Chapter 2

Crystal Structures and ab initio Calculations of New Dicationic Telluranes, [10–Te–4(C2X2)] (X = Se, N)

CONTENTS

I. Introduction

Recently, considerable interest has focused on the study of organic compounds with hypervalent chalcogens and as a result a number of neutral chalcogenuranes were reported.[1), 2)] However, to date only a few examples of positively charged hypervalent chalcogenuranes have been known.[3)] The majority of these compounds involves a three-center transannular interaction in a cyclic or an acyclic framework as exemplified by types A and B as shown in Figure 2-1.
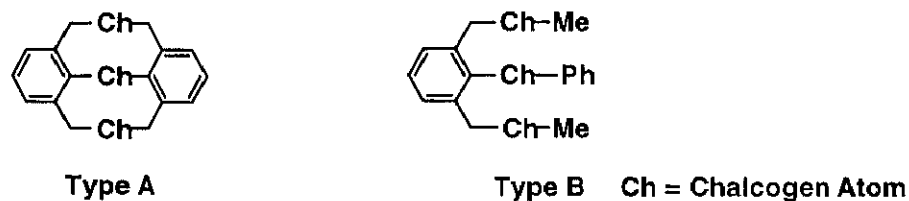

Type A   **Type B   Ch = Chalcogen Atom**

Figure 2-1

Recently, dicationic σ-telluranes were synthesized and isolated by Furukawa's group at first time. A new type of dicationic σ-telluranes (λ^4-tellane), $[10\text{–Te–}4(\text{C2S2})]^{2+}\cdot2\text{X}^-$ (X = BF$_4$ **2a** or CF$_3$SO$_3$ **2b**) was prepared from the new flexible acyclic tris-chalcogenide, 2,6-bis[(phenylthio)methyl]phenyl phenyl telluride **1**, and the corresponding telluroxide **3** via transannular bond formation (Scheme 2-1).
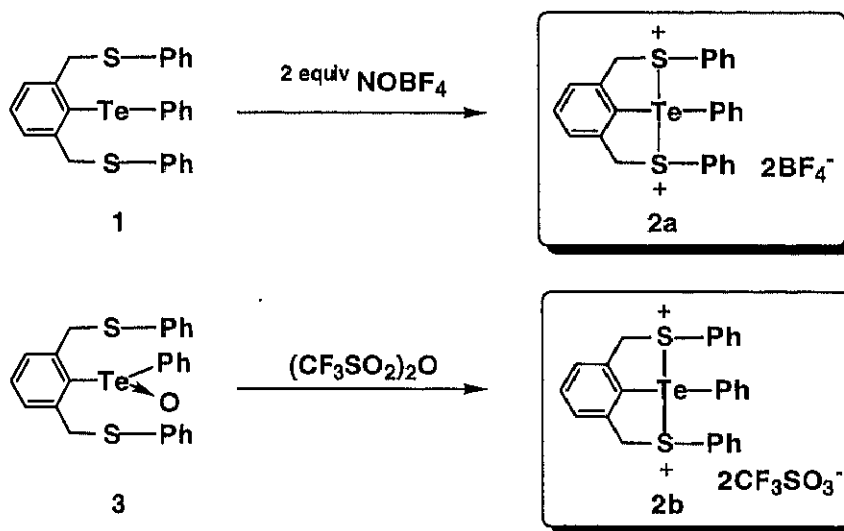
Scheme 2-1

Single crystal X-ray structure determinations of **2a** revealed that two apical sulfonio ligands bond to the central tellurium atom as shown in Figure 2-2. The tellurium atoms of **2a** have a distorted trigonal bipyramidal bonding geometry with two apical Te–S bonds, two equatorial Te–C bonds and the lone-pair of electrons occupying the third equatorial position.

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This chapter reports new dicationic σ-telluranes (λ^4-tellane) prepared from the new flexible acyclic tris-chalcogenides.

