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New Cyclic Dichalcogenonio-Selenuranes Induced by Transannular Multichalcogenides Participation

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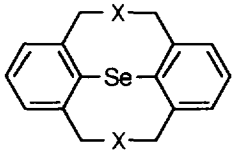
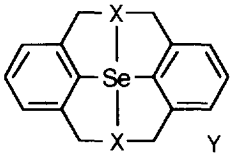
Abstract: The significant conformational change was found when cyclic chalcogenides, 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocin (**1**) and 1,11-(methanothiomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]selenathiocin (**3**), were dissolved in concentrated H_2SO_4; *i.e.*, the twin-chair forms of **1** and **3** in $CHCl_3$ were converted completely into the twin-boat forms of the selenurane dications **2** and **4** in H_2SO_4. Two-electron oxidation of **1** or **3** with 2 equiv of $NOPF_6$ gave the cyclic selenurane dication $2PF_6^-$ salt **2a** or **4a** which contains two selenonium or two sulfonium cations at the apical positions. The selenurane **2a** or **4a** could be reduced readily to neutral **1** or **3** upon treatment with PhSH, Ph_3P, phenothiazine, or SmI_2; that is, **2a** or **4a** acts as an oxidizing agent. Copyright © 1996 Elsevier Science Ltd

The chemistry of hypervalent selenuranes is much less developed than that of hypervalent sulfuranes, and sulfuranes with apical chalcogen or nitrogen ligands are little known.[1,2] Generally, sulfuranes and selenuranes bear two electronegative groups such as oxygen atoms or halogen atoms at the apical positions. Although we recently showed that the transannular interaction between two heteroatoms (Se-Se) of selenium heterocycles produced the diselenide dication, such behavior by fourth-row elements and multiheteroatoms has received less attention. As such an example, two-electron oxidation of a cyclic bis-selenide, 1,5-diselenacyclooctane, with nitrosyl tetrafluoroborate gave the diselenide dication salt.[3]

Most recently, we have found that the transannular multiheteroatoms interaction in quadruply *ortho*-bridged biphenyl ring system induced the hypervalent selenuranes containing transannular three-center bond. Namely, the transannular bond between the three chalcogen atoms (Se, S) of new cyclic chalcogenides, 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocin (**1**) and 1,11-(methanothiomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]selenathiocin (**3**), was formed in the oxidation of **1** and **3** with concd H_2SO_4 or 2 equiv of $NOPF_6$.[4] This multicenter chalcogenide participation provides a new hypervalent σ-selenurane with two apical selenonio or sulfonio ligands. Its selenurane dication undergoes a reversible two-electron reduction. Thus, two-electron redox reaction of **1** or **3** is accompanied by conformational changes of the chair and boat forms. This paper presents the preparation and the chemical property of new cyclic σ-selenuranes having two apical selenonio or sulfonio ligands, together with their interconvertible redox structures by multicenter heteroatom participation.



1 : X = Se
3 : X = S



2 : X = Se$^+$, Y = 2HSO_4^-
2a : X = Se$^+$, Y = 2PF_6^-
4 : X = S$^+$, Y = 2HSO_4^-
4a : X = S$^+$, Y = 2PF_6^-

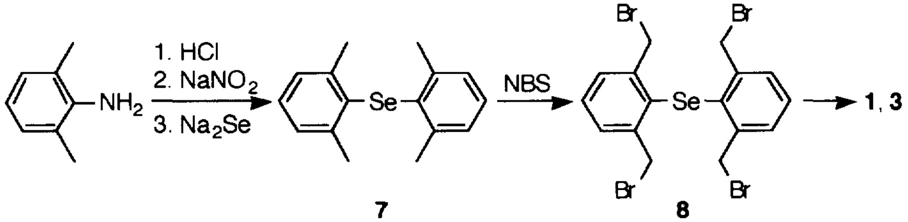
Results and Discussion

Synthesis of Cyclic Selenides

Compounds **1** and **3** were prepared as follows (Scheme 1). Treatment of the diazonium salt of 2,6-dimethylaniline with Na_2Se gave bis(2,6-dimethylphenyl)selenide (**7**) which was irradiated using a high-pressure mercury lamp after addition of *N*-bromosuccinimide (NBS) to afford the tetra-bromide **8**. The compound **8** was treated with Na_2Se or Na_2S using a high dilution technique at room temperature to give the compound **1** or **3**.

