J. Org. Chem. 1990, 55, 263-269

in the crystal were s-cis. Therefore, it is suggested that there is no major intrinsic stability difference between the two conformational states in the trans free amides: the observed forms in the crystal are probably determined by the crystal packing. Overall, from our viewpoints, the potent retinoidal activities of these free amides seem to be a consequence of the trans extended conformation with the s-cis or the s-trans form.

Conclusion

The three *N*-methylanilide molecules examined adopt cis amide conformations in the crystalline state, whereas the corresponding free amides take the trans amide conformation. The structures in solution are considered to be similar to those in the crystal on the basis of various spectroscopic studies. From the structure–activity relationships of various synthetic retinoidal active compounds,[12] we conclude that the trans extended conformation is required for specific binding to the target receptor. This fact strongly supports our postulation. The loss of activity upon N-methylation of retinoidal active benzanilides should not be ascribed to the steric hindrance of the methyl group or to the potential loss of a hydrogen bond from amide nitrogen to the receptor but to the large conformational change unfavorable for binding. The reasons for stabilization of the cis amide conformation in *N*-methylanilide are under investigation by computational methods, using molecular mechanics and molecular orbital calculations. The generality of this cis stabilization by N-methylation from benzanilide to other anilide compounds will be discussed elsewhere.

Registry No. Am80, 94497-51-5; Am580, 102121-60-8; Am581, 102121-59-5; Am90, 110383-33-0; Am590, 116193-58-9; Am591, 116233-28-4.

Supplementary Material Available: Find atomic coordinates, thermal parameters, bond lengths, and bond angles (28 pages). Ordering information is given on any current masthead page.

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[12] Kagechika, H.; Himi, T.; Namikawa, K.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1989**, *32*, 1098.

Synthesis and Unusual Selenium Extrusion Reaction of a Cyclic Triselenide

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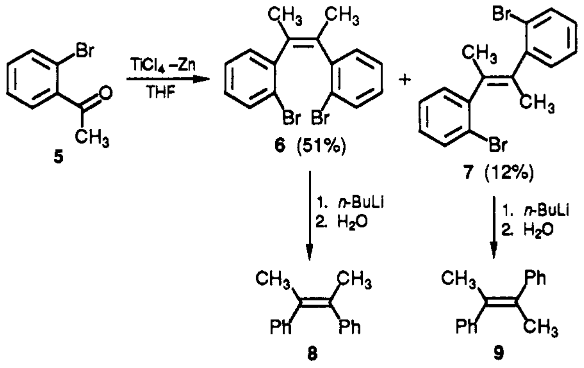
Reaction of (*Z*)-2,3-bis(2-lithiophenyl)-2-butene (**10**) with selenium gave 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**) rather than either 11,12-dimethyldibenzo[*c*,*g*]-1,2-diselenocine (**2**) or 13,14-dimethyldibenzo-[*e*,*i*]-1,2,3,4-tetraselenecine (**4**). Thermolysis and photolysis of **3** gave 5a,10a-dihydro-5a,10a-dimethyldibenzo-[*b*,*f*]seleno[3,2-*b*]selenophene (**12**) via extrusion of a selenium atom and a novel intramolecular addition of arylselenyls to a double bond. Ab initio molecular orbital calculations and X-ray structural analyses are made to elucidate the reaction mechanism of **10** → **3** → **12**.

Introduction

The chemistry of cyclic polysulfides[1] has attracted attention, because of chemical, theoretical, and biological interest. They exhibit unique chemical properties such as skeletal rearrangements, unusual structures, and the transfer of sulfur atoms to acceptors. Compared to syntheses and reactions of sulfur compounds, few examples of those of cyclic di-, tri-, and polyselenides have been reported.[2] We have examined the preparation and a reaction of a cyclic triselenide. We now report a reaction of (*Z*)-2,3-bis(2-lithiophenyl)-2-butene (**10**) with selenium, giving 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**) and the result of thermal and photochemical reactions of **3**.

Scheme I



The aim of this work is to examine how the Se–Se bond is incorporated into a cyclic polyselenide and the polyselenide linkage is converted to C–Se bonds thermally or photochemically. On the basis of the present result, the

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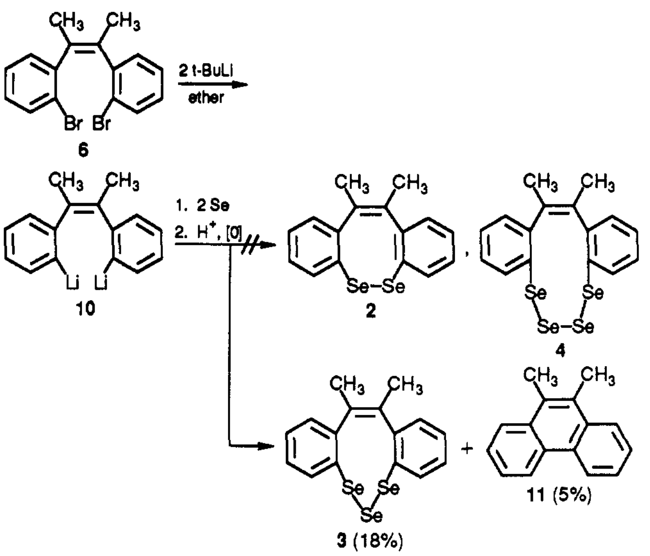
[1] For some recent papers for cyclic polysulfides, see: (a) Nicolaou, K. C.; Hwang, C.-K.; DeFrees, S.; Stylianides, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 4868. (b) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926. (c) Chenard, B. L.; Dixon, D. A.; Harlow, R. L.; Roe, D. C.; Fukunaga, T. *J. Org. Chem.* **1987**, *52*, 2411 and references cited therein.

[2] For reviews, see: (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, Chapter 13. (b) Claus, P. K. *Organic Compounds of Sulphur, Selenium, and Tellurium* **1981**, *6*, 233.

0022-3263/90/1955-0263$02.50/0

Scheme II



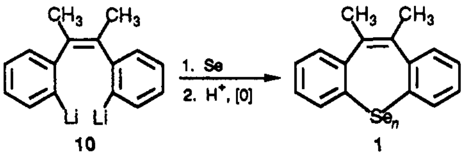
Scheme III

$10 \xrightarrow[2.\ H^+,\ [O]]{1.\ 3\,Se} 3$ (68%) $10 \xrightarrow[2.\ H^+,\ [O]]{1.\ 4\,Se} 3$ (60%)

factors which control the ring size and the skeletal rearrangement mechanism of heterocycles are discussed. Also, it is demonstrated that the combination of X-ray analysis and ab initio MO calculations on such unprecedented heterocycles is indispensable to search for the reaction mechanism as well as for the product analysis.

Results and Discussion

1. Synthesis. In order to prepare a new class of selenium-containing heterocycles[3,4] **1**, insertion of selenium into carbon–lithium bonds of **10** and oxidative ring closure[5] were attempted.



