PERKIN 2

Olefin–olefin reactions mediated by Lewis acids may afford cyclopropanes rather than cyclobutanes: a mechanistic study of cyclopropane formation using a 1-seleno-2-silylethene †

Shoko Yamazaki and Shinichi Yamabe *

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan

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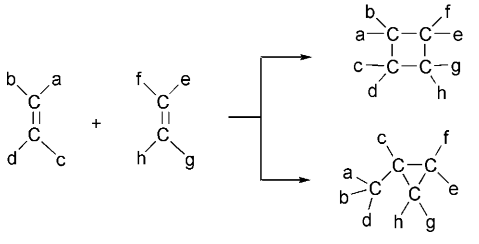
The mechanism of the novel [2 + 1] cycloaddition reaction of 1-seleno-2-silylethenes has been investigated using DFT (density functional theory) calculations. This study revealed a remarkable reaction path; the silicon migration and cyclopropane ring closure occur concertedly with the aid of eight-membered cyclic Se–metal (in the Lewis acid) coordination. The transition state for the crucial silicon-shift and ring-closure steps was obtained. The structures show that a through-space Se–metal (Sn or Zn) interaction causes three-membered ring closure. Cyclopropane *vs.* cyclobutane product selectivity was elucidated by these calculations.

Introduction

In principle, when two olefins (abC=Ccd and efC=Cgh) react, cyclobutanes and/or cyclopropanes can be produced (Scheme 1), and cyclobutane formation is "symmetry forbidden" according to the Woodward–Hoffmann rule.[1] In cases where substituents a, b, c and d are electron-donating and e, f, g and h are electron-withdrawing groups, cyclobutanes are probably formed *via* zwitterionic intermediates.[2]

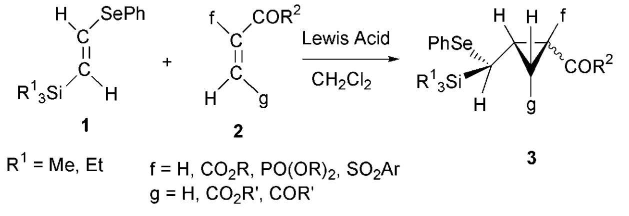


Scheme 1

Reactions between electron-donating and electron-deficient olefins with and without Lewis acids have been extensively studied and the major reaction products are the [2 + 2] cycloadducts, cyclobutanes.[2,3] Other pathways than those in Scheme 1 are known to give acyclic products such as Michael adducts[4] and ene adducts,[5] and hetero Diels–Alder cycloadditions occur to form six-membered rings, when conjugated systems participate in the reaction path.[6]

In Scheme 1, cyclopropane formation must be accompanied by a 1,2-shift of substituent d. A 1,2-silicon shift is well precedented[7] and may be expected to direct the cyclopropanation, however, a Si 1,2-shift alone is too weak to be the driving force for formation of highly strained three-membered rings. Some other structural functions are needed to obtain cyclopropane products from two olefins, but what exactly are the functions that are required to go together with a Si 1,2-shift?

Vinyl selenides are considered as electron-donating olefins,[8] and we have recently found novel [2 + 1] cycloaddition reactions of (*E*)-1-(phenylseleno)-2-silylethene **1** with electrophilic olefins **2** to afford cyclopropane products **3** with high stereoselectivity in the presence of Lewis acids (Scheme 2).[9] This new [2 + 1] cycloaddition reaction, which involves a 1,2-silicon migration process, is an example of the formation of cyclopropanes presented in Scheme 1. The 1,2-silicon migration mechanism in the cyclopropanation was confirmed by a deuterium-labelling study.[10]



R^1 = Me, Et

f = H, CO_2R, $PO(OR)_2$, SO_2Ar

g = H, CO_2R', COR'

R^2 = Alkyl, Ph, OR

Scheme 2

Cyclopropane-forming reactions are important for the synthesis of biologically interesting compounds.[11] In addition, cyclopropanes are useful intermediates in organic synthesis owing to their unique structural and reactivity properties,[12] and numerous synthetic reactions for the preparation of cyclopropanes have been developed.[13] The common cyclopropane-forming steps involve carbene and carbenoid additions and intramolecular nucleophilic substitutions, and because of the strain in the cyclopropane products, unstable and reactive intermediates such as carbenes or kinetically preferable stereoelectronic requirements are needed.[14] Also, mild conditions are required to avoid further ring-opening reactions. Although mechanistic understanding of the three-membered ring-closure step is of much interest in view of the largest ring strain amongst the cycloalkanes, few detailed analyses have been reported so far.[15]

The mechanism of the above-mentioned unique [2 + 1] cycloaddition reaction to give a three-membered ring and not a four-membered ring was difficult to rationalize. Preliminary computational efforts to elucidate the reaction mechanism of this cyclopropane forming reaction and the initial addition mechanism have been attempted.[9a,c–g] However, the precise features of the critical silicon-migration and ring-closure steps still remain unclear. There must be factors ("structural functions") that influence the [2 + 1] cycloaddition leading to strained cyclopropanes with silicon shift and the [2 + 2]

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† Table S1 (total energies and zero-point vibrational energies) and Figs. S1–S16 (optimized geometries) are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b007390n/

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cycloaddition leading to the less strained cyclobutanes without silicon shift. The fundamental chemoselectivity of small cycloalkanes in Scheme 1 needs to be elucidated. We have now performed theoretical calculations on the mechanism of the [2 + 1] cycloaddition reactions of (*E*)-1-(phenylseleno)-2-silylethene **1** with electrophilic olefins in the presence of Lewis acids. We report unprecedented ring-closing transition-state structures caused by multi-atom interactions. Thus, silicon migration and ring-closure occur concertedly with the aid of eight-membered cyclic Se–metal (in the Lewis acid) coordination. Highly strained cyclopropane rings can be obtained by through-space attraction. The metal center of the Lewis acid helps to form the cyclopropane ring.

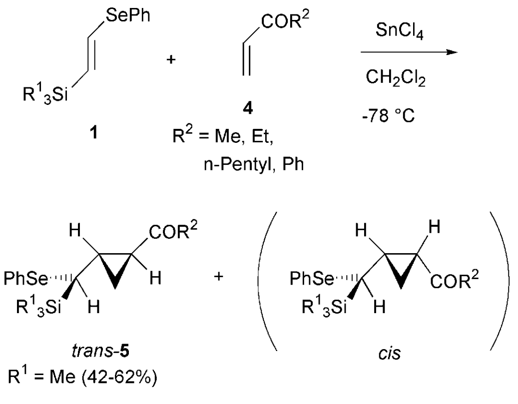
Computational methods

Geometries were fully optimized with the B3LYP density functional method[16] together with the SCRF[17] solvent effect (CH_2Cl_2, relative permittivity = 7.77) using Gaussian 98.[18]‡ The basis set is "spliced" and is composed of 6-31G* for reactant atoms (C, H, O, Si and Se) and 3-21G* for Lewis acid atoms (Sn, Cl, Zn, and Br). Unfortunately, the 6-31G* basis set of Sn is not available in spite of its importance as a Lewis-acid metal. For systematic comparison of the catalytic strength of Lewis acids, the 3-21G* basis set was used. Vibrational frequency calculations were carried out for all structures. The vibrational frequency calculations for all transition structures gave a sole imaginary frequency, which verifies that the obtained geometries are those of the saddle point. Energies were obtained by single-point calculations at the B3LYP/6-311+G(2d,p) and 3-21G* level with SCRF, and zero-point vibrational energy corrections were made.

