

## Synthesis, Structure, and Chemistry of New, Mixed Group 14 and 16 Heterocycles: Nucleophile-Induced Ring Contraction of Mesocyclic Dications

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**Abstract:** More than 40 new 4- to 12-membered ring heterocycles containing various combinations of Group 14 and 16 elements Si, Sn, S, Se, and Te have been synthesized and fully characterized. Synthesis of these small-ring as well as medium-ring (mesocyclic) heterocycles from  $\alpha,\omega$ -dihalides is facilitated by the presence of *gem*-dialkylsilyl and *gem*-dialkylstannyl groups in the precursors. Conformations of several of the new ring systems in the solid state have been determined by X-ray crystal structure analysis. Oxidation of mixed S(Se, Te)/Si eight-membered ring mesocycles with  $\text{NOPF}_6$  or  $\text{Br}_2$  gives dications or a bicyclic dibromide, respectively, which can be characterized by NMR methods. On treatment with nucleophiles, mesocyclic dications, or the corresponding radical cations undergo ring contraction, giving five- or six-membered ring heterocycles. Photolysis of a S/Se four-membered ring heterocycle gives selenoformaldehyde, trapped in 80% yield with 2,3-dimethyl-1,3-butadiene.

### Introduction

Sulfur-containing heterocycles with one or more ring  $\text{R}_2\text{Si}$  or  $\text{R}_2\text{Sn}$  groups, separated from S by  $\text{CH}_2$  groups (e.g. **7–14** (E = S), Chart 1), are virtually unknown, despite novel properties which might be anticipated by analogy with those of well-studied polysulfur systems **1–6**.<sup>1</sup> Also unknown are analogous Se- or Te-containing heterocycles with similarly positioned  $\text{R}_2\text{Si}$  or  $\text{R}_2\text{Sn}$  groups. It is known that the oxidation potential of **4** (1,5-dithiocane; Scheme 1) is lowered, owing to transannular bond formation, and that the radical cation **4'** and dication **4''**, formed on oxidation, are stabilized. Similar effects are also seen with **5** and with **15** and **16**, the Se and Te analogues of **4**, respectively.<sup>2</sup> Compounds **4**, **5**, **15**, and **16** show unusual redox chemistry,<sup>1,2</sup> catalytic activity,<sup>3</sup> and metal coordination abilities.<sup>4</sup> In **1** and its bicyclic analogues **20** (Chart 2), facilitation of oxidation depends not only on the  $\text{S}\cdots\text{S}$  distance but also on the angular relationship of the interacting lone-pair orbitals, e.g., compare planar **1** (higher ionization energy ( $I_E$ )) and puckered **20** (lower  $I_E$ ).<sup>5</sup> Exocyclic  $\beta$ -silicon and  $\beta$ -tin groups, e.g., in 2-substituted derivatives of 1,3-dithiane **21**,<sup>2f</sup> 1,3-dithioles,<sup>6a</sup> and oxiranes and thiiranes **22**,<sup>6b</sup> can also significantly facilitate one-electron oxidation at the chalcogen atom(s) by the well-known  $\beta$ -effect of these elements<sup>7</sup> when the angular relationship of the C–Si or C–Sn orbitals with adjacent chalcogen *p*-type lone-pair orbitals is optimum (eclipsed). The lowering of  $I_E$  and facilitation of oxidation in **1–6** as well as in **15** and **16** has

been evaluated using photoelectron spectroscopy (PES), cyclic voltammetry (CV), MO calculations, and/or more qualitatively by measuring the  $I_E$ -proportional  $\lambda_{\text{max}}$  of their tetracyanoethylene charge-transfer (TCNE-CT) complexes.<sup>2a,f,6</sup>

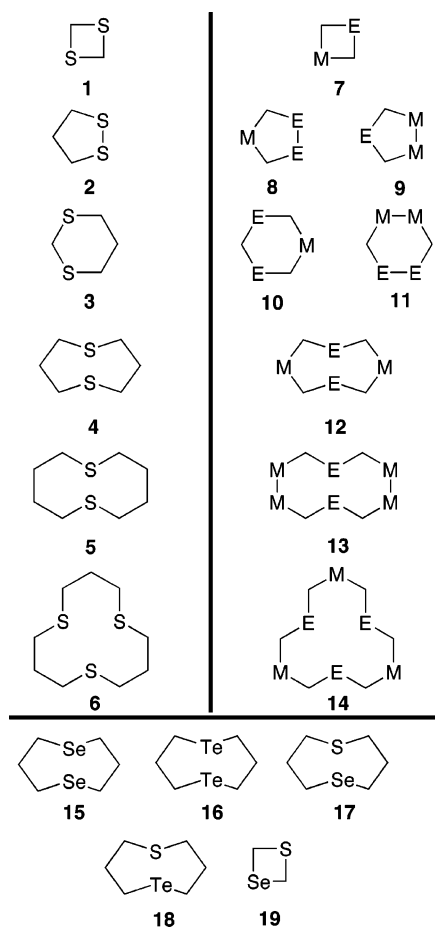
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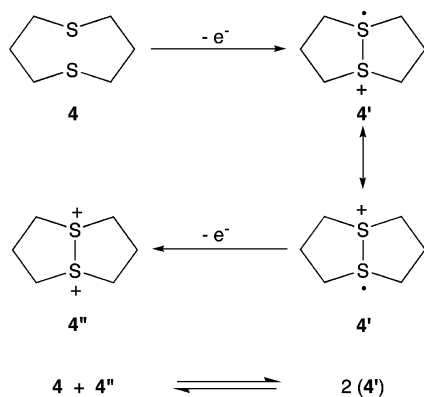
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(1) Detailed discussions of each of these ring systems may be found in appropriate chapters of *Comprehensive Heterocyclic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1996.

**Chart 1.** Di- and Trithiaheterocycles (1–6), Analogous Mixed Group 14/16 Homologs 7–14, and Related Heterocycles 15–19 Prepared in This Work (E = S, Se or Te; M = R<sub>2</sub>Si or R<sub>2</sub>Sn)

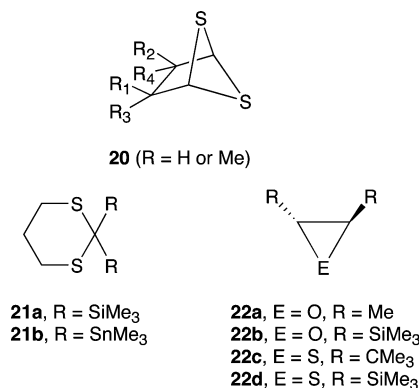


**Scheme 1.** Radical Cation (4') and Dication (4'') Formation in 1,5-Dithiocane (4)



The goal of the present work was to synthesize unknown heterocycles 7–14, having endocyclic or exocyclic C–Si, C–Sn, and Si–Si orbitals (Si–Si orbitals are *exocyclic* when M = (Me<sub>3</sub>Si)<sub>2</sub>Si) at various angles to the chalcogen *p*-orbitals,

**Chart 2.** Heterocycles Illustrating Angular Dependence of Orbital Interaction with Chalcogen Lone Pair *p*-Orbitals



and to examine the ease of their one- and two-electron oxidation. This study reports the synthesis of more than 40 new 4- to 12-membered ring heterocycles including mixed S–Si, S–Sn, Se–Si, Se–Sn, and Te–Si systems, together with their characterization and determination of conformation in the solid state by X-ray crystallography. Radical cations and dications of **12** were generated in solution using stoichiometric NOPF<sub>6</sub>. Stoichiometric Br<sub>2</sub> affords a bicyclic dibromide of **12** (E = Te, M = Me<sub>2</sub>Si). In some cases, the dications of **12** can be characterized by NMR spectroscopic methods and are found to undergo novel rearrangements on treatment with nucleophiles. In view of these interesting findings, we have re-examined the formation of dications from **15** and **16** and have prepared for the first time mesocycles **17** and **18** having two different chalcogen atoms. Finally, we have extended our studies to new four-membered ring system **19** for comparison with properties of **1** and **7**, where E = Se. For selected four-membered rings, we describe photochemical ring cleavage and formation of metal complexes. Ionization energies and oxidation potentials for 7–13 and 16–18 have been obtained using PES and CV; these studies will be reported separately.<sup>8</sup>

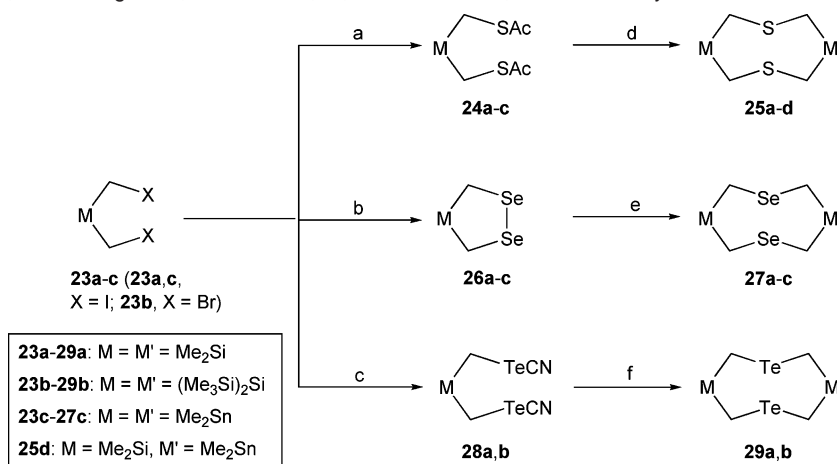
## Results and Discussion

**I. Eight-Membered Ring Systems. Ia. Synthesis of 1,5-Dichalcogena-3,7-disilocanes, -3,7-distannocanes, and Related Systems.** Synthesis of medium-sized ring (mesocyclic) heterocycles lacking rigid groups can be problematic, often requiring high-dilution techniques or use of metal templates,<sup>4e,9a–c</sup> or the *gem*-dialkyl (“Thorpe-Ingold”) effect.<sup>9d–g</sup> A limited number of Se- or Te-containing mesocycles lacking rigid groups are known.<sup>1</sup> We find that new mesocycles **25**, **27**, and **29** (Scheme 2) bearing two *gem*-dimethyl or *gem*-bis(trimethylsilyl) groups can be easily prepared in fair to good yields without resorting to special techniques by combining bis(halomethyl)silanes or -stannanes with appropriate S(Se,Te)/Si(Sn) reagents including bis-thioacetates **24**, cyclic diselenides **26** (prepared using Na<sub>2</sub>Se<sub>2</sub>),<sup>10b,c,f</sup> and bis-tellurocyanate **28**.<sup>10e,11a</sup> In these

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**Scheme 2.** Synthesis of 1,5-Dichalcogena-3,7-disilocanes, -3,7-distannocanes, and Related Systems<sup>a</sup>

<sup>a</sup> Conditions: (a) KSAc, THF, rt (**24a**, 81%; **24b**, 74%; **24c**, 73%). (b) Na<sub>2</sub>Se<sub>2</sub>, EtOH, 0 °C (**26a**, 71%; **26b**, 55%; **26c**, 89%). (c) For **28a**, Te, KCN, DMSO, 100 °C, then **23a**, DMSO, rt; for **28b**, Te, KCN, DMSO, 100 °C, then **23b**, DMSO, rt. (d) For **25a**, **23a** + **24a**, KOH, EtOH, rt 2 h (34%); for **25b**, **23b** + **24b**, KOH, EtOH, rt 2 h (22%); for **25c**, **23c** + **24c**, KOH, EtOH, rt 2 h (42%); for **25d**, **23c** + **24a**, KOH, EtOH, rt 2 h (34%); (e) For **27a**, **23a** + **26a**, NaBH<sub>4</sub>, EtOH, THF (73%); for **27b**, **23b** + **26b**, NaBH<sub>4</sub>, EtOH, THF (76%); for **27c**, **23c** + **26c**, NaBH<sub>4</sub>, EtOH, THF (58%). (f) For **29a**, **23a** + **28a**, NaBH<sub>4</sub>, EtOH, DMSO (23%); for **29b**, **23b** + **28b**, NaBH<sub>4</sub>, EtOH, DMSO (21%; two step yield).

syntheses, in contrast to syntheses of **15** and **16**,<sup>2e,11b</sup> it is imperative to produce the dichalcogen dianions *in the presence of the 1,3-dihalides* because the former dianions are unstable and must be immediately trapped. This is accomplished by dropwise addition of a 1:1 mixture of **23** and **24** to dilute ethanolic KOH giving **25** (22–42% yield), of **23** and **26** to dilute NaBH<sub>4</sub> in EtOH-THF giving **27** (58–76% yield), and of **23** and **28** to dilute NaBH<sub>4</sub> in EtOH-DMSO giving **29** (21–23% yield). Bis-tellurocyanate **28** is only stable in DMSO solution, polymerizing on concentration. Compounds **25a**, **27a**, **27c**, **29a**, and **29b** are crystalline solids further characterized by X-ray crystallography, as discussed below. To facilitate discussion, heterocycles are identified below by a short-hand descriptor as well as by number.<sup>12</sup>

The majority of compounds **25**, **27**, and **29** give intense molecular ions (M<sup>+</sup>) in their mass spectra, whose composition can be confirmed by HR-MS; these compounds are volatile and stable enough for characterization by GC-MS. For compounds with multiple isotopes (e.g., Te–Sn heterocycles), the predicted patterns for the molecular ions are in excellent agreement with the complex observed patterns. Most new heterocycles show singlets in their NMR spectra for the ring CH<sub>2</sub> protons even at –85 °C, indicative of conformational mobility. Compound **29a** shows <sup>125</sup>Te NMR δ 75.2 (relative to Me<sub>2</sub>Te). Efforts to prepare 3,3,7,7-tetramethyl-1,5-ditellura-3,7-distannocane (**29**, M = Me<sub>2</sub>Sn) led to a complex mixture in which only minor amounts of the target compound could be detected by GC-MS.

