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Preparation and Reactivity of Dichalcogenide (S, Se) Dication Salts from Medium-sized Cyclic Bis-sulfide and Bis-selenides

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Abstract: The disulfide dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (3), was isolated from the reaction of 1,5-dithiacyclooctane 1-oxide with trifluoromethanesulfonic anhydride. Two-electron oxidation of 1,5-diselenacyclooctane with two equivalents of $NOPF_6$ or $NOBF_4$ gave the first diselenide dication salt, 1,5-diselenoniabicyclo-[3.3.0]octane bis(hexafluorophosphate) or bis(tetrafluoroborate) (5). The disulfide and diselenide dication salts (3 and 5) act as an oxidant or as an electrophile depending on the added reagents.

The formation of disulfide dication containing sulfur-sulfur bond has been reported, but the reactivity of disulfide dication has not been well explored.[1-3] As typical example, Musker and co-workers reported that the oxidation of 1,5-dithiacyclooctane (**1**) and related compounds with 2 equiv of nitrosyl tetrafluoroborate gave the disulfide dications which were assigned their structures by ^{13}C NMR spectroscopy and elemental analyses.[1] We found that the reaction of 1,5-dithiacyclooctane 1-oxide (**2**) with concd H_2SO_4 afforded the bis(hydrogensulfate) salt of the dication of **1** which was very hygroscopic, becoming liquid on exposure to air .[2] Recently, we reported that the reaction of the sulfoxide **2** with trifluoromethanesulfonic anhydride gave the disulfide dication, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**3**), as a stable crystalline salt which was first analyzed its crystal structure by X-ray method.[3]

In contrast, no clear-cut example of transannular interaction between the two selenium atoms of cyclic bis-selenides and formation of diselenide dication has been hitherto known, except for our recent result.[4] Namely, we found that the two-electron oxidation of a new cyclic bis-selenide, 1,5-diselenacyclooctane (**4**), with nitrosyl hexafluorophosphate or tetrafluoroborate gave the diselenide dication, 1,5-diselenoniabicyclo-[3.3.0]octane bis(tetrafluoroborate) or bis(hexafluorophosphate) (**5**), as a remarkably stable crystalline salt in which the X-ray crystallographic analysis of **5** is consistent with the dicationic structure. This was the first example of an isolable dication salt containing a selenium-selenium σ-bond.[5] The diselenide dication salts of 1,6-diselenacyclodecane (**6**) and 1,4-diselenacyclohexane (**8**) were also formed in the two-electron oxidation of the selenides (**6** and **8**) with $NOBF_4$. This paper reports the preparation and the reactivity of the tetraalkyl substituted disulfide and diselenide dication salts from cyclic bis-sulfide and bis-selenides.

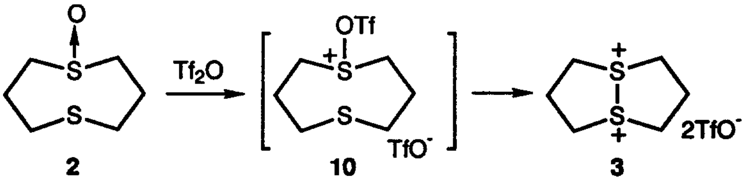
Results and Discussion

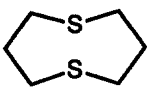
Preparation and Characterization of Disulfide and Diselenide Dication Salts

The disulfide dication $2CF_3SO_3^-$ salt **3** was obtained in the reaction of sulfoxide **2** with triflic anhydride, $(CF_3SO_2)_2O$, Tf_2O (Scheme 1). This reaction should proceed *via* the initial formation of the trifluoromethylsulfonyloxy sulfonium salt (**10**) which subsequently should be converted into the dication by a nucleophilic displacement of the trifluoromethanesulfonate ion by the remote second sulfur atom. The Pummerer rearranged products were not obtained at all. The ^1H NMR spectrum of **3** in CD_3CN shows multiplet peaks at δ 3.6-2.9 and 2.7-2.2 with a ratio of 2:1. The UV spectrum of **3** in CD_3CN exhibits λ_{max} at 231 nm with an extinction coefficient of 1.3×10^4. The X-ray analysis of dication triflate salt **3** indicates that the bond length of S(1)-S(5) is 2.126 Å which is only slightly longer than the normal S-S single bond (2.08 Å) in disulfides.[3b]

2,2,8,8-Tetradeuterated disulfide dication triflate salt **3**-d_4 was prepared by treatment of 2,2,8,8-tetradeuterated 1,5-dithiacyclooctane 1-oxide **2a**-d_4 with triflic anhydride.

Scheme 1





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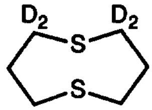
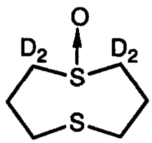
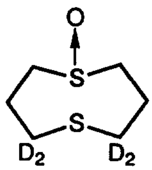


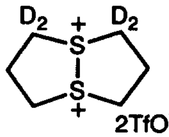
1-d_4



2a-d_4



2b-d_4

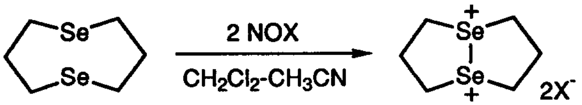


3-d_4

Two-electron oxidation of selenide **4** (1 equiv) with a one-electron-oxidizing agent, nitrosyl hexafluorophosphate, $NO^+PF_6^-$ (2 equiv) in anhydrous CH_2Cl_2-CH_3CN gave a diselenide dication, 1,5-diselenoniabicyclo[3.3.0]octane bis(hexafluorophosphate) (**5**), as a stable crystalline salt (Scheme 2). The dication salt **5** in solution was characterized by spectroscopic means. The ^{13}C NMR spectrum of **5** in CD_3CN shows two peaks at δ 52.6 and 35.3, while the ^1H NMR spectrum of **5** in CD_3CN shows multiplet peaks at δ 4.39-3.91 and 3.85-2.92 in a ratio of 2 : 1 (Table 1). Both the ^1H and ^{13}C NMR spectra indicate downfield shifts for the dication **5** compared to its starting selenide **4**. The ^{77}Se NMR spectrum of selenide **4** in $CHCl_3$ shows a singlet peak at δ 141.3 (relative to Me_2Se), while the dication **5** in CH_3CN shows a singlet at δ 806.5. This is a remarkable downfield shift, consistent with a dicationic structure for **5**. Generally, the ^{77}Se chemical shifts of dialkyl-selenide, -diselenide, and -selenonium salt (relative to Me_2Se) are: δ 217 for Et_2Se, 319 for $(EtSe)_2$, and 325 for $Et_2MeSe^+ I^-$.[6] The UV spectrum of **5** in CH_3CN exhibits λ_{max} at 248 nm with an extinction coefficient of 1.3×10^4. The dicationic $2BF_4^-$ salt **5a** was also prepared by the oxidation of **4** with 2 equiv of $NOBF_4$ in CH_2Cl_2-CH_3CN. The X-ray crystal structure of dication salt **5a** shows that the Se(1)-