Results and discussion

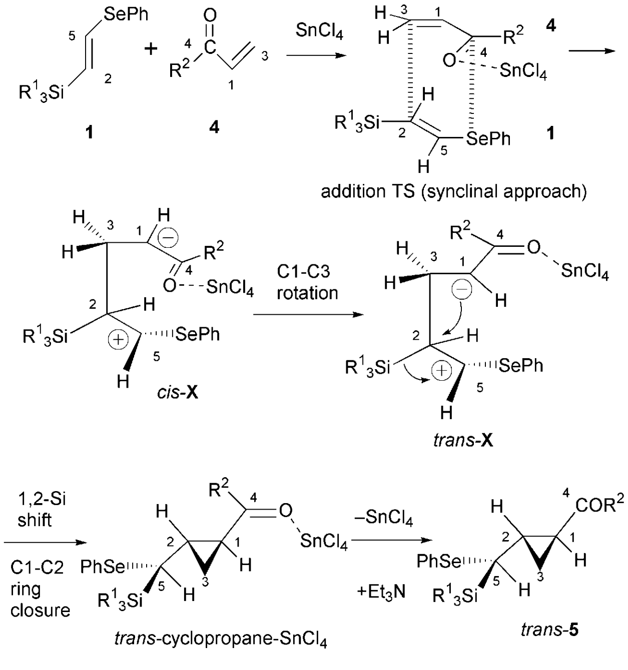
A. $SnCl_4$-mediated [2 + 1] cycloaddition

The reaction of 1-seleno-2-silylethene ($H_3SiHC{=}CHSeMe$) **6** and acrolein–$SnCl_4$ complex **7** was chosen as a model of our synthetic reactions (**1**, vinyl ketone **4**, $SnCl_4$, in Scheme 3).[9a] The characteristic of this [2 + 1] cycloaddition reaction is formation of *trans* (CHSeSi group and carbonyl group COR^2) cyclopropanes **5**. Reactions with other electrophilic olefins such as 2-phosphonoacrylates and 2-sulfonylacrylates gave *cis* (CHSeSi and carbonyl groups) cyclopropanes.[9d,e,g]

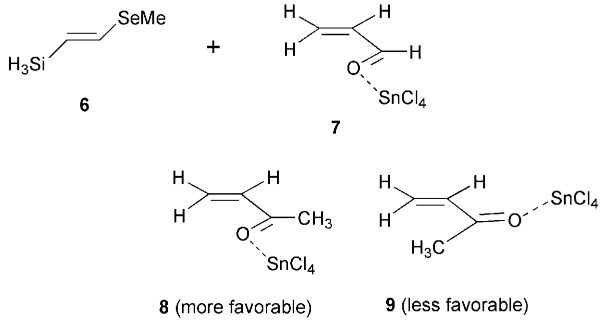


Scheme 3

Scheme 4 outlines a possible reaction course for the [2 + 1] cycloaddition. In the first step, addition of nucleophilic vinyl selenide **1** to vinyl ketone **4** activated by $SnCl_4$ gives carbenium ion *cis*-**X**. In the resulting zwitterionic intermediate, C1–C3 bond rotation is required to give *trans*-cyclopropane. Silicon shift and ring closure leads to cyclopropane, with presumed assistance from the undefined "structural functions" mentioned in the Introduction. For the acrolein–$SnCl_4$ complex **7**, the s-*cis* conformation was chosen for the following reason: the s-*cis* isomer of the methyl vinyl ketone–$SnCl_4$ complex **8** is 3.7 kcal mol^{-1} more stable than the s-*trans* isomer **9** (Scheme 5). In addition, it was shown by *ab initio* calculations that the s-*cis* conformation of a Lewis acid complex of acrolein is preferred in the Diels–Alder reaction.[19] The s-*cis* conformer is more electrophilic and its geometry leads to better secondary orbital interactions.[20] It was proposed previously, and also will be shown in this study, that the [2 + 1] cycloaddition reactions involve a Se···C=O secondary orbital interaction in the first addition step ("addition complex" in Scheme 4). Since the addition step is similar to that in concerted Diels–Alder reactions, the preferred conformations in Diels–Alder reactions can be applied to the synclinal approach in Scheme 4.



Scheme 4 A possible reaction mechanism for [2 + 1] cycloaddition of **1** with vinyl ketones **4** which affords *trans*-cyclopropanes **5**.



Scheme 5

1. Addition step. Prior to the addition transition state, Se–Sn coordinated stable complexes were calculated because it was found out that in the later stages, the Se–Sn coordination becomes very important in causing the cyclopropanation. Two substantially stable Se–Sn coordinated complexes **10** (Scheme 6) and **13** (Scheme 7) were obtained as stereoisomers, respectively. Their energies indicate that the six-coordination of the tin center significantly stabilizes the complexed system.

In addition to the Se–Sn coordinated complexes, selenium–carbonyl carbon interacting complexes **11** and **14** were

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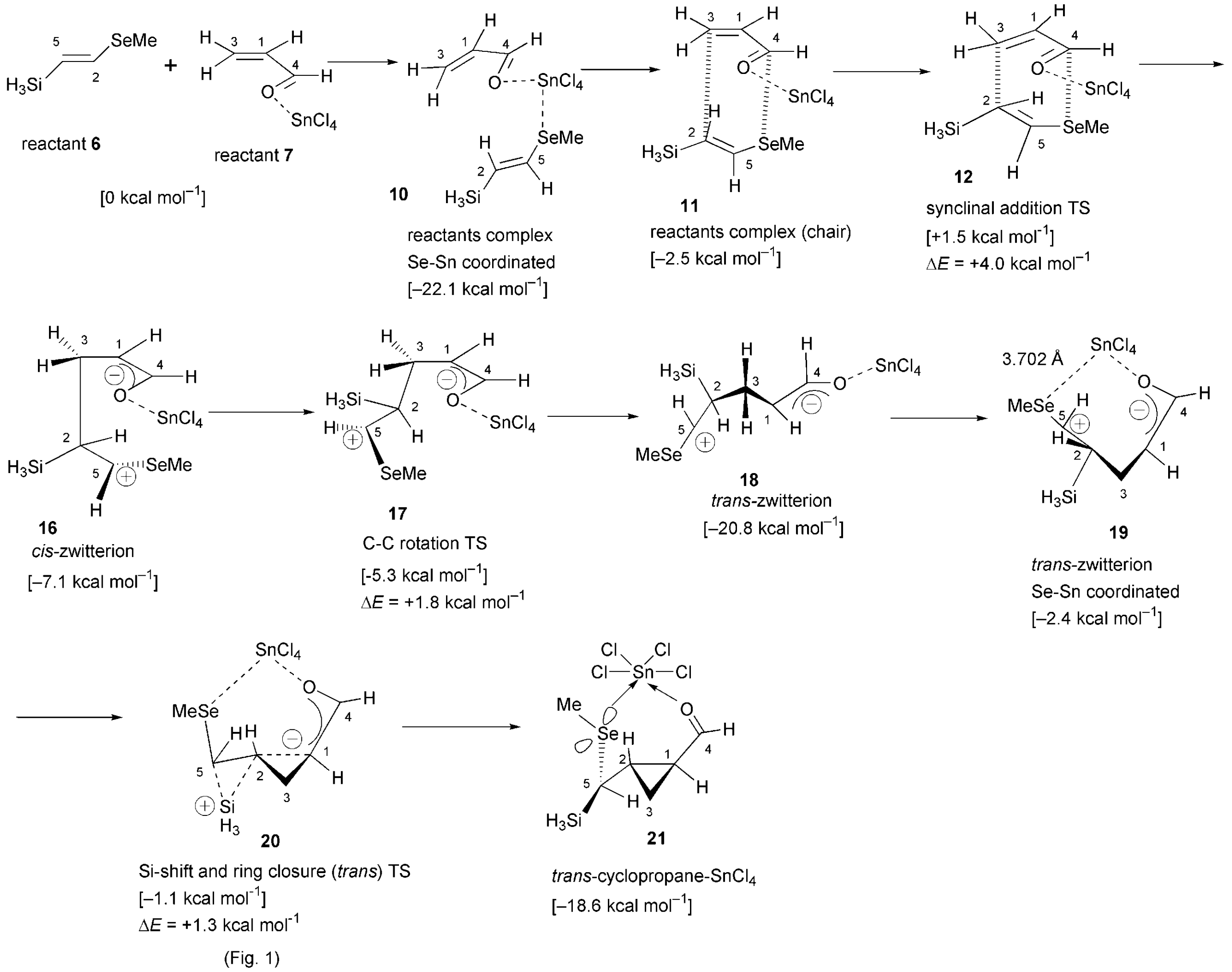
‡ MO calculations using Gaussian 98 were made on the CONVEX SPP1200/XA at the Information Processing Center (Nara University of Education).



