Syntheses, Structures, and Reactions of Sulfur and Selenium Insertion Products of 1,1-Di-*tert*-butylsiliranes

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One-atom and two-atom sulfur and selenium ring expansion products of *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane (**1**), 6,6-di-*tert*-butyl-6-silabicyclo[3.1.0]hexane (**4**), and 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (**7**) are prepared by stirring the silirane and the chalcogen in the presence of tetrabutylammonium halide salts and/or alkali-metal halide salts with crown ethers. Potassium fluoride, 18-crown-6, and selenium in benzene react with **1** to give the novel ring system *trans*-2,2-di-*tert*-butyl-3,4-dimethyl-1,2-selenasiletane (**17**) in 85% yield. When tetrabutylammonium chloride (TBAC) is stirred with selenium and **1** or **17** in benzene, *trans*-3,3-di-*tert*-butyl-4,5-dimethyl-1,2-diselena-3-silacyclopentane (**18**) is formed in 87% and 82% yields, respectively. Similar results are observed for analogous reactions with sulfur. The mechanism responsible for the differences in product distributions seems to involve chalcogen activation by salts and crown ethers. Control of chalcogen insertions is demonstrated by reaction of **17** and sulfur in the presence of TBAC, which results in a new ring system, *trans*-3,3-di-*tert*-butyl-4,5-dimethyl-1-thia-2-selena-3-silacyclopentane (**21**) in 64% yield. *trans*-2,2-Di-*tert*-butyl-3,4-dimethyl-1,2-thiasiletane (**2**) and *cis*-7,7-di-*tert*-butyl-6-thia-7-silabicyclo[3.2.0]heptane (**5**), prepared from reactions of sulfur with **1** and **4**, respectively, are thermolyzed and photolyzed. Products consistent with the generation of a di-*tert*-butylsilathione fragment are observed, but bimolecular processes are not excluded. Three-dimensional structures of the bicyclic insertion products **7**–**9**, **15**, and **27** are elucidated using 1D and 2D NMR techniques. Experimental data are correlated with geometries calculated by molecular mechanics methods. The stereochemistries of 4,4-di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (**8**) and of 4,4-di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (**15**), prepared from reactions with **7** and sulfur and selenium, respectively, are further confirmed by single-crystal X-ray crystallography.

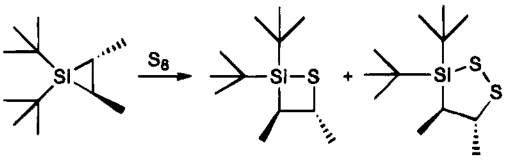
Introduction

Insertion of sulfur into cyclic carbosilanes is a well-known and useful method of preparing sulfur-containing heterocycles.[1] With the exception of *cis*- and *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilacyclopropane,[2] all known siliranes react with sulfur to give products resulting from insertion of two atoms of sulfur into the Si—C bond without forming a 1,2-thiasiletane.[3]

In this paper we report the details of the synthesis and characterization of several new compounds resulting from inserting sulfur and selenium atoms into siliranes. The effects of salts on these insertion reactions are also presented, as are detailed structural analyses in the form of two-dimensional NMR studies of **7**–**9**, **15**, and **27** in solution and the molecular structures of **8** and **15** using X-ray crystallography. Mechanistic pathways for ring expansion of siliranes, as well as for the thermolytic and photolytic decompositions of some of these ring systems, are discussed.

Results and Discussion

Reactions with Sulfur. When sulfur is stirred with approximately 1 equiv of *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane (**1**) is degassed hexane at room temperature, the sulfur dissolves to produce a colorless solution. Removal of solvent followed by preparative gas chromatography leads to the isolation of *trans*-2,2-di-*tert*-butyl-3,4-dimethyl-1,2-thiasiletane (**2**) and *trans*-3,3-di-*tert*-butyl-4,5-dimethyl-1,2-dithia-3-silacyclopentane (**3**) in 60% and 19% yields, respectively (eq 1).[4]



(1)

1 **2** **3**

GC–MS analysis detected a minor product (<2%) of slightly longer retention time than **3** with the same molecular weight. Presumably, this is the *cis* isomer of **3**. When thiasiletane **2** is treated with sulfur, **3** is not produced, implying that **3** arises from the direct reaction of **1** and sulfur. When the *cis* isomer of **1** is used, identical results are obtained, suggesting a stepwise radical mechanism (Scheme 1).[4]

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[‡] Wayne State University.

[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) (a) Weidenbruch, M.; Schäfer, A. *J. Organomet. Chem.* **1984**, *269*, 231. (b) West, R.; Carlson, C. W. *Organometallics* **1983**, *2*, 1798. (c) Dubac, J.; Mazerolles, P. *C. R. Seances Acad. Sci., Ser. C* **1968**, *267*, 411.

(2) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

(3) Seyferth, D.; Duncan, D. P.; Haas, C. K. *J. Oragnomet. Chem.* **1979**, *164*, 305.

(4) Boudjouk, P.; Samaraweera, U. *Organometallics* **1990**, *9*, 2205.

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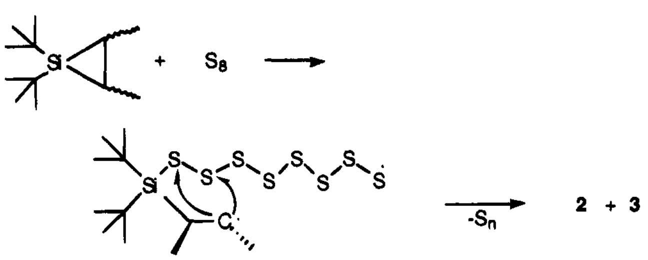
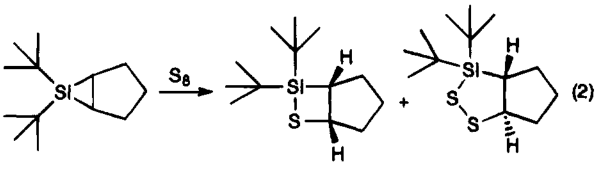
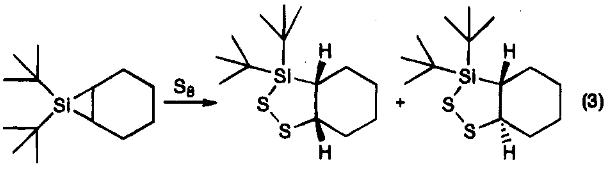
Scheme 1



Fused-ring siliranes follow similar chemistry. For example, 6,6-di-*tert*-butyl-6-silabicyclo[3.1.0]hexane (**4**) reacts with sulfur to give the thiasiletane, 7,7-di-*tert*-butyl-6-thia-7-silabicyclo[3.2.0]heptane (**5**) and a two-atom insertion product, *cis*-8,8-di-*tert*-butyl-6,7-dithia-8-silabicyclo[3.3.0]octane (**6**), in 44% and 20% yields, respectively (eq 2). The *cis* geometries of **5** and **6** were deduced from 2D NMR experiments (see below). The products of the reaction of sulfur with *cis*-7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (**7**) differ slightly from those with **4** in that, in spite of repeated attempts to detect one, a monosulfur insertion product was not observed. The products were the disulfur *cis* (**8**) and *trans* (**9**) isomers (eq 3). Isomer **8** does not convert to **9** under the conditions of the reaction, i.e., stirring of the reagents at room temperature, but will form **9** in 17% yield, at 350 °C.



4 **5** **6**



7 **8** **9**

Effects of Added Salts. Silirane **7** is prepared by the reaction of lithium with di-*tert*-butyldichlorosilane in the presence of excess cyclohexene.[5] When this product mixture is treated with sulfur, only the *cis*-disulfur addition product **8** is obtained in 46% yield. This is in sharp contrast to the isomer mixture obtained when sulfur is added to purified **7** (eq 3). Product distributions were monitored for sulfur insertions into samples of **7** that were first distilled, doped with salts, and then treated with sulfur. The results of these studies are summarized in Table 1. Similar observations were recorded for **4**. For example, in the absence of a salt, silirane **4** gives **5** and **6**, as indicated in Scheme 2. However, if alkali-metal halide is present when sulfur is added, *only* the monoinsertion product **5** is obtained.

Table 1. Effect of Salts on the Insertion of Sulfur into 6,6-Di-*tert*-butyl-6-silabicyclo[4.1.0]heptane (7)

salts	time, min	yield of **8**, %	yield of **9**, %
none	30	12[a]	33
KF[b]	30	55	9
LiCl	10	72	0
LiBr	45	68	3
LiI	45	40	5
NaI	60	44	5
$NaClO_4$	10	21	47

[a] All yields reported are GC yields. [b] 10 mol %; all other salts at approximately 2:1 mole ratio to silirane.

Table 2. Effect of Salts and Crown Ethers on the Insertion of Sulfur into 1,1-Di-*tert*-butyl-2,3-dimethylsilirane (1)

entry no.	conditions	time, min	yield of **2**, %	yield of **3**, %
1	10% KF, 10% 18-crown-6	<1	100[a]	0
2	10% LiF, 10% 12-crown-4	<1	55	21
3	10% LiCl, 10% 12-crown-4	10	86	6
4	10% KF	15	69	27
5	10% LiF	10	59	23
6	10% LiCl	15	64	22
7	10% TBAF[b]	<1	96	4
8	10% TBAC	<1	60	40
		<3	0	100
9	10% TBAB	5	88	12
10	10% TBAP	<1	59	21
11	crown, no salt	10	81	12
12	no crown, no salt	20	48	16

[a] All yields listed are GC yields. [b] TBAF, TBAC, TBAB, and TBAP are tetrabutylammonium fluoride, chloride, bromide, and perchlorate, respectively.

The efficiency with which nucleophilic anions suppress **9** suggests that attack by the halide leading to a pentacoordinate intermediate, such as **10** in Scheme 2, which maintains the integrity of the ring, is an important part of the mechanism. Recently, we reported that fluoride-promoted ring opening of siliranes accelerates the silylation of alcohols and postulated the intermediacy of a pentacoordinated species such as **10** in which X = F.[6] Such an intermediate would be expected to favor *cis* addition over *trans* addition because of greater access to the Si—C bonds on the face of the ring opposite to the *cis* hydrogens of the silirane.

The weakly nucleophilic perchlorate anion accelerated the reaction with sulfur and favored the formation of **9**. A tetracoordinate species such as **11**, in which X is the perchlorate covalently bound to silicon, and the charge is borne by a ring carbon, is consistent with these observations. Carbanions react readily with suflur,[7] and the preferred *trans* orientation is probably the result of steric considerations.

Effects of Added Salts in the Presence of Crown Ethers. Changes in the nucleophile and its environment have measurable effects on the insertion of sulfur into siliranes. We examined these effects using *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane (**1**). Product distributions for the sulfur insertions into **1** to produce **2** and **3** vary as a function of the nucleophile. These results are summarized in Table 2.