Se(5) length is 2.382 Å which is only slightly longer than the normal Se-Se single bond (2.34 Å).[5] The NMR spectral data are shown in Table 1.

Scheme 2



4

5 : X = PF_6
5a : X = BF_4

Table 1. NMR Spectral Data for Compounds 4-9[a]

Compd	Chemical shift, δ		
	^1H	^{13}C	^{77}Se
4	3.02-2.71 (m, 8H), 2.42-2.05 (m, 4H)	30.9, 23.4	141.3
5	4.39-3.91 (m, 8H), 3.85-2.92 (m, 4H)	52.6, 35.3	806.5
6	3.25-2.88 (m, 8H), 2.28-1.89 (m, 8H)	30.2, 28.1	165.7
7	4.02-3.61 (m, 8H), 2.45-2.05 (m, 8H)	37.8, 21.1	439.1
8	3.08 (s)	20.4	206.9
9	4.25 (br s)	47.0	1202.0

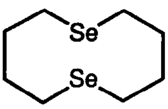
a) ^1H and ^{13}C NMR data for 4, 6, and 8 in $CDCl_3$; 5, 7, and 9 in CD_3CN relative to Me_4Si. ^{77}Se NMR data for 4, 6, and 8 in $CHCl_3$; 5, 7, and 9 in CH_3CN relative to Me_2Se.

Meanwhile, treatment of bis-selenide 4 with *m*-chloroperbenzoic acid (mCPBA) gave a complex mixture, and none of the corresponding selenoxide of 4 was obtained. Normally selenoxides having β-hydrogen atoms undergo elimination to afford olefins.[6]

Two-Electron Oxidation of Six- and Ten-Membered Ring Bis-selenides

The ten-membered ring bis-selenide, 1,6-diselenacyclodecane (6), was treated with 2 equiv of $NOBF_4$ in the same manner as 5 to give the dication salt 7 which gives the correct elemental analysis. The ^1H, ^{13}C, and ^{77}Se-NMR spectral data of 7 are consistent with the dicationic structure (Table 1).

In 1,4-diselenacyclohexane (8), the transannular interaction of the two selenium atoms at 1,4-positions should be minimal. However, the stable diselenide dication, 1,4-diselenoniabicyclo[2.2.0]hexane bis(tetrafluoroborate) (9) could be obtained from the oxidation of 8 with 2 equiv of $NOBF_4$. The ^{77}Se NMR spectrum of 9 in CH_3CN shows a remarkable downfield shift compared to those of the dications 5 and 7 (Table 1).



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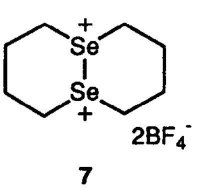

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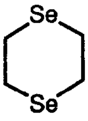

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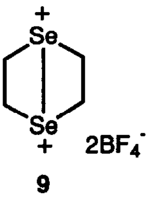

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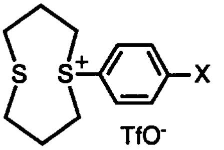
Reactivity of Dication Salts toward Nucleophiles

The possible reaction modes of dications **3** and **5** with nucleophiles and bases are as follows; *i.e.*, nucleophiles are expected to attack on either the sulfur and the selenium atoms or the α-carbons of **3** and **5**, and bases are expected to abstract the α-protons of **3** and **5**.

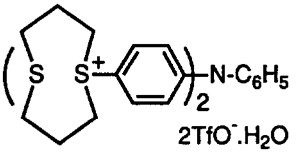
S-Dication **3** reacted with H_2O to give the mono-sulfoxide **2** in quantitative yield. While, hydrolysis of the triflate salt **3**-d_4 led to the *S*-oxide in 93% yield, and its ^{1}H NMR spectrum of the *S*-oxide formed indicates that it is a 1:1 mixture of 2,2,8,8- and 4,4,6,6-tetradeuterated *S*-oxides **2a**-d_4 and **2b**-d_4. This result shows that the two sulfur atoms in **3**-d_4 should have the positive charges equivalently. In contrast to **3**, *Se*-dication **5** was stable in H_2O (*vide infra*).

The reaction of *S*-dication **3** (1 equiv) with aniline (**11**) in CH_3CN at 0 °C for 3 h gave the corresponding *para*-substituted sulfonium salt **15** in 63% yield. Similar treatment of triphenylamine (**12**) with **3** led to the corresponding monosulfonium salt **16** (40%) together with disubstituted product **16a** (22%). When phenol (**13**) was similarly treated with **3**, the sulfonium salt **17** was obtained in 81% yield. On the other hand, anisole (**14**) did not react with **3**, though it is well known that **14** reacts with heterosulfonium cations to produce the corresponding aryl sulfonium salts.[7] The unreactivity of **14** toward **3** seems to be due to the higher oxidation potential of **14** than those of **11**, **12**, and **13**.[8] These observations are quite different from those of the reactions of aromatic sulfide cation radical such as thianthrene cation radical ($Th^{\cdot +}$) with **11** and **14**. Namely, $Th^{\cdot +}$ reacts with **14** to give the *para*-substituted product,[9,10] whereas the reaction of $Th^{\cdot +}$ with **11** affords the oxidation products instead of the substitution products.[10] This distinct difference in reactivity between **3** and $Th^{\cdot +}$ is probably due to the difference in the oxidation potentials of their precursors.[11]

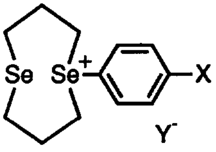
The reaction of *Se*-dication **5** with aniline in CH_3CN at room temperature afforded the corresponding *para*-substituted selenonium salt, 1-(4-aminophenyl)-5-selena-1-selenoniacyclooctane hexafluorophosphate (**18**), in 55% yield. Similar treatment of *N,N*-dimethylaniline with the dication $2BF_4^-$ salt **5a** led to the selenonium salt **19** in 68% yield. Thus, the dications **3** and **5** act as an electrophile toward aromatics.