Scheme 6 Mechanism of the cyclopropane-forming reaction mediated by $SnCl_4$. Energies in square brackets are relative to those of reactants **6** and **7** (negative values mean stabilized systems). ΔE values are energy differences between TSs and their preceding intermediates.

obtained.§ The complexes could be formed by Se 1,3-shift from **10** and **13**. Selenium–carbonyl carbon interacting complexes, **11** (Scheme 6) leading to the chair (synclinal) transition state and **14** (Scheme 7) leading to the boat transition state were obtained, respectively. The C2–C3 distances in **11** and **14** become smaller than those in **10** and **13**. In complex **11**, C4 · · · Se and C3 · · · C2 distances are 2.237 and 4.419 Å, respectively. In complex **14**, C4 · · · Se and C3 · · · C2 distances are 2.741 and 3.609 Å, respectively. In the chair reactant complex **11**, the C4 · · · Se distance is remarkably small as an intermolecular interaction (*cf.* the covalent bond C5–Se = 1.923 Å). The C4 · · · Se attraction controls primarily the synclinal addition path. The transition states of the chair and boat addition steps (**12** in Scheme 6 and **15** in Scheme 7) between **6** and **7** were calculated next.¶ ΔE values (energy barriers) of these addition steps were obtained and were compared. The ΔE value for chair-like TS **12** (+4.0 kcal mol^{-1}) is smaller than that for the boat-like TS **15** (+6.4 kcal mol^{-1}).|| Both transition states benefit from frontier orbital interaction (C3–C2 and Se–C4) between the HOMO of **6** and the LUMO of **7**, as discussed previously (Scheme 8).[9,20] A chair-like alignment of **12** which avoids the C1–C5 orbital-phase cancellation appears to be more favorable than the boat-like alignment of **15** which does not avoid the cancellation (*vide infra*). In the chair-like transition state **12**, the C4 · · · Se and C3 · · · C2 distances are 3.080 and 2.107 Å, respectively. The reaction-coordinate vectors in the transition state structure of the addition step indicate predominantly C3 · · · C2 bond formation. There is no C4 · · · Se vector component. In spite of the primary interaction for formation of the Mulliken CT complex **11**, the C4 · · · Se site cannot become a covalent bond. This explicitly shows the feature of a secondary orbital interaction.**

After the transition state **12**, a zwitterion **16** forms. Se–C4 interaction becomes weaker (Se–C4 4.229 Å for **16** relative to 3.080 Å for **12**) but the Se and Sn interact more strongly than in TS **12** (Se–Sn 4.422 Å for **16** relative to 4.897 Å for **12**).

2. C1–C3 Bond rotation in intermediates. As shown in Scheme 4, the characteristic feature of this [2 + 1] cycloaddition reaction is formation of *trans* (CHSeSi and carbonyl groups) cyclopropanes. This stereochemistry arises from facile rotation around the C1–C3 bond in the intermediate **16** leading to the

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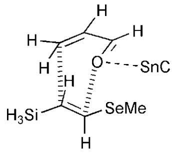
§ We obtained weakly interacting complexes for **1** and dimethyl acrylate–$ZnBr_2$ by RHF-3-21G* previously. See ref. 9*f*.

¶ Calculation of the TS structure related to **15** which has Se–Sn coordination was attempted, but it converged to structure **15** which does not have Se–Sn coordination.

|| Calculation of a further structure after the boat-like TS **15** gave **18**. Because of the lower energy barrier of TS **12** than that of **15**, the path to **18** is considered as **12**→**16**→**17**→**18**.

** The transition state **57** of the reverse electron-demand hetero Diels–Alder [4 + 2] reaction between **6** and **7** was also examined. However, the hetero Diels–Alder TS structure collapsed to the Se–C=O interacting chair-like (synclinal) TS structure **12**.



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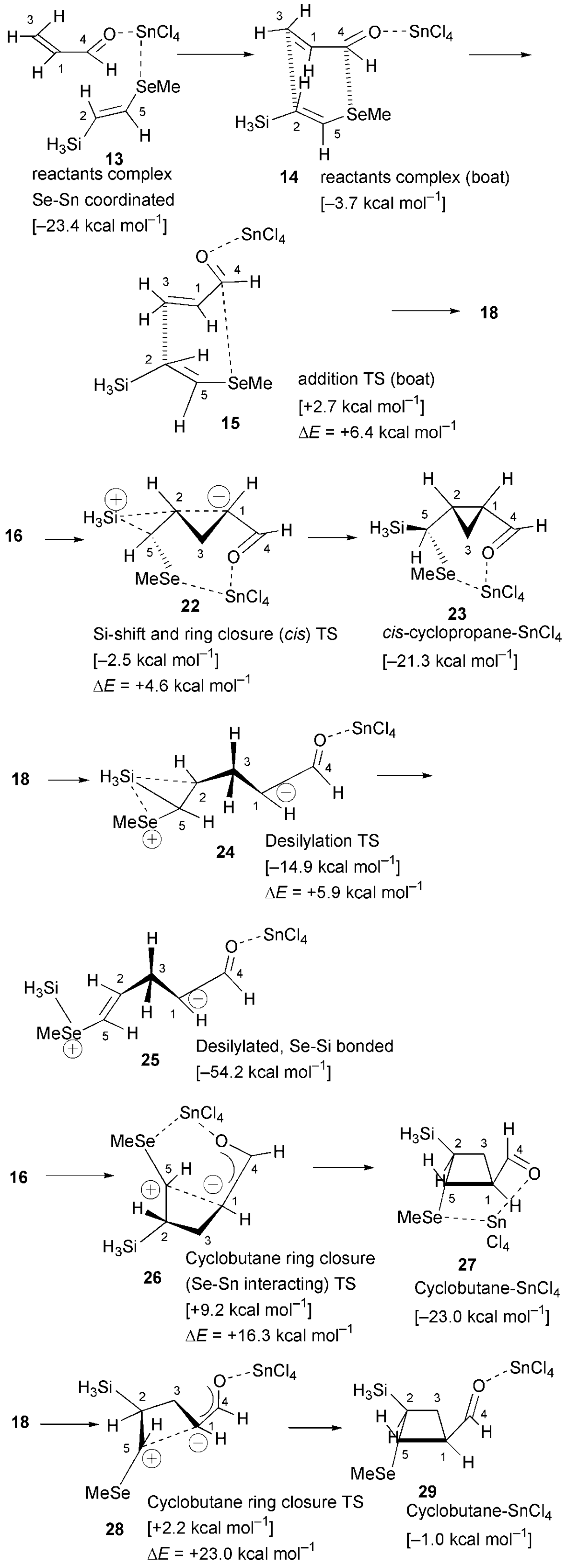
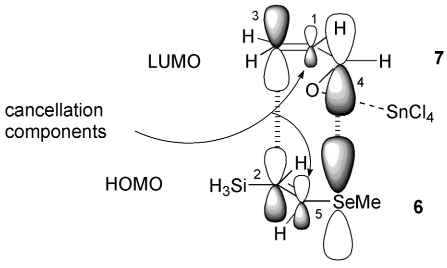