(*Z*)-2,3-Bis(2-bromophenyl)-2-butene (**6**), which is the precursor of **10**, was prepared as follows. Reaction of *o*-bromoacetophenone (**5**) and $TiCl_4$–Zn[6] gave **6** (51%) and *E* isomer **7** (12%); **6** and **7** were separated by fractional crystallization. The structures of these *Z* and *E* isomers were confirmed by lithiation and protonation to the known (*Z*)-dimethylstilbene (**8**)[7] and (*E*)-dimethylstilbene (**9**),[7] respectively (Scheme I).

In Scheme II, **10** was prepared from **6** and *tert*-butyllithium in ether. Then, the reaction of **10** with 2 equiv of selenium and subsequent protonation (2 N HCl) and air oxidation gave 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**) (18%) and 9,10-dimethylphenanthrene (**11**)[8] (5%) as isolable products. The structure of **3** was confirmed by its X-ray analysis (Figure 1). In Scheme III,

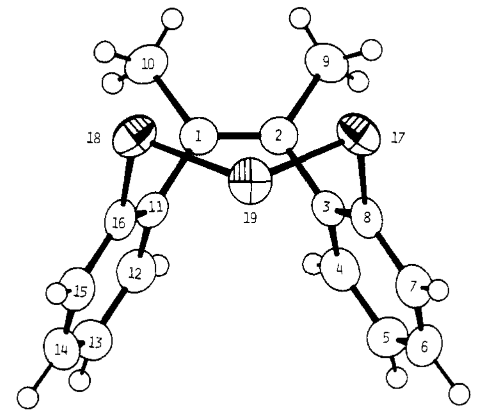


Figure 1. ORTEP drawing of 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**). No. 1 and 2 denote olefin carbons, No. 9 and 10 denote methyl carbons. No. 17, 18, and 19 stand for selenium atoms. Other 12 atoms form two benzene rings. This numbering is different from that of the IUPAC format. The detailed geometric parameters are given in Appendix 1. The geometry belongs to the C_s symmetry.

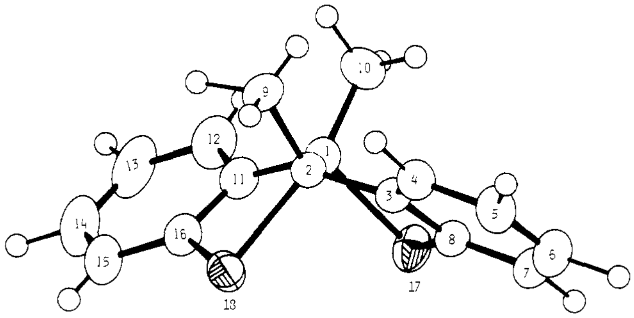
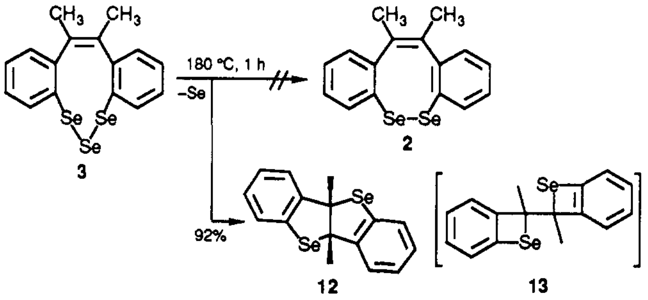


Figure 2. ORTEP drawing of 5a,10a-dihydro-5a,10a-dimethyldibenzo[*b*,*f*]seleno[3,2-*b*]selenophene (**12**). Geometric parameters are given in Appendix 2. The geometry belongs to the C_2 symmetry.

Scheme IV



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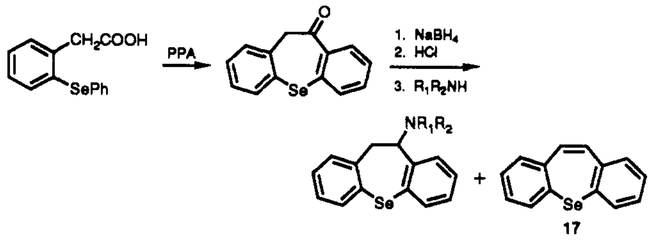
[3] 7-membered compound, dibenzo[*b*,*f*]selenepine **17** is a known compound. **17** has been obtained as follows, which is different from our synthetic route. Sindelar, K.; Metysova, J.; Protiva, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 3801.



[4] For references of acyclic triselenides and polyselenides, see: (a) Reinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 1. (b) Eggert, H.; Nielsen, O.; Hentrksen, L. *J. Am. Chem. Soc.* **1986**, *108*, 1725.

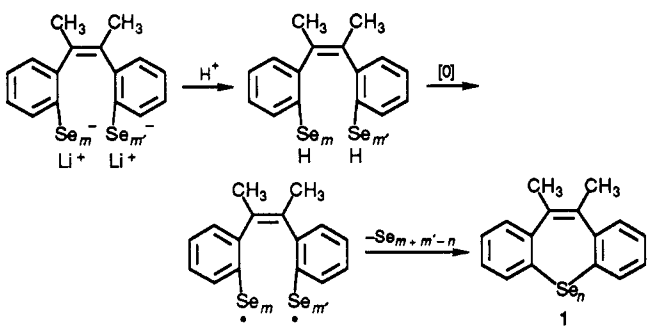
[5] (a) Meinwald, J.; Dauplaise, D.; Wudl, F.; Hauser, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 255. (b) Engman, L. *J. Heterocycl. Chem.* **1984**, *21*, 413.

[6] Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.

[7] Kharash, M. S.; Klieman, M. *J. Am. Chem. Soc.* **1943**, *65*, 11.

[8] Bradsher, C. K.; Jackson, Jr., W. J. *J. Am. Chem. Soc.* **1954**, *76*, 4140.

Scheme V



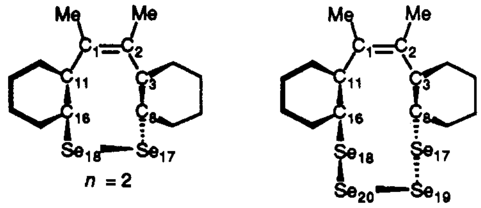
reaction of **10** and 3 equiv of selenium and similar subsequent workup gave **3** in 68% yield. Reaction of **10** and 4 equiv of selenium also gave **3** (60%) as a major product.

