

[4 + 2] Dimerization and Cycloaddition Reactions of α,β -Unsaturated Selenoaldehydes and Selenoketones

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The reactions of α,β -unsaturated aldehydes and ketones with bis(dimethylaluminum) selenide, $(\text{Me}_2\text{-Al})_2\text{Se}$, yield the corresponding α,β -unsaturated selenoaldehydes and selenoketones. They are too unstable to be isolated in the monomeric form, but they undergo regioselective [4 + 2] dimerization via a “head-to-head” oriented transition state to afford diselenin derivatives (trans and cis isomers). Theoretical calculations at the density functional theory level show that this selectivity occurs because the “head-to-head” dimerization is thermodynamically favored over the “head-to-tail” by about 14 kcal/mol. Both dimerization reactions have low energy barriers: 1.5 and 2.8 kcal/mol for the former and 0.9 and 1.3 kcal/mol for the latter. In the presence of norbornadiene, these compounds function as 4π heterodienes ($\text{C}=\text{C}-\text{C}=\text{Se}$) to give the respective cycloadduct products. On the other hand, they act as 2π dienophiles ($\text{C}=\text{Se}$) in the reactions with cyclopentadiene except for selenoacrolein which serves as a 4π diene and only one $\text{C}=\text{C}$ bond (2π) in cyclopentadiene is involved in the reaction. Theoretical calculations have been carried out in order to better understand these observations.

Introduction

In recent years, our knowledge about the chemistry of highly reactive carbon–sulfur, carbon–selenium, and carbon–tellurium doubly bonded compounds has expanded greatly.¹ It is well recognized that these carbon–chalcogen double bonds ($\text{C}=\text{E}$, E is S, Se, or Te) serve as 2π dienophiles in the Diels–Alder reaction to afford the corresponding chalcogen-containing heterocycles.^{1,2} When conjugated with another double bond, the $\text{C}=\text{E}$ can be expected to comprise a component of the 4π heterodiene system. In contrast to the extensive studies of hetero-

dienes bearing N, O, or S atoms,³ much less is known about the selenium analogues.⁴ In a preliminary communication,^{4d} we reported that α,β -unsaturated selenoaldehydes and selenoketones selectively underwent “head-to-head” [4 + 2] dimerization to afford six-membered cyclic diselenides. They also functioned as 4π heterodienes ($\text{C}=\text{C}-\text{C}=\text{Se}$) in the Diels–Alder reaction with norbornadiene or as 2π dienophiles ($\text{C}=\text{Se}$) when reacting with cyclopentadiene. In the present work, we have further investigated experimentally and theoretically these reactions in order to better understand the mechanisms which lead to the observed regio- and stereo-selectivity.

Results and Discussion

We have reported that bis(dimethylaluminum) selenide (**2**), prepared by the Sn–Al trans-metalation between $(\text{Bu}_3\text{Sn})_2\text{Se}$ (**1**) and 2 equiv of a Me_3Al /toluene solution, effectively converts carbonyl ($\text{C}=\text{O}$) compounds to sele-

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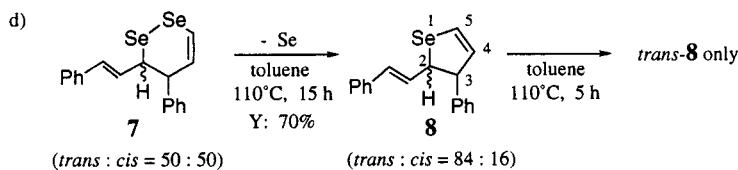
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Table 1. [4 + 2] Dimerization of α,β -Unsaturated Selenoaldehydes and Selenoketones

entry	R	Se	R'	product		
				structure	yield (%) ^a	trans : cis ^b
1					X = O 91	85 : 15
2					S 80	82 : 18
3					X = O 82	85 : 15
4	Br				S 71	80 : 20
5 ^{c,d}	Ph				53	50 : 50
6	Ph		R'		R' = Me 56 ^e	57 : 43
7	Ph		R'		Ph 49 ^e	62 : 38

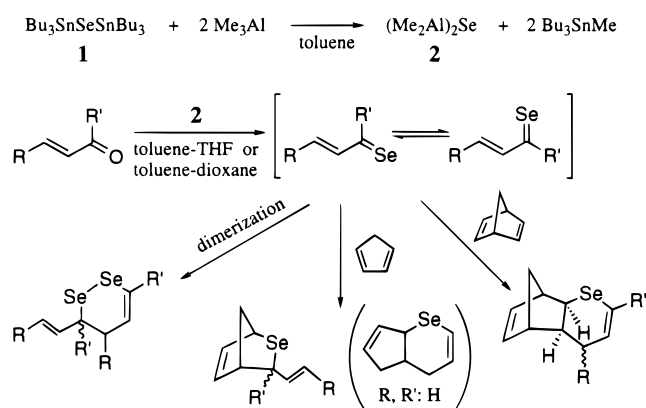
a) Isolated yields. b) Determined by ¹H NMR. c) Reaction temperature: 40–50°C.



e) Impurity included.

nocarbonyls (C=Se).⁵ α,β -Unsaturated selenoaldehydes and selenoketones are prepared in situ by the reaction of the corresponding α,β -unsaturated carbonyl compounds with **2** and simultaneously subjected to [4 + 2] dimerization or cycloaddition reactions with norbornadiene or cyclopentadiene (Scheme 1).

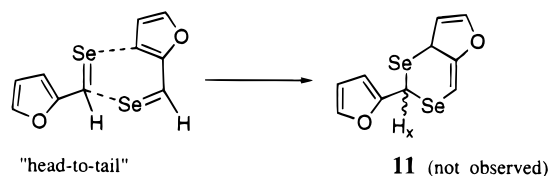
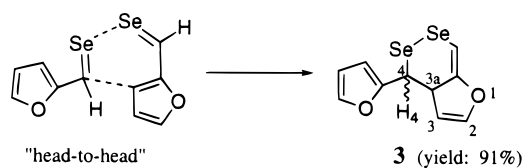
[4+2] Dimerization of α,β -Unsaturated Selenoaldehydes and Selenoketones. α,β -Unsaturated selenoaldehydes and selenoketones undergo regioselective [4 + 2] dimerization via the transition state with a “head-to-head” orientation to afford the dimers. The results are summarized in Table 1. The structures of all products (**3–10**) were characterized by NMR (¹H, ¹³C), mass spectrometry, and elemental analysis. The reaction of 2-furaldehyde with (Me₂Al)₂Se (**2**) at 65 °C for 4 h in a toluene–THF solution resulted in the formation of the dimer (**3**) of 2-selenoformylfuran (entry 1). This dimer was isolated in 91% yield as a mixture of trans and cis isomers. In the ¹H NMR spectrum, two doublets at δ 4.52 ($J_{H4-H3a} = 10.3$ Hz) and δ 5.81 (6.8 Hz) were assigned to the H₄ protons of trans and cis isomers, respectively. The ratio of trans:cis is 85:15 as calculated from ¹H NMR

Scheme 1

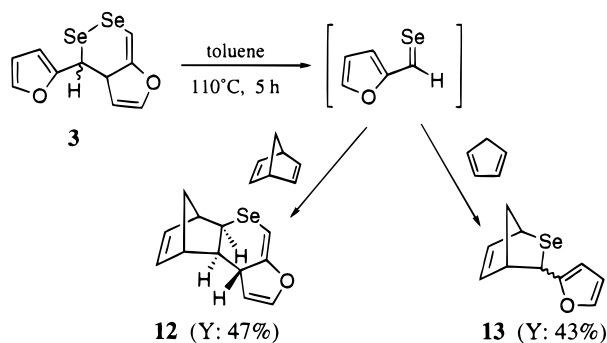
integrations. Another regioisomeric dimer (**11**) was not observed (Scheme 2), whose proton H_x should appear in the ¹H NMR spectrum without such large coupling constants due to the absence of protons on the neighboring carbon atoms. Similarly, 2-thiophenecarboxaldehyde and other related aldehydes undergo reaction with **2** to give the corresponding dimers in good yields (entries 2–4). The bromo-substituted compounds (**5**, **6**) are somewhat unstable. They decompose during storage. Using cinnamaldehyde as the starting material, a mixture of dimer (**7**) of selenocinnamaldehyde and a five-membered cyclic selenide (**8**) was isolated. At lower temperatures (40–50 °C), the reaction produced pure dimer **7** which

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Scheme 2



Scheme 3

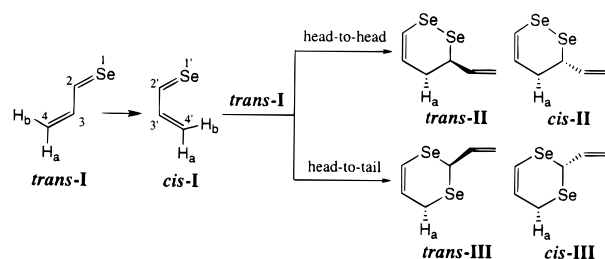


was characterized by satisfactory NMR (^1H , ^{13}C) and mass spectra. However, this dimer decomposed quickly following the NMR measurement to give the mixture of **7** and **8**. Dimer **7** was completely converted to **8** when heated at 110 °C for 15 h in toluene. After heating, the ratio of *trans*:*cis* changed from 50:50 in **7** to 84:16 in **8**. ^1H NMR measurements showed that, when heated for additional 5 h, *cis*-**8** was completely transformed into *trans*-**8**. This *cis* \rightarrow *trans* transformation can be explained in that *cis*-**8** is thermodynamically unstable due to the steric hindrance between the phenyl and styryl groups so that it converts to the stable *trans* isomer during heating. Compound **8** (*trans* isomer only) was also prepared by Takigawa and co-workers using the reaction of cinnamaldehyde with 9-BBN-selenide.⁶ In their procedure, however, it was not possible to isolate dimer **7** (the precursor of **8**) or to observe the transformation from *cis*-**8** to *trans*-**8**. In the cases of 4-phenyl-3-buten-2-selone and selenochalcon (entries 6 and 7), only the five-membered ring compounds (**9** and **10**) together with some impurities were obtained. These results suggest that the dimers of selenocinnamoyl derivatives are more unstable than those of selenoformylfuran and selenoformylthiophene.