Scheme 7 Other mechanisms for the reaction between **6** and **7**. Energies in square brackets are relative to those of reactants **6** and **7**.

sterically stable intermediate **18**. The transition state of C1–C3 rotation **17** was also obtained. The energy barrier for the C1–C3 rotation is +1.8 kcal mol^{-1} and is small. The isomer of zwitterion **18**, **19**, which has Se–Sn interaction, was also calculated.†† The transformation of rotamers **16**, **18** and **19** involves only single-bond free rotations. In the three zwitterionic intermediates, the Si–C2–C5 bond angles (101.6° in **16**, 98.8° in **18** and 98.7° in **19**) are smaller than the standard sp^3 angle, 109.5°. Also, the Si–C2 bonds (1.980 Å in **16**, 1.998 Å in **18** and 2.003 Å in **19**) are longer than those in reactants complexes (1.880–1.895 Å in **10**, **11**, **13** and **14**). These angles and distances show a β-silicon effect.[21] The C2–C5 silicon shift will be brought about readily. The Se–Sn interacting zwitterion **19** proceeds to the next important silicon-shift transition state.



Scheme 8 Orbital interaction in the complex, **11**, and chair-like (synclinal) TS, **12** in Scheme 7.

3. Silicon shift and concomitant ring closure. Next, the crucial silicon-migration step was examined.‡‡ The silicon-migration transition state is shown in Fig. 1. The obtained TS structure **20** showed a highly surprising feature. The silicon C2→C5 shift and C1–C2 ring closure occur concertedly. Thus, in the TS structure **20**, the C1–C2 distance is 2.549 Å and is shorter than that of the precursor **19** (2.613 Å) and the reaction-coordinate vectors indicate C1 · · · C2 bond formation clearly along with Si migration from C2 to C5. In addition, the Se–Sn distance becomes shorter than in the intermediate **19** (Se–Sn 3.400 Å for **20** compared to 3.702 Å for **19**). The Se–Sn distance becomes even shorter in the resulting *trans*-substituted cyclopropane **21** (Se–Sn 2.847 Å). The intramolecular Se–Sn coordination to form a large eight-membered ring leading to the stable six-coordinated tin seems to cause cyclopropanation accompanied by silicon shift.

The similar transition state structure **22**, which leads to *cis*-cyclopropane **23** from the *cis*-zwitterion intermediate **16**, was also obtained (Scheme 7). The TS structure **22** showed features similar to **20** leading to the *trans*-cyclopropane **21**. The C2→C5 silicon shift and C1–C2 ring closure occur concertedly. In the TS structure **22**, the C1–C2 distance is 2.342 Å and is shorter than that of the precursor **16** (2.512 Å) and the reaction-coordinate vectors indicate C1 · · · C2 bond formation along with Si migration from C2 to C5. The Se–Sn distance becomes shorter than in the intermediate **16** (Se–Sn 3.296 Å for **22** compared to 4.422 Å for **16**). The Se–Sn distance becomes even shorter in the resulting *cis*-substituted cyclopropane **23** (Se–Sn 2.818 Å). The *cis*-substituted cyclopropane was isolated as a minor product in the SnCl$_4$-promoted reaction of **1** (R^1 = Et in Scheme 3) and methyl vinyl ketone **4** (R^2 = Me, in Scheme 3).[9a] Also, *cis*-cyclopropanes are major products for AlCl$_3$-[9a] and chiral Ti-promoted[9c] [2 + 1] cycloaddition reactions. Thus, the ring closing process to give *cis*-cyclopropane and the C1–C3 bond rotation from **16** are competitive to give *cis* and *trans* isomers.

The Sn–Se linkage and the resultant eight-membered ring formation are key factors, and control calculations without them are needed. Various transition state structures for Si

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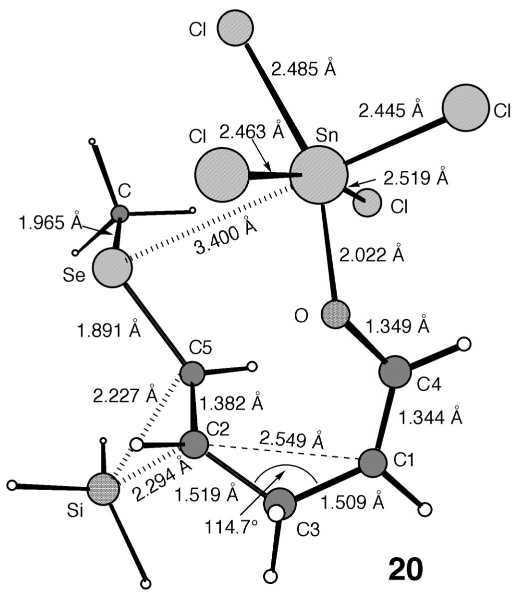
†† The *trans*-zwitterion **18** [−20.8 kcal mol^{-1}] is slightly more stable than the cyclopropane–SnCl$_4$ **21** [−18.6 kcal mol^{-1}], which is curious. In the gas phase (without SCRF = dipole), the relative energies are [+54.5 kcal mol^{-1}] for **18** and [−17.6 kcal mol^{-1}] for **21**, respectively. The intermediate **18** is stabilized significantly by the solvent effect. Thus, the apparent curiosity would come from the somewhat overestimated stabilization of **18** by the SCRF solvent effect.

‡‡ Previously, we proposed a β-selenium stabilized cation intermediate after silicon migration which was supported by primitive model calculations.[9a]



Si-shift and ring closure (*trans*) TS
[−1.1 kcal mol^{-1}]
ΔE = +1.3 kcal mol^{-1}

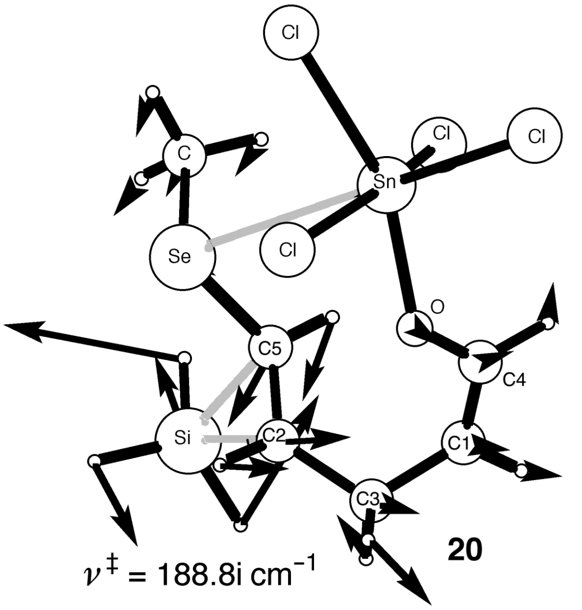
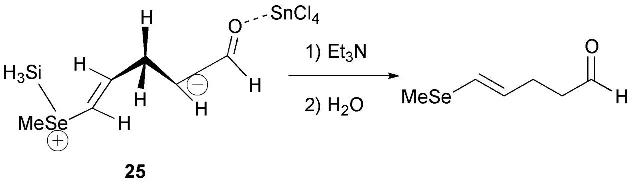


Fig. 1 Geometry of the transition state of the cyclopropane ring-forming step with the through-space Se···Sn attraction and silicon C2→C5 shift (TS **20** in Scheme 6). Energy in square brackets is relative to that of reactants **6** and **7** (negative values mean stabilized systems). Energy barrier ΔE is relative to that of intermediate **19**. Small white circles denote hydrogen atoms. The atomic numbering follows that in Scheme 4. Reaction-coordinate vectors corresponding to the sole imaginary frequencies $\nu^{\ddagger}$ are sketched.