In the above syntheses, we initially employed the known bisiodides Me<sub>2</sub>Si(CH<sub>2</sub>I)<sub>2</sub> (**23a**), prepared from commercially available Me<sub>2</sub>Si(CH<sub>2</sub>Cl)<sub>2</sub>,<sup>13</sup> and Me<sub>2</sub>Sn(CH<sub>2</sub>I)<sub>2</sub> (**23c**).<sup>14a</sup> In an effort to improve the stability and reduce the reactivity of the new heterocycles, we sought to increase the steric bulk at silicon.

We found that the very useful reagent BrCH<sub>2</sub>Li (prepared from CH<sub>2</sub>Br<sub>2</sub> and *n*-BuLi in the presence of LiBr in THF at –78 °C)<sup>13b,14c,d</sup> can be employed for one-pot conversion of compounds of type R<sub>2</sub>SiCl<sub>2</sub> to R<sub>2</sub>Si(CH<sub>2</sub>Br)<sub>2</sub>.<sup>14b</sup> This method is used to prepare the new dibromide (Me<sub>3</sub>Si)<sub>2</sub>Si(CH<sub>2</sub>Br)<sub>2</sub> (**23b**) from (Me<sub>3</sub>Si)<sub>2</sub>SiCl<sub>2</sub><sup>15</sup> in 57% yield, as well as *t*-BuMeSi(CH<sub>2</sub>Br)<sub>2</sub> (**23d**) and [BrCH<sub>2</sub>SiMe<sub>2</sub>]<sub>2</sub>,<sup>10a</sup> from *t*-BuMeSiCl<sub>2</sub> and [ClSiMe<sub>2</sub>]<sub>2</sub>, respectively. In the cyclization steps leading to **27** and **29**, it is essential to use diiodides or dibromides rather than dichlorides, so that reactions can be run at the lowest possible temperatures, to avoid decomposition of unstable Se and Te compounds. Fortunately, the silicon facilitates α-carbon S<sub>N</sub>2 processes (discussed below). In the syntheses of **29**, the unstable bis(tellurocyanates)<sup>10e</sup> are not isolated but rather directly taken on to the next step.

**Ib. Structure of 1,5-Dichalcogena-3,7-disilocanes, -3,7-distannocanes, and Related Systems.** X-ray crystal structures of **25a**, **27a**, **27c**, **29a**, and **29b** (Figure 1) were determined. Calculations indicate that **4** adopts a boat–chair and/or chair–chair conformation in which the transannular S atoms are relatively close to each other.<sup>16a</sup> The solid-state structure of **25a** shows that in the crystal lattice, the molecule adopts a boat–boat<sup>16a</sup> conformation where transannular S atoms are 4.735 Å apart. This conformation is an energy-minimum in the gas phase, as shown by DFT calculations.<sup>8b</sup> In this conformation, the S

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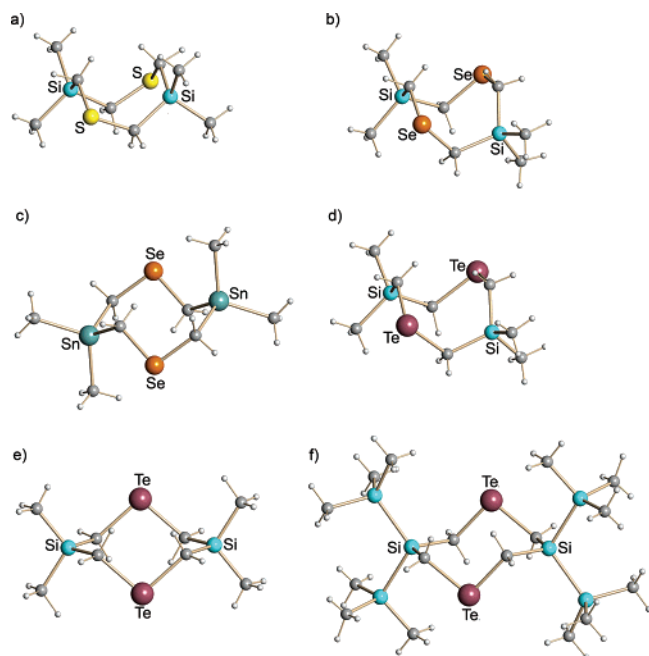
(12) The crown-ether like descriptors we use gives ring size (bracketed), number and identity of Group 16 and 14 elements (contiguous pairs of heteroatoms parenthesized), and nonmethyl heteroatom substituents, e.g.: [8]Se<sub>2</sub>, [8]Te<sub>2</sub>, [8]SSe, [8]STe, [4]SSe, [8]S<sub>2</sub>Si<sub>2</sub>, [8]S<sub>2</sub>(Si(TMS)<sub>2</sub>)<sub>2</sub>, [8]S<sub>2</sub>Sn<sub>2</sub>, and [8]S<sub>2</sub>SiSn (for **15–19**, **25a–25d**, respectively). It is assumed that methylene groups separate noncontiguous heteroatoms. Descriptors for each compound are given in the experimental material.

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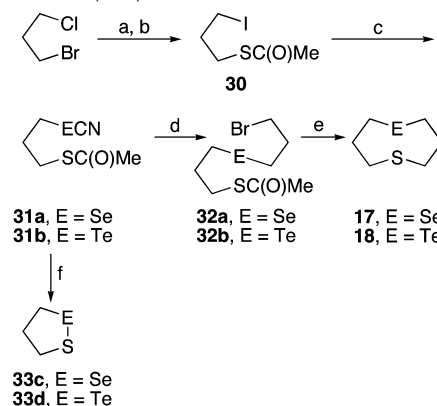


**Figure 1.** (a) Molecular structure of **25a**. Boat–boat conformation (BB2),<sup>16</sup> intramolecular contacts S···S 4.7347(6), intermolecular contacts S···S 4.522(1), 4.615(1), S–C<sub>av</sub> 1.8109(15), Si–C<sub>av</sub> 1.8696(15) Å, C–S–C<sub>av</sub> 105.33(7)°. (b) Molecular structure of **27a**. Boat–boat conformation (BB2), intramolecular contacts Se···Se 4.7686(3) Å, intermolecular contacts Se···Se 4.298(1), 4.952(1), Se–C<sub>av</sub> 1.9538(17), Si–C<sub>av</sub> 1.869(2) Å, C–Se–C<sub>av</sub> 102.17(7)°. (c) Molecular structure of **27c**. Twist–chair conformation (TC), intramolecular contacts Se···Se 4.6526(14), intermolecular contacts Se···Se 4.110(2), Se–C<sub>av</sub> 1.957(6), Sn–C<sub>av</sub> 2.145(6) Å, C–Se–C 98.9(3)°. (d) Molecular structure of **29a**. Boat–boat conformation (BB2), intramolecular contacts Te(1)···Te(2) 5.0332(3), intermolecular contacts Te(1)···Te(2) 4.064(1), Te–C<sub>av</sub> 2.159(2), Si–C<sub>av</sub> 1.866(2) Å, C–Te–C 99.18(9)°. (e) Molecular structure of **29a**. Twist–chair conformation (TC)<sup>1</sup>, intramolecular contacts Te(3)···Te(3A) 4.3025(3), Te–C<sub>av</sub> 2.162(2), Si–C<sub>av</sub> 1.864(3) Å, C–Te–C 96.44(10)°. Contacts from different conformation Te(1)···Te(3) 4.687(1) Å. (f) Molecular structure of **29b**. Twist–chair conformation (TC), intramolecular contacts Te(1)···Te(1A) 4.2574(3), Te–C<sub>av</sub> 2.162(2), Si–C<sub>av</sub> 1.873(3) Å, C–Te–C 96.16(10)° (see Supporting Information for further details).

atoms are substantially far apart (the van der Waals S···S distance is 3.7 Å)<sup>2k,16b</sup> and would be expected to interact less than in **4** (S···S distance 3.58 Å),<sup>2k</sup> presumably a consequence of replacing ring C–C bonds and C–C–C angles with longer C–Si bonds and wider C–Si–C angles. The C–Si bonds sustain an angle of 37.4° to the C–S–C planes, facilitating interaction of the C–Si orbitals with the lone pair *p*-orbitals on the S atoms.

The boat–boat and twist–chair conformations adopted by **27a** and **27c** in their solid-state structures place the transannular Se atoms far from each other, e.g. Se···Se 4.769 and 4.653 Å in the X-ray structures for **27a** and **27c**, respectively. These distances are considerably longer than that (3.780 Å) found in 3,3,7,7-tetramethyl-1,5-diselenocane<sup>4g</sup> and longer than the van der Waals Se···Se distance of 4.0 Å,<sup>16b</sup> likely a consequence, as discussed for **25a**, of substituting Si or Sn for C. In the conformations adopted, the C–Si and C–Sn bonds are oriented for interaction with the lone pair *p*-type orbitals on Se perpendicular to the C–Se–C planes. An unusual distorted twist–chair conformation is adopted in the solid state for **27c** (reminiscent of a chair cyclooctatetraene arrangement for the ring atoms).

**Scheme 3.** Synthesis of 1,5-Thiaselenocane (**17**), 1,5-Thiatellurocane (**18**), 1,2-Thiaselenolane (**33c**), and 1,2-Thiatelluroloane (**33d**)<sup>a</sup>



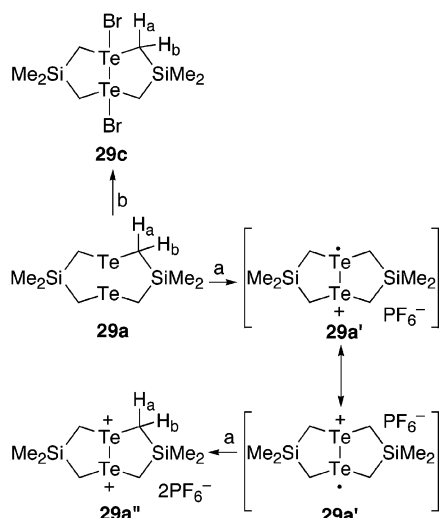
<sup>a</sup> Conditions: (a) KSeCN, THF, reflux 1 h. (b) NaI, acetone, rt, 6 d (99% two steps). (c) KSeCN or KTeCN, DMSO, rt. (d) Br(CH<sub>2</sub>)<sub>3</sub>Br, NaBH<sub>4</sub>, EtOH, rt (**32a**, 48%; **32b**, 32%; each two steps). (e) KOH, EtOH, rt (**17**, 88%; **18**, 37%). (f) KOH, EtOH, 0 °C (**33c**, 25% from **30**; **33d**, 40% from **30**).

The solid-state structure of ditelluroether **29a** reveals molecules of two different conformations in the unit cell (Figure 1): boat–boat (BB2)<sup>16</sup> and twist–chair (TC)<sup>16</sup> in a 2:1 ratio. In the BB2 conformation, all atoms are crystallographically independent, whereas in the TC conformation, the ring sits on an inversion center (only half of the molecule is crystallographically independent). The Te···Te distances in the two different conformations are 5.033 and 4.303 Å, respectively. The structure of **29b** shows a twist–chair (TC) conformation with a Te···Te distance of 4.257 Å, which is smaller than the calculated Te···Te separation in 1,5-ditellurocane (**16**) as well as the van der Waals distance (4.4 Å).<sup>16b</sup> The extent of interaction between the chalcogen *p*-type lone pair orbitals and C–Si, Si–Si and C–Sn  $\sigma$ -orbitals in **25**, **27** and **29**, is evaluated from TCNE-CT complex spectroscopic data and PES and computational studies on **25**, **27**, and **29** to be reported elsewhere.<sup>8</sup> Electrochemical studies provide oxidation potentials for these compounds and relative stabilities of the corresponding oxidized products.<sup>8b</sup>

**1c. Synthesis of 1,5-Thiaselenocane (17) and 1,5-Thiatellurocane (18).** In connection with our exploration of the chemistry of radical cations and dications of **25**, **27**, and **29**, discussed below, we also examined aspects of the reactivity of radical cations and dications of heterocycles **4**, **15**, and **16**, as well as new heterocycles **17** and **18**. The previously unknown 1,5-dichalcogenocanes containing two different chalcogen atoms **17** and **18** (Scheme 3) were prepared using a stepwise process starting from 1-bromo-3-chloropropane via intermediates **30**–**32**. Dibenzo analogues of **17** and **18** are known.<sup>17</sup> 1,2-Thiaselenolane (**33c**) and 1,2-thiatelluroloane (**33d**), required for other purposes (see below), were also synthesized from **31**.