In addition, as shown in Scheme 3, heating the mixture of dimer **3** and excess norbornadiene gave the Diels-Alder adduct (**12**), in which 2-selenoformylfuran acted as a heterodiene ($\text{C}=\text{C}-\text{C}=\text{Se}$). With the use of cyclopentadiene instead of norbornadiene, the Diels-Alder adduct (**13**),⁷ in which 2-selenoformylfuran acted as a dienophile ($\text{C}=\text{Se}$), was formed. This shows that a selenoaldehyde (unstable) can be regenerated by heating its stable dimer.

In previous work,^{4g-1} Krafft and Meinke showed that in the presence of cyclopentadiene the selenoaldehydes

Scheme 4



readily undergo the Diels-Alder reaction to form the bicyclic adducts at 0 °C. Thus, the division of dimer **3** is the rate-determining step in forming **12** and **13**. Together these results indicate that the dimerization reaction of α,β -unsaturated selenoaldehydes should be a low-temperature process and conversion of carbonyl compounds to selenocarbonyl is the rate-determining step from α,β -unsaturated carbonyl compounds through α,β -unsaturated selenoaldehydes to the corresponding Diels-Alder adducts.

Calculations. To elucidate the regio- and stereoselectivity of [4 + 2] dimerization of α,β -unsaturated selenoaldehydes and selenoketones, theoretical calculations were performed on the model compound, selenoacrolein (**I**, $\text{CH}_2=\text{CH}-\text{CH}=\text{Se}$). Density functional theory (DFT),⁸ specifically the Becke three-parameter hybrid exchange functional⁹ and the Lee-Yang-Parr correlation functional (B3LYP),¹⁰ has been used to carry out geometric optimizations of the reactants, transition states, and products along the possible reaction paths as shown in Scheme 4. It can be seen that *trans*-I initially rotates through the transition state (**TS_I**, see Figure 1) to *cis*-I and then they dimerize via "head-to-head" and "head-to-tail" orientations to give four isomeric dimers: *trans*-II, *cis*-II, *trans*-III, and *cis*-III.

The DFT calculated stationary points and their energy profiles are shown in Figure 1. DFT relative energies of the reactions are summarized in Table 2.

The rotation from the *trans*-selenoacrolein to the *cis* form is endothermic by 3.2 kcal/mol with a barrier of 10.7 kcal/mol. The rotational transition state **TS_I** has a twist of 94.9° with respect to planar *trans*-I or *cis*-I. Since both the $\text{Se}=\text{C}$ and $\text{C}=\text{C}$ orbitals of *trans*-I can act as a 2π dienophile to react with *cis*-I, it is necessary to investigate its regioselectivity. The natural bond orbital (NBO) π electron density and π orbital energy of *trans*-I and *cis*-I are illustrated in Table 3.¹¹ For both *trans*-I and *cis*-I, the $\pi_{\text{Se1-C2}}$ orbital has a larger π electron density than the $\pi_{\text{C3-C4}}$ orbital. In addition, the calculations show that the $\pi_{\text{Se1-C2}}$ orbital of *trans*-I is more high-lying than the $\pi_{\text{C3-C4}}$ orbital. The higher electron density and smaller energy gap between the occupied $\pi_{\text{Se1-C2}}$ orbital of *trans*-I and the unoccupied π orbital of *cis*-I should lead to a lower activation barrier and a stronger stabilizing interaction for the [4 + 2] Diels-Alder reaction of *trans*-I and *cis*-I. Thus, the $\text{Se}=\text{C}$ orbital of *trans*-I is favored to act as the 2π dienophile over the $\text{C}=\text{C}$ orbital in the Diels-

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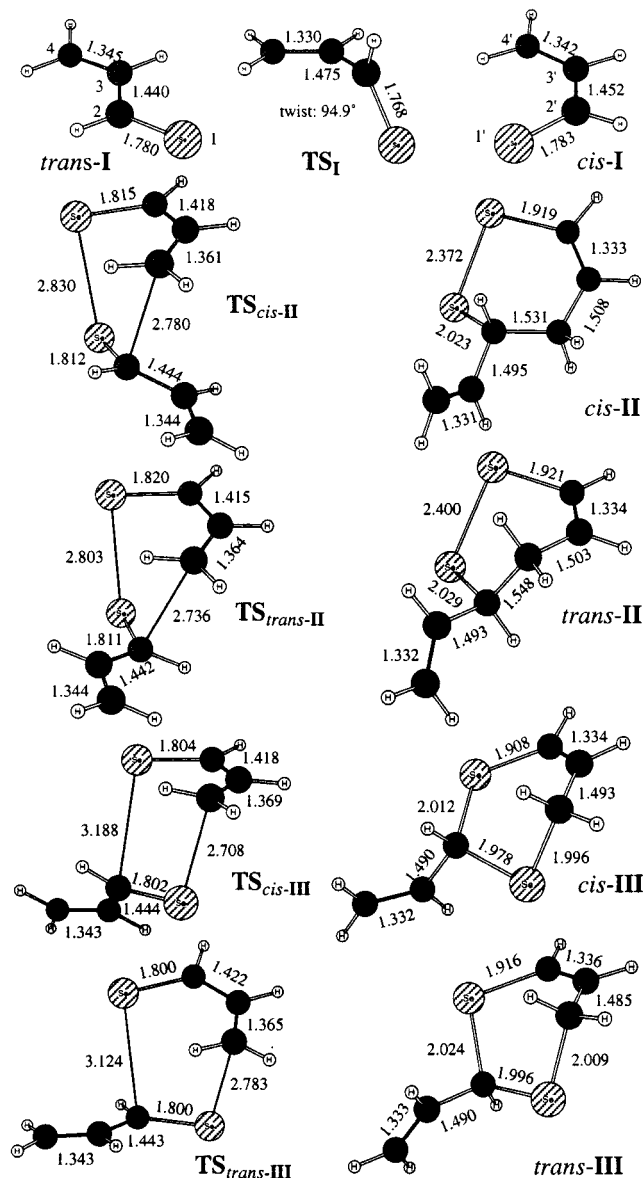


Figure 1. B3LYP optimized stationary points along the reaction pathways of [4 + 2] dimerization of selenoacrolein (Scheme 4) through intermediates (*trans-I*, *cis-I*) and transition states (**TS_I**, **TS_{cis-II}**, **TS_{trans-II}**, **TS_{cis-III}**, and **TS_{trans-III}**) to products (*cis-II*, *trans-II*, *cis-III*, and *trans-III*).

Table 2. Relative Energies (ΔE) of [4 + 2] Dimerization of Selenoacrolein Calculated Using B3LYP

structure	ΔE (kcal/mol) ^a	structure	ΔE (kcal/mol) ^a
<i>trans-I</i> + TS_I	10.66	<i>trans-I</i> + <i>cis-I</i>	3.16
TS_{cis-II}	6.04	<i>cis-II</i>	-34.60
TS_{trans-II}	4.70	<i>trans-II</i>	-34.26
TS_{cis-III}	4.47	<i>cis-III</i>	-20.68
TS_{trans-III}	4.07	<i>trans-III</i>	-20.46

^a All energies are relative to *trans-I* + *trans-I* (0.00 kcal/mol), and the BSSE correction is included.

Alder reaction with a 4 π diene. In the following discussion, those cases, where the C=C orbital of *trans-I* acts as the 2 π dienophile, are neglected.

The B3LYP optimized geometries show that, for both the "head-to-head" and "head-to-tail" type dimeric products, *cis-II* and *cis-III* prefer the "half-chair" (puckered) conformation, while *trans-II* and *trans-III* favor the "boat" conformation (Figure 1). The Se₁-Se₁' distances

Table 3. NBO π Electron Density and π Orbital Energy of Selenoacrolein (*trans-I* and *cis-I*)

	π Electron Density (e)			
	Se1	C2	C3	C4
<i>trans-I</i>	1.092	0.839	0.953	0.882
<i>cis-I</i>	1.105	0.842	0.997	0.847
	π Orbital Energy (au)			
	π Se1-C2	π C3-C4	π^* Se1-C2	π^* C3-C4
<i>trans-I</i>	-0.28966	-0.29544	-0.08205	0.01224
<i>cis-I</i>	-0.28880	-0.29224	-0.08079	0.01695

in "head-to-head" dimers *trans-II* and *cis-II* are shortened by 17–19% as compared to the values in transition states **TS_{trans-II}** and **TS_{cis-II}**. This is much smaller than the C₂-C₄' distance change (77–82%). Clearly, the Se-Se bond forms in the early stage of the "head-to-head" dimerization, while the C-C bond forms in the later stage. Also, the Se₁-C₄' distances in the "head-to-tail" dimers *trans-III* and *cis-III* are shortened by 36–39% as compared to the values in transition states **TS_{trans-III}** and **TS_{cis-III}**, while the Se₁-C₂ distances are shortened by 54–58%. Thus, the formations of the two new bonds in the dimerization reactions are not completely synchronous.