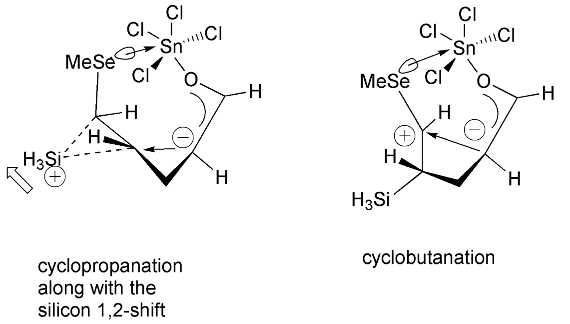
migration from **18** that have no Se–Sn interaction were also examined. However, no TS structures were obtained except the desilylation TS **24** (Scheme 7). The reaction-coordinate vectors for **24** do not indicate C1···C2 bond formation, but indicate Si migration towards Se. After the desilylation TS **24**, the resulting intermediate obtained by calculations was a Se–Si bonded species **25**. Work-up with Et_3N, followed by water, leads to removal of an H_3Si^+ (a model for Me_3Si^+) cation from Se and protonation of the enolate part of **25**, which affords the desilylation products (Scheme 9).§§ In fact, desilylation reactions have often been observed under these [2 + 1] cycloaddition reaction conditions.[9b,d,f,g] Experimentally, suppression of the facile desilylation path by using appropriate Lewis acids and avoiding drastic conditions (*e.g.* reaction at low temperature) is necessary for a successful cycloaddition process.



Scheme 9

4. Cyclopropanation *vs.* cyclobutanation. In Scheme 2, the reactants are nucleophilic olefins **1** and very electrophilic olefins **2** (mediated by Lewis acids). They are thought to mainly afford [2 + 2] cycloadducts as stated in the Introduction. Thus, it is necessary to rationalize the preference for [2 + 1] cycloaddition leading to strained cyclopropanes over [2 + 2] cycloaddition without silicon shift. The transition states for cyclobutane ring closure **26** and **28** were obtained, respectively (Scheme 7). The TS **26** starts from the zwitterion (*cis*) **16** and has an Se–Sn interaction through the ring closure and results in the cyclobutane **27**. The TS **28** starts from (*trans*) **18** and does not have the Se–Sn interaction. The TS **28** leads to the cyclobutane **29**. As shown in Scheme 7, the ΔE values are high for both processes (ΔE for **26**: +16.3 kcal mol^{-1}, ΔE for **28**: +23.0 kcal mol^{-1}) regardless of the Se–Sn interaction compared to those of the cyclopropanation processes (ΔE for **20**: +1.3 kcal mol^{-1}). Therefore, the cyclobutanation is an unfavorable process.

The reactivity contrast is explicable in terms of the directions of formation of C–C and Se–Sn bonds (Scheme 10). In cyclopropanation, these directions are almost parallel to each other (see TS structure **20** in Fig. 1 and **22** in the supplementary data), and the Se–Sn linkage contributes effectively to closure of the three-membered ring. On the other hand, the directions of Se–Sn and C–C formation in cyclobutanation (TS structure **26** in the supplementary data) are not parallel and the Se–Sn linkage does not contribute effectively to closure of the four-membered ring.



Scheme 10 Formation of the eight-membered ring *via* the Se···Sn linkage may work effectively for cyclopropanation rather than for cyclobutanation.

B. $ZnBr_2$-mediated [2 + 1] cycloaddition along with minor [2 + 2] cycloaddition

For the [2 + 1] cycloaddition reactions of **1** with methylenemalonates and β-carbonyl-substituted methylenemalonates, zinc halides ($ZnBr_2$, ZnI_2) are suitable Lewis acids.[9b,d] The reaction of 1-seleno-2-silylethene **6** and the $CH_2{=}C(CHO)_2{-}ZnBr_2$ complex **30** was investigated as a model of these reactions

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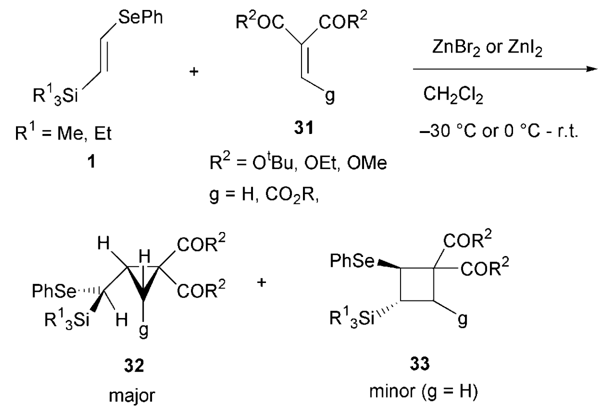
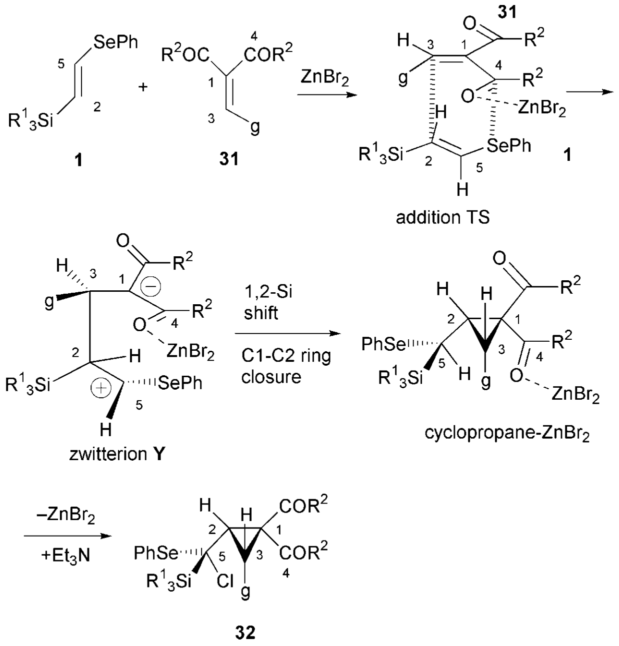
§§ Species **25** is highly stable (−54.2 kcal mol^{-1}). In the gas phase (without SCRF = dipole), the relative energy is +66.6 kcal mol^{-1}. The desilylated product **25** is stabilized too much by the solvent effect, in a similar fashion to the overstabilization of **18** (see footnote §§§).



Scheme 11

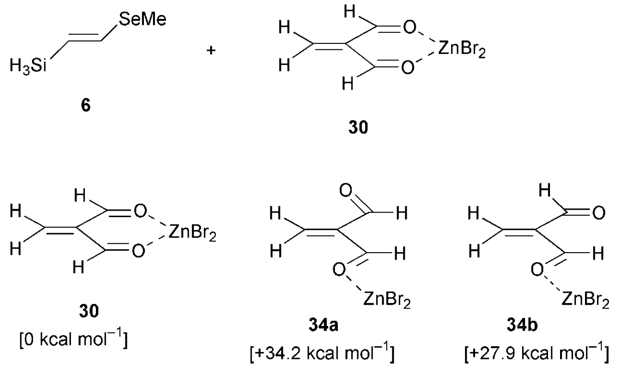


Scheme 12 A possible reaction mechanism for [2 + 1] cycloaddition of **1** with methylenemalonate which affords cyclopropanes.

