[2 + 1] Cycloaddition of 1-Seleno-2-silylethenes. Selenium-Assisted 1,2-Silicon Shift for Cyclopropanation

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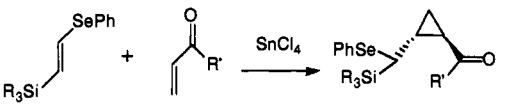
Received June 28, 1993®

Abstract: A novel one-step [2 + 1] cycloaddition synthesis of cyclopropanes has been developed. Reaction of (*E*)-1-(phenylseleno)-2-silylethenes **1a,b** with vinyl ketones **2a-d** and acrolein (**2e**) in the presence of $SnCl_4$ gave cyclopropane products by a formal [2 + 1] cycloaddition accompanied by 1,2-silicon migration rather than by [2 + 2] cycloaddition. This facile 1,2-silicon shift is rationalized by a remarkable selenium effect. A generated β-silicon-stabilized zwitterion **A** is transformed by a 1,2-silicon shift to the more stable selenium-bridged intermediate **C**. Ab initio MO calculations for model compounds clearly demonstrate that the intermediate **C** is more stable than **A**. The selenium-bridged geometry of **C** shows that preference is for formation of a cyclopropane ring instead of a cyclobutane ring.

Introduction

The challenge to synthetic methodology of cyclopropane derivatives has stimulated much activity,[1] in part because the cyclopropyl group is found as a basic structural unit in a wide range of important naturally occurring compounds.[2] Additionally, cyclopropanes are useful intermediates in organic synthesis owing to unusual bonding and strain.[3] For example, the combination of a cyclopropane ring with multiple bonds and hydroxy and sulfur groups leads to composite functional groups.[4] The importance of cyclopropanes requires general methodology for three-membered ring construction. Although [2 + 1] approaches such as carbene or carbenoid additions to olefins (including the Simmons–Smith reaction[5] and decomposition of diazo compounds[6]) are widely used for the synthesis of cyclopropanes, these reactions provide relatively few highly-substituted cyclopropanes, with high regio- and stereoselectivity.

Scheme 1



1a: R = Me
1b: R = Et

2 3

Recently we discovered a novel [2 + 1] cycloaddition synthesis of cyclopropanes involving the combination of (*E*)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1a**) and vinyl ketones in the presence of $SnCl_4$ accompanied by 1,2-silicon migration.[7] This cyclopropanation provides synthetically useful unsymmetrically substituted cyclopropane products in a single step and can also generate cyclopropanes with high stereoselectivity. In this work we provide full accounts of our investigation defining the scope of this novel cyclopropanation and report a remarkable selenium effect for this facile 1,2-silicon migration leading to a strained three-membered ring (Scheme 1). Ab initio geometry optimizations of possible intermediates were carried out, and the results are discussed in relation to a possible reaction mechanism.

Results

Scope of the [2 + 1] Cycloaddition. The silicon–selenium mixed reagent (*E*)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1a**) was obtained by treatment of (*E*)-(2-(trimethylsilyl)vinyl)lithium, which is prepared *in situ* from (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene and *n*-butyllithium,[8] with diphenyl diselenide.[9] Table 1 summarizes the [2 + 1] cycloaddition reactions of **1a**. In the presence of $SnCl_4$ (1.5 equiv for **2a-c** and 2.4 equiv for **2d**), the reaction of **1a** (1 equiv) and vinyl ketones **2a-d** (1.3 equiv) was carried out in CH_2Cl_2 at −78 °C for 3 h. Quenching with triethylamine (2.3–6.9 equiv) gave single stereoisomers **3a-d** exclusively in 42–62% yields after chromatographic purification (entries 1–4). In entry 5, the reaction of **1a** and acrolein (**2e**) also gave the cyclopropane product **3e** in 11% yield along with **13** (6%) and an unidentified mixture. In entry 6, the reaction of **1a** and the ketone **5** gave the cyclopropane product **10** in only 14% yield, due in part to the stability of the product toward chromatographic purification. The structure of **3a** was established by ^1H NMR, ^{13}C NMR, $^{13}C/^1H$ COSY, long-range $^{13}C/^1H$

• Abstract published in *Advance ACS Abstracts*, February 15, 1994.

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0002-7863/94/1516-2356$04.50/0

Table 1. [2 + 1] Cycloaddition of 1-(Phenylseleno)-2-silylethenes **1a** (in Entries 1–9) and **1b** (in Entries 10–13)

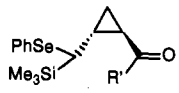
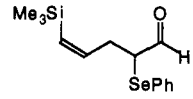
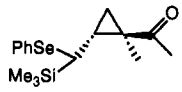
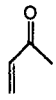
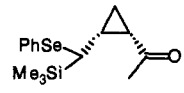
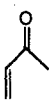
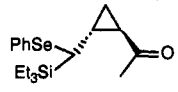
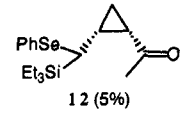
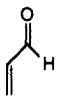
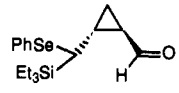
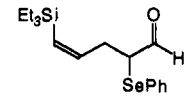
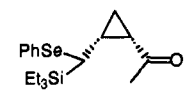
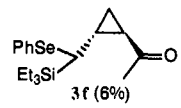
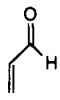
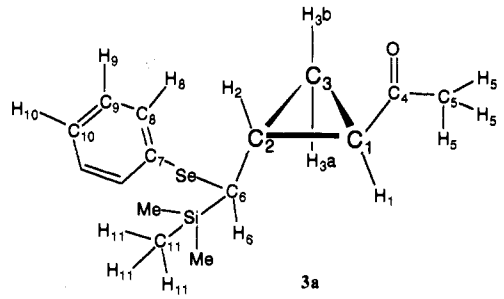
entry	α,β-unsaturated ketone and aldehyde	Lewis acid	product (yield)
			
1	**2a**: R' = Me	$SnCl_4$	**3a**: R' = Me (62%)
2	**2b**: R' = Et	$SnCl_4$	**3b**: R' = Et (62%)
3	**2c**: R' = n-Pentyl	$SnCl_4$	**3c**: R' = n-Pentyl (55%)
4	**2d**: R' = Ph	$SnCl_4$	**3d**: R' = Ph (42%)
5	**2e**: R' = H	$SnCl_4$	**3e**: R' = H (11%)
			 **14** (6%) (Z : E = 8 : 1)
			
6	**5**	$SnCl_4$	**10** (14%)
			
7	**2a**	$AlCl_3$	**11** (25%)
8	**2a**	$EtAlCl_2$	**11** (6%)
			
9	**2e**	$AlCl_3$	complex mixture
			
10	**2a**	$SnCl_4$	**3f** (48%)
			 **12** (5%)
			
11	**2e**	$SnCl_4$	**3g** (28%)
			 **14** (12%)
			
12	**2a**	$AlCl_3$	**12** (29%)
			 **3f** (6%)
			
13	**2e**	$AlCl_3$	complex mixture

Table 2. ^1H and ^{13}C NMR Spectra of **3a**

^1H	δ (ppm)	J_{HH} (Hz)	^{13}C	δ (ppm)	$^1J_{CH}$ (Hz)
H_{11}	0.166 (s, 9H)		C_{11}	−1.897	120 (q)
H_{3a}	0.747 (ddd, 1H)	3.97	C_3	19.72	164 (t)
		6.37			
		8.19			
H_{3b}	1.32 (ddd, 1H)	3.97			
		4.56			
		8.63			
H_1	1.53 (ddd, 1H)	4.17	C_1	29.98	163 (d)
		4.56			
		8.19			
H_2	1.72 (dddd, 1H)	4.17	C_2	29.91	163 (d)
		6.37			
		8.63			
		10.7			
H_5	1.93 (s, 3H)		C_5	30.43	127 (q)
H_6	2.09 (d, 1H)	10.7	C_6	36.26	129 (d)
$H_{9,10}$	7.24–7.30 (m, 3H)		$C_{8,9,10}$	127.5	161 (d)
				129.1	164 (d)
H_8	7.55–7.59 (m, 2H)			134.4	163 (d)
			C_7	130.6	(s)
			C_4	207.7	(s)



3a

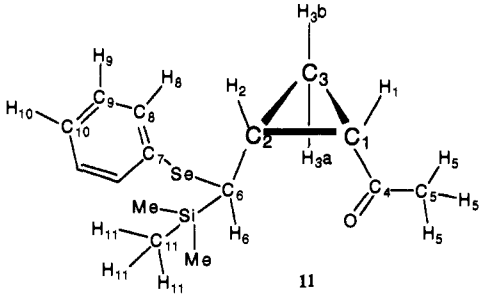
Table 3. Observed NOE and Long-Range $^{13}C/^1H$ Coupling of **3a**

NOE	long-range $^{13}C/^1H$ coupling	
H_1–H_{3a}	C_1–H_2	$^2J_{CH}$
H_1–H_6	C_1–H_{3b}	$^2J_{CH}$
H_2–H_{3b}	C_1–H_5	$^3J_{CH}$
H_2–H_6	C_2–H_6	$^2J_{CH}$
H_{3a}–H_{3b}	C_3–H_1	$^2J_{CH}$
H_{3a}–H_6	C_4–H_1	$^2J_{CH}$
H_6–H_8	C_4–H_5	$^2J_{CH}$
	C_6–H_{11}	$^3J_{CH}$
	C_7–H_6	$^3J_{CH}$

COSY, and 2D-NOESY spectra. All data are in complete agreement with the cyclopropane structure (Table 2). The observation that H_1, H_2, H_{3a}, and H_{3b} are coupled to each other, while H_6 is coupled only with H_2, supports the structure **3a** (see numbering of H and C atoms in Table 2). $^1J_{CH}$ values (J = 163–164 Hz ($C_{1,2,3}$)) in the ^{13}C NMR spectrum, which are characteristic of cyclopropanes, also support the structure **3a**. The existence of long-range couplings, $^3J_{CH}$, C_6–Si–C_{11}–H_{11}, and $^3J_{CH}$, C_7–Se–C_6–H_6, indicates that Se and Si atoms reside on the same carbon (C_6) (Table 3). The assignment of the *trans* stereochemistry of the acetyl and CH(SePh)($SiMe_3$) groups is based on 2D-NOESY (Table 3). The relative configuration at C_2 and C_6 could not be determined from the NMR. Therefore, an X-ray structural analysis of **3a** or its derivatives, which to date has been unsuccessful, is to be carried out. However, the relative configuration at C_2 and C_6 was deduced from the proposed mechanism discussed later as (*R*,*R*) or (*S*,*S*) (*vide post*). The NMR spectra of the cycloadducts **3b-e** and **10** were also in complete agreement with the cyclopropane structures. The stereochemistries of **3e** and **10** were determined by 2D-NOESY and NOE difference spectra. The IR spectra (1688–1698 cm^{-1}) agree with the cyclopropyl ketone structures **3a-d** and **10**. The reaction pathway may be ring formation *via* a 1,2-silicon

Table 4. ^1H and ^{13}C NMR Spectra and Observed NOE of **11**

^1H	δ (ppm)	J_{HH} (Hz)	^{13}C	δ (ppm)	$^1J_{CH}$ (Hz)	NOE
H_{11}	0.060 (s, 9H)		C_{11}	−1.734	119 (q)	H_1–$H_{3a,3b}$
$H_{3a,3b}$	1.21 (dd, 2H)	6.5	C_3	18.68	162 (t)	H_1–H_2
		8.1				
						H_2–$H_{3a,3b}$
H_2	1.67 (dddd, 1H)	8.1	$C_{1,2}$	27.29	163 (d)	
		8.1		29.59	157 (d)	$H_{3a,3b}$–H_6
		8.1				
		12.1				$H_{3a,3b}$–H_{11}
H_5	2.07 (s, 3H)		C_5	32.28	127 (q)	H_5–H_8
H_1	2.16 (ddd, 1H)	6.5				H_6–H_8
		6.5				
		8.1				
H_6	2.66 (d, 1H)	12.1	C_6	28.54	135 (d)	
$H_{9,10}$	7.19–7.23 (m, 3H)		$C_{8,9,10}$	127.2	160 (d)	
				128.8	160 (d)	
H_8	7.48–7.52 (m, 2H)			134.7	163 (d)	
			C_7	129.9	(s)	
			C_4	206.9	(s)	



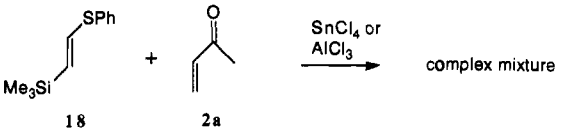
11

migration[10] to give cyclopropane derivatives. A more detailed mechanism will be explained in the Discussion.

