Supplementary Data

Olefin-olefin Reactions Mediated by Lewis Acids may afford Cyclopropanes rather than Cyclobutanes: A Mechanistic Study of Cyclopropane Formation Reaction using a 1-Seleno-2-silylethene

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Table. Total energies and zero-point vibrational energies

compound No.[a)]	Total energy (a.u.)[b)]	Zero-point vibrational energy (kcal/mol)[c)]
6	-2810.22117045	59.73019
7	-8023.47842931	43.15797
8	-8062.81740206	60.29502
9	-8062.81160687	60.38861
10	-10833.7369119	104.20855
11	-10833.7059180	104.40912
12 TS	-10833.7000807	104.64084
13	-10833.7388056	104.10806
14	-10833.7072417	103.94361
15 TS	-10833.6968380	103.89124
16	-10833.7156622	105.93634
17 TS	-10833.7123823	105.61291
18	-10833.7357338	104.81444
19	-10833.7086967	106.13861
20 TS	-10833.7057029	105.55750

21	-10833.7351719	106.63839
22 TS	-10833.7083564	105.89247
23	-10833.7401155	107.03479
24 TS	-10833.7264861	104.87628
25	-10833.7887735	104.69457
26 TS	-10833.6889465	105.35962
27	-10833.7424719	106.75357
28 TS	-10833.703123	105.48107
29	-10833.7063676	106.08025
30	-7199.94579400	48.06287
34a	-7199.88997920	47.24652
34b	-7199.90023697	47.40261
35	-10010.1926431	108.39035
36 TS	-10010.1772782	107.56229
37	-10010.1868761	108.11501
38	-10010.1839886	108.18431
39	-10010.1748949	107.81931
40 TS	-10010.1368023	109.95803
41	-10010.1772059	109.95021
42 TS	-10010.1562192	109.70635
43	-10010.1859858	110.52408
44	-10010.1825455	108.63807
45 TS	-10010.1751035	108.99215
46	-10010.1974084	109.92319
47 TS	-10010.1700920	109.93637
48	-10010.1694843	110.42960
51	-11480.1713476	157.51345

52 TS	-11480.1713420	157.53455
53	-11480.1884537	158.47952
54	-10123.5257080	115.36999
55 TS	-10123.4994176	115.02155
56	-10123.5283200	115.67335
s-trans of **38**	-10010.1880766	108.26353
s-trans of **40** TS	-10010.1340729	109.94048
s-trans of **41**	-10010.1774454	109.90118
s-trans of **42** TS	-10010.1596368	109.60582
s-trans of **43**	-10010.1905423	110.54862
acrolein (s-cis)-$ZnBr_2$	-7086.53802993	41.44264
acrolein-$ZnBr_2$-**1** complex (corresponding to **39**)	-9896.83010670	102.41608
acrolein-$ZnBr_2$-**1** addition TS (corresponding to **40**) TS	-9896.76918072	104.25077
acrolein-$ZnBr_2$-**1** zwitter-ion (corresponding to **41**)	-9896.80471299	104.16327

a) TSs stand for transition states which have sole imaginary frequencies.

b) Total energies were calculated by B3LYP/6-311+G(2d,p) & 3-21G* SCRF.

c) Zero-point vibrational energies were obtained by vibrational analyses of B3LYP/6-31G* & 3-21G* SCRF.

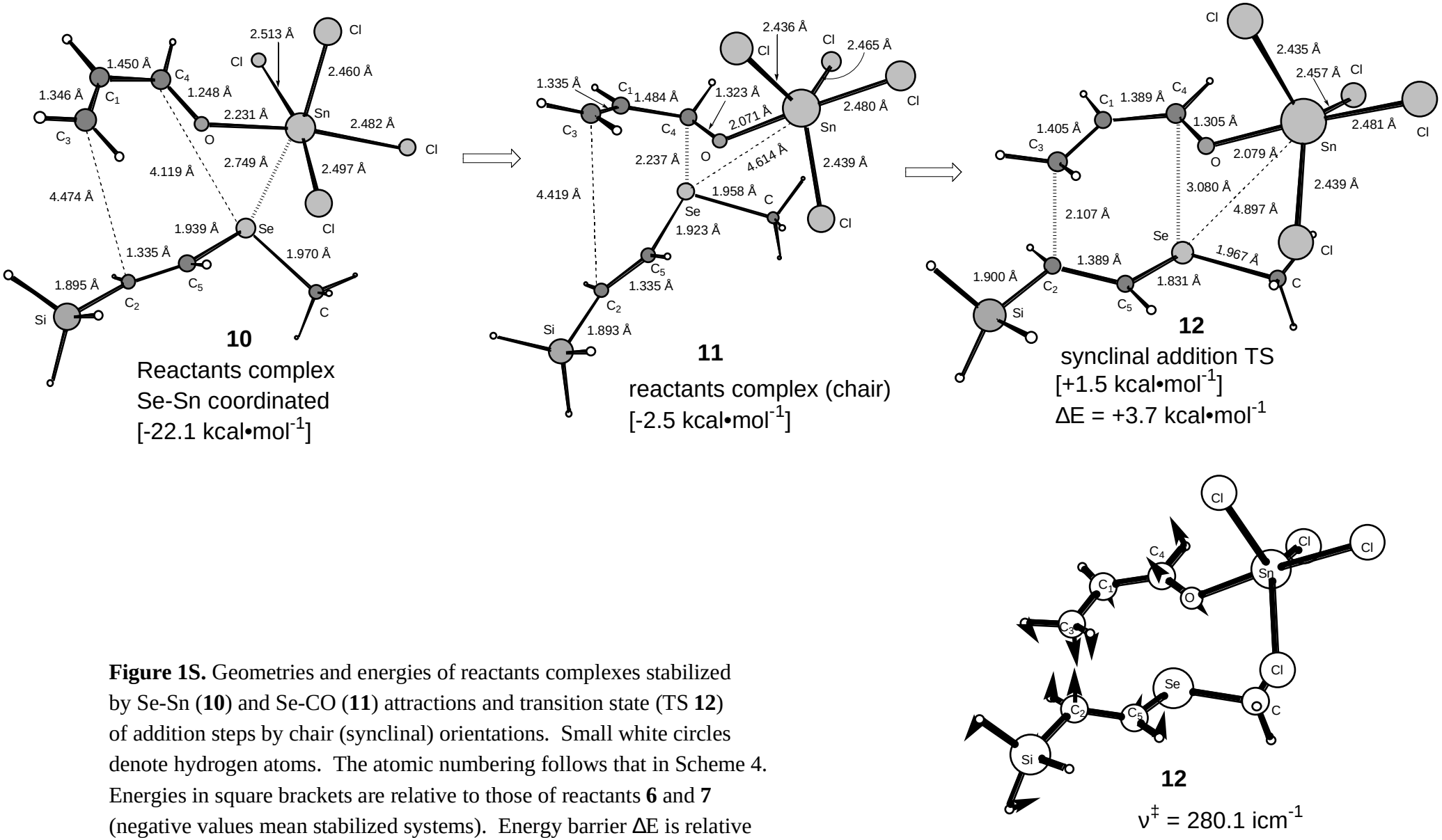
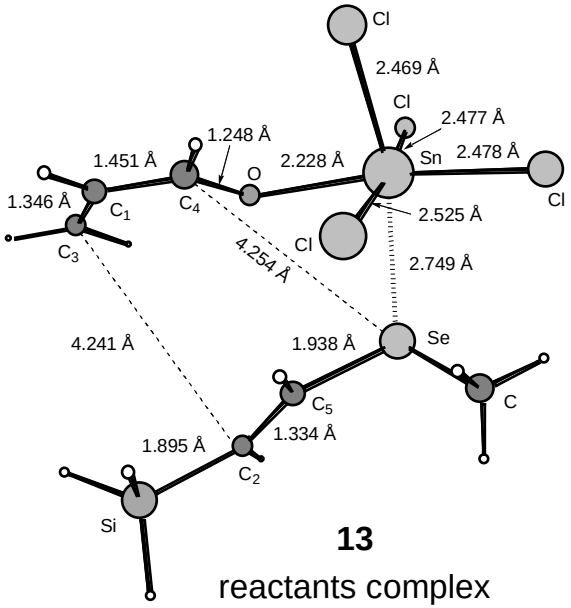
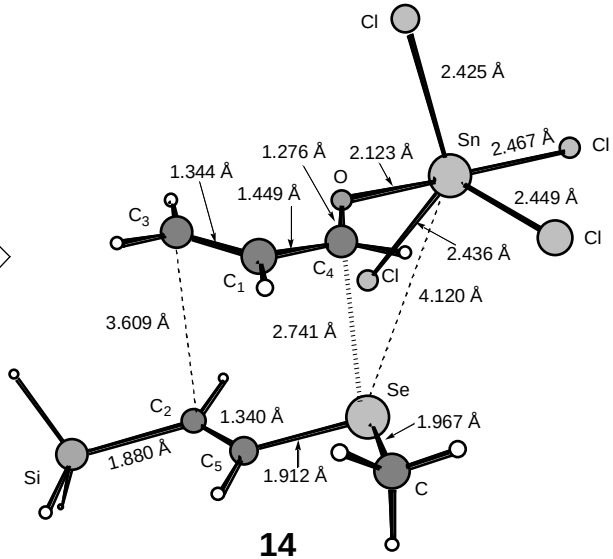


Figure 1S. Geometries and energies of reactants complexes stabilized by Se-Sn (**10**) and Se-CO (**11**) attractions and transition state (TS **12**) of addition steps by chair (synclinal) orientations. Small white circles denote hydrogen atoms. The atomic numbering follows that in Scheme 4. Energies in square brackets are relative to those of reactants **6** and **7** (negative values mean stabilized systems). Energy barrier ΔE is relative to that of reactants complex **11**. For TS, reaction-coordinate vectors corresponding to the sole imaginary frequencies $\nu^{\ddagger}$ are sketched.