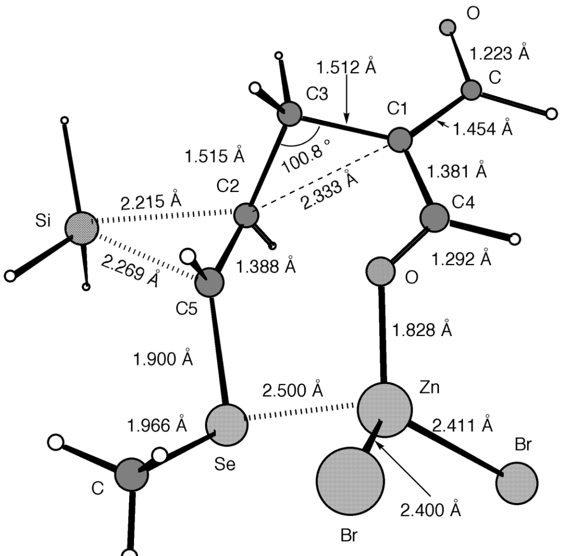
(**1**, methylenemalonate **31** and $ZnBr_2$ in Scheme 11).[¶¶] In zinc halide-promoted reactions of **1** with di-*tert*-butyl methylenemalonate, cyclobutane products **33** were formed as by-products in addition to cyclopropanes **32**.[9b]

Scheme 12 outlines a possible reaction course for the [2 + 1] cycloaddition.[||||] In the first step, addition of nucleophilic vinyl selenide **1** to methylenemalonate **31** activated by $ZnBr_2$ gives a zwitterion **Y**. In the resulting intermediate, silicon shift and ring closure lead to cyclopropane **32**.

For the reactant $H_2C{=}C(CHO)_2$–$ZnBr_2$ complex, the Zn–2(O=C) bidentate structure **30** was chosen, because it is 34.2 and 27.9 kcal mol^{-1} more stable than the s-*cis*/s-*trans* Zn–O=C monodentate complex **34a** and s-*cis*/s-*cis* Zn–O=C monodentate complex **34b**, respectively (Scheme 13).



Scheme 13



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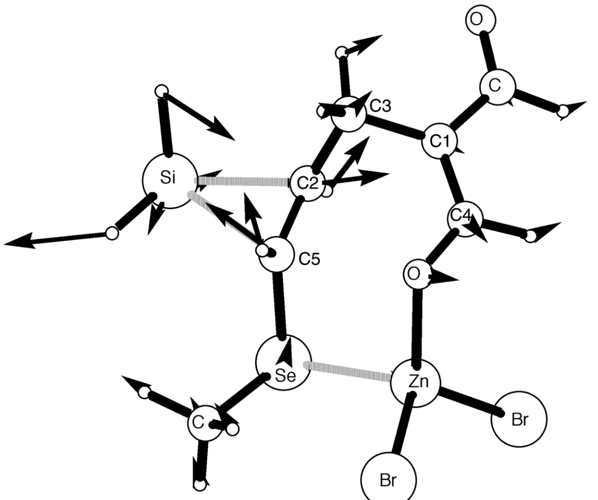
Si-shift and ring closure TS
[+8.6 kcal mol^{-1}]
ΔE = +12.8 kcal mol^{-1}



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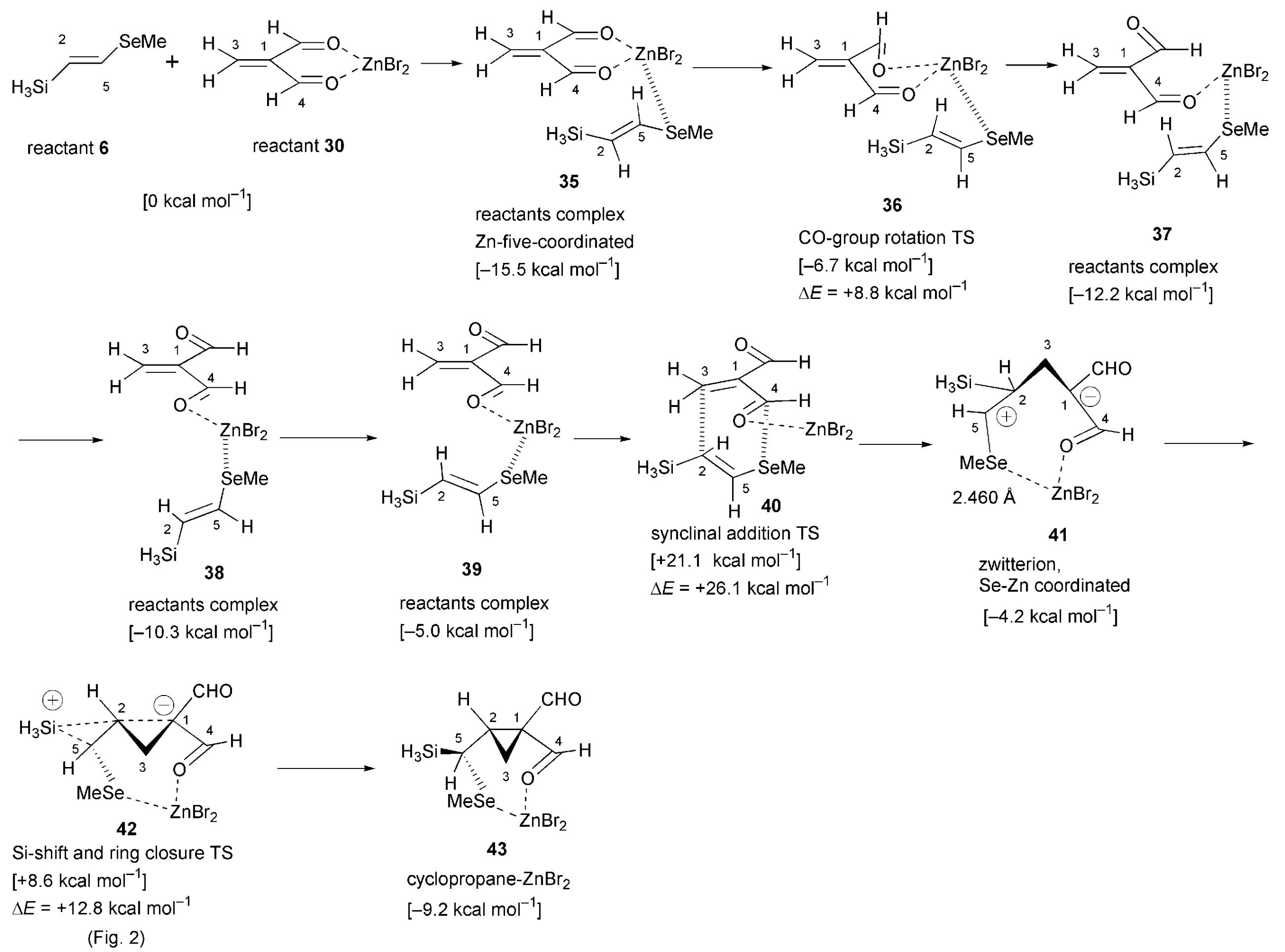
$\nu^{\ddagger}$ = 291.0i cm^{-1}

Fig. 2 Geometry of the transition state of the cyclopropane ring-forming step with the Se···Zn coordination and silicon C2→C5 shift (TS **42** in Scheme 14). Energy in square brackets is relative to that of reactants **6** and **30**. Energy barrier ΔE is relative to that of intermediate **41**. Reaction-coordinate vectors corresponding to the sole imaginary frequencies $\nu^{\ddagger}$ are sketched.

[¶¶] We examined experimentally the vinyl ketone–$ZnBr_2$ system previously (unpublished results). However, the reaction did not proceed, probably because the initial addition step is unfavorable due to the low electrophilicity of the vinyl ketone–$ZnBr_2$ complex towards 1-seleno-2-silylethene. The addition step of 1-seleno-2-silylethene **6** and acrolein–$ZnBr_2$ was examined as a simple variation of acrolein–$SnCl_4$. The energy barrier to addition is +40.1 kcal mol^{-1} and is much higher than that of **6** and acrolein–$SnCl_4$ (+4.0 kcal mol^{-1} for **12**) and that of **6** and $CH_2{=}C(CHO)_2$-$ZnBr_2$ (+26.1 kcal mol^{-1} for **40**). The computed result is consistent with the above experimental evidence; the low reactivity is due to the weak Lewis acidity of $ZnBr_2$ compared to $SnCl_4$ and due to the absence of an additional electron-withdrawing group (CHO) in the electrophilic olefin, acrolein.

