Lewis Acid Promoted [2 + 1] Cycloaddition Reactions of 1-Seleno-2-silylethene with Tricarbonyl-Substituted Olefins

Shoko Yamazaki,* Hitoshi Kumagai, Takashi Takada, and Shinichi Yamabe

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630, Japan

Kagetoshi Yamamoto

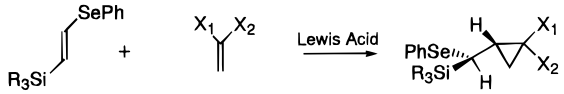
Department of Chemistry, Graduate School of Science, Osaka University , Toyonaka, Osaka 560, Japan

Received December 3, 1996[⊗]

The reactions of 1-seleno-2-silylethenes **1** with highly electrophilic tricarbonyl-substitued olefins in the presence of Lewis acids have been investigated. The reaction of 1-(phenylseleno)-2-(trimethylsilyl)ethene (**1a**) with tris(alkoxycarbonyl) olefins **2** or 1,1-bis(alkoxycarbonyl)-2-acyl olefins **3** in the presence of $ZnBr_2$ at −30 °C gave *cis*-substituted cyclopropanes exclusively. The origin of the *cis* stereochemistry is ascribed to the synclinal addition path of the $ZnBr_2$-coordinated electrophilic olefin to **1**. Application of the highly functionalized selenium- and silicon-substituted cyclopropane products to the preparation of a useful synthetic intermediate **20** for the pyrethroid class of insecticides is also demonstrated.

Introduction

Due to the importance of cyclopropanes in the fields of biologically active compounds,[1] utilization in organic synthesis,[2] mechanistic probes to determine reaction pathways,[3] and potential scaffolds for generation of molecular diversity,[4] the development of new methodology for the preparation of cyclopropane derivatives is of major interest. One of today's challenges in this field is to devise and develop new cyclopropanation reactions which can produce diversely functionalized cyclopropanes with excellent control of the diastereo- and enantioselectivities. We have recently reported that reaction of (*E*)-1-(phenylseleno)-2-silylethenes (**1**) with vinyl ketones or methylenemalonate esters gave di- and trisubstituted cyclopropane products in the presence of Lewis acids. The reaction has high stereoselectivity and proceeds *via* an unprecedented selenium-stabilized silicon migration (eq 1).[5]



1a: R = Me X_1 = COR', X_2 = H

1b: R = Et X_1, X_2 = COOR' (eq 1)

Since relatively few methods for the synthesis of tri- and tetrasubstituted cyclopropanes have been reported so far,[6] further development of this novel reaction *via* investigation of new substrates which can lead to polyfunctionalized cyclopropanes is desirable. The potential for asymmetric synthesis has been also demonstrated.[5c] Additionally, further improvements in, and understanding of, the cyclopropane *vs* cyclobutane chemoselectivity are especially required, since we have previously observed an unusual [2 + 1] and [2 + 2] cycloaddition competition in the reaction between **1** and methylenemalonate esters.[5b]

We now present the results of the reaction of **1** with tricarbonyl-substituted olefins and the transformation of the selenosilicon-substituted cyclopropane products into useful synthetic intermediates for biologically significant compounds. In order to expand the scope of [2 + 1] cycloadditions of **1**, a relatively unreactive olefin, we have investigated highly reactive electrophilic olefins with *three* electron-withdrawing substituents. Such types of highly reactive olefins have so far only been employed in a limited number of reactions such as free-radical copolymerization, Diels−Alder, [2 + 2], and carbanionic [2 + 1] cycloadditions. However, reactions in the presence of Lewis acid have not been fully investigated.[7]

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) For a recent review, see: (a) Salaün, J.; Baird, M. S. *Curr. Med. Chem.* **1995**, *2*, 511. For recent papers, see: (b) White, J. D.; Kim, T-S.; Mambu, M. *J. Am. Chem. Soc.* **1995**, *117*, 5612. (c) Onada, T.; Shirai, R.; Koiso, Y.; Iwasaki, S. *Tetrahedron Lett.* **1995**, *36*, 5765. (d) Hoemann, M. Z.; Agrios, K. A.; Aubé, J. *Tetrahedron Lett.* **1996**, *37*, 953. (e) Burgess, K.; Ho, K.-K.; Pettitt, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 54. (f) Charette, A. B.; Côté B. *J. Am. Chem. Soc.* **1995**, *117*, 12721. (g) Shuto, S.; Ono, S.; Hase, Y.; Kamiyama, N.; Takada, H.; Yamashita, K.; Matsuda, A. *J. Org. Chem.* **1996**, *61*, 915. (h) Barrett, A. G. M.; Kasdorf, K. *J. Chem. Soc., Chem. Commun.* **1996**, 325. (i) Barrett, A. G. M.; Hamprecht, D.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 7863. (j) Jiao, Y.; Yoshihara, T.; Ishikuri, S.; Uchino, H.; Ichihara, A. *Tetrahedron Lett.* **1996**, *37*, 1039. (k) Critcher, D. I.; Connolly, S.; Wills, M. *Tetrahedron Lett.* **1995**, *36*, 3763. (l) White, J. D.; Jensen, M. S. *Synlett* **1996**, 31. (m) White, J. D.; Jensen, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6224.

(2) (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (c) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229. (d) Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733. (e) de Meijere, A.; Wessjohann, L. *Synlett* **1990**, 20. (f) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. (g) Monti, H.; Rizzotto, D.; Leandri, G.; Monti, J.-P. *Tetrahedron Lett.* **1994**, *35*, 2885.

(3) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) He, M.; Dowd, P. *J. Am. Chem. Soc.* **1996**, *118*, 711. (c) Mattalia, J.-M.; Chanon, M.; Stirling, C. J. M. *J. Org. Chem.* **1996**, *61*, 1153. (d) Suckling, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 537.

(4) For examples of carbocyclic scaffolds, see: (a) Patek, M.; Drake, B.; Lebl, M. *Tetrahedron Lett.* **1994**, *35*, 9169. (b) Kocis, P.; Issakova, O.; Sepetov, N. F.; Lebl, M. *Tetrahedron Lett.* **1995**, *36*, 6623.

(5) (a) Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356. (b) Yamazaki, S.; Tanaka, M.; Inoue, T.; Morimoto, N.; Kumagai, H. *J. Org. Chem.* **1995**, *60*, 6546. (c) Yamazaki, S.; Tanaka, M.; Yamabe, S. *J. Org. Chem.* **1996**, *61*, 4046.

(6) (a) *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 1987. (b) *The Chemistry of the Cyclopropyl Group, Vol. 2*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 1995. (c) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, pp 951−1067. (d) Romo, D.; Meyers, A. I. *J. Org. Chem.* **1992**, *57*, 6265. (e) Martin, S. F.; Spaller, M. R.; Liras, S.; Hartmann, B. *J. Am. Chem. Soc.* **1994**, *116*, 4493. (f) Hanessian, S.; Andreotti, D.; Gomtsyan, A. *J. Am. Chem. Soc.* **1995**, *117*, 10393.