**1d. Sequential One-Electron Oxidation of 25a, 27a, and 29a Giving Radical Cations and Dications.** Treatment of **29a** ([8]Te<sub>2</sub>Si<sub>2</sub>) with 2 equiv of the one-electron oxidant NOPF<sub>6</sub> gives the corresponding dication **29a''** (Scheme 4) as shown by the <sup>1</sup>H (see Figure 5), <sup>13</sup>C, and <sup>125</sup>Te NMR spectra. When 1.0 equiv of NOPF<sub>6</sub> is added, the reaction mixture takes on a

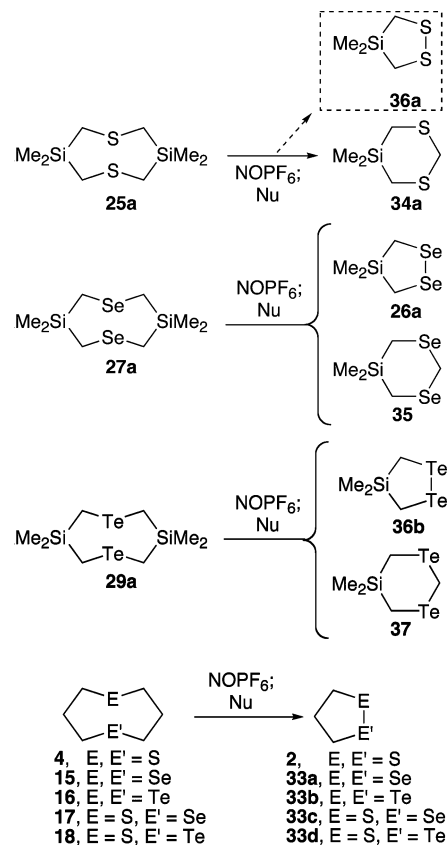
(17) (a) Fujihara, H.; Mima, H.; Chiu, J. J.; Furukawa, N. *Tetrahedron Lett.* **1990**, *31*, 2307–2310. (b) Takaguchi, Y.; Fujihara, H.; Furukawa, N. *Organometallics* **1996**, *15*, 1913–1919.

**Scheme 4.** Radical Cation, Dication, and Dibromide Formation in **29a<sup>a</sup>**

<sup>a</sup> Conditions: (a) NOPF<sub>6</sub>, CD<sub>3</sub>CN–CD<sub>2</sub>Cl<sub>2</sub>, –78 °C to room temperature. (b) Br<sub>2</sub>.

red color, presumably due to formation of a radical cation. After 2.0 equiv of NOPF<sub>6</sub> is added, the solution of **29a''** becomes colorless. A comparison of the NMR data for **29a** (<sup>1</sup>H δ 1.67 (s, 8H, CH<sub>2</sub>), 0.18 (s, 12H, Me); <sup>13</sup>C δ 0.4 (CH<sub>3</sub>), –17.0 (CH<sub>2</sub>); <sup>125</sup>Te δ 75.2) and **29a''** (<sup>1</sup>H δ 2.73 (d, *J* = 12.8 Hz, 4H), 2.49 (d, *J* = 12.8 Hz, 4H), 0.30 (s, 6H), 0.26 (s, 6H); <sup>13</sup>C δ 15.2 [TeC], 2.19 [CH<sub>3</sub>]; <sup>125</sup>Te δ 1068; Table 1) shows a notable deshielding at tellurium (δ 75.2 versus 1068 ppm) along with smaller but still significant deshielding at all protons and carbon atoms. Both the methyl groups on silicon and the methylene protons (H<sub>a</sub>, H<sub>b</sub>) in **29a''** are nonequivalent. These NMR results are in good agreement with <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR data on dication **16''** from 1,5-ditellurocane **16**.<sup>2e</sup> Efforts to characterize the intermediate radical cation **29a'** by ESR under a variety of conditions were not successful. Treatment of **29a** with 1 equiv of bromine gives a bicyclic dibromide **29c**, whose NMR spectra in DMSO-*d*<sub>6</sub> are similar to those of **29a''** (<sup>1</sup>H NMR δ 2.76 (d, *J* = 13.2 Hz, 2H), 2.62 (d, *J* = 13.2 Hz, 4H), 0.31 (s, 6H), 0.30 (s, 6H); <sup>13</sup>C δ 17.2, [TeC] 3.3 [CH<sub>3</sub>], 2.7 [CH<sub>3</sub>]; <sup>125</sup>Te δ 867).

From **25a** ([8]S<sub>2</sub>Si<sub>2</sub>) and **27a** ([8]Se<sub>2</sub>Si<sub>2</sub>), dications **25a''** (<sup>1</sup>H NMR δ 2.26 (d, *J* = 15.1 Hz, 4 H), 1.74 (d, *J* = 15.1 Hz, 4 H), 0.44 (s, 6 H), 0.42 (s, 6 H)) and **27a''** (<sup>1</sup>H NMR δ 2.39 (d, *J* = 13.6 Hz, 4 H), 1.96 (d, *J* = 13.6 Hz, 4 H), 0.41 (s, 6 H), 0.39 (s, 6 H)), respectively, can be prepared. For the dication series **25a''**, **27a''**, **29a''**, *J*<sub>HaHb</sub>, and Δ*δ*<sub>H<sub>a</sub> – H<sub>b</sub></sub> decrease, the CH<sub>2</sub> protons become more deshielded, and the Si–Me protons become more shielded. Our results are notable because of the simplicity of the <sup>1</sup>H NMR spectra of the dications (see Figure 5) due to the absence of adjacent CH<sub>2</sub> groups, which greatly complicate the <sup>1</sup>H NMR spectra of dications of 1,5-dichalcogenocanes.<sup>2e,18</sup> Heterocycles **17** ([8]SSe) and **18** ([8]STe) also undergo ready oxidation with NOPF<sub>6</sub>. Because the consequences of oxidation are different than what is observed for **25a** ([8]S<sub>2</sub>Si<sub>2</sub>), **27a** ([8]Se<sub>2</sub>Si<sub>2</sub>), and **29a** ([8]Te<sub>2</sub>Si<sub>2</sub>), these results are discussed elsewhere.<sup>8b</sup>

**Scheme 5.** Ring Contraction Products Formed upon One- and Two-Electron Oxidation of Eight-Membered Chalcogen-Containing Mesocyclic Rings with NOPF<sub>6</sub>

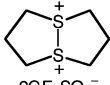
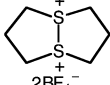
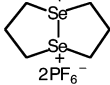
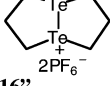
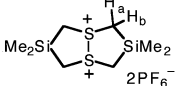
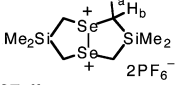
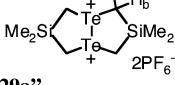
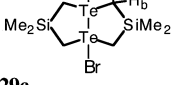
#### Ie. Formation of Five- and Six-Membered Rings by Fragmentation of Eight-Membered Ring Radical Cations and/or Dications.

When mesocycles **25a**, **27a**, and **29a** are sequentially treated at –78 °C with one and then two equivalents of NOPF<sub>6</sub>, the solutions first take on a red-orange color, which lightens with the addition of the second equivalent of NOPF<sub>6</sub> and warming. At –78 °C, <sup>1</sup>H NMR spectra of dications **25a''**, **27a''**, and **29a''** can be obtained; for **29a''**, <sup>13</sup>C NMR spectra can also be obtained. Dication **29a''** is stable up to ca. 10 °C, whereas **25a''** and **27a''** are somewhat less kinetically stable. In most cases, quenching the reactions with thiols (ethanethiol or 2-propanethiol), alcohols (methanol or ethanol), or water following the addition of 1 or 2 equiv of NOPF<sub>6</sub> leads to mixtures of five- and six-membered ring heterocycles (Scheme 5) along with the recovered mesocycles, together with disulfide when thiols are used. An exception is the dication **29a''**, which gives a complex mixture upon quenching. The ratio of the five- and six-membered ring heterocycles shows considerable variation in these reactions, as summarized in Table 2. Disulfide formation with regeneration of starting material may occur either by electron transfer or by nucleophilic attack of thiol on the dication followed by thiol attack on chalcogen-bound thiolate.

Analogous reactions are also found with 1,5-dithiocane (**4**, [8]S<sub>2</sub>), and related mesocycles **15** ([8]Se<sub>2</sub>) and **16** ([8]Te<sub>2</sub>), which give 1,2-dithiolane (**2**) and 1,2-dichalcogenolanes **33a** and **33b**, respectively. In all cases products were identified through comparison with authentic materials, synthesized as described below, or in the case of known compounds 1,2-diselenolane (**33a**)<sup>10f</sup> and 1,2-ditellurolane (**33b**),<sup>19a</sup> as described

(18) (a) Musker, W. K.; Wolford, T. L.; Roush, P. *J. Am. Chem. Soc.* **1978**, *100*, 6416–6421. (b) Fujihara, H.; Kawada, A.; Furukawa, N. *J. Org. Chem.* **1987**, *52*, 4254–4257. (c) Fujihara, H.; Akaishi, R.; Furukawa, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 616–617. (d) Fujihara, H.; Akaishi, R.; Erata, T.; Furukawa, N. *J. Chem. Soc., Chem. Commun.* **1989**, *23*, 1789–1790.

**Table 1.** NMR Spectral Data for Dications and Bicyclic Dibromide from 1,5-Dichalcogenocanes

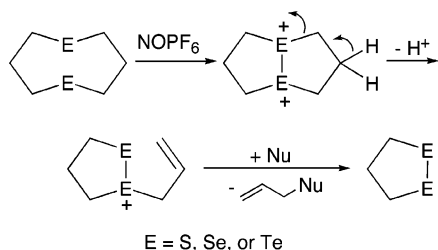
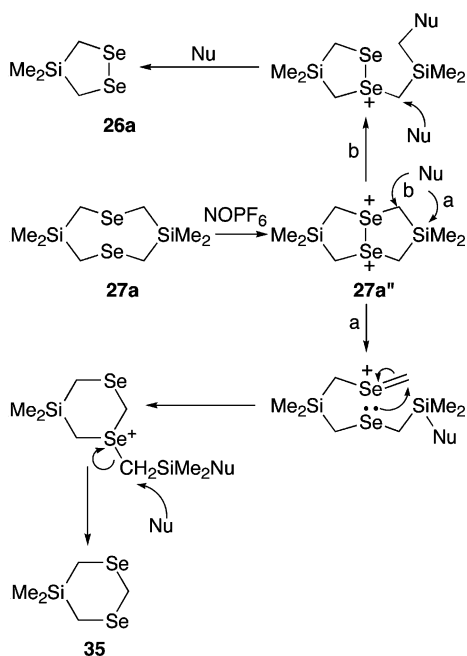
compound	$\delta$ $^1\text{H}$	$\delta$ $^{13}\text{C}$	$\delta$ $^{77}\text{Se}$	$\delta$ $^{125}\text{Te}$
 <b>4''</b> $2\text{CF}_3\text{SO}_3^-$	3.60-2.90 (m, 8H), 2.70-2.20 (m, 4H) <sup>a,c</sup>			
 <b>4''</b> $2\text{BF}_4^-$		53.0, 35.0 <sup>d</sup>		
 <b>15''</b> $2\text{PF}_6^-$	4.39-3.91 (m, 8H), 3.85-2.92 (m, 4H) <sup>a,e,j</sup>	52.6, 35.3 <sup>a,j</sup>	806.5 <sup>a,g</sup>	
 <b>16''</b> $2\text{PF}_6^-$	3.03-2.89 (m, 8H), 2.10-1.74 (m, 4H) <sup>b,f</sup>	36.1, 17.8 <sup>b</sup>		1303.7 <sup>b,h</sup>
 <b>25a''</b> $2\text{PF}_6^-$	2.26 (d, $J = 15.1$ Hz, 4 H), 1.74 (d, $J = 15.1$ Hz, 4 H), 0.44 (s, 6 H), 0.42 (s, 6 H)	--		
 <b>27a''</b> $2\text{PF}_6^-$	2.39 (d, $J = 13.6$ Hz, 4 H), 1.96 (d, $J = 13.6$ Hz, 4 H), 0.41 (s, 6 H), 0.39 (s, 6 H)	--	--	
 <b>29a''</b> $2\text{PF}_6^-$	2.73 (d, $J = 12.8$ , 4H), 2.49 (d, $J = 12.8$ , 4H), 0.30 (s, 6H), 0.26 (s, 6H)	15.2 [TeC], 2.19 [CH <sub>3</sub> ]		1068
 <b>29c</b>	2.76 (d, $J = 13.2$ Hz, 2H), 2.62 (d, $J = 13.2$ Hz, 4H), 0.31 (s, 6H), 0.30 (s, 6H)	17.2 [TeC], 3.3 [CH <sub>3</sub> ], 2.7 [CH <sub>3</sub> ]		867

<sup>a</sup> In  $\text{CD}_3\text{CN}$ . <sup>b</sup> In  $(\text{CD}_3)_2\text{SO}$ . <sup>c</sup> Reference 18c. <sup>d</sup> Reference 18a. <sup>e</sup> Reference 18d. <sup>f</sup> Reference 2e. <sup>g</sup> Precursor **15** showed  $^{77}\text{Se}$  at  $\delta$  141.3. <sup>h</sup> Precursor **16** shows  $^{125}\text{Te}$  at  $\delta$  163.5. <sup>i</sup> Precursor **29a** shows  $^{125}\text{Te}$  at 75.2. <sup>j</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR data on the bis- $\text{CF}_3\text{SO}_3$  salt of **15''** in  $\text{CH}_3\text{CN}$  agrees with the data for the  $\text{PF}_6^-$  salt (ref 2j).