A number of other Lewis acids such as $TiCl_4$, $TiCl_4$–Ti(O-*i*-Pr)$_4$ (1:1), BF_3·Et_2O, $AlCl_3$, and $EtAlCl_2$ were examined for the reaction between **1a** and **2a**. Using $TiCl_4$ or $TiCl_4$–Ti(O-i-Pr)$_4$ resulted in a complex mixture. When BF_3·Et_2O was used, no reaction occurred. Reaction in the presence of $AlCl_3$ or $EtAlCl_2$ required a large excess amount (4.5 equiv) of **2a** to give *cis*-substituted cyclopropane product **11** as the only isolable product in low yield (25% for $AlCl_3$ and 6% for $EtAlCl_2$ in entries 7 and 8, respectively, of Table 1). The *cis* structure of **11** was established by 2D-NOESY spectra (Table 4). The relative configuration at C_2 and C_6 could not be determined from the NMR.

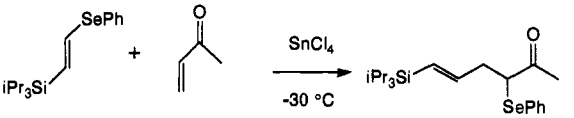
When **3a** was treated with $AlCl_3$ at −78 °C for 3 h, it was recovered with partial decomposition and was not isomerized to **11**. Thus, the Lewis acid dependence of *cis–trans* stereochemistry is determined prior to the ring closure.[11] Reaction of **1a** with excess **2e** (4 equiv) in the presence of $AlCl_3$ gave a complex mixture (entry 9).

The sulfur analog of **1a**, **18**,[12] was examined for S/Se comparison. Reaction of **18** with **2a** in the presence of $SnCl_4$ or $AlCl_3$ gave a complex mixture, and no cyclopropane product was isolated. Thus, sulfur seems to be ineffective for the [2 + 1] cycloaddition accompanied by a 1,2-silicon shift.



18 2a

1-Seleno-2-silyl olefins bearing sterically bulky silyl groups were examined in order to improve product yields. (*E*)-1-(phenylseleno)-2-(triethylsilyl)ethene (**1b**) and (*E*)-1-(phenylseleno)-2-(triisopropylsilyl)ethene (**1c**) were employed. **1b**,**c** were synthesized from the corresponding (*E*)-1-silyl-2-(tributylstannyl)ethenes[13] as for **1a**. In entry 10, the reaction of **1b** with methyl vinyl ketone (**2a**) (2 equiv) in the presence of $SnCl_4$ for 4 h at −78 °C gave **3f** and its *cis* isomer **12** in 48 and 5% yields, respectively. In entry 11, the reaction of **1b** with excess acrolein (**2e**) (4 equiv) in the presence of $SnCl_4$ gave **3g** and **14** in 28 and 12%, respectively. In entry 12, the reaction of **1b** with **2a** (4 equiv) in the presence of $AlCl_3$ gave **12** and **3f** in 29 and 6% yields, respectively. In entry 13, the reaction of **1b** with excess **2e** (4 equiv) in the presence of $AlCl_3$ gave a complex mixture. **1c** did not react with **2a** or excess **2e** in the presence of $SnCl_4$ at −78 °C. At −30 °C, the reaction of **1c** with **2a** in the presence of $SnCl_4$ gave **15**(*vide infra*) in ca. 15% yield and no cyclopropane



1c 2a 15 (ca. 15%)

product was obtained. The vinyl silanes, **15**, **13** (entry 5), and **14** (entry 11) also appear to be the products of 1,2-silicon migration. Thus, the triethylsilyl derivative **1b** improved product yields in some cases, although steric hindrance at the silyl substituent seems to retard the first conjugate addition step of the reaction and consume excess amount of electrophiles.

Unfortunately, in the presence of $SnCl_4$, no reaction occurred upon exposure of **1a** to less reactive electrophilic olefins such as 2-cyclohexen-1-one, *trans*-3-penten-2-one, 4-methyl-3-penten-2-one, dimethyl fumarate, 3-acryloyl-1,3-oxazolidin-2-one, ethyl α-cyano-*trans*-cinnamate, and nitroethylene[14] under the same condition. Higher temperature (−30∼0 °C) of the reaction of **1a** and 2-cyclohexen-1-one in the presence of $SnCl_4$ caused decomposition of **1a**. Low reactivity of **1a** to those electrophilic olefins and instability in the presence of Lewis acid at higher temperatures seem to be the problem.

Attempts to extend the [2 + 1] cycloaddition to alkyl-substituted 1-(phenylseleno)-2-(trimethylsilyl)ethene have proven unsuccessful. **19** and **17** were synthesized from the known (*E*)- and (*Z*)-2-(tributylstannyl)-1-(trimethylsilyl)-1-hexene (**22**[15] and **23**[16]) by the same procedure as for **1a**. Reaction of **19** with **2a** in the presence of $SnCl_4$ or $AlCl_3$ at −78 °C results in the formation

(10) 1,2-Cationic silicon migration was elegantly applied to five-membered ring synthesis originally by Danheiser, and the synthetic strategy has been extensively developed: (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513. Danheiser, R. L.; Fink, D. M.; Tsai, Y.-M. *Org. Synth.* **1988**, *66*, 8. (b) Danheiser, R. L.; Kwasigroth, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277. (d) Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 389. (e) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407. (f) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094. (g) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 9868. (h) Panek, J. S.; Beresis, R. *J. Org. Chem.* **1993**, *58*, 809. (i) Knölker, H.-J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1081 and references cited therein.

(11) The reaction of **1a** and **2a** with $SnCl_4$ in CH_2Cl_2 (−78 °C, 3 h), followed by quenching with water instead of triethylamine, gave **3a** (51%) as a major product along with the Michael adduct (*E*)-6-(phenylseleno)-5-hexen-2-one (8%); see ref 7. The possibility of a *cis–trans* equilibration during workup with triethylamine is therefore excluded.

(12) (a) Magnus, P.; Quagliato, D. A.; Huffman, J. C. *Organometallics* **1982**, *1*, 1240. (b) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621.

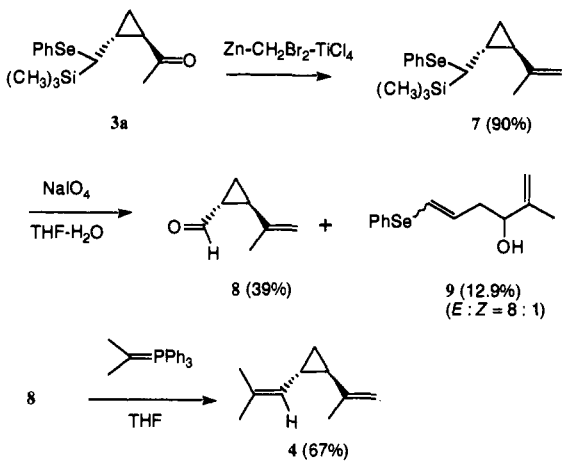
(13) Denmark, S. E.; Jones, T. K. *Helv. Chim. Acta* **1983**, *66*, 2397.

(14) Lewis acid catalyzed Michael reactions of nitro olefins with nucleophiles such as silyl enol ethers and ketone silyl acetals have been reported. Reaction of silyl enol ethers in the presence of $SnCl_4$, $TiCl_4$, and $AlCl_3$ affords the Michael adduct, while reaction of ketone silyl acetals in the presence of $SnCl_4$ failed, succeeding only with $TiCl_4$: Miyashita, M.; Yamani, T.; Kumazawa, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1984**, *106*, 2149.

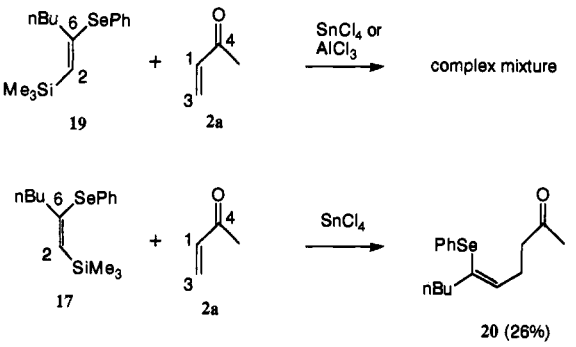
(15) Zhang, H. X.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

(16) (a) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561. (b) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868.

Scheme 2



of a complex mixture of products. Reaction of **17** with **2a** in the presence of $SnCl_4$ proceeds to afford the desilylated Michael adduct **20** in 26% yield with retention of the stereochemistry of olefin **17**.



Synthetic Utility of the [2 + 1] Cycloadducts. To demonstrate the synthetic utility of the [2 + 1] cycloadducts, **3a** was converted by three steps to the three-membered natural product (±)-rothrockene (**4**)[17] (Scheme 2). Methylenation of the carbonyl group of **3a** by the modified Nozaki reagent $Zn–CH_2Br_2–TiCl_4$[18] gave **7** in 90% yield. Olefin **7** was oxidized with $NaIO_4$ in THF–H_2O solution at room temperature to give the sila-Pummerer products **8** and **9**.[19] Aldehyde **8** was obtained in 39% yield as the major product along with the ring-opened byproduct **9** (12.9% yield, $E:Z$ = 8:1). Wittig reaction of **8** with isopropylidenetriphenylphosphorane in THF gave (±)-rothrockene (**4**) in 67% yield. The spectral data of **4** are in accord with the reported data.[17] Thus, the synthetic utility of the unsymmetrically substituted cyclopropane products obtained here is well documented.

Discussion

In order to rationalize the observed preference for cyclopropanation instead of four-membered ring formation, the reaction mechanism was considered in detail. Scheme 3 outlines the proposed course of the [2 + 1] cycloaddition process. In the first step, the nucleophilic vinyl selenides **1** attack the electrophilic olefins **2** activated by a Lewis acid to give carbenium ion **A**. The regioselectivity of this reaction with respect to selenium is the same as it is in the reaction between **1a** or 1-(phenylseleno)-1-(trimethylsilyl)ethene (**21**) and unsaturated acid chlorides and between **21** and vinyl ketones in the presence of Lewis acids.[9,20] Concerning the stereochemistry of this step, the preferred transition state would be chairlike (synclinal) (Figure 1). This arrangement may benefit from a stabilizing secondary orbital interaction (Se–C_4).