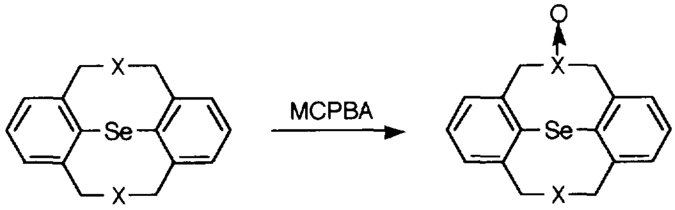
Oxidation of the selenides **1** and **3** with *m*-chloroperbenzoic acid (MCPBA) gave the corresponding oxides **5** and **6** (Scheme 2).

Scheme 1



7 **8**

Scheme 2



1 : X = Se
3 : X = S

5 : X = Se
6 : X = S

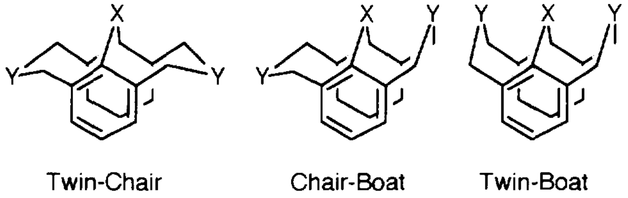
Conformation of Cyclic Selenides

The conformational behaviors in cyclic selenides **1** and **3** concerning eight-membered ring are of interest, because in general, three different conformers, *i.e.*, twin-chair, boat-chair, and twin-boat forms can exist as shown in Chart 1.

The conformers can be assigned by the ^{1}H NMR spectral data for the benzylic protons of the eight-membered ring.[5] The ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as an AB quartet peak at δ 3.88 and 5.33 (J = 12.8 Hz) which is assigned to the twin-chair form. The ^{1}H NMR spectra of **1** do not change over the temperature range from -50 °C (in $CDCl_3$) to +180 °C [in $(CD_3)_2SO$], indicating that **1** is conformationally rigid. The proton-coupled ^{77}Se NMR spectrum of **1** in $CHCl_3$ shows the two peaks at δ 209 (s, -SeAr) and at δ 366 (t, $^2J_{Se-H}$ = 31 Hz, $-SeCH_2Ar$).[6,7] Similarly, the ^{1}H NMR spectrum of **3** shows that **3** exists as a twin-chair form. These conformational analyses are consistent with that of the sulfur analogous compound of **1** and **3** which was characterized by X-ray diffraction method and the ^{1}H NMR spectroscopy.[8]

In such compounds, if one could generate a cationic species on the one group, the other functional group could interact to stabilize the cationic species, resulting in the generation of a transannular bond.

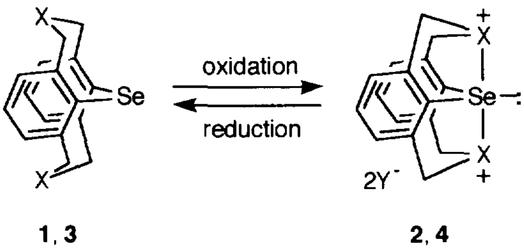
Chart 1



Dichalcogenoselenurane Dications

When tris-selenide **1** was dissolved in concd D_2SO_4 (98%) at room temperature,[9] the conformation of **1** in $CDCl_3$ was changed completely to the twin-boat form **2** in D_2SO_4 as shown by ^{1}H NMR spectroscopy, *i.e.*, the benzylic methylene protons appear at δ 4.07 and 4.59 (ABq, J = 16.0 Hz) (Scheme 3). This D_2SO_4 solution **2** was stable for several weeks and no deuterium exchange was observed at all. More significant spectroscopic evidence for the formation of **2** was obtained in the ^{77}Se NMR spectrum. The proton-noise-decoupled ^{77}Se NMR spectrum of the H_2SO_4 solution **2** exhibits two resonances at δ 544 ($-SeCH_2Ar$)[10] and at δ 817 (-SeAr) (ratio 2:1) indicating the remarkable downfield shift; the former resonance is assigned to the selenonium cation, and the latter peak to the selenurane structure, particularly, each peak exhibits two clearly resolved satellite peaks due to the ^{77}Se-^{77}Se coupling (large coupling constant of $^1J_{Se-Se}$ = 210 Hz) about each central peak. This observation of ^{77}Se satellites clearly indicates the occurrence of bond formation between the three selenium atoms.