15 X = NH_2
16 X = $N(C_6H_5)_2$
17 X = OH



16a



18 X = NH_2 Y = PF_6
19 X = NMe_2 Y = BF_4

In contrast to the above aromatics, treatment of benzenethiol (PhSH) (2 equiv) with *S*-dication **3** gave diphenyl disulfide (86%) as the oxidation product and sulfide **1** (84%) as the reduction product. Analogous result was obtained in the reaction of *Se*-dication **5** with benzenethiol. In these cases, the dications work as an oxidizing agent.

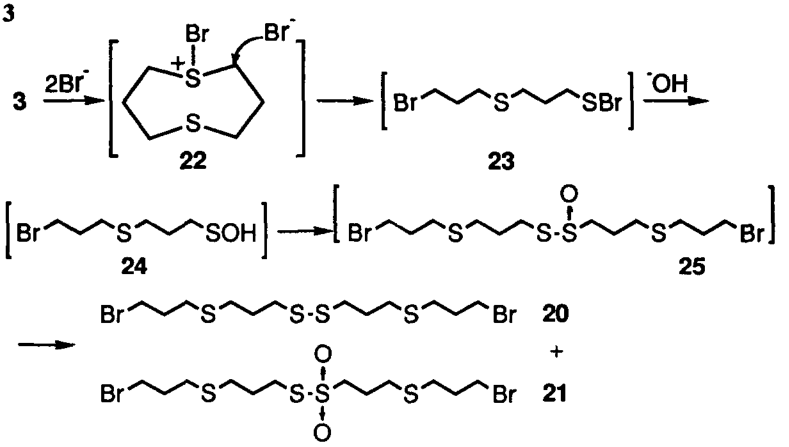
$$3 + PhSH \longrightarrow 1 + PhSSPh$$

Similarly, the reaction of *S*-dication **3** (1 equiv) with 1,2-diphenylhydrazine (PhNHNHPh) (1 equiv) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) gave the redox products such as sulfide **1** (73%) and azobenzene (PhN=NPh) (71%), and none of substitution products were obtained.

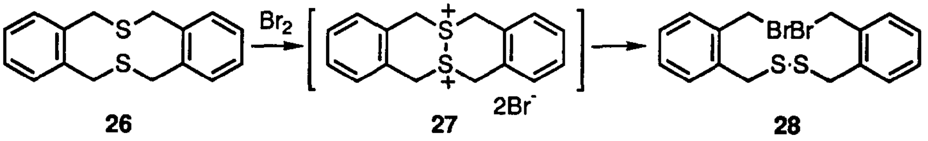
$$\mathbf{3} + \mathrm{PhNHNHPh} \longrightarrow \mathbf{1} + \mathrm{PhN{=}NPh}$$

The *S*-dication **3** could be reduced to the sulfide **1** upon treatment with 2 equiv of KI or n-$Bu_4N^+I^-$, and KCl, and KF in CH_3CN at room temperature for 1 h. The following yields are given: sulfide **1** (50%) and sulfoxide **2** (49%) for KI, **1** (52%) for KCl, and **1** (25%) and **2** (72%) for KF. The sulfoxide **2** was produced after treatment of the reaction mixture with H_2O. However, when *S*-dication **3** was treated similarly with KBr, the disulfide **20** (15%), the thiosulfonate **21** (16%), and **2** (61%) were obtained (Scheme 3). These compounds **20** and **21** might be formed in the following pathway. The sulfenylbromide **23** was generated *via* a sulfonium cation **22**, which converts the sulfenic acid **24** by the hydrolysis and then **24** dimerized to form the thiosulfinate **25** which finally undergoes disproportionation to give **20** and **21**. Similar reaction mechanism has been proposed that the reaction of 2,5,7,10-tetrahydrodibenzo[*c*,*h*]-1,6-dithiecin (**26**) with bromine gave disulfide **28** presumably *via* an intermediacy of disulfide dication **27** (Scheme 4).[1b]

Scheme 3



Scheme 4



On the other hand, the reaction of *Se*-dication **5** with halide ions resulted in the formation of a complex mixture which could not be characterized.

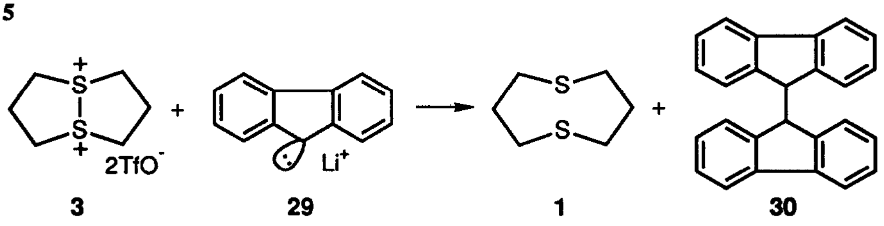
Redox Reaction of Dications with Carbanion and Alkoxide

Surprisingly, when the *S*-dication **3** was treated with organolithium reagent, only the redox reaction took place. No hydrogen atom abstraction of **3** by the strong base was observed, although normal sulfonium ion salts bearing α-protons do easily undergo deprotonation to give the sulfur ylides.[12]