The generated zwitterionic intermediate **A** is stabilized by interaction with the adjacent carbon–silicon (C_2–Si) bond ("β-silicon effect") and expected to undergo rapid and reversible rearrangement (1,2-silicon shift) to give another β-silicon-stabilized intermediate **B**. The intermediate **B** could be transformed to the more stable selenium-bridged intermediate **C**.

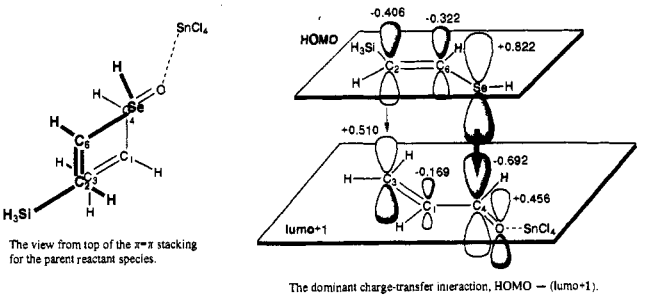
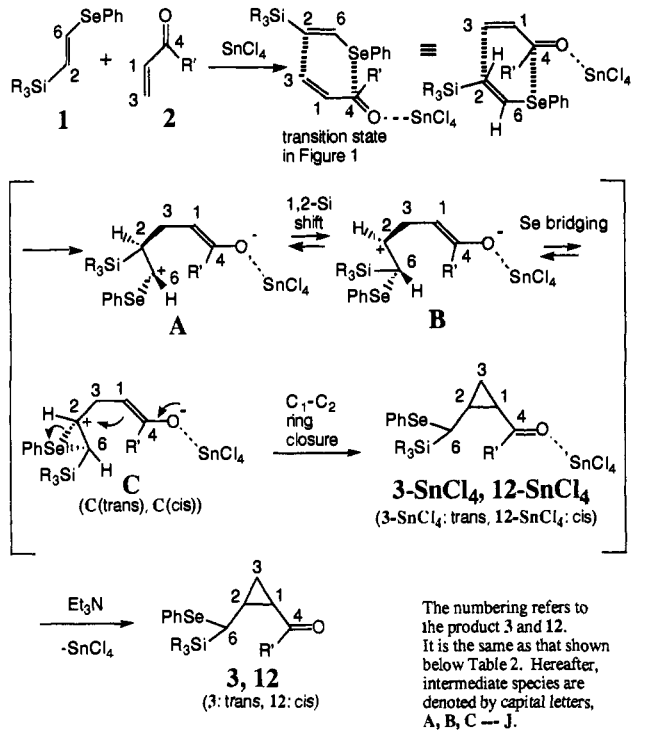


Figure 1. Synclinal (chairlike) transition state. At the right, ab initio orbital coefficients of the HOMO of a model compound, 1-(hydroseleno)-2-silylethene, and the lumo + 1 of $SnCl_4$-coordinated acrolein are shown. These coefficients are of RHF/LANL1MB[33] implemented in GAUSSIAN 90.[34] The LUMO of acrolein–$SnCl_4$, which is not shown, has the orbital extension almost localized on the tin 5s atomic orbital. Therefore, while the LUMO is generally the most electron-accepting orbital, it is not involved with the interaction with the HOMO in this case. For the view from the top, each reactant geometry is that optimized at the isolated state.

Scheme 3



(17) (a) Epstein, W. W.; Grudioso, L. A. *J. Org. Chem.* **1982**, *47*, 176. (b) Barbachyn, M. R.; Johnson, C. R.; Glick, M. D. *J. Org. Chem.* **1984**, *49*, 2746. (c) Epstein, W. W.; Graudioso, L. A.; Brewster, G. B. *J. Org. Chem.* **1984**, *49*, 2748.

(18) (a) Oshima, K.; Takai, K.; Hotta, Y.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417. (b) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1698. (c) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293.

(19) (a) Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977**, *42*, 1773. (b) Brook, A. G.; Anderson, D. G. *Can. J. Chem.* **1968**, *46*, 2115. (c) Carey, F. A.; Hernandez, O. *J. Org. Chem.* **1973**, *38*, 2670. (d) Vedejs, E.; Mullins, M. *Tetrahedron Lett.* **1975**, 2017.

(20) (a) Yamazaki, S.; Mizuno, W.; Yamabe, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1555. (b) Yamazaki, S.; Fujitsuka, H.; Yamabe, S. *J. Org. Chem.* **1992**, *57*, 5610.

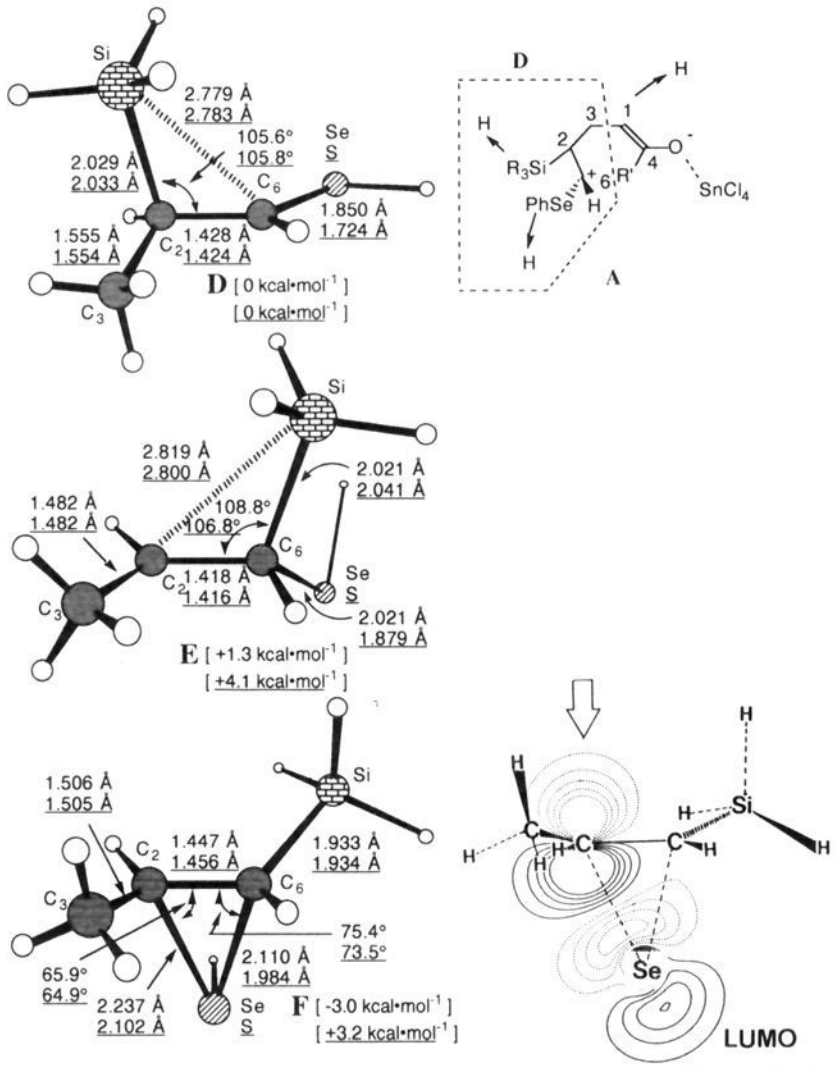
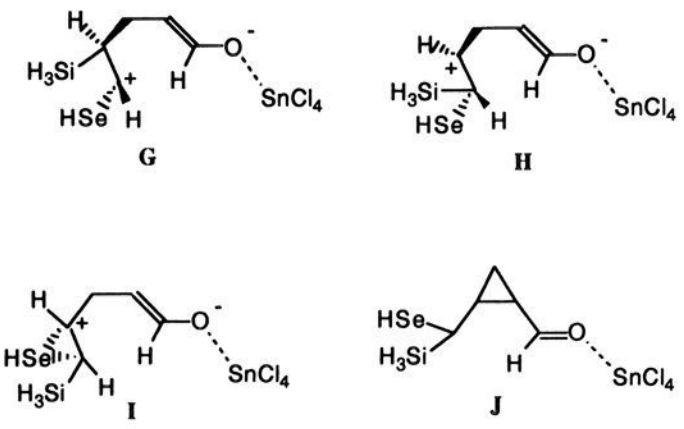


Figure 2. Ab initio RHF/LANL1DZ[33]-optimized geometries of three cation models **D**, **E**, and **F** of $H_3CCHCH(SeH)(SiH_3)^+$. The modeling of **A** → **D** is exemplified. Energies in square brackets are relative ones (positive, less stable). Underlined numbers in **D**, **E**, and **F** are for the corresponding sulfur intermediates. White circles denote hydrogen atoms.

Nucleophilic attack of C_2 by C_1 in the intermediate **C** generates the cyclopropane ring. The intermediacy of a stable species **C** seems to be responsible for this facile 1,2-silicon shift and the subsequent cyclopropanation. In this mechanism, one reasonable assumption is needed for the relative configuration of C_2 and C_6 as (*R*,*R*) or (*S*,*S*) in the *trans*-cyclopropane products. That is, after the synclinal stereoselective addition, there should be minimum motion (*i.e.*, the dihedral-angle rotation, ca. 60°) in the process leading to 1,2-silicon migration and the selenium-bridged intermediate. Thus, the generation of a single stereoisomer could be explained.

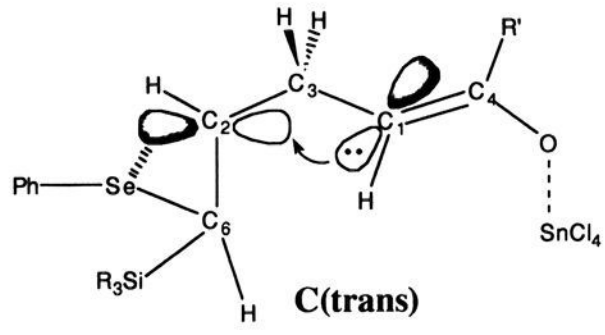
To support this hypothetical pathway, ab initio MO calculations for model compounds were carried out. First, the corresponding cation-part models **D**, **E**, and **F** were calculated (Figure 2). The optimized geometries of β-silicon-stabilized cations **D** and **E** were given as open forms.[21] The conformation obtained by the C–C bond rotation of **E** by 49° (the dihedral angle C_3–C_2–C_6–Se set to 90°) was used as a starting structure. The optimization gave the selenium-bridged cation (episelenonium ion) **F**. The total energies of **D**, **E**, and **F** show that **F** is 3.0 kcal/mol more stable than **D** and 4.3 kcal/mol more stable than **E**, respectively (in upper square brackets in Figure 2). The difference in stability between **E** and **F** suggests that a combination of the silicon shift and the selenium bridging is a driving force for the reaction progress. A similar comparison of the stabilities of three isomers of the sulfur intermediate is made in Figure 2. The underlined energies (in the lower square brackets) do demonstrate that the

Chart 1



stability order is **D** > **F** > **E** for the sulfur in contrast to that, **F** > **D** > **E**, for the selenium. Clearly, the sulfur–selenium difference is shown in spite of geometric similarity: **D** with the sulfur is too stable to undergo the 1,2-silicon migration and the subsequent 1,2-sulfur bridging. This computational result is consistent with the reported data that the PhS group is about seven times more effective than the PhSe group in stabilizing an α-carbocation.[22,23] The failure of cyclopropanation between **18** and **2a** would therefore stem from the fact that the 1,2-silicon shift is not assisted by sulfur bridging. In spite of the small difference between C_2–Se (2.237 Å) and C_6–Se (2.110 Å) distances, the LUMO is localized at the C_2 carbon and a nucleophilic attack occurs as the bold arrow shows. The attack gives rise to the C_2–Se bond scission according to the antibonding nature (node) and is of the same pattern as the bromide ion antiattack on the cyclic bromonium ion.