2. **Reaction.** We have explored the reactivities of the unique compound **3** in Scheme IV. Thermolysis of **3** at 180 °C gave **12** having the molecular formula $C_{16}H_{14}Se_2$ in 92% yield. The ^{13}C NMR spectrum of **12** exhibited six sp^2 carbons (125.56, 125.63, 125.68, 128.6, 138.4, and 144.3 ppm) and two sp^3 carbons (22.54 and 75.47 ppm), whereas that of **3** exhibited seven sp^2 carbons (127.5, 128.8, 129.5, 130.4, 135.7, 138.2, and 149.2 ppm) and one sp^3 carbon (21.67 ppm). Therefore **12** is not diselenide **2**, although it has been reported that thermolysis of linear diaryl triselenides gives diselenides.[4b] Because ^{77}Se NMR shows one peak at 535.2 ppm, the two selenium atoms are equivalent. From these spectral features, the structure of **12** may be assigned to 5a,10a-dihydro-5a,10a-dimethyldibenzo[*b*,*f*]seleno[3,2-*b*]selenophene or possibly strained 4-membered compound **13**.[9] Structure and stereochemistry of **12** were established by X-ray analysis (Figure 2) as 5a,10a-dihydro-5a,10a-dimethyldibenzo[*b*,*f*]seleno[3,2-*b*]selenophene.

Photolysis of **3** with a 100-W high-pressure mercury lamp (Pyrex filter, $\lambda > 290$ nm) in THF (0 °C) gave **12** in 51% yield as an isolable product. Furthermore, the thermal transformation (80 °C) of **3** into **12** in refluxing benzene (0.01 M) proceeded very slowly (for 53 h, **3**:**12** = 73:27). When **3** in benzene (0.01 M) was refluxed in the presence of 30 mol % of azobisisobutyronitrile (AIBN), **12** and the recovered **3** were obtained after 6 h in 76% and 24% yields, respectively. The reaction was accelerated by the radical initiator, AIBN. These thermal and photochemical intramolecular additions of **3**, accompanied by extrusion of selenium, presumably proceeds via a radical mechanism.[10] This point will be discussed in detail in the next subsection.

3. **Analysis of Structures and Reactions.** In view of results of synthesis, crystal structures, and reaction, two questions arise. One is (i) why the triselenide **3** ($n = 3$) has been obtained exclusively ($n = 2$ and 4 heterocycles have not been generated). The other is (ii) how **3** is converted to **12** via the Se extrusion; (i) is concerned with structures of heterocycles of ring strain, and (ii) is related to the mechanistic classification, radical or concerted intramolecular addition.

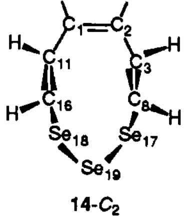
(i) **Structure of 3 ($n = 3$).** Generally, the formation of compounds **1** can be rationalized by three steps. The first is the selenium insertion, the second is the oxidation, and the third is the extrusion of selenium (Scheme V). Suffixes *m*, *m'*, and *n* stand for the number of selenium atoms. We compared the stabilities of **1** by structures of heterocycles of ring strain. At the process of the Se extrusion **3** → **12**, the molecular symmetry has been switched from C_s to C_2. The possibility of the polyselenide **1** with the C_2 symmetry must be checked to decide that the C_s $n = 3$ (in Figure 1) is the sole obtainable form. In the framework of C_2, molecular models using standard bond lengths and angles are constructed; $n = 2$ and $n = 4$ compounds with C_2 symmetry are found to have unreasonable ∠CSeSe angles and Se–Se distances regardless of the C_2 dihedral angle rotation.



$n = 2$ $n = 4$

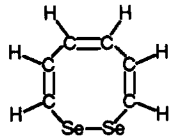
C_2 geometries absent

Only the $n = 3$ C_2 structure has reasonable angles and distances. To determine it accurately, an ab initio molecular orbital calculation was carried out on the model (parent) compound, **14**-C_2. The partially optimized geometry of **14** is given in Appendix 3, where sp^2 ∠HCC angles and C(11)–C(16) and C(3)–C(8) distances are kept to those of benzene ring at C(3), C(8), C(11), and C(16). The Se(17)–Se(19) or Se(18)–Se(19) bond length (3.67 Å) is computed to be much larger than the standard length, 2.33 Å, and the C(8)–Se(17) or C(16)–Se(18) length (1.73 Å) is noticeably shorter than the standard length, 1.91 Å. The ∠C(16)Se(18)Se(19) or ∠C(8)Se(17)Se(19) is 39.3°, which is an abnormal angle. That is, the MO calculation has judged that the C_2 symmetry structure of **3** is of extraordinary geometric parameters. In fact, the C_2 geometry is 103 kcal/mol less stable than **14**-C_s geometry shown in Appendix 3.



14-C_2

Next, C_s symmetry geometries of **1** are examined. The $n = 4$ C_s structure is of reasonable bond angles and distances by the molecular-model search. The $n = 2$ C_s structure is checked by the use of another model compound, **15**, and is calculated to have possible ∠CSeSe (107°) angle in Appendix 4. Although the $n = 2$ and 4 C_s structures appear to be likely according to the criterion of bond lengths and angles, they may be ruled out in the



15

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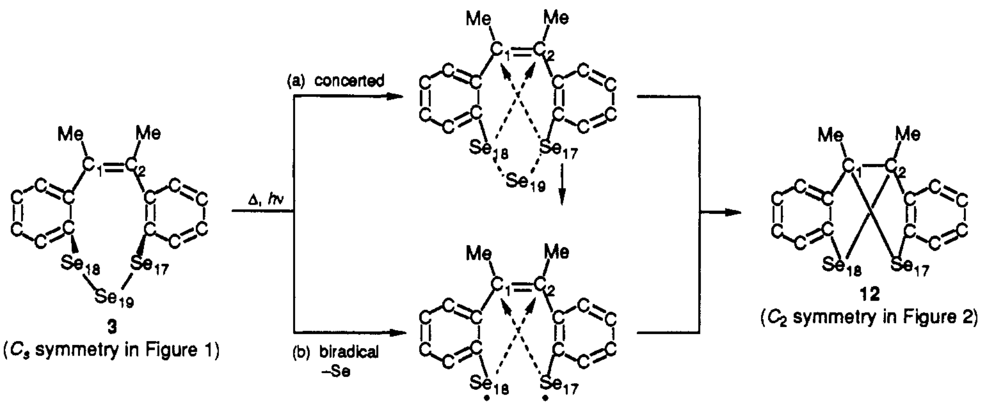
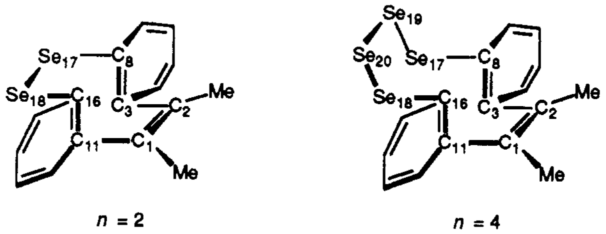
(9) Recently, we attempted to synthesize a benzoselenete derivative. Yamazaki, S.; Kohgami, K.; Okazaki, M.; Yamabe, S.; Arai, T. *J. Org. Chem.* **1989**, *54*, 243.