Scheme 3



A selenurane $2PF_6^-$ salt **2a** was isolated from the two-electron oxidation of **1** with 2 equiv of $NOPF_6$, a one-electron-oxidant. The selenurane **2a** was stable and easily handled. The structure of **2a** in CH_3CN was analyzed by multinuclear NMR spectroscopy. Specially, the ^{77}Se NMR spectrum of **2a** shows two resonances at δ 535 ($-SeCH_2Ar$) and δ 830 (-SeAr), and the ^{77}Se satellites in the proton-decoupled ^{77}Se NMR spectrum of **2a** give a value of 200 Hz for $^1J_{Se\text{-}Se}$; *i.e.*, **2a** has the selenurane structure having two apical selenonium cations. The selenurane **2a** exists solely as a single conformer from -40 to +75 °C as evidenced by its ^1H NMR spectrum. The conformation of **2a** was fixed as the boat form by transannular bonds between the three selenium atoms, although normally the chair conformer has been shown to be more stable and rigid than the boat conformer.

Similarly, oxidation of **3** with concd H_2SO_4 or 2 equiv of $NOPF_6$ gave the selenurane **4** or its salt **4a**. The ^{77}Se NMR spectrum of **3** in $CHCl_3$ shows a singlet peak at δ 207, while **4a** in CH_3CN shows a singlet at δ 947 as characteristic of a selenurane. This is the first example of multicentered bond formation involving two-different chalcogens.

Reactivity of Dichalcogenoselenurane Dications

Reaction of benzenethiol (PhSH) (2 equiv) with **2a** (1 equiv) in CH_3CN under an Ar atmosphere at room temperature for 1 h gave diphenyl disulfide (PhSSPh) (87%) as the oxidation product and the neutral **1** (85%) as the reduction product.

Similar treatment of **2a** with triphenylphosphine (Ph_3P, 2 equiv) afforded **1** (90%) and the phosphine oxide ($Ph_3P{=}O$) (76%) after treatment with H_2O. Ph_3P is known to transfer electron to suitable acceptor resulting in the formation of its phosphinium cation radical which reacts with H_2O to give $Ph_3P{=}O$.[11]

The selenurane **2a** could also be reduced by phenothiazine (PTz, 2 equiv) in CH_3CN to give **1** (91%) by two-electron transfer, accompanied by the formation of the cation radical of PTz as evidenced by the UV-visible spectrum (λ_{max} = 437 and 515 nm).[12]

Interestingly, **2a** undergoes two-electron reduction to give **1** in quantitative yield by treatment with samarium (II) iodide, SmI_2,[13] at room temperature. From these novel results, an electron-transfer pathway is likely and **2a** is a good oxidant.

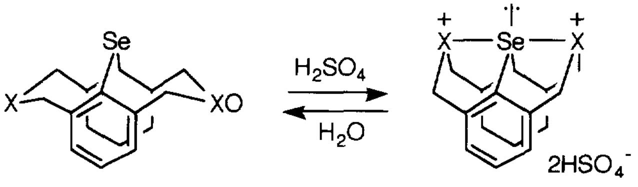
Reduction of **2a** was also facile electrochemically; the cyclic voltammetry of **2a** in CH_3CN revealed that the reduction potential is remarkably lower (-0.10 V *vs.* Ag/0.01 M $AgNO_3$) than that of some selenonium salts (ca. -1.5 to -1.8 V *vs.* Ag/0.01 M $AgNO_3$), though the electrochemistry of selenuranes and selenonium salts is virtually unknown.

Selenurane Dications from *Se*- and *S*-Oxides

The selenurane dication salts **2a** and **4a** reacted with H_2O to give the corresponding oxides **5** and **6**. The benzylic methylene protons in the ^1H NMR spectrum of the selenoxide **5** ($CDCl_3$) appears as two types of AB quartet peaks at δ 3.91, 5.29 (ABq, J = 13.5 Hz, 4H, CH_2) and 4.18, 5.94 (ABq, J = 11 Hz, 4H, CH_2) which are assigned to the twin-chair form. While, the ^{77}Se NMR spectrum of **5** in $CDCl_3$ exhibits three absorptions at δ 230 (s), 370 (t, $J_{Se\text{-}H}$ = 30.3 Hz) and 936 (t, $J_{Se\text{-}H}$ = 12.3 Hz), and its ^{13}C NMR spectrum shows the benzylic carbons at δ 32.4 and 61.4. Dissolution of the selenoxide **5** in concd D_2SO_4 led to the selenurane dication **2** as evidenced from the ^1H, ^{13}C and ^{77}Se NMR spectra (Scheme 4). Hydrolysis of a solution of the selenurane **2** in D_2SO_4 afforded exclusively the selenoxide **5**.

