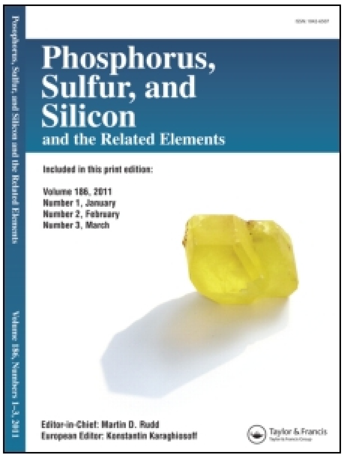

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Creation of Organo-Sulfur, -Selenium- and - Tellurium Multi-Cation Species

Naomichi Furukawa

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CREATION OF ORGANO-SULFUR, -SELENIUM- AND -TELLURIUM MULTI-CATION SPECIES

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Preparation and structures of several dithia-, diselena- and ditellura-dications of 2-center-2-electron and 3-center-4-electron systems are described. 1,5-Dithia- diselena- and ditellura cyclooctane dications are stable, while those obtained from 1,8-bis(dichalcogeno)naphthalenes and 2,2'-bis(dichalcogeno) biphenyls undergo readily carbon-chalcogen bond cleavage to generate reactive chemical species such as quinodimethane, and carbocations. Diphenyl chalcogenides bearing 2,6-bis(methylthiomethyl)-, -selenomethyl and dimethylaminomethyl substituents afforded the hypervalent chalcogenuranes and their structures were determined by X-ray crystallographic analysis. Their electronic structures were also determined by ab initio MO calculations. Molecular and electronic structures of the dication of 1,11-(methanoselenomethano)-*5H,7H*-dibenzoselenocin were determined by X-ray crystallographic analysis and MO calculation.

Keywords: Dichalcogena dications Transannular interaction Hypervalent molecules Quinodimethane Pummerer rearrangement Selenium cation Tellurium cation Molecular hysteresis

INTRODUCTION

Transannular interaction is a well known phenomenon in organic compounds bearing more than two chalcogen atoms arranged appropriately in space[1]. On removal of one or two electrons from the chalcogen atom, an attractive force operates between the two chalcogen atoms to create a new chemical bond, called a "dication": 2-center-2-electron [2c-2e] bond (I) [2]. Furthermore, when a lone pair of electrons attached to a third chalcogen atom transannularly participate in the formation of dichalcogena dications, new dication species in which the central atom is a hypervalent tetra-coordinated atom are formed: 3-center-4-electron [3c-4e] bond (II). These molecular models are schematically illustrated in Fig. 1

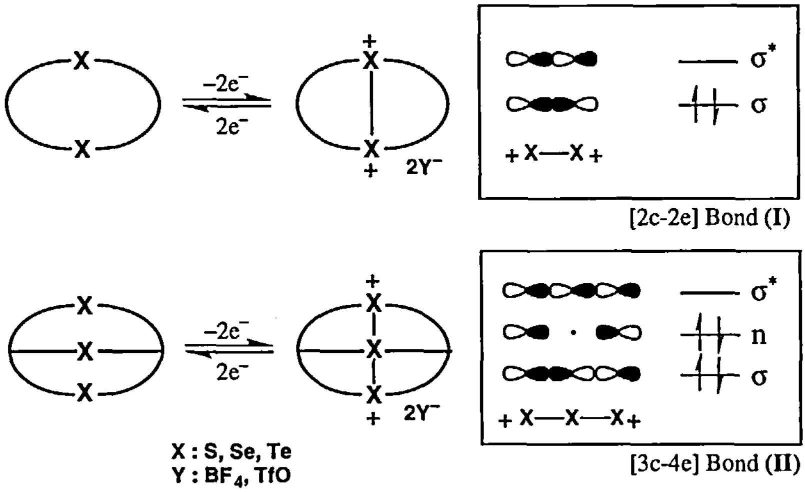


FIGURE 1 Schematic illustration of two types of bonds of dication species.

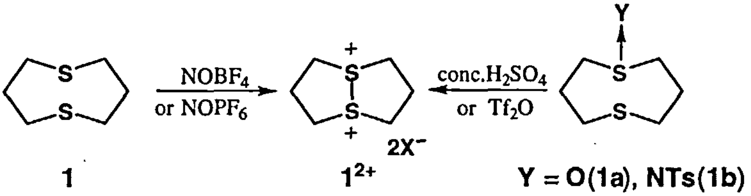
This article presents our recent investigations on the dichalcogena dications bearing the [2c-2e] and the [3c-4e] bonds.