(10) A few types such as selenosulfonates, selenylthiocarboxylates, and diselenides have been reported to undergo free-radical 1,2-additions to olefins or acetylenes. (a) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438. (b) Toru, T.; Seko, T.; Maekawa, E. *Tetrahedron Lett.* **1985**, *26*, 3263. (c) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533.

Scheme VI



sense of dihedral angles. That is, they have unreasonably much smaller CSeSeC (in n = 2) and SeSeSeSe (in n = 4) dihedral angles (~0°) than standard ones (e.g., 87.5° in Me_2Se_2 and 101° in Se_8).

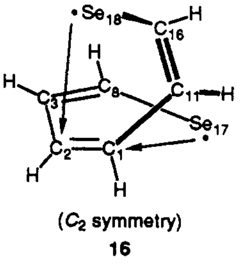


n = 2 n = 4

C_s geometries absent

Through the combination of the molecular-model simulation and the ab initio MO geometric optimization, it is confirmed that 1 may be present exclusively as 3 with the C_s symmetry.

(ii) Mechanism of the Intramolecular Bicyclization (3 → 12) via the Se Extrusion. Whereas 3 is found to be of the C_s symmetry, 12 is of the C_2 symmetry by the X-ray analysis. To switch the ($C_s \rightarrow C_2$), the Se(19) atom must be extruded from 3. If the reaction proceeds concertedly, (a) in Scheme VI, the spatial extension of frontier orbitals (HOMO and LUMO) in 3 must be localized on Se(17) (or Se(18) and the ethylenic moiety [C(1)=C(2)]. However, in these orbitals, major components of the ethylenic bond are absent, leading to the improbability of the concerted mechanism. Thus, the first step of reaction b is the stepwise Se–Se bond scission through the thermolysis or the photolysis of 3. To test whether the biradical intermediate is present or not, the geometry optimization of the UHF (triplet) ab initio MO on the model compound, 16, is made and gives a stable species in the C_2 symmetry in the Appendix 5. It is noteworthy that lobes of two radical frontier orbitals on Se atoms are directed toward the ethylenic π orbitals to form not 13 but 12. Therefore, the intervention of the biradical intermediate is the key process for the intramolecular C–Se bond formation, i.e., the bicyclization. This theoretical consideration is in accord with experimental evidence that the reaction is enhanced by AIBN.



(C_2 symmetry)

16

Conclusion

We have demonstrated that reaction of 10 with selenium gave exclusively triselenide 3 and thermolysis and photolysis of 3 gave a tetracyclic compound 12 via extrusion of a selenium atom and a novel intramolecular addition of arylselenyls to a double bond.

The structure and reactivity of polyselenides have been interpreted on the basis of ab initio calculations. While 12 is of the C_2 symmetry, 3 is of the C_s symmetry. To switch the point group, the Se atom is extruded. Consequently, the biradical intermediate is generated which has frontier orbitals on Se atoms directed to the C=C bond. According to this directionality, the cross bicyclization takes place to form 12. The size of the Se atom seems to have a crucial role for this novel cyclization.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a JEOL FX-200 spectrometer. For the ^1H and ^{13}C spectra, Me_4Si was used as an internal reference. Mass spectra were determined on a JEOL JMS-01SG-2 spectrometer and UV/vis spectra were measured with a Hitachi 200-20 spectrometer. All reactions were carried out under a nitrogen or argon atmosphere.

Preparation of (*Z*)-2,3-Bis(2-bromophenyl)-2-butene (6) and (*E*)-2,3-Bis(2-bromophenyl)-2-butene (7) in Scheme I. The suspension of zinc powder (1.45 g, 22.2 mmol) in 11.6 mL of THF was added slowly into a mixture of *o*-bromoacetophenone (1.48 g, 7.42 mmol) and $TiCl_4$ (1.41 g, 7.43 mmol) in 23.1 mL of THF at −10 °C. The reaction mixture was refluxed for 3 h. After the addition of water the mixture was extracted with hexane. The extracts were dried over anhydrous sodium sulfate. Removal of the solvent gave the mixture of 6 and 7; 6 and 7 were separated by fractional crystallization from hexane. The hexane-soluble component of the mixture is 6 (686 mg, 51%). The hexane-insoluble component of the mixture is 7 (166 mg, 12%). 6: colorless crystals; mp 50.5–52.0 °C (recrystallized from methanol); ^1H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 6.88 (td, J = 7.4, 2.0 Hz, 2 H), 6.97 (td, J = 7.4, 1.3 Hz, 2 H), 7.09 (dd, J = 7.5, 2.1 Hz, 2 H), 7.39 (dd, J = 7.7, 1.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.48, 122.7, 127.0, 127.7, 129.6, 132.0, 134.3, 145.0; IR (KBr) 3040, 2890, 1460, 1420, 1020 cm^{-1}; MS (70 eV) m/z (relative intensity) 368 (13), 366 (24), 364 (17), 206 (100). Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; Br, 43.65. Found: C, 52.73; H, 3.90; Br, 43.42. 7: colorless crystals; mp 154–155 °C (recrystallized from hexane); ^1H NMR ($CDCl_3$) δ 1.67 (s, relative intensity, 4 H), 1.70 (s, 2 H), 7.09–7.37 (m, 6 H), 7.61 (d, J = 7.9 Hz, 2 H); IR (KBr) 3040, 2970, 2890, 1460, 1420, 1020 cm^{-1}; MS (70 eV) m/z (relative intensity) 368 (27), 366 (52), 364 (27), 206 (100). Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; Br, 43.65. Found: C, 52.79; H, 3.94; Br, 42.95.

***cis*-Dimethylstilbene (8) in Scheme I.** To a solution of 6 (170.2 mg, 0.465 mmol) in 2.79 mL of ether at −78 °C was added dropwise 0.886 mL of a 1.05 N hexane solution of *n*-butyllithium

(0.930 mmol). The solution was warmed to room temperature and stirred for 1 h. To the reaction mixture at −20 °C was added water. The mixture was extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to give *cis*-dimethylstilbene (**8**) quantitatively. **8**: colorless crystals; mp 59–61 °C (recrystallized from methanol) (lit.[7] mp 66–67 °C); ^1H NMR ($CDCl_3$) δ 2.17 (s, 6 H), 6.93–7.11 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 21.43, 125.5, 127.5, 129.2, 132.9, 144.7; MS (70 eV) m/z (relative intensity) 208 (100), 193 (64), 178 (32).