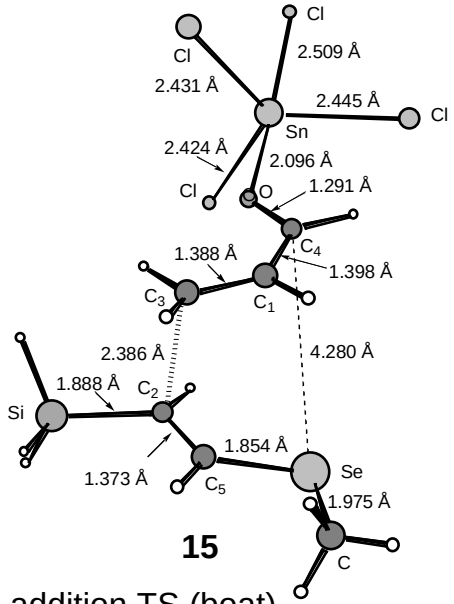
13

reactants complex
Se-Sn coordinated
[-23.4 kcal•mol^{-1}]



14

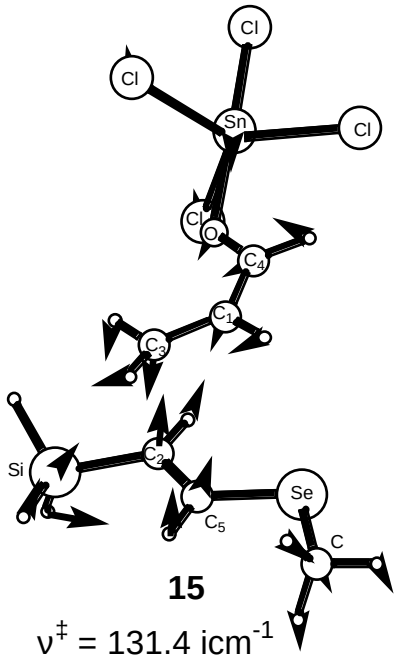
reactants complex (boat)
[-3.7 kcal•mol^{-1}]



15

addition TS (boat)
[+2.7 kcal•mol^{-1}]
ΔE = +6.4 kcal•mol^{-1}

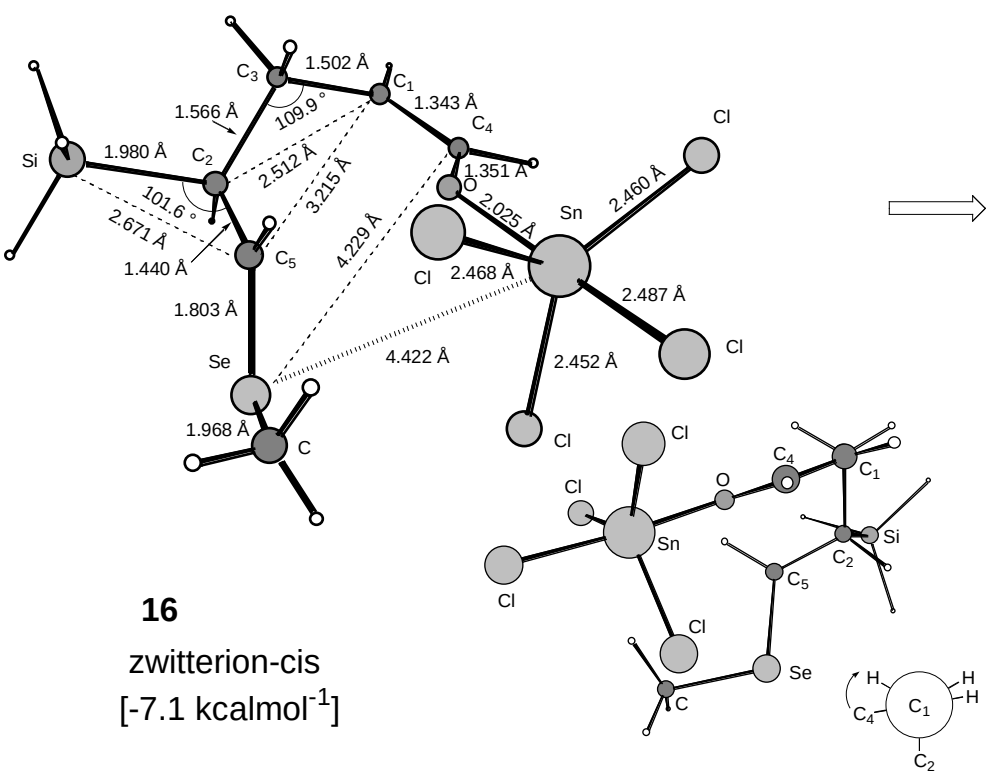
18 (see Figure 3S)



15

$\nu^{\ddagger}$ = 131.4 icm^{-1}

Figure 2S. Geometries and energies of reactants complexes stabilized by Se-Sn (**13**) and Se-CO (**14**) attractions and transition state (TS **15**) of addition step by boat orientations. Energy barrier ΔE is relative to that of reactants complex **14**.

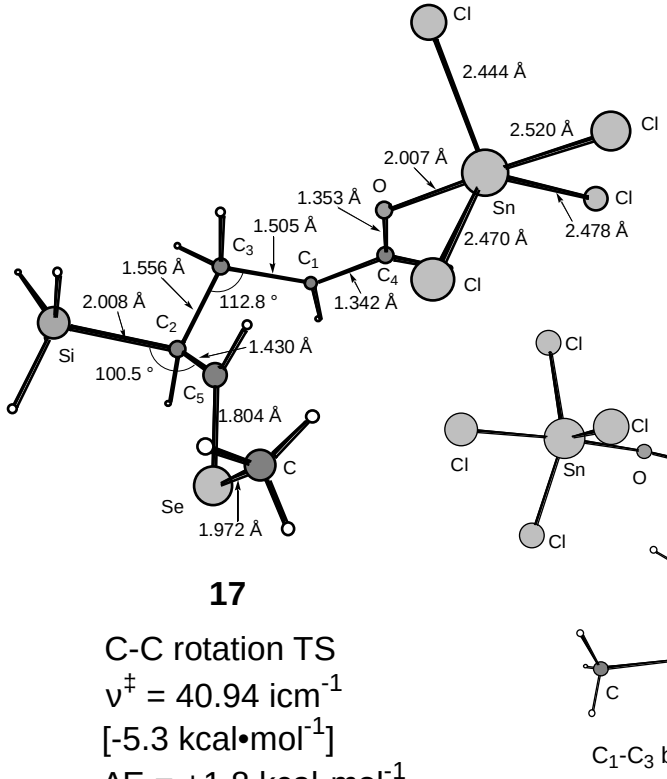


16

zwitterion-cis

[-7.1 kcalmol^{-1}]

C_1-C_3 bond view of **16**



17

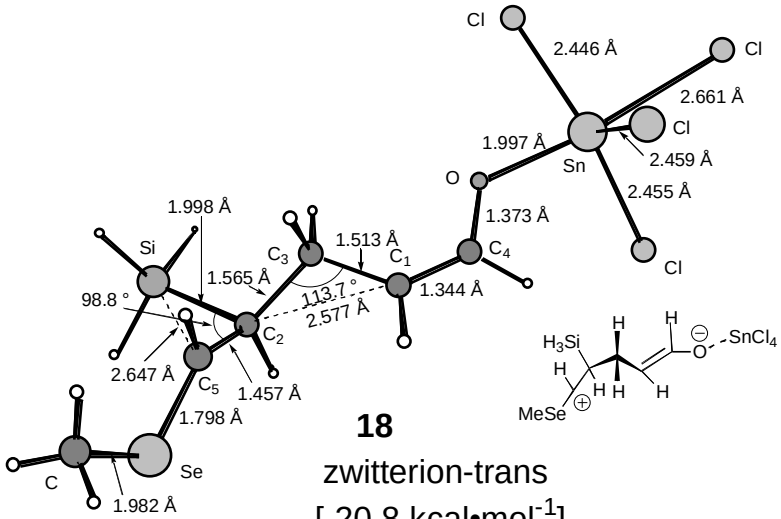
C-C rotation TS

$\nu^{\ddagger}$ = 40.94 icm^{-1}

[-5.3 kcal•mol^{-1}]

ΔE = +1.8 kcal•mol^{-1}

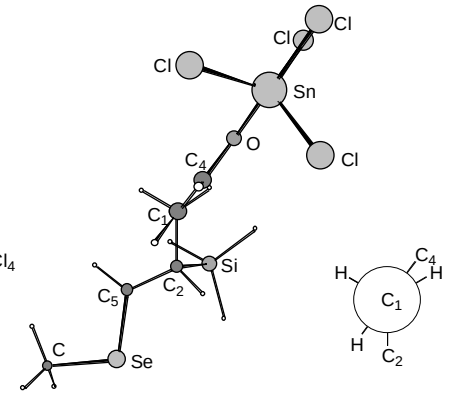
C_1-C_3 bond view of **17**



18

zwitterion-trans

[-20.8 kcal•mol^{-1}]



C_1-C_3 bond view of **18**

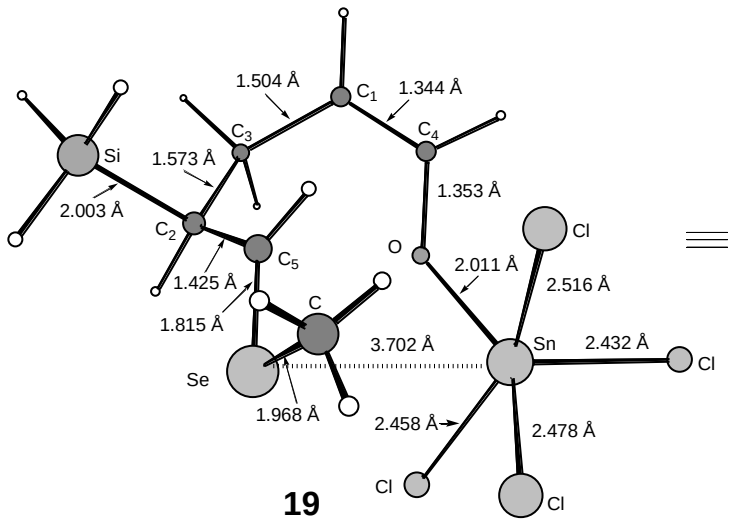
19

zwitterion-trans,

Se-Sn coordinated

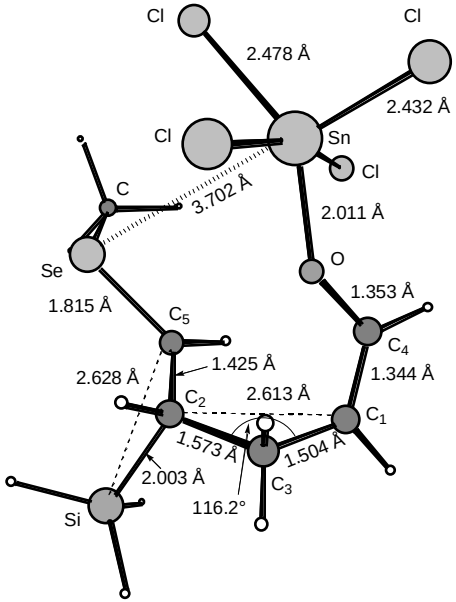
[-2.4 kcal•mol^{-1}]

Figure 3S. Isomerization processes of zwitterionic species via rotation around the C-C single bond. The zwitterion **16** is generated from TS **12** in Figure 1S.