I. Dications of [2c-2e] (I) bond

I-1) 1,5-Dichalcogena cyclooctane (1,5-DXCO) dications (X=S,Se,Te)

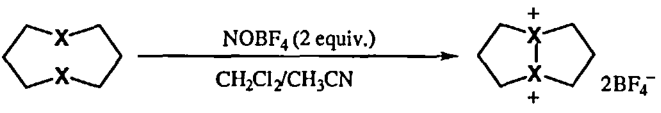
1,5-Dithiacyclooctane (**1**) and its selenium (**2**) and tellurium (**3**) analogs are the best candidates to prepare the dichalcogena dications. We found that the dications (1^{2+}), (2^{2+}) and (3^{2+}) are produced by treating the corresponding monooxide (**1a**) or monoimine (**1b**) with conc. H_2SO_4 or by an acid anhydride such as $(CF_3SO_2)_2O$ [Tf_2O] [3]. (Scheme. 1)

SCHEME 1



^{77}Se and ^{125}Te-NMR spectroscopies are also efficient techniques for the detection of the dications of Se (2^{2+})[4] and Te (3^{2+})[5]. Several examples are shown in Scheme 2.

SCHEME 2



2 (X = Se): ^{77}Se δ 141 ppm
3 (X = Te): ^{125}Te δ 163 ppm

2^{2+} (X = Se): ^{77}Se δ 806 ppm
3^{2+} (X = Te): ^{125}Te δ 1303 ppm

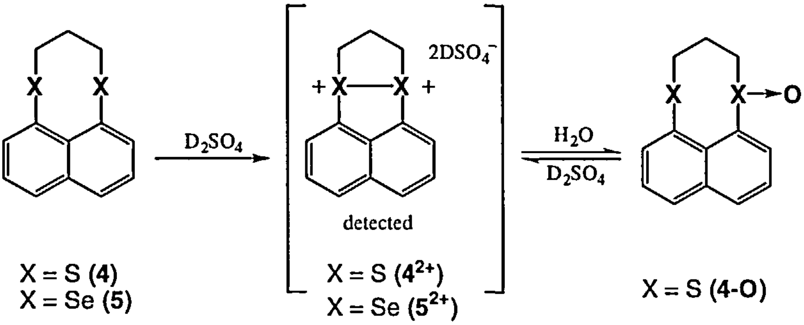
Finally the structure of 2^{2+} was determined by X-ray crystallographic analyses [6].

I-2) Aromatic ring-fused dichalcogena dications

As a further extension, we tried to prepare dichalcogena dications bearing sterically congested aromatic rings such as 1,8-bis(chalcogen-substituted) naphthalenes and 2,2'-bis(chalcogen-substituted) 1,1'-biphenyls. Dithia dications from these compounds are obtained using one of the following two common procedures: (i) the sulfides are treated with 2 equivalents of $NOBF_4$ or $NOPF_6$; (ii) the monosulfoxides are treated with conc. H_2SO_4 or Tf_2O. Similarly, the selenium and tellurium analogs can be converted to the diselena and ditellura dications.

Glass and his co-workers reported the preparation of dications (4^{2+}) from dithiocin (**4**) and its monooxide (**4-O**) [7]. Although, on the basis of an MO calculation, it was proposed that there is no bond formation between the two sulfur atoms in **4-O**, on dissolution in conc. H_2SO_4, **4-O** is converted to $\mathbf{4^{2+}}$, which after hydrolysis with H_2O, **4-O** was recovered with retention of the configuration at the sulfinyl sulfur atom. We have also examined the oxygen exchange reaction of **4-O** in conc. H_2SO_4 and obtained results identical with those by Glass *et al.* In the case of the selenium derivative, even the bis-selenide (**5**) gives the diselena dication ($\mathbf{5^{2+}}$) directly in conc. D_2SO_4. as shown in Scheme 3[8][9].