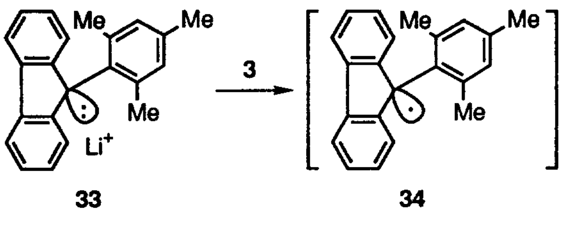
Treatment of fluorenyllithium **29** (1 equiv) with dication **3** (1 equiv) gave the oxidative coupling dimer, $\Delta^{9,9'}$-bifluorene (**30**) (20%), **1** (42%), fluorene (**31**) (58%), and **2** (46%) (Scheme 5). The products **2** and **31** could be formed mainly when the reaction mixture was treated with H_2O. In this reaction the carbanion **29** can act as one electron donor toward dication **3** to form the corresponding radical which dimerizes to produce the oxidative dimer **30**. Carbanion **29** has been known to transfer the electrons to suitable acceptors resulting in the formation of oxidative dimer.[13] In order to confirm the formation of radical intermediate in the reaction of carbanion with dication **3**, 9-mesitylfluorene (**32**) was prepared. When a solution of 9-mesitylfluorenyl-lithium (**33**) (1 equiv) in anhydrous THF was added to a solution of **3** (1 equiv) in anhydrous THF under an Ar atmosphere at -78 °C, the solution became immediately green. Its UV-visible spectrum shows at λ_{max} 494, 464, 338, 329, 289, and 280 nm which are consistent with that previously reported for the 9-mesitylfluorenyl radical **34** (Scheme 6).[14] The ESR spectrum of the radical **34** is quite complex.[14] The corresponding radical cation derived from dication **3** could not be characterized, since the absorption of the cation radical of **1** overlaps at 420 nm in CH_3CN.[1] This finding shows that 9-mesitylfluorenide (**33**) was oxidized to its radical **34** by dication **3**. The free radical **34** does not dimerize due to the steric hindrance.[14] Treatment of this solution with H_2O gave sulfide **1** as the reduction product (50%) together with **2** (20%) and **32** (62%). This result clearly indicates that the reaction of dication **3** with carbanion **29** or **33** should proceed *via* an electron-transfer as a major pathway. Similarly, several bases such as sodium methoxide, *tert*-butoxide, *tert*-butyllithium, and lithium diisopropylamide also act as reductant toward dication **3**.

The reaction of *Se*-dication **5** (1 equiv) with fluorenyllithium **29** (1 equiv) afforded the bis-selenide **4** (43%), $\Delta^{9,9'}$-bifluorene **30** (22%), and fluorene **31** (47%).

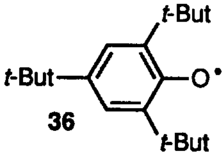
Scheme 5



Scheme 6



Diselenide dication **5** was reduced to selenide **4** upon treatment with sodium 2,4,6-tri-*tert*-butylphenoxide (**35**) (1 equiv). This reaction likely proceeds *via* an electron transfer process as evidenced from its UV-visible spectrum; *i.e.*, the UV-visible spectrum of a solution of **5** and **35** in THF exhibits the absorptions at λ_{max} = 401 and 382 nm which indicate the formation of the corresponding phenoxy radical (**36**).[15b] The dimeric peroxide **37** from **36** was obtained after work-up of the reaction mixture, namely the radical **36** reacted with oxygen to give the peroxide **37**.[15a]



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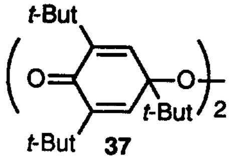

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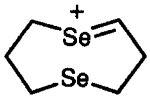
Reduction of Diselenide Dication Salt

The *Se*-dication salt **5** could not be hydrolyzed with H_2O as evidenced by ^1H, ^{13}C, ^{77}Se, and ^{31}P-NMR spectroscopy, although the disulfide dication salt **3** was easily hydrolyzed to the corresponding sulfoxide (*vide supra*). A solution of **5** in D_2O-CD_3CN was followed by NMR spectroscopy and no significant changes were observed over several hours.[16] Compound **5** was recovered in a good yield after addition of H_2O, and could again act as an oxidant, *e.g.*, the reaction of 1,2-diphenylhydrazine (**38**) with the dication in the presence of DABCO afforded azobenzene (**39**) (90%) and selenide **4** (72%).

The *Se*-dication **5** in H_2O-CH_3CN also works as an oxidant toward Na_2S. Treatment of **5** (1 equiv) with sodium sulfide ($Na_2S \cdot 9H_2O$, 1 equiv) in CH_3CN-H_2O under an Ar atmosphere at room temperature for 3 h resulted in selenide **4** as the reduction product (76%) and elemental sulfur as the oxidation product (72%).

The *Se*-dication salt **5** can be reduced quantitatively to selenide **4** on treatment with sodium borohydride ($NaBH_4$, 2.5 equiv) in H_2O-EtOH at room temperature. In contrast, Alder and co-workers reported the deprotonation of the hydrazinium dication salt, namely, the reduction of a hydrazinium dication, 1,5-diazoniatricyclo[3.3.3.0]undecane bis(tetrafluoroborate) (**48**), with $NaBD_4$ in either H_2O or D_2O gives the [3.3.3]-diamine with one deuteriun incorporated at α-carbon; this reaction proceeds *via* the corresponding iminium intermediate.[16] Accordingly, the dication **5** was treated with sodium borodeuteride, $NaBD_4$, in H_2O or D_2O. However, no H-D exchange was observed in the bis-selenide **4** at all after the reaction. This result indicates that the mechanism involving the intermediate formation of **40** can be ruled out. This borohydride reduction probably goes *via* an electron transfer mechanism rather than the elimination-addition in the case of the hydrazinium dication **48**.[17] Analogously, $LiAlH_4$ (or $LiAlD_4$) also acts as a reductant toward **5**.



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We have discovered a simple direct means of preparing new dichalcogenide dications; *i.e.*, the disulfide dication salt was formed by the substitution reaction of 1,5-dithiacyclooctane *S*-oxide with triflic anhydride and the diselenide dication was prepared from the two-electron oxidation of cyclic bis-selenide. The X-ray crystal analyses of those dications provide the first evidence for the σ-bonding dichalcogenide dication. The diselenide dication acts as an oxidizing agent even in the presence of water, however the disulfide dication is easily hydrolyzed to the sulfoxide. Both dichalcogenide dications behave as an oxidant and as an electrophile.

