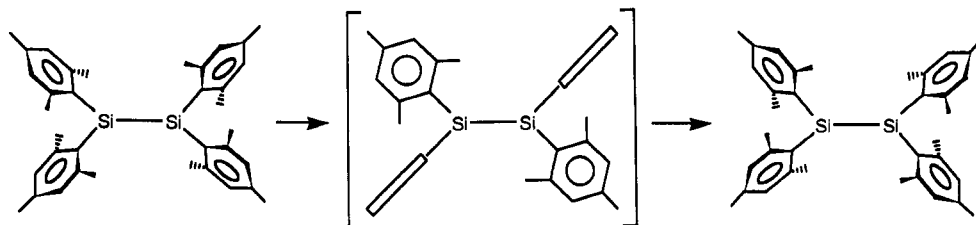


Figure 5. Schematic representation of the two-ring flip mechanism for compounds 1–4, in a view down the plane formed by the two silicon atoms and the corresponding chalcogen atom (the chalcogen atom is omitted for clarity).

however, are slightly longer than some of the Si–Te bond lengths reported for various telluro analogues of silicates, which range from 2.494 to 2.506 Å in Ba_2SiTe_4 ¹³ and 2.498 to 2.503 Å in $\text{Na}_6\text{Si}_2\text{Te}_6$.¹⁶

The internal Si–Te–Si angle is 55.2 (1)°, and the Te–Si(1)–Si(2) and Te–Si(2)–Si(1) angles are both 62.4 (1)°. The independent Si–C bond lengths are 1.889 (11), 1.891 (10), 1.892 (11), and 1.894 (10) Å. The C–C bond lengths and angles in the mesityl groups are normal; the endocyclic distances range from 1.361 (16) to 1.438 (15) Å, and the exocyclic distances range from 1.469 (18) to 1.536 (19) Å. Other bond lengths and angles for 4 are listed in Tables IV and V.

Comparison of Structures 1–4. An interesting feature of compounds 1–4 is that the Si–Si bond lengths in all four compounds are shorter than a normal Si–Si single bond (2.35 Å). The Si–Si bond lengths increase gradually from 1 through 4, as the electronegativity of the chalcogen atom decreases. In compound 1, the Si–Si bond length (2.227 (2) Å) is actually closer to that of a Si–Si double bond (2.14 Å)¹⁷ than that of a Si–Si single bond. The Si–Si bond lengths are almost identical for 2 (2.289 (2) Å) and 3 (2.303 (3) Å). In 4 the bond length (2.337 (4) Å) is only 0.01 Å shorter than the normal Si–Si single bond. The short Si–Si bond distances are not necessary features of three-membered rings, since hexakis(2,6-dimethylphenyl)cyclo-trisilane has a longer than average Si–Si bond of 2.407 Å.¹⁸

To account for the short Si–Si bond distances in 1 and 2, a bonding model was proposed in which a significant amount of double-bond character of the disilene is retained in the three-membered rings.^{3,4} This model is similar to the one developed by Dewar¹⁹ (later amplified by Chatt and Duncanson²⁰) to explain the bonding of olefins to transition metals. In this model, the bonding is viewed in terms of donation from the π orbitals of the olefin into a vacant orbital on the metal, accompanied by back-donation from the metal d orbital into the π^* orbital of the olefin. In 1–4, such back-bonding can take place from a filled orbital on the chalcogen atom of the appropriate symmetry into the π^* orbital of the disilene. The structures arising from these interactions lie on a continuum between a three-membered ring and a π complex. As the chalcogen becomes more electronegative, there is less back-bonding and the compounds tend toward the π -complex structure and, hence, shorter Si–Si bond lengths. This model suitably accounts for both the short Si–Si bond distances in compounds 1–3 and the observed trend of

increasing bond lengths on going from 1 to 4.