As shown in Figure 2, the "head-to-head" dimerization reactions between *trans-I* and *cis-I*, which give dimers *trans-II* and *cis-II* through transition states **TS_{trans-II}** and **TS_{cis-II}**, are exothermic by 31.1 and 31.4 kcal/mol with the barriers of 1.5 and 2.8 kcal/mol, respectively. The formations of "head-to-tail" type dimers *trans-III* and *cis-III*, through the transition states **TS_{trans-III}** and **TS_{cis-III}**, are exothermic by 17.3 and 17.5 kcal/mol with the barriers of 0.9 and 1.3 kcal/mol, respectively. The "head-to-head" dimerization is thermodynamically favored over the "head-to-tail" dimerization because the former is more exothermic by about 14 kcal/mol; but both reactions have small barriers. These results suggest that the [4 + 2] dimerization of α,β -unsaturated selenoaldehydes and selenoketones should be a thermodynamically controlled process to give "head-to-head" oriented dimers selectively. This is consistent with the experimental observations that the "head-to-tail" type dimers have never been obtained despite their low kinetic barriers. On the other hand, the transition state **TS_{cis-II}** is the most sensitive to the steric properties of the dienes. The sterically hindered transition state effect leads to the *trans* product (*trans-II*) to be favored over the *cis* product (*cis-II*).

Cycloaddition Reactions of α,β -Unsaturated Selenoaldehydes and Selenoketones with Norbornadiene or Cyclopentadiene. The results obtained in the dimerization of α,β -unsaturated selenoaldehydes and selenoketones prompted us to investigate their reactions with norbornadiene (a dienophile) and cyclopentadiene (an enophile). In the presence of excess norbornadiene, the reaction of 2-furaldehyde with (Me₂Al)₂Se (**2**) at 100 °C gave the Diels-Alder adduct (**12**) of 2-selenoformylfuran and norbornadiene as the sole isomeric product in 45% yield (Table 4, entry 1). Also, in the cases of 2-selenoformylthiophene and 2-selenoacetylfuran or 2-selenoacetylthiophene, the cycloadducts (**14**, **17**, and **18**) were obtained in moderate yields (entries 2, 5, and 6). When cinnamoyl derivatives were used as the starting material, the yields of the corresponding cycloadducts were much lower; the five-membered ring compounds were obtained as the major product (entries 7–9). The

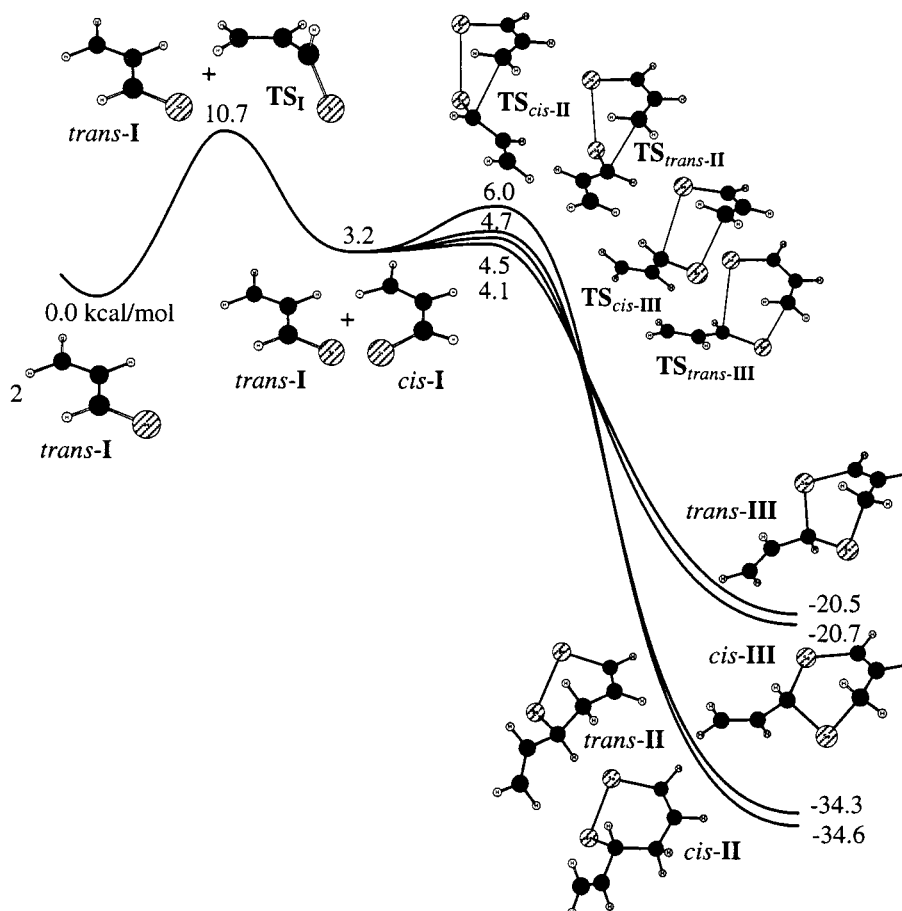


Figure 2. B3LYP energy profiles along the reaction pathways shown in Scheme 4.

structures of all compounds were determined by NMR, mass spectrometry, and elemental analysis.

When **12** or **14** was treated with aqueous HCl (pH = 1) or the original reaction mixture was quenched with aqueous HCl, the re-aromatized compounds **15** and **16** were obtained (entries 3 and 4 and Scheme 5).

The compounds obtained before and after re-aromatization are easily distinguished by their NMR spectra. For example, in the ^1H NMR spectrum of **12**, the large coupling constant ($J = 10.1$ Hz) between protons H_9 (δ 3.20) and H_{10} (δ 1.71) suggests they are in the trans relationship, and the long-distance couplings of $\text{H}_2 - \text{H}_{14b}$ ($J = 1.9$ Hz) and $\text{H}_{10} - \text{H}_{14b}$ ($J = 1.4$ Hz) indicate that both H_2 and H_{10} are in the "W" form with H_{14b} . Therefore, this compound (**12**) has the exo configuration. In its ^{13}C NMR spectrum, the bridge carbon (C_{14}) resonated at a higher field (δ 40.2) than the carbon (δ 48.8) in the same position of norbornene due to the steric compression shift.¹² This also supports the exo configuration. For the re-aromatized compound **15**, in the ^1H NMR spectrum, protons H_7 (δ 7.24) and H_8 (δ 6.30) appeared as doublets with a small coupling constant ($J = 1.9$ Hz) due to the disappearance of proton H_9 . Also, two doublets at δ 3.67 and 3.56 with a large coupling of $J = 14.1$ Hz were observed; they arise from the methylene protons (CH_2) adjacent to the selenium atom. In the ^{13}C NMR spectrum, C_4 appeared upfield (δ 11.1) due to the heavy atom effect of selenium.¹³ In addition, the chemical shift of proton

H_{14a} changed from δ 2.41 (in **12**) to a higher field at δ 1.42–1.47 (in **15**) since the double bond between C_4 and C_5 moved to C_5 and C_9 after re-aromatization. Also, this is because proton H_{14a} in **15** is shielded by the furan ring. Proton H_{10} resonances at δ 2.79 in **15**, downshifted from δ 1.71 in **12**, due to the formation of the furan ring.

As a representative example, the structure of compound **14** (a yellow solid) was also determined by single-crystal X-ray diffraction.¹⁴ The crystal structure is shown in Figure 3. This confirmed the exo configuration and trans relationship as established from proton and carbon-13 NMR spectra.

On the other hand, when cyclopentadiene was used in place of norbornadiene, 2-selenoformylfuran and 2-selenoformylthiophene behaved as 2π dienophiles ($\text{C}=\text{Se}$) to give their Diels–Alder adducts (**13** and **22**) with cyclopentadiene in high yields with low endo selectivity (entries 10 and 11). However, in the reaction with selenoacrolein, cyclopentadiene (one of the most reactive dienes) functioned only as a 2π dienophile to afford compound **23** as the sole product (entry 12). Formation of the other regioisomer **24** was not observed. The

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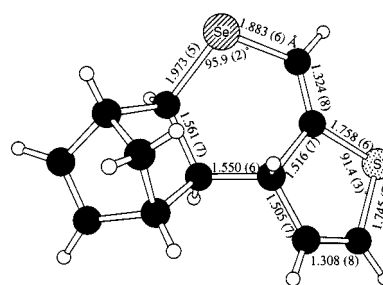
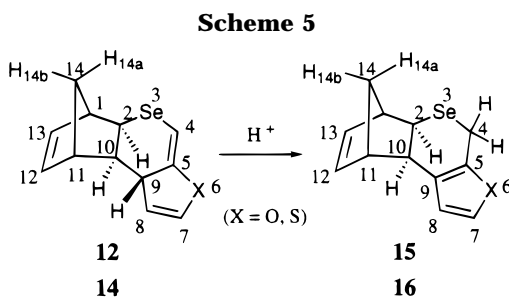
(14) Crystal data for **14**: $\text{C}_{12}\text{H}_{12}\text{SSe}$, MW = 267.25, a yellow plate, monoclinic, space group $P2_1/n$, $a = 7.0649$ (14) Å, $b = 17.227$ (3) Å, $c = 9.546$ (2) Å, $\beta = 110.72$ (3)°, $V = 1086.6$ (4) Å³, $Z = 4$, D_{calc} = 1.634 g/cm³, $R_1 [I > 2\theta(I)] = 0.0412$, $wR_2 [I > 2\theta(I)] = 0.1209$, R_1 (all data) = 0.0713, wR_2 (all data) = 0.1506. Preliminary examination and data collection were performed on a Siemens P4 single-crystal diffractometer (oriented graphite monochromator; Mo $K\alpha$ radiation, wavelength 0.71073 Å) at 297 (2) K. The structure was solved by direct methods¹⁵ and refined by full-matrix least-squares methods.¹⁶

(12) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: 1987; p 195.