***trans*-Dimethylstilbene (9) in Scheme I.** To a solution of **7** (75.1 mg, 0.205 mmol) in 1.23 mL of ether at −78 °C was added dropwise 0.391 mL of a 1.05 N hexane solution of *n*-butyllithium (0.411 mmol). The solution was warmed to room temperature and stirred for 1 h and then cooled down to −78 °C. To the reaction mixture was added water. The mixture was extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to give *trans*-dimethylstilbene (**9**) quantitatively. **9**: colorless crystals; mp 104–104.5 °C (recrystallized from methanol) (lit.[7] mp 105 °C); ^1H NMR ($CDCl_3$) δ 1.89 (s, 6 H), 7.22–7.42 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 22.56, 126.3, 128.2, 128.4, 133.1, 144.6; MS (70 eV) m/z (relative intensity) 208 (100), 193 (68), 178 (35).

Reaction of 10 with Selenium. A. 2 Equiv of Selenium in Scheme II. To a solution of **6** (0.279 g, 0.76 mmol) in 9.1 mL of ether at −78 °C was added dropwise 1.27 mL of a 1.2 N pentane solution of *tert*-butyllithium (1.52 mmol). The solution was warmed to room temperature and stirred for 1 h. To the mixture at −78 °C was added selenium (0.120 g, 1.52 mmol). After further stirring at −20 °C for 2 h, water was added to the reaction mixture. The mixture was acidified by 2 N HCl and extracted with ether. The organic layer was dried ($MgSO_4$) and evaporated to give the crude products containing **3** and **11**. The hexane-insoluble component of the crude products was purified by column chromatography on silica gel with hexane/$CHCl_3$ (8:2) to give 60.3 mg of **3** (18%) (R_f 0.4). The hexane-soluble component of the crude products was purified by preparative TLC (silica gel, hexane) to give 16.9 mg of **11** (5%) (R_f 0.5). **3**: orange crystals (from benzene); mp 175–176 °C dec; ^1H NMR ($CDCl_3$) δ 2.13 (s, 6 H), 6.93–7.12 (m, 6 H), 7.61 (d, 2 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.67, 127.6, 128.8, 129.5, 130.4, 135.7, 138.2, 149.2; ^{77}Se NMR ($CDCl_3$, relative to $(CH_3)_2Se$) δ 530.5, 782.0 ppm; IR (KBr) 3040, 1455 cm^{-1}; UV (methanol) λ_{max} (log ϵ) 273 nm (3.91), 345 (3.36) sh; MS (70 eV) m/z (relative intensity) 448 (6), 446 (14), 444 (18), 442 (14), 440 (8), 367 (12), 365 (36), 363 (34), 361 (20), 284 (64), 282 (36), 206 (34), 191 (100). Anal. Calcd for $C_{16}H_{14}Se_3$: C, 43.36; H, 3.18. Found: C, 43.72; H, 3.32. **11**: colorless crystals (from methanol); mp 144–144.5 °C (lit.[8] mp 143.5–144.5 °C); ^1H NMR ($CDCl_3$) δ 2.74 (s, 6 H), 7.59–7.64 (m, 4 H), 8.10–8.14 (m, 2 H), 8.69–8.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.05, 122.9, 124.7, 125.5, 126.6, 129.4, 129.5, 132.3; MS (70 eV) m/z (relative intensity) 206 (100), 191 (59).

B. 3 Equiv of Selenium in Scheme III. To a solution of **6** (0.211 g, 0.575 mmol) in 13.8 mL of ether at −78 °C was added dropwise 0.958 mL of a 1.2 N pentane solution of *tert*-butyllithium (1.52 mmol). The solution was warmed to room temperature and stirred for 1 h. To the mixture at −78 °C was added selenium (136.2 mg, 1.72 mmol). After further stirring at −20 °C for 4 h, water was added to the reaction mixture. The mixture was acidified by 2 N HCl and extracted with ether. The organic layer was dried ($MgSO_4$) and evaporated to give the crude products. The hexane-insoluble component of the crude products gave 173 mg (68%) of **3**.

C. 4 Equiv of Selenium in Scheme III. The same procedure as described above except using 4 equiv of selenium gave **3** in 60%.

Thermolysis of 3 in Scheme IV. The crystals of **3** (50 mg, 0.113 mmol) were heated without solvent at 180 °C for 1 h. After cooling to room temperature, chloroform was added to the solidified product and liberated selenium. The chloroform solution was filtered and concentrated in vacuo gave 38 mg (92%) of **12**. **12**: pale yellow crystals, mp 175–176 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.94 (s, 6 H), 7.16–7.35 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 22.54, 75.47, 125.56, 125.68, 128.6, 138.4, 144.3; ^{77}Se NMR ($CDCl_3$, relative to $(CH_3)_2Se$) δ 535.2 ppm; MS (70 eV) m/z (relative intensity) 366 (100), 364 (92), 362 (54); IR (KBr) 3040, 2960, 1575, 1420 cm^{-1}; UV (methanol) λ_{max} (log ϵ) 255 nm (4.27), 301 (3.50). Anal. Calcd for $C_{16}H_{14}Se_2$: C, 52.77; H, 3.87. Found: C, 52.56; H, 3.87.

Photolysis of 3. A solution of **3** (50 mg, 0.113 mmol) in 50 mL of THF was irradiated with a 100-W high-pressure mercury lamp and a Pyrex apparatus for 2.3 h at 0 °C. Removal of the solvent and column chromatography on silica gel with hexane/$CHCl_3$ (3:1) of the photolysate (R_f 0.3) gave **12** (21 mg, 51%) as an isolable product.

Thermolysis of 3 in Benzene. A. In the Absence of AIBN. A solution of **3** (194.0 mg, 0.438 mmol) in 46 mL of benzene was refluxed for 53 h. After cooling to room temperature, the solvent was removed in vacuo. ^1H NMR analysis showed that the residue consists of **3** and **12** in 73:27 ratio.

B. In the Presence of AIBN. A solution of **3** (21.6 mg, 0.049 mmol) and azobisisobutyronitrile (2.4 mg, 0.0146 mmol) in 5.1 mL of benzene was refluxed for 6 h. After cooling to room temperature, the solvent was removed in vacuo. Column chromatography (silica gel, hexane/$CHCl_3$ (8:2)) of the residue gave 5.3 mg of **3** (24%) (R_f = 0.4) and 13.5 mg of **12** (76%) (R_f = 0.3).