Two recent theoretical papers, one by Schaefer and Grev²¹ and the other by Cremer et al.,²² on bonding in silicon three-membered-ring compounds reported calculations that predict unusually short Si–Si bond lengths in compounds such as 1 and 2. They also found that the Si–Si bond distances in the three-membered-ring compounds increase with decreasing electronegativity of the substituents, in agreement with the experimental results we obtained for compounds 1–4. Both groups interpreted the short Si–Si bonds in terms of partial π -complex character in the three-membered-ring compounds. Another recent paper by Gordon and Boatz²³ on this subject, however, attributed the short Si–Si bond distances to extreme bond bending of the Si–Si bond, rather than to partial Si–Si π character. Cremer, in his paper,²² also calculated similar bond bending of the Si–Si bonds; he, however, attributed the bond bending to the π -complex character of the rings.

According to Cremer,²² the short Si–Si bond distance may also be caused by geometrical constraints resulting from the size of the atom E at the apex of the ring. When the Si–E bond distance is smaller than the Si–Si bond distance in a three-membered ring, there exists Baeyer strain resulting from a small (<60°) Si–Si–E angle. In order to avoid this increase in Baeyer strain for small Si–Si–E angles, as in the case of 1, Si–E distances are elongated and Si–Si distances reduced. In line with this interpretation, we note that as the Si–Si–E angles increase (or Si–E–Si angles decrease) on going from 1 to 4, Si–Si bond distances increase accordingly (Table I). In 1, where the Si–Si–E angles are smallest (50.0°), the Si–Si bond length is shorter than the a normal Si–Si single bond and the Si–O bond lengths are longer (1.732 (2) and 1.733 (3) Å) than the normal Si–O bond length found for other cyclic siloxanes (1.61–1.65 Å).²⁴

Another interesting structural feature of compounds 1–4 is the planar or nearly planar arrangement of carbon and silicon atoms around each silicon atom. In compound 1, the sum of the bond angles C–Si–Si, C'–Si–Si, and C–Si–C' around each silicon atom is 360.0 (2)°. The corresponding values in compounds 2–4 are only slightly smaller, ranging from 357.5 (2)° in 2 to 355.3 (6)° in 4 (see Table I). This planar arrangement of C, C, Si atoms around each silicon atom had previously been attributed to the π character of such compounds.^{3,4} The gradual decrease in planarity could be due to the decreasing π character in the com-

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Table VII. Dynamic NMR Data

compd	$\Delta G_{T_c}^*$, kcal/mol (T , °C)	$\Delta\nu$, Hz ^a	k_c , Hz
1 (E = O)	9.9 (-65)	41.1	92.0
2 (E = S)	9.6 (-73)	26.6	59.1
3 (E = Se)	9.8 (-70)	26.5	58.9
4 (E = Te)	9.3 (-83)	18.6	41.3

^a Difference in chemical shifts, at the coalescence temperature, of the *p*-methyl signals. $\Delta\nu$ at the coalescence temperature was obtained by extrapolation of values of $\Delta\nu$ at three or more temperatures in the slow-exchange region.

pounds on going from 1 to 4, in accordance with our proposed model.

Torsional distortion along the silicon-silicon axis results in twist angles ranging from 10.0° in 1 to 14.5° in 4, with no apparent trend as the size of the chalcogen increases (see Table I).

Dynamic NMR Results. The three-membered-ring compounds 1-4 possess an idealized C_2 rotational axis (actual in the case of 4) and are chiral as a result of their propeller-like conformation in the ground state. They are analogous to triarylmethanes,²⁵ triarylsilanes,²⁶ and other related compounds that are chiral due to their propeller-like conformations. Enantiomerization in such compounds has been found to occur by various ring flip mechanisms; in particular, the two-ring flip mechanism has been found to be the predominant pathway followed by many triarylmethanes²⁷ and triarylsilanes.²⁶ From examination of molecular models, it appears that a similar two-ring flip mechanism would provide the lowest energy pathway for enantiomerization in our disilane compounds (see Figure 5).