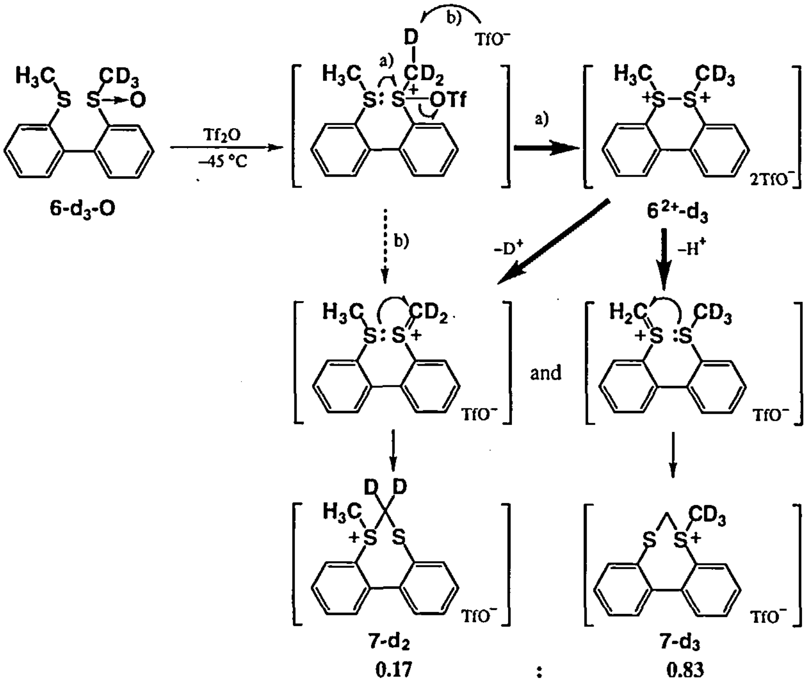
SCHEME 3



I-3) Facile dealkylation *via* S•••S through-space interaction

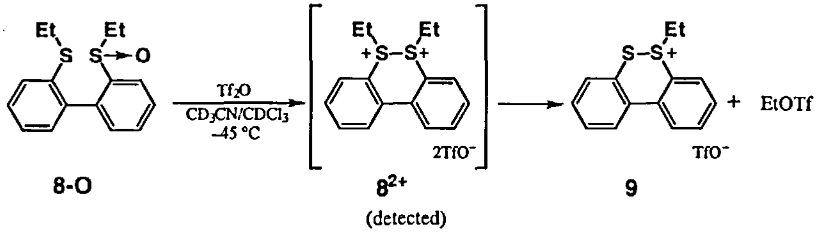
2,2'-Bis(methylthio) 1,1'-biphenyl monosulfoxide (**6-O**) was prepared and treated with Tf_2O at -45 °C in $CD_3CN/CDCl_3$[10]. Surprisingly, the formation of dication ($\mathbf{6}^{2+}$) was not observed by ^{1}H-NMR spectroscopy at -45 °C, but **6-O** was converted to the cyclic sulfonium salt (**7**) in high yield. Normally, one would think that in this reaction the Pummerer-type reaction should take place. However, when the trideuterated sulfoxide (**6-d$_3$-O**) was treated with Tf_2O at -45 °C, the deuterium atoms in the sulfonium salt (**7-d$_2$**) and (**7-d$_3$**) were observed at the methylene groups of **7-d$_2$** and the methyl groups of **7-d$_3$** in 0.17 : 0.83 ratio. The present result strongly supports the formation of the dication ($\mathbf{6}^{2+}$**-d$_3$**) prior to proton abstraction. The isotope ratio reflects on the isotope effect due to the proton abstraction from $\mathbf{6}^{2+}$**-d$_3$**. (Scheme 4).

SCHEME 4



Furthermore, when the mono-sulfoxide of diethyl derivative (**8-O**) was treated with Tf_2O in an NMR tube at -45 °C, two ethyl-^{1}H-NMR signals in **8-O** coalesced to give a symmetrically coupled ethyl-signal in ^{1}H-NMR spectroscopy indicating the formation of the bis(sulfonium) dication (8^{2+}) which on elevating the temperature to -20 °C, two new ethyl signals were observed[11]. In a large scale preparation, a crystalline compound was isolated and its ^{1}H, ^{13}C, and ^{19}F-NMR spectroscopies indicate the formation of the monosulfonium salt (**9**)[12]. Similarly, isopropyl, *t*-butyl- and benzyl- substituted biphenyl derivatives afford the corresponding monosulfonium salts.(Scheme 5)

SCHEME 5



I-3) Molecular activation and generation of active species *via* dithia or diselena dications

Another possible procedure to activate the molecules is the photolysis of the compounds by n-π* excitation. This photo-excitation produces an electron-deficient radical-cation-like state at the one chalcogen group, from which the S-S or Se-Se bond formation takes place transannularly to convert the molecules into highly activated states. From this activated state, the substituents attached at the chalcogen atoms are released to liberate the active species together with thermodynamically stable disulfides or diselenides. This concept may create a new methodology for generating new reactive species.