S0022-3263(96)02248-7 CCC: $14.00

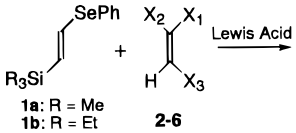
Table 1. [2 + 1] Cycloadditions of 1 and Electrophilic Olefins[a]

entry	seleno olefin	electrophilic olefin	Lewis acid	temp/°C	time/h	product (yield/%)	recovered **1** (yield/%)
1	**1a**	**2a**	$ZnBr_2$	−30	12	**7a** (63)	
2	**1b**	**2a**	$ZnBr_2$	−30	10	**8a** (21)	**1b** (61)
3	**1a**	**2b**	$ZnBr_2$	−30	12	**7b** (69)	
4	**1a**	**2c**	$ZnBr_2$	−30	14	**7c** (67)	
5	**1a**	**2d**	$ZnBr_2$	−30	12	**7d** (53)	**1a** (17)
6	**1a**	**2e**	$ZnBr_2$	−30	8	**7e** (37) diastereomer ratio 2:1	**1a** (39)
7	**1a**	**3a**	$ZnBr_2$	−30	1	**9a** (55)	
8	**1b**	**3a**	$ZnBr_2$	−30	4.5	**10a** (47)	**1b** (48)
9	**1a**	**3b**	$ZnBr_2$	−30	3	**9b** (74)	
10	**1a**	**4**	$ZnBr_2$	−30	2	**11a** (2.5) **12a** (5.3)	
11	**1a**	**5**	$ZnCl_2$	−78	3	**13** (23)[b]	
12	**1b**	**6**	$SnCl_4$	−78	3	**14** (19)	**1b** (81)

[a] All reactions were carried out using 1−3 mmol of **1**, 1.3 equiv of **2**−**6**, and 1.5 equiv of Lewis acid at ~0.4 M for **1** in CH_2Cl_2. [b] X_1/X_2 *cis*/*trans* diastereomer mixture.

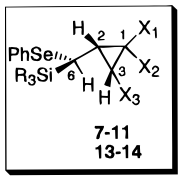
A. [2 + 1] Cycloaddition with Reactive Trisubstituted Olefins. Table 1 summarizes the [2 + 1] cycloaddition reactions of **1** and electrophilic olefins **2**−**6** with three (or two for comparison) electron-withdrawing substituents in the presence of Lewis acids. Reaction of **1a** with tris(alkoxycarbonyl) olefins **2a**−**d** in the presence of $ZnBr_2$ at −30 °C for 12−14 h gave [2 + 1] cycloadducts **7a**−**d** as single products in 53−69% yields (entries 1 and 3−5). Reaction of **1b** with **2a** proceeds slowly compared to the reaction of **1a**, probably because of steric hindrance (entry 2). The reaction of **1a,b** with **2a** using $SnCl_4$ as a Lewis acid (−78 °C) or the reaction using $ZnBr_2$ at higher temperature (0 °C) gave only desilylated products which could not be isolated in pure form. Reaction of **1a** with the chiral electrophile **2e** gave a 2:1 mixture of diastereomers (entry 6). The absolute configuration of **7e** was not determined. Reactions of **1a** with 1,1-bis(ethoxycarbonyl)-2-acyl olefins **3a,b** (entries 7−9) proceed much faster than those with triesters **2a**−**e**. In the reaction of **1a** with diethyl 2-acetylethene-1,1-dicarboxylate (**3a**), a longer reaction time (5 h) results in contamination of **9a** by desilylated byproducts. Reaction of **1a** with **4** gave mainly an intractable desilylated mixture, accompanied by cyclopropane **11a** and cyclobutane **12a** in low yields (entry 10). At −78 °C for 3 h, the reaction did not proceed. Use of $ZnCl_2$ at −30 °C for 6 h also gave mainly a desilylated mixture and **11a** in 6.2% yield. The structures of cyclopropane **11a** and cyclobutane **12a** are distinguished by characteristic $^1J_{CH}$ values in ^{13}C NMR spectra (J = 175 (C_3) and 168 (C_2) Hz for the cyclopropane ring, J = 132 (C_3), 146 (C_4), 152 (C_2) Hz for cyclobutane ring). Also, the structures of **11a** and **12a** are fully consistent with the observed HMBC spectra (Chart 1 in the Supporting Information). Reaction of **1a** with unstable 1,1-dicarbonyl-substituted olefin **5** in the presence of $ZnCl_2$ gave **13** in 23% isolated yield; this reaction could not be improved because of difficulty in handling **5** (entry 11). The product **13** is presumably a *cis*/*trans* diastereomer mixture; however, stereochemistry was not determined. Use of $ZnBr_2$ gave only a desilylated mixture.

No reaction occurred upon exposure of **1a** to olefins with electron-donating or steric substituents in the β-position (X_3) **15**, **16**, and **17**[8] or symmetrically substituted di- and tetraesters **18**[9] and **19**[10] in the presence of $ZnBr_2$ and/or $SnCl_4$. This is probably because of low reactivity of their Lewis acid complexes. The reaction of **1b** and **6** with $SnCl_4$ afforded *cis*-cyclopropane **14** in 19% yield (entry 12).[11]

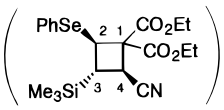


1a: R = Me
1b: R = Et

2-6



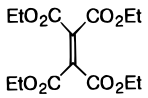
7-11
13-14



12a

(eq 2)

	X_1 =	X_2 =	X_3 =	cyclopropane products
2a	CO_2Et	CO_2Et	CO_2Me	**7a** (R =Me), **8a** (R = Et)
2b	CO_2Et	CO_2Et	$CO_2{}^tBu$	**7b** (R =Me)
2c	CO_2Me	CO_2Me	$CO_2{}^tBu$	**7c** (R =Me)
2d	CO_2Me	CO_2Me	CO_2Me	**7d** (R =Me)
2e	CO_2Et	CO_2Et	CO_2-(*l*)-menthyl	**7e** (R =Me)
3a	CO_2Et	CO_2Et	$COCH_3$	**9a** (R =Me), **10a** (R = Et)
3b	CO_2Et	CO_2Et	COPh	**9b** (R =Me)
4	CO_2Et	CO_2Et	CN	**11a** (R =Me)
5	$COCH_3$	$CO_2{}^tBu$	H	**13** (R =Me)
6	CO_2Me	CO_2Me	CH_3	**14** (R = Et)
15	CO_2Et	CO_2Et	OEt	-
16	CO_2Et	CO_2Et	Ph	-
17	$COCH_3$	CO_2Et	CH_3 (*cis*/*trans* mixture)	-
18	CO_2Et	H	CO_2Et	-



19

Stereochemistry of the X_3 and CH(SePh)($SiMe_3$) groups in cyclopropanes **7a**, **8a**, **11a**, and **14** was confirmed as *cis* by 2D-NOESY.[12] The stereochemistry of the other

(7) (a) Srisiri, W.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1994**, *59*, 5424. (b) Hall, H. K., Jr.; Ykman, P. *Macromolecules* **1977**, *10*, 464. (c) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22. (d) Corey, E. J.; Munroe, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 6129. (e) Krief, A.; Devos, M. J.; Sevrin, M. *Tetrahedron Lett.* **1986**, *27*, 2283.