Next, ab initio geometry optimizations of three zwitterion models, **G**, **H**, and **I**, and a cyclopropane–$SnCl_4$ complex, **J**, shown in Chart 1 were carried out. Those structures of parent systems **G**, **I**, and **J** corresponding to the species **A**, **C**, and **3**–$SnCl_4$, **12**–$SnCl_4$ in the large square bracket of the Scheme 3 are shown in Figure 3. A stable structure for **H** could not be obtained, which corresponds to the instability of **E** in Figure 2. However, those of **G**, **I**, and **J** were successfully obtained. For **I**, two stable conformational species **I** (*trans*) and **I** (*cis*) were obtained. Also, for **J**, two stable structures **J** (*trans*) and **J** (*cis*) were obtained. **I** (*trans*) gives *trans*-cyclopropane via **J** (*trans*), while **I** (*cis*) gives *cis*-cyclopropane via **J** (*cis*). In **G**, the enolate ion and the α-selenium-stabilized carbenium ion (C_6) are confirmed. The Si–C_2–C_6 bond angle is 104.0° and is similar to 105.8° of **D** in Figure 2, which shows that the silyl group is ready to migrate to C_6. **I** (*trans*) is the silicon-migrated and selenium-bridged structure, where the Se---C_2 length of 2.317 Å is larger than the Se---C_6 one, 2.153 Å. Cyclopropanation is therefore prefered to cyclobutanation.[24] Ring closure of **C**(*trans*) would give the *trans*-



substituted cyclopropane–$SnCl_4$ complex **3**–$SnCl_4$. Workup with

(21) For recent theoretical studies of the β-silicon effect, see: (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. For recent solvolysis studies of the β-silicon effect, see: (c) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (d) Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120. (e) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317. See also: (f) Mayr, H.; Pock, R. *Tetrahedron* **1986**, *42*, 4211.

(22) (a) McClelland, R. A.; Leung, M. *J. Org. Chem.* **1980**, *45*, 187. (b) Hevesi, H.; Piquard, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 870. See also: (c) Heveshi, L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 155.

(23) We appreciate the suggestion of the reviewers on the sulfur–selenium comparison.

(24) The formation of 3- vs 4-membered rings is also explicable in terms of geometrical constraints (Baldwin's rules[25]) and the ring closure rate differences. However, our discussion is more precise.

(25) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

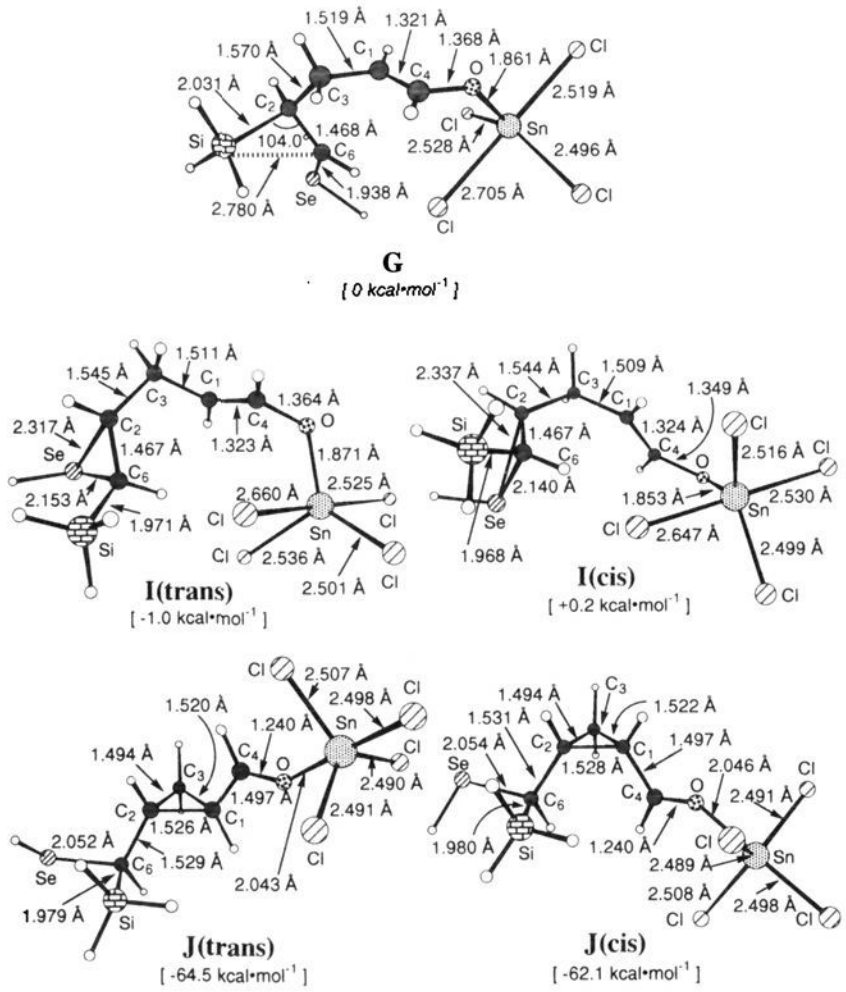


Figure 3. Structures of intermediates shown in Chart 1 and obtained by geometry optimizations of RHF/LANL1MB. Energies in square brackets are ones relative to that of **G**.

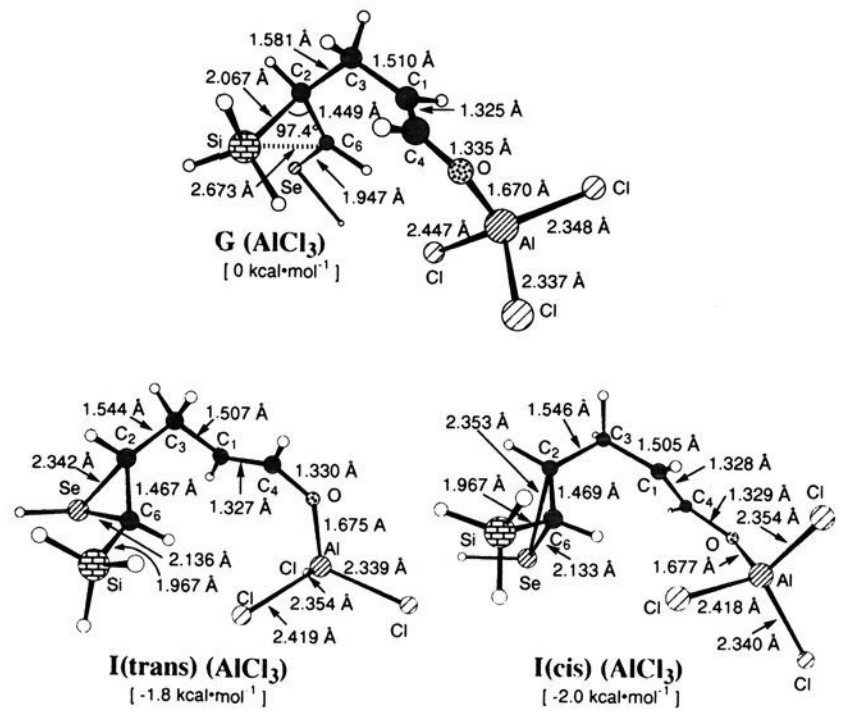
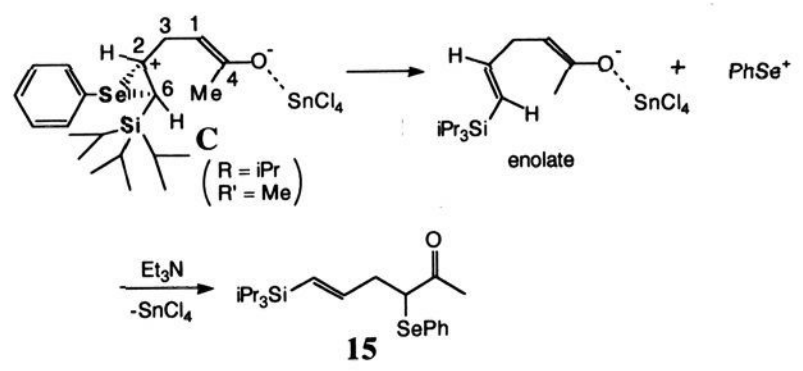


Figure 4. Ab initio RHF/LANL1MB-optimized geometries of **G**, **I** (*trans*), and **I** (*cis*) with $AlCl_3$. Energies in square brackets are ones relative to **G** ($AlCl_3$).

Et_3N, which removes $SnCl_4$ from the carbonyl group of 3-$SnCl_4$, affords **3**. The calculated model compounds, **I** (*cis*) and **J** (*cis*), shown in Figure 3 are for a minor product **12** in entry 10 (Table 1).

When the Lewis acid is $AlCl_3$, the reaction would proceed by a mechanism similar to that for $SnCl_4$. The corresponding intermediate models **G**, **I** (*cis*), and **I** (*trans*) with $AlCl_3$ were calculated (Figure 4). The differences leading to *cis* products with $AlCl_3$ and *trans* products with $SnCl_4$ preferentially could be explained in terms of the energy difference between **I** (*cis*) and **I** (*trans*). With $SnCl_4$, **I** (*trans*) is 1.2 kcal/mol more stable than **I** (*cis*) in Figure 3. On the contrary, with $AlCl_3$, **I** (*cis*) is 0.2 kcal/mol more stable than **I** (*trans*) in Figure 4. The energy difference would come from steric requirements (O–$SnCl_4$ is bigger than O–$AlCl_3$).[26]

Failure of cyclopropanation with the triisopropylsilyl derivative **1c** can be explained as follows. Nucleophilic attack of C_2 by C_1 in the intermediate **C** is prevented by steric hindrance. Instead, deselenation occurs and the resulting $PhSe^+$ attacks the enolate *in situ* to give **15**. Similar selenophenyl group migration in the



presence of Lewis acid was observed previously.[9,20a] Failure of cyclopropanation with the alkyl-substituted (on C_6) derivatives **17** and **19** would arise from the facile desilylation. In the desired route, the silyl group should migrate from C_2 to C_6 (see Scheme 3). When the C_6 is the tertiary cation in **A** by the alkyl substitution, it is too stable to accept the silyl group. Thus, even if the *n*-Bu group is replaced by Me, Et, or propyl, the desired [2 + 1] reaction does not seem to occur. The C_6 should be the secondary carbenium ion in the intermediate **A**.[27] The present cyclopropanation has required two conditions. One is the coordination of a Lewis acid ($SnCl_4$ or $AlCl_3$) to the carbonyl group to cause the chairlike addition path in Figure 1 and to yield a zwitterionic intermediate **A** with the enolate structure. The other is the combination of the Si 1,2-shift and the subsequent Se bridging for the "anti" intramolecular nucleophilic attack of C_2 by C_1.