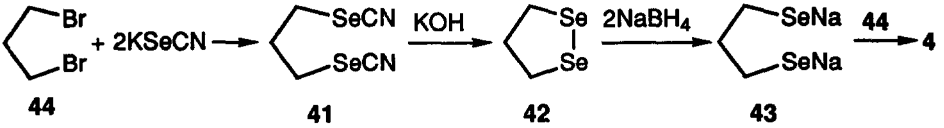
Experimental Section

IR spectra were obtained on a JASCO A-3 spectrometer. UV spectra were obtained on a JASCO Ubest-50 spectrometer. ^1H and ^{13}C NMR spectra were measured on a Hitachi R-600 FT-NMR, a JEOL FX 100, or a Bruker A 500 spectrometer. For the ^1H and ^{13}C NMR spectra, the chemical shifts are given in δ values from tetramethylsilane (TMS) as the internal standard. ^{77}Se NMR (76 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker MSL 400 NMR spectrometer. The chemical shifts of ^{77}Se NMR spectra are given in δ values from dimethyl selenide as the external standard and the chemical shifts of ^{31}P NMR spectra are given in δ values from phosphoric acid as the external standard. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this University.

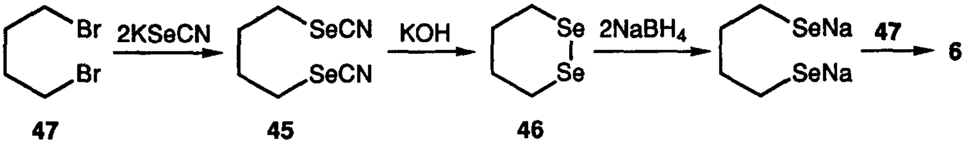
All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. Nitrosyl hexafluorophosphate ($NOPF_6$) was supplied by Morton Thiokol, Inc. The reagents used as reaction solvents were further purified by general methods.

1,5-Dithiacyclooctane (**1**), 1,5-dithiacyclooctane 1-oxide (**2**), and 2,2,8,8-tetradeuterated 1,5-dithiacyclooctane 1-oxide (**2a**-d_4) were prepared according to our previous paper.[2,18]

Scheme 7



Scheme 8



Synthesis of Cyclic Bis-selenides. The cyclic bis-selenides (**4** and **6**) were synthesized by the methods as illustrated in Schemes 7 and 8. 1,3-Diselenacyanopropane (**41**), 1,2-diselenolane (**42**), 1,4-diselenocyanobutane (**45**), cyclodiselenohexane (**46**), and 1,4-diselenacyclohexane (**8**) were prepared according to the methods reported in the literature;[19-21] **41**: mp 50-51 °C (lit.[19] 51 °C); **42**: mp 58-59 °C (lit.[19] 59 °C); **45**: mp 40-41 °C (lit.[20] 40 °C); **46**: mp 40-41 °C (lit.[20] 41-42 °C); **8**: mp 112-113 °C (lit.[21] 112 °C).

1,5-Diselenacyclooctane (**4**). To a solution of cyclic diselenide **42** (4.08 g, 20.4 mmol) in benzene-ethanol (500 mL, 2/3) was added sodium borohydride ($NaBH_4$) (1.71 g, 45.2 mmol) at room temperature. The diselenide **42** was reduced quantitatively to sodium propane-1,3-diselenolate **43**. To a solution of **43** (5.01 g, 20.4 mmol) in benzene-ethanol (500 mL, 2/3) was added a solution of 1,3-dibromopropane (4.12 g, 20.4 mmol) in benzene (100 mL) at 50 °C. The whole mixture was stirred for 6 h. After evaporation of the solvent, the residue was extracted with benzene. The organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the yellow oil was purified by silica-gel column chromatography (eluent, hexane-benzene, 1/1) to give 1,5-diselenacyclooctane (**4**) in 45% yield. Bis-selenide **4** was further purified by preparative liquid chromatography (Japan Analytical Co. Ltd.; Model LC-09). **4**: colorless liquid; IR (neat, cm^{-1}) 608 and 571; MS, *m/z* 244 (M^+, ^{80}Se). Anal. Calcd for $C_6H_{12}Se_2$: C, 29.77; H, 5.00. Found: C, 29.75; H, 5.02. The spectral data are listed in Table 1.

1,6-Diselenacyclodecane (6). Compound **6** was synthesized by the same procedure as **4**. 1,6-Diselenacyclodecane (**6**): yield 3%; colorless solid; mp 65-66 °C; IR (KBr, cm^{-1}) 604 and 568; MS, *m/z* 272 (M^+, ^{80}Se). Anal. Calcd for $C_8H_{16}Se_2$: C, 35.57; H, 5.97. Found: C, 35.55; H, 6.04. The spectral data are listed in Table 1.

Preparation of 1,5-Dithioniabicyclo[3.3.0]octane Bis(trifluoromethanesulfonate) (3). To a solution of 1,5-dithiacyclooctane 1-oxide (**2**) (215 mg, 1.31 mmol) in anhydrous CH_2Cl_2 (10 mL) was added a solution of triflic anhydride (369 mg, 1.31 mmol) in anhydrous CH_2Cl_2 (10 mL) at -20 °C under an Ar atmosphere. Standing for 3 h, colorless solid was precipitated. After filtration, the solid was dried in vacuo to give the dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**3**) in 83% yield. The dication **3** was recrystallized from anhydrous CH_3CN. **3**: colorless crystals; mp 100-102 °C; UV (CH_3CN) λ_{max} 231 nm (ε=1.3 X 10^4); ^1H NMR (CD_3CN) δ 3.6-2.9 (m, 8H, S^+CH_2) and 2.7-2.2 (m, 4H, CH_2). Anal. Calcd for $C_8H_{12}F_6O_6S_4$: C, 21.42; H, 2.71. Found: C, 21.52; H, 2.70.

2,2,8,8-Tetradeuterated disulfide dication salt, **3**-*d*$_4$, was obtained by the reaction of the corresponding 2,2,8,8-tetradeuterated sulfoxide, **2a**-*d*$_4$, with $(CF_3SO_2)_2O$ according to the same procedures as dication salt **3**. The deuterium content was determined by ^1H NMR spectroscopy.