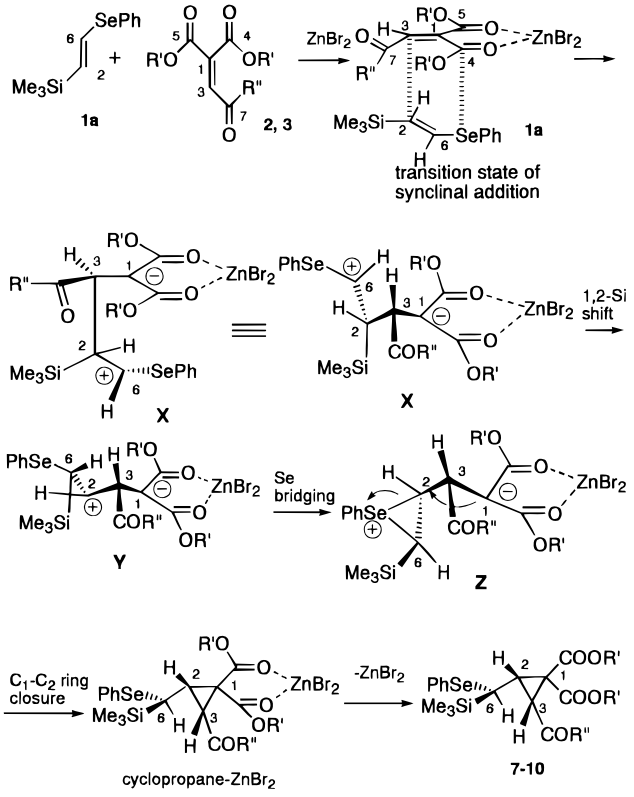
(8) Lehnert, W. *Tetrahedron* **1972**, *28*, 663.

(9) In the reaction with **18** in the presence of $SnCl_4$, 6% of isomerized ethyl fumarate was obtained along with unchanged **18** (80% recovered) and **1a**. Methyl fumarate also did not react with **1a**.[5a]

(10) Corson, B. B.; Benson, W. L. *Organic Syntheses*; John Wiley: New York, 1943; Collect. Vol. II, p 273.

(11) The reaction of **1a** and **6** with $SnCl_4$ gave a small amount of desilylated adduct as a mixture with recovered **6**, and 68% of **1a** was recovered. The cyclopropane, possibly produced in low yield, could be unstable to these reaction conditions.

Scheme 1. Reaction Mechanism for Cyclopropanation Proposed Based on ab Initio Calculations

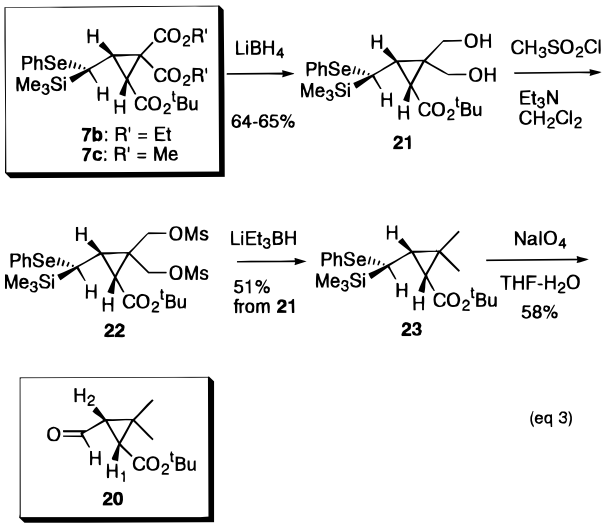


cyclopropane products **7b**−**e**, **9a**,**b**, and **10a** was also assigned as *cis* from the observed vicinal coupling constants. The coupling constants of vicinal protons in cyclopropane rings are characteristic, and the *J* values are in the region of *cis*-vicinal protons (9.1−9.6 Hz for **7a**−**e**, **8a**, **9a**,**b**, **10a**, **11a**, and **14**).[1m,13] The origin of the *cis* stereochemistry of X_3 and the CH(SePh)($SiMe_3$) groups in cyclopropanes **7a**−**e**, **8a**, **9a**,**b**, **10a**, and **11a** will be discussed in section C.

On the whole, tricarbonyl-substituted olefins **2** and **3** have proven to be good substrates. In contrast, alkyl-, aryl-, and alkoxy-substitued olefins **6** and **15**−**17** do not have high enough reactivity to participate in this novel [2 + 1] cycloaddition.

B. Synthetic Application. To demonstrate the synthetic utility of the [2 + 1] cycloaddition, the selenium- and silicon-containing cyclopropane products were converted to *tert*-butyl (±)-3,3-dimethyl-2-formyl-1,2-*cis*-cyclopropanecarboxylate (**20**).[14] This ester is a well-known synthetic intermediate for the biologically important compounds, pyrethroid insecticides.

The cyclopropanes **7b**/**7c** were converted to **20** by the following chemical transformations (eq 3). The ethyl ester or methyl ester groups (X_1 and X_2) were reduced to the diol **21** chemoselectively by use of $LiBH_4$[15] in THF in 64−65% yields, after extensive experimentation with various reducing reagents and conditions. The *tert*-butyl ester group was unaffected due to its lower reactivity as a result of steric effects. Transformation of **21** to the dimesylate **22** was performed with methanesulfonyl chloride in dichloromethane in the presence of triethylamine. Treatment of **22** with lithium triethylborohydride in THF gave **23** (51% yield from **21**).[16] Compound **23** was oxidized with $NaIO_4$ in THF−H_2O solution at room temperature to give the *cis*-aldehyde **20** in 58% yield.[14] The ^1H and ^{13}C NMR spectra were in complete accord with those of an authentic sample.[17] The $J_{1,2}$ coupling constant of 8.6 Hz confirms the *cis* stereochemistry in **20**.[1m,13]



C. Origin of the Stereochemistry. In order to explain the origin of the *cis* stereoselectivity of the X_3 (COR′) and CH(SePh)($SiMe_3$) groups in cyclopropanes **7a**−**e**, **8a**, **9a,b**, and **10a**, the total reaction mechanism was depicted in Scheme 1, which is based on our previous results.[5]

Initially the complex of **2** or **3** with $ZnBr_2$ is formed. The crucial conformation of the complex will be discussed later. Next, this electrophile is attacked by the selenosilyl nucleophile **1a**. Synclinal stereoselective addition (due to a stabilizing secondary orbital interaction, Se- - C_4=O) may affect the observed *cis*-selectivity regarding X_3 (COR″) and CH(SePh)($SiMe_3$) groups. Subsequent 1,2-silicon migration from the first produced zwitterion **X** leads to the second intermediate **Y**. This is followed by generation of a selenium-bridged intermediate **Z** by minimum motion, and ring closure then gives the cyclopropanes **7**−**10**. Thus, single-bond rotation as well as C_2−C_3 rotation must be a slower process than ring closure. Since the stereochemistry of the original syn-

(12) The relative configuration at C_2 and C_6 was deduced as (*R*,*R*) or (*S*,*S*) assuming the same stereochemical course as previously discussed.[5a,b] For **7a**, **8a**, **11a**, and **14**, the combination of large vicinal coupling constants ($J_{2,6}$ = 13.0−13.5 Hz), which indicate that ∠H_2−C_2−C_6−H_6 is close to 180°, and the observed NOE's (H_9−H_{13} for **7a**, H_{11}−H_{13}, H_{11}−$H_{14,15}$, H_{16}−H_{18}, H_{17}−H_{18} for **8a**, H_{11}−H_{13}, H_{11}−$H_{14,15}$ for **11a**, H_7−H_{14}, H_7−H_{15}, H_8−H_{11}, H_8−$H_{12,13}$ for **14** (see the numbering in Chart 1 of Supporting Information)), support the above hypothesis as previously discussed.[5b]

(13) (a) Williamson, K. L.; Lanford, C. A.; Nicholson, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 762. (b) Gey, C.; Perraud, R.; Pierre, J. L.; Cousse, H.; Dussourd D'Hinterland, L.; Mouzin, G. *Org. Magn. Reson.* **1977**, *10*, 75.