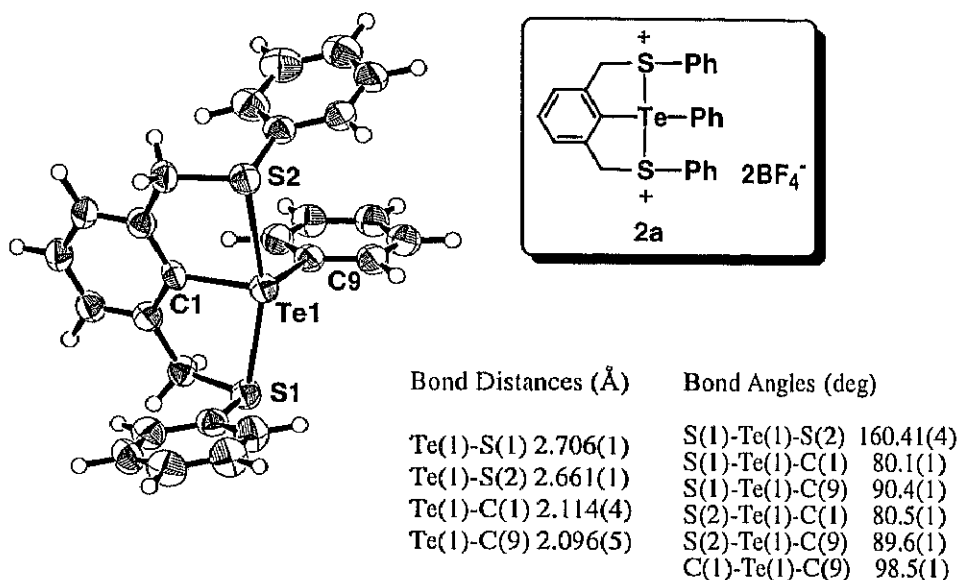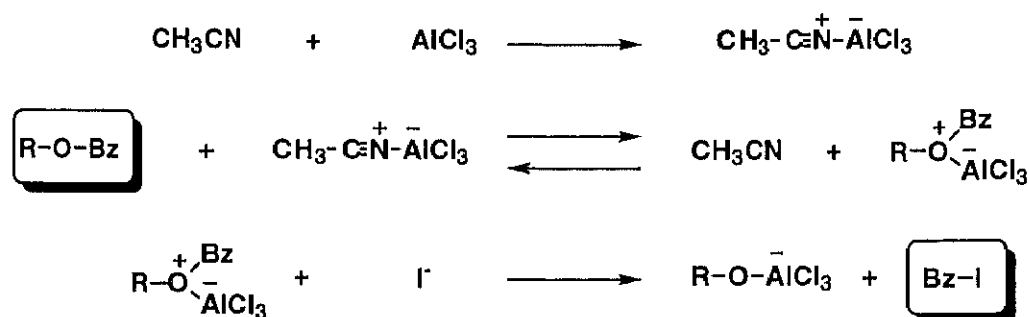| Bond Distances (Å)	Bond Angles (deg)	
Te(1)-S(1) 2.706(1)	S(1)-Te(1)-S(2)	160.41(4)
Te(1)-S(2) 2.661(1)	S(1)-Te(1)-C(1)	80.1(1)
Te(1)-C(1) 2.114(4)	S(1)-Te(1)-C(9)	90.4(1)
Te(1)-C(9) 2.096(5)	S(2)-Te(1)-C(1)	80.5(1)
	S(2)-Te(1)-C(9)	89.6(1)
	C(1)-Te(1)-C(9)	98.5(1)