In each case where an alkali-metal halide is included in the reaction mixture, acceleration of the disappearance of starting silirane **1** is observed. Fluoride, the better nucleophile, gives faster reactions than does chloride. Also, when the cation is complexed by a crown

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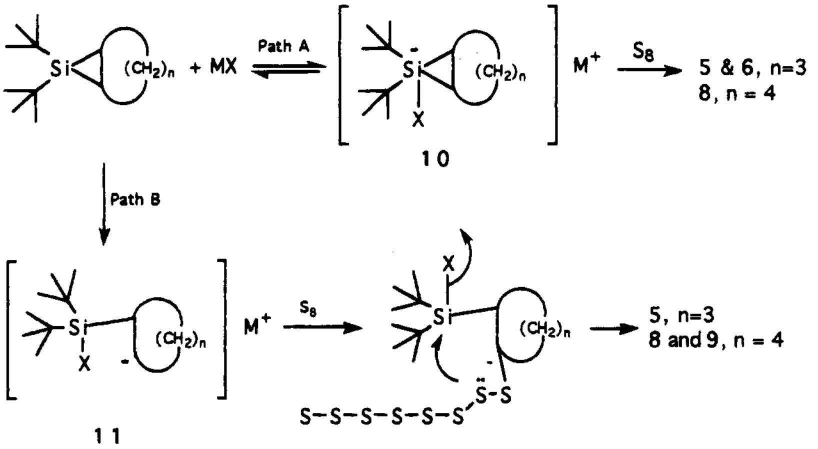
[5] Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095.

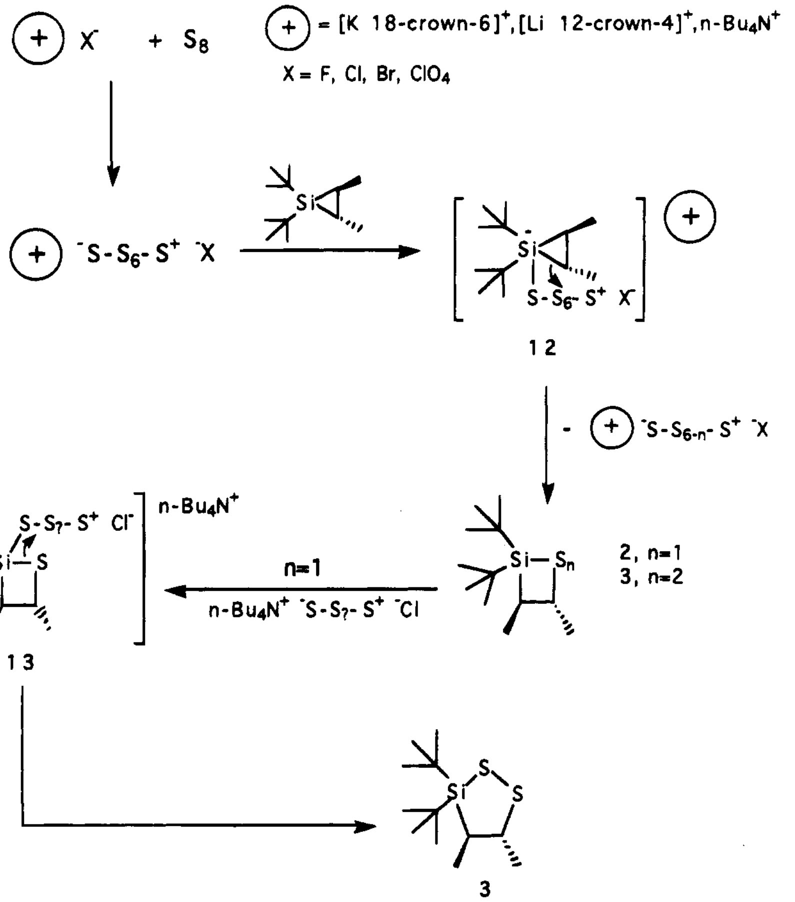
[6] Kumarathasan, R.; Boudjouk, P. *Tetrahedron Lett.* **1990**, *31*, 3987.

[7] Mayer, R. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977.

Scheme 2



Scheme 3



ether, faster reactions are noted in each case where a "freer" nucleophile is present. This enhancement of speed could be the result of an intermediate similar to **10** as an important part of the reaction; however, results from reactions with tetrabutylammonium chloride (TBAC) and 18-crown-6 seem to suggest otherwise (entries 8 and 11).

For example, treating **1** with sulfur in the presence of TBAC in THF gives a mixture of **2** and **3** initially, but upon further stirring for 3 min, only **3** remains. When both **2** and **3** are present, the solution color is an intense red, which changes to yellow upon complete conversion to **3**. The yellow color is attributed to **3**, and the red color could be indicative of an activated sulfur complex. A similar reaction using the *cis* isomer of **1**[2,8] yields a mixture of *cis* and *trans* isomers in a ratio of 85:15, respectively. This is indicative of **2** undergoing a second ring opening followed by expansion to produce **3** with some loss of stereochemistry.

Chalcogen activation by the salts and/or crown ethers present would explain the enhancement of yield and selectivity observed when only crown ether is present. Reaction of an activated chalcogen complex to give an intermediate such as **12** in Scheme 3, in which subtle differences in the molecular environment determine the reaction speed and selectivity, could explain the differences observed when different combinations of crown

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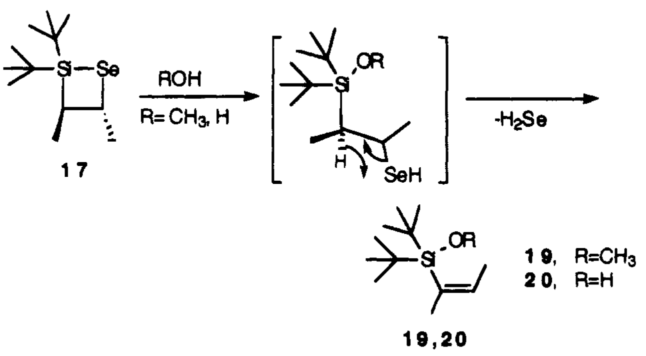
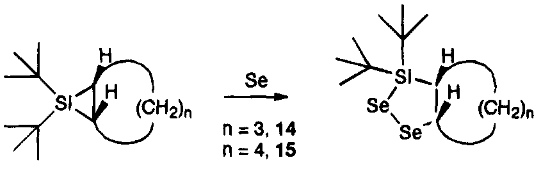
[8] There is a 5% *trans* impurity in the starting *cis*-**1**, as the *cis*-butene used to prepare this silirane is only 95% pure, with the remainder being *trans*.

Scheme 4



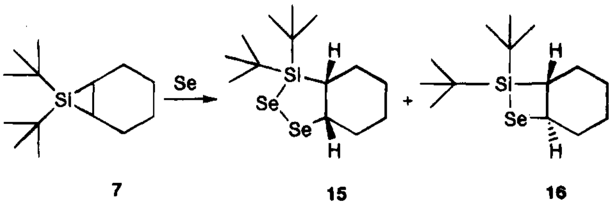
ethers and salts are used. The formation of an intermediate such as **13** *en route* to **3** is reasonable, but it is not clear why TBAC enjoys such unique reactivity. It is the only reagent that promotes the insertion of sulfur into a thiasiletane. We exploited this capability to expand selenetanes by the insertion of one sulfur atom between selenium and silicon (eq 7). It is interesting to note that sulfur in the presence of KF and 18-crown-6 in THF heated in a sealed tube produces the familiar red color that could be indicative of a sulfur reactive intermediate which may exist in these reactions.

Reactions with Selenium. Siliranes **1**, **4**, and **7** are practically inert toward selenium.[9] However, in the presence of lithium chloride, conversion is rapid and good yields of insertion products are obtained. Treatment of **4** with selenium powder gives only one two-atom insertion product, *cis*-8,8-di-*tert*-butyl-6,7-diselena-8-silabicyclo[3.3.0]octane (**14**), in 70% yield. As with **4**, compound **7** and selenium gave only the *cis* product **15** (eq 4).



(4)

When silirane **7** is stirred with 18-crown-6, potassium fluoride, and selenium in benzene or THF, evidence for the formation of the selenasiletane **16** by ^{29}Si and ^{77}Se NMR was observed in addition to signals for **15** (eq 5).



(5)

7 **15** **16**

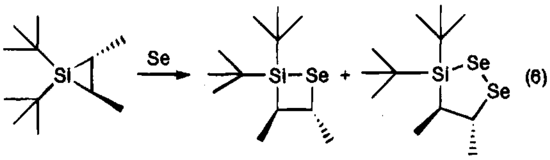
However, **16** was not isolable and attempts to generate it exclusively in the absence of **15** were unsuccessful. Thus, we could not make definitive assignments for **16** in the ^{1}H and ^{13}C NMR.

When **1** is stirred in the presence of potassium fluoride and 18-crown-6 in benzene, *trans*-2,2-di-*tert*-butyl-3,4-dimethyl-1,2-selenasiletane (**17**) is produced in 85–100% yield with less than 1% of the two-atom insertion product **18** detected (eq 6).

Table 3. Effect of Salts and Crown Ethers on the Insertion of Selenium into 1

entry no.	conditions	reacn time	yield of 17, %	yield of 18, %
1	THF	48 h	32[a]	<1
2	THF, 10% KF	48 h[b]	21	<1
3	THF, 10% 18-crown-6	4.5 h	74	13
4	THF, 10% 12-crown-4	12 h	94	<1
5	THF, 10% 12-crown-4, 10% LiCl	2.5 h	81	<1
6	THF, 10% 18-crown-6, 10% KF	2 h	62	38
7	THF, 10% TBAC	<1 min	65	24
		>5 min	0	87
8	THF, 10% TBAF	<1 min	51	42
9	benzene	NR[c]	0	0
10	benzene, 10% KF	NR	0	0
11	benzene, 10% 18-crown-6	24 h[b]	12	<1
12	benzene, 10% 18-crown-6, 10% KF	45 min	85	<1

[a] All yields are GC yields. [b] Starting material remains. [c] NR = no reaction.



(6)

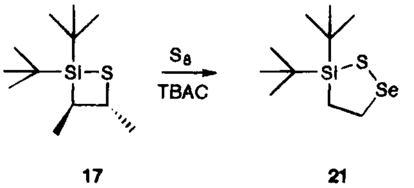
1 **17** **18**

Attempts to isolate **17** by distillation or preparative gas chromatography failed. However, **17** could be generated in benzene and stored frozen for several days. The neat selenasiletane has a half-life of about 2 h. In solution the half-life is about 6 h.

Reactions with methanol and water did not give stable derivatives resulting directly from ring opening (Scheme 4). Instead, **17** gave the vinylmethoxysilane **19** and the vinylsilanol **20**, respectively, as isolable products. These result, presumably, from a process involving the anticipated cleavage of the silicon–selenium bond in **17** followed by β-elimination of H$_2$Se.

As with sulfur, the effects of different salt and crown ether combinations on the reaction of **1** with selenium were investigated (Table 3). The conditions used to prepare *trans*-2,2-di-*tert*-butyl-3,4-dimethyl-1,2-thiasiletane (**2**) exclusively (Table 2, entry 1) produced a mixture of **17** and **18** (Table 3, entry 6). However, as mentioned above, the same reaction with selenium in benzene yielded **17** almost exclusively (Table 3, entry 12). Similar results in the cases involving TBAC and the cases involving crown ethers in the absence of salts support the mechanism of chalcogen activation (Scheme 3) as an important step in these reactions. Treatment of **1** or **17** with a catalytic amount of TBAC and excess selenium leads to exclusive formation of **18**, isolated as a red viscous oil by distillation in 87% and 82% yield, respectively. In contrast to **17**, **18** is stable. It is inert to air and moisture, is stable to 200 °C, and undergoes no further ring expansion when exposed to selenium even in the presence of TBAC.