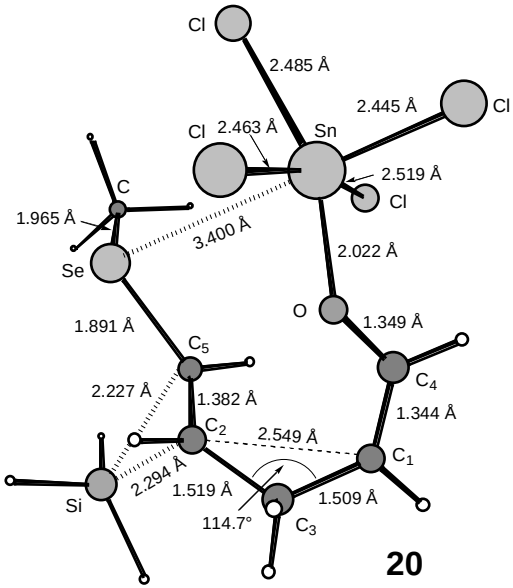


19

zwitterion-trans, Se-Sn coordinated
[-2.4 kcal•mol^{-1}]

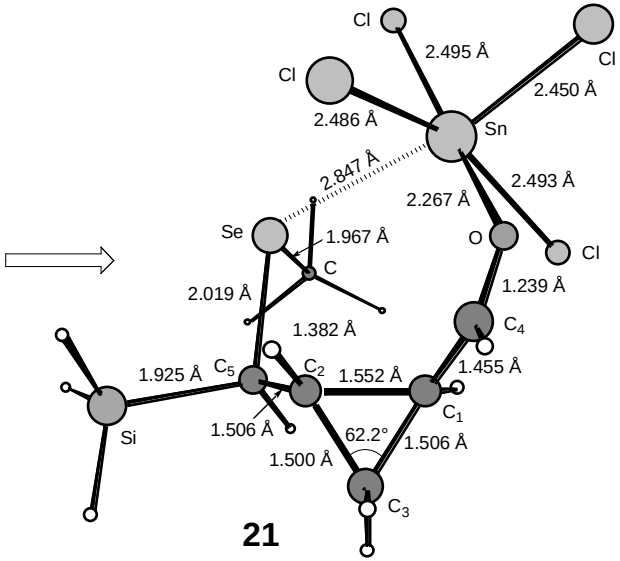


19



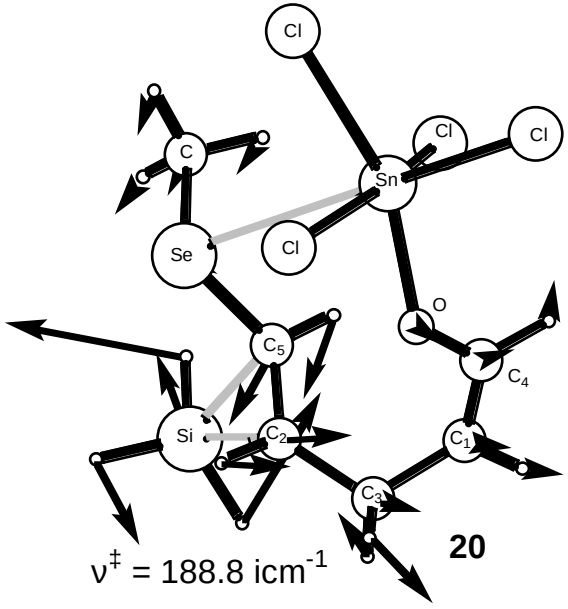
20

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



21

trans-cyclopropane-SnCl$_4$
[-18.6 kcal•mol^{-1}]



20

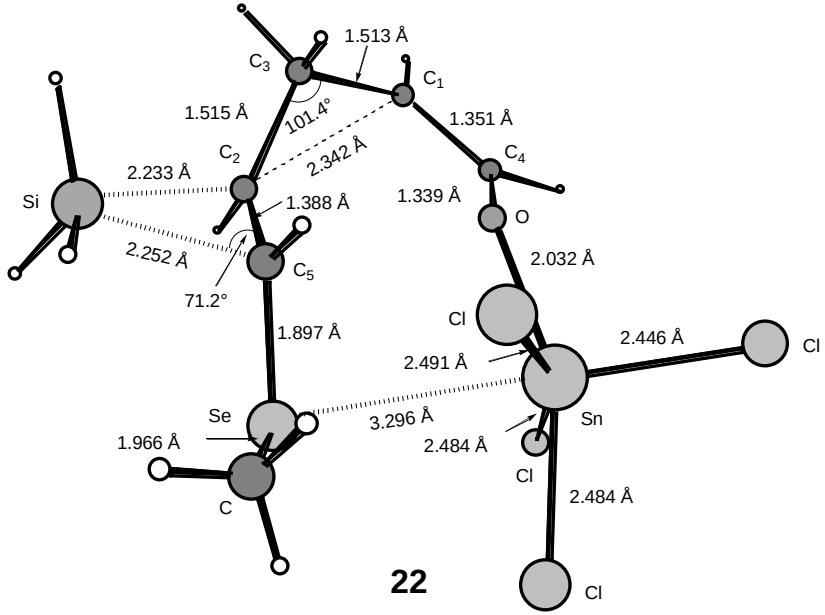
$\nu^{\ddagger}$ = 188.8 icm^{-1}

Figure 4S. The cyclopropane-ring forming step with the through-space Se---Sn attraction and silicon C_2 → C_5 shift, **19**→**20**→**21**.

16

zwitterion-cis

[-7.1 kcalmol^{-1}]

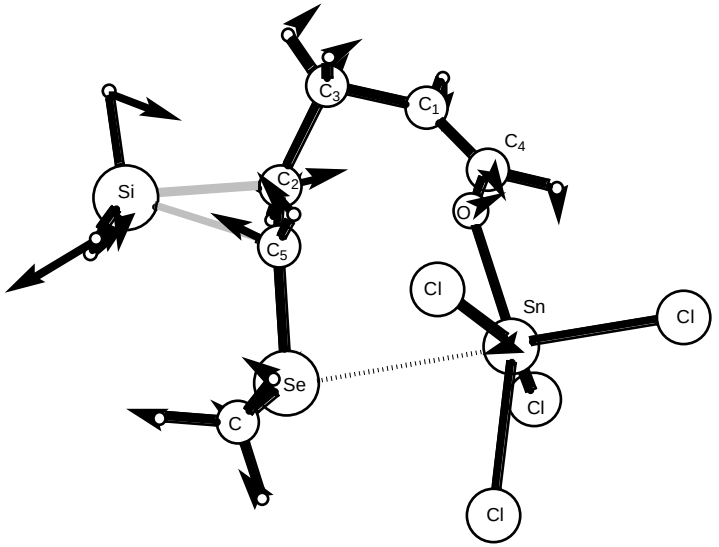


22

Si-shift and ring closure (cis) TS

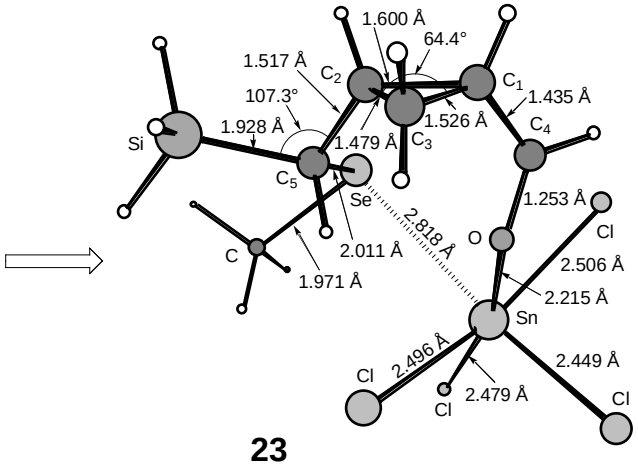
[-2.5 kcal•mol^{-1}]

ΔE = +4.6 kcal•mol^{-1}



$\nu^{\ddagger}$ = 227.0 icm^{-1}

22



23

cis-cyclopropane-$SnCl_4$

[-21.3 kcal•mol^{-1}]

Figure 5S. The cyclopropanation step starting from the *cis* zwitterionic intermediate **16** (shown in Figure 3S), **16**→**22**→**23**.