[||||] In Scheme 12, the C3 stereochemistry for g ≠ H was experimentally determined and the mechanism was discussed in ref. 9*d*. In this paper, the C3 stereochemistry was not examined in detail.



Scheme 14 Mechanism of the cyclopropane forming reaction mediated by $ZnBr_2$. Energies in square brackets are relative to those of reactants **6** and **30**.

Prior to the addition transition state, the zinc five-coordinated complex bearing the Se–Zn bond **35** was obtained (Scheme 14). Complex **35** then gives monocarbonyl coordinated complex **37** *via* carbonyl rotation TS **36**. The complex **37** could be transformed into its rotamers: the Se–Zn coordinated complexes **38** and **39**. The transformation of **37** to the rotamer **38** involves C1–C4 (1.456 Å) rotation. The complex **39** directly leads to the synclinal addition transition state **40**.††† In the TS structure **40**, the C4–Se and C3–C2 distances are 3.083 and 2.129 Å, respectively. These distances are similar to those of **12** and show the C–Se secondary orbital interaction in the TS. The reaction-coordinate vectors in the transition state structure indicate C3 · · · C2 bond formation. After transition state **40**, the Se–Zn coordinated species **41** with tetrahedral zinc was obtained. The Se–Zn distance is 2.460 Å and the Se–Zn interaction seems to be stronger than that of Se–Sn (3.702 Å in the corresponding intermediate **19** in Scheme 6).‡‡‡

The zwitterion **41** proceeds to TS **42** (Fig. 2). In the TS structure, the C1–C2 distance is 2.333 Å and is shorter than that of the precursor **41** (2.513 Å) and the reaction-coordinate vectors indicate C1 · · · C2 bond formation clearly along with Si migration from C2 to C5. The intramolecular Se–Zn coordination to form an eight-membered ring with the stable tetrahedral coordinated zinc seems to cause cyclopropanation accompanied by silicon shift. Thus, TS **20** (Fig. 1) and TS **42** (Fig. 2) have demonstrated unprecedented cyclopropanation patterns. Characteristic of the cyclopropane-forming reaction mediated by $ZnBr_2$ is that the bidentate form Zn–2(O=C) of the reactant **30** is transformed to a monodentate form with Se–Zn coordination (**37**, **38** and **39**). This transformation and the subsequent isomerization of these rotamers are required to take the path outlined in Scheme 12.

The cyclobutane-forming reaction was also examined. First, the reaction path from an intermediate (**37**, **38**, **39** or **41**) involving monodentate Zn–O=C and an Se–Zn linkage was probed, but no results could be obtained. Second, the path with Zn–2(O=C) bidentate coordination retained was traced. Scheme 15 shows the addition reaction between reactants **6** and **30** yielding the zwitterionic intermediate **46**. From **46**, the transition state for cyclobutane ring closure **47** was obtained.§§§ As shown, the ΔE value is slightly higher than that of the cyclopropanation process (ΔE for **47**: +17.1 kcal mol^{-1}, ΔE for **42**: +12.8 kcal mol^{-1} in Scheme 14). The ΔE for cyclobutanation is comparable with those of the $SnCl_4$-mediated reactions (ΔE for **26**: +16.3 kcal mol^{-1}, ΔE for **28**: +23.0 kcal mol^{-1} in Scheme 7). However, the ΔE values for cyclopropanation with $SnCl_4$ (ΔE for **20**:

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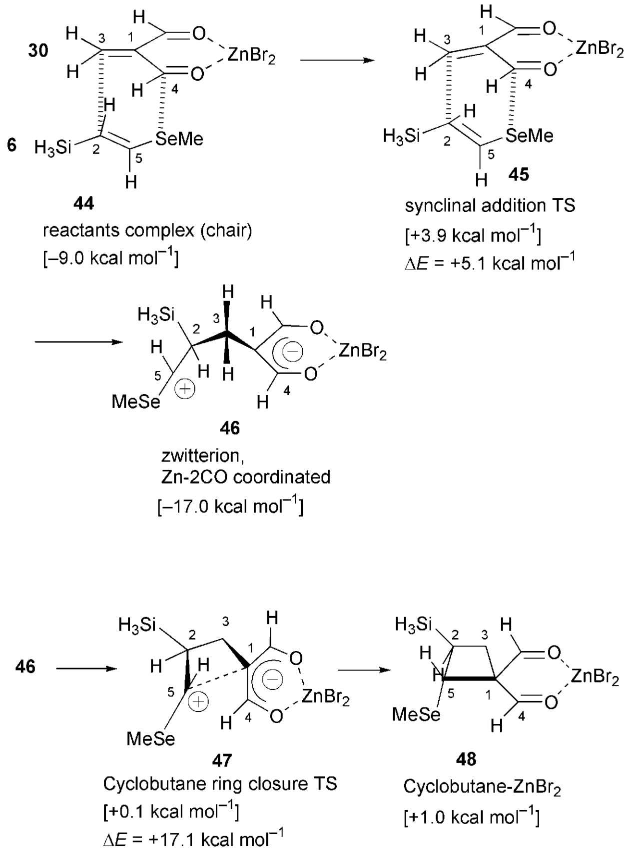
††† The energies for the obtained s-*cis*/s-*trans* isomers of **38** and **40**–**43** are similar to their s-*trans*/s-*trans* complexes (the differences are −2.8 ~ +1.3 kcal mol^{-1}). Thus, the s-*cis* or s-*trans* conformation of the uncomplexed carbonyl group in the intermediates does not have a large effect on reactivities.

‡‡‡ The model calculations of $Me_2Se \cdots ZnBr_2$ by B3LYP/6-31G* (for all atoms) and by B3LYP/6-31G* for C, H, O, Si and Se and 3-21G* for Zn and Br were carried out in order to compare the bond lengths. The Se–Zn distances are 2.451 Å by the full 6-31G* and 2.239 Å by the spliced method. This result shows the spliced calculation gives a *ca.* 0.2 Å shorter Zn–Br bond length than that of the full 6-31G* method. This difference is understandable in view of the somewhat large polarity of the 3-21G* basis set. However, the Se · · · Zn and Se · · · Sn linking mechanism presented here would be not affected by the choice of basis set for the Lewis acids.

§§§ The energy of cyclobutane **48** is 0.9 kcal mol^{-1} higher (less stable) than that of the ring-closure transition state **47**. The problem probably comes from the calculation of solvation energies. The relative energy of **48** is 5.6 kcal mol^{-1} lower than that of **47** in the gas phase (without SCRF).



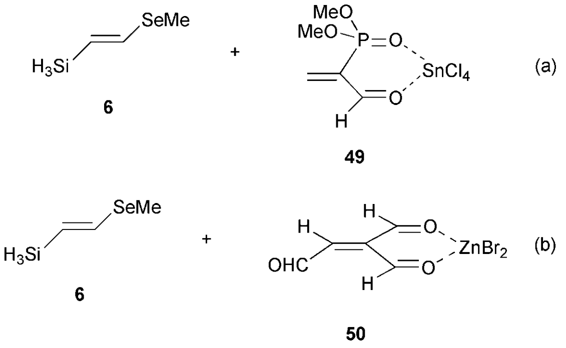
Scheme 15 Other mechanisms for the reaction between **6** and **30**. Energies in square brackets are relative to those of reactants **6** and **30** in Scheme 14.