To further explore the result that catalytic TBAC converts **2** to **3** and **17** to **18**, **17** was stirred with TBAC and sulfur, forming **21** in 64% isolated yield (eq 7). This



(7)

17 **21**

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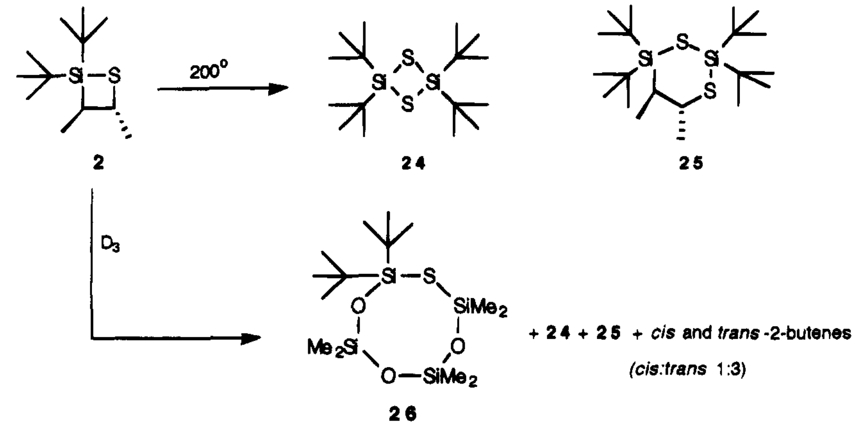
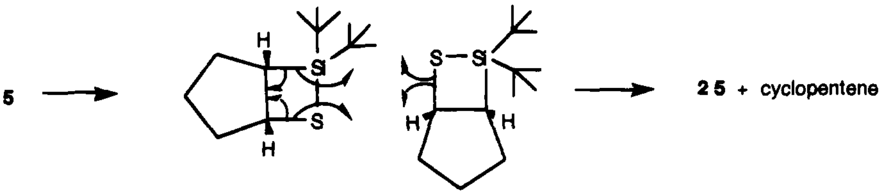
[9] For a review of recent developments in the chemistry of silicon selenides see: Boudjouk, P. *Polyhedron* **1991**, *10*, 1231.

Scheme 5



Scheme 6

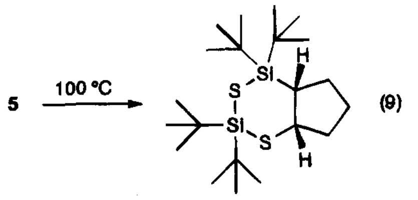


result is noteworthy in that a trapped product of **17** is obtained. Also, an intermediate similar to **13** (Scheme 3) occurring during the second ring opening is implied once again, and control over the order of heteroatom insertions in the preparation of a heterocycle such as **19** is established.

Ring Expansion of Silacyclobutanes. We have been able to extend our use of salt and crown ether aided chalcogen insertions to silacyclobutanes. When 1,1-dimethyl-1-silacyclobutane (**22**) is refluxed in tetrahydrofuran in the presence of potassium fluoride and 18-crown-6, 2,2-dimethyl-1-thia-2-silacyclopentane (**23**) is obtained in 72% yield (eq 8). This compound was previously prepared in 30% yield, from sulfur and **22** under high-temperature conditions (270 °C).[1c] Similar attempts with 1,1-dimethyl-1-silacyclopentane gave no reaction.

Thermolysis of Silathietanes. Pyrolysis of *trans*-2,2-di-*tert*-butyl-3,4-dimethyl-1,2-thiasiletane (**2**) in benzene at 200 °C yields 2,2,4,4-tetra-*tert*-butyl-1,3-dithia-2,4-disilacyclobutane (**24**) and 2,2,4,4-tetra-*tert*-butyl-*trans*-4,5-dimethyl-1,3-dithia-2,4-disilacyclohexane (**25**) in 33% and 30% yields, respectively, and a mixture of *cis*- and *trans*-2-butenes. Cyclobutane **24** is formally the dimer of di-*tert*-butylsilanethione, *t*-$Bu_2Si{=}S$, and cyclohexane **25** is the result of insertion of the *t*-$Bu_2Si{-}S$ fragment into the 1,2-thiasiletane **2**. When a mixture of **2**, hexane, and hexamethylcyclotrisiloxane (D_3) is pyrolyzed (200 °C, 4 h), 2,2-di-*tert*-butyl-4,4,6,6,8,8-hexamethyl-1,5,7-trioxa-3-thia-2,4,6,8-tetrasilacyclooctane (**26**), is obtained in 27% yield in addition to **24** (24%), **25** (40%), and *cis*- and *trans*-2-butenes (Scheme 5). **26** could be the result of the insertion of di-*tert*-butylsilanethione into one of the Si−O bonds of D_3. Increasing the temperature to 340 °C for 6 h leads to an increase in **26** at the expense of **25** with essentially no change in the amount of **24**. When **25** is heated to 350 °C, a complex mixture results but cyclobutane **24** is not detected. On the other hand, when **25** is pyrolyzed in the presence of D_3, **26** is produced. These results suggest that both **2** and **25** deliver the *t*-Bu_2-Si−S fragment to D_3 in a bimolecular reaction but may not actually generate *t*-$Bu_2Si{=}S$.[10]

When thiasiletane **5** was thermolyzed in hexane at 100 °C for 3 days, one major product, **27**, was observed (eq 9). The stereochemistry of **27** was determined to be *cis* by NMR spectroscopy (see below). The thermolysis of thiasiletane **5** at this temperature in the presence of D_3 gave no *t*-$Bu_2Si{=}S$ insertion product, only compound **27**. **24** was not observed in either reaction. The product **27** could be formed via a stepwise bimolecular reaction of thiasiletane, or by the insertion of *t*-$Bu_2Si{=}S$ into thiasiletane. Since no oligomer of *t*-$Bu_2Si{=}S$ was observed, and D_3 did not trap a detectable quantity, a stepwise bimolecular fragmentation reaction is a more likely mechanism at 100 °C (Scheme 6). However, when the thermolysis is carried out at 150 °C in the absence of a trap, compounds **27** and **24** are obtained in 69% and 18% yields, respectively. In the presence of D_3, **26**, resulting from the insertion of *t*-$Bu_2Si{=}S$ into D_3, was observed, in addition to **24** and **27** in 61%, 12%, and19%



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[10] It is relevant to note that a convincing case against the intermediacy of silanones in the thermolysis of siloxetanes and in support of a bimolecular mechanism to explain the products of "R_2-Si=O insertion" has been made: Barton, T. J.; Hussman, G. P. *Organometallics* **1983**, *2*, 692.

Scheme 7

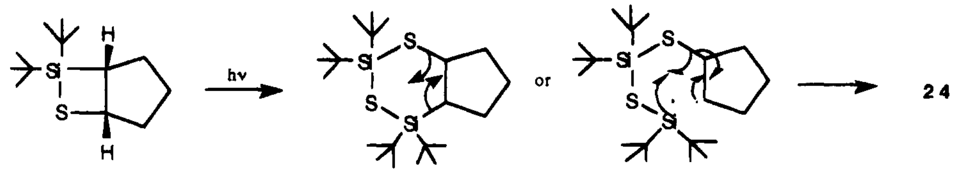
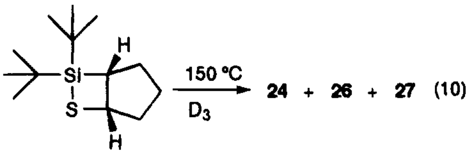


Table 4. Calculated and Experimental $^3J_{H-H}$ Coupling Constants for 8 and 9

H—H	*trans*		*cis* (Si eq)		*cis* (Si ax)		obsd ^3J (Hz)	
	^3J (Hz)	angle[a] (deg)	^3J (Hz)	angle[a] (deg)	^3J (Hz)	angle[a] (deg)	**8**	**9**
1—2a	12.3	174.7	2.0	48.6	12.3	176.4	<4.0	~12.0
1—2e	3.8	3.8	4.7	67.3	3.5	58.0	~4.0	3.4
1—6	13.3	179.8	5.1	46.5	6.2	43.7	~4.0	~12.0
5a—6	13.5	179.3	13.2	169.6	6.3	42.5	12.7	na
5e—6	2.8	60.3	4.6	50.3	1.1	71.8	~4.0	na

[a] Dihedral angle.

yields, respectively (eq 10). These results suggest that,



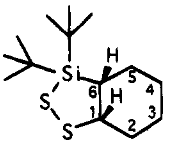
5

at 150 °C, thiosiletane **5** generates the di-*tert*-butylsilanethione intermediate to give **24** and **26**. However, a bimolecular process is by no means excluded.[10,11]

When thiosiletane **5** was photolyzed in the presence of D_3 using 254 nm irradiation for 45 min, **27** and **24** were observed, and no product resulting from the insertion of t-$Bu_2Si{=}S$ into D_3 was detected. Further irradiation resulted in the decrease of product **27** and an increase of **24**. This experiment clearly indicates the formation of **24** from the decomposition of **27** and not from the dimerization of t-$Bu_2Si{=}S$. The conversion of **27** to **24** could take place by a concerted or a nonconcerted pathway (Scheme 7).

Solution Structures of Bicyclic Compounds. The relatively simple ^{13}C spectra of the bicyclic products were assigned on the basis of chemical shift and $^1J_{C-H}$ coupling data. 2D HETCOR[12] experiments were then used to correlate the ^{13}C assignments to directly bonded protons. Finally, the complete $^3J_{H-H}$ coupling network was determined using 2D COSY[13] experiments. It was essential to include a double-quantum filter in these experiments to eliminate dynamic range problems in analyzing 2D maps due to the intensity of the *tert*-butyl resonances.[14] Once the bridgehead methine protons were identified, the stereochemistry of the compound was determined by analysis of the $^3J_{H-H}$ coupling constants, which were translated into dihedral angles through the Karplus relationship.[15] The data were then compared with geometries calculated by molecular mechanics methods.

The disulfur insertion into compound **7** can give rise two configurational isomers: *cis* (**8**) and *trans* (**9**). In addition, the *cis* configuration can exist in two chair conformations. Molecular mechanics calculations[16] predict the *trans* configuration (**9**) to be more stable than the minimum energy conformation for the *cis* isomer by3.5 kcal/mol. Furthermore, the calculations predict unique $^3J_{H-H}$ coupling patterns for the bridgehead protons for each isomer and conformer. Listed in Table 4 are the calculated dihedral angles and corresponding $^3J_{H-H}$ coupling constants for the *cis* and *trans* configurations.



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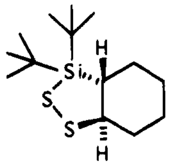

9

Since the bicyclic structures are fairly rigid, only small-angle librations are expected to exist in the carbon backbone. Thus, the calculated coupling constants are expected to be in good agreement with the experimental values. The presence of two large (~12—13 Hz) axial—axial coupling constants distinguishes the *trans* isomer from the *cis* configurations. One would expect to see a coupling pattern resembling a triplet of doublets (td) as opposed to a first-order doublet of doublet of doublets (ddd), since the values of the large coupling constants for the *trans* isomer are very similar.

Both *cis* conformers are predicted to have a single large axial—axial coupling constant, on the basis of the calculations. The presence of a large coupling between H_6 and H_{5a} distinguishes the conformer in which the silicon is occupying the equatorial position from the conformer where the silicon is in an axial disposition. In the latter case, the large coupling constant is located between H_1 and H_{2a}. Similar magnitudes for the axial—equatorial coupling constants in both *cis* conformers can result in non-first-order patterns. Rapid interconver-

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(16) All molecular mechanics calculations were conducted on a Silicon Graphics Personal Iris using the MMX force field and interactive graphics in the PCMODEL program (Serena Software, Bloomington, IN 47402).

sion of the two *cis* conformers on the NMR time scale would result in a population-weighted averaging of all the coupling constants.