(14) (a) Elliott, M.; Janes, N. F. *Chem. Soc. Rev.* **1978**, *7*, 473. (b) Arlt, D.; Jautelat, M.; Lantzsch, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 703. (c) De Vos, M.-J.; Krief, A. *J. Am. Chem. Soc.* **1982**, *104*, 4282. (d) Ueda, K.; Matsui, M. *Agr. Biol. Chem.* **1970**, *34*, 1119. (e) Elliott, M.; Janes, N. F.; Pulman, D. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2470.

(15) Brown, H. C.; Narasimhan, S.; Choi, Y. M. *J. Org. Chem.* **1982**, *47*, 4702.

(16) Zimmerman, H. E.; Heydinger, J. A. *J. Org. Chem.* **1991**, *56*, 1747.

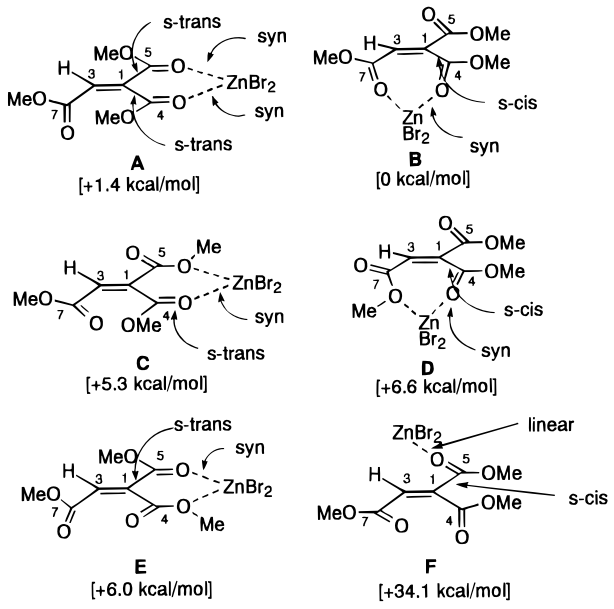
(17) The ^1H and ^{13}C NMR spectra of an authentic sample **20** were kindly provided by Sumitomo Chemical Co., Ltd. 2-1, Takatsukasa 4-chome, Takarazuka, Hyogo 665, Japan.

clinal addition step may be retained throughout this proposed mechanism, the origin of the observed *cis* selectivity in **7**−**10** may arise from the conformation of the initial complex of **2** or **3** and $ZnBr_2$ and the first synclinal addition step.

Since the stereochemical function of the complex has not been investigated, the conformation of the initial complex of the electrophilic olefin **2** or **3** and the Lewis acid $ZnBr_2$ was examined in more detail by using ab initio MO calculations.[18]

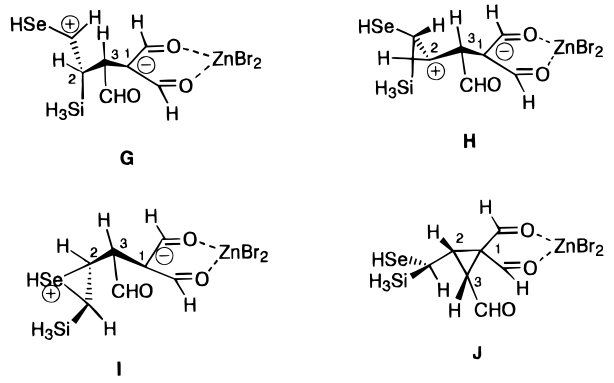
Two conformations **A** and **B** for **2d**:$ZnBr_2$ were found to be most stable (see Scheme 2). Our interest is in the orientation (transition state of synclinal addition in Scheme 1) of the $ZnBr_2$-coordinated electrophilic olefins **2** or **3** toward the nucleophilic olefin **1**. Frontier orbitals

Scheme 2. Geometrical Isomers of the 2d−$ZnBr_2$ Complex[a]



[a] Energies in square brakets obtained by ab initio RHF/LANL2MB calculations are relative ones (positive, less stable).

Scheme 3. Models of Intermediates for X−Z and a Cyclopropane−$ZnBr_2$ Complex Shown in Scheme 1 Generated by the Combination of 1a and A



of **A** and **B** are LUMO's. Their effective overlap with the HOMO of **1** determines the orientation. LUMO's of **A** and **B** are now compared (Figure 3 in the Supporting Information). The coefficient of C_3 where the new C−C bond is formed is 0.682 in **A** and is much larger than that in **B** (0.515). This result together with the C_3 cationic character in **A** discussed in ref 18 suggests that the complex **A** is a more reactive species than the complex **B** toward the addition step in Scheme 1. Therefore, complex **A** is probably the actual electrophile in this reaction, even though it is 1.4 kcal/mol thermodynamically less stable than **B**. The low FMO reactivity of **B** (*i.e.* the poorer selectivity at C_3 and C_4) can also be deduced by the failure of reactions with diethyl maleate (**18**).

To support this hypothetical pathway, ab initio geometry optimizations of the zwitterion model **G** for **X** and the cyclopropane−$ZnBr_2$ complex model **J** shown in Scheme 3 were carried out by the LANL2MB method. The structures of **G** and **J** were successfully obtained (Figure 4 in the Supporting Information). Stable structures of models **H** and **I** for **Y** and **Z**, respectively, could not be obtained, probably because of their transient

(18) A 1:1 interacting system was reasonably assumed because of the ability of **2** or **3** to form bidentate complexes and since the experimental conditions included **2** or **3**−$ZnBr_2$ in a 1:1.5 molar ratio. We have carried out ab initio MO calculations for the possible structures of the **2d**−$ZnBr_2$ complex as a model by using the LANL2MB method.[19,20] All the molecular orbital calculations were performed using Gaussian 94 program packages.[21] The geometries **A**−**F** for the **2d**−$ZnBr_2$ complex (Scheme 2) were optimized with respect to all structural variables. Their relative energies are shown in Scheme 2. Structures **A** and **B** are carbonyl oxygen bidentate complexes, **C**−**E** are carbonyl and ether oxygens (mixed) bidentate complexes, and **F** is a monodentate complex. The total energies of these six complexes indicate that bidentate complexes **A**−**E** are much more stable than monodentate complex **F** and that carbonyl oxygen bidentate complexes **A**−**B** are 3.9−6.6 kcal/mol more stable than the mixed bidentate complexes **C**−**E**. These results are consistent with the fact that chelate structures between bidentate ligands and a Lewis acid with two empty coordination sites are preferentially observed by X-ray and NMR.[22] The lower stability of **C**−**E** compared to that of **A**−**B** comes from the lower basicity of the alkoxy oxygen. As for the geometrical coordination modes for C=C−C=O···$ZnBr_2$, we have checked all eight possible structures (*s-cis*/syn, *s-cis*/anti, *s-trans*/syn, *s-trans*/anti for both C_4=O and C_5=O $ZnBr_2$-coordinated conformers) as listed in Table 2. **F** is *s-trans* and has an almost linear geometry for C=O···$ZnBr_2$. Since the energy differences between *s-cis* and *s-trans* of C=C−C=O without Lewis acid may be as small as ∼0.7−0.8 kcal/mol for methyl acrylate, according to earlier calculations,[23] we believe that the diversity of the models presented in this work is sufficient. As shown in Scheme 2, two conformations **A** and **B** were found to be most stable. In order to examine more the nature of these complexes, the conformations of free **2d**, **A** and **B**, are compared. The two uncomplexed conformations, **2d** (*s-trans*) and **2d** (*s-cis*), which would produce **A** and **B**, respectively, are optimized. In both **2d** (*s-trans*) and **2d** (*s-cis*) C_4=O is twisted 97° out of the C_1=C_3 plane due to steric repulsion. On the other hand, complexation of **2d** with $ZnBr_2$ fixes the C_4=O bond to the C_1=C_3 plane. The $ZnBr_2$-complexed C=O lengths are increased by 0.015−0.021 Å for **A** and **B**. The change in the atomic charge in C_3 from **2d** (*s-trans*) to **A** shows that the C_3 cationic character is enhanced (−0.060 → +0.010) for **A**. The LUMO's of **2d** (*s-trans*), **2d** (*s-cis*), **A** and **B**, are shown in the Supporting Information. It is obvious that LUMO energy levels are decreased (*i.e.* electrophilicity raised) for both **A** and **B** by complexation with $ZnBr_2$.