This is the first example of the utilization of a 1,2-silicon shift to generate a cyclopropane ring. Our computational study clearly demonstrates that the intervention of the stable selenium-bridged intermediate **C** caused by a 1,2-silicon shift leads to cyclopropanation. On the contrary, the sulfur-bridged intermediate is not stable enough to intervene during the corresponding reaction. The Se–Si combination allows the strained ring formation. The remarkable selenium effect for the 1,2-silicon shift elucidated here should allow creation of stereoselective synthetic methods for highly-substituted compounds. Recently, the usefulness of Lewis acids for promoting high stereoselectivity has been shown in many kinds of C–C bond formation including asymmetric synthesis, and this cyclopropanation has much potential for wide applicability.[28] Further studies are under way in our laboratory to demonstrate the utility of 1,2-silicon shifts assisted by selenium.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded with a JASCO FT-IR 5000 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a JEOL FX-200 or JNM-GSX400, or JNM-GX500 spectrometer. For the ^1H and ^{13}C spectra, Me_4Si was used as an internal reference. Mass spectra were determined on a JEOL JMS-SX102 spectrometer. All reactions were carried out under a nitrogen atmosphere. 1-Octen-3-one (**2c**) was prepared by the reaction of *n*-pentyl magnesium bromide and acrolein, followed by oxidation according to the literature procedure.[29] Phenyl vinyl ketone (**2d**)[30] and 3-methyl-3-buten-2-one (**5**)[31] were prepared according to the literature.

(*E*)-1-(Phenylseleno)-2-(trimethylsilyl)ethene (1a).[9] A solution of 1.45 M *n*-BuLi (11.0 mL, 16.6 mmol) in hexane was added to a precooled (–78 °C) solution of (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene[8] (5.93 g, 15.2 mmol) in THF (43.5 mL) with stirring. The solution was allowed

(26) We appreciate the suggestions of the reviewers on the *cis–trans* stereochemistry of the cyclopropane products.

(27) The valuable comment of a reviewer on the effect of the alkyl substituent is acknowledged.

(28) Yamazaki, S.; Tanaka, M.; Yamabe, S. To be published.

(29) Vanstone, A. E.; Whitehurst, J. S. *J. Chem. Soc. C* **1966**, 1972.

(30) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(31) Cook, K. L.; Waring, A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 529.

to warm to −30 °C slowly. After 2 h at −30 °C, the solution was recooled to −78 °C. To the solution was added diphenyl diselenide (4.56 g, 15.2 mmol). The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and stirred for an additional 1 h. After the addition of water, the mixture was extracted with hexane–ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel, hexane) of the residue gave **1a** (2.93 g, 76%) (R_f = 0.5). **1a**: colorless oil; bp 80–82 °C (1 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.072 (s, 9H), 6.18 (d, J = 18.1 Hz, 1H), 7.02 (d, J = 18.1 Hz, 1H), 7.31–7.35 (m, 3H), 7.51–7.56 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.18 (CH_3), 127.8 (CH), 129.4 (CH), 129.5 (C), 133.9 (CH), 134.3 (CH), 134.5 (CH) (^{13}C multiplicities were determined by INEPT); IR (neat) 3062, 2958, 2900, 1580, 1544, 1478, 1439, 1248, 736, 690 cm^{-1}; MS (70 eV) m/z (relative intensity) 256 (8), 254 (4), 157 (29), 76 (38), 73 (100). Anal. Calcd for $C_9H_{16}SeSi$: C, 51.75; H, 6.32. Found: C, 52.01; H, 6.53.

Typical Experimental Procedure for the Preparation of 3a-c and 10 in Table 1 (Entries 1–3 and 6). A typical experimental procedure in Table 1 (entries 1–3 and 6) is described for **3a**. To a solution of $SnCl_4$ (366 mg, 1.40 mmol) in dichloromethane (1.8 mL), cooled to −78 °C, was added **1a** (234 mg, 0.917 mmol) in dichloromethane (0.4 mL), followed by methyl vinyl ketone (**2a**) (82.2 mg, 1.17 mmol). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (213 mg, 2.1 mmol), and then water was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **3a** (184 mg, 62%).

***trans*-1-Acetyl-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (3a) (Entry 1)**: 62%; R_f = 0.4 (hexane–ether (4:1)); colorless crystals; mp 45–46.5 °C (hexane); for ^{1}H NMR (400 and 500 MHz, $CDCl_3$) and ^{13}C NMR (125.65, 100, and 50.1 MHz, $CDCl_3$), see Tables 1 and 2; IR (KBr) 1692, 1392, 1249, 839, 739 cm^{-1}; MS (70 eV) m/z (relative intensity) 326 (100), 283 (22), 215 (35), 169 (100); exact mass M$^+$ 326.0610 (calcd for $C_{15}H_{22}OSeSi$ 326.0605). Anal. Calcd for $C_{15}H_{22}OSeSi$: C, 55.37; H, 6.81. Found: C, 55.30; H, 6.94.

***trans*-1-Propionyl-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (3b) (Entry 2)**: 62%; R_f = 0.3 (hexane–ether (4:1)); pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.162 (s, 9H), 0.735 (ddd, J = 3.9, 6.4, 8.1 Hz, 1H), 0.942 (t, J = 7.3 Hz, 3H), 1.303 (ddd, J = 3.9, 4.9, 8.5 Hz, 1H), 1.531 (ddd, J = 4.1, 4.9, 8.1 Hz, 1H), 1.711 (dddd, J = 4.1, 6.4, 8.5, 10.7 Hz, 1H), 2.10 (d, J = 10.7 Hz, 1H), 2.12–2.26 (m, 2H), 7.25–7.28 (m, 3H), 7.54–7.58 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.822, 7.842, 19.67, 29.19, 29.48, 36.37, 36.51, 127.4, 129.1, 130.7, 134.3, 210.5; IR (neat) 3060, 2960, 2900, 1698, 1578, 1477, 1437, 1394, 1251, 1125, 1029, 841, 741, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 340 (12), 338 (8), 183 (60), 109 (40), 73 (100); exact mass M$^+$ 340.0781 (calcd for $C_{16}H_{24}OSeSi$ 340.0762). Anal. Calcd for $C_{16}H_{24}OSeSi$: C, 56.62; H, 7.13. Found: C, 56.82; H, 7.31.

***trans*-1-Hexanoyl-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (3c) (Entry 3)**: 55%; R_f = 0.5 (hexane–ether (4:1)); pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.160 (s, 9H), 0.733 (ddd, J = 3.9, 6.4, 8.1 Hz, 1H), 0.879 (t, 6.8 Hz, 3H), 1.16–1.59 (m, 8H), 1.708 (dddd, J = 4.1, 6.4, 8.5, 10.7 Hz, 1H), 2.11–2.21 (m, 2H), 7.25–7.28 (m, 3H), 7.53–7.58 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.822, 14.03, 19.73, 22.53, 23.52, 29.36, 29.57, 31.49, 36.34, 43.52, 127.4, 129.1, 130.8, 134.2, 210.2; IR (neat) 2958, 2934, 2864, 1696, 1578, 1477, 1437, 1394, 1251, 857, 839, 739, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 382 (9), 380 (6), 225 (56), 151 (33), 129 (17), 73 (100); exact mass M$^+$ 382.1245 (calcd for $C_{19}H_{30}OSeSi$ 382.1231).

***r*-1-Acetyl-1-methyl-*t*-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)-cyclopropane. (10) (Entry 6)**: 14%; R_f = 0.3 hexane–ether (4:1)); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.144 (s, 9H, Si(CH_3)$_3$), 0.381 (dd, J = 3.7, 6.8, 1H, C*H*H), 0.972 (s, 3H, CH_3), 1.56 (dd, J = 3.7, 9.3 Hz, 1H, CH*H*), 1.65–1.79 (m, 1H), 1.99 (s, 3H, $COCH_3$), 2.18 (d, J = 11.7 Hz, 1H, C*H*SePhSi(CH_3)$_3$), 7.20–7.33 (m, 3H), 7.53–7.63 (m, 2H); NOE's were observed between δ 0.381 and δ 1.56 and between δ 0.972 and δ 2.18 by NOE difference spectrum; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.588 (CH_3), 14.82 (CH_3), 26.76 (CH_2), 27.29 (CH_3), 31.35 (CH), 32.05 (C), 33.92 (CH), 127.8 (CH), 129.0 (CH), 129.5 (C), 135.8 (CH), 210.0 (C) (^{13}C multiplicities were determined by INEPT); IR (neat) 2964, 1688, 1578, 1477, 1437, 1354, 1249, 859, 839, 739, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 340 (2), 183 (60), 129 (34), 109 (25), 73 (100); exact mass M$^+$ 340.0782 (calcd for $C_{16}H_{24}OSeSi$ 340.0762).

***trans*-1-Benzoyl-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (3d) (Entry 4).** To a solution of $SnCl_4$ (574 mg, 2.21 mmol) in dichloromethane (1.8 mL), cooled to −78 °C, was added **1a** (234 mg, 0.917 mmol) in dichloromethane (0.4 mL), followed by phenyl vinyl ketone (**2d**) (154 mg, 1.17 mmol). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (638 mg, 6.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1), followed by recrystallization from hexane to give **3d** (148 mg, 42%) (R_f = 0.7). **3d**: colorless crystals; mp 94–95 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.188 (s, 9H), 0.968 (ddd, J = 3.8, 6.4, 8.1 Hz, 1H), 1.57 (ddd, J = 3.8, 4.7, 8.8 Hz, 1H), 1.99 (dddd, J = 3.9, 6.4, 8.8 Hz, 1H), 2.21 (d, J = 10.7 Hz, 1H), 2.34 (ddd, J = 3.9, 4.7, 8.1 Hz, 1H), 7.11–7.14 (m, 3H), 7.32–7.40 (m, 2H), 7.46–7.52 (m, 3H), 7.65–7.69 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.793, 21.68, 26.29, 30.97, 36.51, 127.2, 128.1, 128.3, 129.1, 130.8, 132.6, 133.9, 137.7, 199.6; IR (KBr) 3056, 2958, 1661, 1448, 1396, 1253, 1232, 1021, 870, 830, 758, 731, 690 cm^{-1}; MS (70 eV) m/z (relative intensity) 388 (4), 231 (50), 157 (58), 105 (45), 73 (100), 28 (50); exact mass M$^+$ 388.0069 (calcd for $C_{20}H_{24}OSeSi$ 388.0769). Anal. Calcd for $C_{20}H_{24}OSeSi$: C, 62.00; H, 6.24. Found: C, 61.90; H, 6.28.