The HETCOR experiment for compound **8** identified the bridgehead protons H_1 and H_6 at 3.61 and 1.67 ppm, respectively. H_1 is a well-resolved dt, while H_6 appears as a broad td pattern. The magnitude of the coupling constants identifies this compound as the *cis* isomer, with the silicon occupying the equatorial position. There is excellent agreement between the calculated and experimental coupling constants for **8** (Table 4). The remaining protons were also assigned by the COSY experiment. Table 5 lists the observed $^3J_{H-H}$ coupling constants, calculated dihedral angles, the corresponding coupling constant based on the Karplus relationship, and the dihedral angles based on the X-ray coordinates for **8** (see below). The excellent agreement between the solution and solid-state structures confirms both the configuration and conformation of compound **8**. Furthermore, these data affirm use of NMR coupling constant analysis, of rigid structures such as these, to determine molecular geometries through Karplus relationships.

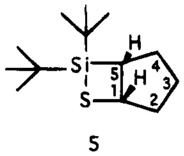
The *trans* isomer, **9**, was also characterized by 2D NMR methods. H_6 is coincident with one of the H_2 resonances and a *tert*-butyl peak at approximately 1.2 ppm. Therefore, H_6 could not be used to determine the configuration of the compound. H_1 was identified as an apparent td pattern at 2.88 ppm. This pattern is due to the presence of two large coupling constants, both on the order of 12 Hz, and a small coupling constant. These data are consistent with the *trans* isomer (Table 4).

The selenium insertion product of **7** can be analyzed in a similar fashion to determine the configuration at the bridgehead carbons. The H_1 resonance, which is adjacent to the sulfur, is located at 4.21 ppm and appears as a seven-line multiplet which cannot be analyzed as a first-order spin pattern. The complexity of the H_1 pattern is due to long-range "W" four-bond coupling.[17] Decoupling studies reveal that the large 14.5 Hz coupling constant is due to the vicinal H_5 axial proton, while the H_1–H_6 coupling is equal to approximately 3.9 Hz. These data confirm the assignment of a *cis* configuration for **15** in which the Si occupies the equatorial position. H_6 is a doublet of multiplets at 1.92 ppm with a large coupling constant of approximately 14.5 Hz. Each of the multiplets in this pattern contains eight lines which cannot be treated as a first-order splitting pattern. The additional coupling constants to H_6 also appear to be due to long-range coupling. The magnitudes of these coupling constants are in the same range as axial–equatorial or equatorial–equatorial vicinal coupling constants.

Compound **6** can be viewed as a bicyclo[3.3.0]octane derivative. The corresponding carbocyclic system has been prepared in both the *cis* and *trans* geometries; however, the *trans* isomer is 6.0 kcal/mol higher in energy than the *cis* isomer.[18] Our molecular mechanics calculations predict the most stable *cis* isomer of **6** to be energetically favored by approximately 8.2 kcal/mol. The *cis* isomer appears to contain a family of conformers which differ only slightly in energy according to the molecular mechanics calculations. These differences can be attributed to changes in the atom which occupies the "flap" position in the envelope-like conformation.

Analysis of the $^3J_{H-H}$ coupling constants for the bridgehead protons can be used to distinguish the two isomers. On the basis of the molecular mechanics calculations, three of the five $^3J_{H-H}$ coupling constants associated with the bridgehead positions of the *trans* isomer should be in the range of approximately 11–13 Hz, characteristic of axial–axial interactions. In contrast, only two large vicinal coupling constants are expected for the *cis* isomer. The H_1 and H_6 resonances were identified using the COSY and HETCOR experiments. The proton adjacent to the sulfur, H_1, appears as a td at 3.80 ppm with coupling constants of 7.0 and 3.2 Hz, respectively. H_6, which is adjacent to the silicon, is an apparent dt at 1.42 ppm with coupling constants of 11.8 and 7.0 Hz, respectively. The bridgehead H_1–H_6 coupling constant is approximately 7 Hz, which translates to a dihedral angle of approximately 37°. These data are most consistent with the *cis* isomer. Slight variations in calculated and observed $^3J_{H-H}$ coupling constants are most likely due to population averaging of energetically similar *cis* conformations.

Compound **5** is expected to exist as the *cis* isomer only because of the strain associated with a *trans* bicyclo[3.2.0]heptane geometry. Molecular mechanics calculations predict the *cis* geometry of **5** to be more stable than the corresponding *trans* configuration by approximately 17 kcal/mol. H_1 and H_5 assignments were completed using 2D correlation experiments and are at 3.71 and 2.24 ppm, respectively. Both H_1 and H_5 appear as non-first-order multiplets. Decoupling studies reveal that the H_1–H_5 vicinal coupling constant is approximately 8 Hz while the calculated value is 11.2 Hz (dihedral angle 0.6°). The remaining H_1 coupling constants are approximately 6.4, 6.4, and 2.1 Hz. The presence of an additional coupling constant beyond which is expected for the vicinal coupling constants is due to $^4J_{H-H}$ "W" coupling between the bridghead H's and axial H_3. The fit between calculated coupling constants and the experiment values is not as close in this case due to the strain associated with small rings.



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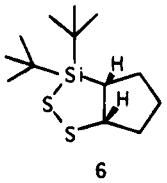

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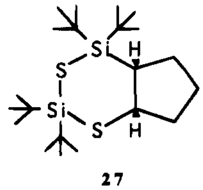

27

Determining the stereochemistry of compound **27** proved to be the most challenging task, due to significant chemical shift coincidence at 400 MHz. Semiem-

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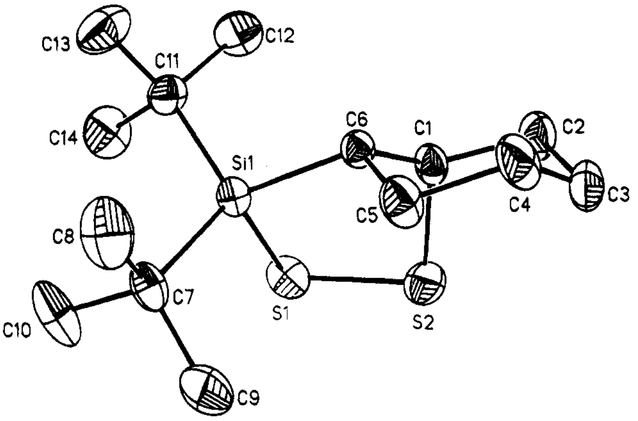

Figure 1. ORTEP diagram of 4,4-di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (**8**) with the non-hydrogen atoms represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for the sake of clarity.

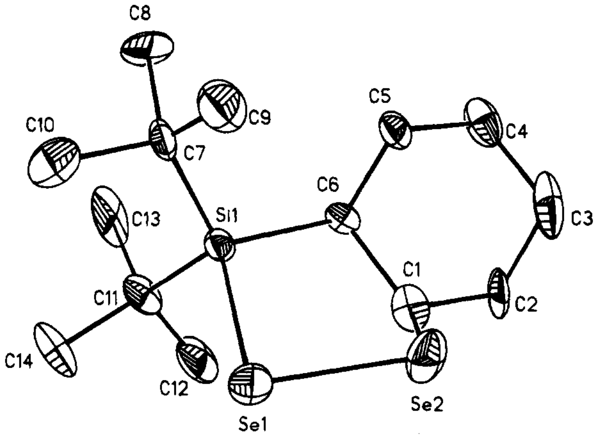

Figure 2. ORTEP diagram of 4,4-di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (**15**) with the non-hydrogen atoms represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for the sake of clarity.

Table 5. ^{3}J **Coupling Constants and Dihedral Angles for 8**

H—H	NMR ^{3}J (Hz)	calcd ^{3}J (Hz)	calcd angle (deg)	X-ray dihedral angle (deg)
1—2a	<4.0	2.0	48.6	49.4
1—2e	~4.0	4.7	67.3	69.2
1—6	~4.0	5.1	46.5	50.4
5a—6	12.7	13.2	169.6	172.2
5e—6	~4.0	4.6	50.3	53.1

pirical calculations[19] predict the *cis* isomer to be more stable than the *trans* isomer by 5 kcal/mol. The calculated *cis*$^{3}J_{\mathrm{H-H}}$ coupling constants of the bridgehead methine proton adjacent to the sulfur atom (H_1) are approximately 12, 10, and 5 Hz due to interactions with H_2, H_5, and H_2', respectively. The *trans* isomer was calculated to have coupling constants of 11, 11, and 7 Hz for the same spin couplings. The H_1 resonance at 3.99 ppm appears as a non-first-order quartet with additional small coupling. The largest apparent coupling constant is approximately 5 Hz. Decoupling at the chemical shifts for H_5, H_2, and H_2' did not result in a first-order pattern. The apparent lack of a large coupling constant (>5 Hz) and the fact that the entire spin pattern is only 11 Hz wide suggest that the calculated conformers are not consistent with the experimental data. The data are consistent with conformational averaging of the *cis* configuration on the NMR time scale. The barrier for inversion of *cis*-hydrindane is lower than that of cyclohexane.[20] Additional support for the *cis* assignment was gained through a 2D NOESY experiment, which indicated that the strongest cross-relaxation present was between H_1 and H_5, which are separated by approximately 1.7 Å in the *cis* structure and 2.9 Å in the *trans* isomer on the basis of the calculations.

Solid-State Structures. The stereochemical assignments of **8** and **15** were confirmed by single-crystal X-ray analysis. The structures of **8** and **15** consist of discrete bicyclic molecular units with four molecules in general positions per unit cell. The structures of **8** and **15** can be viewed as derivatives of bicyclo[4.3.0]nonane with the silicon and two sulfur [or selenium] atoms substituting for carbon atoms on the smaller ring. Carbon atoms 1–6 form a cyclohexane ring in the chair conformation. Carbons 2, 3, 5, and 6 comprise the equatorial carbons of the chair, while carbons 1 and 4 occupy the apical positions. Carbons 2, 3, 5, and 6 are coplanar within 0.007(2) Å [0.04(1) Å], indicating that the ring is rigidly held in the chair conformation. Carbon 4 lies 0.694(5) Å [0.65(1) Å] above the plane, while C1 lies 0.617(4) Å [0.70(2) Å] below this plane. These displacements would be 0.73 Å for a cyclohexane ring in an ideal chair conformation assuming tetrahedral valency angles and carbon–carbon bond lengths of 1.545 Å.[21] The bond lengths and angles within the ring are normal. The largest deviation from tetrahedral valency in **8** are seen in the C2—C3—C4 angle at 112.2(3)° and C1—C6—C5 angle, at 114.0(4)°. In **15** the variations from tetrahedral valency at carbon are somewhat larger with a range in angles from 109° for C3—C4—C5 to 116° for C2—C1—C6.