I-4-1) Quinodimethane formation

8,13-Dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]dithionin (**10**) and diselenonin (**11**) was prepared and was exposed to sunlight in the presence of air. The decomposition of **10** and **11** took place gradually to give incipiently *o*-quinodimethane (**12**) which was identified by the trapping experiment in the presence of olefins under UV irradiation. This reaction gives tetrahydronaphthalene derivatives **13** in high yields, together with 100% recovery of naphthalene-selenole (**14**) as shown in Scheme 6 and the results are summarized in Table II[13].

SCHEME 6

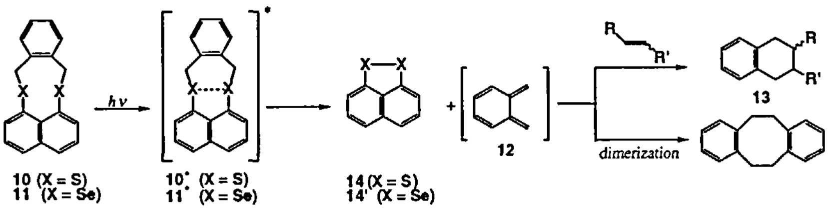


TABLE II. Trapping Experiment of *o*-Quinodimethane (**12**)

Substrates	Olefins			Yield(%)
	R	R'		**13**
10	H	CO_2Me		62
	CO_2Me	CO_2Me	(cis)	54
	CO_2Me	CO_2Me	(trans)	79
11	H	CO_2Me		97
	CO_2Me	CO_2Me	(cis)	94
	CN	CN	(trans)	99

I-4-2) Photochemical reactions of 2-substituted and 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiin derivatives.

As an extension of the photolysis, we prepared various derivatives of 2- and 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiin (**15**) and converted them to the corresponding monooxides (**15-O**), mono-sulfilimines (**15-NTs**) and mono-*S*-ylides (**15-C⁻R$_2$**), respectively. These three dithiin derivatives undergo photolysis to give aldehydes, ketones (**16**), imine derivatives (**17**) and olefins (**18**) in almost quantitative yields with the recovery of naphto[1,8-*cd*]-1,2-dithiole (**14'**) as shown in Scheme 7[14]. Typically, the results of the photolysis of sulfoxides obtained are summarized in Table III[15].

SCHEME 7

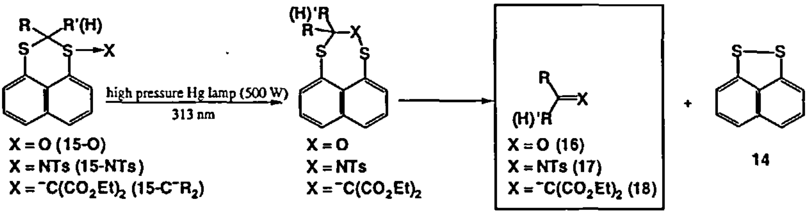


TABLE III Photolysis of Dithioacetal Monooxide and Diketal Monooxide in Benzene[a)]

Substrates(15-O)		Yield(%)[b)]	
R	R'	aldehyde or ketone	dithiole or diselenole
Ph	H	>99	>99
$CH_3(CH_2)_5$	H	>99	>99
PhCH=CH	H	>99	>99
Ph	CH_3	>99	>99
Ph	Py	>99	>99
Ph	PhCH(OH)-	>99	>99

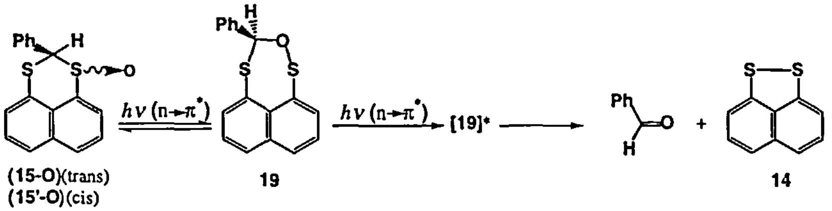
a) 400 W high pressure Hg lamp, λ> 300 nm, Substrates (0.1 mmol), Benzene (5 ml)

b) Yields were determined by gas chromatography and ^{1}H-nmr spectroscopy

During the photolysis, the rearranged intermediate product (sulfenate) (**19**) was identified as the cyclic sulfenate by examining the ^{1}H-, ^{13}C-NMR and mass-spectra after the isolation of the crude compound. Finally the spectra were converted to that of a 1 : 1 mixture of dithiole (**14**) and benzaldehyde.