***trans*-1-Formyl-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (3e) (Entry 5).** To a solution of $SnCl_4$ (445 mg, 1.71 mmol) in dichloromethane (2.2 mL), cooled to −78 °C, was added **1a** (280 mg, 1.10 mmol) in dichloromethane (0.5 mL), followed by acrolein (**2e**) (84 mg, 1.49 mmol) in dichloromethane (0.2 mL). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (254 mg, 2.51 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **13** (20 mg, 6%) (R_f = 0.7, hexane–ether (2:1)) and crude **3e** (R_f = 0.35, hexane–ether (2:1)). The crude **3e** was further purified by column chromatography (silica gel) eluting with CH_2Cl_2 to give **3e** (38 mg, 11%) (R_f = 0.7, CH_2Cl_2). **3e**: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.190 (s, 9H, Si(CH_3)$_3$), 0.794–0.913 (m, 1H, C*H*H), 1.21–1.43 (m, 2H, CH*H*, *CH*CHO), 1.67–1.82 (m, 1H, C*H*), 2.08 (d, J = 10.5 Hz, 1H, C*H*SePhSi(CH_3)$_3$), 7.26–7.30 (m, 3H, Ph), 7.56–7.60 (m, 2H, Ph), 9.04 (d, J = 3.7 Hz, 1H, C*H*O). NOE's were observed between δ 0.794–0.913 and δ 1.21–1.43, δ 0.794–0.913 and δ 2.08, δ 1.21–1.43 and δ 1.67–1.82, δ 1.21–1.43 and δ 2.08, δ 1.21–1.43 and δ 9.04, δ 1.67–1.82 and δ 2.08, 1.67–1.82 and 9.04, and δ 2.08 and δ 7.56–7.60 by 2D-NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.909 (q, $^1J_{CH}$ = 119 Hz, Si(CH_3)$_3$), 16.87 (t, $^1J_{CH}$ = 165 Hz, CH_2), 28.10 (d, $^1J_{CH}$ = 166 Hz, *C*HCHSePhTMS), 31.08 (dd, $^1J_{CH}$ = 166 Hz, $^2J_{CH}$ = 28 Hz, *C*HCHO), 35.58 (d, $^1J_{CH}$ = 132 Hz, *C*HSePhTMS), 127.9 (d, $^1J_{CH}$ = 161 Hz, Ph), 129.0 (d, $^1J_{CH}$ = 161 Hz, Ph), 129.7 (s, Ph), 135.4 (d, $^1J_{CH}$ = 163 Hz, Ph), 200.5 (dd, $^1J_{CH}$ = 171 Hz, $^2J_{CH}$ = 4.4 Hz, *C*HO); IR (neat) 2960, 1707, 1578, 1477, 1437, 1251, 839, 741, 692 cm^{-1}; MS (70 eV) m/z (relative intensity) 312 (13), 155 (42), 73 (67), 28 (100); exact mass M$^+$ 312.0433 (calcd for $C_{14}H_{20}OSeSi$ 312.0448). **13**: pale yellow oil (*Z*:*E* = 8:1 by ^{1}H NMR); the *Z* stereochemistry for the major isomer was determined by comparison of the observed olefin vicinal coupling constant (J = 14.1 Hz) with the reported values of vinylsilanes;[32] ^{1}H NMR (200 MHz, $CDCl_3$) for the major isomer δ (ppm) 0.106 (s, 9H), 2.42–2.74 (m, 2H), 3.61 (dt, J = 3.1, 7.5 Hz, 1H), 5.68 (d, J = 14.1 Hz, 1H), 6.32 (td, J = 7.1, 14.1 Hz, 1H), 7.26–7.38 (m, 3H), 7.50–7.56 (m, 2H), 9.43 (d, J = 3.1 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) for the major isomer δ (ppm) 0.134, 31.40, 52.16, 129.1, 129.4, 132.9, 136.1, 136.2, 143.5, 192.6; IR (neat) 2958, 1711, 1605, 1477, 1437, 1249, 837, 739, 690 cm^{-1}; MS (70 eV)

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m/z (relative intensity) 312 (13), 215 (13), 155 (60), 84 (40), 73 (100); exact mass M^+ 312.0439 (calcd for $C_{14}H_{20}OSeSi$ 312.0449).

***cis*-1-Acetyl-2-(1-phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (11) (Entry 7).** To a solution of **1a** (234 mg, 0.917 mmol) and methyl vinyl ketone (**2a**) (289 mg, 4.12 mmol) in dichloromethane (2.2 mL) was added $AlCl_3$ (187 mg, 1.40 mmol) by portions at −78 °C. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (638 mg, 6.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **11** (74 mg, 25%) (R_f = 0.4). **11**: colorless crystals; mp 50–51 °C (hexane); for ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (50.1 MHz, $CDCl_3$), see Table 4; IR (neat) 2958, 1692, 1578, 1479, 1437, 1386, 1249, 901, 839, 739, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 326 (17), 169 (75), 95 (33), 73 (100); exact mass M^+ 326.0604 (calcd for $C_{15}H_{22}O^{80}SeSi$ 326.0605), 324.0598 (calcd for $C_{15}H_{22}O^{78}SeSi$ 324.0613). Anal. Calcd for $C_{15}H_{22}OSeSi$: C, 55.37; H, 6.81. Found: C, 55.34; H, 6.93.

(*E*)-1-(Phenylseleno)-2-(triethylsilyl)ethene (1b). A mixture of *n*-Bu_3SnH (4.92 g, 16.9 mmol) and triethylsilylacetylene (2.98 g, 21.2 mmol) was heated at 120 °C for 25 h. Distillation afforded (*E*)-1-(triethylsilyl)-2-(tri-*n*-butylsilyl)ethene (4.91 g, 67%): bp 127–130 °C (1 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.563 (q, *J* = 7.5 Hz, 6H), 0.842–0.968 (m, 24H), 1.25–1.55 (m, 12H), 6.53 (d, *J* = 23 Hz, 1H), 6.97 (d, *J* = 23 Hz, 1H). A solution of 1.52 M *n*-BuLi (8.24 mL, 12.5 mmol) in hexane was added to a precooled (−78 °C) solution of (*E*)-1-(triethylsilyl)-2-(tri-*n*-butylstannyl)ethene (4.91 g, 11.4 mmol) in THF (36.6 mL) with stirring. The solution was allowed to warm to −30 °C slowly. After 2 h at −30 °C, the solution was recooled to −78 °C. To the solution was added diphenyl diselenide (3.55 g, 11.4 mmol). The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and stirred for an additional 2 h. After the addition of water, the mixture was extracted with hexane–ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel, hexane) of the residue gave **1b** (2.55 g, 75%) (R_f = 0.4). **1b**: pale yellow oil; ^1H NMR (200 Mhz, $CDCl_3$) δ (ppm) 0.568 (q, *J* = 7.8 Hz, 6H), 0.928 (t, *J* = 7.8 Hz, 9H), 6.16 (d, *J* = 18.1 Hz, 1H), 7.02 (d, *J* = 18.1 Hz, 1H), 7.28–7.32 (m, 3H), 7.49–7.54 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 3.550, 7.404, 127.6, 129.4, 129.8, 131.3, 133.5, 135.1; IR (neat) 2956, 2912, 2876, 1555, 1539, 1479, 1017, 961, 774, 735, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 298 (95), 296 (97), 243 (100), 215 (43), 187 (17), 115 (34); exact mass M^+ 298.0688 (calcd for $C_{14}H_{22}SeSi$ 298.0656). Anal. Calcd for $C_{14}H_{22}SeSi$: C, 56.55; H, 7.46. Found: C, 56.78; H, 7.52.

Reaction of 1b with 2a in the Presence of $SnCl_4$ (Entry 10). To a solution of $SnCl_4$ (391 mg, 1.5 mmol) in dichloromethane (2.0 mL), cooled to −78 °C, was added **1b** (300 mg, 1.0 mmol) in dichloromethane (0.5 mL), followed by methyl vinyl ketone (**2a**) (140 mg, 2.0 mmol). The mixture was stirred at −78 °C for 4 h. The reaction mixture was quenched by triethylamine (232 mg, 2.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give recovered **1b** (44 mg, 15%) (R_f = 0.4, hexane), **12** (20 mg, 5.4%) (R_f = 0.5, hexane–ether (2:1)) and **3f** (176 mg, 48%) (R_f = 0.4, hexane–ether (2:1)). *trans*-1-Acetyl-2-(1-(phenylseleno)-1-(triethylsilyl)methyl)cyclopropane (**3f**): pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.611–0.787 (m, 7H, CH_2CH_3, CHH), 1.02 (t, *J* = 7.7 Hz, 9H, CH_2CH_3), 1.27 (ddd, *J* = 4.3, 4.4, 8.7 Hz, 1H, CH*H*), 1.46 (ddd, *J* = 4.2, 4.3, 8.2 Hz, 1H, C*H*$COCH_3$), 1.71–1.81 (m, 1H, C*H*), 1.87 (s, 3H, $COCH_3$), 2.24 (d, *J* = 11.0 Hz, 1H, C*H*SePhSiEt$_3$), 7.26–7.29 (m, 3H, Ph), 7.55–7.60 (m, 2H, Ph); NOE's were observed between δ 0.611–0.787 and δ 1.02, δ 0.611–0.787 and δ 1.27, δ 0.611–0.787 and δ 1.46, δ 0.611–0.787 and δ 2.24, δ 1.27 and δ 1.71–1.81, δ 1.46 and δ 2.24, δ 1.71–1.81 and δ 2.24, and δ 2.24 and δ 7.55–7.60 by 2D-NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 3.258 (t, $^1J_{CH}$ = 116 Hz, CH_2CH_3), 7.667 (q, $^1J_{CH}$ = 127 Hz, CH_2CH_3), 19.58 (t, $^1J_{CH}$ = 163 Hz, CH_2), 30.27 (d, $^1J_{CH}$ = 166 Hz, CH), 30.44 (q, $^1J_{CH}$ = 127 Hz, $COCH_3$), 30.53 (d, $^1J_{CH}$ = 161 Hz, CH), 33.51 (d, $^1J_{CH}$ = 132 Hz, CHSePhSiEt$_3$), 127.4 (d, $^1J_{CH}$ = 161 Hz, Ph), 129.1 (d, $^1J_{CH}$ = 161 Hz, Ph), 131.1 (s, Ph), 134.2 (d, $^1J_{CH}$ = 163 Hz, Ph), 207.7 (s, CO); IR (neat) 2958, 2914, 2878, 1696, 1578, 1477, 1392, 1174, 1021, 735, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 368 (28), 254 (10), 243 (14), 211 (100), 181 (9), 157 (11), 115 (100), 97 (35), 87 (61); exact mass M^+ 368.1079 (calcd for $C_{18}H_{28}OSeSi$ 368.1074). *cis*-1-Acetyl-2-(1-(phenylseleno)-1-(triethylsilyl)methyl)cyclopropane (**12**): pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.661 (q, *J* = 7.9 Hz, 6H, CH_2CH_3), 0.957 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 1.15–1.21 (m, 2H, CH_2), 1.77 (dddd, *J* = 7.9, 8.1, 8.1, 11.9 Hz, 1H, C*H*), 1.91 (s, 3H, $COCH_3$), 2.11 (ddd, *J* = 5.9, 7.7, 7.9 Hz, 1H, C*H*$COCH_3$), 2.86 (d, *J* = 11.9 Hz, 1H, C*H*SePhSiEt$_3$), 7.19–7.24 (m, 3H, Ph), 7.50–7.53 (m, 2H, Ph); NOE's were observed between δ 0.661 and δ 0.957, δ 0.661 and δ 1.15–1.21, δ 0.957 and δ 2.86, δ 1.15–1.21 and δ 1.77, δ 1.15–1.21 and δ 2.11, δ 1.15–1.21 and δ 2.86, δ 1.77 and δ 2.11, and δ 1.91 and δ 2.11, δ 1.91 and δ 7.19–7.24, δ 1.91 and δ 7.50–7.54, δ 2.86 and δ 7.50–7.54 by 2D-NOESY; ^{13}C NMR (50.1 Mhz, $CDCl_3$) δ (ppm) 3.346, 7.667, 18.62, 25.56, 27.40, 30.62, 32.05, 127.3, 128.8, 129.7, 134.9, 206.9); IR (neat) 2956, 2914, 2878, 1692, 1578, 1477, 1386, 1168, 735, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 368 (9), 269 (7), 243 (16), 211 (72), 181 (9), 157 (17), 115 (100), 95 (48), 87 (79); exact mass M^+ 368.1088 (calcd for $C_{18}H_{28}OSeSi$ 368.1074).