Crystal Structure Determination. 3. $C_{16}H_{14}Se_3$ in Figure 1 and Appendix 1. Single crystals of $C_{16}H_{14}Se_3$ were grown by slow evaporation from a benzene solution. A fragment, 0.2 × 0.2 × 0.4 mm was cut from a much larger crystal. The crystals are orthorhombic, space group *Pnma*,[11] with a = 12.527 (3), b = 15.796 (4), c = 7.782 (1) Å; V = 1540 (1) Å^3; d_{calc} = 1.91 g cm^{-3} for Z = 4 (M_r = 443.17). Intensity data were measured by the $\omega - 2\theta$ scan technique on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromatized Mo Kα radiation. Of 2587 reflections collected up to $2\theta = 60°$, 1234 reflections with $F_o > 3\sigma(F_o)$ were used in calculation. Empirical absorption correction was made (μ (Mo Kα) = 76.8 cm^{-1}). The structure was solved by the heavy atom method and refined by the full-matrix least-squares method. The function minimized was $\sum w(F_o - |F_c|)^2$, with $w = 1/(\sigma(F_o))^2$. All hydrogen atoms were located from difference syntheses. The final discrepancy indices were R = 0.030 and R_w = 0.038. Max. $\Delta\rho$ and min $\Delta\rho$ in the final difference Fourier map were 0.39 and −0.42 e Å^{-3}, respectively. The molecule has exact C_s symmetry. All calculations were carried out on a MicroVax II computer at Faculty of Science, Osaka University, with the TEXSAN structure analysis package.[12]

12. $C_{16}H_{14}Se_2$ in Figure 2 and Appendix 2. Single crystals of $C_{16}H_{14}Se_2$ were obtained from a benzene–hexane solution. The crystals are monoclinic, space group $P2_1/n$, with a = 10.3004 (8), b = 16.271 (2), and c = 8.2439 (7) Å; β = 98.62 (2)°; V = 1366.1 (2) Å^3; d_{calc} = 1.77 g cm^{-3} for Z = 4 (M_r = 364.21). Intensity data were measured by the ω–2θ scan technique on a Rigaku AFC-5R four-circle diffractometer with Ni-filtered Cu Kα radiation. The size of the crystal used for collection was 0.2 × 0.3 × 0.3 mm. Of 2178 reflections collected up to $2\theta = 125°$, 1975 reflections with $F_o > 2\sigma(F_o)$ were used in calculation. No absorption correction was made (μ (Cu Kα) = 74.5 cm^{-1}). The structure was solved by the heavy atom method[13] and refined by the block-diagonal least-squares method. The function minimized was $\sum w(F_o - |F_c|)^2$, with $w = \{(\sigma(F_o))^2 + 0.0323|F_o| + 0.0029|F_o|^2\}^{-1}$. All hydrogen atoms were located from difference Fourier map and their isotropic temperature factors were assumed to be equal to B_{eq} of their parent carbon atoms. The final discrepancy indices were R = 0.055 and R_w = 0.073. Max. $\Delta\rho$ and min $\Delta\rho$ in the final difference Fourier map were 2.03 and −2.0 e Å^{-3}, respectively. All calculations were carried out on an ACOSS-S900 computer at Research Center for Protein Engineering, Institute for Protein Research, Osaka University, with The Universal Crystallographic Computing System—Osaka.[14]

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(11) The systematic absences, $0kl$: $k + l = 2n$ and $hk0$: $h = 2n$, indicate the probable space group *Pnma* (No. 62) or $Pn2_1a$ (No. 33). The former was confirmed by a statistical distribution of E values and a successful refinement of the structure.

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Molecular Orbital (MO) Calculation of Model Compounds. A theoretical determination of the geometry is made using a model parent compound, 14, 15, or 16. This simplification comes from the computational restriction on the triselenide moiety. All the electrons are explicitly considered in the STO-3G basis set. All the MO calculations are carried out by using the GAUSSIAN 82 program.[15] Computed geometric parameters of 14 of C_s form are found to reproduce satisfactorily those of 3 in Figure 1 and Appendix 1. For instance, 2.333 Å of Se(19)–Se(18) bond in 14 is almost the same 2.3259 Å in 3. The MO calculation is needed to seek both possible isomers of 1 and transient 16-like intermediates during the reaction 3 → 12. Calculated results are given in Appendices 3 (14), 4 (15), and 5 (16), respectively.

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Appendix 1

(a) Positional and thermal parameters of 3 in the X-ray analysis. H(101) denotes, for instance, the first hydrogen attached to the methyl (the tenth) carbon.

	x	y	z	B_{eq}/B
Se(19)	0.06988(5)	1/4	0.14417(9)	4.09(3)
Se(18)	0.02848(4)	0.36763(3)	-.02278(6)	4.13(2)
C(16)	-.1223(4)	0.3790(2)	0.0183(5)	3.2(2)
C(15)	-.1554(4)	0.4270(3)	0.1587(5)	3.7(2)
C(14)	-.2625(4)	0.4396(3)	0.1881(6)	4.2(2)
C(13)	-.3366(4)	0.4046(3)	0.0788(7)	4.2(2)
C(12)	-.3036(4)	0.3566(3)	-.0601(6)	3.7(2)
C(11)	-.1962(3)	0.3424(2)	-.0927(5)	2.9(2)
C(1)	-.1635(3)	0.2918(2)	-.2475(5)	3.2(2)
C(10)	-.1359(5)	0.3446(4)	-.4036(7)	4.5(3)
H(15)	-.100(3)	0.450(2)	0.234(5)	3.2(9)
H(14)	-.284(3)	0.476(3)	0.291(5)	4(1)
H(13)	-.410(4)	0.416(3)	0.099(6)	5(1)
H(12)	-.354(3)	0.331(3)	-.134(5)	4(1)
H(101)	-.081(5)	0.390(4)	-.373(8)	8(2)
H(102)	-.101(6)	0.317(4)	-.483(8)	10(2)
H(103)	-.194(4)	0.379(3)	-.422(7)	7(2)

(b) Anisotropic thermal parameters of 3 in the X-ray analysis. The form is

$$\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$$

	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Se(19)	0.0486(4)	0.0540(4)	0.0529(4)	0	-.0099(3)	0
Se(18)	0.0479(3)	0.0552(3)	0.0536(3)	-.0111(2)	0.0014(2)	0.0074(2)
C(16)	0.054(2)	0.029(2)	0.037(2)	0.001(2)	-.004(2)	0.008(2)
C(15)	0.066(3)	0.039(2)	0.038(2)	-.006(2)	-.005(2)	0.000(2)
C(14)	0.077(3)	0.038(2)	0.045(2)	0.009(2)	0.007(2)	0.000(2)
C(13)	0.054(3)	0.048(3)	0.057(3)	0.012(2)	0.011(2)	0.005(2)
C(12)	0.051(3)	0.045(2)	0.047(3)	-.002(2)	-.004(2)	0.005(2)
C(11)	0.050(2)	0.031(2)	0.028(2)	-.000(2)	-.000(2)	0.008(2)
C(1)	0.047(2)	0.042(2)	0.031(2)	0.003(2)	-.003(2)	0.002(2)
C(10)	0.080(4)	0.054(3)	0.038(3)	0.000(3)	0.009(3)	0.011(2)

(c) Bond lengths (Å) and angles (deg) of 3 in Figure 1.