The effect of light intensity on the photolysis of **15-O** and the quantum yield measurements demonstrate that photoreaction of **15-O** proceeds *via* the mechanism shown in Scheme 8.

SCHEME 8



II) Dications of hypervalent species of [3c-4e] bond

II-1) Preparation of hyperdications

Diphenyl chalcogenides bearing 2,6-bis(phenylthiomethyl) groups (**20**~**22**) were prepared and their Ep values *vs.* Ag/AgCl in 3M KCl/CH$_3$CN were measured (Fig.2). Subsequently, these compounds were converted to the dications[16].

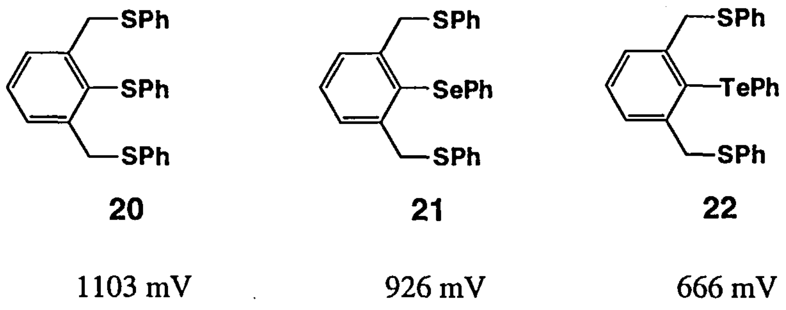
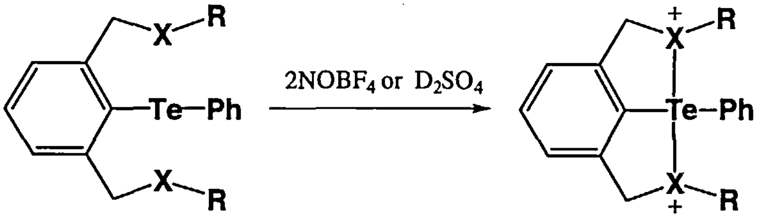


FIGURE 2 Oxidation potentials of 2,6-bis(phenylthiomethyl)phenyl phenyl sulfide (**20**) -selenide (**21**) and telluride (**22**)

The three compounds **20**, **21** and **22** have one cathodic and anodic peaks between -1500 mV to +1500 mV in the CV measurement, and the oxidizing ability order of the three chalcogenides is Te>Se>S, which is the same as the trend observed for the oxidation potentials of the chalcogen atoms[16].

The tellurides **22**, **23** and **24** and their monooxides were prepared and treated with either conc. D_2SO_4 or $NOBF_4$ as an oxidant in an NMR-tube (Scheme 9).

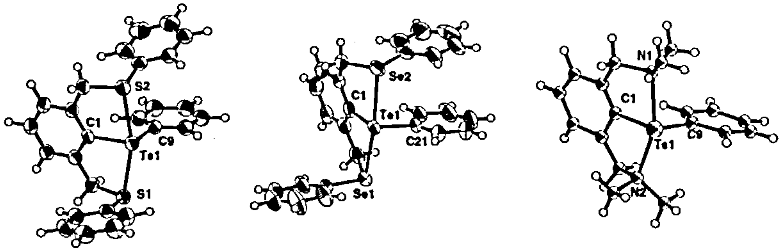
SCHEME 9



RX = SPh (**22**)
RX = SePh (**23**)
RX = $N(CH_3)_2$ (**24**)

RX = SPh (**25**)
RX = SePh (**26**)
RX = $N(CH_3)_2$ (**27**)

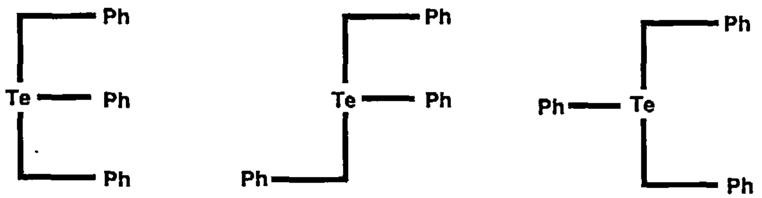
The ^1H-NMR spectra of these compounds show the formation of the dication species **25**, **26** and **27**. The structures of these chalcogen dications were determined by X-ray crystallographic analysis after isolation. The ORTEP drawings of telluranes **25**, **26** and **27** are shown in Fig.3.