In compounds 1-4, the two *o*-methyl groups and the two meta protons on each mesityl ring are diastereotopic due to their positions relative to the three-membered ring. In addition, the *o*- and *p*-methyl groups and the meta protons on adjacent mesityl rings are diastereotopic; therefore, there are four sets of diastereotopic *o*-methyl groups and meta protons and two sets of *p*-methyl groups within the four mesityl rings. If the rotation about the Si-C_{Ar} bonds were sufficiently slowed, we would expect to see signals corresponding to the diastereotopic *o*- and *p*-methyl groups and meta protons in the ¹H NMR spectrum.

The ¹H NMR spectra of 1-4 were found to be temperature-dependent. The *o*- and *p*-methyl groups and the meta protons each appear as singlets at room temperature. When the samples are cooled, each of the singlet peaks decoalesces, and eventually the signals due to the *o*-methyl groups and the meta protons each split into four peaks and the *p*-methyl signal splits into a doublet. The rate constants k_c for the exchange of chemical environments of the *p*-methyl groups at their coalescence temperatures were found by using the approximate equation $k_c = \pi(\Delta\nu)/2^{1/2}$.

On the assumption that enantiomerization in our compounds occurs via the two-ring flip mechanism, the rate of enantiomerization equals $2k_c$. The free energy of activation for enantiomerization of compounds 1-4 was then calculated from the Eyring equation (Table VII). The free energy values all fall within the narrow range of 9.3 kcal/mol for 4 and 9.9 kcal/mol for 1. These values are

slightly smaller than those obtained for the ring rotations of hindered triarylsilanes: (Mes)₃SiH, $\Delta G_{T_c}^* = 10.9$ kcal/mol; (2,6-xylyl)₃SiH, $\Delta G_{T_c}^* = 11.1$ kcal/mol.^{26b}

Experimental Section

Proton NMR spectra were recorded on a Bruker WP-200 FT spectrometer; ²⁹Si, ⁷⁷Se, ¹²⁵Te, and variable-temperature ¹H NMR spectra were obtained on a Bruker AM-500 instrument. ¹H and ²⁹Si chemical shifts were respectively referenced to an internal and external standard of tetramethylsilane in the appropriate solvents. The ⁷⁷Se chemical shift was referenced to an external standard of Me₂Se in CDCl₃. The ¹²⁵Te chemical shift was referenced to an external standard of Me₂Te in CD₂Cl₂. For the dynamic NMR studies, samples of 2-4 were dissolved in THF-*d*₆ and 1 was dissolved in toluene-*d*₆. High-resolution mass spectral analyses were obtained with a Kratos MS-80 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. All reactions were carried out under an atmosphere of argon. Solids were manipulated under nitrogen in a glovebox. All solvents were dried, distilled, and degassed, and all glassware was baked at 120 °C for several hours prior to use. Melting points were not calibrated.

Tetramesityldisilene was prepared as previously reported²⁸ with the exception that in the photolysis step a solvent mixture of 2:1 pentane/THF was used instead of straight pentane. This results in a high yield of analytically pure disilene. Syntheses of 1 and 2 have been previously described.^{3,4}