(19) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.*, **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(20) (a) We have also carried out semiempirical MO (PM3) calculations[20b] for the $ZnBr_2$ complexes of **2d**; however, the optimized structure and their relative energies gave unreliable results. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221. Stewart, J. J. P. MOPAC, Version 6, QCPE program No. 455, Indiana University, Oct 1990.

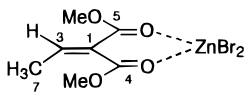
(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian *94*, *Revision B.1*, Gaussian, Inc., Pittsburgh, PA, 1995. MO calculations using Gaussian 94 were made on the CONVEX spp1200/XA at the Information Processing Center (Nara University of Education).

(22) (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (b) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, p 283.

(23) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

characters.[24] The result of **G** supports the intermediacy of the zwitterion **X** which is generated by nucleophilic attack of **1a** to **A** and the subsequent stereochemical pathway. Thus, the observed stereochemistry probably arises from the effective Se−C_4 secondary orbital interaction between **A** and **1a** as suggested in our earlier papers.[5]

The low reactivity of olefins **6** and **15**−**17** with electron-donating or steric substituents (X_3's) in the β-position can be interpreted in terms of a large HOMO−LUMO gap between nucleophile **1** and the electrophiles. Thus, the LUMO energy levels in those unreactive olefin−$ZnBr_2$ complexes may be much higher than those of reactive olefins (with three electron-withdrawing substituents)−$ZnBr_2$ complexes. As an example, the structure of **6**−$ZnBr_2$ complex **K** was calculated (Figure 5 in the Supporting Information), and its LUMO level was compared to that of **2d**−$ZnBr_2$ complex **A**. The LUMO level of **K** is +0.101 63 au, which is much higher than that of **A** (+0.086 98 au). Thus, the high LUMO energy level of **6**−$ZnBr_2$ causes a large HOMO−LUMO gap between **1** and **6**−$ZnBr_2$, leading to the small charge-transfer interaction and accordingly low reactivity. It is clear that the LUMO levels of electrophilic olefin−Lewis acid complexes are practical criteria for prediction of their reactivity.



K

In summary, we have shown new stereoselective cyclopropanation reactions of 1-seleno-2-silylethene **1** with highly electrophilic *tri*carbonyl-substitued olefins in the presence of Lewis acids and illustrated their synthetic utility. It was also demonstrated that suitable reactivity of the electrophilic olefins in this cyclopropanation can be predicted by computational study. The stereochemical consequence of the synclinal approach based on the FMO interaction has been elucidated. The low-energy level of LUMO and its localized orbital extension (as in **A**) are required for efficient cyclopropanations. Further developments toward an asymmetric version of this methodology are under way in our laboratory.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded in the FT mode. ^{1}H NMR spectra were recorded in $CDCl_3$ at 200, 400, or 600 MHz. ^{13}C NMR spectra were recorded at $CDCl_3$ at 50.1 or 150.9 MHz. Chemical shifts are reported in ppm relative to Me_4Si or residual nondeuterated solvent. Mass spectra were recorded at an ionizing voltage of 70 eV by EI or FAB. All reactions were carried out under a nitrogen atmosphere. Only representative compounds are described here, and others are compiled in the Supporting Information.

Preparation of Electrophilic Olefins. 2a−**c**,**e**,**3a**,**b**, and **4** were prepared by reaction of diethyl oxomalonate or dimethyl oxomalonate with substituted triphenylmethylenephosphoranes according to the preparation of the corresponding dimethyl ester of **4**.[7b] **2d** was prepared by the literature method.[7c]

1,1-Diethyl 2-*tert*-Butyl Ethene-1,1,2-tricarboxylate (2b). To an ice−water-cooled solution of diethyl oxomalonate (3.48 g, 20.0 mmol) in 40 mL of benzene was added over 5 min *tert*-butyl (triphenylphosphoranylidene)acetate[25] (7.53 g, 20.0 mmol). The mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature and stirred for 1 h. The benzene was evaporated, and ether was added. The precipitated triphenylphosphine oxide and side product were removed by filtration. The filtrate was concentrated, and the residue was distilled with a small amount of hydroquinone to give **2b** (3.35 g, 62%). **2b**: R_f = 0.8 (hexane:ether = 1:1); colorless oil; bp 100 °C/3 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.49 (s, 9H), 4.29 (q, J = 7.2 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 6.80 (s, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 13.83, 13.92, 27.78, 61.80, 62.26, 82.76, 132.1, 137.5, 162.5, 162.6, 164.3; IR (neat) 2984, 1717, 1647, 1450, 1373, 1350, 1253, 1201, 1154, 1067, 1023, 849, 777 cm^{-1}; MS (FAB) m/z 273 (MH^+). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.09; H, 7.46.

Typical Experimental Procedure (Entry 3 in Table 1). To a solution of **1a** (768 mg, 3.0 mmol) in dichloromethane (7.5 mL), cooled to −78 °C, was added $ZnBr_2$ (1.01 g, 4.5 mmol), followed by **2b** (1.06 g, 3.9 mmol). The mixture was allowed to warm to −30 °C and stirred for 12 h. The reaction was quenched by triethylamine (1.08 mL, 7.7 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 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 **7b** (1.10 g, 69%).

1,1-Diethyl 2-*tert*-butyl 3-[(phenylseleno)(trimethylsilyl)methyl]-2,3-*cis*-cyclopropane-1,1,2-tricarboxylate (7b): R_f = 0.6 (hexane:ether = 2:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.24 (q, J = 7.6 Hz, 6H), 1.45 (s, 9H), 1.99 (dd, J = 13.4, 9.4 Hz, 1H), 2.62 (d, J = 9.4 Hz, 1H), 3.32 (d, J = 13.4 Hz, 1H), 4.00−4.27 (m, 4H), 7.19−7.22 (m, 3H), 7.61−7.66 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.617 (q, J = 119 Hz), 14.12 (q, J = 127 Hz), 23.34 (d, J = 135 Hz), 28.10 (q, J = 127 Hz), 34.38 (d, J = 170 Hz), 35.78 (dd, J = 163, 7.3 Hz), 39.41 (s), 61.16 (td, J = 148, 3.9 Hz), 62.21 (td, J = 148, 3.9 Hz), 82.03 (s), 127.2 (dt, J = 160, 7.3 Hz), 128.6 (d, J = 160 Hz), 129.7 (t, J = 4.4 Hz), 135.1 (dd, J = 158, 7.3 Hz), 164.5 (s), 167.9 (d, J = 4.4 Hz), 169.4 (s); IR (neat) 2982, 1725, 1578, 1479, 1394, 1369, 1323, 1261, 1224, 1151, 1025, 913, 859, 839, 735 cm^{-1}; MS (EI) m/z (relative intensity) 528 (21), 427 (6.5), 355 (15), 309 (26), 269 (16), 241 (23), 217 (100); exact mass M^+ 528.1455 (calcd for $C_{24}H_{36}O_6SeSi$ 528.1446).