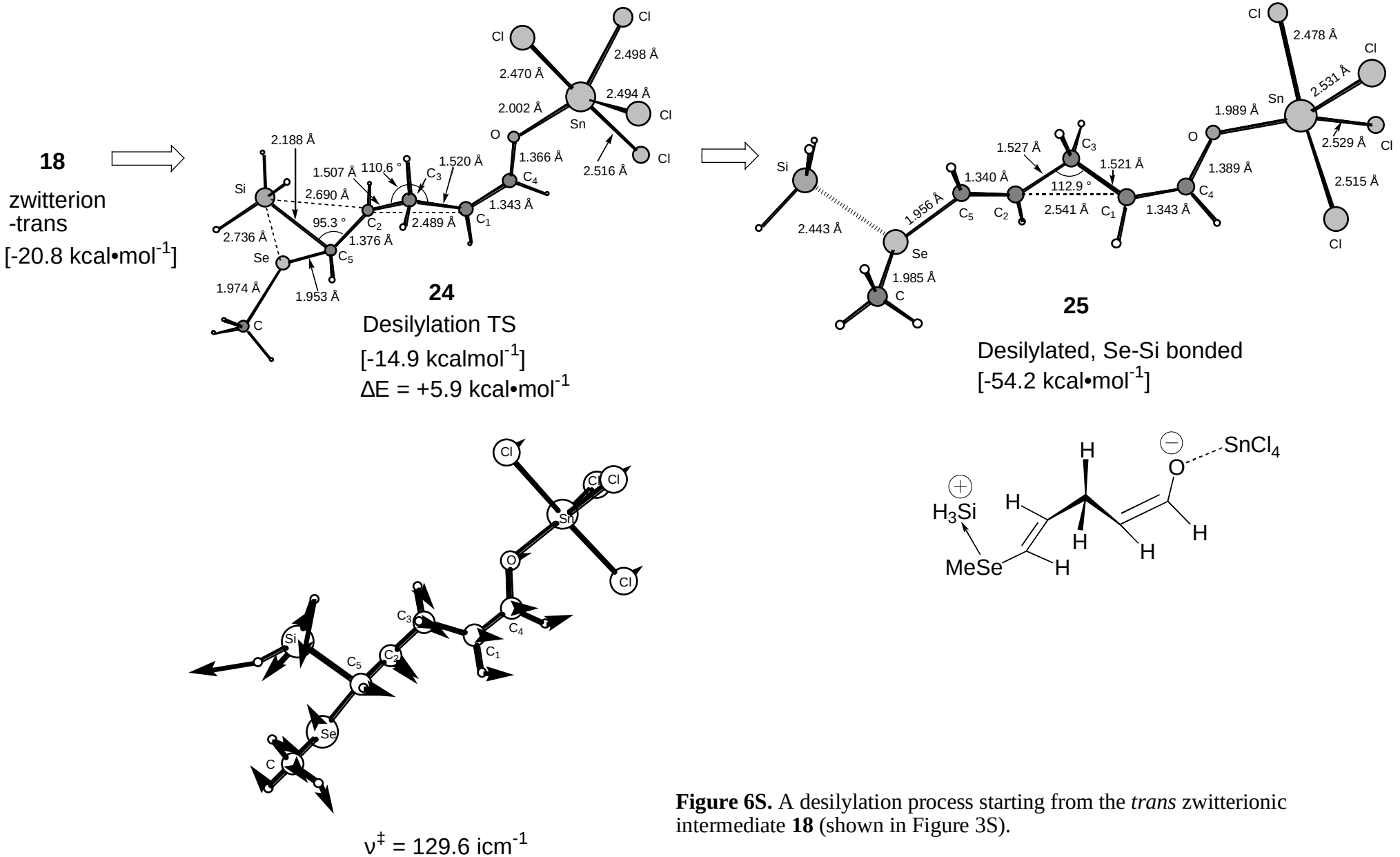
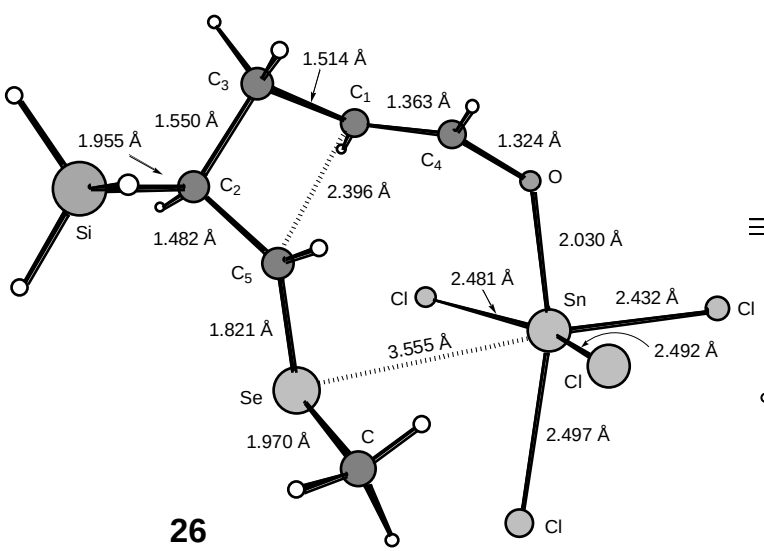


Figure 6S. A desilylation process starting from the *trans* zwitterionic intermediate **18** (shown in Figure 3S).

16

zwitterion-cis

[-7.1 kcalmol^{-1}]



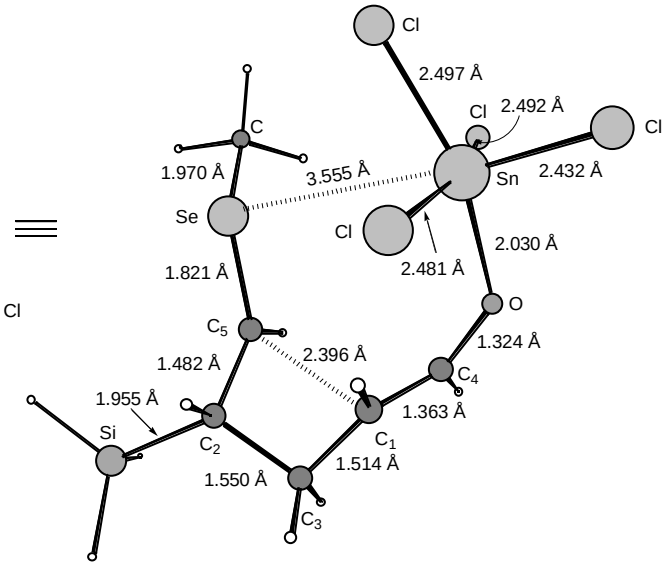
26

Cyclobutane ring closure

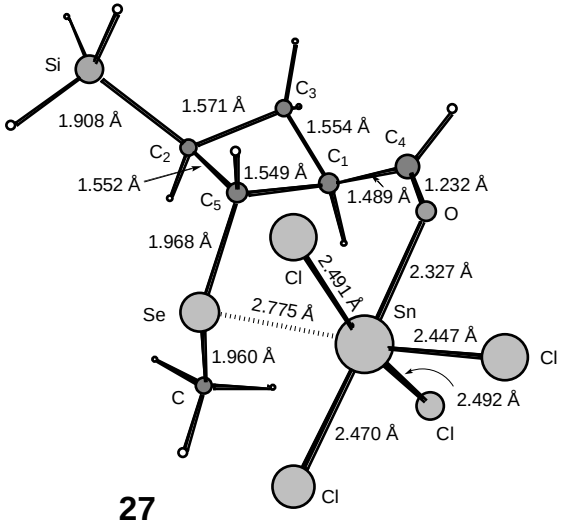
(Se-Sn interacting) TS

[+9.2 kcal•mol^{-1}]

ΔE = +16.3 kcal•mol^{-1}



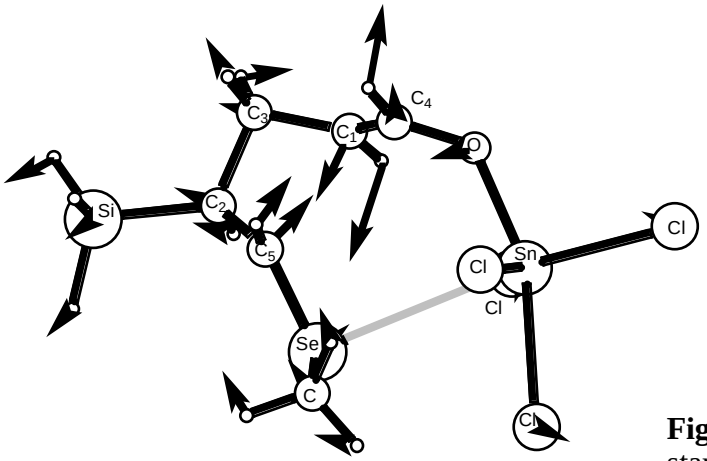
26



27

Cyclobutane-$SnCl_4$

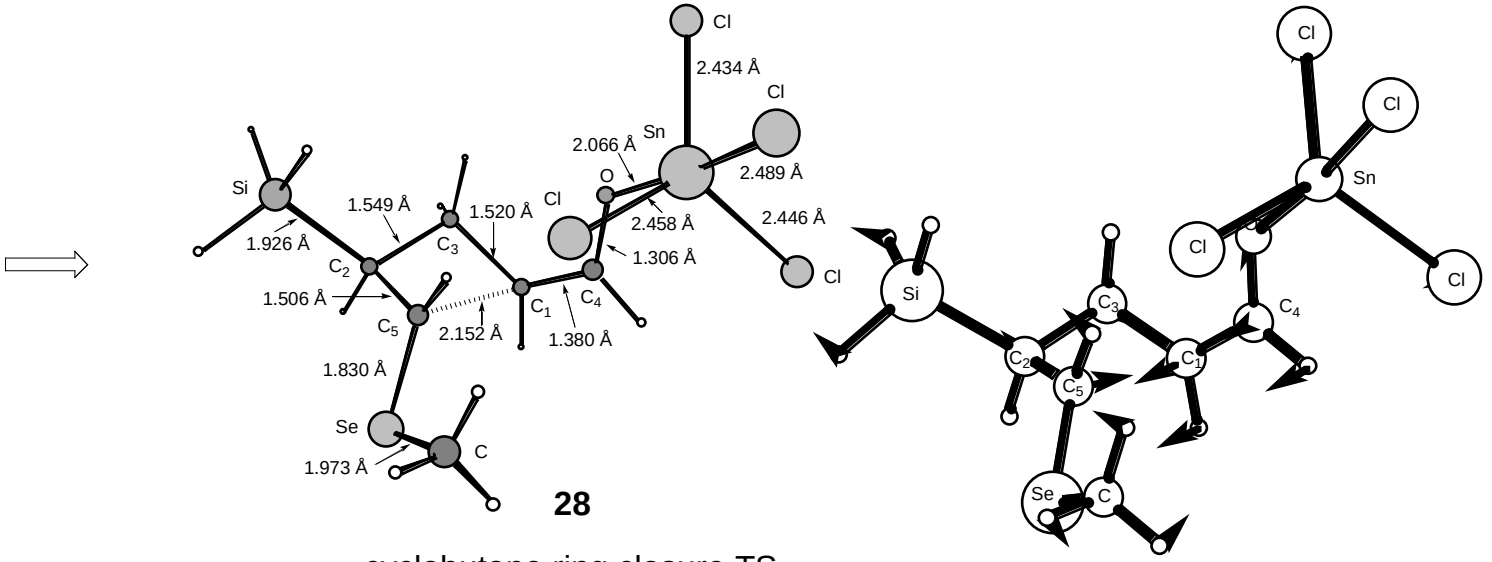
[-23.0 kcal•mol^{-1}]



$\nu^{\ddagger}$ = 158.1 icm^{-1}

Figure 7S. A cyclobutane formation process starting from the *cis* zwitterionic intermediate **16** (shown in Figure 3S).