Figure 2-2

II. Synthesis of the Tellurides

At first, the author tried to synthesize 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluride **6** as a precursor of the new σ-tellurane having seleno ligands. When n-BuLi was added to the bromobenzene derivative **4**, the attack of the n-Bu anion to the selenium atom was predominant to the lithium halogen exchange, so the compound **4** could not be lithiated with n-BuLi directly.
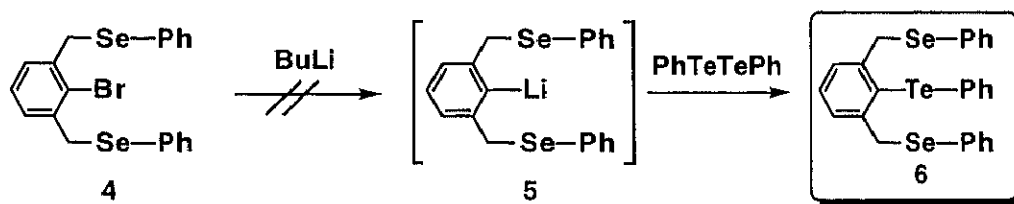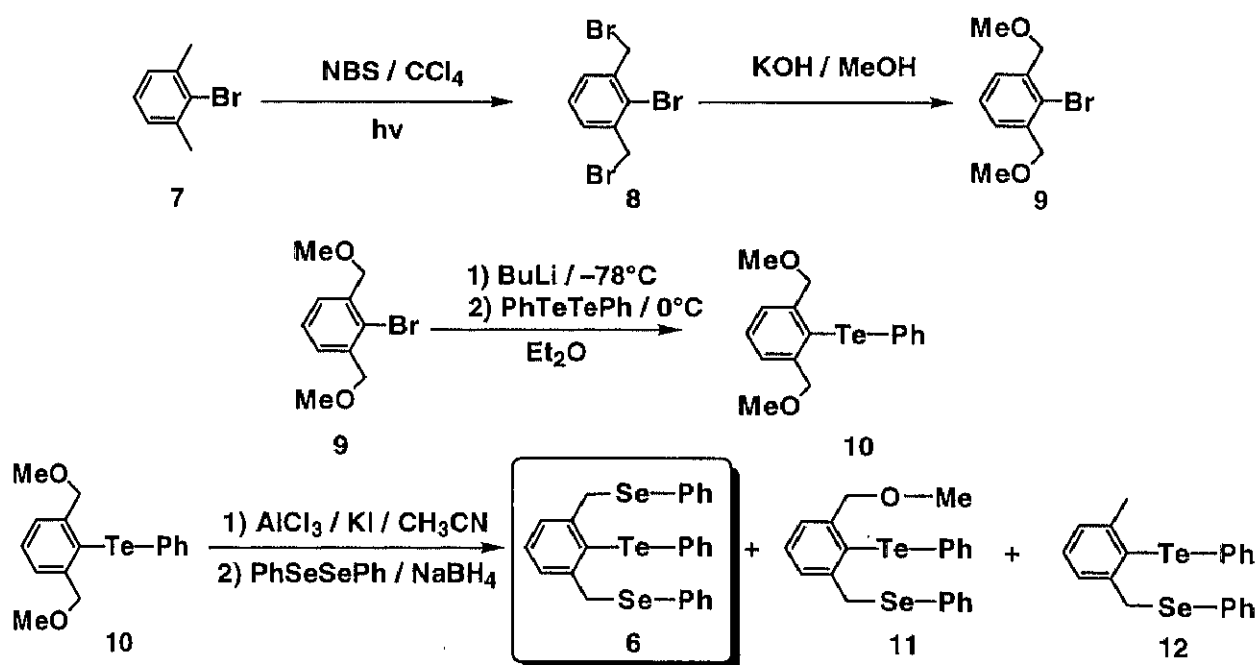

Scheme 2-2

Because of the reason, methoxy group was used as a protecting group for lithiation. And the deprotection of the methoxy group was carried out by the reaction using $AlCl_3$ and KI. It has been known that the bond cleavage reaction of benzylic ether proceeds smoothly on using the CH_3CN solution of $AlCl_3$, as a hard Lewis acid, and I⁻ anion as a soft nucleophile[4]. The mechanism for this reaction can be expected to proceed through three steps shown in Scheme 2-3.