Preparation of 1,5-Diselenoniabicyclo[3.3.0]octane Bis(hexafluorophosphate) (5). To a solution of 1,5-diselenacyclooctane (**4**) (518 mg, 2.14 mmol) in anhydrous CH_2Cl_2 (20 mL) was added a solution of nitrosyl hexafluorophosphate ($NOPF_6$) (749 mg, 4.28 mmol) in anhydrous CH_2Cl_2-CH_3CN (10 mL, 2/3) at -78 °C under an Ar atmosphere. The mixture was stirred at -78 °C under an Ar atmospher for 1 h and allowed to come to 0 °C for 2 h. NO gas was removed several times in vacuo during the reaction. A colorless crystal precipitated was separated by filtration and dried in vacuo to give the salt **5** in 86% yield, which was recrystallized from CH_2Cl_2-CH_3CN. Dication $2PF_6^-$ salt **5**: colorless crystals; mp 116-117 °C (decomp); UV (CH_3CN) λ_{max} 248 nm (ε=1.3 X 10^4); ^{31}P NMR (CH_3CN) δ -143.4 (sept, J_{PF} = 708 Hz) (relative to H_3PO_4). Anal. Calcd for $C_6H_{12}F_{12}P_2Se_2$: C, 13.55; H, 2.27. Found: C, 13.95; H, 2.43. The spectral data are listed in Table 1.

The dication $2BF_4^-$ salt **5a** was obtained by the reaction of **4** with 2 equiv of $NOBF_4$ in CH_2Cl_2-CH_3CN. **5a**: colorless crystals, mp 91-92 °C (decomp). Anal. Calcd for $C_6H_{12}F_8B_2Se_2$: C, 17.34; H, 2.91. Found: C, 17.18; H, 2.88.

Other diselenide dications, 1,6-diselenoniabicyclo[4.4.0]decane bis(tetrafluoroborate) (**7**) (76%) and 1,4-diselenoniabicyclo[2.2.0]hexane bis(tetrafluoroborate) (**9**) (72%) were obtained by the same procedure as **5**. **7**: colorless crystals; mp 116-117 °C (decomp). Anal. Calcd for $C_8H_{16}B_2F_8Se_2$: C, 21.65; H, 3.63. Found: C, 21.29; H, 3.76. **9**: colorless crystals; mp 130-131 °C (decomp). Anal. Calcd for $C_4H_8B_2F_8Se_2 \cdot 2CH_2Cl_2$: C, 12.93; H, 2.17. Found: C, 13.24; H, 2.37. The spectral data of **7** and **9** are listed in Table 1.

Hydrolysis of Disulfide Dication Salt 3. Disulfide dication salt **3** was treated with aqueous $NaHCO_3$ solution in ice-bath. The mixture was extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous $MgSO_4$. After removal of the solvent, the sulfoxide **2** was obtained in quantitative yield.

Hydrolysis of 2,2,8,8-tetradeuterated disulfide dication salt **2a**-d_4 was carried out by the same procedure described above to give a mixture of sulfoxide **2a**-d_4 and **2b**-d_4 in 93% yield.

Reaction of Disulfide Dication Salt 3 with Aniline. To a solution of disulfide dication **3** (150 mg, 0.34 mmol) in anhydrous CH_3CN (5 mL) was added a solution of aniline (50 mg, 0.34 mmol) in anhydrous CH_3CN (8 mL) at 0 °C under an Ar atmosphere. After 3 h, to a solution was added aqueous $NaHCO_3$ solution (5%, 3 mL). Then the products were extracted with CH_2Cl_2. The organic layer was separated and dried over $MgSO_4$. After removal of the solvent, the crude was chromatographed on silica-gel (eluent, $CHCl_3$-MeOH) to give 1-(4-aminophenyl)-1-thionia-5-thiacyclooctane trifluoromethanesulfonate (**15**) in 63% yield. **15**: mp 167 °C (decomp); IR (KBr, cm^{-1}) 3454, 3356 (NH_2), and 1310-1229 (CF_3SO_3); ^1H NMR ($CDCl_3$) δ 7.47 (d, J=9 Hz, 2H, ArH), 6.78 (d, J=9 Hz, 2H, ArH), 5.19-4.81 (br s, 2H, NH_2), 3.97-3.33 (m, 4H, S^+CH_2), 2.95-2.67 (m, 4H, SCH_2), and 2.51-2.24 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 154.1, 132.4, 116.7, 116.0, 47.6, 31.0, and 26.6. Anal. Calcd for $C_{13}H_{18}F_3NO_3S_3$: C, 40.09; H, 4.66; N, 3.60. Found: C, 39.84; H, 4.64; N, 3.51.

Reaction of Disulfide Dication Salt 3 with Triphenylamine. To a solution of disulfide dication salt **3** (150 mg, 0.34 mmol) was added a solution of triphenylamine (82 mg, 0.34 mmol) in the same condition as described above. After 3 h, the reaction mixture was treated with usual work-up and chromatographed on silica-gel (eluent, $CHCl_3$-MeOH) to give mono-sulfonium salt, 4-(*N,N*-diphenylamino)-phenyl-1-thionia-5-thiacyclooctane trifluoromethanesulfonate (**16**) in 40% and bis-sulfonium salt, *N,N*-bis[4-(1-thionia-5-thiacyclooctyl)-phenyl]aniline (**16a**) in 22% yields. **16**: IR (neat, cm^{-1}) 1310-1225 (CF_3SO_3); ^1H NMR ($CDCl_3$) δ 7.68 (d, J=9 Hz, 2H, ArH), 7.50-6.86 (m, 12H, ArH), 4.64-4.26 (m, 2H, S^+CH_2), 3.68-3.27 (m, 2H, S^+CH_2), and 3.10-2.12 (m, 8H, SCH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 152.9, 145.4, 131.1, 129.9, 126.3, 125.8, 120.5, 119.7, 47.6, 31.0, and 26.5; MS, *m/z* 392 (M^+-CF_3SO_3). (**16a**): mp 199-201 °C (decomp); IR (KBr, cm^{-1}) 3438 (OH) and 1310-1230 (CF_3SO_3); ^1H NMR (CD_3CN) δ 7.71 (d, J=9 Hz, 4H, ArH), 7.60-7.05 (m, 9H, ArH), 4.07-3.44 (m, 8H, S^+CH_2), 3.10-2.59 (m, 8H, SCH_2), and 2.55-2.22 (m, 8H, CH_2); ^{13}C NMR (CD_3CN) δ 151.9, 132.4, 131.3, 128.2, 126.0, 124.9, 47.2, 31.2, and 26.7. Anal. Calcd for $C_{32}H_{39}F_6NO_7S_6$: C, 44.90; H, 4.59; N, 1.64. Found: C, 44.68; H, 4.34; N, 1.63.