1,1-Diethyl 2-methyl 3-[(phenylseleno)(trimethylsilyl)-methyl]-2,3-*cis*-cyclopropane-1,1,2-tricarboxylate (7a): R_f = 0.4 (hexane:ether = 4:1); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ −0.005 (s, 9H, H_{16}), 1.21 (t, J = 7.0 Hz, 3H, H_9), 1.27 (t, J = 7.1 Hz, 3H, H_{11}), 2.11 (dd, J = 13.2 Hz, 9.5 Hz, 1H, H_2), 2.72 (d, J = 9.5 Hz, 1H, H_3), 3.24 (d, J = 13.2 Hz, 1H, H_6), 3.68 (s, 3H, H_{17}), 4.05−4.16 (m, 3H, $H_{8,10}$), 4.18−4.24 (m, 1H, $H_{10'}$), 7.19−7.22 (m, 3H, $H_{14,15}$), 7.60−7.62 (m, 2H, H_{13}) (see the numbering in Chart 1 of Supporting Information); observed NOE's were H_2−H_3, H_2−H_6, H_2−H_{13}, H_3−H_{17}, H_6−H_{13}, H_8−H_9, H_9−H_{13}, H_9−H_{17}, H_{10}−$H_{10'}$, H_{10}−H_{11}, $H_{10'}$−H_{11}, H_{13}−$H_{14,15}$; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.851 (q, J = 119 Hz), 13.97 (q, J = 127 Hz), 23.34 (d, J = 138 Hz), 33.36 (d, J = 170 Hz), 35.99 (dd, J = 164, 7.3 Hz), 39.73 (s), 52.08 (q, J = 147 Hz), 61.36 (t, J = 147 Hz), 62.33 (t, J = 148 Hz), 127.4 (dt, J = 161, 7.7 Hz), 128.7 (d, J = 158 Hz), 129.6 (s), 135.1 (d, J = 164 Hz), 164.5 (s), 168.9 (s), 169.0 (s); IR (neat) 2956, 2906, 1729, 1578, 1479, 1439, 1369, 1323, 1261, 1205, 1025, 859, 839, 737, 692 cm^{-1}; MS (EI) m/z (relative intensity) 486 (43), 427 (13), 413 (50), 315 (65), 283 (100), 241 (41), 165 (33); exact mass M^+ 486.0994 (calcd for $C_{21}H_{30}O_6SeSi$ 486.0977). Anal. Calcd for $C_{21}H_{30}O_6SeSi$: C, 51.95; H, 6.23. Found: C, 51.76; H, 6.21.

(24) An alternative mechanism was suggested by a reviewer involving direct C−C bond formation from **X** accompanied by silicon migration (Scheme 4). The mechanism avoids an unstable β-carbonyl carbocation **Y**. However, as discussed previously, formation of the relatively stable selenium-bridged intermediate **Z** can be the driving force to three-membered-ring formation.[5] On the other hand, the mechanism in Scheme 4 cannot explain the selectivity of three-membered-ring and four-membered-ring formations. A detailed investigation of the intermediacy of **Y** and **Z** in this system is now underway. We appreciate the suggestion of the reviewer on the possibility of this alternative mechanism.

(25) Cooke, M. P., Jr.; Burman, D. L. *J. Org. Chem.* **1982**, *47*, 4955.

Diethyl 2-cyano-3-[(phenylseleno)(trimethylsilyl)methyl]-2,3-*cis*-cyclopropane-1,1-dicarboxylate (11a): R_f = 0.4 (hexane:ether = 4:1); pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.145 (s, 9H, H_{16}), 1.21 (t, $J_{8,9} = J_{8',9}$ = 7.1 Hz, 3H, H_9), 1.33 (t, $J_{10,11}$ = 7.1 Hz, 3H, H_{11}), 2.31 (dd, $J_{2,6}$ = 13.0 Hz, $J_{2,3}$ = 9.1 Hz, 1H, H_2), 2.55 (d, $J_{2,3}$ = 9.1 Hz, 1H, H_3), 2.84 (d, $J_{2,6}$ = 13.0 Hz, 1H, H_6), 3.94 (dq, $J_{8,8'}$ = 10.9 Hz, $J_{8,9}$ = 7.1 Hz, 1H, H_8), 4.08 (dq, $J_{8,8'}$ = 10.9 Hz, $J_{8',9}$ = 7.1 Hz, 1H, $H_{8'}$), 4.23−4.29 (m, 2H, H_{10}), 7.22−7.28 (m, 3H, $H_{14,15}$), 7.57−7.61 (m, 2H, H_{13}) (see the numbering in Chart 1 of Supporting Information); observed NOE's were H_2-H_3, H_2-H_6, H_2-H_{10}, H_2-H_{11}, H_2-H_{13}, H_2-H_{16}, H_3-H_{10}, H_3-H_{11}, H_3-H_{16}, H_6-H_9, H_6-H_{13}, H_6-H_{16}, $H_8-H_{8'}$, H_8-H_9, H_8-H_{13}, $H_{8'}-H_9$, H_9-H_{13}, $H_{10}-H_{11}$, $H_{11}-H_{13}$, $H_{13}-H_{14,15}$, $H_{13}-H_{16}$, $H_{14,15}-H_{16}$; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ −1.74 (q, J = 120 Hz, C_{16}), 13.81 (q, J = 127 Hz, C_9), 13.97 (q, J = 128 Hz, C_{11}), 20.67 (d, J = 175 Hz, C_3), 24.55 (d, J = 135 Hz, C_6), 34.67 (dd, J = 168, 5.8 Hz, C_2), 38.55 (s, C_1), 62.28 (t, J = 145 Hz, C_8), 62.67 (t, 148 Hz, C_{10}), 114.9 (s, C_7), 127.7 (d, 161 Hz, C_{15}), 128.9 (dd, J = 160, 7.2 Hz, C_{14}), 129.0 (s, C_{12}), 134.9 (d, J = 162 Hz, C_{13}), 164.4 (s, C_4), 167.1 (s, C_5) (^{1}H and ^{13}C assignments were determined by HMQC, HMBC, and NOESY); observed HMBC spectra were H_2-C_1, H_2-C_3, H_2-C_7, H_3-C_1, H_3-C_2, H_3-C_6, H_3-C_7, H_6-C_1, H_6-C_2, H_6-C_3, H_6-C_{12}, H_6-C_{16}, H_8-C_9, $H_{8'}-C_9$, H_9-C_8, $H_{10}-C_{11}$, $H_{11}-C_{10}$, $H_{13}-C_{12}$, $H_{15}-C_{13}$, $H_{15}-C_{14}$, $H_{16}-C_6$; IR (neat) 2966, 2250, 1734, 1578, 1479, 1439, 1371, 1313, 1265, 1216, 1064, 1023, 859, 841, 741, 692 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 453 (6.5), 380 (28), 296 (6.5), 178 (4.3), 73 (25), 28 (15), 18 (100); exact mass M^+ 453.0883 (calcd for $C_{20}H_{27}NO_4SeSi$ 453.0874).