**Table 2.** Products Formed by Quenching Mesocyclic Radical Cations and Dications<sup>a</sup>

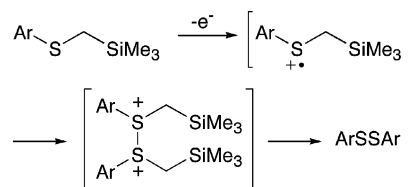
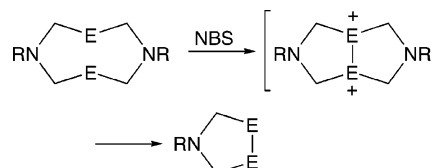
entry	reactants (color of intermediate)	quench reagent	products (ratio) <sup>b</sup>
1	<b>4</b> , 1 equiv NOPF <sub>6</sub> (yellow)	2-propanethiol	<i>i</i> -Pr <sub>2</sub> S <sub>2</sub> ; 2.4:1 <b>4:2</b>
2	<b>15</b> , 1 equiv NOPF <sub>6</sub> (orange)	2-propanethiol	<i>i</i> -Pr <sub>2</sub> S <sub>2</sub> ; 6.8:1 <b>15:33a</b>
3	<b>16</b> , 1 equiv NOPF <sub>6</sub> (yellow)	ethanethiol	Et <sub>2</sub> S <sub>2</sub> ; <b>33b</b>
4	<b>25a</b> , 1 equiv NOPF <sub>6</sub> (orange)	ethanethiol	Et <sub>2</sub> S <sub>2</sub> ; recovered <b>25a</b>
5	<b>25a</b> , 2 equiv NOPF <sub>6</sub> (light yellow)	ethanethiol	Et <sub>2</sub> S <sub>2</sub> ; 17:1 <b>25a:34a</b>
6	<b>27a</b> , 1 equiv NOPF <sub>6</sub> (orange red)	ethanethiol	Et <sub>2</sub> S <sub>2</sub> ; 55:3:1 <b>27a:35:26a</b>
7	<b>27a</b> , 2 equiv NOPF <sub>6</sub> (light yellow)	ethanethiol	Et <sub>2</sub> S <sub>2</sub> ; 5.5:1 <b>35:26a</b>
8	<b>27a</b> , 2 equiv NOPF <sub>6</sub> (light yellow)	methanol	8.6:1 <b>35:26a</b>
9	<b>29a</b> , 1 equiv NOPF <sub>6</sub> (red)	ethanethiol	<b>37:36b</b> 1:4.3
10	<b>29a</b> , 1 equiv NOPF <sub>6</sub> (red)	ethanol	<b>37:36b</b> 3.3:1

<sup>a</sup> Solvent,  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ ; **2**, 1,2-dithiolane; **4**, 1,5-dithiocane; **15**, 1,5-diselenocane; **16**, 1,5-ditellurocane; **25a**, 3,3,7,7-tetramethyl-1,5-dithia-3,7-disilocane; **26a**, 4,4-dimethyl-1,2,4-diselenasilolane; **27a**, 3,3,7,7-tetramethyl-1,5-diselena-3,7-disilocane; **29a**, 3,3,7,7-tetramethyl-1,5-ditellura-3,7-disilocane; **33a**, 1,2-diselenolane; **33b**, 1,2-ditellurane; **33c**, 1,2-thiaselenolane; **33d**, 1,2-thiatellurane; **34a**, 5,5-dimethyl-1,3,5-dithiasilane; **35**, 5,5-dimethyl-1,3,5-diselenasilane; **36b**, 4,4-dimethyl-1,2,4-ditellurasilane; **37**, 5,5-dimethyl-1,3,5-ditellurasilane (see Scheme 5 for structures). <sup>b</sup> Analysis by GC-MS.

**Scheme 6.** Proposed Mechanism for 1,2-Dichalcogenolane Formation from 1,5-Dichalcogenocane Dications**Scheme 7.** Proposed Mechanism for Ring Contraction of Dication **27a''** to **26a** and **35**<sup>a</sup>

in the literature. Formation of 1,2-dichalcogenolanes **2**, **33a**, and **33b** from mesocycles **4**, **15**, and **16**, respectively, following NOPF<sub>6</sub> oxidation, can be rationalized by fragmentation initiated by proton loss<sup>21a</sup> followed by nucleophile-induced C–E' (chalcogen) cleavage (Scheme 6).<sup>21f</sup> In the case of **4** and **15–18**, gas-phase fragmentation giving **2** and **33**, respectively, is also seen in the mass spectrum, as previously noted for **4**.<sup>19b</sup> It is relevant that the stable radical cation of 1,2-dithiolane **2** is easily formed by AlCl<sub>3</sub> oxidation.<sup>19c</sup> Interestingly, the mass spectrum of **29a** ([8]Te<sub>2</sub>Si<sub>2</sub>) shows a cluster of peaks (50% abundance relative to base peak **29a**) corresponding to **36b** (Scheme 5),

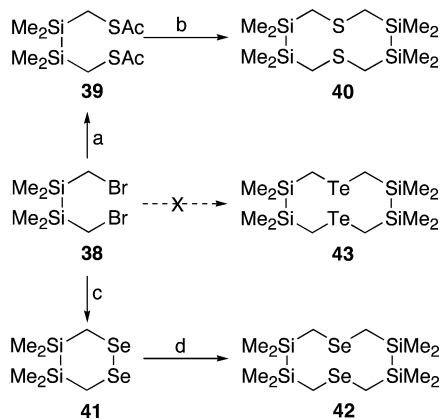
- (19) (a) Lakshmikantham, M. V.; Cava, M. P.; Gunther, W. H. H.; Nugara, P. N.; Belmore, K. A.; Atwood, J. L.; Craig, P. *J. Am. Chem. Soc.* **1993**, *115*, 885–887. (b) Musker, W. K.; Gorewit, B. V.; Roush, P. B.; Wolford, T. L. *J. Org. Chem.* **1978**, *43*, 3235–3236. (c) Bock, H.; Stein, U. *Angew. Chem., Int. Ed.* **1980**, *19*, 834–835.
- (20) Suslova, E. N.; Albanov, A. I.; Shainyan, B. A. *J. Organomet. Chem.* **2003**, *677*, 73–79.
- (21) (a) Furukawa, N.; Shima, H.; Ogawa, S. *Heteroatom Chem.* **1995**, *6*, 559–565. (b) Takikawa, Y.; Koyama, Y.; Yoshida, T.; Shimada, K.; Kabuto, C. *Chem. Lett.* **1995**, 277–278. (c) Takikawa, Y.; Yoshida, T.; Koyama, Y.; Sato, K.; Shibata, Y.; Aoyagi, S.; Shimada, K.; Kabuto, C. *Chem. Lett.* **2000**, 870–871. (d) A short Se...Se distance of 3.858 Å is reported in 1,5,3,7-diselenadiazocane.<sup>21b</sup> (e) Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. *Tetrahedron* **1981**, *37*, 2743–2747. (f) A reviewer proposed an alternative mechanism in which the α-proton of the dication is removed to generate an ylide, which undergoes C–E cleavage to generate a carbene. The carbene then undergoes C–H insertion forming the allylic intermediate shown in Scheme 6. We prefer the mechanism shown in Scheme 6 because we believe that the proposed ylide would more likely undergo rapid E–E cleavage with concomitant formation of –E<sup>+</sup>=CH, which could then cyclize to a six-membered ring.

**Scheme 8.** Disulfide Formation upon Electrochemical Oxidation of a β-Silylsulfide**Scheme 9.** Oxidative Syntheses of 1,2,4-Diselenazolidines and 1,2,4-Ditellurazolidines from 1,5,3,7-Diselenadiazocane and 1,5,3,7-Ditelluradiazocane Precursors, Respectively (E = Se or Te)

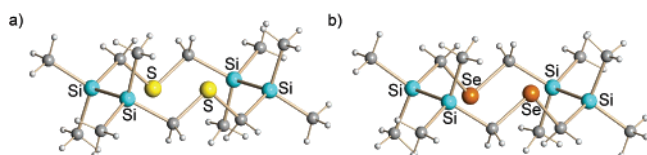
e.g., from loss of 1,1-dimethylsilirane (Me<sub>2</sub>Si(CH<sub>2</sub>)<sub>2</sub>). In the case of **25a** ([8]S<sub>2</sub>Si<sub>2</sub>), **27a** ([8]Se<sub>2</sub>Si<sub>2</sub>), and **29a** ([8]Te<sub>2</sub>Si<sub>2</sub>), we suggest (Scheme 7, path a) that nucleophilic attack by oxygen or sulfur at the silicon atom in the respective bicyclic dications results in C–Si bond cleavage and ring fragmentation, giving a chalcogen-stabilized carbocation, which recycles to a six-membered ring, followed by nucleophilic cleavage of the carbon–oxygen chalcogen bond.

1-Alkyl 1,3-thiasilacycloalkane salts are particularly susceptible to attack at silicon by methanol and water.<sup>20</sup> Alternatively, nucleophilic attack at carbon (twice) would result in carbon–chalcogen bond cleavage (path b), giving five-membered ring heterocycle **26a**, analogous to processes occurring during electrolysis of acyclic β-silyl sulfides affording disulfides (Scheme 8).<sup>7c</sup> The preference for path a versus path b should be governed by the comparative reactivity of the nucleophile toward silicon and carbon as well as the relative strength of the carbon–chalcogen bonds. This proposal is supported by the preference following oxidation of tellurium mesocycle **29a** for formation of the six-membered ring **37** over five-membered ring **36b** with the more silaphilic reagent ethanol, whereas the less silaphilic but better carbon-nucleophile ethanethiol favors **36** over **37**. The fact that 4,4-dimethyl-1,2,4-dithiasilolane (**36a**; see below for synthesis) could not be detected in experiments involving radical cation and dications **25a'** and **25a''** may be a consequence of the relative strength of the C–S bond compared to the C–Se and C–Te bonds, disfavoring path b in the case of dication **25a''**. Because the cation radicals can disproportionate to dications and the parent mesocycles (Scheme 1), in some cases the dications may also be responsible for nucleophile-induced processes when one equivalent of NOPF<sub>6</sub> is used. Precedence for the above processes includes reactions in cyclic systems<sup>21a</sup> analogous to that shown in Scheme 8<sup>7c</sup> as well as oxidative syntheses of 1,2,4-diselenazolidines and 1,2,4-ditellurazolidines (Scheme 9).<sup>21b–d</sup> Ring-contractions have not been previously reported for dications from **4** ([8]S<sub>2</sub>), **15** ([8]Se<sub>2</sub>), and **16** ([8]Te<sub>2</sub>). Enhanced ring contraction associated with radical cations or dications from **25**, **27**, and **29** compared to **4**, **15**, and **16** is presumably due to ease of nucleophilic attack at silicon, or at an α-silyl carbon, compared to deprotonation-induced fragmentation.

**II. Ten-Membered Ring Systems. IIa. Synthesis of 1,6-Dichalcogeno-3,4,8,9-tetrasilocanes.** The ready availability of

**Scheme 10.** Synthesis of 1,6-Dichalcogena-3,4,8,9-disilocanes<sup>a</sup>

<sup>a</sup> Conditions: (a) KSAc, THF (73%); (b) **38**, KOH, EtOH (30%); (c)  $\text{Na}_2\text{Se}_2$ , EtOH (40%); (d) **38**,  $\text{NaBH}_4$ , EtOH/THF (41%).

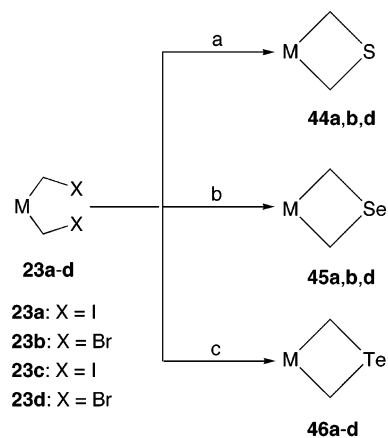


**Figure 2.** (a) Molecular structure of **40**. [1414] conformation,<sup>21e</sup> intramolecular contacts  $\text{S}\cdots\text{S}$  3.6648(5), Si–Si 2.3450(4), S–Si 3.0511(4), 4.2566(4), S–C<sub>av</sub> 1.8068(11), Si–C<sub>av</sub> 1.8915(12), intermolecular contacts  $\text{S}\cdots\text{S}$  4.855(1) Å, C–S–C<sub>av</sub> 102.39(5)°, C–Si–Si<sub>av</sub> 109.86(4)°, torsion angles C–S–C–Si 160.36(6)°, S–C–Si–Si<sub>av</sub> 81.87(6)°. (b) Molecular structure of **42**. [1414] conformation, intramolecular contacts  $\text{Se}\cdots\text{Se}$  3.8136(3), Si–Si 2.3464(6), Se–Si<sub>av</sub> 3.1652(4), 4.3495(5), Se–C<sub>av</sub> 1.9554(16), Si–C<sub>av</sub> 1.8868(16), intermolecular contacts  $\text{Se}\cdots\text{Se}$  4.901(1) Å, C–Se–C<sub>av</sub> 99.48(7)°, C–Si–Si<sub>av</sub> 110.15(5)°, torsion angles C–Se–C–Si 157.66(8)°, Se–C–Si–Si<sub>av</sub> 83.16(8)° (see Supporting Information for further details).