Table 4. Cycloaddition Reaction of α,β -Unsaturated Selenoaldehydes and Selenoketones with Norbornadiene or Cyclopentadiene

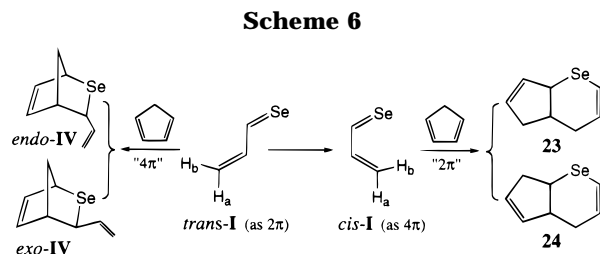
entry		trapping agent	adduct	
			structure	yield (%) ^a
1				45
2				51
3 ^b				48
4 ^b				44
5				52
6				56
7				18 (85 : 15) ^c
8 ^d				27 (82 : 18) ^c
9 ^d				34 (85 : 15) ^c
10				91 (57 : 43) ^e
11				91 (67 : 33) ^e
12 ^f				

^a Isolated yields. ^b The reaction mixture was quenched with aqueous HCl (pH = 1). ^c Trans:cis determined by ¹H NMR. ^d Some impurity included in compounds **9** and **10**. ^e endo:exo determined by ¹H NMR. ^f Acrolein diethyl acetal was used as the starting material.

**Figure 3.** Crystal structure of **14**.

structure of **23** was evaluated from NMR spectra. The assignment of protons and H–H coupling constants (*J*) were determined by the ¹H NMR decoupling experiment. Olefinic protons appear at δ 6.03–5.97 (m, 1H) and 5.95–5.88 (m, 3H). The doublet–triplet at a relatively lower field (δ 4.07, *J* = 6.10, 1.83 Hz) is assigned to proton H_{7a} in structure **23** due to the electronic effect of both selenium atom and C₆–C₇ double bond. For compound **24**, no protons except for olefinic ones should appear so far downfield.

Calculations. To better understand these results, we have investigated cycloaddition reactions of selenoacrolein with cyclopentadiene along different reaction paths (Scheme 6) using B3LYP calculations. On the left side of



Scheme 6, *trans-I* acts as a 2 π dienophile (C=Se) in reaction with cyclopentadiene (4 π) to afford their Diels–Alder products (*exo-IV* and *endo-IV*). Alternatively, *trans-I*

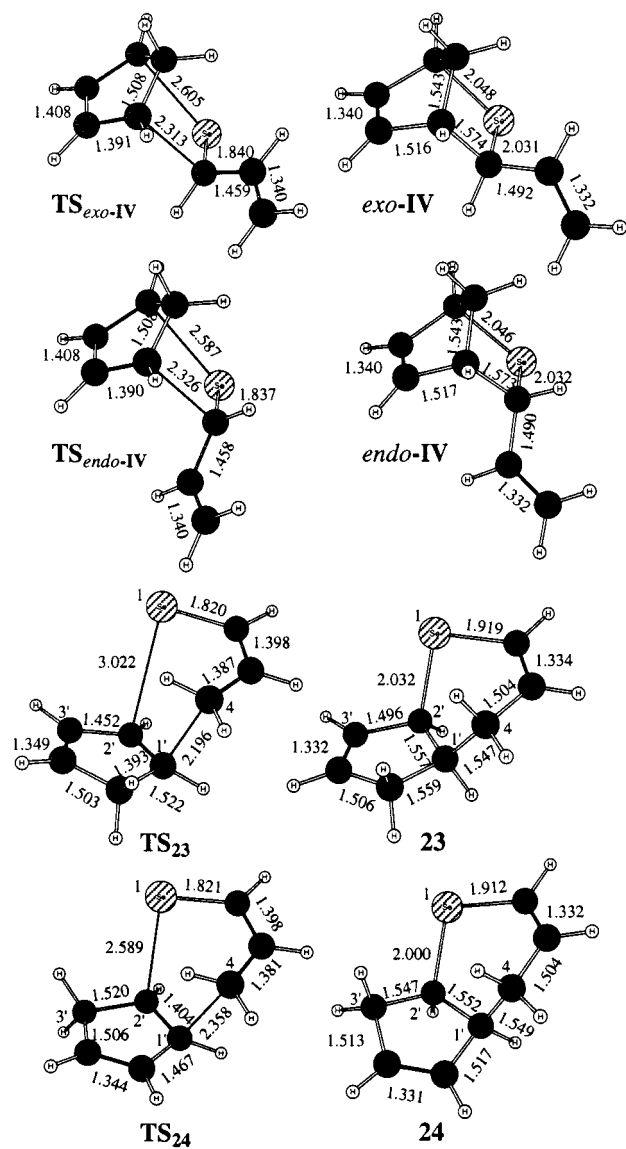


Figure 4. B3LYP optimized stationary points along the reaction pathways shown in Scheme 6: from selenoacrolein and cyclopentadiene to products *exo-IV* and *endo-IV* through transition states **TS_{exo-IV}** and **TS_{endo-IV}** or to **23** and **24** through **TS₂₃** and **TS₂₄**.

can rotate first to form *cis-I* and the latter reacts as a 4π diene with one C=C bond of cyclopentadiene to yield Diels–Alder type products (**23** and **24**), as shown on the right side of Scheme 6. **23** and **24** are regioisomers. The DFT calculated stationary points and the energy profiles are shown in Figures 4 and 5, respectively. DFT relative energies of the reactions are summarized in Table 5.

The B3LYP optimized geometries show that the products *exo-IV* and *endo-IV* have very similar geometrical features; also their transition states **TS_{exo-IV}** and **TS_{endo-IV}** display very small differences. As discussed in the dimerization section, in a similar manner, the formations of the new C–Se and C–C bonds in the cycloaddition reactions through **TS_{exo-IV}** to *exo-IV* and **TS_{endo-IV}** to *endo-IV* are not completely synchronous. The Se–C distance changes (26–27%) are much smaller than that of the C–C distance (47–48%). Both reaction pathways to *exo-IV* and *endo-IV* showed similar energy profiles; they are exothermic by 16 kcal/mol with a barrier of 11 kcal/mol. The six-membered rings in **23** and **24** show “boat”

Table 5. Relative Energies (ΔE) of Selenoacrolein–Cyclopentadiene Cycloaddition Reaction Calculated Using B3LYP

structure	ΔE (kcal/mol) ^a	structure	ΔE (kcal/mol) ^a
TS_{exo-IV}	11.05	<i>exo-IV</i>	–15.84
TS_{endo-IV}	11.00	<i>endo-IV</i>	–15.96
CP^b + TS_I	10.66	CP^b + cis-I	3.16
TS₂₃	13.32	23	–24.10
TS₂₄	15.53	24	–23.67

^a All energies are relative to *trans-I* + cyclopentadiene (0.00 kcal/mol), and the BSSE correction is included. ^b CP stands for cyclopentadiene.

structural features and only differ in the site of the double bond in the five-membered rings. In comparison with *exo-IV* and *endo-IV*, the new Se–C and C–C bond distances in **23** and **24** are shorter by about 0.031 and 0.025 Å. Thus, the binding energy of **23** and **24** is larger by about 11 kcal/mol than that of *exo-V* and *endo-V*, where the Diels–Alder reaction leads to a larger geometrical distortion of the five-membered rings. Because of the large thermodynamic preference for the six-membered products, **23** and **24**, over *exo-V* and *endo-V*, the latter species are not seen. The large differences in the Se–C bond (Se₁–C_{2'} and Se₁–C_{1'}) distance (0.032 Å) and C₂–C₃ bond distance (0.021 Å) between **23** and **24** indicate that the C=C bond in the five-membered ring clearly influences other bond lengths of both compounds. The orbital analyses show that the charge density delocalization from the $\sigma_{\text{Se-C}}$ bonding orbital to the unoccupied $\pi^*_{\text{C-C}}$ orbital of the five-membered ring of **23** leads to a decrease in energy of the $\sigma_{\text{Se-C}}$ bond orbital (Figure 6).¹⁷ Since the $\sigma_{\text{C-C}}$ bond orbital of *cis-I* is lower-lying than the $\sigma_{\text{Se-C}}$ bond orbital, the interaction between the $\sigma_{\text{C-C}}$ bond orbital and the unoccupied $\pi^*_{\text{C-C}}$ orbital of the five-membered ring in **24** is weaker than that between $\sigma_{\text{Se-C}}$ and $\pi^*_{\text{C-C}}$ in **23**. This stabilizes structure **23** slightly over **24**. It is noteworthy that in the late stage of the cycloaddition the Se–C distance change (29%) from **TS₂₄** to **24** is much smaller than that from **TS₂₃** to **23** (49%). Clearly, the reaction pathway through **TS₂₃** to **23** has a very early transition state, which partially arises from the charge density delocalization of the forming $\sigma_{\text{Se-C}}$ bond orbital to the unoccupied $\pi^*_{\text{C-C}}$ orbital of the five-membered ring in **TS₂₃**. Overall, the early transition state **TS₂₃** leads to a lower barrier of 10.1 kcal/mol, which is smaller by 2.2 kcal/mol than that of **TS₂₄**. This means that the formation of **23** is kinetically favored over **24**. The calculations are in good agreement with the experimental results as only **23** has been obtained.