25 **26** **27**

FIGURE 3 ORTEP drawings of the telluranes **25**, **26**, and **27**

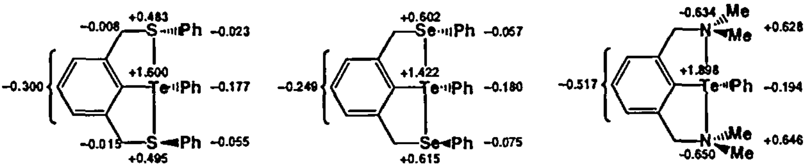
The telluruane **25** has a trigonal bipyramidal structure at the central Te atom, in which the two sulfonio groups occupy the axial positions, while the two phenyl rings and the lone electron-pair compose the equatorial ligands with significantly longer Te–S bond distances: 2.652 and 2.654 Å, compared with the normal Te–S σ-bond length of 2.36 Å. From the view of **25** down the Te(1)–C(1) axis, it is seen that the phenyl rings are almost perpendicular to the S(1)–Te(1)–S(2) bond. Furthermore, surprisingly, the arrangement of the three phenyl groups are of a *cis-trans*-conformation, which is marked contrast to the expected *trans-trans* conformation, as shown in Fig.4 indicating that π - π stacking may play an important role of this conformer of **25** in the solid state.



cis-cis conformation *cis-trans* conformation *trans-trans* conformation

FIGURE 4 Three types of conformers of the tellurane **25**

The charge densities and bond orders of the hypervalent bond of these telluranes **25**, **26** and **27** were calculated by an *ab* initio RHF-method on the basis of 3-21G(*). The results are shown in Fig.5.



25 **26** **27**

FIGURE 5 Charge distribution of the telluranes **25**, **26**, and **27**

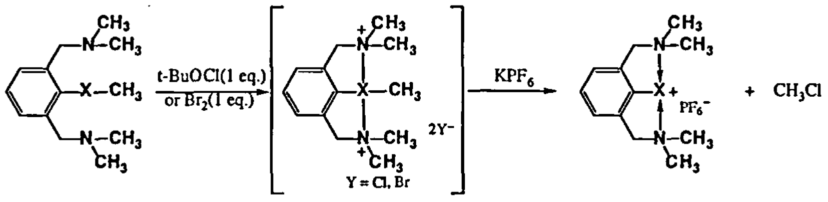
Accordingly, these telluranes **25**, **26** and **27** should have doubly positively charged structures at the Te atom rather than the hypervalent bonds.

II-2) First RSe^+ and RTe^+ salt; 2,6-bis(dimethylaminomethyl) phenyl selenenium and tellurenium cationic compounds

As described in the previous sections, selenides and tellurides with two 2,6-dimethylaminomethyl groups called a Koten's arm (ligand) [17] can stabilize the cations generated at the central Se and Te atoms. Furthermore, the formation of dications highly activates the molecules to release the alkyl substituents attached at the central chalcogen atom as electrophiles.

We prepared the following selenide (**28**) and telluride (**29**) and treated them with *t*-BuOCl and then KPF_6 for the anion exchange. As we expected, the selenenium salt (**30**) and tellurenium analog (**31**) were isolated, as shown in Scheme 10[18].

SCHEME 10



X = Se (**28**) ^{77}Se: 90.0 ppm
X = Te (**29**) ^{125}Te: 287.2 ppm

X = Se (**30**) ^{77}Se: 1208.3 ppm
X = Te (**31**) ^{125}Te: 1949.4 ppm

The selenenium salt (**30**) was isolated and the structure was determined by X-ray crystallographic analysis as shown in Fig.6. The PF_6^- anion is separated from the cationic center and makes no contact within the van der Waals contact. The bond lengths between the Se and two nitrogen atoms are 2.154(7) and 2.180(7) Å, which are slightly longer than the sum of a covalent radii of Se–N bond. The enormous down-field shift of the ^{77}Se NMR in cationic species **30** as compared with that of the starting material **28** demonstrates the formation of a positive charge at the Se atom. The tellurenium species **31** was also confirmed by ^{125}Te-NMR spectroscopy. *Ab initio* RHF calculations with STO-3-21G$^{(*)}$ as a basis set of these two new chalcogen species also confirm their existence.