The silicon atom is bonded in a tetrahedral manner to C1 and S1 [Se1] in addition to two *tert*-butyl groups. The Si—C bond lengths are typical for Si—alkyl carbon bonds, occurring in the range 1.912(4)-1.934(4) Å [1.88(2)–1.98(2) Å]. The Si—S bond of 2.173(2) Å is slightly longer than the 2.138(2) Å reported for methylthiophenylsilane[22] and the average Si—S bond lengths of 2.146(1) and 2.221(4) Å reported for S—Ge bonds in a structure incorporating S and Ge in six-membered heterocycles.[23] Steric crowding about the silicon results in deviations from tetrahedral valency (C6—Si—C7, 116.5(2)°; C11—Si—C7, 115.2(2)°; C11—Si—S1, 105.0(2)°; C6—Si—S1, 100.0(1)°; C7—Si—S1, 108.1(2)°). The S1—S2 bond length of 2.064(2) Å is typical of many disulfide compounds and is similar to the S—S distance reported for $LMnS_4(H_2O)$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane),[24] which incorporated a five-membered ring including the Mn as well as four sulfur atoms, and also a series of binary metal sulfides reported by Coucovanis.[25] The five-membered ring is strongly puckered with C1 lying 0.784(4) Å above the Si—S1—S2—C2 plane. The valence angles about the sulfur atoms

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Table 6. Experimental Parameters for the X-ray Diffraction Study of 4,4-Di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (8) and 4,4-Di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (15)

	8, $C_{14}H_{28}SiS_2$	**15**, $C_{14}H_{28}SiSe_2$
mol wt	288.50	383.38
cryst habit	rectangular fragment	nearly spherical ground fragment
cryst color; dimens, (mm)	pale yellow; 0.32 × 0.46 × 0.28	rust color; 0.38 diam
cryst syst	primitive monoclinic	primitive monoclinic
space group	$P2/1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4
constrained cell constants from 25 rflns for 2θ (deg)	$20.0 \le 2\theta \le 34.2$	$20.0 \le 2\theta \le 32.2$
a (Å)	6.694(4)	6.888(5)
b (Å)	14.987(4)	15.2000(3)
c (Å)	16.785(4)	16.717(2)
β (deg)	98.13(4)	96.76(9)
vol (Å^3)	1667(1)	1748(1)
density (calcd) (g cm^{-3})	1.149	1.461
$F(000)$ (e)	752	776
radiation type	Mo Kα, $\lambda = 0.710\,73$ Å, graphite monochromator	Mo Kα, $\lambda = 0.710\,73$ Å, graphite monochromator
temp	ambient	ambient
type of data collection	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range (deg)	5−50	5−50
octants used	$+h,+k,\pm l$ (h, 0−9; k, 0−18; l −20 to +20)	$+h,+k,\pm l$ (h, 0−9; k, 0−19; l, −20 to +20)
scan rate (deg min^{-1})	3−6, variable	3−6, variable
scan width (deg)	1.0 below $K\alpha_1$ to 1.1 above $K\alpha_2$	1.0 below $K\alpha_1$ to 1.0 above $K\alpha_2$
bkgd/scan ratio	0.5	0.5
std rflns	3 measd per every 100 rflns; max dev 2%	3 measd every 100 rflns, linear decay about 2%
no. of data collected	3464	3597
no. of unique rflns	2946, $R_{int} = 0.0097$	3078, $R_{int} = 0.0775$
no. of obsd rflns with $F_o \ge 3.0\sigma(F)$	1683	1331
linear abs coeff, μ (cm^{-1})	3.3	45.93
abs cor	empirical, ψ scans	none applied
R (merge) before/after cor	0.0275/0.0163	
max/min transmission	0.854/0.676	
no. of param refined	156	156
observn/param ratio	10.8	8.53
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.050	0.075
$R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$, $w^{-1} = \sigma^2(F_o)$	0.028	0.047
overall shift/esd	0.000	0.000
max shift/esd	0.002	0.001
secondary extinction	$[1.1(2)] \times 10^{-7}$, 1 rfln excluded	6rflns excluded
residual electron density (e Å^{-3})	0.30, near C3	0.93, 0.76 Å away from Se1
coordinates (x, y, z)	0.3310, 0.0776, 0.8222	0.2264, 0.1835, 0.3577

Table 7. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in 4,4-Di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (8)

atom	x	y	z	U(eq),[a] Å^2
S1	0.7436(2)	0.17083(8)	0.77039(7)	0.0606(5)
S2	0.6729(2)	0.17987(9)	0.88587(7)	0.0689(6)
Si1	0.4848(2)	0.08919(8)	0.72399(7)	0.0400(4)
C1	0.4027(6)	0.1870(3)	0.8571(2)	0.051(2)
C2	0.2935(8)	0.2027(3)	0.9307(2)	0.074(2)
C3	0.2913(8)	0.1225(3)	0.9847(2)	0.082(3)
C4	0.1978(7)	0.0435(3)	0.9355(3)	0.078(2)
C5	0.3162(7)	0.0228(3)	0.8663(2)	0.059(2)
C6	0.3232(6)	0.1043(3)	0.8083(2)	0.041(2)
C7	0.5798(7)	−0.0304(3)	0.7076(3)	0.053(2)
C8	0.4006(7)	−0.0954(3)	0.6867(3)	0.090(3)
C9	0.7172(7)	−0.0638(3)	0.7821(3)	0.087(3)
C10	0.7046(7)	−0.0318(3)	0.6381(3)	0.097(3)
C11	0.3629(7)	0.1493(3)	0.6284(3)	0.054(2)
C12	0.2650(7)	0.2369(3)	0.6514(2)	0.085(2)
C13	0.1967(7)	0.0935(3)	0.5804(2)	0.091(2)
C14	0.5202(7)	0.1742(3)	0.5732(2)	0.087(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$.

Table 8. Atomic Coordinates and Isotropic Thermal Parameters for 4,4-Di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (15)

atom	x	y	z	U(eq),[a] Å^2
Se1	0.7619(3)	0.1717(2)	0.7649(1)	0.0560(8)
Se2	0.6780(3)	0.1813(2)	0.8964(1)	0.069(1)
Si1	0.4879(7)	0.0864(3)	0.7242(3)	0.037(2)
C1	0.394(2)	0.188(1)	0.865(1)	0.058(8)
C2	0.281(2)	0.205(1)	0.9338(9)	0.062(9)
C3	0.276(3)	0.123(1)	0.987(1)	0.09(1)
C4	0.194(3)	0.043(1)	0.937(1)	0.07(1)
C5	0.331(3)	0.021(1)	0.8717(9)	0.053(8)
C6	0.337(2)	0.100(1)	0.8141(9)	0.033(7)
C7	0.566(3)	−0.030(1)	0.708(1)	0.054(9)
C8	0.411(2)	−0.099(1)	0.688(1)	0.08(1)
C9	0.700(3)	−0.068(1)	0.778(1)	0.09(1)
C10	0.680(3)	−0.037(1)	0.636(1)	0.09(1)
C11	0.359(3)	0.147(1)	0.628(1)	0.055(9)
C12	0.281(3)	0.239(1)	0.652(1)	0.09(1)
C13	0.190(3)	0.088(1)	0.585(1)	0.11(1)
C14	0.509(2)	0.166(1)	0.5659(9)	0.081(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$.

(S2−S1−Si, 95.5(1)°; C1−S2−S1, 96.1(1)°) are typical of small ring systems incorporating sulfur.[26]

The Se−Se distance of 2.343(3) Å is in good agreement with the mean Se−Se length of 2.355(6) Å found for 100 entries in the Cambridge structural database. The Si−Se bond length found for **15** of 2.324(5) Å is no longer than that reported for $Si(SeC_6H_5)_6$[27] and significantly longer than the analogous Si−S bond of **8**, as expected for the larger Se atom. The silicon atom is bonded in a tetrahedral manner to two *tert*-butyl groups in a fashion similar to that for **8**. The five-membered ring is

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Table 9. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 4,4-Di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (8) and 4,4-Di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (15)

compd **8**		compd **15**	
	Bond Distances		
S1—S2	2.064(1)	Se1—Se2	2.343(2)
S1—Si1	2.173(2)	Se1—Si1	2.324(5)
Si1—C6	1.912(3)	Si1—C6	1.94(1)
Si1—C7	1.934(4)	Si1—C7	1.88(2)
Si1—C11	1.919(4)	Si1—C11	1.98(2)
	Bond Angles		
S1—S2—C1	96.1(1)	Se1—Se2—C1	95.5(4)
S2—S1—Si1	95.53(7)	Se2—Se1—Si1	91.6(1)
S1—Si1—C6	100.0(1)	Se1—Si1—C6	110(1)
S1—Si1—C7	108.1(2)	Se1—Si1—C7	109.4(6)
S1—Si1—C11	105.0(1)	Se1—Si1—C11	104.4(6)
C6—Si1—C7	116.5(2)	C6—Si1—C7	113.7(7)
C6—Si1—C11	110.2(2)	C6—Si1—C11	110.7(7)
C7—Si1—C11	115.2(2)	C7—Si1—C11	115.4(7)

torsion angle[a]	compd **8**	compd **15**
E1—E2—C1—C2	−175.3(3)	−173(1)
E1—E2—C1—C6	58.8(2)	58.7(9)
E1—Si1—C6—C1	17.8(3)	23(1)
E1—Si1—C6—C5	−105.2(3)	−105(1)
E2—E1—Si1—C6	14.6(1)	12.5(5)
E2—C1—C2—C3	−72.0(4)	−72(2)
E2—C1—C6—Si1	−50.8(3)	−55(1)
E2—C1—C6—C5	76.0(3)	77(1)
Si1—E1—E2—C1	−37.1(2)	−36.6(6)
Si1—C6—C1—C2	−176.1(3)	178(1)
Si1—C6—C5—C4	175.4(3)	−176(1)
C1—C2—C3—C4	−56.0(5)	−55(2)
C1—C6—C5—C4	53.5(4)	53(2)
C2—C1—C6—C5	−49.3(4)	−48(2)
C2—C3—C4—C5	58.5(5)	63(2)
C3—C2—C1—C6	52.8(5)	49(2)
C3—C4—C5—C6	−58.9(5)	−61(2)

[a] E1, E2 = S1, S2 or Se1, Se2.

strongly puckered, with C1 lying 0.92(2) Å above the Si—Se1—Se2—C6 plane. The valency angles at the selenium atoms (Si—Se1—Se2, 91.6(1)°; Se1—Se2—C1, 95.2(5)°) are typical of selenium incorporated into small cages such as P_4Se_5[28] and P_4Se_3.[29]

Experimental Section

The ^{1}H (399.78 MHz), ^{13}C (100.52 MHz), ^{29}Si (79.43 MHz), and ^{77}Se (76.22 MHz) NMR were obtained on a JEOL GSX400 spectrometer. Data were collected in C_6D_6. The ^{29}Si NMR spectra were acquired by using a refocused INEPT pulse sequence.[30] The ^{77}Se chemical shifts were measured with respect to a 25% solution of Me_2Se in $CDCl_3$.[31] UV—vis is spectra were obtained using a Hewlett-Packard 8451A spectrophotometer.

Gas chromatography analyses were carried out on a Hewlett-Packard Model 5880A gas chromatograph equipped with a flame ionization detector and methyl silicon capillary column. The GC yields were calculated using decane as the internal standard. Preparative chromatography was performed on a Varian Aerograph Model 920. GC—MS analyses were performed on a Hewlett-Packard Model 5992. High-resolution mass spectra were taken on a MAT CH-5DF or CH7 mass spectrometer at 70 eV. Infrared spectra were obtained on a Mattson Model 2020 Galaxy series FT-IR spectrometer.

Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). Melting points were measuring using a Thomas Hoover capillary melting point apparatus and are uncorrected. Photolyses were carried out in an Rayonet Model RPR 1000 reactor. Sonication was performed on a Branson Model 220 (110−120 V, 50−60 Hz, 125 W) ultrasonic cleaner filled with distilled water. The reaction flask was positioned at a point that gave maximum cavitation. All glassware was oven-dried, assembled hot, and cooled under a stream of nitrogen before use. All reactions were run under a nitrogen atmosphere.

Tetrahydofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl immediately before use. All alcohols were dried and distilled using standard procedures.[32] Commercially available anhydrous potassium fluoride was stored in a drybox and used without further purification. Tetrabutylammonium fluoride was purchased as a THF solution from Aldrich. Other tetrabutylammonium halide salts were recrystallized from acetone/diethyl ether prior to use. Di-*tert*-butyldichlorosilane was obtained by chlorinating di-*tert*-butylchlorosilane (Aldrich) using benzoyl peroxide and carbon tetrachloride.

Reaction of *trans*-1,1-Di-*tert*-butyl-2,3-dimethylsilirane (1) with Sulfur.[2] **1** (1 g, 5 mmol) was added to a three-neck flask charged with sulfur (170 mg, 0.66 mmol) and 5 mL of degassed hexane. The reactants were stirred for 6 h and then allowed to settle. GLC analysis showed **2** and **3** in 60% and 19% yields, respectively. The solution was filtered under nitrogen, and the hexane layer was concentrated *in vacuo*. Further purification was accomplished by preparative GLC as follows. **2** was isolated as a colorless liquid with the detector and injector temperatures kept below 170 °C, while the column (10% SE 30, on Chromosorb A) was kept at 140 °C to avoid thermal decomposition. **3** was isolated as a thermally stable bright yellow liquid with normal preparative GLC techniques.

2: ^{1}H NMR (C_6D_6) δ 3.29 (m, 1H, CH), 1.88 (m, 1H, CH), 1.46 (d, J = 7.33 Hz, 3H, CCH_3), 1.31 (s, 9H, *t*-Bu), 1.18 (s, 9H, *t*-Bu), 1.10 (d, J = 7.52 Hz, 3H, CCH_3); ^{13}C NMR (C_6D_6) δ 44.4 ($SCCH_3$), 35.5 (CCH_3), 28.3, 25.2 (*t*-Bu), 26.3 (CCH_3), 23.1, 21.5 (*t*-Bu), 15.4 (CCH_3); ^{29}Si NMR (C_6D_6) δ 26.4; UV λ_{max} 214 ($\epsilon = 1.4 \times 10^3$); MS *m/e* (relative intensity) 230 (M^+, 5%), 173 ($M^+ - 57$, 37%). Anal. Calcd for $C_{12}H_{26}SiS$: C, 63.53; H, 11.37. Found: C, 62.77; H, 11.64.

3: ^{1}H NMR (C_6D_6) δ 3.06 (m, 1H, CH), 1.29 (m, 1H, CH), 1.26 (s, 9H, *t*-Bu), 1.19 (d, J = 6.35 Hz, 3H, CCH_3), 1.18 (s, 9H, *t*-Bu), 1.10 (d, J = 7.5 Hz, 3H, CCH_3); ^{13}C NMR (C_6D_6) δ 54.0 ($SCCH_3$), 34.8 (CCH_3), 28.8, 28.3 (*t*-Bu), 22.6, 17.7 (*t*-Bu), 13.2 ($SiCCH_3$); ^{29}Si NMR (C_6D_6) δ 48.2; UV λ_{max} 214 ($\epsilon = 1.15 \times 10^2$); MS *m/e* (relative intensity) 262 (M^+, 50%), 205 ($M^+ - 57$, 72%). Anal. Calcd for $C_{12}H_{26}SiS_2$: C, 54.89; H, 9.98. Found: C, 55.02; H, 10.06.

Synthesis of *cis*-6,6-Di-*tert*-butyl-6-silabicyclo[3.1.0]hexane (4). A three-neck 100 mL round-bottom flask equipped with a condenser and a N_2 inlet was charged with lithium dispersion (0.45 g, 64 mmol), 20 mL of THF, and cyclopentane (10 mL, 114 mmol, passed through neutral Al_2O_3 before use). Di-*tert*-butyldichlorosilane (3 mL, 14.1 mmol) was added to this slurry, and the mixture was sonicated for 5−7 h. After lithium chloride settled, the supernatant liquid was transferred to another flask, and the solvent was removed on a pump. The residue was extracted with degassed hexane and concentrated. **4** was isolated by molecular distillation at 50 °C at 2 Torr, in 45−55% yield.

4: ^{1}H NMR (C_6D_6) δ 2.1−2.2 (m, 2H, cyclopentyl), 1.81−2.0 (m, 4H, cyclopentyl), 1.11 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 33.93 (CH_2, cyclopentyl), 31.41 (CH_3, *t*-Bu), 29.88 (CH_3, *t*-Bu), 27.87 (CH_2, cyclopentyl), 21.45 (*t*-Bu), 21.18 (CH, cyclopentyl), 19.34 (*t*-Bu); ^{29}Si NMR (C_6D_6) −39.6; UV λ_{max} 230 nm ($\epsilon = 3 \times 10^2$); HR-MS calcd for $C_{13}H_{26}Si$ *m/e* 210.1804, found 210.1802.

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Reaction of 4 with Sulfur. In a 10 mL round-bottom flask equipped with nitrogen inlet and stirbar were added 2 mL of THF and sulfur (21 mg, 0.082 mmol). To this slurry was added **4** (0.1 g, 0.476 mmol) and the mixture was stirred for 5 min. GC analysis of the reaction mixture showed the presence of *cis*-7,7-di-*tert*-butyl-6-thia-7-silabicyclo[3.2.0]heptane (**5**) and *cis*-3,3-di-*tert*-butyl-1,2-dithia-3-silabicyclo[3.3.0]octane (**6**) in 44% and 20% yields, respectively. The supernatant liquid of the reaction mixture was transferred to another flask and concentrated, and a molecular distillation was carried out at 50 °C under a pressure of 2 Torr, to separate **5** as a colorless liquid from **6**. **6** was isolated from the residue as a yellowish green viscous liquid by preparative GC.

5: ^{1}H NMR (C_6D_6) δ 3.71 (m, J = 8, 6 Hz, 1H, S—CH), 2.23 (m, 1H), 1.44–2.1 (m, 7H, cyclopentyl), 1.15 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 45.94 (CH—S), 39.13 (CH_2, cyclopentyl), 33.34 (CH—Si), 28.47, 27.51 (CH_3, *t*-Bu), 27.3, 26.78 (CH_2, cyclopentyl), 23.38, 21.97 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 24.1; UV λ_{max} 214 ($\epsilon = 3.62 \times 10^2$); MS *m/e* (relative intensity) 242 (M^+, 5.84), 185 ($M^+ - 57$, 47.61). Anal. Calcd for $C_{13}H_{26}SiS$: C, 64.39; H, 10.81. Found: C, 64.17; H, 10.87.

6: ^{1}H NMR (C_6D_6) δ 3.81 (m, J = 7 Hz, 3 Hz, 1H, S—CH), 1.25–1.94 (m, 7H, cyclopentyl), 1.2 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 61.89 (S—CH), 38.97, 30.38, 30.03 (CH_2, cyclopentyl), 29.18, 28.95 (CH_3, *t*-Bu), 28.03 (cyclopentyl), 23.05, 21.91 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 52.0; MS *m/e* (relative intensity) 274 (M^+, 11.156). Anal. Calcd for $C_{13}H_{26}SiS_2$: C, 56.87; H, 9.54. Found: C, 56.76; H, 9.84.

Reaction of *cis*-7,7-Di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (7) with Sulfur. In a 25 mL three-neck round-bottom flask equipped with a N_2 inlet and stirbar were added 2 mL of hexane and sulfur (20 mg, 0.078 mmol). To this slurry was added (0.1 g, 0.446 mmol), and the mixture was stirred for 0.5 h. GC analysis of the reaction mixture showed the presence of **8** and **9** in 12% and 33% yields, respectively. The products were separated as a pale yellow solid (**8**) and a green viscous liquid (**9**) by preparative GC.

8: mp 94–96 °C; ^{1}H NMR (C_6D_6) δ 3.65 (bs, 1H, CH—S), 1.35–2.1 (m, 9H, cyclohexyl), 1.15 (s, 9H, *t*-Bu), 1.0 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 57.34 (S—CH), 33.64 (Si—CH), 30.13 (cyclohexyl), 29.84, 29.16 (CH_3, *t*-Bu), 24.38, 23.6 (cyclohexyl), 22.6, 22.3 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 51.59; MS *m/e* (relative intensity) 288 (M^+, 2.5). Anal. Calcd for $C_{14}H_{28}SiS_2$: C, 58.27; H, 9.78. Found: C, 58.48; H, 9.64.

9: ^{1}H NMR (C_6D_6) δ 2.85–2.45 (m, J = 12.3, 3.2 Hz, 1H, CH—S), 1.3–1.95 (m, 9H, cyclohexyl), 1.12 (s, 9H, *t*-Bu), 1.05 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 56.43 (CH—S), 40.24, 32.24 (cyclohexyl), 28.93, 28.44 (*t*-Bu), 27.17, 26.0, 22.59 (cyclohexyl); ^{29}Si NMR (C_6D_6) δ 45.17; MS *m/e* (relative intensity) 288 (M^+, 15.7). Anal. Calcd for $C_{14}H_{28}SiS_2$: C, 58.27; H, 9.78. Found: C, 58.24; H, 9.43.

Thermolysis of 8 at 350 °C. A solution of **8** (50 mg, 0.173 mmol) in 1 mL of hexane was placed in a sealed tube and thermolyzed at 350 °C for 26 h. The GC of the reaction mixture showed the presence of **9** in 17% yield with no other volatile products noted.

Treatment of the Reaction Product of Di-*tert*-butyldichlorosilane with Lithium in the Presence of Cyclohexene with Sulfur. A three-neck 50 mL round-bottom flask equipped with condenser and N_2 inlet was charged with di-*tert*-butyldichlorosilane (3.0 g, 14 mmol), cyclohexene (10.0 mL, 98.7 mmol), lithium dispersion (0.45 g, 0.064 mmol), and 20 mL of THF. The reaction mixture was sonicated for 7 h and the supernatant liquid transferred to another flask containing sulfur (0.631 g, 2.46 mmol); this mixture was stirred for 10 min. The GC showed **8** in 46% yield. The product was isolated by removing the THF, extracting with hexane, and cooling the extract in a refrigerator to precipitate pale yellow crystals.

Reaction of Silirane 4 with Sulfur in the Presence of 10% Lithium Chloride. To a 25 mL round-bottom flask equipped with a nitrogen inlet and a stirbar were added 5 mL of THF, lithium chloride (16 mg, 0.377 mmol), and silirane **4** (0.80 g, 3.8 mmol). To this solution was added sulfur (122 mg, 0.48 mmol) in five equal portions. After each addition, the solution was stirred until the yellow color of the solution disappeared. GC analysis of the reaction mixture showed the presence of **5** and **6** in 93% and <5% yields, respectively. The supernatant liquid was transferred to another flask and concentrated; a molecular distillation was carried out at 50 °C under a pressure of 2 Torr, to isolate **5**.

Reaction of Silirane 7 with Sulfur in the Presence of Salts. In a 25 mL three-neck round-bottom flask equipped with a N_2 inlet and stirbar were added lithium chloride (0.020 g, 0.47 mmol), sulfur (0.010 g, 0.039 mmol), and 1 mL of THF. To this was slowly added silirane **7** (50 mg, 0.22 mmol), and this mixture was stirred for 10 min at room temperature. The solvent was removed and the product was extracted with hexane. The GC of the reaction mixture showed the presence of **8** in 72% yield. The extracts were combined, concentrated, and cooled in the refrigerator to obtain crystals.

The above procedure was followed with LiBr, LiI, NaI, $NaClO_4$, and KF. The results are summarized in Table 1.