Conclusions

The [4 + 2] dimerization and cycloaddition reactions of α,β -unsaturated selenoaldehydes and selenoketones have been investigated experimentally and theoretically. These α,β -unsaturated selenocarbonyl compounds function as both 4π and 2π components in the “head-to-head” [4 + 2] dimerization to afford six-membered cyclic diselenides. In reactions with norbornadiene, they served

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(17) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

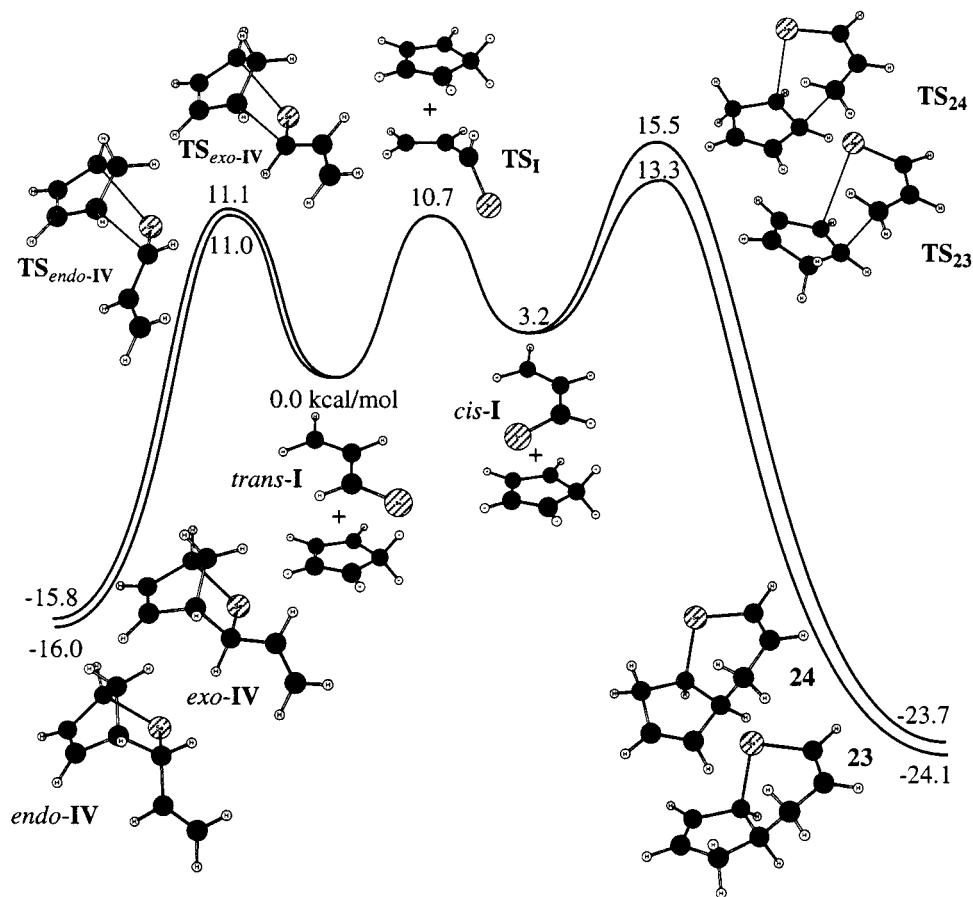


Figure 5. B3LYP energy profiles along the reaction pathways shown in Scheme 6.

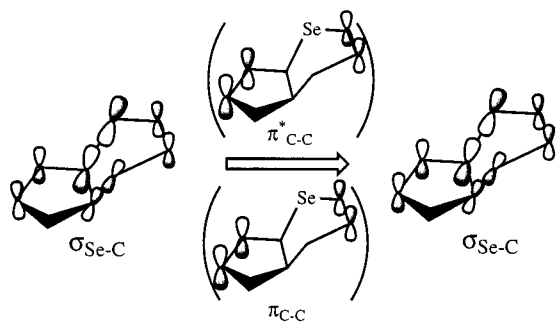


Figure 6. Generation of the orbital description of the $\sigma_{\text{Se-C}}$ bond of **23**.

as 4π dienes ($\text{C}=\text{C}-\text{C}=\text{Se}$) to give the Diels–Alder adducts. In reactions with cyclopentadiene, most of these compounds acted as 2π dienophiles ($\text{C}=\text{Se}$), as expected. However, selenoacrolein functioned only as a 4π diene in the reaction with cyclopentadiene. The calculations at the DFT level show that (1) the rate-determining step of the $[4 + 2]$ dimerization of α,β -unsaturated selenocarbonyl compounds is the rotation from the trans form to the cis form, (2) the experimentally obtained “head-to-head” dimeric products are much more thermodynamically stable than the unobserved “head-to-tail” type dimers, and (3) there is not much energy difference between trans and cis isomeric dimers (“head-to-head” type) in both transition state and ground state (product), so that mixtures of trans and cis isomers are obtained in all cases. The calculations also helped us to understand the formation of compound **23** in the reaction of sele-

noacrolein with cyclopentadiene from the views of relative energies and bond orbital interactions.

Experimental Section

General Considerations. Toluene, THF, and 1,4-dioxane were carefully refluxed over sodium or potassium metal and distilled under argon prior to use. Reactions were carried out under an atmosphere of dry argon. All laboratory reagents were purchased from the Aldrich Chemical Co. Selenium powder was provided by the Phelps Dodge Co. The ^1H and ^{13}C NMR spectra were recorded on 200 or 400 MHz FT-NMR spectrometers in CDCl_3 with TMS as the internal standard. The ^{77}Se NMR spectra were measured using a 400 MHz FT-NMR spectrometer (76.2 MHz for ^{77}Se) in CDCl_3 solution with Me_2Se as the external standard. Mass spectra were run in the EI or FAB mode. IR spectra were obtained on a JASCOA-202 spectrometer. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., and Canadian Microanalytical Service, Ltd. Bis(tributyltin) selenide (**1**), $(\text{Bu}_3\text{Sn})_2\text{Se}$, was prepared according to the previously reported procedures.^{5e}

Theoretical Details. All DFT calculations were performed using GAUSSIAN94 programs,¹⁸ at the Supercomputer Center and the Department of Chemistry of Texas A&M University

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on Silicon Graphics Power Challenge, Origin 2000, and the Cray J90 servers. The transition states (TS) were optimized using a quasi-Newton method,¹⁹ in which the final updated Hessian shows only one negative eigenvalue, and were characterized by one and only one imaginary frequency for every unique TS in a separate calculation.²⁰ The triple- ζ basis sets 6-311G with polarization functions (6-311G**) were used for selenium and carbon atoms,²¹ and the double- ζ basis set 6-31G was used for hydrogen atoms.²² The relative energies have been corrected for the basis-set superposition error (BSSE).²³ Since the geometries of our model systems are very similar, the zero-point vibrational energy (ZPVE) differences will be small. As a check of this assertion, we performed a ZPVE calculations for **23** and *endo-IV*, which are among the most geometrically different in this system, and found the ZPVE correction to the energy difference to be only +0.42 kcal/mol, which is small compared to their uncorrected $\Delta E = -8.14$ kcal/mol. Furthermore, the calculated enthalpy and free energy differences between **23** and *endo-IV*, -7.45 and -7.79 kcal/mol, show that both the temperature and entropic contributions to the energy are small and of opposite sign. Since our conclusions depend on large energy differences between stable species, we have not included these corrections in our discussion.

General Procedure for Dimerization of α,β -Unsaturated Selenoaldehydes and Selenoketones. Under a dry argon atmosphere, to a white suspension of $(\text{Me}_2\text{Al})_2\text{Se}$ (**2**) in toluene (10 mL), prepared in situ from 660 mg (1.0 mmol) of $(\text{Bu}_3\text{Sn})_2\text{Se}$ (**1**) and 1.1 mL (2.2 mmol) of Me_3Al (2 M in toluene) as described in our previous article,^{5e} was added THF (5 mL) followed by 1.3 mmol of a α,β -unsaturated aldehyde or ketone. The mixture was stirred at 65 °C for 4–5 h and then poured into ice–water (20 mL) and extracted with CH_2Cl_2 (30 mL \times 3). The organic extract was washed with brine (100 mL) and dried over MgSO_4 followed by filtration and evaporation. The residue was chromatographed through a silica gel (230–400 mesh) column with hexane and then hexane– CH_2Cl_2 (5:1) as the solvents. Evaporation of the eluate gave the dimer of the respective α,β -unsaturated selenoaldehyde or selenoketone as a mixture of trans and cis isomers (Table 1).