18
zwitterion-trans
[-20.8 kcalmol^{-1}]

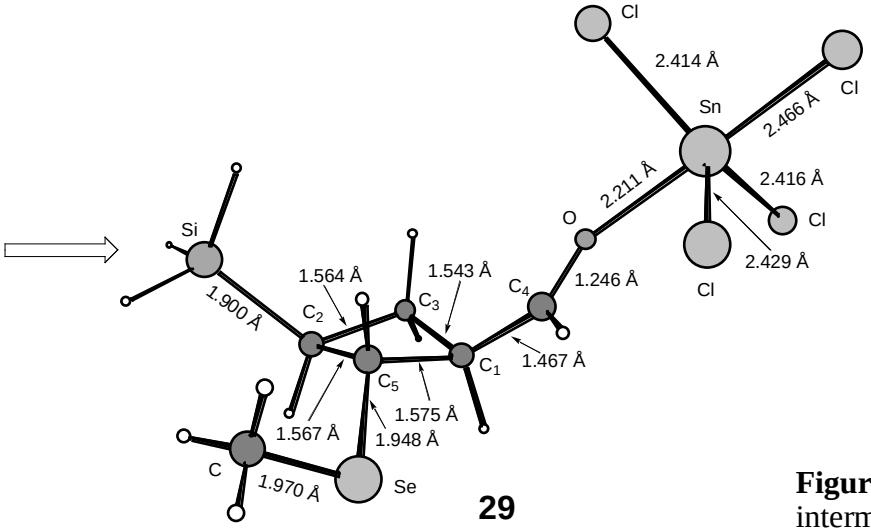


28

cyclobutane ring closure TS
[+2.2 kcal•mol^{-1}]
ΔE = +23.0 kcal•mol^{-1}

28

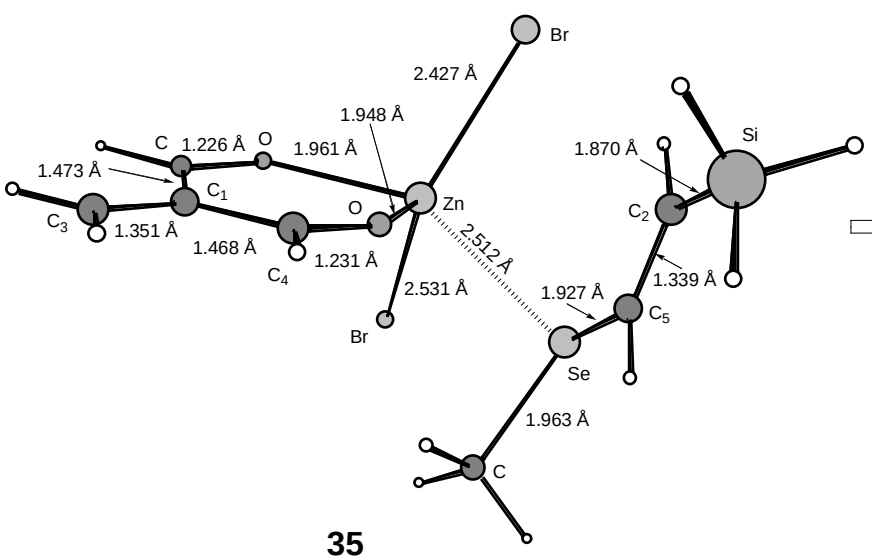
$\nu^{\ddagger}$ = 217.6 icm^{-1}



29

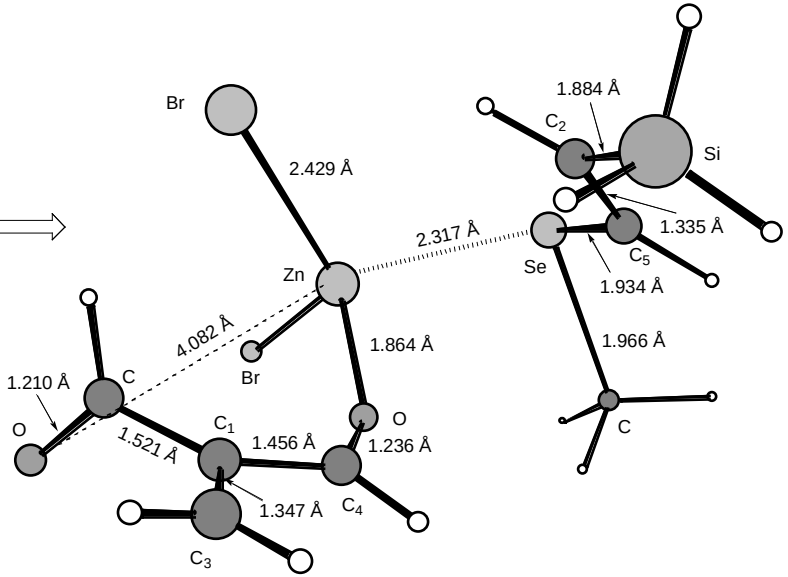
cyclobutane-$SnCl_4$
[-1.0 kcal•mol^{-1}]

Figure 8S. A second cyclobutane formation process starting from the *trans* zwitterionic intermediate **18** (shown in Figure 3S).



35

reactants complex
Zn five-coordinated
[-15.5 kcal•mol^{-1}]

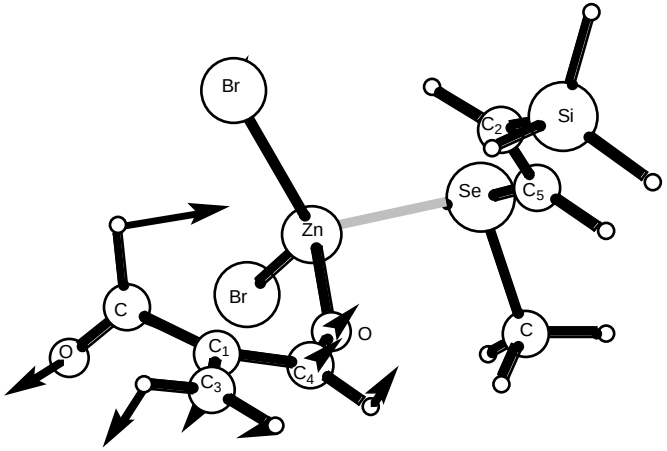


36

CO-group rotation TS
[-6.7 kcal•mol^{-1}]
ΔE = +8.8 kcal/mol

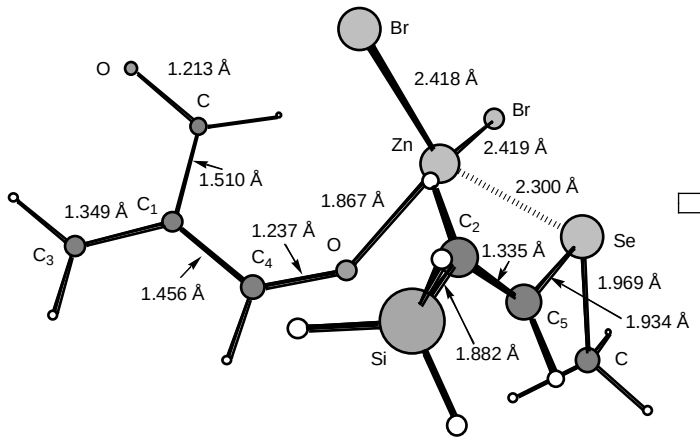
37

reactants complex
Se-Zn coordinated
[-12.2 kcal•mol^{-1}]



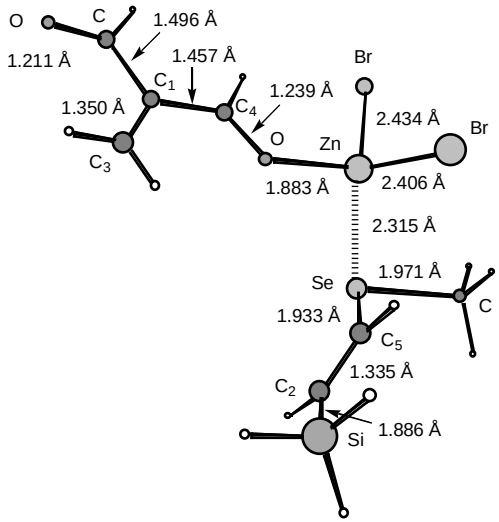
$\nu^{\ddagger}$ = 133.3 icm^{-1}

Figure 9S. Geometries and energies of the five-coordinated complex bearing the Se-Zn bond (**35**) and transition state (TS **36**) of the carbonyl rotation. The atomic numbering follows that in Scheme 12. Energies in square brackets are relative to those of reactants **6** and **30** (negative values mean stabilized systems). Energy barrier ΔE is relative to that of reactants complex **35**.



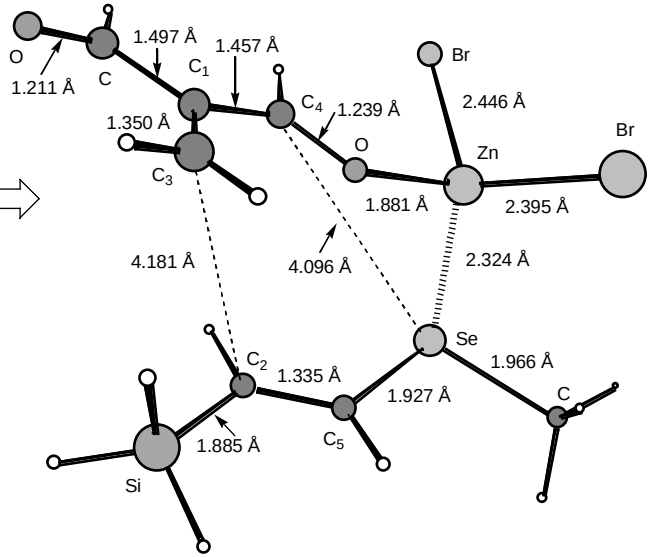
37

reactants complex
Se-Zn coordinated
[-12.2 kcal•mol^{-1}]



38

reactants complex
Se-Zn coordinated
[-10.3 kcal•mol^{-1}]



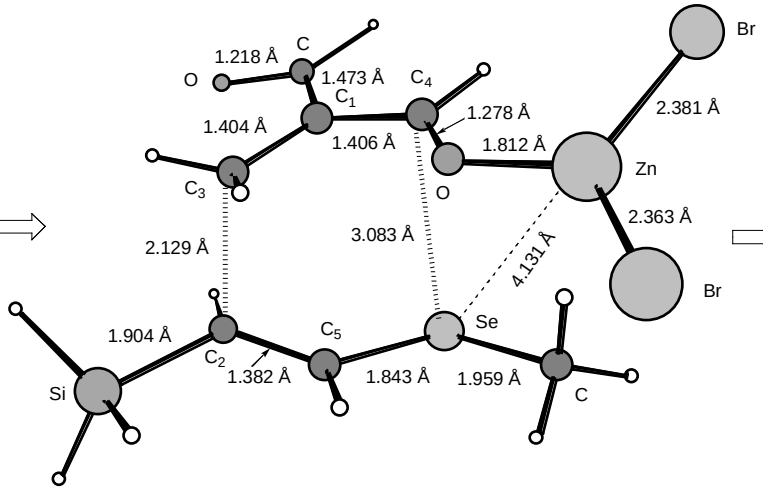
39

reactants complex
Se-Zn coordinated
[-5.0 kcal•mol^{-1}]

Figure 10S. Transformation of complex **37** to its rotamers, Se-Zn coordinated complexes **38** and **39**.

