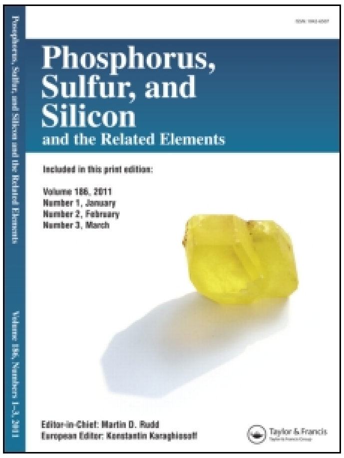

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σ-Bonded Dications from Medium-Sized Selenium and Tellurium Heterocycles

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σ-BONDED DICATIONS FROM MEDIUM-SIZED SELENIUM AND TELLURIUM HETEROCYCLES

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Abstract The two-electron oxidation of 1,5-diselenacyclooctane (**1**) or 1,5-ditelluracyclooctane (**3**) with 2 equiv of $NOBF_4$ gave the diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]octane bis(tetrafluoroborate) (**2**), or the ditelluride dication salt **4**. The structures of the dications were characterized by ^{77}Se and ^{125}Te NMR spectroscopy and X-ray crystallographic analysis. The diselenide dication salt **6** having aromatic ring was formed in the reaction of *5H,7H*-dibenzo[*b,g*][1,5]diselenocin *6*-oxide (**5**) with 2 equiv of silylating reagent, $CF_3SO_3SiMe_3$. These dications react either as an oxidant or as an electrophile depending on the added reagent.

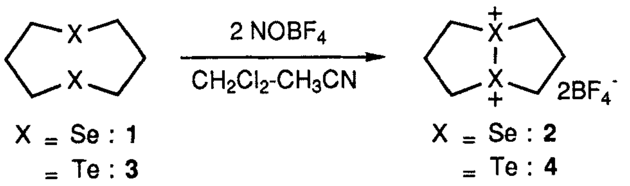
Dications bonded by two positively charged heteroatoms have received little attention.[1-3] However, σ-bonded dications containing selenium and tellurium atoms have been hitherto unknown, except for our recent results.[4-6] This paper presents the preparation, structure, and properties of σ-bonded dications from the medium-sized cyclic compounds containing Se and Te atoms, and the electrochemical property of cyclic bis-selenides and tellurides.

Electrochemical Oxidation of Cyclic Bis-Selenides and Tellurides

The electrochemical oxidation of selenide **1** and telluride **3** was performed by cyclic voltammetry. The cyclic voltammogram (CV) of **1** and **3** showed one reversible oxidation wave with remarkably low oxidation potential. Normally, dialkylselenides and tellurides showed the irreversible redox behaviors in electrochemical oxidations. The oxidation potentials (*vs.* Ag/0.01 M $AgNO_3$) of **1** and **3** are: **1**, +0.25 V and **3**, -0.02 V. These facile oxidations of **1** and **3**, and the unusual stabilities of the cationic species of **1** and **3** are attributed to the destabilization of **1** and **3** by transannular lone-pair-lone-pair repulsion and the stabilization of the oxidized products by neighboring-group participations, *i.e.*, bond formation between the two selenium or tellurium atoms.

σ-Bonded Dications from Cyclic Bis-Selenides and Tellurides

The two-electron oxidation of **1** with 2 equiv of $NOBF_4$ gave a novel diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]octane bis(tetrafluoroborate) (**2**) (Scheme 1). This dication salt **2** is stable that it is easily isolated and handled. The ^{77}Se NMR spectrum of bis-selenide **1** in $CHCl_3$ shows a singlet peak at δ 141.3 (relative to Me_2Se), while the dication **2** in CH_3CN shows a singlet at δ 806.5.[4a] Analogously, the tetraalkyl substituted ditelluride dication salt **4** was obtained by treatment of **3** with 2 equiv of $NOBF_4$; the ^{125}Te NMR spectrum of **3** in $CHCl_3$ shows a singlet peak at δ 163.5 (relative to Me_2Te), while dication **4** in $(CH_3)_2SO$ shows a one peak at δ 1303.7.[5]



Scheme 1

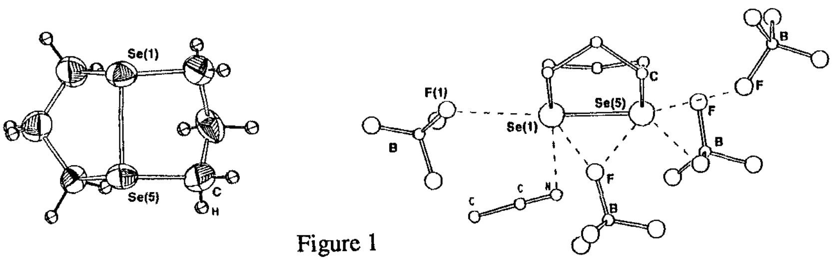
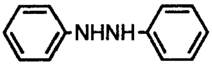