Diethyl 4-cyano-2-(phenylseleno)-3-(trimethylsilyl)cyclobutane-1,1-dicarboxylate (12a): R_f = 0.5 (hexane:ether = 4:1); pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.00 (s, 9H, H_{16}), 1.20 (t, J = 7.1 Hz, 3H, H_{11}), 1.33 (t, J = 7.1 Hz, 3H, H_9), 2.53 (dd, $J_{3,4}$ = 11.6, $J_{2,3}$ = 11.7 Hz, 1H, H_3), 3.13 (d, $J_{3,4}$ = 11.6 Hz, 1H, H_4), 3.80 (d, $J_{2,3}$ = 11.7 Hz, 1H, H_2), 4.20 (q, J = 7.1 Hz, 2H, H_{10}), 4.37 (q, J = 7.1 Hz, 2H, H_8), 7.20−7.24 (m, 3H, $H_{14,15}$), 7.52−7.54 (m, 2H, H_{13}) (see the numbering in Chart 1 of Supporting Information); observed NOE's were H_2-H_4, H_2-H_{13}, H_2-H_{16}, H_3-H_{16}, H_4-H_{16}, H_8-H_9, $H_{10}-H_{11}$, $H_{11}-H_{13}$, $H_{13}-H_{14,15}$, $H_{13}-H_{16}$, $H_{14,15}-H_{16}$; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ −3.504 (q, J = 119 Hz, C_{16}), 13.97 (q, J = 128 Hz, C_{11}), 14.17 (q, J = 128 Hz, C_9), 27.74 (dd, J = 146, 6.3 Hz, C_4), 34.27 (d, J = 132 Hz, C_3), 43.06 (dd, J = 152, 8.0 Hz, C_2), 62.13 (td, J = 149, 4.3 Hz, C_{10}), 62.69 (td, J = 149, 4.4 Hz, C_8), 63.50 (s, C_1), 117.7 (t, J = 7.2 Hz, C_7), 127.9 (dt, J = 161, 7.5 Hz, C_{15}), 129.1 (dd, J = 161, 7.8 Hz, C_{14}), 130.6 (s, C_{12}), 134.2 (dd, J = 162, 6.6 Hz, C_{13}), 166.5 (s, C_5), 168.4 (s, C_6) (^{1}H and ^{13}C assignments were determined by HMQC, HMBC, and NOESY); observed HMBC spectra were H_2-C_1, H_2-C_3, H_2-C_5, H_2-C_6, H_2-C_{12}, H_3-C_2, H_3-C_4, H_3-C_7, H_3-C_{16}, H_4-C_1, H_4-C_3, H_4-C_5, H_4-C_6, H_4-C_7, H_8-C_5, H_8-C_9, H_9-C_8, $H_{10}-C_6$, $H_{10}-C_{11}$, $H_{11}-C_{10}$, $H_{13}-C_{12}$, $H_{13}-C_{15}$, $H_{14}-C_{12}$, $H_{14,15}-C_{13}$, $H_{15}-C_{14}$, $H_{16}-C_3$; IR (neat) 2986, 2960, 2244, 1734, 1580, 1479, 1439, 1371, 1255, 1218, 1143, 1023, 843, 743, 692 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 453 (26), 380 (19), 296 (19), 256 (8.6), 178 (37), 157 (28), 84 (49), 73 (100); exact mass M^+ 453.0874 (calcd for $C_{20}H_{27}NO_4SeSi$ 453.0874).

Dimethyl 2-[(Phenylseleno)(triethylsilyl)methyl]-3-methyl-2,3-*cis*-cyclopropane-1,1-dicarboxylate (14). To a solution of **1b** (297 mg, 1.0 mmol) in dichloromethane (2.4 mL), cooled to −78 °C, was added $SnCl_4$ (0.173 mL, 1.5 mmol), followed by dimethyl ethylidenemalonate (**6**) (206 mg, 1.3 mmol). The mixture was stirred at −78 °C for 3 h. The reaction was quenched by triethylamine (0.32 mL, 2.3 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 (1:1) to give **14** (85.5 mg, 19%). **14**: R_f = 0.7 (hexane:ether = 1:1); pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.600−0.639 (m, 6H, H_{14}), 0.914 (t, J = 7.8 Hz, 9H, H_{15}), 1.31 (d, J = 6.6 Hz, 3H, H_7), 2.06 (dq, J = 9.6, 6.6 Hz, 1H, H_3), 2.20 (dd, J = 13.3, 9.6 Hz, 1H, H_2), 2.92 (d, J = 13.3, 1H, H_6), 3.53 (s, 3H, H_8), 3.75 (s, 3H, H_9), 7.21−7.23 (m, 3H, $H_{12,13}$), 7.62−7.65 (m, 2H, H_{11}) (see the numbering in Chart 1 of Supporting Information); observed NOE's were H_2-H_3, H_2-H_6, H_2-H_{11}, H_2-H_{14}, H_3-H_7, H_3-H_{14}, H_3-H_{15}, H_6-H_7, H_6-H_{11}, H_6-H_{14}, H_6-H_{15}, H_7-H_{14}, H_7-H_{15}, H_8-H_{11}, $H_8-H_{12,13}$, $H_{11}-H_{14}$, $H_{11}-H_{15}$, $H_{12,13}-H_{14}$, $H_{12,13}-H_{15}$, $H_{14}-H_{15}$; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 3.141 (t, J = 114 Hz), 7.667 (q, J = 125 Hz), 8.923 (q, J = 129 Hz), 22.94 (q, J = 133 Hz), 31.23 (d, J = 163 Hz), 37.04 (d, J = 163 Hz), 37.57 (s), 51.96 (q, J = 147 Hz), 52.75 (q, J = 148 Hz), 127.2 (dt, J = 160, 7.3 Hz), 128.7 (d, J = 158 Hz), 130.3 (s), 134.7 (d, J = 164 Hz), 168.1 (s), 171.0 (s); IR (neat) 2956, 2878, 1723, 1578, 1437, 1325, 1276, 1224, 1149, 1125, 1023, 739 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 456 (4.3), 342 (10), 314 (4.3), 271 (100), 255 (15); exact mass M^+ 456.1217 (calcd for $C_{21}H_{32}O_4SeSi$ 456.1235).

***tert*-Butyl 3,3-Bis(hydroxymethyl)-2-[(phenylseleno)(trimethylsilyl)methyl]-1,2-*cis*-cyclopropanecarboxylate (21).** To a solution of **7c** (451 mg, 0.90 mmol) in THF (2.0 mL) was added lithium borohydride (220 mg, 10 mmol) at 0 °C. The solution was warmed to room temperature and stirred for 18 h. The reaction mixture was cooled with ice−water, acidified by the gradual addition of 10% aqueous citric acid (c.a. 3.0 mL), and 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−ether (2:1) to give **21** (258 mg, 65%). **21**: R_f = 0.2 (hexane:ether = 2:1); colorless crystals; mp 98−100 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.050 (s, 9H), 1.44 (s, 9H), 1.57 (dd, J = 12.9, 8.6 Hz, 1H), 1.86 (d, J = 8.6 Hz, 1H), 2.43 (dd, J = 8.1, 4.6 Hz, 1H, OH), 2.75 (bt, J = 5.7 Hz, 1H, OH), 3.25 (d, J = 12.9 Hz, 1H), 3.51−3.70 (m, 2H), 3.83 (dd, J = 12.2, 8.1 Hz, 1H), 3.97 (dd, J = 12.2, 4.6 Hz, 1H), 7.26−7.29 (m, 3H), 7.57−7.62 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.968 (q, J = 119 Hz), 25.53 (d, J = 135 Hz), 28.16 (q, J = 129 Hz), 30.97 (d, J = 161 Hz), 32.75 (d, J = 160 Hz), 36.69 (s), 59.73 (t, J = 145 Hz), 70.18 (t, J = 141 Hz), 81.01 (s), 127.6 (dd, J = 161, 7.3 Hz), 129.2 (d, J = 163 Hz), 129.8 (s), 134.0 (d, J = 166 Hz), 170.4 (s); IR (KBr) 3412, 1715, 1477, 1367, 1251, 1152, 1067, 1015, 849, 737, 690 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 444 (67), 413 (9.8), 387 (11), 370 (18), 339 (41), 256 (93), 231 (58), 213 (100); exact mass M^+ 444.1207 (calcd for $C_{20}H_{32}O_4SeSi$ 444.1235).