Analogous results were obtained in the sulfoxide **6**.

Scheme 4



5 : X = Se
6 : X = S

2, 4

Summary

The facile structural changes between chair and boat forms in the redox reactions of **1** and **3** are ascribed to the stabilization of the oxidized species by multicenter chalcogenide participation, *i.e.*, the formation of selenurane dications **2** and **4**, and the destabilization by transannular lone pair-lone pair repulsion of the neutral boat-forms derived from the reduction of the dications. Hydrolysis of the selenurane dications **2** and **4** led to the selenoxide **5** and the sulfoxide **6** which were converted into the dications **2** and **4** upon treatment with concd H_2SO_4. These hypervalent dichalocogenoselenuranes **2** and **4** containing Se-Se-Se and S-Se-S bond are new functional groups.

Experimental Section

All NMR spectra were measured on a JEOL LMN-EX-270, or a BRUKER MSL-400 spectrometer. IR spectra were obtained on a JASCO A-3 spectrometer. Mass spectra were taken with a Shimazu QP-2000 and a JEOL JMX SX102 mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this university. For cyclic voltammetry measurements, Hokuto Denko Co. Model HB-104 electrochemical apparatus was used in conjunction with a Yokokawa Co. Model 3025A X-Y recorder.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of Cyclic Tris-selenides 1 and 3. To 2,6-dimethylaniline (77 g, 0.6 mol) was added 6 N hydrochloric acid (160 ml). After cooling the resulting hydrochloride at 0 °C, to the stirred mixture was added an aqueous $NaNO_2$ (46 g, 0.64 mol) solution. Then, to a stirred solution of K_2Se (0.6 mol) was added the solution of the diazonium salt of 2,6-dimethylaniline at 40 °C and then the mixture was heated at 65 °C for 2 h. The organic layer was extracted with n-hexane. The mixture was purified by column chromatography (silica gel, eluent; n-hexane) and recrystallized from n-hexane to afford bis(2,6-dimethylphenyl)selenide (**7**) as white crystals in 11% yield. **7**: mp 84-85 °C; ^{1}H-NMR ($CDCl_3$) δ 2.27 (s, 12H, Me), 6.97-7.10 (m, 6H, ArH); ^{13}C-NMR ($CDCl_3$) δ 23.6. 127.3, 128.0, 133.0, 141.5; ^{77}Se-NMR ($CDCl_3$) δ 255 (s); MS, *m/z* 290 (M^+). Anal. Calcd for $C_{16}H_{18}Se$: C, 66.43; H, 6.27. Found: C, 66.41; H, 6.28.

The mixture of selenide **7** (6.4 g, 22.1 mmol) and *N*-bromosuccinimide (16.6 g, 92.8 mmol) in dry CCl_4 (350 ml) was irradiated using a high-pressure mercury lamp under an Ar atmosphere for 24 h. The resulting white precipitates were filtered and the mixture was purified by column chromatography (silica gel, eluent; n-hexane-$CHCl_3$) to afford tetra-bromide (**8**) as white crystals in 21% yield. **8**: mp 160-168 °C; ^{1}H-NMR ($CDCl_3$) δ 4.63 (s, 8H, Me), 7.28-7.36 (m, 2H, ArH), 7.40-7.46 (m, 4H, ArH); ^{13}C-NMR ($CDCl_3$) δ 34.2, 129.5, 132.0, 132.3, 141.9. Anal. Calcd for $C_{16}H_{14}SeBr_4$: C, 31.77; H, 2.33. Found: C, 31.59; H, 2.22.

To a stirred soluiton of tetra-bromide **8** (1.12 g, 1.85 mmol) in EtOH-CH_2Cl_2 (320 ml; 1:1) was added a solution of Na_2Se (3.7 mmol) in EtOH. After stirring at room temperature for 5 h, the resulting solid was separated by filtration and the residue was concentrated under vacuum. The mixture was purified by column chromatography (silica gel, eluent; $CHCl_3$) to give tris-selenide **1** in 32% yield. The tris-selenide **1** was further purified by recrystallization. **1**: mp 273-275 °C (decomp); ^{1}H-NMR ($CDCl_3$) δ 3.88, 5.33 (ABq, J = 12.8 Hz, 8H, CH_2), 6.97-7.01 (m, 4H, ArH), 7.07-7.13 (m, 2H, ArH); ^{13}C-NMR ($CDCl_3$) δ 32.9, 127.1, 130.3, 133.7, 149.3; ^{77}Se-NMR ($CDCl_3$) δ 209 (s), 366 (t, $J_{Se\text{-}H}$ = 31 Hz); MS, *m/z* 444 (M^+). Anal. Calcd for $C_{16}H_{14}Se_3$: C, 43.36; H, 3.18. Found: C, 43.33; H, 3.07.