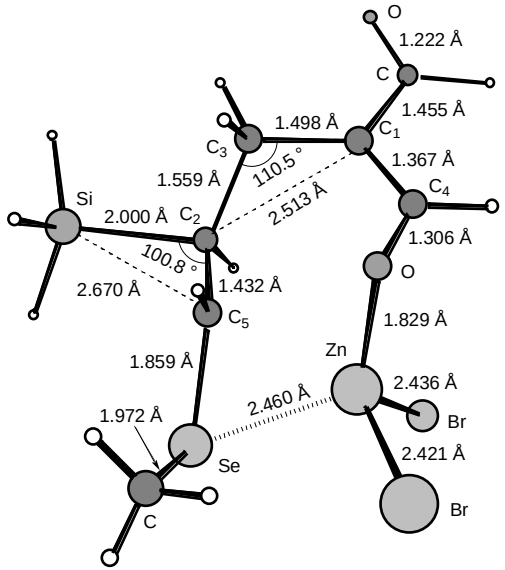
39

reactants complex
Se-Zn coordinated
[-5.0 kcal•mol^{-1}]



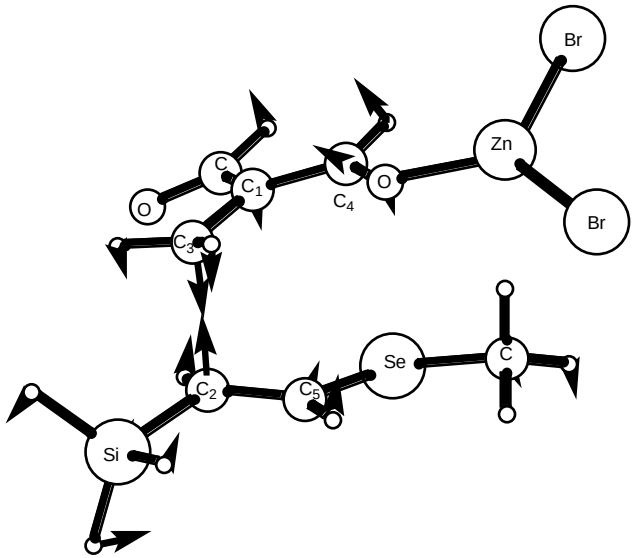
40

synclinal addition TS
[+21.1 kcal•mol^{-1}]
ΔE = +26.1 kcal/mol



41

zwitterion, Se-Zn coordinated
[-4.2 kcal•mol^{-1}]

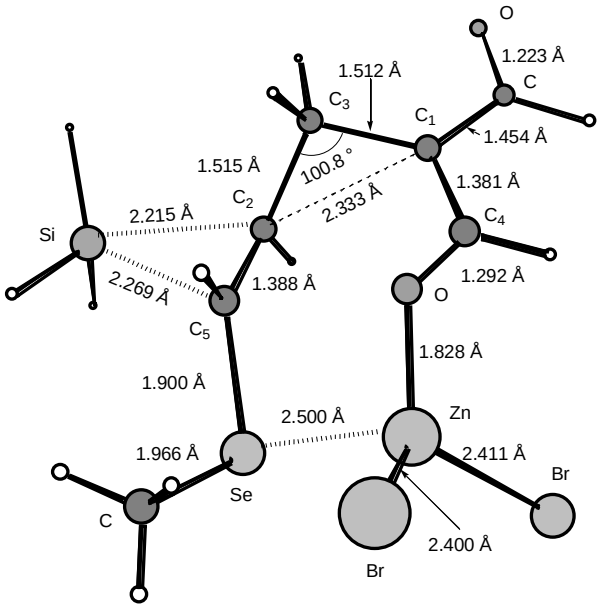


$\nu^{\ddagger}$ = 241.3 icm^{-1}

Figure 11S. An addition process through synclinal orientation. Energy barrier ΔE is relative to that of reactants complex **39** (in Figure 10S).

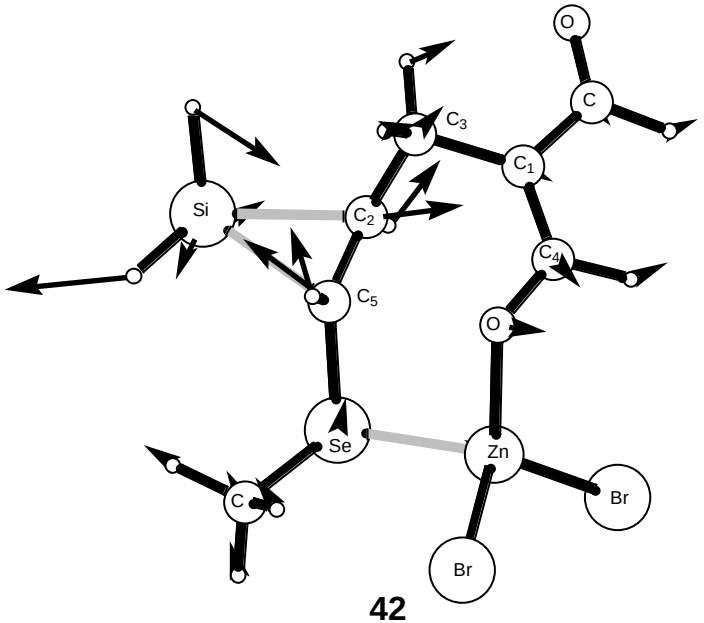
41

zwitterion, Se-Zn coordinated
[-4.2 kcal•mol^{-1}]



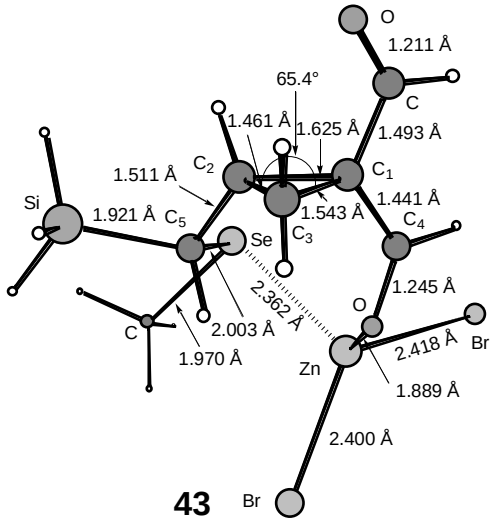
42

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



42

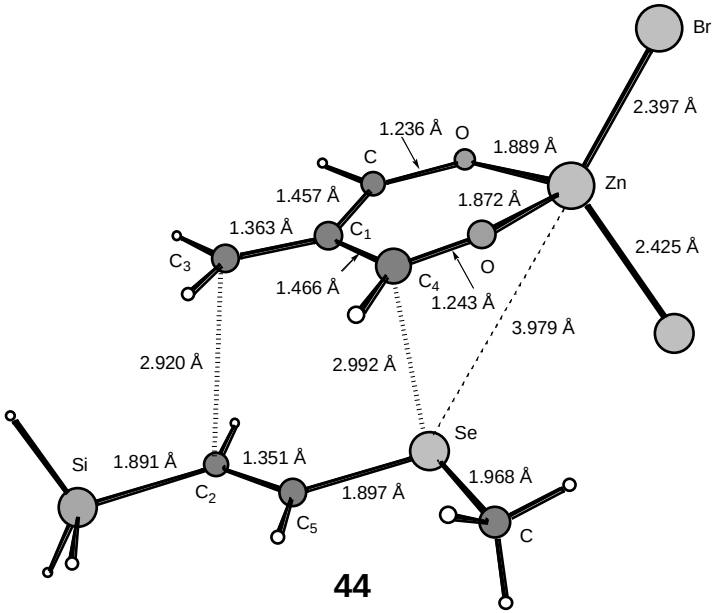
$\nu^{\ddagger}$ = 291.0 icm^{-1}



43

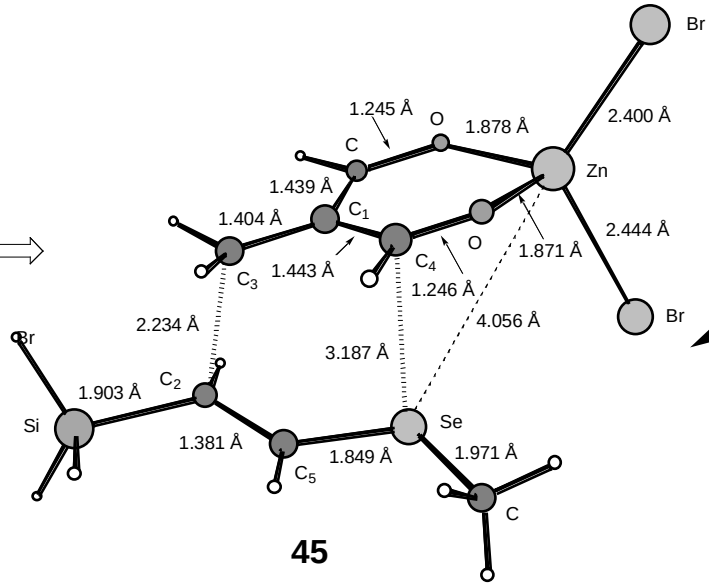
cyclopropane-$ZnBr_2$
[-9.2 kcal•mol^{-1}]

Figure 12S. The cyclopropane-ring forming step with the Se---Zn coordination and silicon C2 → C5 shift, **41**(in Figure 11S)→**42**→**43**.