4-(2-Furyl)-3a,4-dihydro-1-oxa-5,6-diselena-indene 3: orange-red oil. ¹H NMR (CDCl_3 ; δ , ppm): trans 7.46 (dd, $J = 1.7, 0.7$ Hz, 1H), 6.80 (dd, $J = 2.7, 1.7$ Hz, 1H), 6.60 (dd, $J = 2.4, 1.2$ Hz, 1H), 6.37 (dd, $J = 3.2, 1.7$ Hz, 1H), 6.32 (brd, $J = 3.2$ Hz, 1H), 5.56 (ddd, $J = 2.7, 2.6, 1.2$ Hz, 1H), 4.52 (d, $J = 10.3$ Hz, 1H), 3.68 (ddd, $J = 10.3, 4.2, 2.4$ Hz, 1H); cis 7.26 (brd, $J = 2.2$ Hz, 1H), 6.64 (dd, $J = 2.4, 1$ Hz, 1H), 6.62 (dd, $J = 2.9, 1.7$ Hz, 1H), 6.20 (dd, $J = 3.2, 1.7$ Hz, 1H), 6.09 (d, $J = 3.2$ Hz, 1H), 5.81 (d, $J = 6.8$ Hz, 1H), 5.43 (ddd, $J = 2.7, 2.7, 1$ Hz, 1H), 3.36 (ddd, $J = 6.8, 4.4, 2.4$ Hz, 1H). ¹³C NMR (CDCl_3 ; δ , ppm): trans 165.0, 153.0, 145.7, 142.8, 110.8, 108.3, 106.9, 93.4, 51.4, 51.3. ⁷⁷Se NMR (CDCl_3 ; δ , ppm): trans 452.8, 321.2; cis 435.0, 323.7. IR (NaCl, neat; cm^{-1}): 3025, 2975, 1610, 1580, 1480. Mass (EI mode; m/e): 320 (M^+ , ⁸⁰Se), 239 ($[\text{M} - \text{SeH}]^+$), 160 (2-selenoformylfuran). HRMS: calcd for $\text{C}_{10}\text{H}_8\text{O}_2\text{Se}_2$: 319.8855. Found: m/e 319.8856. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_2\text{Se}_2$: C 37.76, H 2.53. Found: C 37.50, H 2.42.

4-(2-Thienyl)-3a,4-dihydro-1-thia-5,6-diselena-indene 4: orange-red oil. ¹H NMR (CDCl_3 ; δ , ppm): trans 7.33 (dd, $J = 5.2, 1.8$ Hz, 1H), 7.32 (dd, $J = 3.4, 1.8$ Hz, 1H), 7.07 (dd, $J = 2.4, 1.2$ Hz, 1H), 6.95 (dd, $J = 5.2, 3.4$ Hz, 1H), 6.56 (dd, $J =$

$6.1, 1.5$ Hz, 1H), 5.85 (ddd, $J = 6.1, 2.4, 1.2$ Hz, 1H), 4.64 (d, $J = 10.4$ Hz, 1H), 3.80 (ddd, $J = 10.4, 2.4, 1.5$ Hz, 1H); cis 7.22–7.13 (m, 2H), 6.90–6.88 (m, 1H), 6.82 (dd, $J = 5.2, 3.4$ Hz, 1H), 6.44 (dd, $J = 6.1, 1.5$ Hz, 1H), 6.10 (d, $J = 6.1$ Hz, 1H), 5.88–5.86 (m, 1H), 3.60–3.50 (m, 1H). ¹³C NMR (CDCl_3 ; δ , ppm): trans 151.2, 145.5, 126.8, 126.2, 125.7, 125.5, 125.3, 113.3, 64.0, 52.6. IR (NaCl, neat; cm^{-1}): 3075, 3050, 1670, 1580, 1550. Mass (EI mode; m/e): 352 (M^+ , ⁸⁰Se), 272 ($[\text{M} - \text{Se}]^+$), 192 ($[\text{M} - 2\text{Se}]^+$), 176 (2-selenoformylthiophene). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{S}_2\text{Se}_2$: C 34.30, H 2.30. Found: C 33.94, H 2.28.

2-Bromo-4-(5-bromo-2-furyl)-3a,4-dihydro-1-oxa-5,6-diselena-a-indene 5: dark-red oil. ¹H NMR (CDCl_3 ; δ , ppm): trans 6.69 (dd, $J = 1.3, 1$ Hz, 1H), 6.29 (brd, $J = 3.3$ Hz, 1H), 6.27 (d, $J = 3.2$ Hz, 1H), 5.57 (dd, $J = 2.4, 1$ Hz, 1H), 4.55 (d, $J = 10.2$ Hz, 1H), 3.64 (dt, $J = 10.2, 2.4$ Hz, 1H); cis 6.80–6.60 (m, 1H), 6.14 (d, $J = 3.3$ Hz, 1H), 6.06 (d, $J = 3.3$ Hz, 1H), 5.69 (d, $J = 6.6$ Hz, 1H), 5.41 (dd, $J = 2.5, 1$ Hz, 1H), 3.38 (dt, $J = 6.6, 2.4$ Hz, 1H). ¹³C NMR (CDCl_3 ; δ , ppm): trans 163.7, 154.5, 130.5, 122.2, 112.6, 109.8, 108.2, 95.6, 52.7, 50.0. Anal. Calcd for $\text{C}_{10}\text{H}_6\text{Br}_2\text{O}_2\text{Se}_2$: C 25.24, H 1.27. Found: C 24.45, H 1.84.

2-Bromo-4-(5-bromo-2-thienyl)-3a,4-dihydro-1-thia-5,6-diselena-indene 6: dark-red oil. ¹H NMR (CDCl_3 ; δ , ppm): trans 7.29 (dd, $J = 2.2, 0.8$ Hz, 1H), 6.88 (brd, $J = 3.8$ Hz, 1H), 6.81 (d, $J = 3.8$ Hz, 1H), 5.94 (brd, $J = 2.8$ Hz, 1H), 4.64 (d, $J = 10.3$ Hz, 1H), 3.65 (dt, $J = 10.3, 2.8$ Hz, 1H); cis 7.35–7.31 (m, 1H), 6.79 (d, $J = 3.8$ Hz, 1H), 6.65 (d, $J = 3.8$ Hz, 1H), 5.93 (dd, $J = 2.8, 0.8$ Hz, 1H), 5.89 (d, $J = 5.8$ Hz, 1H), 3.52 (dt, $J = 5.8, 2.8$ Hz, 1H). ¹³C NMR (CDCl_3 ; δ , ppm): trans 150.7, 146.6, 129.6, 126.8, 125.8, 114.5, 113.8, 112.8, 64.6, 51.5.

4-Phenyl-3-((E)-phenylvinyl)-3,4-dihydro-1,2-disele-nin 7: red oil. ¹H NMR (CDCl_3 ; δ , ppm): trans and cis 7.40–7.00 (m, 20H), 6.88 (dd, $J = 9.8, 2$ Hz, 1H), 6.79 (dd, $J = 10.3, 1.9$ Hz, 1H), 6.44 (dd, $J = 9.8, 5.3$ Hz, 1H), 6.40–6.24 (m, 4H), 5.95 (dd, $J = 15.7, 10.3$ Hz, 1H), 4.49 (dd, $J = 10.3, 4.2$ Hz, 1H), 4.08 (t, $J = 7.1$ Hz, 1H), 3.88–3.76 (m, 1H), 3.76–3.62 (m, 1H). ¹³C NMR (CDCl_3 ; δ , ppm): trans and cis 142.3, 140.3, 136.5, 134.9, 134.8, 132.5, 131.9, 129.8, 129.0, 128.8, 128.5, 128.1, 127.7, 127.5, 127.1, 126.5, 126.4, 117.8, 116.3, 48.5, 48.1, 44.8. Mass (+FAB mode; m/e): 393 ($[\text{M} + \text{H}]^+$, ⁸⁰Se).

3-Phenyl-2-(E-phenylvinyl)-2,3-dihydrosele-nophene 8: light yellow solid, mp 90.0–94.0 °C. ¹H NMR (CDCl_3 ; δ , ppm): cis 7.50–7.10 (m, 10H), 6.95 (dd, $J = 6.4, 2.0$ Hz, 1H), 6.48–6.35 (m, 2H), 6.21 (dd, $J = 6.4, 2.8$ Hz, 1H), 5.03 (dd, $J = 10.6, 8.0$ Hz, 1H), 4.29 (dt, $J = 7.8, 2.0$ Hz, 1H). The spectral data for *trans-8* are the same as that reported in the literature.⁶

2,5-Dimethyl-3-phenyl-2-((E)-phenylvinyl)-2,3-dihydrosele-nophene 9: orange oil, impurities included. ¹H NMR (CDCl_3 ; δ , ppm): 7.40–7.07 (m, 10H), 6.88 (d, $J = 16.2$ Hz, 1H), 6.25 (d, $J = 16.2$ Hz, 1H), 5.80–5.77 (m, 1H), 4.29 (dq, $J = 2.4, 2.1$ Hz, 1H), 2.17 (dd, $J = 2.4, 1.5$ Hz, 3H), 1.46 (s, 3H). Mass (EI mode; m/e): 340 (M^+ , ⁸⁰Se), 259 ($[\text{M} - \text{SeH}]^+$), 249 ($[\text{M} - 91]^+$), 170 ($[\text{M} - \text{PhCHSe}]^+$ or $[\text{PhCHSe}]^+$).