Cyclic selenide **3** was prepared by the similar procedures as **1**. **3**: mp 271-274 °C (decomp); ^{1}H-NMR ($CDCl_3$) δ 3.79, 5.27 (ABq, J = 14.4 Hz, 8H, CH_2), 6.97-7.03 (m, 4H, ArH), 7.08-7.15 (m, 2H, ArH); ^{13}C-NMR ($CDCl_3$) δ 42.3, 127.8, 130.3, 134.5, 148.0; ^{77}Se-NMR ($CDCl_3$) δ 207 (s); MS, *m/z* 350 (M^+). Anal. Calcd for $C_{16}H_{14}S_2Se$: C, 55.00; H, 4.04. Found: C, 54.86; H, 3.94.

Preparation of Selenoxide 5 and Sulfoxide 6. To a solution of selenide **1** (200 mg, 0.45 mmol) in $CHCl_3$ (50 ml) was added a solution of *m*-chloroperbezoic acid (MCPBA; 97 mg, 0.45 mmol) in $CHCl_3$ (15 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for 3 h. The mixture was treated with ammonia and the crude product was purified with column chromatography (silica gel, eluent; $CHCl_3$-MeOH) to yield the selenoxide **5** (24% yield) and the recovered **1** (61%). ***Se*-oxide 5:** mp 230-235 °C (decomp); FT-IR (KBr) 820 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.91, 5.29 (ABq, J = 13.5 Hz, 4H, CH_2), 4.18, 5.94 (ABq, J = 11 Hz, 4H, CH_2), 7.08-7.14 (m, 2H, ArH), 7.19-7.30 (m, 4H, ArH); ^{13}C-NMR ($CDCl_3$) δ 32.4, 61.4, 128.7, 129.6, 130.9, 135.6, 137.1, 150.1; ^{77}Se-NMR ($CDCl_3$) δ 230 (s), 370 (t, $J_{Se\text{-}H}$ = 30.3 Hz), 936 (t, $J_{Se\text{-}H}$ = 12.3 Hz); MS, *m/z* 444 (M^+-16). Anal. Calcd for $C_{16}H_{14}OSe_3$: C, 41.85; H, 3.07. Found: C, 41.53; H, 3.17.

Similar oxidation of the sulfide **3** with MCPBA gave the sulfoxide **6** (54% yield). ***S*-oxide 6**: mp 287-290 °C (decomp); FT-IR (KBr) 1040, 1015 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.75, 5.27 (ABq, J = 14.6 Hz, 4H, CH_2), 4.45, 5.09 (ABq, J = 13.5 Hz, 4H, CH_2), 7.02-7.20 (m, 6H, ArH); ^{13}C-NMR ($CDCl_3$) δ 41.4, 58.6, 129.4, 129.8, 132.2, 134.0, 137.3, 146.7; ^{77}Se-NMR ($CDCl_3$) δ 227 (s); MS, *m/z* 366 (M^+). Anal. Calcd for $C_{16}H_{14}OS_2Se$: C, 52.60; H, 3.86. Found: C, 52.25; H, 3.87.

Reaction of Selenide 1 or 3 with Concentrated D_2SO_4. Selenide **1** or **3** was dissolved in concd D_2SO_4 (98%) at room temperature. The reaction was followed immediately by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. The D_2SO_4 solution was then poured into ice-water, and the solution was neutralized with dilute sodium hydroxide solution. The solution was extracted with chloroform and evaporated in vacuo. The product was purified by preparative liquid chromatography to afford the selenoxide **5** (71%) or the sulfoxide **6** (92%).