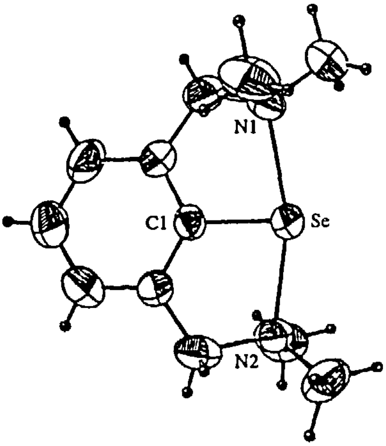
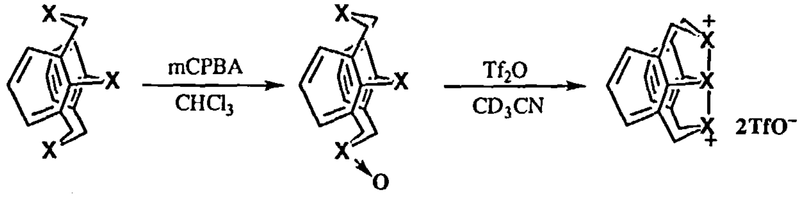


FIGURE 6 ORTEP drawing of **30**

II-3) Preparation of selenium dications bearing selenurane bonds: dication of diselenocin

Recently, 1,11-(methanothiomethano)-*5H,7H*-dibenzo [*b,g*][1,5]dithiocin (**32**) and its monooxide (**33**) were converted to the dication (**34**) on treatment with two equivalents of $NOBF_4$ or conc. H_2SO_4[19]. The dication **34** was isolated as a solid material. However, the structure determination has not been succeeded as yet. Therefore, the Se-analog **37** was prepared similarly on treatment with Tf_2O in crystalline compound as shown in Scheme 11[20].

SCHEME 11



X = S (**32**)
X = Se (**35**)

X = S (**33**)
X = Se (**36**)

X = S (**34**)
X = Se (**37**)

The ^{77}Se-NMR chemical shifts of **37** reveal that the selenurane dication is generated. The crystal structure of **37** was determined by X-ray crystallographic analysis indicating that the dication **37** has a central selenurane structure bearing two selenonium groups as apical ligands. The conformation of **35** is a twin chair form while that of **37** is a twin boat form. The electronic structure of **37** was determined by an *ab* initio RHF calculation using 3-21G$^{(*)}$ basis set. The calculated electronic structure of **37** is nearly identical with that determined by X-ray analysis. The crystal structure is shown in Fig.7.

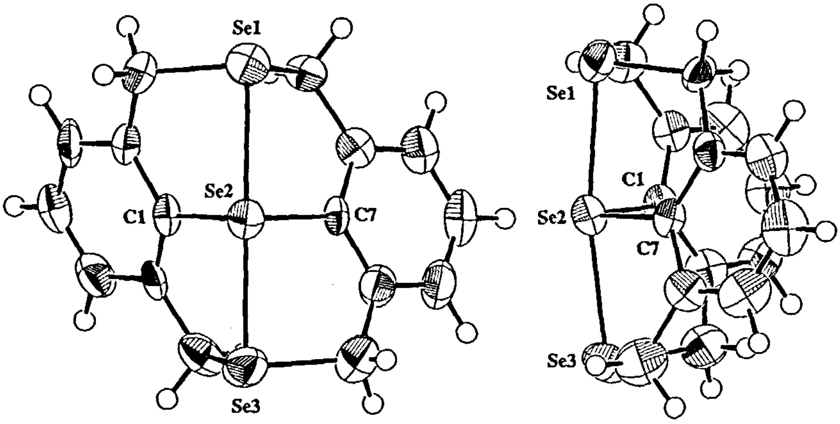


FIGURE 7 ORTEP Drawing of **37**

The compound **37** was converted to **35** on treatment with 2 equivalents of PhSH quantitatively.Therefore, the compounds **35** and **37** form a redox system which has a possibility to be used as a "hysteresis molecule"

As a conclusion of this study, transannular interaction between or among multiple chalcogen atoms in the molecules creates dication species to provide many interesting and valuable compounds.

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