Reaction of 1 with Sulfur in the Presence of Salts and Crown Ethers. **1** (165 mg, 0.818 mmol) was added to a 10 mL two-neck flask, equipped with N_2 inlet and a rubber septum, containing sulfur (48 mg, 1.5 mmol), 5 mL of solvent, and 10 mol % of crown ether and/or salt. The reaction mixtures were stirred at room temperature and monitored by GLC using decane as an inert internal standard. **2** and **3** were the only products observed. The results are summarized in Table 2. When THF, 18-crown-6, and potassium fluoride are used, **2** is the only product and may be isolated by molecular distillation (bp 48 °C, 2 Torr) in 60% yield.

Reaction of 4 with Selenium in the Presence of Lithium Chloride. To a 25 mL round-bottom flask equipped with a nitrogen inlet and a stirbar were added lithium chloride (0.20 g, 4.7 mmol), selenium (0.26 g, 3.3 mmol), and 5 mL of THF. To this solution was added **4** (0.5 g, 2.4 mmol), and the mixture was stirred for 0.5 h. GC analysis of the reaction mixture showed the presence of *cis*-3,3-di-*tert*-butyl-1,2-diselena-3-silabicyclo[3.3.0]octane (**14**) in 70% yield. The pure product was isolated as a red viscous liquid by preparative GC.

14: ^{1}H NMR (C_6D_6) δ 4.24 (m, J = 7, 2 Hz, 1H, CH—Se), 2.13–1.25 (m, 7H, cyclopentyl), 1.22 (s, 3H, *t*-Bu), 1.1 (s, 3H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 55.64 (CH—Se), 42.13 (CH—Si), 31.35 (cyclopentyl), 29.59, 29.16 (CH_3, *t*-Bu), 29.02, 28.34 (cyclopentyl), 23.51, 22.49 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 57.4; ^{77}Se NMR (C_6D_6) δ 410 (Se—CH), −58 (Si—Se); MS *m/e* (relative intensity) 370 (M^+, 22).

Treatment of the Reaction Product of Di-*tert*-butyldichlorosilane with Lithium in the Presence of Cyclohexene with Selenium. The procedure above was followed with selenium (1.56 g, 19.7 mmol). The reaction mixture was stirred for 0.5 h at room temperature. The GC of the reaction mixture showed the presence of **15** in 57% yield. Analytical samples were obtained by repeated crystallization from hexane.

15: mp 76–78 °C; ^{1}H NMR (C_6D_6) δ 4.2 (bs, 1H, CH—Se), 1.45–2.25 (m, 9H, cyclohexyl), 1.2 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 53.9 (Se—CH), 37.02 (Si—CH), 32.15 (cyclohexyl), 30.1, 29.32 (CH_3, *t*-Bu), 29.02, 25.32, 23.86 (cyclohexyl), 23.17, 22.69 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 55.43; ^{77}Se NMR (C_6D_6) δ 384 (Se—CH), −72 (Si—Se); MS *m/e* (relative intensity) 288 (M^+, 82.5). Anal. Calcd for $C_{14}H_{28}SiSe_2$: C, 43.97; H, 7.38. Found: C, 43.77; H, 7.32.

Reaction of Silirane 7 with Selenium in the Presence of Lithium Chloride. Lithium chloride (0.32 g, 7.6 mmol), selenium (0.395 g, 4.99 mmol), and 10 mL of THF were combined in a 25 mL flask. **7** (0.80 g, 3.6 mmol) was added, and the reaction mixture was stirred for 30 min. GC of the reaction mixture showed the presence of compound **15** in 62% yield.

Reaction of 7 with Selenium in the Presence of Potassium Fluoride and 18-crown-6. **7** (33 mg, 0.15 mmol) was added to a dry, N_2-flushed NMR tube containing 0.6 mL of benzene-d_6, selenium (13 mg, 0.16 mmol), potassium fluoride (1.0 mg, 0.015 mmol), and 18-crown-6 (4.0 mg, 0.016 mmol). The tube was mixed by shaking for 5 min and examined spectroscopically. Peaks assigned to **15** are present along with peaks presumably belonging to **16**. Due to the presence of **15**, ^{77}Se and ^{29}Si NMR signals were the only interpretable spectra. The ^{13}C and ^{1}H NMR spectra contained too many overlapping peaks to make accurate assignments.

16: ^{29}Si NMR (C_6D_6) δ 19.0; ^{77}Se NMR (C_6D_6) δ 54.7.

Synthesis of *trans*-2,2-Di-*tert*-butyl-3,4-dimethyl-1,2-selenasiletane (17). In a 10 mL flask equipped with a magnetic stirbar, rubber septum, and N_2 inlet, selenium (20 mg, 0.25 mmol), 18-crown-6 (8 mg, 0.025 mmol), KF (1 mg, 0.025 mmol), and 1 mL of benzene-d_6 were stirred under N_2 at room temperature. To this mixture was added **1** (45 mg, 0.25 mmol), and the mixture was stirred for 45 min. The contents of the flask were transferred by syringe to a dry N_2-flushed NMR tube. The tube may then be frozen for future use of the selenasiletane product. The yield of **17** was determined by ^{1}H NMR using the crown ether as an internal standard and ranged from 85 to 100%.

17: ^{1}H NMR (C_6D_6) δ 0.96 (d, J = 7.52 Hz, 3H, SiCHCH_3), 1.10 (s, 9H, *t*-Bu), 1.24 (s, 9H, *t*-Bu), 1.46 (d, J = 6.45 Hz, 3H, SeCHCH_3), 1.96 (dq, J = 10.21, 7.52 Hz, 1H, SiC*H*), 3.31 (dq, J = 10.21, 6.45 Hz, 1H, SeC*H*); ^{13}C NMR (C_6D_6) δ 16.7 (SiCH), 20.8 (*t*-Bu), 22.5 (*t*-Bu), 26.4 (SeCH), 28.4 (*t*-Bu), 28.7 (*t*-Bu), 35.5 (SiCH*C*H_3), 35.9 (SeCH*C*H_3); ^{29}Si NMR (THF-d_8) δ 18.9; ^{77}Se NMR (C_6D_6) δ 3.7; MS (electron impact) *m/e* (relative intensity) 278 (3, M^+), 222 (24, $M^+ - 56$), 166 (22, $M^+ - 56 - 56$).

Synthesis of *trans*-3,3-Di-*tert*-butyl-4,5-dimethyl-1,2-diselena-3-silacyclopentane (18). Selenium (517 mg, 6.5 mmol), TBAC (83 mg, 0.3 mmol), and 12 mL of THF were stirred in a 25 mL flask under nitrogen. To this slurry was added **1** (648 mg, 3.27 mmol), yielding a slightly exothermic reaction. The solution was stirred at room temperature for 90 min, at which point GLC indicates reaction completion. The solvent was removed under vacuum, and the residue was distilled (bp 102 °C, 2 Torr) to give 677 mg (58%) of the product as a red viscous oil.

18: ^{1}H NMR (C_6D_6) δ 0.97 (d, J = 7.32 Hz, 3H, SiCHCH_3), 1.07 (s, 9H, *t*-Bu), 1.10 (d, J = 6.6 Hz, 3H, SeCHCH_3), 1.19 (s, 9H, *t*-Bu), 1.35 (m, 1H, SiC*H*), 3.34 (dq, J = 11.72, 6.59 Hz, 1H, SeC*H*); ^{13}C NMR (C_6D_6) δ 15.4 (CH_3), 18.5 (CH_3), 22.9 (*t*-Bu), 23.3 (*t*-Bu), 28.6 (*t*-Bu), 29.1 (*t*-Bu), 37.6 (CH), 46.5 (CH); ^{29}Si NMR (C_6D_6) δ 53.2; ^{77}Se NMR (C_6D_6) δ 414 (SeC), −133 (SeSi); UV−vis ($c = 1.3 \times 10^{-3}$ M, hexane) λ_{max} 418 (ϵ = 148) nm; MS (electron impact) *m/e* (relative intensity) 354 (11, M^+). Anal. Calcd for $C_{12}H_{26}SiSe_2$: C, 40.45; H, 7.35. Found: C, 40.42; H, 7.64.

Reaction of 1 with Selenium in the Presence of Salts and Crown Ethers. **1** (165 mg, 0.818 mmol) was added to a 10 mL two-neck flask, equipped with a N_2 inlet and a rubber septum, containing selenium (120 mg, 1.5 mmol), 5 mL of solvent, and 10 mol % of crown ether and/or salt. The reaction mixtures were stirred at room temperature and monitored by GLC using decane as an inert internal standard. **17** and **18** were the only products observed. The results are summarized in Table 3.

Reaction of 17 with Methanol. **17** was prepared as above and quenched with methanol (52 mg, 1.64 mmol). Purification by preparative GLC gave **19** as a clear liquid.

19: ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 18H, *t*-Bu), 1.64 (m, 6H, CH_3), 3.53 (s, 3H, OCH_3), 5.97 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 16.1 (CH_3), 20.3 (*t*-Bu), 28.1 (*t*-Bu), 52.6 (OCH_3), 136.7 (Si−C), 137.6 (CH); ^{29}Si NMR ($CDCl_3$) δ 3.0; MS (electron impact) *m/e* (relative intensity) 228 (1, M^+), 171 (28, $M^+ - 57$), 89 (100). Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 67.71; H, 12.49.

Reaction of 17 with Water. **17** was prepared as above, and excess selenium is removed by filtering through a medium-porosity sintered-glass frit. The solution was exposed to atmospheric moisture and stirred overnight. The clear vinylsilanol **20** was purified by preparative GLC.

20: ^{1}H NMR (C_6D_6) δ 1.10 (s, 18H, *t*-Bu), 1.63 (dt, J = 7.33, 2.20 Hz, 3H, $CHCH_3$), 1.75 (t, J = 2.20 Hz, 3H, CCH_3), 3.60 (s, 1H, OH), 6.08 (m, 1H, CH); ^{13}C NMR (C_6D_6) δ 13.9 (CH_3), 16.2 (CH_3), 20.5 (*t*-Bu), 28.3 (*t*-Bu), 133.5 (C), 136.8 (CH); ^{29}Si NMR (C_6D_6) δ 1.9; IR (neat) 3700, 3550−3300, 823 cm^{-1}; MS (electron impact) *m/e* (relative intensity) 214 (1, M^+), 157 (37, $M^+ - 57$), 75 (100). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 66.79, H, 12.15.

Preparation of *trans*-3,3-Di-*tert*-butyl-4,5-dimethyl-1-thia-2-selena-3-silacyclopentane (21). A 50 mL flask was charged with selenium (360 mg, 4.5 mmol), potassium fluoride (25 mg, 0.43 mmol), 18-crown-6 (100 mg, 0.39 mmol), and 28 mL of benzene. To this was added **1** (900 mg, 4.5 mmol), and the mixture was stirred at room temperature for 3 h. After unreacted selenium was allowed to settle, the supernatant liquid, composed primarily of **17**, was added by syringe into another flask containing sulfur (146 mg, 0.57 mmol) and TBAC (120 mg, 0.43 mmol). After 8 h of stirring, GLC showed reaction completion. The benzene was stripped away by vacuum, and the remaining liquid was distilled on a molecular distillation apparatus (bp 98 °C, 2 Torr), yielding 900 mg (64%) of **21** as a viscous red liquid.