Spectral data for selenurane dications **2** and **4** in D_2SO_4 are presented as follows. **2**: ^{1}H-NMR (D_2SO_4) δ 4.07, 4.59 (ABq, *J* = 16.0 Hz, 8H, CH_2), 7.04 (d, *J* = 7.6 Hz, 4H, ArH), 7.33 (t, *J* = 7.6 Hz, 2H, ArH); ^{13}C-NMR (D_2SO_4) δ 41.3, 131.9, 134.8, 138.6, 142.3; ^{77}Se-NMR (D_2SO_4) δ 544 (t, $J_{Se\text{-}H}$ = 28.3 Hz), 817 (s). **4**: ^{1}H-NMR (D_2SO_4) δ 4.05, 4.61 (ABq, *J* = 17.3 Hz, 8H, CH_2), 7.13 (d, *J* = 7.6 Hz, 4H, ArH), 7.34 (t, *J* = 7.6 Hz, 2H, ArH); ^{13}C-NMR (D_2SO_4) δ 44.9, 130.1, 133.7, 139.1, 141.0; ^{77}Se-NMR (D_2SO_4) δ 918 (s).

Isolation of Diselenaselenurane Dication PF_6^- Salt (2a). A solution of $NOPF_6$ (83 mg, 0.45 mmol) in CH_3CN (7 ml) was added to tris-selenide **1** (100 mg, 0.23 mmol) in CH_2Cl_2 (15 ml) at -78 °C, and after 2 h the solution was allowed to come to 0 °C and stirred for an additional 3 h. After removal of solvent, the crude was recrystallized from ether-CH_2Cl_2-CH_3CN to afford the crystal **2a**. **2a**: 190 °C (decomp); ^{1}H-NMR (CD_3CN) δ 4.56, 5.06 (ABq, *J* = 15.8 Hz, 8H, CH_2), 7.53 (d, *J* = 7.6 Hz, 4H, ArH), 7.79 (t, *J* = 7.6 Hz, 2H, ArH); ^{13}C-NMR (CD_3CN) δ 39.7, 132.2, 135.3, 141.6; ^{77}Se-NMR (CD_3CN) δ 535 (t, $J_{Se\text{-}H}$ = 27.8 Hz), 830 (s); ^{31}P-NMR spectrum shows ^{31}P peak at δ -145 (sept, J_{PF} = 707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-. Anal. Calcd for $C_{16}H_{14}Se_3P_2F_{12}$: C, 26.21; H, 1.92. Found: C, 26.39; H, 1.82.

Isolation of Dithiaselenurane Dication PF_6^- Salt (4a). The selenurane **4a** was prepared by the same procedures as **2a**. **4a:** 180 °C (decomp); ^{1}H-NMR (CD_3CN) δ 4.60, 5.10 (ABq, *J* = 16.2 Hz, 8H, CH_2), 7.59 (d, *J* = 7.6 Hz, 4H, ArH), 7.78 (t, *J* = 7.6 Hz, 2H, ArH); ^{13}C-NMR (CD_3CN) δ 43.4, 131.0, 135.7, 140.5; ^{77}Se-NMR (CD_3CN) δ 947 (s); ^{31}P-NMR (CD_3CN) δ -145 (sept, J_{PF} = 707 Hz).

Reaction of Selenurane 2a with Benzenethiol. To a solution of selenurane dication salt **2a** (20 mg, 0.027 mmol) in anhydrous CH_3CN (3 ml) was added a solution of benzenethiol (5.5 μl, 0.054 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min. After usual work-up, the products were purified by silica-gel column chromatography (eluent, hexane-$CHCl_3$) to give selenide **1** (85% yield) and diphenyl disulfide (87% yield).

Reaction of Selenurane 2a with Triphenylphosphine. To a solution of selenurane dication salt **2a** (20 mg, 0.027 mmol) in anhydrous CH_3CN (3 ml) was added a solution of triphenylphosphine (15.4 mg, 0.059 mmol) in anhydrous CH_3CN (2.5 ml) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min. After usual work-up, the products were purified by silica-gel column chromatography (eluent, hexane-$CHCl_3$) to give selenide **1** (90% yield) and triphenylphosphine oxide (76% yield).

Reaction of Selenurane 2a with Samarium Iodide. To a solution of selenurane dication salt **2a** (10 mg, 0.014 mmol) in anhydrous THF (5 ml) was added a solution of SmI_2 (0.03 mmol) in anhydrous THF (5 ml) at 0 °C under an Ar atmosphere. The mixture was stirred for 30 min. After usual work-up, the products were purified by silica-gel column chromatography (eluent, hexane-$CHCl_3$) to give selenide **1** (99% yield).

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