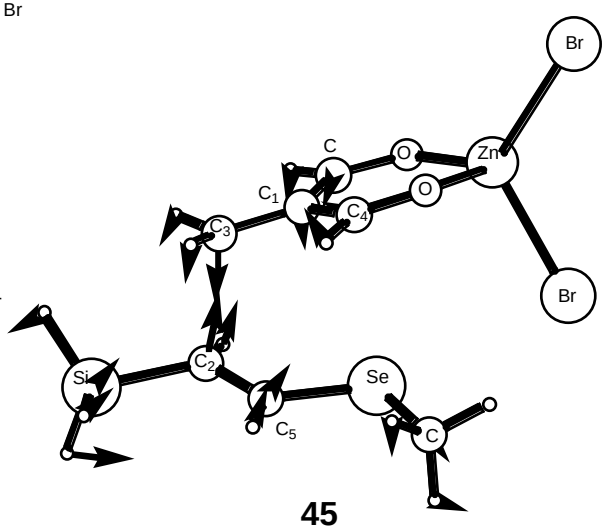
44

reactants complex (chair)
[-9.0 kcal•mol^{-1}]



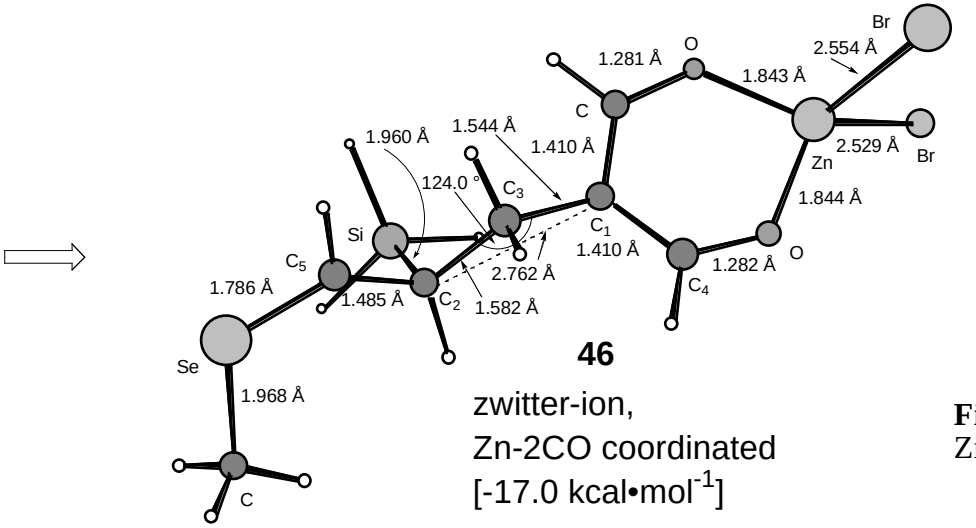
45

synclinal addition TS
[-3.9 kcal•mol^{-1}]
ΔE = +5.1 kcal/mol



45

$\nu^{\ddagger}$ = 207.1 icm^{-1}



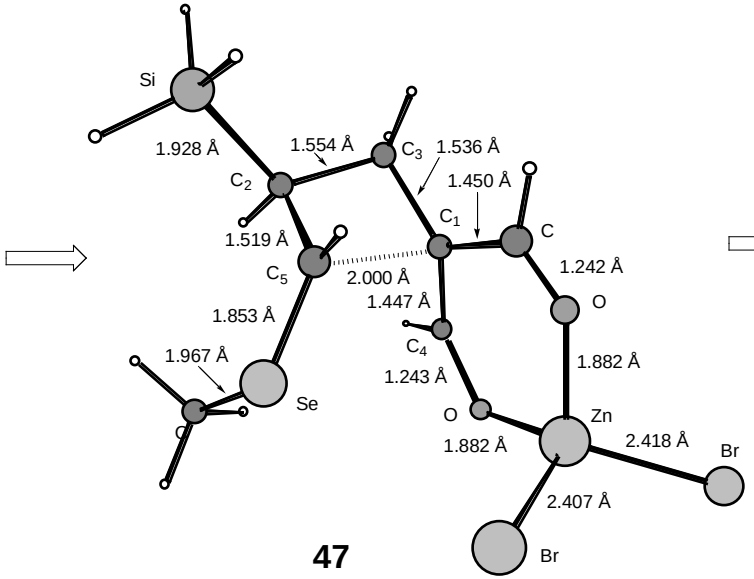
46

zwitter-ion,
Zn-2CO coordinated
[-17.0 kcal•mol^{-1}]

Figure 13S. Synclinal addition process of reactants **6** and **30** with the Zn-2(O=C) bidentate form retained.

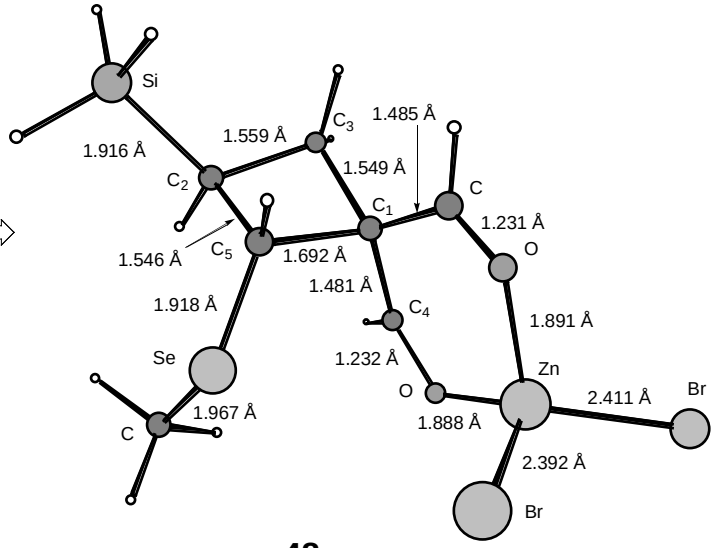
46

zwitter-ion,
Zn-2CO coordinated
[-17.0 kcal•mol^{-1}]



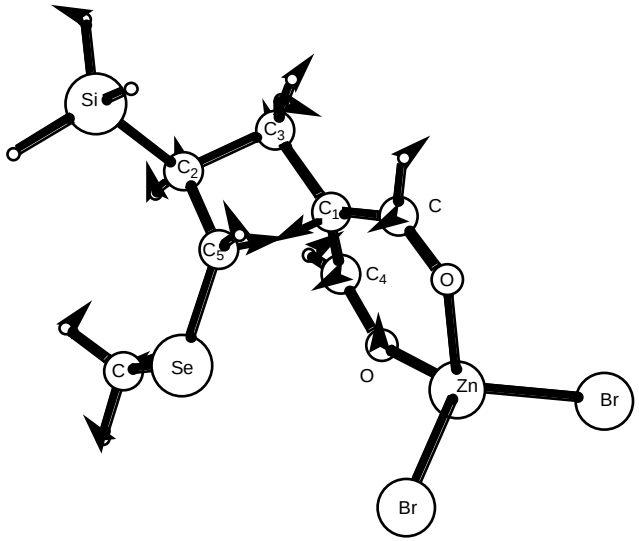
47

Cyclobutane ring closure TS
[+0.1 kcal•mol^{-1}]
ΔE = +17.1 kcal/mol



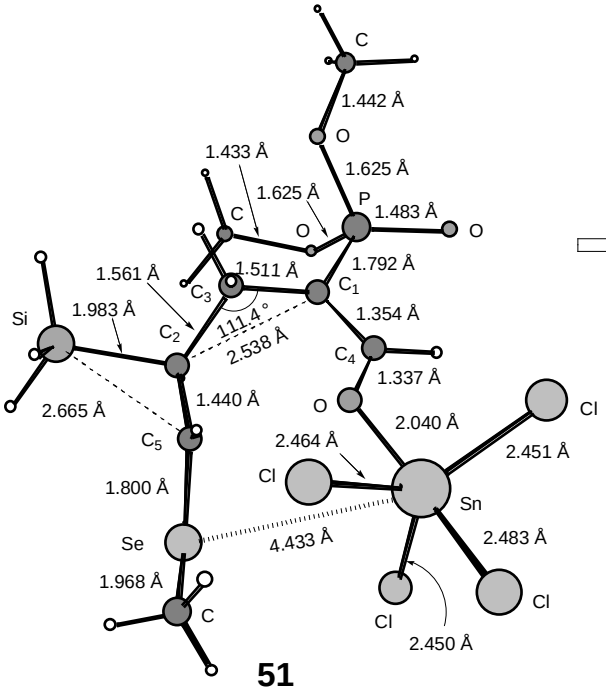
48

cyclobutane-$ZnBr_2$
[+1.0 kcal•mol^{-1}]



$\nu^{\ddagger}$ = 282.4 icm^{-1}

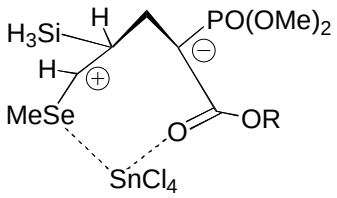
Figure 14S. A cyclobutane formation process starting from the zwitterionic intermediate **46** (shown in Figure 13S).