Se(19)-Se(18)	2.3259(7)	C(13)-C(12)	1.383(7)
Se(18)-C(16)	1.924(5)	C(12)-C(11)	1.388(6)
C(16)-C(15)	1.392(6)	C(11)-C(1)	1.502(5)
C(16)-C(11)	1.392(6)	C(1)-C(10)	1.514(6)
C(15)-C(14)	1.376(6)	C(1)-C(2)	1.320(8)
C(14)-C(13)	1.375(7)		

Se(18)-Se(19)-Se(17)	106.05(4)	C(13)-C(12)-C(11)	121.5(4)
Se(19)-Se(18)-C(16)	101.5(1)	C(12)-C(11)-C(16)	117.6(4)
C(15)-C(16)-C(11)	121.0(4)	C(16)-C(11)-C(1)	122.6(4)
Se(18)-C(16)-C(11)	120.7(3)	C(11)-C(1)-C(2)	122.1(2)
C(16)-C(15)-C(14)	120.0(4)	C(11)-C(1)-C(10)	114.4(4)
C(15)-C(14)-C(13)	119.8(4)	C(10)-C(1)-C(2)	123.4(3)
C(14)-C(13)-C(12)	120.1(5)		

Appendix 2

(a) Positional and thermal parameters of 12 in the X-ray analysis.

	x	y	z	B_{eq}/B
Se(17)	0.14330(7)	0.15413(4)	0.42080(7)	2.58(2)
Se(18)	-.02075(6)	0.30957(4)	0.61301(8)	2.45(2)
C(1)	0.2192(5)	0.2594(3)	0.5248(6)	2.1(1)
C(2)	0.1603(5)	0.2647(3)	0.6858(6)	1.9(1)
C(3)	0.1492(5)	0.1792(3)	0.7531(6)	1.9(1)
C(4)	0.1511(5)	0.1600(4)	0.9154(7)	2.4(2)
C(5)	0.1365(6)	0.0781(4)	0.9637(8)	2.7(2)
C(6)	0.1193(6)	0.0174(4)	0.8463(8)	2.9(2)
C(7)	0.1202(6)	0.0346(4)	0.6831(8)	2.8(2)
C(8)	0.1349(5)	0.1162(3)	0.6372(7)	2.1(1)
C(9)	0.2314(6)	0.3261(4)	0.8077(7)	2.4(1)
C(10)	0.3688(6)	0.2492(4)	0.5519(8)	2.7(2)
C(11)	0.1685(6)	0.3299(4)	0.4136(6)	2.2(1)
C(12)	0.2343(7)	0.3657(4)	0.2947(8)	3.2(2)
C(13)	0.1770(8)	0.4319(4)	0.2039(8)	3.7(2)
C(14)	0.0549(8)	0.4620(4)	0.2296(8)	3.7(2)
C(15)	-.0090(7)	0.4286(4)	0.3468(8)	3.1(2)
C(16)	0.0486(6)	0.3628(3)	0.4405(7)	2.3(1)
H(4)	0.169(7)	0.206(4)	1.016(8)	2.4
H(5)	0.153(6)	0.074(4)	1.093(8)	2.7
H(6)	0.110(6)	-.050(5)	0.871(8)	2.9
H(7)	0.110(6)	-.011(5)	0.581(8)	2.8
H(12)	0.313(7)	0.353(5)	0.296(8)	3.2
H(13)	0.214(7)	0.466(5)	0.125(9)	3.7
H(14)	0.006(7)	0.514(5)	0.168(10)	3.7
H(15)	-.089(7)	0.447(5)	0.358(9)	3.1
H(91)	0.229(7)	0.390(4)	0.736(8)	2.4
H(92)	0.171(7)	0.329(5)	0.903(8)	2.4
H(93)	0.313(7)	0.309(4)	0.834(9)	2.4
H(101)	0.414(7)	0.295(5)	0.636(8)	2.7
H(102)	0.406(6)	0.238(4)	0.453(8)	2.7
H(103)	0.398(7)	0.204(5)	0.619(8)	2.7

(b) Anisotropic thermal parameters of 12 in the X-ray analysis. The form is

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
Se(17)	0.01188(8)	0.00258(3)	0.0094(1)	0.00017(7)	0.0013(1)	-.00182(7)
Se(18)	0.00710(6)	0.00298(3)	0.0136(1)	0.00123(6)	0.0028(1)	0.00101(8)
C(1)	0.0076(6)	0.0024(2)	0.0093(8)	0.0001(5)	0.003(1)	-.0001(7)
C(2)	0.0060(5)	0.0023(2)	0.0099(8)	-.0001(5)	0.002(1)	-.0011(7)
C(3)	0.0058(5)	0.0024(2)	0.0098(8)	-.0004(5)	0.002(1)	0.0000(7)
C(4)	0.0070(6)	0.0028(2)	0.014(1)	0.0001(6)	0.005(1)	0.0005(8)
C(5)	0.0095(7)	0.0031(2)	0.014(1)	0.0007(7)	0.008(1)	0.0041(8)
C(6)	0.0102(7)	0.0026(2)	0.017(1)	-.0007(7)	0.009(1)	0.0023(8)
C(7)	0.0085(6)	0.0025(2)	0.018(1)	-.0007(6)	0.002(1)	-.0018(9)
C(8)	0.0068(5)	0.0022(2)	0.0119(9)	-.0006(5)	0.000(1)	0.0003(7)
C(9)	0.0084(6)	0.0028(2)	0.0117(9)	-.0016(6)	-.000(1)	-.0020(8)
C(10)	0.0073(6)	0.0041(3)	0.013(1)	0.0010(6)	0.003(1)	0.0012(8)
C(11)	0.0092(6)	0.0027(2)	0.0083(8)	-.0005(6)	0.001(1)	-.0003(7)
C(12)	0.0138(9)	0.0036(3)	0.012(1)	-.0002(8)	0.008(1)	0.0006(9)
C(13)	0.021(1)	0.0028(2)	0.011(1)	-.0020(9)	0.008(2)	0.0012(8)
C(14)	0.020(1)	0.0028(3)	0.012(1)	0.0016(9)	-.001(2)	0.0017(9)
C(15)	0.0132(8)	0.0027(2)	0.014(1)	0.0014(7)	-.003(1)	0.0008(9)
C(16)	0.0096(6)	0.0025(2)	0.0094(8)	-.0001(6)	0.000(1)	-.0007(7)

(c) Bond lengths (Å) and angles (deg) of 12 in Figure 2.