2,3,5-Triphenyl-2-((E)-phenylvinyl)-2,3-dihydrosele-nophene 10: orange oil, impurities included. ¹H NMR (CDCl_3 ; δ , ppm): 7.60–7.00 (m, 20H), 6.61 (d, $J = 3.7$ Hz, 1H), 6.40 (d, $J = 15.9$ Hz, 1H), 6.21 (d, $J = 15.9$ Hz, 1H), 4.50 (d, $J = 3.7$ Hz, 1H). Mass (EI mode; m/e): 464 (M^+ , ⁸⁰Se), 383 ($[\text{M} - \text{SeH}]^+$), 373 ($[\text{M} - 91]^+$), 294 ($[\text{M} - \text{PhCHSe}]^+$), 192 ($[\text{PhCH}=\text{CHCPh}]^+$).

General Procedure for Cycloaddition Reactions of α,β -Unsaturated Selenoaldehydes and Selenoketones with Norbornadiene or Cyclopentadiene. Under a dry argon atmosphere, to a white suspension of $(\text{Me}_2\text{Al})_2\text{Se}$ in toluene (10 mL), prepared in situ from 660 mg (1.0 mmol) of $(\text{Bu}_3\text{Sn})_2\text{Se}$ and 1.1 mL (2.2 mmol) of Me_3Al (2 M in toluene) as described previously,^{5e} was added dioxane (5 mL) followed by 5 mmol of norbornadiene (or cyclopentadiene) and 1.3 mmol of an α,β -unsaturated aldehyde or ketone. The mixture was stirred at 100 °C for 4–5 h and then treated in the same manner described for the dimerization of α,β -unsaturated selenoaldehyde or -ketone. The Diels–Alder cycloadduct product of α,β -unsaturated selenoaldehyde or -ketone with norbornadiene (or cyclopentadiene) was isolated by column chro-

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(23) (a) Davidson, E. R.; Feller, A. *Chem. Rev.* **1986**, *86*, 681. (b) *Ab Initio Methods in Quantum Chemistry-Part I*; Lawley, K. P., Ed.; John Wiley & Sons: New York, 1987. (c) The calculations show that the BSSE of the current basis sets for relative energy calculations is less than 2 kcal/mol.

matography on silica gel (230–400 mesh) with hexane followed by hexane–CH₂Cl₂ (5:1) as the solvents.

exo-9,10-trans-6-Oxa-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene 12: orange oil. ¹H NMR (CDCl₃; δ, ppm): 6.63 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.18 (dd, *J* = 5.7, 2.9 Hz, 1H), 6.11 (dd, *J* = 5.7, 2.9 Hz, 1H), 5.88 (dd, *J* = 2.9, 1.1 Hz, 1H), 5.50 (ddd, *J* = 2.5, 2.5, 1.1 Hz, 1H), 3.20 (dq, *J* = 10.1, 1.1 Hz, 1H), 3.02 (dd, *J* = 7.8, 1.9 Hz, 1H), 2.83 (brs, 1H), 2.75 (brs, 1H), 2.41 (brd, *J* = 8.9 Hz, 1H), 1.71 (ddd, *J* = 10.1, 7.8, 1.4 Hz, 1H), 1.63 (dt, *J* = 8.9, 1.9 Hz, 1H). ¹³C NMR (CDCl₃; δ, ppm): 160.7, 145.2, 138.2, 137.1, 107.7, 84.3, 55.5, 50.5, 47.6, 47.0, 43.6, 40.2. ⁷⁷Se NMR (CDCl₃, δ, ppm): 266.9. IR (NaCl, neat; cm⁻¹): 3025, 2925, 1640, 1590. Mass (EI mode, *m/e*): 252 (M⁺, ⁸⁰Se), 186 ([M – cyclopentadiene]⁺), 160 ([M – norbornadiene]⁺). HRMS: calcd for C₁₂H₁₂OSe 252.0053. Found: *m/e* 252.0057. Anal. Calcd for C₁₂H₁₂OSe: C 57.38, H 4.82. Found: C 57.40, H 5.08.

exo-9,10-trans-6-Thia-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene 14: yellow solid, mp 84.5–85.5 °C. ¹H NMR (CDCl₃; δ, ppm): 6.56 (dd, *J* = 3.0, 1.1 Hz, 1H), 6.40 (dd, *J* = 6.2, 1.8 Hz, 1H), 6.21 (dd, *J* = 5.7, 3.0 Hz, 1H), 6.11 (dd, *J* = 5.7, 3.0 Hz, 1H), 5.94 (ddd, *J* = 6.2, 2.6, 1.1 Hz, 1H), 3.40 (ddd, *J* = 10.5, 4.6, 2.7 Hz, 1H), 2.95 (dd, *J* = 7.5, 1.9 Hz, 1H), 2.94 (brs, 1H), 2.82 (brs, 1H), 2.50 (brd, *J* = 9 Hz, 1H), 1.71 (ddd, *J* = 10.5, 7.8, 1.4 Hz, 1H), 1.63 (dt, *J* = 9, 1.9 Hz, 1H). ¹³C NMR (CDCl₃; δ, ppm): 144.5, 138.6, 136.7, 125.7, 124.5, 104.6, 60.0, 53.8, 47.6, 47.4, 43.5, 40.3. ⁷⁷Se NMR (CDCl₃, δ, ppm): 321.9. IR (NaCl, neat; cm⁻¹): 3050, 2950, 2850, 1660, 1585. Mass (EI mode, *m/e*): 268 (M⁺, ⁸⁰Se), 202 ([M – cyclopentadiene]⁺), 176 ([M – norbornadiene]⁺). Anal. Calcd for C₁₂H₁₂SSe: C 53.93, H 4.53. Found: C 53.58, H 4.53. Crystals of **14** for X-ray analysis were prepared by recrystallization from a hexane–CH₂Cl₂ solution under refrigeration. Full details of the crystal structure determination are given in the Supporting Information.

exo-6-Oxa-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-5,7,12-triene 15: orange oil. ¹H NMR (CDCl₃; δ, ppm): 7.24 (brd, *J* = 1.9 Hz, 1H), 6.30 (brd, *J* = 1.9 Hz, 1H), 6.27 (ddd, *J* = 5.7, 2.8, 0.7 Hz, 1H), 6.20 (ddd, *J* = 5.7, 2.9, 0.9 Hz, 1H), 3.67 (d, *J* = 14.1 Hz, 1H), 3.56 (dd, *J* = 14.1, 1.4 Hz, 1H), 3.14 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.96 (brs, 1H), 2.88 (brs, 1H), 2.79 (d, *J* = 8.0 Hz, 1H), 1.47–1.42 (m, 2H). ¹³C NMR (CDCl₃; δ, ppm): 147.0, 139.4, 137.5, 136.9, 122.5, 111.1, 52.0, 50.4, 44.9, 38.8, 36.8, 11.1. ⁷⁷Se NMR (CDCl₃, δ, ppm): 277.2. Mass (EI mode, *m/e*): 252 (M⁺, ⁸⁰Se), 186 ([M – cyclopentadiene]⁺), 160 ([M – norbornadiene]⁺).

exo-6-Thia-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-5,7,12-triene 16: red oil. ¹H NMR (CDCl₃; δ, ppm): 7.04 (brd, *J* = 5.4 Hz, 1H), 6.94 (d, *J* = 5.4 Hz, 1H), 6.31 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.24 (dd, *J* = 5.4, 3.4 Hz, 1H), 3.81 (d, *J* = 14.2 Hz, 1H), 3.69 (d, *J* = 14.2 Hz, 1H), 3.22 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.03–3.01 (br, 2H), 2.82 (d, *J* = 8.3 Hz, 1H), 1.50–1.43 (m, 2H). ¹³C NMR (CDCl₃; δ, ppm): 140.5, 137.7, 137.3, 133.4, 129.0, 120.7, 51.9, 51.1, 45.1, 40.1, 36.8, 14.0. Mass (EI mode, *m/e*): 268 (M⁺, ⁸⁰Se), 202 ([M – cyclopentadiene]⁺), 176 ([M – norbornadiene]⁺).