21: ^{1}H NMR (C_6D_6) δ 1.00 (d, J = 7.32 Hz, 3H), 1.09 (s, 9H), 1.12 (d, J = 5.13 Hz, 3H), 1.17 (s, 9H), 1.42 (m, 1H), 3.38 (m, 1H); ^{13}C NMR (C_6D_6) δ 14.7 (CH_3), 17.4 (CH_3), 23.0 (*t*-Bu), 26.8 (*t*-Bu), 28.4 (*t*-Bu), 28.9 (*t*-Bu), 36.9 (CH), 47.5 (CH); ^{29}Si NMR (C_6D_6) δ 48.7; ^{77}Se NMR (C_6D_6) δ 516; MS (electron impact) *m/e* (relative intensity) 310 (15, M^+), 253 (18, $M^+ - 57$), 197 (27, $M^+ - 57 - 56$). Anal. Calcd for $C_{16}H_{26}SSeSi$: C, 46.58; H, 8.47. Found: C, 46.57; H, 8.49.

Reaction of 1,1-Dimethylsilacyclobutane with Sulfur in the Presence of KF and 18-crown-6. A 25 mL flask was charged with 1,1-dimethylsilacyclobutane (**22**; 150 mg, 1.5 mmol), sulfur (48 mg, 1.5 mmol), potassium fluoride (6 mg, 0.10 mmol), 18-crown-6 (48 mg, 0.18 mmol), and 4 mL of THF. The mixture was refluxed for 16 h, whereupon GLC indicated 2,2-dimethyl-1-thia-2-silathiacyclopentane (**23**) in 72% yield. Analytically pure **23** was obtained by preparative GLC. The rate was negligible at room temperature.

23: ^{1}H NMR (C_6D_6) δ 0.26 (s, 6H, $SiMe_2$), 0.63 (t, 2H, CH_2-Si), 1.69 (m, 2H, CCH_2C), 2.67 (t, 2H, SCH_2); ^{29}Si NMR (C_6D_6) δ 33.67.

Thermolysis of 2. **2** (0.30 g, 1.3 mmol) was added to 2 mL of degassed hexane, and this solution was thermolyzed at 200 °C for 4 h in a sealed tube. The reaction mixture consists of two major products, **24** and **25**, in 33% and 30% yields, respectively. **24** and **25** were isolated in pure form by HPLC as crystalline solids.

24: mp 128 °C; ^{1}H NMR (C_6D_6) δ 1.38 (s, *t*-Bu); ^{13}C NMR (C_6D_6) δ 29.5, 25.7 (*t*-Bu); ^{29}Si NMR (C_6D_6): δ 29.7; UV λ_{max} 215 nm ($\epsilon = 9.2 \times 10^3$); MS *m/e* (relative intensity) 291 ($M^+ -$ 57, 31%). Anal. Calcd for $C_{16}H_{36}Si_2S_2$: C, 55.10; H, 10.40. Found: C, 55.51; H, 10.38.

25: mp 121−123 °C; ^{1}H NMR (C_6D_6) δ 3.45 (m, 1H, SCH), 1.63 (m, 1H, SiCH), 1.29 (d, J = 6.98 Hz, 3H, $CHCH_3$), 1.26, 1.23, 1.22, 1.18 (s, 9H each, *t*-Bu), 1.02 (d, J = 7.29 Hz, 3H, $CHCH_3$); ^{13}C NMR (C_6D_6) δ 38.6 ($SCCH_3$), 30.2, 30.0, 29.3, 28.7 (*t*-Bu), 28.5, 27.5, 25.4, 24.5 (*t*-Bu), 23.4, 15.6, 14.3; ^{29}Si NMR (C_6D_6) δ 30.6, 25.9; UV λ_{max} 214 nm ($\epsilon = 1.1 \times 10^3$); MS *m/e* (relative intensity) 347 ($M^+ -$ 57, 23%). Anal. Calcd for $C_{20}H_{44}Si_2S_2$: C, 59.33; H, 10.95. Found: C, 59.08; H, 11.17.

Thermolysis of 2 in the Presence of Hexamethylcyclotrisiloxane (D_3) at 200 °C. **2** (0.2 g, 0.87 mmol) was added to 2 mL of degassed hexane and D_3 (5g, 18 mmol) and was thermolyzed at 200 °C for 12 h in a sealed tube. The products were **24**−**26** in 24%, 40%, and 27% GC yields, respectively. **26** was isolated by preparative GLC as a colorless liquid.

26: ^{1}H NMR (C_6D_6) δ 1.30 (s, 18H, *t*-Bu), 0.60 (s, 6H, $SiCH_3$), 0.33, 0.26 (s, 6H each, $SiCH_3$); ^{13}C NMR (C_6D_6) δ 27.9 (*t*-Bu), 25.0 (*t*-Bu), 6.6, 1.4, 0.9 (CH_3); ^{29}Si NMR (C_6D_6) δ 9.7, 4.6, −17.5, −19.9; MS *m/e* (relative intensity) 339 ($M^+ - 57$, 100%). Anal. Calcd for $C_{14}H_{36}Si_4O_3S$: C, 42.37; H, 9.14. Found: C, 42.36; H, 9.38.

Thermolysis of 5 at 100 °C. 5 (75 mg, 0.31 mmol) and 1.5 mL of hexane were placed in a sealed tube and heated at 100 °C for 4 days. GC analysis of the reaction mixture showed 2,2,4,4-tetra-*tert*-butyl-1,3-dithia-2,4-disilabicyclo[4.3.0]-nonane (**27**) in 75% yield. Pure **27** was obtained as a pale yellow solid by preparative GC.

27: mp 117–118 °C; ^{1}H NMR (C_6D_6) δ 3.85 (m, J = 5.3, 3.2 Hz, 1H, S—CH), 1.75–2.11 (m, 5H, cyclopentyl), 1.28 (s, 9H, *t*-Bu), 1.25 (s, 18H, *t*-Bu), 1.14–1.2 (m, 2H, cyclopentyl), 1.12 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 46.58 (S—CH), 38.39 (cyclopentyl), 30.15, 29.29, 29.21 (CH_3, *t*-Bu), 27.27, 24.49 (cyclopentyl), 24.21 (Si—CH), 23.95, 23.37 (*t*-Bu); ^{29}Si NMR (C_6D_6) δ 28.78, 23.58; UV λ_{max} 218 ($\epsilon = 7.5 \times 10^4$); MS *m/e* (relative intensity) 359 ($M^+ - 57$, 14.23). Anal. Calcd for $C_{21}H_{44}Si_2S_2$: C, 60.50; H, 10.64. Found: C, 60.14; H, 10.67.

Thermolysis of 5 in the Presence of D_3 at 100 °C. 5 (75 mg, 0.31 mmol), D_3 (1.72 g, 7.74 mmol), and 1.5 mL of hexane were placed in a sealed tube and heated at 100 °C for 4 days. GC analysis of the reaction mixture showed the presence of **27** in 44% yield.

Thermolysis of 5 in the Presence of D_3 at 150 °C. 5 (50 mg, 0.21 mmol), D_3 (1.15 g, 5.2 mmol), and 1 mL of hexane were placed in a sealed tube and heated at 150 °C for 5 h. GC analysis of the reaction mixture showed the presence of **27**, **24**, and **26** in 61%, 12%, and 19% yields, respectively. When the reaction was carried out in the absence of D_3, **27** and **24** were obtained in 69% and 18% yields, respectively.

Photolysis of 5 in the Presence of D_3. In a quartz Erlenmeyer flask equipped with a nitrogen inlet and a reflux condenser were added **5** (50 mg, 0.206 mmol), D_3 (1.15, 5.2 mmol), and 1 mL of degassed hexane. This solution was irradiated (254 nm) for 45 min. GC analysis of the reaction mixture showed **27** and **24** in 48% and 19% yields, respectively. Irradiation for an additional 9 h resulted in a decrease of **27** and an increase of **24**. GC analysis showed **27** and **24** in 10% and 62% yields, respectively. The products were identified by comparison with authentic samples.[4]

Crystal Selection and Data Collection for 4,4-Di-*tert*-butyl-2,3-dithia-4-silabicyclo[4.3.0]nonane (8) and 4,4-Di-*tert*-butyl-2,3-diselena-4-silabicyclo[4.3.0]nonane (15). All manipulations were carried out in a Vacuum Atmospheres drybox. A number of crystals were selected and placed in thin-walled glass capiliaries which were plugged with silicone grease, removed from the drybox, and quickly flame-sealed. The crystals were examined under optical and polarizing microscopes, and the best-looking crystal was selected for data collection, placed on a goniometer head, and mounted on a Nicolet R3 diffractometer.

After optical alignment of the crystal, a rotation photograph was taken and 15 low-angle reflections were selected for precise centering, autoindexing, preliminary cell constants with standard deviations, and calculation of the orientation matrix. An index transformation was applied which indicated that the probable Bravais lattice was primitive monoclinic. Axial photographs were taken to confirm the axial lengths and revealed the required mirror plane perpendicular to the *b* axis.

The crystal and data collection parameters are given in Table 6 for **8** and **15**. The cell reduction program TRACER II[33] was run to check for higher symmetry lattices. Corrections were made for decay, background, Lorentz, and polarization effects using the program XTAPE.[34]

Reported cell parameters were obtained by precise centering of 25 reflections extracted from the full data set, followed by application of an autoindexing program and a least-squares fit to the refined angular settings of the 25 reflections. For **8**, a set of 12 moderately strong reflections with a distribution in 2θ having an χ range of 70–90 or 270–290° were selected from the data set. An empirical absorption correction was applied on the basis of ψ scans collected for each reflection with the diffraction vector varied from 0 to 180° in 10° increments. The merging *R* was lowered from 0.0275 before to 0.0163 after correction. For **15** the data were not corrected for absorption due to the accidental loss of the crystal; however, the nearly spherical shape of the crystal minimizes any large errors due to absorption.

Solution and Refinement of Structures. Compounds **8** and **15** were found to crystallize in the monoclinic crystal system and were assigned to the space group $P2_1/n$, an alternate setting of $P2_1/c$ (No. 14), on the basis of systematic absences. The structures were solved by the direct-methods routine of SHELX-76,[35] which gave the silicon, two sulfur, and some carbon atom positions for **8** and silicon, two selenium, and some carbon atoms in **15**. The remaining non-hydrogen atoms were located by successive applications of difference Fourier maps and least-squares refinement. Atomic coordinates and isotropic and anisotropic thermal parameters for all non-hydrogen atoms were refined using full-matrix least squares. All hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å) using the riding model of the AFIX utility of SHELX-76 and given a common isotropic temperature factor which was refined as a free variable. An isotropic secondary extinction parameter was refined to a value of $[1.1(2)] \times 10^{-7}$. The final difference Fourier map showed a residual electron density of 0.30 e/Å^3 near C3. There were no peaks of chemical significance. The refinement of the data for **15** followed that for **8**, and the compound was found to be isostructural with **8**. The final difference Fourier map showed a residual electron density of 0.93 e/Å^3 located 0.76 Å from Se2 at x = 0.2264, y = 0.1835, and z = 0.3577. There were no peaks of chemical significance. Neutral atom scattering factors were used[36] and were corrected for anomalous dispersion. Atomic coordinates and isotropic temperature factors for **8** and **15** are given in Tables 7 and 8, respectively. Selected bond distances, bond angles, and torsion angles for both compounds are listed in Table 9. ORTEP views of **8** and **15** are given in Figures 1 and 2, respectively.

Complete listings of interatomic bond lengths and bond angles, anisotropic thermal parameters for all non-hydrogen atoms, and hydrogen atom positional parameters are available for **8** and **15**. See the paragraph at the end of the paper for ordering information.

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Supplementary Material Available: Complete listings of bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates and isotropic thermal parameters, and torsion angles for **8** and **15** (7 pages). Ordering information is given on any current masthead page.

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