***tert*-Butyl 3,3-Bis[(methanesulfonyloxy)methyl]-2-[(phenylseleno)(trimethylsilyl)methyl]-1,2-*cis*-cyclopropanecarboxylate (22).** To an ice-cooled solution of **21** (464 mg, 1.04 mmol) in dichloromethane (16 mL) was added triethylamine (0.44 mL, 3.16 mmol). After 15 min, methanesulfonyl chloride (0.16 mL, 2.12 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 24 h. The reaction mixture was poured into the mixture of saturated aqueous $NaHCO_3$ and dichloromethane, extracted, washed with water, and dried. The solvent was removed *in vacuo* to give crude **22** (617 mg, 99%). **22**: R_f = 0.5 (hexane:ether = 2:1); pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.103 (s, 9H), 1.45 (s, 9H), 1.82−1.98 (m, 2H), 3.09 (s, 6H), 3.19−3.34 (m, 2H), 3.58 (d, J = 10.5 Hz, 1H), 3.69 (d, J = 12.0 Hz, 1H), 3.56−3.72 (m, 2H), 4.44 (d, J = 10.5 Hz, 1H), 7.26−7.29 (m, 3H), 7.57−7.62 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −2.172, 25.71, 27.90, 30.38, 34.32, 37.24, 37.39, 40.89, 72.95, 81.30, 81.39, 127.6, 129.0, 130.1, 134.5, 168.5.

***tert*-Butyl 3,3-Dimethyl-2-[(phenylseleno)(trimethylsilyl)methyl]-1,2-*cis*-cyclopropanecarboxylate (23).** A solution of crude **22** (617 mg, 1.03 mmol) in THF (34 mL) was added slowly to 1.0 M lithium triethylborohydride in THF (10 mL, 10.0 mmol) at 0 °C. After addition was complete, the reaction was refluxed for 18 h, cooled, and quenched with water. The mixture was extracted with ether, and the organic phase was washed with saturated aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel, eluting with hexane−ether (9:1) to give **23** (236 mg, 51% from **20**, including a trace amount of unidentified impurity). **23**: R_f = 0.6 (hexane:ether = 9:1); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.070 (s, 9H), 0.899 (s, 3H), 1.12 (s, 3H), 1.25 (m, 1H), 1.42 (s, 9H), 1.51 (d, J = 8.5 Hz, 1H), 3.30 (d, J = 12.9 Hz, 1H), 7.20−7.24 (m, 3H), 7.56−7.58 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ −1.763, 14.30, 26.82, 27.43, 28.43, 29.33, 33.59, 35.99, 79.99, 127.0, 128.8, 129.0, 134.4, 171.2; IR (neat) 3400, 2960, 1717, 1640,

1578, 1367, 1249, 1154, 1123, 861, 841, 737 cm^{-1}; MS (EI) *m/z* (relative intensity) 412 (20), 340 (4.3), 311 (11), 256 (52), 220 (15), 201 (52), 73 (100); exact mass M^+ 412.1339 (calcd for $C_{20}H_{32}O_2SeSi$ 412.1336).

***tert*-Butyl (±)-3,3-Dimethyl-2-formyl-1,2-*cis*-cyclopropanecarboxylate (20).** To a solution of **23** (96 mg, 0.23 mmol) in THF (4.2 mL) and water (0.66 mL) was added $NaIO_4$ (118 mg, 0.50 mmol) with vigorous stirring. After 4 h, $NaIO_4$ (88 mg, 0.23 mmol) was added, and the mixture was stirred for an additional 2 h. The reaction mixture was poured into ether and saturated aqueous $NaHCO_3$ solution. The organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by distillation to give **20** (27 mg, 58%): R_f = 0.3 (hexane:ether = 4:1); colorless oil; bp 70−90 °C/20 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.46 (s, 9H), 1.55 (s, 3H), 1.76 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.07 (d, *J* = 8.6 Hz, 1H), 9.73 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 0.075 (q, *J* = 119 Hz), 15.00 (q, *J* = 127 Hz), 28.22 (q, *J* = 127 Hz), 28.34 (q, *J* = 127 Hz), 29.42 (s), 38.09 (d, *J* = 167 Hz), 40.57 (dd, *J* = 164, 26 Hz), 81.77 (s), 169.1 (s), 200.9 (d, *J* = 182 Hz); IR (neat) 2980, 2936, 2892, 2746, 1720, 1702, 1393, 1370, 1333, 1228, 1166, 1134, 831 cm^{-1}; MS (EI) *m/z* (relative intensity) 142 (22) (M^+ − 56, 125 (13), 97 (14), 57 (43), 41 (21), 28 (43), 18 (100); MS (FAB) *m/z* 199 (MH^+).

Acknowledgment. We are grateful to Dr. T. Umemura (Sumitomo Chemical Co., Ltd.) for kindly providing us the ^{1}H and ^{13}C NMR spectra of **20** and its *trans* isomer.

Appendix

Table 2, listing the eight possible structures for both C_4=O and C_5=O $ZnBr_2$-coordinated conformers,[18] and Scheme 4, an alternative mechanism involving direct C−C bond formation from **X** accompanied by silicon migration.[24]

Supporting Information Available: Experimental procedures and characterization for **2a**,**c**,**e**, **3a**,**b**, **4**, **5**, **7c**−**e**, **8a**, **9a**,**b**, **10a**, and **13**; ^{1}H and ^{13}C NMR spectra for compounds **7b**−**e**, **9a**, **10a**, **11a**, **12a**, **13**, **14**, **20**, **21**, and **23**; 2D-NOESY spectra for **7a**, **8a**, **11a**, **12a**, and **14**; HMQC and HMBC spectra for **11a** and **12a**; ab initio RHF/LANL2MB optimized geometries of **A**−**F**, **2d** (*s-trans*), **2d** (*s-cis*), **G**, **J**, and **K**; Frontier orbital coefficients of LUMO of **2d** (*s-trans*) and **2d** (*s-cis*), **A**, and **B** (57 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9622486

Table 2. Geometrical Coordination Modes of 1:1 2d−$ZnBr_2$ Complex Regarding the C=C−C=O···Zn Moiety

coordination modes	LANL2MB-optimized structures
C_4=O/*s-cis*/syn	**B** (two carbonyl bidentate)
C_4=O/*s-cis*/anti	converged to **B**
C_4=O/*s-trans*/syn	**A** (two carbonyl bidentate)
	C (carbonyl-ether bidentate)
C_4=O/*s-trans*/anti	converged to **C**
C_5=O/*s-cis*/syn	converged to **F** (monodentate)
C_5=O/*s-cis*/anti	converged to **F**
C_5=O/*s-trans*/syn	**A**
	E (carbonyl−ether bidentate)
C_5=O/*s-trans*/anti	converged to **E**

Scheme 4. An Alternative Mechanism for Cyclopropanation