exo-9,10-trans-2-Methyl-6-oxa-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene 17: orange oil. ¹H NMR (CDCl₃; δ, ppm): 6.63 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.18 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.09 (dd, *J* = 5.6, 3.0 Hz, 1H), 5.44 (dd, *J* = 2.9, 2.4 Hz, 1H), 3.21 (dq, *J* = 10.2, 2.4 Hz, 1H), 3.14 (dd, *J* = 7.8, 1.9 Hz, 1H), 2.81 (brs, 1H), 2.75 (brs, 1H), 2.37 (brd, *J* = 9.4 Hz, 1H), 2.07 (d, *J* = 2.8 Hz, 3H), 1.74–1.54 (m, 2H). ¹³C NMR (CDCl₃; δ, ppm): 154.1, 145.0, 138.2, 136.8, 107.4, 96.6, 54.5, 50.9, 47.3, 47.0, 43.5, 40.9, 17.7. IR (NaCl, neat; cm⁻¹): 3025, 2925, 1680, 1660, 1600, 1560. Mass (EI mode, *m/e*): 266 (M⁺, ⁸⁰Se), 200 ([M – cyclopentadiene]⁺), 174 ([M – norbornadiene]⁺). Anal. Calcd for C₁₃H₁₄OSe: C 58.87, H 5.32. Found: C 59.10, H 5.32.

exo-9,10-trans-2-Methyl-6-thia-3-selenatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene 18: brown solid, mp 88.5–89.0 °C. ¹H NMR (CDCl₃; δ, ppm): 6.40 (dd, *J* = 6.2, 1.8 Hz, 1H), 6.20 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.10 (dd, *J* = 5.6, 3.0 Hz, 1H), 5.90 (dd, *J* = 6.2, 2.7 Hz, 1H), 3.40 (dq, *J* = 10.7, 2.4 Hz, 1H), 3.07 (dd, *J* = 7.8, 1.7 Hz, 1H), 2.90 (brs, 1H), 2.79

(brs, 1H), 2.46 (brd, *J* = 9.0 Hz, 1H), 2.10 (d, *J* = 2.7 Hz, 3H), 1.68–1.60 (m, 2H). ¹³C NMR (CDCl₃; δ, ppm): 138.5, 137.1, 136.5, 126.2, 124.2, 115.1, 60.6, 53.0, 47.4, 47.2, 43.5, 41.5, 24.3. ⁷⁷Se NMR (CDCl₃; δ, ppm): 370.9. IR (NaCl, neat; cm⁻¹): 3020, 2950, 2900, 2800, 1650, 1560. Mass (EI mode, *m/e*): 282 (M⁺, ⁸⁰Se), 216 ([M – cyclopentadiene]⁺), 190 ([M – norbornadiene]⁺). Anal. Calcd for C₁₃H₁₄SSe: C 55.51, H 5.02. Found: C 55.50, H 5.12.

exo-6-Phenyl-3-selenatetracyclo[6.2.1.0^{2,7}]-undeca-4,9-diene 19: orange oil. ¹H NMR (CDCl₃; δ, ppm): trans 7.40–7.20 (m, 5H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.46 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.06 (dd, *J* = 5.9, 2.9 Hz, 1H), 6.01 (dd, *J* = 5.9, 2.9 Hz, 1H), 3.32 (dd, *J* = 7.8, 1.9 Hz, 1H), 3.10 (ddd, *J* = 10.5, 4.0, 2.4 Hz, 1H), 2.84 (brs, 1H), 2.53 (d, *J* = 9.0 Hz, 1H), 2.51 (brs, 1H), 1.95 (ddd, *J* = 10.5, 7.8, 1.2 Hz, 1H), 1.58 (dt, *J* = 9.0, 1.7 Hz, 1H); cis 7.40–7.20 (m, 5H), 6.99 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H), 6.64 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.08 (dd, *J* = 5.9, 2.9 Hz, 1H), 6.00 (dd, *J* = 5.9, 2.9 Hz, 1H), 3.62–3.60 (m, 1H), 3.28 (brd, *J* = 9.0 Hz, 1H), 3.01 (brs, 1H), 2.61 (brs, 1H), 2.26 (brd, *J* = 9.0 Hz, 1H), 2.05–1.96 (ddd, 1H), 1.35–1.25 (dt, 1H). ¹³C NMR (CDCl₃; δ, ppm): trans 145.0, 139.7, 138.9, 136.3, 128.6, 128.5, 126.5, 120.8, 54.1, 52.3, 48.6, 46.8, 43.8, 43.2. ⁷⁷Se NMR (CDCl₃; δ, ppm): trans 262.2; cis 282.0. IR (NaCl, neat; cm⁻¹): 3000, 2950, 1590, 1490. Mass (EI mode, *m/e*): 288 (M⁺, ⁸⁰Se), 222 ([M – cyclopentadiene]⁺), 196 ([M – norbornadiene]⁺). Anal. Calcd for C₁₆H₁₆Se: C 66.90, H 5.61. Found: C 67.13, H 5.54.

exo-4-Methyl-6-phenyl-3-selenatetracyclo[6.2.1.0^{2,7}]-undeca-4,9-diene 20: yellow oil. ¹H NMR (CDCl₃; δ, ppm): trans 7.40–7.20 (m, 5H), 6.10–5.95 (m, 3H), 3.37 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.10 (m, 1H), 2.82 (brs, 1H), 2.48 (brs, 1H), 2.47 (d, *J* = 8.3 Hz, 1H), 2.13 (m, 3H), 1.95–1.85 (m, 1H), 1.55 (brd, *J* = 9.0 Hz, 1H). ¹³C NMR (CDCl₃; δ, ppm): trans 145.4, 139.0, 136.2, 133.4, 128.8, 128.6, 128.5, 126.1, 53.2, 53.1, 48.4, 46.5, 44.0, 43.9, 25.4. ⁷⁷Se NMR (CDCl₃; δ, ppm): trans 308.5; cis 323.6. IR (NaCl, neat; cm⁻¹): 3000, 2950, 1590, 1485. Mass (EI mode, *m/e*): 302 (M⁺, ⁸⁰Se), 236 ([M – cyclopentadiene]⁺), 210 ([M – norbornadiene]⁺).

exo-4,6-Diphenyl-3-selenatetracyclo[6.2.1.0^{2,7}]-undeca-4,9-diene 21: yellow solid, mp 90.0–92.0 °C. ¹H NMR (CDCl₃; δ, ppm): trans 7.70–7.20 (m, 10H), 6.63 (d, *J* = 4.4 Hz, 1H), 6.20–6.00 (m, 2H), 3.51 (dd, *J* = 7.6, 1.8 Hz, 1H), 3.35 (dd, *J* = 10.9, 4.4 Hz, 1H), 2.93 (brs, 1H), 2.58 (brd, *J* = 8.7 Hz, 1H), 2.55 (brs, 1H), 2.04 (ddd, *J* = 10.9, 7.8, 1.4 Hz, 1H), 1.62 (dt, *J* = 8.7, 1.6 Hz, 1H). ¹³C NMR (CDCl₃; δ, ppm): trans 145.0, 142.0, 140.0, 139.2, 137.3, 136.3, 135.3, 128.7, 128.6, 128.3, 127.9, 126.9, 126.6, 54.5, 54.3, 48.4, 46.6, 44.9, 43.8. ⁷⁷Se NMR (CDCl₃; δ, ppm): trans 282.8. Mass (+FAB mode, *m/e*): 365 ([M + H]⁺, ⁸⁰Se). Anal. Calcd for C₂₂H₂₀Se: C 72.72, H 5.55. Found: C 72.32, H 5.66.

3-(2-Thienyl)-2-selenabicyclo[2.2.1]hept-5-ene 22: yellow-orange oil. ¹H NMR (CDCl₃, δ, ppm): endo 7.25–6.80 (m, 3H), 6.63 (dd, *J* = 5.4, 2.9 Hz, 1H), 5.68 (dd, *J* = 5.4, 2.9 Hz, 1H), 5.49 (d, *J* = 3.9 Hz, 1H), 4.44 (brs, 1H), 3.37 (brs, 1H), 1.90–1.80 (m, 2H); exo 7.25–6.80 (m, 3H), 6.44 (dd, *J* = 5.4, 2.9 Hz, 1H), 5.91 (dd, *J* = 5.4, 2.9 Hz, 1H), 4.52 (brs, 1H), 4.50 (s, 1H), 3.13 (brs, 1H), 2.18 (d, *J* = 10.0 Hz, 1H), 1.98–1.80 (m, 1H). IR (NaCl, neat; cm⁻¹): 2950, 2930. Mass (EI mode, *m/e*): 242 (M⁺, ⁸⁰Se), 176 ([M – cyclopentadiene]⁺).

4H,5H-4a,7a-Dihydrocyclopent[*b*]selenin 23: orange oil. ¹H NMR (CDCl₃, δ, ppm): 6.03–5.97 (m, 1H), 5.95–5.88 (m, 3H), 4.07 (dt, *J* = 6.1, 1.8 Hz, 1H), 3.27 (dq, *J* = 15.6, 2.8 Hz, 1H), 2.88 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.62–2.53 (m, 1H), 2.46 (ddd, *J* = 16.2, 7.9, 1.8 Hz, 1H), 2.18 (ddq, *J* = 16.2, 9.2, 1.8 Hz, 1H). ¹³C NMR (CDCl₃, δ, ppm): 133.0, 132.7, 124.0, 40.5, 38.4, 37.8, 15.9. IR (NaCl, neat; cm⁻¹): 3010, 3000, 2910, 1650. Mass (EI mode, *m/e*): 186 (M⁺, ⁸⁰Se), 105 ([M – SeH]⁺).

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Supporting Information Available: NMR spectra (^1H , ^{13}C , ^{77}Se) for representative compounds. Packing diagram, tables of crystal data and structure refinement, atomic coordinates and isotropic and anisotropic displacement parameters, and

bond distances and angles for **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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