$$CH_3CN \quad + \quad AlCl_3 \quad \longrightarrow \quad CH_3\text{-}C\overset{+}{\equiv}N\text{-}\overset{-}{AlCl_3}$$

$$R\text{-}O\text{-}Bz \quad + \quad CH_3\text{-}C\overset{+}{\equiv}N\text{-}\overset{-}{AlCl_3} \quad \rightleftharpoons \quad CH_3CN \quad + \quad R\text{-}\overset{+}{O}\overset{Bz}{\underset{AlCl_3}{-}}$$

$$R\text{-}\overset{+}{O}\overset{Bz}{\underset{AlCl_3}{-}} \quad + \quad I^- \quad \longrightarrow \quad R\text{-}O\text{-}\overset{-}{AlCl_3} \quad + \quad Bz\text{-}I$$

Scheme 2-3

In the first step, the hard acid suitable for the S_N2 reaction is generated by the coordination of $AlCl_3$ to the nitrogen atom of CH_3CN. In the second step, this acid gives rise to the equilibrium between benzylic ether by exchanging of the ligand ($AlCl_3$). In the final step, the oxonium ion generated by the ligand ($AlCl_3$) exchange reaction, is attacked by the I⁻ ion from back side of the benzylic carbon atom affording the final product.

By using this reaction, 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluride **6** was synthesized as shown in Scheme 2-4.

Scheme 2-4

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Interestingly, two byproducts **11** and **12**, having a similar structure as **6**, were obtained at the final step of the synthesis. The telluride **12** was produced from the reaction that only one side of the methyl groups was deprotected. And the excess $NaBH_4$ reduced the benzylic iodide to methyl group, instead of unucleophilic attack of PhSe⁻, to form the telluride **11**.

Furthermore, 2,6-[bis(dimethylamino)methyl]phenyl phenyl telluride **14** was synthesized as shown in Scheme 2-5.
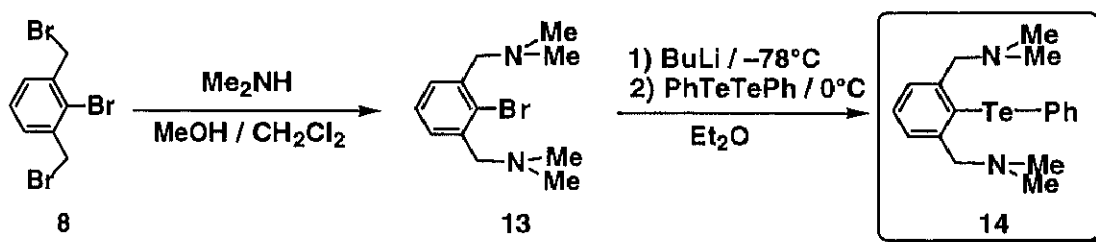
Scheme 2-5

Interestingly, the ^{77}Se and ^{125}Te NMR spectra of compounds **6** and **11** show satellite peaks between the selenium and tellurium atoms in spite of the fact that there are no bonding interactions between these atoms. The coupling constants (J_{Se-Te}) are 100 Hz (**6**) and 121 Hz (**11**) respectively. This spin-spin coupling may be due to an interaction through the carbon bonds between selenium and tellurium atoms, as opposed to a through space one.

This type of coupling has not been reported, but there is an example, in which the coupling was observed between the selenium and tellurium atoms. This compound **15** is shown in Figure 2-3, and this coupling is considered to be a through bond one[5].
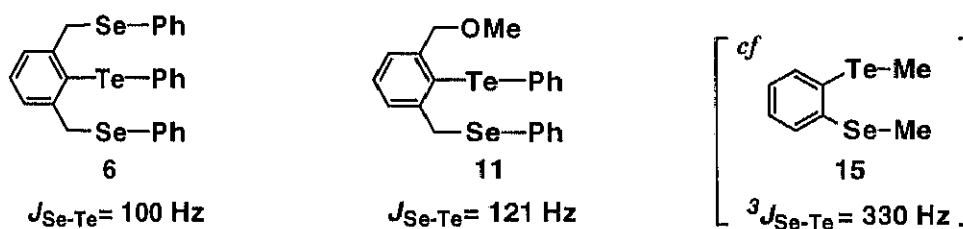