**38**<sup>10a</sup> encouraged us to attempt syntheses of previously unknown mesocycles **40–43** (Scheme 10) by the protocol used to prepare **25**, **27**, and **29**. This approach proved partially successful, affording nicely crystalline 10-membered rings **40** ([10]S<sub>2</sub>(Si<sub>2</sub>)<sub>2</sub>) and **42** ([10]Se<sub>2</sub>(Si<sub>2</sub>)<sub>2</sub>), both of which can be characterized by X-ray crystallography (Figure 2). Unfortunately, 10-membered ring tellurium compound **43** ([10]Te<sub>2</sub>(Si<sub>2</sub>)<sub>2</sub>) cannot be prepared by methods that worked for **29**, instead giving **52c** ([5]Te(Si<sub>2</sub>)), Scheme 13, below). Like 8-membered rings **25a** and **27a**, 10-membered rings **40** and **42** show sharp singlets for their ring CH<sub>2</sub> protons. The <sup>1</sup>H and <sup>13</sup>C NMR shifts for both **40** and **42** are slightly deshielded relative to those in **25a** and **27a**, respectively. Mesocycles **40** and **42** offer the opportunity to examine the interaction of the sulfur and selenium upon electron loss with β-C–Si as well as γ-Si–Si orbitals associated with a pair of endocyclic Si–Si bonds as well as the conformational consequences of replacing four CH<sub>2</sub> groups in **5** with four SiMe<sub>2</sub> groups.

### Ib. Structure of 1,6-Dichalcogena-3,4,8,9-tetrasilocanes.

X-ray crystal structures of **40** and **42** (Figure 2) show that in both cases the Si–Si bonds are almost perpendicular to the CSC or CSeC planes, ideal for interaction of the Si–Si orbitals with the sulfur or selenium *p*-type lone-pair orbitals, which are normal to the CSC and CSeC planes, respectively. The S⋯S distance in **40** is 3.6648(5) Å while the Se⋯Se distance in **42** is 3.8136(3) Å. These values are slightly shorter than the van der Waals S⋯S and Se⋯Se radii of 3.7 and 4.0 Å,<sup>16b</sup> respectively. The extent of interaction between the endocyclic Si–Si orbitals in

**Scheme 11.** Synthesis of 1,3-Thiasiletanes, 1,3-Selenasiletanes, 1,3-Tellurasiletanes, and 1,3-Tellurastannetanes<sup>a</sup>

**23a:** X = I  
**23b:** X = Br  
**23c:** X = I  
**23d:** X = Br

**a:** M = Me<sub>2</sub>Si; **b:** M = (Me<sub>3</sub>Si)<sub>2</sub>Si; **c:** M = Me<sub>2</sub>Sn; **d:** M = Me(<sup>t</sup>Bu)Si

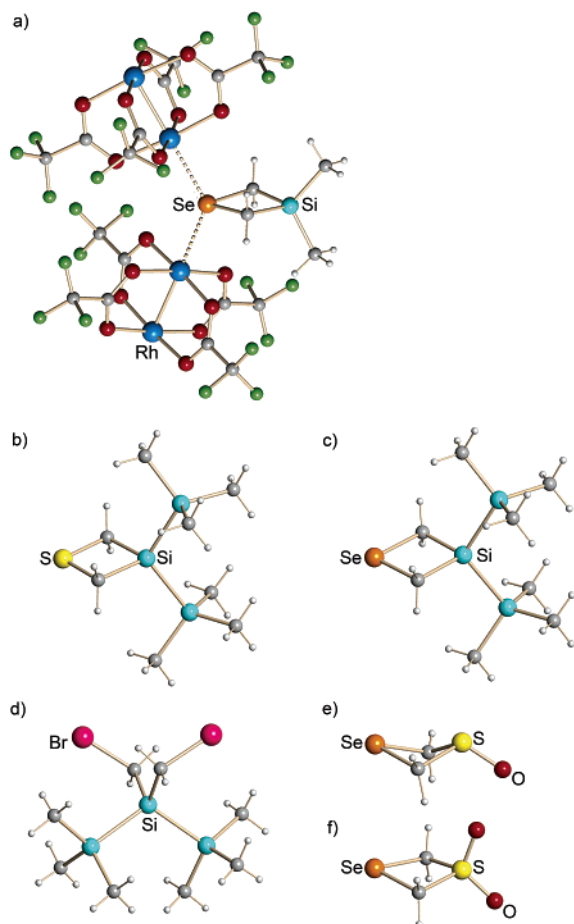
<sup>a</sup> Conditions: (a) KHS, EtOH (**44a**, 55%); Li<sub>2</sub>S, THF (**44b**, 43%); Li<sub>2</sub>S, THF (**44d**, 31%). (b) Li<sub>2</sub>Se (**45a**, 60%; **45b**, 57%; **45d**, 47%). (c) Na<sub>2</sub>Te, EtOH (**46b**, 66%; **46d**, 68%; **46a**, **46c**, yields not determined).

**40** and **42** and the filled *3p* and *4p* orbitals on sulfur and selenium, respectively, has been evaluated through measurement of TCNE-CT complex  $\lambda_{\text{max}}$  values along with PES and electrochemical studies, discussed elsewhere.<sup>8</sup> The conformations of ten-membered rings have been previously described; compounds **40** and **42** can be said to have [1414] conformations.<sup>21e</sup>

**III. Four-Membered Ring Systems. IIIa. 1,3-Thia-, 1,3-Selena-, and 1,3-Tellurasiletanes.** Of the 1,3-diheterocyclobutanes containing both Group 14 and 16 elements, 1,3-oxasiletanes, 1,3-thiasiletanes (e.g. 3,3-dimethyl-1,3-thiasiletane, **44a** ([4]SSi), Scheme 11)<sup>22a–e</sup> and 1,3-thiagermetanes<sup>22f–i</sup> are known, but heterocycles containing other combinations of S(Se,Te) and Si(Sn) are unknown.<sup>22j,k</sup> We initially examined the reaction of **23** with chalcogenide anions (S<sup>2–</sup>, Se<sup>2–</sup>, Te<sup>2–</sup>) as a possible one-step approach to mesocycles **25**, **27**, and **29** but discovered that the major products of these reactions were instead 1,3-diheterocyclobutanes **44–46**, with at best trace amounts of **25**, **27**, and **29**. Under optimized conditions, **23a** reacted smoothly with Li<sub>2</sub>Se to give 3,3-dimethyl-1,3-selenasiletane (**45a**, [4]SeSi) a new heterocycle, in 60% yield. Although commercially available bis(chloromethyl)dimethylsilane can also be used, **23a** gives higher yields and cleaner reactions with Li<sub>2</sub>Se. As in the case of synthesis of **25**, **27**, and **29**, in ring closures using α,ω-dihalides with Li<sub>2</sub>S, Li<sub>2</sub>Se or Na<sub>2</sub>Te, diiodides or dibromides are preferred over dichlorides, allowing displacements to be carried out at the lowest possible

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**Figure 3.** (a) Molecular structure of  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot 45\text{a}$ . Rh–Rh<sub>av</sub> 2.4256(8), Rh–Se 2.5901(7), 2.5970(7) Å, Rh–Se–Rh 130.35(3), C–Se–C 85.8(3)°. (b) Molecular structure of **44b**. Intramolecular contact S···Si 2.6589(8), S–C 1.8257(16), Si–C<sub>ring</sub> 1.9113(15) Å, C–S–C 91.91(9), C–Si–C<sub>ring</sub> 86.72(10)°. (c) Molecular structure of **45b**. Intramolecular contact Se···Si 2.7742(6), Se–C 1.9792(15), Si–C<sub>ring</sub> 1.9090(15) Å, C–Se–C 86.94(8), C–Si–C<sub>ring</sub> 91.01(9)°. (d) Molecular structure of **23b**. C–Br 1.953(2), Si–Si 2.3551(7), Si–C 1.886(2) Å, C–Si–C 106.89(16), Si–Si–Si 112.58(4)°. (e) Molecular structure of **48**. Intramolecular contact S···Se 2.6597(7), S–O<sub>av</sub> 1.487(2), S–C<sub>av</sub> 1.798(3), Se–C<sub>av</sub> 1.961(3) Å, C–S–C<sub>av</sub> 84.67(14), C–Se–C<sub>av</sub> 76.28(12)°. (f) Molecular structure of **49**. Intramolecular contact S···Se 2.7029(16), S–O<sub>av</sub> 1.439(5), S–C<sub>av</sub> 1.781(6), Se–C<sub>av</sub> 1.970(7) Å, C–S–C 92.0(3), C–Se–C 81.1(2)° (see Supporting Information for further details).

temperatures, an important consideration for reactive and unstable four-membered ring systems.

Compound **45a**, a colorless volatile liquid, can be fully characterized by spectroscopic methods as well as by X-ray crystallography of its complex with dirhodium tetrakis(trifluoroacetate)  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$  (Figure 3). This latter reagent is particularly useful in characterizing a variety of Lewis bases, including those that are liquids.<sup>23</sup> Reaction of **23a** with  $\text{Na}_2\text{Te}$  under the above conditions gives 3,3-dimethyl-1,3-tellurasiletane **46a** ( $[\text{4TeSi}]$ ), which is stable for less than 24 h in solution, even when refrigerated, but can still be characterized by GC-MS and spectroscopic methods. Ethanol is the preferred solvent for **46a**; all aprotic solvents examined lead to rapid decomposition.

By increasing the steric bulk at silicon in mixed silicon-chalcogen four-membered ring systems, the reactivity of the heterocycles can be reduced, the volatility decreased, and the melting points increased, facilitating isolation, purification, and

characterization. Thus, treatment of **23b** with  $\text{Li}_2\text{S}$ ,<sup>24a</sup>  $\text{Li}_2\text{Se}$ ,<sup>24b</sup> or  $\text{Na}_2\text{Te}$ <sup>24c</sup> gives 3,3-bis(trimethylsilyl)-1,3-thiasiletane, -selenasiletane, and -tellurasiletane (**44b**, **45b**, and **46b** ( $[\text{4SSi}(\text{TMS})_2]$ ,  $[\text{4SeSi}(\text{TMS})_2]$ , and  $[\text{4TeSi}(\text{TMS})_2]$ ), respectively), all low melting crystalline solids, which are fully characterized. Both **44b** and **45b** were further characterized by X-ray crystallography (Figure 3). With the bulkier bis(trimethylsilyl) group, tellurium compound **46b** proved to be somewhat more stable than **46a** ( $[\text{4TeSi}]$ ), although it still was quite reactive.

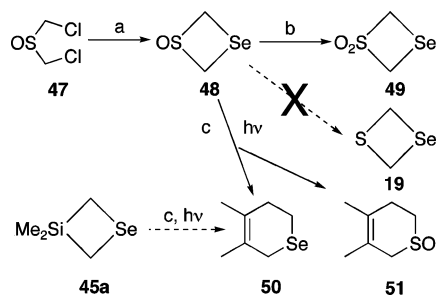
By a similar process, bis(bromomethyl)(*tert*-butyl)methylsilane **23d** can be used to prepare **44d**, **45d**, and **46d** ( $[\text{4SSi}(t\text{-BuMe})]$ ,  $[\text{4SeSi}(t\text{-BuMe})]$ , and  $[\text{4TeSi}(t\text{-BuMe})]$ ) as moderately stable liquids, with diastereotopic ring  $\text{CH}_2$  protons (**44d**,  $J = 13$  Hz; **45d**, **46d**,  $J = 12$  Hz) along with other spectroscopic data consistent with the proposed structures. Tellurium compound **46d** can be stored without decomposition at  $-20$  °C for several days. Reaction of  $\text{Na}_2\text{Te}$  with bis(iodomethyl)dimethylstannane (**23c**) gives 3,3-dimethyl-1,3-tellurastannetane (**46c**,  $[\text{4TeSn}]$ ), which is only stable in solution but can be characterized by NMR and by GC-MS. The predicted pattern for the molecular ion of **46c** containing combinations of isotopes of tin and tellurium is in excellent agreement with the complex observed pattern.