Reaction of 1b with 2e in the Presence of $SnCl_4$ (Entry 11). To a solution of $SnCl_4$ (445 mg, 1.71 mmol) in dichloromethane (2.2 mL), cooled to −78 °C, was added **1b** (333 mg, 1.12 mmol) in dichloromethane (0.5 mL), followed by acrolein (**2e**) (260 mg, 4.64 mmol) in dichloromethane (0.8 mL). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (261 mg, 2.58 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **14** (49 mg, 12%) (R_f = 0.6) and **3g** (110 mg, 28%) (R_f = 0.5). *trans*-1-Formyl-2-(1-(phenylseleno)-1-(triethylsilyl)methyl)cyclopropane (**3g**): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.675–0.869 (m, 7H, CH_2CH_3, CH*H*), 1.03 (t, *J* = 7.6 Hz, 9H, CH_2CH_3), 1.22–1.39 (m, 2H, C*H*CHO, CH*H*), 1.72–1.88 (m, 1H, C*H*), 2.20 (d, *J* = 11.3 Hz, 1H, C*H*SePhSiEt$_3$), 7.26–7.31 (m, 3H, Ph), 7.56–7.62 (m, 2H, Ph), 9.02 (d, *J* = 3.9 Hz, 1H, C*H*O); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 3.200, 7.667, 16.69, 28.66, 31.40, 33.01, 127.9, 129.1, 130.2, 135.2, 200.4; IR (neat) 2956, 2914, 2878, 1707, 1578, 1477, 1437, 1021, 1007, 733, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 354 (17), 325 (4), 243 (13), 205 (9), 197 (100), 157 (15), 115 (78), 103 (47), 87 (48), 75 (27); exact mass M^+ 354.0916 (calcd for $C_{17}H_{26}OSeSi$ 354.0918). **14**: pale yellow oil; the *Z* stereochemistry of **14** was determined by comparison of the observed olefin vicinal coupling constant (*J* = 14.0 Hz) with the reported values of vinylsilanes;[32] ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.595 (q, *J* = 7.9 Hz, 6H), 0.929 (t, *J* = 7.9 Hz, 9H), 2.40–2.73 (m, 2H), 3.61 (dt, *J* = 3.1, 7.5 Hz, 1H), 5.60 (d, *J* = 14.0 Hz, 1H), 6.41 (td, *J* = 7.0, 14.0 Hz, 1H), 7.26–7.40 (m, 3H), 7.51–7.55 (m, 2H), 9.44 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 4.543, 7.550, 31.90, 52.19, 125.7, 129.1, 129.4, 129.4, 136.2, 144.6, 192.6; IR (neat) 2956, 2912, 2876, 1711, 1605, 1019, 737, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 354 (4), 325 (7), 185 (9), 167 (25), 139 (34), 103 (58), 84 (87), 75 (36), 57 (100); exact mass M^+ 354.0895 (calcd for $C_{17}H_{26}OSeSi$ 354.0918).

Reaction of 1b with 2a in the Presence of $AlCl_3$ (Entry 12). To a solution of **1b** (297 mg, 1.0 mmol) and methyl vinyl ketone (**2a**) (315 mg, 4.5 mmol) in dichloromethane (2.5 mL) was added $AlCl_3$ (200 mg, 1.5 mmol) by portions at −78 °C. The mixture was stirred at −78 °C for 4 h. The reaction mixture was quenched by triethylamine (232 mg, 2.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give recovered **1b** (98 mg, 33%), **12** (107 mg, 29%) and **3f** (23 mg, 6%).

(*E*)-1-(Phenylseleno)-2-(triisopropylsilyl)ethene (1c). A solution of 1.45 M *n*-BuLi (2.98 mL, 4.32 mmol) in hexane was added to a precooled (−78 °C) solution of (*E*)-1-(triisopropylsilyl)-2-(tri-*n*-butylstannyl)-ethene[13] (1.70 g, 3.6 mmol) in THF (36.7 mL) with stirring. The solution was allowed to warm to −20 °C. After 20 min at −20 °C, the solution was recooled to −78 °C. To the solution was added diphenyl diselenide (1.12 g, 3.6 mmol). The mixture was allowed to warm to 0 °C and was stirred for 1 h. After the addition of water, the mixture was extracted with hexane–ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel, hexane) of the residue gave **1c** (785 mg, 64%) (R_f = 0.5). **1c**: pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.01–1.07 (m, 21H), 6.13 (d, *J* = 18.3 Hz, 1H), 7.05 (d, *J* = 18.3

Hz, 1H), 7.26–7.35 (m, 3H), 7.47–7.54 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 11.01, 18.65, 127.5, 129.4, 129.7, 130.0, 133.4, 135.3; IR (neat) 2944, 2866, 1549, 1477, 1464, 882, 754, 690, 656 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 340 (6), 297 (16), 255 (4), 229 (5); exact mass M$^+$ 340.1111 (calcd for $C_{17}H_{28}{}^{80}SeSi$ 340.1126), 338.1086 (calcd for $C_{17}H_{28}{}^{78}SeSi$ 338.1134).

Reaction of 1c with 2a in the Presence of $SnCl_4$. To a solution of $SnCl_4$ (365 mg, 1.4 mmol) in dichloromethane (1.8 mL), cooled to −78 °C, was added **1c** (350 mg, 1.0 mmol) in dichloromethane (0.4 mL), followed by methyl vinyl ketone (**2a**) (82 mg, 1.17 mmol). The mixture was stirred at −30 °C for 6 h. The reaction mixture was quenched by triethylamine (212 mg, 2.1 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane, and the organic phase was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **15** (58 mg, ca. 15%) (R_f = 0.4, hexane–ether (2:1)). (A small amount of unidentified compound was present by NMR.) **15**: pale yellow oil; the *E* stereochemistry of **15** was determined by comparison of the observed olefin vicinal coupling constant (J = 18.8 Hz) with the reported values of vinylsilanes;[32] ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.04 (bs, 21H), 2.28 (s, 3H), 2.47–2.68 (m, 2H), 3.74 (t, J = 7.6 Hz, 1H), 5.61 (d, J = 18.8 Hz, 1H), 6.02 (td, J = 6.2, 18.8 Hz, 1H), 7.24–7.35 (m, 3H), 7.47–7.55 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 10.82, 18.65, 27.64, 37.83, 51.08, 127.7, 128.9, 129.2, 129.3, 135.9, 144.7, 203.7; IR (neat) 2944, 2866, 1705, 1615, 1464, 1354, 996, 884, 739 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 410 (5), 367 (100), 312 (25), 271 (25), 229 (9), 211 (83), 167 (58); exact mass M$^+$ 410.1548 (calcd for $C_{21}H_{34}OSeSi$ 410.1544).

(*E*)-2-(Phenylseleno)-1-(trimethylsilyl)-1-hexene (19). A mixture of (*E*)-2-(tributylstannyl)-1-(trimethylsilyl)hexane (**22**) and (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)hexene (**24**) (containing a small amount of the *Z* isomer of **24**) (**22**:**24** = ca. 70:30) was prepared by molybdenum-catalyzed hydrostannation of 1-(trimethylsilyl)-1-hexyne according to the literature.[15] A solution of 1.55 N *n*-BuLi (3.31 mL, 5.13 mmol) in hexane was added to a precooled (−78 °C) solution of a mixture of **15** and **16** (2.11 g, 4.73 mmol) in THF (14.1 mL) with stirring. The solution was allowed to warm to −30 °C. After 1 h at −30 °C, the solution was recooled to −78 °C. To the solution was added diphenyl diselenide (1.48 g, 4.73 mmol). The mixture was stirred at −78 °C for 15 min, allowed to warm to room temperature, and stirred overnight. After the addition of the water, the mixture was extracted with hexane–ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel, hexane) of the residue gave **19** (443 mg, 30.1%) (R_f = 0.5) and 1-(phenylseleno)-1-(trimethylsilyl)-1-hexene (**25**) (a mixture of *E* and *Z* isomers (6:1 by ^{1}H NMR) (51 mg, 3.5%) (R_f = 0.6)). **19**: pale yellow oil; ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) 0.067 (s, 9H, $Si(CH_3)_3$), 0.826 (t, J = 7.2 Hz, 3H, $(CH_2)_3CH_3$), 1.16–1.35 (m, 2H, $(CH_2)_2CH_2CH_3$), 1.61–1.77 (m, 2H, $CH_2CH_2C_2H_5$), 2.42–2.50 (m, 2H, $CH_2nC_3H_7$), 5.81 (s, 1H, =C*H*), 6.97–7.01 (m, 3H), 7.59–7.64 (m, 2H); NOE's were not observed between δ 2.42–2.50 and δ 5.81 by NOE difference spectra; ^{13}C NMR (50.1 MHz, C_6D_6) δ (ppm) 0.321, 14.13, 22.75, 32.91, 38.19, 128.2, 129.4, 129.9, 136.3, 153.4; IR (neat) 2960, 2864, 1576, 1477, 1437, 1249, 841, 739, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 312 (6), 215 (7), 157 (28), 73 (100); exact mass M$^+$ 312.0791 (calcd for $C_{15}H_{24}SeSi$ 312.0812). **25** (*E*:*Z* = 6:1): pale yellow oil; ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) 0.053 (s, *Z* isomer), 0.133 (s, *E* isomer, 9H), 0.805 (t, J = 7.0 Hz, *E*), 0.904 (t, J = 7.3 Hz, *Z*, 3H), 1.12–1.44 (m, 4H), 2.32–2.51 (m, 2H), 5.60 (t, J = 7.4 Hz, *Z*), 6.60 (t, J = 6.7 Hz, *E*, 1H), 6.91–7.03 (m, 3H), 7.35–7.47 (m, 2H); ^{13}C NMR (50.1 MHz, C_6D_6) δ (ppm) −1.112, −0.966, 13.98, 14.16, 22.74, 23.50, 29.95, 31.30, 33.72, 34.68, 126.0, 126.7, 129.1, 129.3, 130.7, 132.4, 132.9, 133.4, 133.6, 153.1; IR (neat) 2960, 2930, 1580, 1477, 1247, 837, 733, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 312 (6), 215 (20), 73 (100); exact mass M$^+$ 312.0797 (calcd for $C_{15}H_{24}SeSi$ 312.0812).