Figure 2-3

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2,6-[Bis(methylthio)methyl]phenyl phenyl telluride **17** was synthesized from 1-bromo-2,6-[bis(methylthio)methyl]benzene **16**, which was prepared from the tris-bromide **8** with 2 equiv of sodium thiomethoxide (Scheme 2-6). And bis[2-(phenylthio)methyl]phenyl telluride **19** was synthesized from the tetrabrommide **18** with 4 equiv of thiophenolate ion (Scheme 2-7). In this reaction, 2 equiv of thiophenolate ion was used for the nucleophilic attack to the benzylic carbon and the rest was used for the reduction of the tellurium atom. These tellurides **17** and **19** were oxidized to the dicationic telluranes as described in the following section.
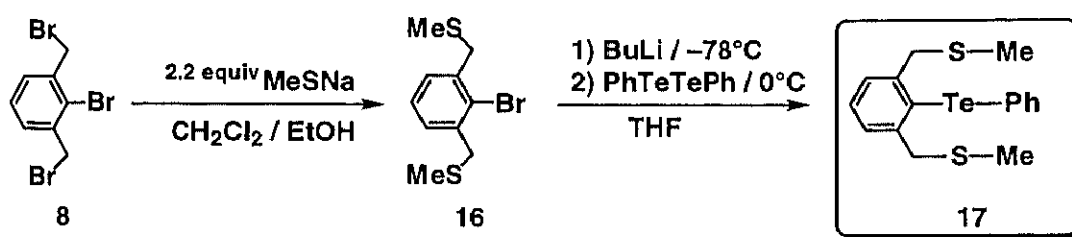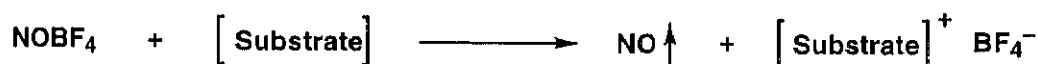
Scheme 2-6
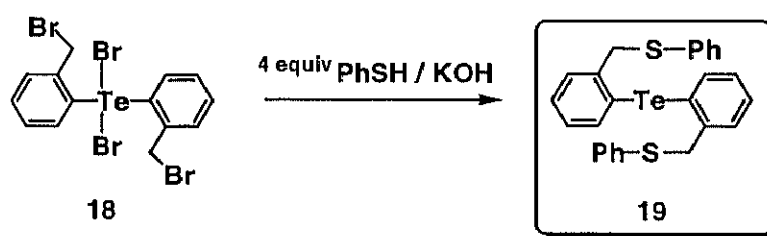
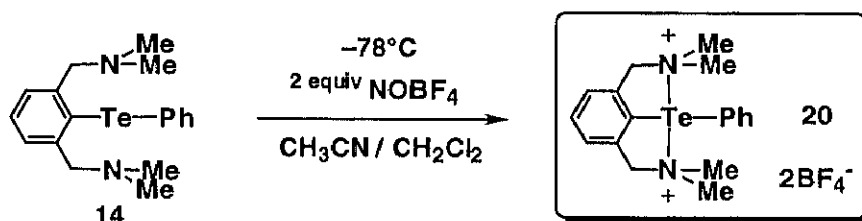Scheme 2-7

III. Synthesis of the Novel Dicationic Telluranes

Nitrosonium tetrafluoroborate (NOBF$_4$) and nitrosonium hexafluorophosphate (NOPF$_6$) are useful oxidizing agents. In the case of oxidation with these reagents, only removable NO gas and BF$_4^-$ or PF$_6^-$ are left after oxidation as shown in Scheme 2-8. And the low nucleophilicity of these counter ions improves the stability of the cationic species.

$$\text{NOBF}_4 \quad + \quad \big[\text{Substrate}\big] \longrightarrow \text{NO}\!\uparrow \quad + \quad \big[\text{Substrate}\big]^+ \text{BF}_4^-$$

Scheme 2-8

### A. Synthesis of the Novel Dicationic Tellurane (+N–Te–N+)

2,6-[Bis(dimethylamino)methyl]phenyl phenyl telluride **14** was readily oxidized by adding a solution of anhydrous CH$_3$CN containing NOBF$_4$ (2 equiv) dropwise to a solution of anhydrous CH$_2$Cl$_2$ with **14** at –78 °C under an argon atmosphere. After removal of solvent, the dicationic σ-tellurane 2BF$_4^-$ salt **20** was isolated in 56% yield as colorless crystals, which were stable to moisture (Scheme 2-9).