Synthesis of Disilaselurane 3. A solution of 400 mg (0.75 mmol) of tetramesityldisilene in 30 mL of degassed benzene was placed in a 100-mL side-arm flask. Selenium granules (59 mg, 0.75 mmol) were added to the flask. The mixture was stirred for 3 days at room temperature; the final solution was light yellow. ¹H NMR analysis showed the exclusive formation of 3. Evaporation of the solvent in vacuo followed by several recrystallizations from hexane gave a fine colorless powdery solid (280 mg, 61%) identified as 3: mp 272-274 °C; ¹H NMR (200 MHz, C₆D₆) δ 2.03 (s, 12 H, *p*-CH₃), 2.56 (s, 24 H, *o*-CH₃), 6.62 (s, 8 H, Ar H); ¹H NMR (200 MHz, CDCl₃) δ 2.20 (s, 12 H, *p*-CH₃), 2.35 (s, 24 H, *o*-CH₃), 6.70 (s, 8 H, Ar H); ²⁹Si{¹H} NMR (99.4 MHz, C₆D₆) δ -64.8 (s, ¹J(Si-Se) = 78 Hz); ⁷⁷Se{¹H} NMR (95.4 MHz, CDCl₃) δ -287.1 (s, ¹J(Si-Se) = 78 Hz); MS (30 eV) *m/e* (relative intensity) 612 (M⁺, 3.0), 493 (M - Mes, 21.9); exact mass calcd for ¹²C₃₆¹H₄₄²⁸Si₂⁸⁰Se 612.2146, found 612.2186. Anal. Calcd for C₃₆H₄₄Si₂Se: C, 70.64; H, 7.27. Found: C, 70.81; H, 7.52.

Synthesis of Disilatellururane 4. A solution of 500 mg (0.94 mmol) of tetramesityldisilene in 35 mL of benzene was placed in a 100-mL side-arm flask. Tellurium granules (120 mg, 0.94 mmol) were added to the mixture. The solution was stirred at room temperature for 20 h; it was almost colorless except for fine gray particles of Te metal. NMR analysis showed the exclusive formation of 4. Excess metal was filtered off and the solvent removed in vacuo. Recrystallization from hexane gave a colorless solid (410 mg, 66%) identified as 4: mp 184 °C; ¹H NMR (200 MHz, C₆D₆) δ 2.03 (s, 12 H, *p*-CH₃), 2.56 (s, 24 H, *o*-CH₃), 6.62 (s, 8 H, Ar H); ¹H NMR (200 MHz, CD₂Cl₂) δ 2.05 (s, 12 H, *p*-CH₃), 2.25 (s, 24 H, *o*-CH₃), 6.60 (s, 8 H, Ar H); ²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂) δ -90.3 (s, ¹J(Si-Te) = 166 Hz); ¹²⁵Te{¹H} NMR (157.7 MHz, CD₂Cl₂) δ -783.8 (s, ¹J(Si-Te) = 166 Hz); MS (30 eV) *m/e* (relative intensity) 662 (M⁺, 10.9), 396 (M - Si(Mes)₂, 6.8); exact mass calcd for ¹²C₃₆¹H₄₄²⁸Si₂¹³⁰Te 662.2051, found 662.2035. Anal. Calcd for C₃₆H₄₄Si₂Te: C, 65.43; H, 6.73. Found: C, 65.83; H, 7.09.

X-ray Structure Determination. Single crystals of 3 for X-ray diffraction experiments were grown by vapor diffusion of hexane into a concentrated solution of 3 in toluene. X-ray-quality crystals, which grew as colorless plates, formed in the toluene solution in about 2 days. A single crystal was selected, coated with Paratone-N, cut to a suitable size, and mounted on a thin glass fiber for X-ray analysis.

X-ray-quality crystals of 4 were obtained from pentane by slow evaporation at room temperature. Crystals were taken from the solution under argon and immediately coated with a layer of Paratone-N. The colorless crystals grew as needles and had to be cut to a suitable length for X-ray studies. A suitable crystal was selected and mounted in a thin-walled glass capillary.

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The X-ray crystallographic experiments were performed on a Nicolet P3/F diffractometer for **3** and on a Syntex-Nicolet P1 diffractometer for **4**; both were equipped with a graphite-monochromated Mo K α X-radiation source ($\lambda = 0.71072 \text{ \AA}$) and a low-temperature device.

Unit cell parameters were determined by least-squares refinements based on 25 centered reflections. Three standard reflections were measured after every 50 reflections during the data collection. No significant decreases in the intensity of the standard reflections were observed during the data collection of both compounds.