(*Z*)-1-(Trimethylsilyl)-2-(phenylseleno)-1-hexene (17). A solution of 1.35 N *n*-BuLi (1.81 mL, 2.45 mmol) in hexane was added to a precooled (−78 °C) solution of (*Z*)-2-(tributylstannyl)-1-(trimethylsilyl)-1-hexene (**23**)[16] (1 g, 2.25 mmol) in THF (6.7 mL) with stirring. The solution was allowed to warm to −30 °C. After 1 h at −30 °C, the solution was recooled to −78 °C. To the solution was added diphenyl diselenide (0.702 g, 2.25 mmol). The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and stirred for an additional 1 h. After the addition of water, the mixture was extracted with hexane–ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel, hexane) of the residue gave **17** (455 mg, 65%) (R_f = 0.6). **17**: pale yellow oil; ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) 0.380 (s, 9H, $Si(CH_3)_3$), 0.808 (t, J = 7.2 Hz, 3H, $(CH_2)_3CH_3$), 1.08–1.26 (m, 2H, $(CH_2)_2CH_2CH_3$), 1.46–1.60 (m, 2H, $CH_2CH_2C_2H_5$), 2.34 (t, J = 7.6 Hz, 2H, $CH_2nC_3H_7$), 6.29 (s, 1H, =C*H*), 7.00–7.06 (m, 3H, Ph), 7.50–7.54 (m, 2H, Ph); NOE's were observed between δ 2.34 and δ 6.29 by NOE difference spectra; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 0.134, 14.03, 21.92, 31.14, 42.06, 127.0, 129.1, 130.7, 133.0, 135.8, 151.7; IR (neat) 2958, 2932, 1578, 1477, 1437, 1247, 1023, 841, 735, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 312 (13), 215 (9), 155 (10), 73 (100); exact mass M$^+$ 312.0808 (calcd for $C_{15}H_{24}O^{80}SeSi$ 312.0813), 310.0766 (calcd for $C_{15}H_{24}O^{78}SeSi$ 310.0820).

Reaction of 17 and 2a in the Presence of $SnCl_4$. To a solution of $SnCl_4$ (354 mg, 1.36 mmol) in dichloromethane (1.7 mL), cooled to −78 °C, was added **17** (276 mg, 0.89 mmol) in dichloromethane (0.4 mL), followed by methyl vinyl ketone (**2a**) (79.8 mg, 1.14 mmol). The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (213 mg, 2.1 mmol) and then saturated aqueous $NaHCO_3$. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **20** (71.3 mg, 26%) (R_f = 0.5). **20**: pale yellow oil; ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 0.785 (t, J = 7.4 Hz, 3H, $(CH_2)_3CH_3$), 1.11–1.20 (m, 2H, $(CH_2)_2CH_2CH_3$), 1.45–1.53 (m, 2H, $CH_2CH_2C_2H_5$), 1.62 (s, 3H, $COCH_3$), 2.04 (t, J = 7.2 Hz, 2H, $COCH_2CH_2$), 2.22 (t, J = 7.5 Hz, 2H, $CH_2nC_3H_7$), 2.59 (td, J = 7.1, 7.1 Hz, 2H, $COCH_2CH_2$), 5.76 (tt, J = 7.1, 1.1 Hz, 1H, =C*H*), 6.93–7.02 (m, 3H, Ph), 7.43–7.46 (m, 2H, Ph); NOE's were observed between δ 2.22 and δ 5.76 by 2D-NOESY; ^{13}C NMR (50.1 MHz, C_6D_6) δ (ppm) 14.04, 22.15, 26.71, 29.16, 31.47, 39.44, 42.80, 126.9, 129.3, 130.8, 132.6, 134.3, 134.5, 205.5; IR (neat) 2960, 2932, 2874, 1717, 1578, 1477, 1437, 1363, 1162, 1023, 739, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 310 (54), 153 (72), 95 (52), 73 (28), 43 (100); exact mass M$^+$ 310.0847 (calcd for $C_{16}H_{22}OSe$ 310.0835).

Products Shown in Scheme 2 Are Described. ***trans*-1-(1-Methylethenyl)-2-(1-(phenylseleno)-1-(trimethylsilyl)methyl)cyclopropane (7).** An ice-cold solution of 18.6 mL of $Zn–CH_2Br_2–TiCl_4$ reagent (ca. 0.58 M, 10.7 mmol), which was prepared according to the literature,[18c] was added portionwise to a stirred solution of **3a** (599 mg, 1.84 mmol) in dichloromethane (16.3 mL) at room temperature. The mixture was stirred for 1 h. The reaction mixture was poured into sodium bicarbonate (47 g)–water (109 mL) and ether. The mixture was extracted with ether. The organic phase was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel eluting with hexane to give **7** (538 mg, 90%) (R_f = 0.4). **7**: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.149 (s, 9H), 0.514 (ddd, J = 4.9, 5.1, 8.5 Hz, 1H), 0.840 (ddd, J = 4.9, 6.0, 7.9 Hz, 1H), 1.06–1.19 (m, 2H), 1.55 (bs, 3H), 2.09 (d, J = 9.8 Hz, 1H), 4.48–4.49 (m, 1H), 4.58–4.60 (m, 1H), 7.20–7.26 (m, 3H), 7.54–7.59 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.676 (CH_3), 15.11 (CH_2), 20.81 (CH_3), 23.26 (CH), 26.18 (CH), 38.12 (CH), 107.9 (CH_2), 127.0 (CH), 128.8 (CH), 131.6 (C), 134.0 (CH), 145.7 (C); ^{13}C multiplicities were determined by INEPT; IR (neat) 3076, 3002, 2958, 2898, 1636, 1578, 1477, 1437, 1249, 1023, 857, 839, 737, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 324 (2), 322 (1), 256 (10), 230 (9), 167 (13), 93 (100), 73 (100); exact mass M$^+$ 324.0807 (calcd for $C_{16}H_{24}SeSi$ 324.0813).

***trans*-1-Formyl-2-(1-methylethenyl)cyclopropane (8).** To a solution of **7** (686 mg, 2.12 mmol) in 36.7 mL of THF was added a solution of $NaIO_4$ (1.06 g, 4.95 mmol) in water (6.0 mL) with vigorous stirring. After 4 h, the reaction mixture was poured into ether and saturated aqueous $NaHCO_3$ solution. The organic layer was washed with H_2O, dried ($MgSO_4$), and concentrated *in vacuo* (with ice-cooling). The residue was eluted through a silica gel column with pentane–ether (4:1), and the fractions containing the R_f = 0.5 product (TLC: silica gel, hexane–ether (2:1)) were combined and concentrated *in vacuo* (with ice-cooling) to give **8** (92 mg, 39%, including a trace amount of impurity). The fractions containing the R_f = 0.2 product (TLC: silica gel, hexane–ether (2:1)) were evaporated to give **9** (73.4 mg, 12.9%). **8**: colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.32 (ddd, J = 4.8, 7.0, 8.4 Hz, 1H), 1.42 (ddd, J = 4.5, 4.8, 9.2 Hz, 1H), 1.67 (s, 3H), 1.96 (dddd, J = 4.2, 4.5, 5.1, 8.4 Hz, 1H), 2.13 (ddd, J = 4.2, 7.0, 9.2 Hz, 1H), 4.82 (m, 2H), 9.16 (d, J = 5.1 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 13.60, 20.28, 28.51, 30.41, 111.6, 142.0, 200.3; IR (neat) 2976, 1709, 1640, 1456, 1168, 992, 893 cm^{-1}; GC–MS (70 eV) *m/z* (relative intensity) 110 (11), 109 (15), 95 (100), 81 (76), 67 (38), 53 (40), 41 (51); exact mass

M^+ 110.0751 (calcd for $C_7H_{10}O$ 110.0732). 9: yellow oil (*E*:*Z* = 8:1), *E*:*Z* ratio was determined by ^1H NMR; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.731 (s, *E*), 1.769 (s, *Z*, 3H), 1.958 (bs, 1H), 2.37–2.44 (m, 2H), 4.14 (t, *J* = 6.2 Hz, *E*), 4.21 (t, *J* = 6.3 Hz, *Z*, 1H), 4.88–4.89 (m, 1H), 4.99–5.01 (m, 1H), 6.02 (ddd, *J* = 7.4, 7.4, 15.2 Hz, *E*), 6.07 (m, *Z*, 1H), 6.53 (ddd, *J* = 1.2, 1.2, 15.2 Hz, *E*), 6.60 (ddd, *J* = 1.2, 1.2, 9.0 Hz, *Z*, 1H), 7.26–7.34 (m, 3H), 7.43–7.50 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) (peaks for the major *E* isomer) δ (ppm) 18.00 (CH_3), 40.11 (CH_2), 74.53 (CH), 111.5 (CH_2), 120.0 (CH), 127.0 (CH), 129.2 (CH), 130.6 (C), 131.9 (CH), 134.4 (CH), 146.5 (C) (^{13}C multiplicities were determined by off-resonance decoupling); IR (neat) 3372, 3074, 2918, 1653, 1578, 1479, 1439, 1023, 901, 737, 690 cm^{-1}; MS (70 eV) *m*/*z* (relative intensity) 268 (19), 266 (14), 198 (42), 157 (18), 116 (100); exact mass M^+ 268.0384 (calcd for $C_{13}H_{16}OSe$ 268.0366).

(±)-*trans*-1-(1-Methylethenyl)-2-(2-methyl-1-propenyl)cyclopropane ((±)-Rothrockene) (4). A solution of *n*-BuLi (1.35 M in *n*-hexane, 1.85 mL, 2.5 mmol) was added dropwise to a stirred and ice-cold suspension of isopropyltriphenylphosphonium iodide (1.08 g, 2.5 mmol) in THF (9.9 mL). The mixture was stirred to 0 °C for 15 min. A solution of **8** (59 mg, 0.536 mmol) in THF (1 mL) was added to the mixture at 0 °C. After the mixture was stirred at 0 °C for 2.5 h, it was allowed to warm to room temperature and was stirred for 1 h. Water was added and the mixture was extracted with *n*-pentane. The pentane layer was separated, washed with water, dried (Na_2SO_4), and concentrated *in vacuo* (with ice-cooling). The residue was eluted through a silica gel column with pentane with cooling, and the fractions containing the R_f = 0.7 product (TLC: silica gel, hexane) were combined and concentrated *in vacuo* (with ice-cooling) to give **4** (49 mg, 67%). **4**: colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.615 (ddd, *J* = 5.0, 5.0, 8.6 Hz, 1H), 0.947 (ddd, *J* = 4.5, 5.7, 8.5 Hz, 1H), 1.32 (ddd, *J* = 4.6, 4.6, 9.0 Hz, 1H), 1.46–1.60 (m, 1H), 1.67 (bs, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.72 (d, *J* = 0.98 Hz, 3H), 4.61–4.67 (m, 3H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 13.86 (CH_2), 18.31 (CH_3), 19.16 (CH), 20.82 (CH_3), 25.58 (CH_3), 27.04 (CH), 108.0 (CH_2), 127.5 (CH), 131.2 (C), 145.8 (C) (^{13}C multiplicities were determined by INEPT); IR (neat) 3082, 3006, 2972, 2924, 2862, 1647, 1636, 1452, 1377, 874 cm^{-1}; MS (70 eV) *m*/*z* (relative intensity) 136 (11), 121 (14), 105 (12), 93 (85), 92 (15), 91 (29), 80 (38), 79 (44), 77 (36), 67 (16), 28 (100); exact mass M^+ 136.1261 (calcd for $C_{10}H_{16}$ 136.1252).

Acknowledgment. We are grateful to Prof. I. Murata and Dr. K. Yamamoto (Osaka University) for measurement of NMR (400 and 500 MHz) and mass spectra and elemental analysis. All the MO calculations were performed on the CONVEX C-220 computer at the Information Processing Center of Nara University of Education.