Reaction of Disulfide Dication 3 with Phenol. To a solution of disulfide dication **3** (240 mg, 0.54 mmol) in anhydrous CH_3CN was added a solution of phenol (51 mg, 0.54 mmol) in anhydrous CH_3CN under the same condition as described above. After 3 h, the reaction mixture was treated by usual work-up and chromatographed on silica-gel (eluent, $CHCl_3$-MeOH) to give the sulfonium salt, 1-(4-hydroxyphenyl)-1-thionia-5-thiacyclooctane trifluoromethanesulfonate (**17**) in 81% yield. **17**: mp 160 °C; IR (KBr, cm^{-1}) 3463 (OH) and 1350-1199 (CF_3SO_3); ^1H NMR (CD_3CN) δ 8.56-8.38 (br s, 1H, OH), 7.67 (d, J=9 Hz, 2H, ArH), 7.07 (d, J=9 Hz, 2H, ArH), 4.04-3.41 (m, 4H, S^+CH_2), 3.10-2.59 (m, 4H, SCH_2), and 2.55-2.21 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 162.6, 132.7, 122.3, 118.5, 47.3, 31.0, and 26.5. Anal. Calcd for $C_{13}H_{17}F_3O_4S_3$: C, 39.99; H, 4.38. Found: C, 39.67; H, 4.46.

Reaction of Diselenide Dication Salt 5 with Aniline or *N,N*-Dimethylaniline. To a stirred solution of dication salt **5** (411 mg, 0.77 mmol) in anhydrous CH_3CN (2 mL) was added a solution of aniline (143 mg, 1.54 mmol) in anhydrous CH_3CN (3 mL) under an Ar atmosphere at room temperature and the whole mixture was stirred for 6 h. The mixture was then treated with H_2O, and after usual work-up, the residue was chromatographed on silica-gel (eluent, $CHCl_3$-MeOH) to afford the selenonium salt, 1-(4-aminophenyl)-5-selena-1-selenoniacyclooctane hexafluorophosphate (**18**) as white crystal in 55% yield. **18**: mp 151-152 °C; ^1H NMR (CD_3CN) δ 7.37 (d, J=9 Hz, 2H, ArH), 6.75 (d, J=9 Hz, 2H, ArH), 3.80-3.31 (m, 4H, Se^+CH_2), 3.16-2.69 (m, 4H, $SeCH_2$), and 2.66-2.20 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 152.9, 132.1, 119.8, 116.2, 46.3, 27.0, and 25.0. Anal. Calcd for $C_{12}H_{18}F_6NPSe_2$: C, 30.08; H, 3.79; N, 2.92. Found: C, 30.24; H, 4.05; N, 2.87. 1-(4-Dimethylaminophenyl)-5-selena-1-selenoniacyclooctane tetrafluoroborate (**19**) was obtained in 68% yield from the reaction of **5** with *N,N*-dimethylaniline: mp 141-142 °C; ^1H NMR (CD_3CN) δ 7.47 (d, J=9 Hz, 2H, ArH), 6.81 (d, J=9 Hz, 2H, ArH), 3.84-3.34 (m, 4H, Se^+-CH_2), 3.19-2.74 (m, 4H, $SeCH_2$), 3.01 (s, 6H, Me), and 2.72-2.28 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 153.7, 131.7, 119.2, 113.8, 46.2, 40.2, 27.0, and 25.0. Anal. Calcd for $C_{14}H_{22}BF_4NSe_2$: C, 37.45; H, 4.93; N, 3.19. Found: C, 37.08; H, 4.79; N, 3.14.

Reaction of Disulfide or Diselenide Dication (3 or 5) with Benzenethiol. To a solution of **3** (240 mg, 0.54 mmol) in anhydrous CH_3CN (5 mL) was added a solution of benzenethiol (118 mg, 1.08 mmol) in anhydrous CH_3CN (3 mL) under an Ar atmosphere at room temperature. The mixture was stirred at room temperature and the reaction was monitored by GLC. After the reaction was complete, the reaction mixture was treated with aqueous $NaHCO_3$ solution (5%). The crude products were chromatographed on silica-gel (eluent, n-hexane-benzene, 1/1) to give diphenyl disulfide in 86% yield and sulfide **1** in 84% yield.

In the case of diselenide dication **5**, diphenyl disulfide (92%) and selenide **4** (76%) were obtained.

Reaction of Disulfide Dication Salt 3 with 1,2-Diphenylhydrazine. To a solution of the dication salt **3** (120 mg, 0.27 mmol) in anhydrous CH_3CN (5 mL) was added a solution of 1,2-diphenylhydrazine (**38**) (50 mg, 0.27 mmol) in CH_3CN (3 mL) in the presence of 1,4-diazabicyclo[2.2.2]-octane (DABCO) (30 mg, 0.27 mmol) at room temperature under an Ar atmosphere. After 3 h, to the reaction mixture was added water (5 mL) and the products were extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous $MgSO_4$. After evaporation of the solvents, the residue was separated by silica-gel column chromatography (eluent, hexane-benzene, 1/1) to give azobenzene (**39**) in 71% yield and sulfide **1** in 73% yield. Azobenzene: mp 67 °C (lit.[23] 68 °C).