The structures were solved by direct methods with the SHELXTL PLUS program on a Microvax II computer and refined by the full-matrix least-squares refinement method by use of the reflections with $F_o > 4.0\sigma(F)$. In the final refinement cycles the non-hydrogen atoms were assumed to vibrate anisotropically while the hydrogen atoms were included as idealized isotropic fixed contributors; the refinement converged to unweighted and

weighted agreement factors of $R = 5.67\%$ and $R_w = 8.14\%$ for **3** and $R = 5.18\%$ and $R_w = 6.22\%$ for **4**. Crystal data and experimental details for the structure determination of **3** and **4** are provided in Table VI.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles for **3** and **4** (15 pages); listings of observed and calculated structure factor amplitudes for **3** and **4** (26 pages). Ordering information is given on any current masthead page.

Preparation of Pre ceramic Polymers via the Metalation of Poly(dimethylsilene)[†]

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Model compound studies employing $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$, $(\text{Me}_3\text{SiCH}_2)_2\text{SiMe}_2$, $(\text{Me}_3\text{Si})_2\text{CHSiMe}_2\text{CH}_2\text{SiMe}_3$, and $c\text{-(Me}_2\text{SiCH}_2)_3$ showed $n\text{-BuLi}/t\text{-BuOK}$ to be the most effective metalation reagent for CH_2 groups in a SiCH_2Si environment. With use of this reagent in 1:1 $n\text{-BuLi}/t\text{-BuOK}$ to SiCH_2 molar ratio, it was found that about every fourth CH_2 group of poly(dimethylsilene), $(\text{Me}_2\text{SiCH}_2)_n$, could be metalated. Reactions of the resulting $[(\text{Me}_3\text{SiCH}_2)_3(\text{Me}_2\text{SiCHK})]_n$ species with Me_2HSiCl , $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$, Me_3SiCl , $\text{Me}_2(\text{ClCH}_2)\text{SiCl}$, and Et_3SiCl are described. Reactions of the $\{(\text{Me}_2\text{SiCH}_2)_3[\text{Me}_2\text{SiCH}(\text{SiMe}_2\text{CH}=\text{CH}_2)]\}_n$ polycarbosilane with the $[(\text{MeSiH})_{0.8}(\text{MeSi})_{0.2}]_x$ polysilane (AIBN catalyst) gave a hybrid polymer whose pyrolysis under a stream of argon at 1500°C gave a ceramic residue that contained about 91% by weight of SiC and 9% free carbon.

Introduction

Since Yajima and his co-workers developed the first polymeric precursor for silicon carbide,¹ there has been much interest in organosilicon polymers whose pyrolysis gives ceramic materials with a high content of silicon carbide.² Among the known organosilicon polymers that might be considered as potentially useful SiC precursors, poly(dimethylsilene), $(\text{Me}_2\text{SiCH}_2)_n$, is of interest. Polysilenes (or polysilmethylenes), $(\text{R}_2\text{SiCH}_2)_n$, linear polymers based formally on the $\text{R}_2\text{Si}=\text{CH}_2$ monomer, are organosilicon polymers that belong to the general class of polycarbosilanes.³ Their preparation and properties have been discussed in a recent review.⁴ Of the known polysilenes, $(\text{Me}_2\text{SiCH}_2)_n$ is the easiest to prepare and it has received the most study. Polymers of this kind, of relatively low molecular weight, have been prepared by active metal condensation of $\text{ClCH}_2\text{SiMe}_2\text{Cl}$,⁵ but material of considerably higher molecular weight is accessible by transition-metal-catalyzed ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.⁶ Such linear polymers, however, are not useful SiC precursors, their

pyrolysis to 1000°C under a stream of argon leaving little or no ceramic residue. The requirements for a good pre ceramic polymer have been discussed in some detail.⁷ Notable among these is that the polymer give as high a yield of ceramic residue on pyrolysis as possible, preferably above 70%. With few exceptions, the polymers with which this requirement can be met are ones that either are highly cross-linked to begin with (network polymers) or that contain a reactive (latent) functionality whose reactivity

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