Se(17)-C(1)	2.019(5)	C(4)-C(5)	1.406(8)
Se(17)-C(8)	1.902(6)	C(5)-C(6)	1.375(9)
Se(18)-C(2)	2.009(5)	C(6)-C(7)	1.376(9)
Se(18)-C(16)	1.894(6)	C(7)-C(8)	1.395(8)
C(1)-C(2)	1.543(7)	C(11)-C(12)	1.400(9)
C(1)-C(10)	1.533(8)	C(11)-C(16)	1.394(8)
C(1)-C(11)	1.512(8)	C(12)-C(13)	1.391(11)
C(2)-C(3)	1.508(7)	C(13)-C(14)	1.396(12)
C(2)-C(9)	1.524(8)	C(14)-C(15)	1.361(11)
C(3)-C(4)	1.371(8)	C(15)-C(16)	1.399(9)
C(3)-C(8)	1.394(8)		

C(1)-Se(17)-C(8)	86.9(2)	C(4)-C(3)-C(8)	119.1(5)
C(2)-Se(18)-C(16)	87.3(2)	C(3)-C(4)-C(5)	120.3(5)
Se(17)-C(1)-C(2)	103.6(3)	C(4)-C(5)-C(6)	119.3(6)
Se(17)-C(1)-C(10)	106.7(4)	C(5)-C(6)-C(7)	121.5(6)
Se(17)-C(1)-C(11)	108.1(4)	C(6)-C(7)-C(8)	118.4(6)
C(2)-C(1)-C(10)	113.4(5)	C(7)-C(8)-C(3)	121.2(5)
C(2)-C(1)-C(11)	109.5(4)	Se(17)-C(8)-C(3)	112.9(4)
C(10)-C(1)-C(11)	114.8(5)	C(1)-C(11)-C(16)	115.4(5)
Se(18)-C(2)-C(1)	103.3(3)	C(12)-C(11)-C(16)	119.0(6)
Se(18)-C(2)-C(3)	109.1(3)	C(11)-C(12)-C(13)	119.2(6)
Se(18)-C(2)-C(9)	106.9(4)	C(12)-C(13)-C(14)	120.7(7)
C(1)-C(2)-C(3)	109.1(4)	C(13)-C(14)-C(15)	120.6(7)
C(1)-C(2)-C(9)	113.1(4)	C(14)-C(15)-C(16)	119.2(7)
C(3)-C(2)-C(9)	114.7(4)	C(15)-C(16)-C(11)	121.2(6)
C(2)-C(3)-C(8)	115.6(4)	Se(18)-C(16)-C(11)	112.8(4)

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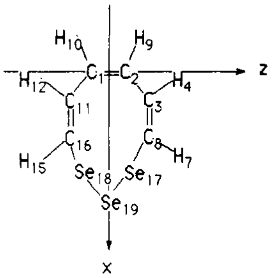
[15] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, PA, 1984.

Appendix 3

Geometries of two isomers (C_s and C_2 symmetries) of **14** given in cartesian coordinates. The ab initio MO calculation is carried out with the STO-3G basis set. Total energies are −7350.581 005 au (C_2) and −7350.745 151 au (C_s) (1 au = 627.52 kcal/mol). Angles ∠H(12)C(11)C(16), ∠H(15)C(16)C(11), ∠H(4)C(3)C(8), and ∠H(7)C(8)C(3) (= 120.0°) and the lengths C(11)–C(16) and C(3)–C(8) (=1.40 Å) are fixed during the optimization.



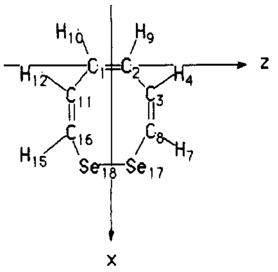
14

C_2	X(Å)	Y(Å)	Z(Å)
C(1)	0.0	0.0	-0.654812
C(2)	0.0	0.0	0.654812
C(3)	1.225931	0.0	1.555517
H(4)	1.707492	-0.947418	1.779626
H(7)	2.614716	1.162894	2.735072
C(8)	1.735274	1.188401	2.092427
H(9)	-0.957715	0.0	1.166828
H(10)	-0.957715	0.0	-1.166828
C(11)	1.225931	0.0	-1.555517
H(12)	1.707492	0.947418	-1.779626
H(15)	2.614716	-1.162894	-2.735072
C(16)	1.735274	-1.188401	-2.092427
Se(17)	1.075214	2.764346	1.823217
Se(18)	1.075214	-2.764346	-1.823217
Se(19)	2.665575	0.0	0.0

C_s	X(Å)	Y(Å)	Z(Å)
C(1)	0.0	0.0	-0.659535
C(2)	0.0	0.0	0.659535
C(3)	1.258189	0.0	1.494176
H(4)	1.664610	-0.993635	1.677347
H(7)	2.804485	1.010865	2.607873
C(8)	1.901622	1.127161	2.019060
H(9)	-0.939649	0.0	1.204055
H(10)	-0.939649	0.0	-1.204055
C(11)	1.258189	0.0	-1.494176
H(12)	1.664610	-0.993635	-1.677347
H(15)	2.804485	1.010865	-2.607873
C(16)	1.901622	1.127161	-2.019060
Se(17)	1.319175	2.919720	1.788618
Se(18)	1.319175	2.919720	-1.788618
Se(19)	2.667559	3.573293	0.0

Appendix 4

The geometry of the $n = 2$ C_s species, **15**, obtained through the RHF ab initio MO calculation with the STO-3G basis set. The total energy is −4976.409 287 au.

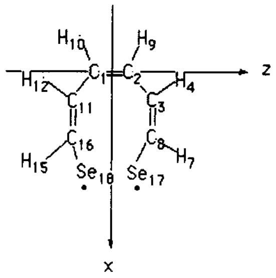


15

C_s	X(Å)	Y(Å)	Z(Å)
C(1)	0.0	0.0	-0.656552
C(2)	0.0	0.0	0.656552
C(3)	1.289480	0.0	1.432479
H(4)	1.636279	-0.962649	1.778076
H(7)	2.949498	1.080951	2.277633
C(8)	2.030813	1.153645	1.714487
H(9)	-0.919712	0.0	1.222705
H(10)	-0.919712	0.0	-1.222705
C(11)	1.289480	0.0	-1.432479
H(12)	1.636279	-0.962649	-1.778076
H(15)	2.949498	1.080951	-2.277633
C(16)	2.030813	1.153645	-1.714487
Se(17)	1.564961	2.904712	1.185118
Se(18)	1.564961	2.904712	-1.185118

Appendix 5

The geometry of the biradical intermediate **16** obtained through the UHF ab initio MO calculation with the STO-3G basis set. The C_2 symmetry is imposed on the geometry optimization. The total energy is −4976.403 302 au.



16

C_2	X(Å)	Y(Å)	Z(Å)
C(1)	0.0	0.0	-0.657854
C(2)	0.0	0.0	0.657854
C(3)	1.208985	0.0	1.544157
H(4)	1.319427	-0.879312	2.174313
H(7)	2.984891	0.847708	2.316613
C(8)	2.171412	1.014166	1.616290
H(9)	-0.958155	0.0	1.169977
H(10)	-0.958155	0.0	-1.169977
C(11)	1.208985	0.0	-1.544157
H(12)	1.319427	0.879312	-2.174313
H(15)	2.984891	-0.847708	-2.316613
C(16)	2.171412	-1.014166	-1.616290
Se(17)	2.188035	2.575842	0.653101
Se(18)	2.188035	-2.575842	-0.653101