Figure 1

The X-ray crystallographic analysis of the dication BF_4^- salt **2** indicates the following characteristic properties (Figure 1).[4b] The Se(1)-Se(5) length is

2.382(2) Å, which is only slightly longer than the normal Se-Se single bond (2.34 Å). The conformation of the eight-membered ring is a chair-boat form, while that in a disulfide dication, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate), is a distorted chair-chair form.[3] The crystal has one acetonitrile molecule as a crystal solvent in an asymmetric unit. Very short contacts are observed between Se atom of the dication and F atoms of counter anions and N atom of CH_3CN; *e.g.*, the distance of Se(1)···F(1) is 2.89(2) Å which is remarkably shorter than the van der Waals' contact of 3.35 Å.

Interestingly, the dication salt **2** could not be hydrolyzed with H_2O as evidenced by ^{1}H, ^{13}C, and ^{77}Se-NMR spectroscopy. A solution of **2** in D_2O-CD_3CN was followed by NMR spectroscopy and no significant changes were observed over several hours. Compound **2** was recovered in a good yield after addition of H_2O, and could again act as an oxidant, *e.g.*, the reaction of hydrazine **7** with the dication gave azobenzene **8** (90%) and **1** (72%). However, disulfide dication salts were easily hydrolyzed to the corresponding *S*-oxides.[1,3]



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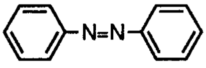

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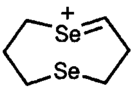


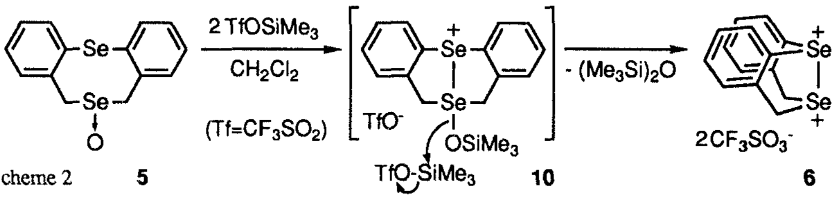
9

The diselenide dication salt **2** can be reduced quantitatively to bis-selenide **1** upon treatment with $NaBH_4$ at room temperature. In contrast, Alder *et al.* reported the deprotonation of the hydrazinium dication salt on treatment with $NaBD_4$.[2] Accordingly, the dication **2** was treated with $NaBD_4$ in H_2O or D_2O; however, no H-D exchange was observed in the bis-selenide **1** at all after the reaction. This result indicates that the mechanism involving the intermediate formation of **9** 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.

It is interesting to study the electrochemical behavior of σ-bonded heteroatom dications, because no clear-cut example of the reversible electrochemical reduction of their dications has been reported. The CV of **2** exhibited that one-reversible reduction peak appeared at extremely low reduction potential, +0.11 V *vs.* Ag/0.01 M $AgNO_3$. While mono-selenonium cations of **1**, *e.g.*, 1-methyl-5-selena-1-

selenonia-cyclooctane iodide and 1-*p*-(aminophenyl)-5-selena-1-selenonia-cyclooctane hexafluorophosphate, showed the irreversible waves with very negative reduction potentials (-1.5 V to -1.8 V *vs.* Ag/0.01 M $AgNO_3$).

A diselenide dication salt **6** containing aromatic ring was formed by a reaction of selenoxide **5** with 2 equiv of $CF_3SO_3SiMe_3$.[6] This reaction may proceed *via* the initial formation of the *O*-silylated selenurane intermediate **10** which subsequently would be converted into the dication **6** (Scheme 2). This is a new method for the preparation of diselenide dication, although the preparative methods of heteroatom dications from medium-sized heterocyclic compounds are little known.[1-3] Hydrolysis of the salt **6** gave the selenoxide **5** (85%). In contrast, a dication salt **2** was stable in H_2O.[4a] The difference in reactivity between **6** and **2** was also observed, *i.e.*, the dication **6** led to the corresponding selenide (70%) on treatment with *N*,*N*-dimethylaniline (DMA, 2 equiv), contrasting with the reaction of **2** with DMA which gave the *para*-substituted product, selenonium salt. Thus the dication **6** can be reduced by DMA, since the oxidation potential of DMA is lower than that of the dication precursor.[6]



Scheme 2

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