+1.3 kcal mol^{-1} in Scheme 6, ΔE for **22**: +4.6 kcal mol^{-1} in Scheme 7) are much smaller than those with $ZnBr_2$, probably because $SnCl_4$ is a stronger Lewis acid than $ZnBr_2$, and Se electrons donate to Sn^{4+} more strongly than to Zn^{2+}. Therefore, the adjacent Si 1,2-shift with $SnCl_4$ occurs more readily than with $ZnBr_2$. As a result, the difference in ΔE between **47** and **42** is small compared to that of $SnCl_4$. This small energy difference is consistent with the experimental result that in zinc halide-promoted reactions of **1** with di-*tert*-butyl methylenemalonate, cyclobutanation occurs along with cyclopropanation as in Scheme 11.[9b]

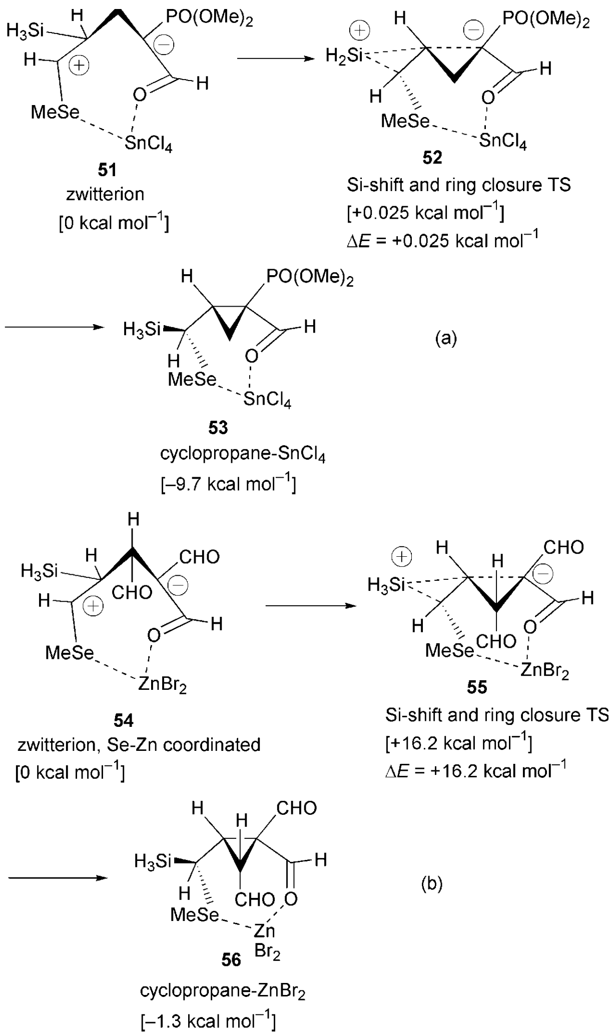
C. $SnCl_4$- and $ZnBr_2$-mediated [2 + 1] cycloadditions of other substrates

In previous sections, the difference between $SnCl_4$- and $ZnBr_2$-mediated [2 + 1] cycloadditions is somewhat complicated because of the different Lewis acid metal coordination patterns. In this sub-section, the difference between $SnCl_4$- and $ZnBr_2$-mediated [2 + 1] cycloadditions is compared more fairly to check the generality of the present mechanism of cyclopropanation. Electrophilic olefins other than **7** (Scheme 5) and **30** (Scheme 13) that work with high yields and high chemo- and stereoselectivity in this reaction were adopted for examination. As model compounds for electrophilic olefins, $SnCl_4$-mediated phosphonoacrylates[9e] and $ZnBr_2$-mediated β-carbonyl-substituted methylenemalonates[9d,f] were employed. Both types of olefin react with **1** highly selectively and only afford cyclopropanes. The model substrates **6**, **49** and **50** are shown in Scheme 16. These cyclopropane ring-formation steps ((a), **51**→**53**) and ((b), **54**→**56**) are shown in Scheme 17, respectively. The structures of these intermediates and the transition states have the above-mentioned through-space Se–metal (Sn or Zn) interaction as well.

There is a noteworthy difference in reactivity between $SnCl_4$ and $ZnBr_2$. Energy barriers for $SnCl_4$-mediated reactions



Scheme 16

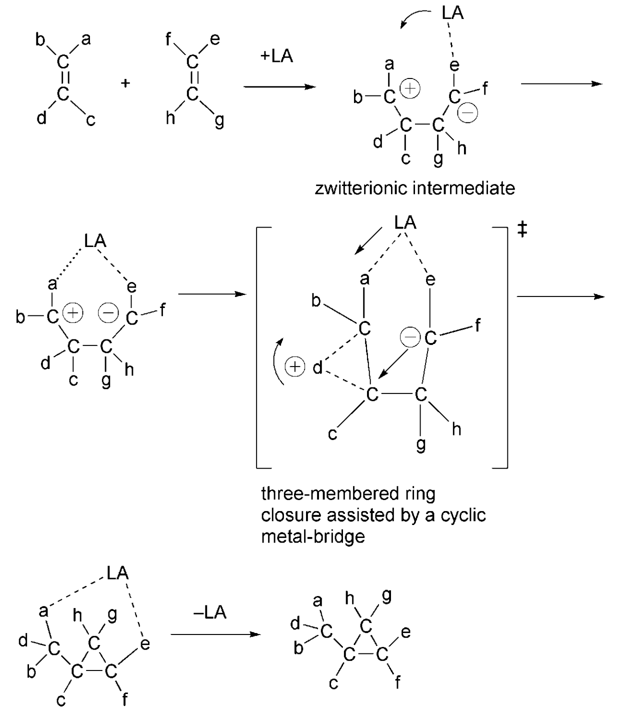


Scheme 17 The cyclopropane ring-forming steps between **6** and **49** and between **6** and **50**. Energies in square brackets are relative to the intermediates **51** and **54**, respectively.

(ΔE = +1.3 kcal mol^{-1} for **20** in Scheme 6, +4.6 kcal mol^{-1} for **22** in Scheme 7, and +0.025 kcal mol^{-1} for **52**) are lower than for $ZnBr_2$-mediated reactions (ΔE = +12.8 kcal mol^{-1} for **42** in Scheme 14 and +16.2 kcal mol^{-1} for **55**). The difference does not depend on mono- or bidentate coordination of the Lewis acids. The low-energy barrier for $SnCl_4$ may explain the effective cyclopropanation observed at low temperature (−78 °C), although $SnCl_4$ is sometimes too strong and causes the desilylation reactions shown in Scheme 7.[9d,f]

Concluding remarks

The mechanism of the novel [2 + 1] cycloaddition reactions of 1-seleno-2-silylethene has been investigated using DFT (density



Scheme 18 Summary of the cyclopropanation of two olefins with the aid of a Lewis acid (LA).

functional theory) calculations. The elementary processes for $SnCl_4$-mediated and $ZnBr_2$-mediated cyclopropane formation are illustrated in Schemes 6 and 14, respectively. Both processes involve synclinal addition of **6** to electrophilic olefin–Lewis acid complexes, leading to zwitterionic intermediates. In the Se–metal (Lewis acid) interacting zwitterionic intermediate, silicon shift and ring closure occurred, leading to cyclopropanes. Calculations on transition states show that the silicon migration and cyclopropane ring closure occur concertedly with the aid of eight-membered cyclic Se–metal coordination. The cyclopropane formation energy barrier is smaller than the possible cyclobutane formation energy barrier. The tin atom tends to make six-coordinated complexes[22] and the zinc atom tends to make tetrahedral four-coordinated complexes. The Se lone-pair electrons are excellent ligands. This driving force originating from the metal center can generate the very strained cyclopropane rings along with Si shift. In short, the cyclopropanation is caused by the ligand–ligand interaction on the metal center which is the structural function raised in the Introduction. Scheme 1 is thus reviewed, and a Lewis (LA) acid that bridges the two substituents a and e is needed to cause the cyclopropanation (Scheme 18).

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