The ring  $\text{CH}_2$   $^1\text{H}$  NMR shifts of **44a** ( $[\text{4SSi}]$ ), **45a** ( $[\text{4SeSi}]$ ), and **46a** ( $[\text{4TeSi}]$ ) are slightly deshielded compared to those of **25a** ( $[\text{8S}_2\text{Si}_2]$ ), **27a** ( $[\text{8Se}_2\text{Si}_2]$ ), and **29a** ( $[\text{8Te}_2\text{Si}_2]$ ), whereas the reverse is true comparing **44b** ( $[\text{4SSi}(\text{TMS})_2]$ ), **45b** ( $[\text{4SeSi}(\text{TMS})_2]$ ), and **46b** ( $[\text{4TeSi}(\text{TMS})_2]$ ) with **25b** ( $[\text{8S}_2[\text{Si}(\text{TMS})_2]_2]$ ), **27b** ( $[\text{8Se}_2[\text{Si}(\text{TMS})_2]_2]$ ), and **29b** ( $[\text{8Te}_2[\text{Si}(\text{TMS})_2]_2]$ ), respectively. The  $^{13}\text{C}$  NMR shifts of **44a,b**, **45a,b**, and **46a,b** are all shielded compared to those of **25a,b**, **27a,b**, and **29a,b**. The  $^{77}\text{Se}$  NMR shift of **45b** is  $\delta$  272, whereas the  $^{125}\text{Te}$  NMR shifts of **46a–c** are  $\delta$  204, 142, and 219, respectively, significantly deshielded from the corresponding chemical shift in eight-membered ring **29a** ( $[\text{8Te}_2\text{Si}_2]$ , ( $\delta$  75.2). Four-membered rings containing a single divalent tellurium are unknown, although 1,3-ditelluretanes and 1,3-selenatelluretanes are known,<sup>25</sup> stannetanes, four-membered rings containing tin, are highly reactive, rare, and little studied.<sup>26</sup> This is the first example of a four-membered ring containing both Te and Sn. We were unable to prepare the analogous S/Sn and Se/Sn heterocycles. Efforts to oxidize selenium in **45a** ( $[\text{4SeSi}]$ ) using *m*-CPBA led to formation of a complex mixture.

Cyclizations of bis(halomethyl)silanes are facilitated compared to cyclizations of analogous 1,3-dihalopropanes. Thus, although conversion of tetrakis(bromomethyl)methane to 2,6-diselenaspiro[3.3]heptane by  $\text{Li}_2\text{Se}$  requires 4 h in refluxing THF,<sup>28c</sup> analogous cyclization of **23d** giving **45d**,  $[\text{4SeSi}(t\text{-BuMe})]$ , occurs in 2 h at 0 °C. The facilitation of cyclization of the silicon (and tin) bis(halomethyl) systems can be attributed

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**Scheme 12.** Synthesis and (S)-Oxidation of **48**: Trapping of Selenoformaldehyde,  $\text{CH}_2=\text{Se}$ , from Photolysis of **48** and **45a**<sup>a</sup>



<sup>a</sup> Conditions: (a)  $\text{Na}_2\text{Se}$ , THF (61%). (b)  $\text{KMnO}_4$ ,  $\text{MgSO}_4$ , acetone,  $-15$  to  $-25$  °C (69%). (c) 2,3-dimethyl-1,3-butadiene,  $\text{CH}_2\text{Cl}_2$ ,  $h\nu$ , 3 h (**50** from **48**, 80%; **51** from **48**, trace; **50** from **45a**, trace).

to a combination of the greater length of Si–C (Sn–C) compared to C–C bonds and the relative enhancement of nucleophilic substitution at carbon attached to silicon (or tin) compared to carbon.<sup>27</sup> Furthermore, **23b**, characterized by X-ray crystallography using low temperature techniques (Figure 3d), shows a significantly contracted BrC–Si–CBr angle of 106.89–(16)°, <sup>28e</sup> favoring ring closure.

In these syntheses, the ratio of the amount of reducing reagent, Super Hydride, relative to the amount of S or Se used to generate the  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{Se}$ , respectively, employed in the cyclizations must be precisely controlled. Although a slight excess of Super Hydride is desirable, too much of an excess will reduce the carbon–halogen bonds. On the other hand, excess of S or Se will lead to formation of  $\text{Li}_2\text{S}_2$  or  $\text{Li}_2\text{Se}_2$  with resultant formation of five-membered rings (see below). Dilute solutions are preferred for synthesis of four-membered rings to avoid contamination with eight-membered rings, which are sometimes found as contaminants. Reaction time (as short as possible), temperature (0 °C), and solvent (THF not EtOH) must be controlled to avoid ring decomposition, e.g., through nucleophilic attack at silicon. Because many of the four-membered ring compounds decompose on silica gel, neutral alumina is favored for chromatography.

**IIIb. 1,3-Thiaselenetanes. Photochemical Generation and Trapping of Selenoformaldehyde.** Our earlier work on 1,3-dithietanes<sup>28a</sup> (e.g. **1**, [4]S<sub>2</sub>) and more recent work on selenetanes (**7**, E = Se, M = CR<sub>2</sub>)<sup>28b–d</sup> inspired efforts to synthesize related, unknown mixed S–Se systems, e.g. 1,3-thiaselenetane (**19**, [4]SSe). Through the use of the same protocol that was successful in the synthesis of 1,3-dithietane 1-oxide,<sup>28a</sup> derivatives of the little known 1,3-thiaselenetane ring system<sup>29</sup> were easily prepared (Scheme 12). Thus, bis(chloromethyl)sulfoxide (**47**) was treated with a suspension of sodium selenide (from reduction of Se with Na in THF in the presence of naphthalene)<sup>10d</sup>

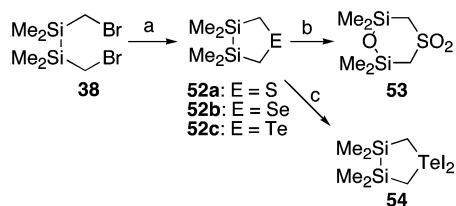
giving 1,3-thiaselenetane 1-oxide (**48**; 61%) as a colorless solid with a garlicky odor and an <sup>1</sup>H NMR spectrum similar to that of 1,3-dithietane 1-oxide<sup>28a</sup> (<sup>77</sup>Se NMR  $\delta$  –14.9, <sup>13</sup>C NMR  $\delta$  41.8, UV  $\lambda_{\text{max}}$  286). Oxidation ( $\text{KMnO}_4/\text{MgSO}_4$ )<sup>30</sup> of **48** gives 1,3-thiaselenetane 1,1-dioxide (**49**; 69%; (<sup>77</sup>Se NMR  $\delta$  –42.5, <sup>13</sup>C NMR  $\delta$  59.6). Interestingly, despite the anticipated electron withdrawing effects of the sulfinyl and sulfonyl groups, in both **48** and **49**, selenium is shielded compared to the <sup>77</sup>Se NMR chemical shift of  $\delta$  592 in **45a**. Recrystallization gives colorless crystals of **48**, mp 86–88 °C, and **49**, mp 141–143 °C. Both **48** and **49** can be characterized by X-ray crystallography (Figure 3). The mode of preparation of the sodium selenide is crucial because traces of residual NaHSe reduce sulfoxide **47**.

Efforts to deoxygenate **48** to the parent compound 1,3-thiaselenetane (**19**) as previously reported for 1,3-dithietane 1-oxide<sup>28a</sup> with  $\text{BH}_3$ -THF or other reagents were unsuccessful, precluding efforts to compare chalcogen–chalcogen interactions in **19** with those seen in **1**.<sup>31</sup> We were also unsuccessful in extending this synthetic procedure to 1,3-thiatelluretane 1-oxide using sodium telluride. The novel selective oxidation of the sulfinyl group of **48** to the sulfonyl function in **49**, rather than oxidation at selenium, is consistent with prior studies by us on the selectivity of  $\text{KMnO}_4$  in the presence of Lewis acids.<sup>30</sup> Efforts to oxidize **48** and **49** at selenium using *m*-CPBA led to an unstable and insoluble mixtures of isomeric sulfoxide/selenoxide which could not be satisfactorily characterized. Efforts to form the dication of **19** by treatment of **48** with acetic anhydride or trifluoroacetic anhydride (a procedure successfully employed to convert 1,5-dithiocane 1-oxide to dication **4''**) were also unsuccessful. Ultraviolet irradiation of **48** in the presence of excess 2,3-dimethyl-1,3-butadiene gives the known 3,4-dimethyl-1-selenacyclohex-3-ene<sup>32a</sup> **50** in 80% yield by a route that presumably involves efficient generation and trapping of selenoformaldehyde,  $\text{CH}_2=\text{Se}$ . Trace amounts of the Diels–Alder adduct **51** of sulfine can also be detected by GC-MS. While this is the first instance of photochemical solution phase generation and trapping of selenoformaldehyde, other methods have been described for generation and trapping of this highly reactive molecule.<sup>32b–e</sup> Repetition of the photochemical procedure substituting **45a** for **48** led only to trace amounts of **50**.

**IIIc. Structures of Four-Membered Rings.** Although **45a** ([4]SeSi) is a liquid, an X-ray structure can be obtained for the complex of **45a** with  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  (Figure 3a). This structure shows **45a** in the complex to be nearly planar (dihedral angle ca. 7°), with a short Se···Si distance of 2.761(2) Å. Crystals of **44b** ([4]SSi(TMS)<sub>2</sub>) and **45b** ([4]SeSi(TMS)<sub>2</sub>) were obtained in hexane at  $-78$  °C. Because both compounds have very low melting points, X-ray crystallography was carried out by manually mounting crystals in dry ice cooled dishes under a flow of cold, dry nitrogen. The crystal structures of **44b** and

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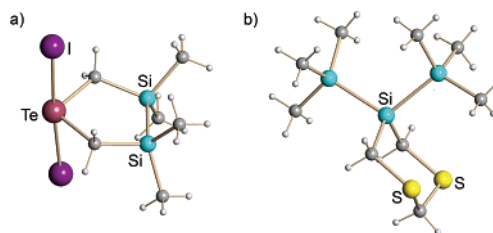
**Scheme 13.** Synthesis and Reactions of 1,3,4-Chalcogenadisilolanes<sup>a</sup>

<sup>a</sup> Conditions: (a) **52a**:  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (68%); **52b**:  $\text{Li}_2\text{Se}$  (33%); **52c**:  $\text{Na}_2\text{Te}$  (74%). (b) *m*-CPBA (71%). (c)  $\text{I}_2$  (52%).

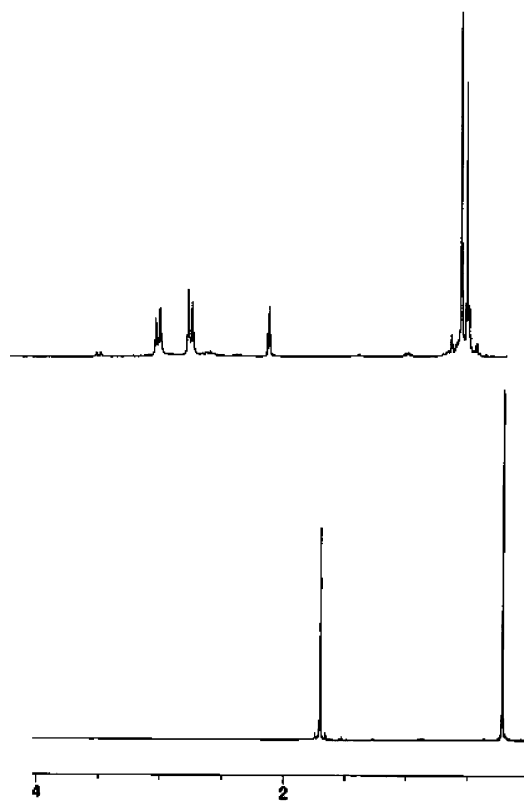
**45b** (Figure 3b,c) show that both rings are nearly planar with very short  $\text{S}\cdots\text{Si}$  and  $\text{Se}\cdots\text{Si}$  distances of 2.66 and 2.77 Å, respectively (the  $\text{S}\cdots\text{Si}$  distance, comparable to that reported for a nonplanar 3-silathietane,<sup>22a,b</sup> is shorter than the sum of the van der Waals radii for these atoms of 3.90 Å), and that the Si–Si bonds sustain angles of ca. 32° to the CSC and CSeC planes, geometries which have important implications to be discussed below. The crystal structure of **48** (Figure 3e) shows a puckered ring with an equatorial oxygen. The average dihedral angle for the ring is 32.3° (compare the corresponding dihedral angle of 39° for 1,3-dithietane 1-oxide as determined by gas-phase microwave spectroscopy)<sup>28a</sup> whereas the short  $\text{S}\cdots\text{Se}$  distance averages 2.6615 Å (2.6597(7)/2.6633(7) Å for two different molecules of **48** measured in the same unit cell). The crystal structure of **49** (Figure 3f) shows a more nearly planar ring with an average dihedral angle for the ring of 12.6° and a short  $\text{S}\cdots\text{Se}$  distance of 2.703(2) Å. The mass spectra (MS) of heterocycles **44**–**46** all show a major fragment  $\text{R}_2\text{ME}^+$ , where M = Si or Sn and E = S, Se or Te. MS fragmentation giving  $\text{Me}_2\text{SiS}^{+}$  is known for **44a** ( $[\text{4SSi}]$ ).<sup>22c</sup>

**IV. Five-Membered Ring Systems. IVa. 1,2,4-Dithia- and 1,2,4-Diselenasilolanes and 1,2,4-Dithia- and 1,2,4-Diselenastannolanes.** Bis(acetylthiomethyl)silanes **24** on sequential treatment with NaOMe and then iodine gives the corresponding 1,2,4-dithiasilolanes, e.g. **36a**,  $[\text{5}](\text{S}_2)\text{Si}$  (Scheme 5). 1,2,4-Dithiasilolanes can also be obtained by reaction of bis(halomethyl)silanes **23** with  $\text{Li}_2\text{S}_2$ , prepared by reduction of sulfur powder with Super Hydride. Five-membered Si- or Sn-containing diselenides **26a–c** ( $[\text{5}](\text{Se}_2)\text{Si}$ ,  $[\text{5}](\text{Se}_2)\text{Si}(\text{TMS})_2$ ,  $[\text{5}](\text{Se}_2)\text{Sn}$ ; Scheme 2) are formed by nucleophilic attack of  $\text{Na}_2\text{Se}_2$  (prepared by reduction of selenium powder with  $\text{NaBH}_4$  at reflux in EtOH) on the corresponding dihalides **23a–c** in EtOH at 0 °C. Efforts to prepare 1,2,4-ditellurasilolanes (e.g. **36b**,  $[\text{5}](\text{Te}_2)\text{Si}$ , Scheme 5) using  $\text{Na}_2\text{Te}_2$  and bis(halomethyl)silanes **23** led to products corresponding to 1,2,4-ditellurasilolanes, which can be detected by GC-MS but decompose during the workup, giving solid precipitates.