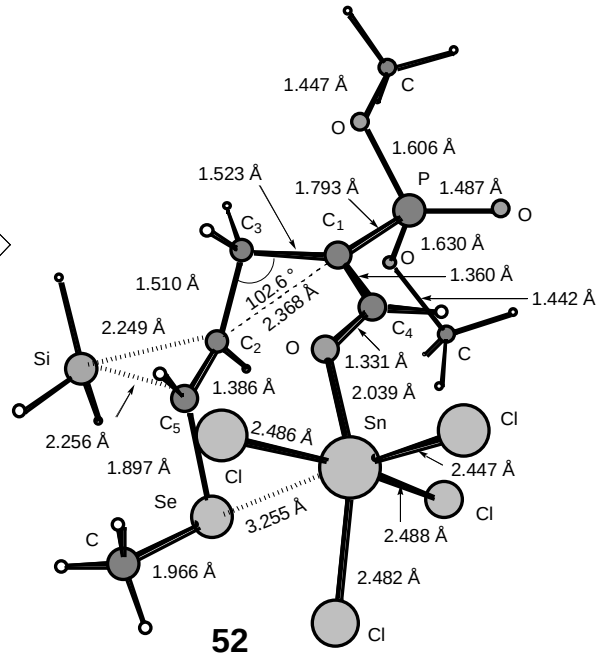


51

zwitter-ion

[0 kcal•mol^{-1}]



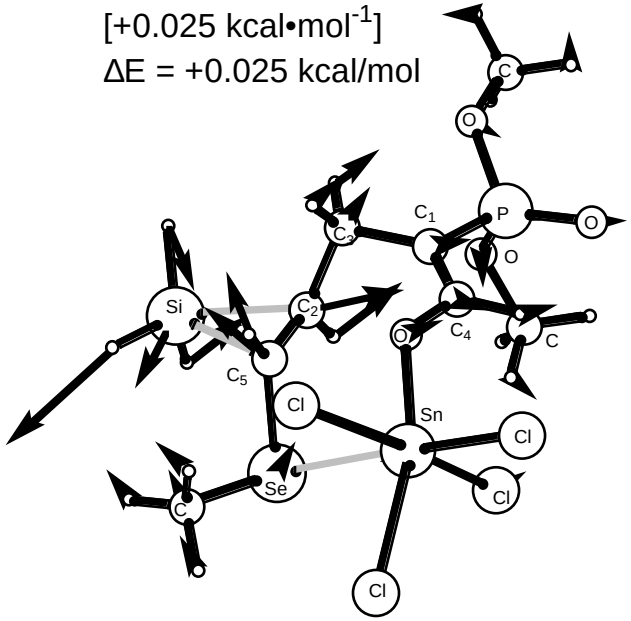


52

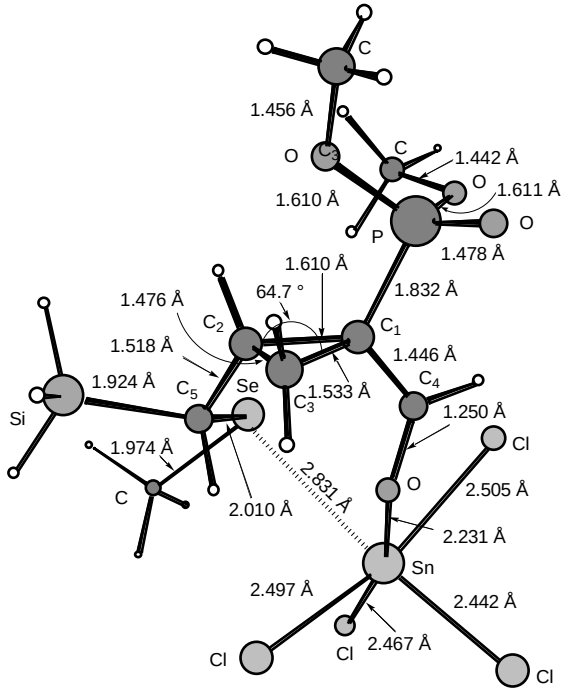
Si-shift and ring closure TS

[+0.025 kcal•mol^{-1}]

ΔE = +0.025 kcal/mol



$\nu^{\ddagger}$ = 197.3 icm^{-1}



53

cyclopropane-$SnCl_4$

[-9.7 kcal•mol^{-1}]

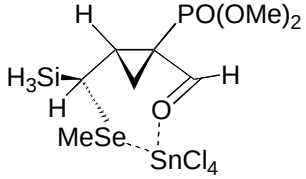
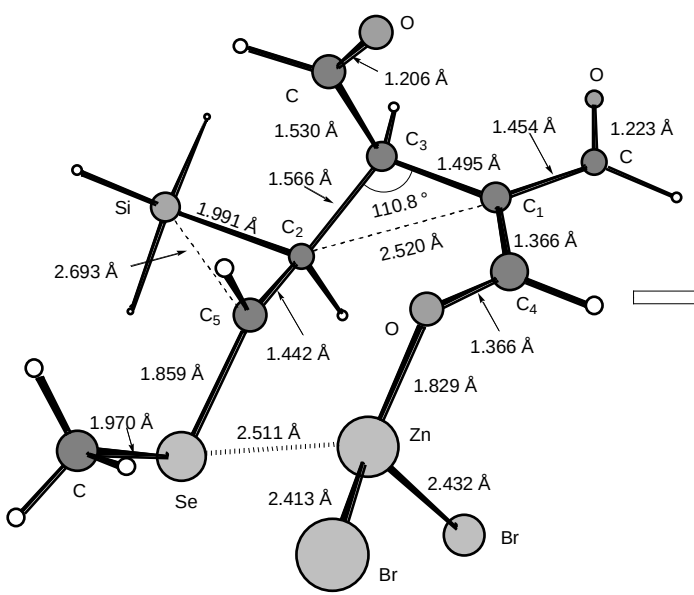
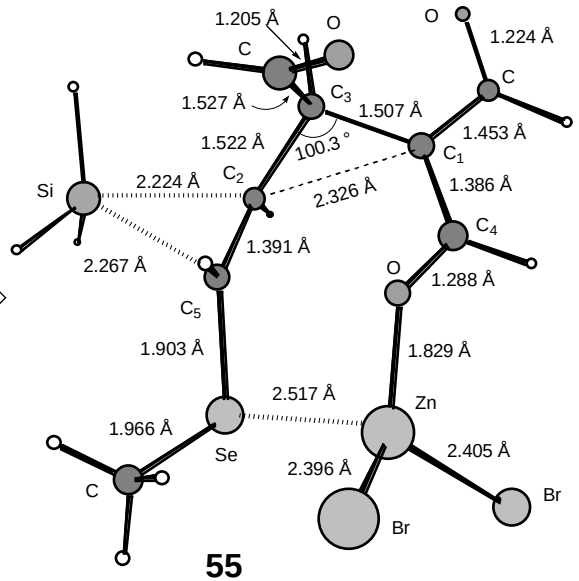


Figure 15S. The cyclopropane-ring forming step for a model reaction of **6** and phosphonoacrylate **49** with the through-space Se---Sn attraction and silicon shift. Energies in square brackets are relative to the intermediate **51**.



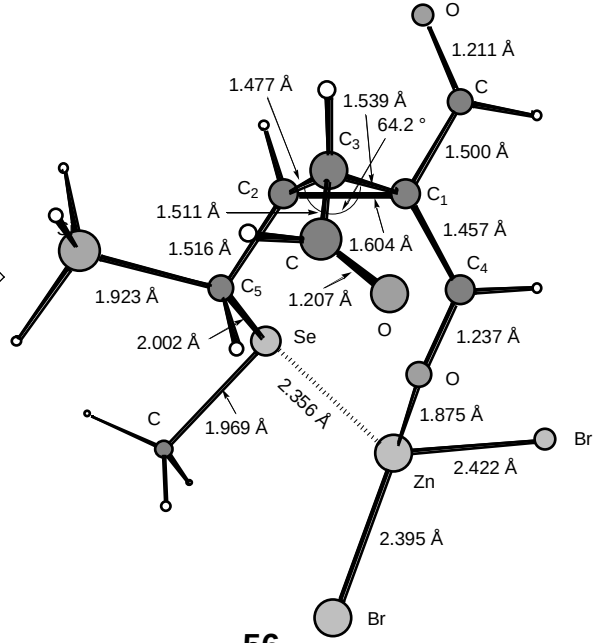
54

zwitter-ion, Se-Zn coordinated
[0 kcal•mol^{-1}]



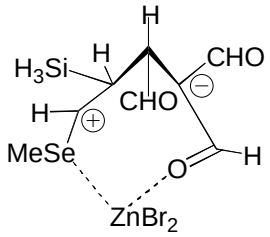
55

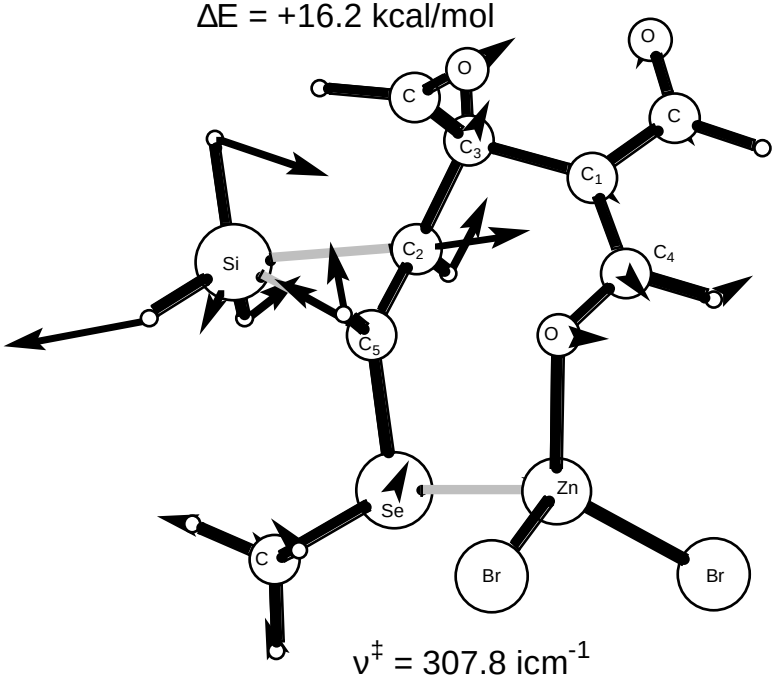
Si-shift and ring closure TS
[+16.2 kcal•mol^{-1}]
ΔE = +16.2 kcal/mol



56

cyclopropane-$ZnBr_2$
[-1.3 kcal•mol^{-1}]





$\nu^{\ddagger}$ = 307.8 icm^{-1}

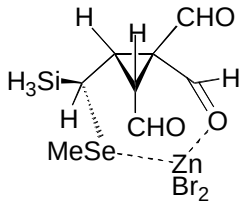


Figure 16S. The cyclopropane-ring forming step for a model reaction of **6** and β-carbonyl-substituted methylenemalonate **50** with the Se---Zn coordination and silicon shift. Energies in square brackets are relative to the intermediate **54**.