Reaction of Disulfide Dication Salt 3 with Potassium Bromide. To a solution of dication salt **3** (240 mg, 0.54 mmol) in CH_3CN (10 mL) was added potassium bromide (129 mg, 1.08 mmol) at room temperature under an Ar atmosphere. After 1 h, the solution was poured into water (10 mL) and treated with 5%-$NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and evaporated in vacuo to give the compounds **20** (15% yield), **21** (16% yield), and sulfoxide **2** (61% yield). Bis[3-(3-bromopropylthio)-propyl]disulfide **20**; IR (neat, cm^{-1}) 1233; MS, *m/z* 228 ($M^+/2$); ^1H NMR ($CDCl_3$) δ 3.46 (t, 4H, J=6 Hz, $BrCH_2$), 2.90-2.39 (m, 12H, CH_2), and 2.30-1.74 (m, 8H, CH_2). Anal. Calcd for $C_{12}H_{24}Br_2S_4$: C, 31.58; H, 5.30. Found: C, 31.84; H, 5.29. *S*-3-(3-Bromopropylthio)propyl 3-(3-bromopropylthio)propylthiosulfonate **21**: IR (neat, cm^{-1}) 1315, 1123 (SO_2), and 1236 (CH_2Br); ^1H NMR ($CDCl_3$) δ 3.45 (t, 4H, J=6 Hz, $BrCH_2$), 3.20 (t, 4H, J=6 Hz, CH_2), 2.79-2.42 (m, 8H, CH_2), and 2.29-1.86 (m, 8H CH_2). Anal. Calcd for $C_{12}H_{24}Br_2O_2S_4$: C, 29.51; H, 4.95. Found: C, 29.62; H, 4.91.

Reaction of Disulfide Dication 3 with Fluorenyl Lithium. To a solution of dication **3** (240 mg, 0.54 mmol) was added a solution of fluorenyl-lithium (**29**) (0.54 mmol) in hexane-THF (1 mL) at -78 °C under an Ar atmosphere. After 3 h, the solution was allowed to come to room temperature. The mixture was treated with aqueous $NaHCO_3$ solution (5%) and the products were extracted with CH_2Cl_2. Then the organic layer was separated and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica-gel (eluent, hexane-benzene followed by $CHCl_3$-MeOH) to give sulfide **1** in 42%, $\Delta^{9,9'}$-bifluorenyl (**30**) in 20%, fluorene in 58%, and the sulfoxide **2** in 46% yields. $\Delta^{9,9'}$-Bifluorenyl (**30**): mp 242-243 °C (lit.[22] 243.5-245.0 °C).

Reaction of Disulfide Dication Salt 3 with 9-Mesitylfluorenyl-lithium. To a solution of dication **3** (178 mg, 0.40 mmol) was added a solution of 9-mesitylfluorenyl-lithium (**33**) (0.54 mmol) in hexane-THF (1 mL) at -78 °C under an Ar atmosphere. Then the solution was stirred at -20 °C for 1 h and allowed to come to room temperature. After 10 h, the solution was treated with aqueous $NaHCO_3$ solution (5%). The products were extracted with CH_2Cl_2. Then the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica-gel (eluent, hexane-benzene followed by $CHCl_3$-MeOH) to give sulfide **1** in 50%, 9-mesitylfluorene in 62%, and sulfoxide **2** in 20% yields.

Reaction of Diselenide Dication Salt 5 with Sodium 2,4,6-tri-*tert*-Butylphenoxide. To a solution of dication salt **5** (245 mg, 0.46 mmol) in anhydrous THF (4 mL) was added a solution of sodium 2,4,6-tri-*tert*-butylphenoxide (132 mg, 0.46 mmol) in anhydrous THF (2 mL) at -78 °C under an Ar atmosphere. Then the solution was stirred for 3 h. To this mixture was added water (2 mL) and the products were extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica-gel (eluent, $CHCl_3$-MeOH) to give selenide **4** (47%) and the peroxide **37** (16%). Bis(1,3,5-tri-*tert*-butyl-2,5-cyclohexadiene-4-one)peroxide (**37**): mp 147-149 °C (lit.[15a] 148-149 °C); MS, *m/z* 277 ($M^+/2$).

Treatment of Diselenide Dication Salt 5 with H_2O and Oxidation of 1,2-Diphenylhydrazine. A solution of **5** (266 mg, 0.5 mmol) in CH_3CN (2 mL) was poured into water (3 mL). The compound was extracted with CH_2Cl_2 and then the organic layer was dried with $MgSO_4$. The organic layer was evaporated in vacuo to give white solid (82%) which was recrystallized from CH_3CN-CH_2Cl_2: mp 121-122 °C (decomp); ^1H NMR (CD_3CN) δ 4.09-3.51 (m, 8H, Se^+CH_2) and 3.33-2.81 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 48.2 and 32.4; ^{77}Se NMR (CD_3CN) δ 739.5 (br s) (relative to Me_2Se); ^{31}P NMR (CD_3CN) δ -141.3 (sept, J_{PF} = 708 Hz) (relative to H_3PO_4).

To a solution of the dication salt **5** (266 mg, 0.5 mmol) obtained from the above treatment in anhydrous CH_3CN (5 mL) was added a solution of 1,2-diphenylhydrazine (**38**) (92.1 mg, 0.5 mmol) in CH_3CN (3 mL) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) (56 mg, 0.5 mmol) at room temperature under an Ar atmosphere. After 3 h, to the reaction mixture was added water (5 mL) and the products were extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous $MgSO_4$. After evaporation of the solvents, the residue was separated by silica-gel column chromatography (eluent, hexane-benzene, 1/1) to give azobenzene (**39**) in 90% yield together with selenide **4** (72%). Azobenzene: mp 67 °C (lit.[23] 68 °C).

Reaction of Diselenide Dication Salt 5 with Sodium Sulfide. To a solution of **5** (173 mg, 0.33 mol) in CH_3CN (3 mL) was added a solution of sodium sulfide ($Na_2S \cdot 9H_2O$) (79 mg, 0.33 mmol) in water (2 mL) at room temperature under an Ar atmosphere. After 3 h, the elemental sulfur precipitated was filtered off. The solution was concentrated in vacuo to give selenide **1** in 76% yield. The yield of elemental sulfur was 72%: mp 112 °C.

Reduction of Diselenide Dication Salt 5 with Sodium Borodeuteride. To a solution of sodium borodeuteride ($NaBD_4$) (21 mg, 0.5 mmol) in water (2 mL) was added dication salt **5** (109 mg, 0.2 mmol) at room temperature under an Ar atmosphere. The mixture was stirred for 3 h. After the reaction, the solution was extracted with CH_2Cl_2 and dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by preparative liquid chromatography to afford the undeuterated bis-selenide **4** (99%) which was characterized by the ^1H NMR spectroscopy and the mass spectrometer. The reaction of **5** with $NaBH_4$, $LiAlH_4$, or $LiAlD_4$ was carried out by the same procedure as $NaBD_4$.

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