**IVb. 1,3,4-Thia-, 1,3,4-Selena-, and 1,3,4-Telluradisilolanes.** Efforts to synthesize **43** (Scheme 10) led instead to five-membered ring compound **52c** (Scheme 13). 1,3,4-Chalcogenadisilolanes **52** could be readily prepared from 1,2-bis-(bromomethyl)-1,1,2,2-tetramethyldisilane (**38**). Thus, treatment of **38** with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ,  $\text{Li}_2\text{Se}$  or  $\text{Na}_2\text{Te}$  gives 3,3,4,4-tetramethyl-1,3,4-thiadisilolanes, -1,3,4-selenadisilolanes, and -1,3,4-telluradisilolanes **52a–c** ( $[\text{5}]\text{S}(\text{Si}_2)$ ,  $[\text{5}]\text{Se}(\text{Si}_2)$ ,  $[\text{5}]\text{Te}(\text{Si}_2)$ ), respectively in 68, 33, and 74% yields as oils. None of the mixed Group 14/16 five-membered ring compounds have been previously reported; theoretical calculations have been performed on the des-methyl analogue of **52a**.<sup>33</sup> Oxidation of **52a** with excess *m*-CPBA results in insertion of oxygen into the Si–Si



**Figure 4.** (a) Molecular structure of **54**. Intramolecular contact  $\text{Te}\cdots\text{Si}_{\text{av}}$  3.3933(16),  $\text{Te}-\text{C}_{\text{av}}$  2.137(6),  $\text{Te}-\text{I}_{\text{av}}$  2.9045(7),  $\text{Si}-\text{Si}$  2.350(2) Å,  $\text{I}-\text{Te}-\text{I}$  176.45(2)°. (b) Molecular structure of **34b**. Chair conformation, intramolecular contacts  $\text{S}\cdots\text{S}$  3.0850(4),  $\text{Si}-\text{Si}_{\text{av}}$  2.3498(4),  $\text{S}-\text{Si}_{\text{av}}$  3.1065(4),  $\text{S}-\text{C}_{\text{av}}$  1.8114(12),  $\text{Si}-\text{C}_{\text{av}}$  1.8949(12), intermolecular contacts  $\text{S}\cdots\text{S}$  4.636(1) Å,  $\text{C}-\text{Si}-\text{C}$  105.50(5)°,  $\text{S}-\text{C}-\text{S}$  117.46(7)°,  $\text{C}-\text{S}-\text{C}$  100.40(6)°, torsion angles  $\text{C}-\text{S}-\text{C}-\text{Si}_{\text{av}}$  59.89(8)° (see Supporting Information for further details).



**Figure 5.**  $^1\text{H}$  NMR spectrum of 3,3,7,7-tetramethyl-1,5-ditellura-3,7-disilolane (**29a**, bottom) and the corresponding dication, 3,3,7,7-tetramethyl-1,5-ditellura-3,7-disilabicyclo[3.3.0]octane bis(hexafluorophosphate) (**29a''**, top); in  $\text{CD}_3\text{CN}-\text{CD}_2\text{Cl}_2$ . The multiplet at ca.  $\delta$  2 is from  $\text{CD}_3\text{CN}$ .

bond as well as oxidation at sulfur to afford the known compound, 2,2,6,6-tetramethyl-1-oxa-4-thia-2,6-disilacyclohexane **53**.<sup>34</sup> Treatment of **52c** with iodine gives 1,1-diiodo-3,3,4,4-tetramethyl-1,3,4-telluradisilolane (**54**), characterized by X-ray crystallography (Figure 4a). The PES of **52a** is reported elsewhere.<sup>8a</sup>

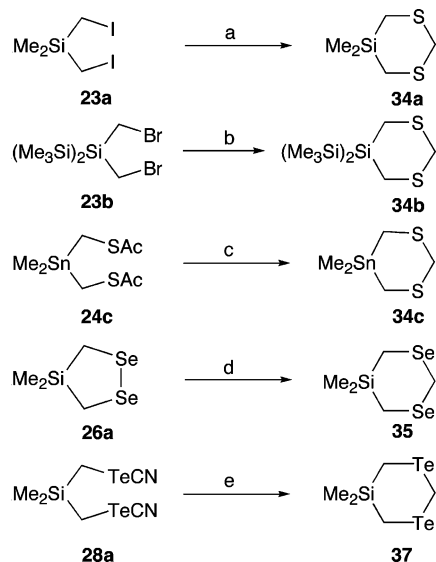
**V. Six-Membered Ring Systems.** Compounds **34a,b** ( $[\text{6}]\text{S}_2\text{Si}$ ,  $[\text{6}]\text{S}_2\text{Si}(\text{TMS})_2$ ) were prepared from **23a,b**, respectively, using  $\text{CS}_2$  as the source of  $\text{CH}_2(\text{S}^-)_2$ ;<sup>35</sup> synthesis of **34c**

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**Scheme 14.** Synthesis of 1,3,5-Dithiasilinananes, 1,3,5-Dithiastanninananes, 1,3,5-Diselenasilinananes, and 1,3,5-Ditellurasilinananes<sup>a</sup>



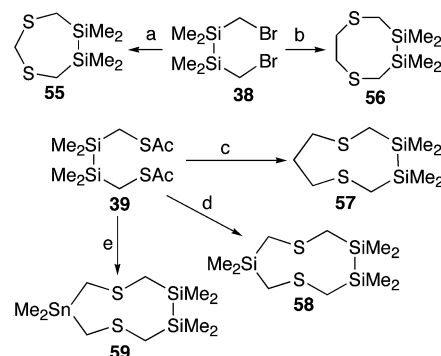
<sup>a</sup> Conditions: (a) CS<sub>2</sub>, NaBH<sub>4</sub>, THF, rt, 16 h (47%). (b) CS<sub>2</sub>, NaBH<sub>4</sub>, EtOH-THF, rt, 2 h (57%). (c) CH<sub>2</sub>I<sub>2</sub>, KOH, EtOH, rt (24%). (d) CH<sub>2</sub>I<sub>2</sub>, NaBH<sub>4</sub>, EtOH-THF, rt (30%). (e) CH<sub>2</sub>I<sub>2</sub>, NaBH<sub>4</sub>, DMSO, rt (28%).

([6]S<sub>2</sub>Sn), **35** ([6]Se<sub>2</sub>Si), and **37** ([6]Te<sub>2</sub>Si) employed **24c**/KOH/CH<sub>2</sub>I<sub>2</sub>, **26a**/NaBH<sub>4</sub>/CH<sub>2</sub>I<sub>2</sub>, and **28a**/NaBH<sub>4</sub>/CH<sub>2</sub>I<sub>2</sub>, respectively (Scheme 14). None of the mixed Group 14/16 six-membered ring compounds have been previously reported. Compound **34b** was characterized by X-ray crystallography, which shows that the Si–Si bonds sustain angles of 60.4 and 56.6° to the C–S–C planes, which correspond to angles of 29.6 and 33.4° to the sulfur *p*-type lone pair orbitals; this geometry should be favorable for interaction of the Si–Si  $\sigma$ -orbitals with the sulfur *p*-type lone pair orbitals (Figure 4b). The consequences of this interaction, evaluated through TCNE CT-complex  $\lambda_{\max}$  data and PES studies, is presented elsewhere.<sup>8</sup> Synthesis of 4,4,5,5-tetramethyl-1,2,4,5-diselenadisilane **41** ([6](Se)<sub>2</sub>(Si)<sub>2</sub>) from **38** is described in Scheme 10.

**VI. Seven-, Eight-, and Nine-Membered Ring Systems with Si–Si Bonds.** To take advantage of the ready availability of intermediates **38** and **39**, to round out our survey of mixed Group 14/16 heterocycles, and to make compounds available for PES, seven-, eight- and nine-membered ring compounds **55–59** were prepared (Scheme 15).

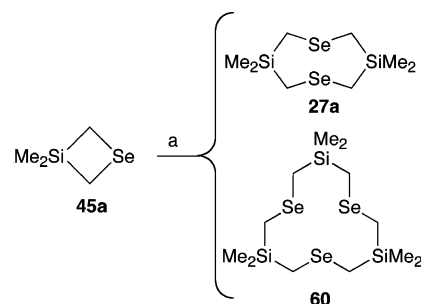
**VII. Twelve-Membered Ring Systems: 1,5,9-Triseleno-3,7,11-trisilacyclododecanes.** Since Adams has reported the rhenium catalyzed cyclooligomerization of thietanes and selenetanes to polythia or polyselena macrocycles,<sup>4e</sup> we examined the reactions of **44a** ([4]SSi) and **45a** ([4]SeSi) with Re<sub>2</sub>(CO)<sub>9</sub>-CH<sub>3</sub>CN under Adams' conditions (Scheme 16). In the case of **44a**, the Si–C bond was cleaved and no macrocycles could be detected by GC-MS analysis. In the case of **45a**, neat reaction at 65 °C gives, after preparative TLC, eight-membered ring 3,3,7,7-tetramethyl-1,5-diselena-3,7-disilocane (**27a**; 3%) and 12-membered ring 3,3,7,7,11,11-hexamethyl-1,5,9-triseleno-3,7,11-trisilacyclododecane (**60**, [12]Se<sub>3</sub>Si<sub>3</sub>, 9%), along with an apparently polymeric material (34%). Compound **60** is a unique example of a silicon- and selenium-containing crown ether.<sup>36</sup>

**Scheme 15.** Synthesis of a 1,3,5,6-Dithiadisilepane (**55**), 1,4,6,7-Dithiadisilocane (**56**), 1,5,7,8-Dithiadisilone (**57**), 1,5-Dithia-3,7,8-trisilone (**58**), and 1,5-Dithia-7,8-disila-3-stannone (**59**)<sup>a</sup>



<sup>a</sup> Conditions: (a) CS<sub>2</sub>, NaBH<sub>4</sub>, THF, rt, 16 h. (b) HS(CH<sub>2</sub>)<sub>2</sub>SH, EtOH, CS<sub>2</sub>CO<sub>3</sub>, 50 °C, 2 h. (c) Br(CH<sub>2</sub>)<sub>3</sub>Br, KOH, EtOH, rt, 2 h. (d) **23a**, EtOH, KOH, rt, 2 h. (e) **23c**, KOH, rt, 2 h.

**Scheme 16.** Rhenium Catalyzed Cyclooligomerization of 3,3-Dimethyl-1,3-selenasiletane (**45a**)<sup>a</sup>



<sup>a</sup> Conditions: (a) Re<sub>2</sub>(CO)<sub>9</sub>CH<sub>3</sub>CN, CH<sub>3</sub>CN (3% **27a**, 9% **60**).

Formation of this compound presumably involves a mechanism proposed by Adams.<sup>4e</sup> The failure to afford the macrocyclization product from **44a** indicates that silicon is the more electrophilic site to be attacked than carbon in **44a** due to the electronegativity: Si < C < S. For **45a**, the weaker Se–C bonds compared to S–C bonds may explain the success of the reaction.

## Summary

We demonstrate that a variety of mixed Group 14/16 heterocycles **7–14** (Chart 1) with 4–12-membered rings can be easily prepared from bis(halomethyl)-silanes or -stannanes or compounds prepared therefrom. Most of these compounds represent previously unknown ring systems, including rare examples of four-membered rings containing a single tin or tellurium atom. Solid-state conformations for many of these new ring systems have been established by X-ray crystallography. 1,5-Dichalcogena-3,7-disilocanes, on treatment with NOPF<sub>6</sub> give dications which can be characterized by low-temperature NMR methods. On treatment with nucleophiles, these dications rearrange to mixtures of five-membered ring 1,2-dichalcogenolanes and six-membered ring 1,3,5-dichalcogenasilinananes. Heterocycles with four- and eight-membered rings containing two different chalcogen atoms, e.g. S/Se or S/Te, have been prepared for the first time. A member of the latter class of compounds, 1,3-thiaselenetane 1-oxide, has been found to be a useful photochemical source of selenoformaldehyde. Given the ease of one-electron oxidation for many of these heterocycles, based on reactivity toward NOPF<sub>6</sub>, it can be anticipated that they should be of interest as ligands and catalysts. Additional aspects

(36) For a recent example of dimethylsiloxane crown ethers see: Decken, A.; Passmore, J.; Wang, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 2773–2777.

of the chemistry of these novel heterocycles will be presented elsewhere.

### Experimental Section<sup>37</sup>

**3,3,7,7-Tetramethyl-1,5-dithia-3,7-disilocane (25a) ([8]S<sub>2</sub>Si<sub>2</sub>).** A solution of bis(acetylthiomethyl)dimethylsilane (**24a**, 0.47 g, 2.0 mmol; from reaction of bis(iodomethyl)dimethylsilane (**23a**) stirred overnight in THF with excess KSAc) and **23a** (0.68 g, 2.0 mmol) in EtOH (20 mL) was added dropwise during 1.5 h to a solution of KOH (0.28 g, 5.0 mmol) in EtOH (100 mL) with stirring under Ar at room temperature. The solution was stirred for an additional 10 min, poured into H<sub>2</sub>O (20 mL), and extracted (CH<sub>2</sub>Cl<sub>2</sub>; 2 × 20 mL). The extracts were washed (H<sub>2</sub>O; 4 × 20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated, and the residue chromatographed (Al<sub>2</sub>O<sub>3</sub>; 1:6 CH<sub>2</sub>Cl<sub>2</sub>:C<sub>6</sub>H<sub>14</sub>) giving **25a** as colorless crystals (0.16 g, 34%), mp 50–51 °C; <sup>1</sup>H NMR δ 1.85 (s, 8H), 0.18 (s, 12H); <sup>13</sup>C NMR δ 17.4 (CH<sub>2</sub>), –2.7 (CH<sub>3</sub>); IR (thin film, cm<sup>–1</sup>): 2955 and 2893 (m, C–H), 2360 (w), 1715 (m), 1252 (m), 1053 (m), 841 (s), 793 (m), 531 (m); LR-EIMS *m/z* 236 (M<sup>+</sup>, 100), 221 (M<sup>+</sup>–Me, 19), 190 (19), 175 (55), 149 (20), 147 (20); HR-MS Calcd for C<sub>8</sub>H<sub>20</sub>S<sub>2</sub>Si<sub>2</sub>: 236.0545. Found: 236.0548. X-ray crystal structure determined.

**3,3,7,7-Tetramethyl-1,5-diselena-3,7-disilocane (27a) ([8]Se<sub>2</sub>Si<sub>2</sub>).** 4,4-Dimethyl-1,2-diselena-4-silolane (**26a**, 0.30 g, 1.2 mmol; from Na<sub>2</sub>Se<sub>2</sub> and **23a** in EtOH at 0 °C) and **23a** (0.41 g, 1.2 mmol) in EtOH-THF (1:1, 10 mL) was added dropwise during 1.5 h to a suspension of NaBH<sub>4</sub> (0.30 g, 7.9 mmol) in EtOH-THF (1:19, 100 mL) with stirring under Ar at room temperature. The solution was stirred for 10 min, concentrated in vacuo, poured into H<sub>2</sub>O (20 mL) and extracted (CH<sub>2</sub>Cl<sub>2</sub>; 2 × 20 mL). The extracts were washed (H<sub>2</sub>O; 4 × 20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo, and the residue was chromatographed (silica gel; 1:7 CH<sub>2</sub>Cl<sub>2</sub>:C<sub>6</sub>H<sub>14</sub>), giving **27a** as colorless crystals (0.29 g, 73%), mp 30–31 °C; <sup>1</sup>H NMR δ 1.75 (s, 8H), 0.19 (s, 12H); <sup>13</sup>C NMR δ 6.5 (CH<sub>2</sub>), –1.7 (CH<sub>3</sub>); MS *m/z* 332 (M<sup>+</sup>, <sup>80</sup>Se, 75), 245 (48), 45 (100); IR (KBr, cm<sup>–1</sup>): 2955 and 2896 (m, C–H), 2355 (w), 1361 (m), 1249 (s), 1102 (m), 1026 (m), 832 (s); HR-MS Calcd for C<sub>8</sub>H<sub>20</sub><sup>80</sup>Se<sup>80</sup>SeSi<sub>2</sub>: 331.9428. Found: 331.9435. X-ray crystal structure determined.

**3,3,7,7-Tetramethyl-1,5-ditellura-3,7-disilocane (29a) ([8]Te<sub>2</sub>Si<sub>2</sub>).** A mixture of Te powder (1.28 g, 10 mmol) and KCN (0.67 g, 10 mmol) in dry DMSO (20 mL) was heated to 100 °C under Ar for 1 h. The mixture was cooled to room temperature, and **23a** (1.7 g, 5 mmol) in DMSO (5 mL) was added dropwise. After stirring for 2 h, a solution of **23a** (1.7 g, 5 mmol) in EtOH (10 mL) was added to the solution of bis-tellurocyanide **28a** (88% yield by NMR; <sup>1</sup>H NMR, DMSO-*d*<sub>6</sub>, δ 1.87 (s, 4H), 0.31 (s, 6H); <sup>13</sup>C, DMSO-*d*<sub>6</sub> δ –1.0, –7.2). The mixture was added dropwise by syringe during 1–1.5 h to a suspension of NaBH<sub>4</sub> (1.16 g, 30 mmol) in EtOH (60 mL) at 0 °C. The solution was stirred for 10 min, poured into H<sub>2</sub>O (50 mL), and extracted (CH<sub>2</sub>Cl<sub>2</sub>; 2 × 30 mL). The extracts were washed (H<sub>2</sub>O, 5 × 30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated, and the residue was chromatographed (basic Al<sub>2</sub>O<sub>3</sub>; hexane), giving **29a** as a pale-yellow oil (0.5 g, 23%). Recrystallization of the product (hexane) gave pale-yellow crystals; mp 56.5–57.5 °C; <sup>1</sup>H NMR δ 1.67 (s, 8H, CH<sub>2</sub>), 0.18 (s, 12H, Me); <sup>13</sup>C NMR δ 0.4 (CH<sub>3</sub>), –17.0 (CH<sub>2</sub>); <sup>125</sup>Te–NMR δ 75.2 (relative to Me<sub>2</sub>Te); MS *m/z* 428 (M<sup>+</sup>, <sup>130</sup>Te, 100), 342 (41), 216 (61); IR (KBr) 2950, 2894, 1240, 827, 769, 705 cm<sup>–1</sup>. HRMS Calcd for C<sub>8</sub>H<sub>20</sub>Si<sub>2</sub>Te<sub>2</sub>: 427.9202. Found 427.9196. An X-ray crystal structure was determined.

**Radical Cation of 29a Quenched with Ethanol.** To **29a** (9 mg, 0.02 mmol) in CDCl<sub>3</sub> (0.5 mL) was added NOPF<sub>6</sub> (3.8 mg, 0.02 mmol) in CD<sub>3</sub>CN (0.5 mL) dropwise at –55 °C. The mixture, which instantly turned red, was stirred for 20 min. Then EtOH (2.8 mg, 0.06 mmol) was added at –55 °C. GC-MS showed 3.3:1 5,5-dimethyl-1,3,5-ditellurasilane (**37**) to 4,4-dimethyl-1,2-ditellurasilolane (**36**).

**5,5-Bis(trimethylsilyl)-1,3,5-dithiasilane (34b) ([6]S<sub>2</sub>Si(TMS)<sub>2</sub>).** 2,2-Bis(bromomethyl)-1,1,1,3,3,3-hexamethyltrisilane (**23b**, 0.36 g, 1.0 mmol) and CS<sub>2</sub> (0.12 g, 1.5 mmol) in THF (10 mL) was added at room temperature to a slurry of NaBH<sub>4</sub> (0.12 g, 3.0 mmol) in EtOH-THF (1:5, 12 mL), and the solution was stirred for 2 h. The solution was concentrated and extracted (CH<sub>2</sub>Cl<sub>2</sub>; 20 mL), the extracts were concentrated, and the residue was chromatographed (silica gel, CH<sub>2</sub>Cl<sub>2</sub>), giving **34b** as colorless crystals (0.16 g, 57%), mp 82–83 °C; <sup>1</sup>H NMR δ 3.74 (s, 2H), 2.09 (s, 4H), 0.18 (s, 18H); <sup>13</sup>C NMR δ 35.9 (SCH<sub>2</sub>S), 9.9 (SCH<sub>2</sub>Si), –0.5 (CH<sub>3</sub>); IR (thin film, cm<sup>–1</sup>) 2948 (s), 2890 (m), 1244 (s), 837 (s); HRMS Calcd for C<sub>9</sub>H<sub>24</sub>S<sub>2</sub>Si<sub>3</sub>: 280.0627. Found: 280.0609. X-ray crystal structure determined.

**3,3,4,4,8,8,9,9-Octamethyl-1,6-diselena-3,4,8,9-tetrasilicane (42) ([10]Se<sub>2</sub>(Si<sub>2</sub>)<sub>2</sub>).** 4,4,5,5-Tetramethyl-1,2-diselena-4,5-disililane (**41**, 0.35 g, 1.2 mmol; from 1,2-bis(bromomethyl)tetramethyldisilane (**38**) and Na<sub>2</sub>Se<sub>2</sub> in EtOH) and **38** (0.35 g, 1.2 mmol) in EtOH-THF (1:1, 10 mL) was added dropwise during 1.5 h to a suspension of NaBH<sub>4</sub> (0.34 g, 9.0 mmol) in EtOH-THF (1:19, 100 mL) with stirring under Ar at room temperature. The solution was concentrated, and the residue was chromatographed (SiO<sub>2</sub>; 1:3 CH<sub>2</sub>Cl<sub>2</sub>:C<sub>6</sub>H<sub>14</sub>), giving **42** as colorless crystals (0.21 g, 41%), mp 103–104 °C; <sup>1</sup>H NMR δ 2.07 (s, 8H), 0.11 (s, 24H); <sup>13</sup>C NMR δ 12.0 (CH<sub>2</sub>), –2.4 (CH<sub>3</sub>); IR (KBr, cm<sup>–1</sup>): 2953 (s), 2891 (s), 1246 (s), 1022 (m); HR-MS Calcd for C<sub>12</sub>H<sub>32</sub>Se<sub>2</sub>Si<sub>4</sub>: 447.9913. Found: 447.9906. An X-ray crystal structure was determined.

**1,3-Thiaselenetane S-Oxide (48).** Bis(chloromethyl) sulfoxide<sup>30</sup> (**47**, 1.47 g, 10 mmol) in THF (10 mL) was added dropwise to an ice cooled Na<sub>2</sub>Se (10 mmol) suspension in THF (25 mL) at 0 °C. The mixture was warmed to room temperature, stirred for 2 h, filtered through Celite, and concentrated. The brown residue was chromatographed (silica gel; EtOAc, *R<sub>f</sub>* 0.4), giving **48** (0.95 g, 61%) as colorless crystals, mp 86–88 °C after recrystallization (EtOAc; 0 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.22 (dd, *J* = 5.3, 2.4 Hz, 2H), 3.95 (dd, *J* = 5.5, 2.4 Hz, 2H); (C<sub>6</sub>D<sub>6</sub>) δ 3.36 (dd, *J* = 5.0, 2.4 Hz, 2H), 2.70 (dd, *J* = 5.5, 2.4 Hz, 2H); (DMSO-*d*<sub>6</sub>) δ 4.58 (dd, *J* = 5.0, 2.4 Hz, 2H), 4.06 (dd, *J* = 5.5, 2.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 41.8; <sup>77</sup>Se–NMR (CDCl<sub>3</sub>) δ –14.9; GC-MS *m/z* 156 (M<sup>+</sup>, <sup>80</sup>Se, 38), 126 (20), 108 (3), 94 (100), 80 (6), 63 (8); IR (KBr) 1114, 1061, 1008 cm<sup>–1</sup> (all s); UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 266 nm (518), 286 nm (476). Anal. Calcd for C<sub>2</sub>H<sub>4</sub>SSeO: C, 15.49; H, 2.60; S, 20.68. Found: C, 15.72; H, 2.44; S, 20.84. An X-ray crystal structure was determined.

**3,4-Dimethyl-1-selena-3-cyclohexene (50).**<sup>32a</sup> Compound **48** (0.35 g, 2.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and 2,3-dimethyl-1,3-butadiene (0.6 g, 6.9 mmol) in a 10 mL Pyrex flask was irradiated for 3 h using a medium pressure 450 W mercury lamp (Hanovia). By GC-MS analysis, 3,4-dimethyl-1-selena-3-cyclohexene (**50**) and 3,4-dimethyl-1-thia-3-cyclohexene 1-oxide (**51**) were formed in a 21:1 ratio. The mixture was concentrated and chromatographed (silica gel, hexane), affording **50** as a light-yellow oil (0.32 g, 80%); <sup>1</sup>H NMR δ 3.02 (s, 2H), 2.70 (t, *J* = 6 Hz, 2H), 2.33 (m, 2H), 1.76 (s, 3H), 1.70 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 129.3, 125.0, 33.0, 20.9, 20.4, 19.9, 18.4; GC-MS *m/z* 176 (M<sup>+</sup>, <sup>80</sup>Se, 100), 161 (10).

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**Supporting Information Available:** Complete experimental procedures and data on new compounds; full X-ray crystallographic data on structures determined. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(37) Representative syntheses are given; full details appear in the Supporting Information.