Scheme 2-9

The ^{125}Te NMR signal of **20** appeared at 1335 ppm. This lower shift indicates that the tellurium atom was oxidized to produce the dicationic hypervalent tellurane. The ^{1}H NMR signals of benzylic protons in **20**, measured in CD$_3$CN at room temperature, appear at 4.24 and 4.44 ppm as one set of AB quartet. And four methyl protons appear at 2.34 and 3.14 ppm as two singlets. These chemical shifts of **20** were lower field than those of the telluride **14**. These results indicate that each amino group coordinates to the tellurium with strong interaction.

Furthermore, the structure of the dicationic σ-tellurane 2 BF$_4^-$ salt **20** in the solid state was determined by X-ray diffraction method. An ORTEP view of **20** is shown in Figure 1. In the solid state, the two neighboring amino nitrogens direct toward the tellurium atom. The bond lengths between the tellurium and two nitrogen atoms are 2.33 and 2.31 Å respectively, which are slightly longer than a single covalent bond (2.02 Å) between tellurium and nitrogen atoms. The angle of N(1)–Te(1)–N(2), 154.9 ° is much distorted from linear arrangement, which is expected for the apical bond in hypervalent compounds. The counter anion, BF$_4^-$, was independent of the cationic part and not located within the van der Waals radii.
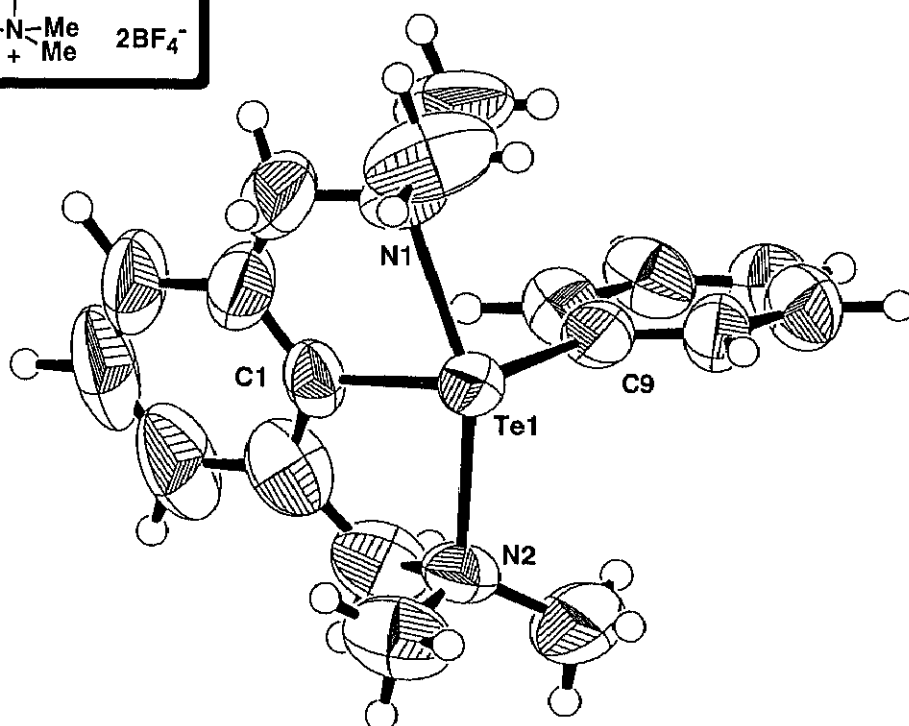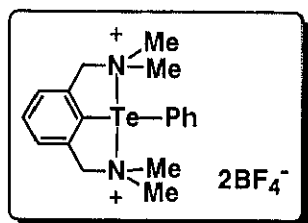
The tetrafluoroborate anions are omitted.

Space Group P21/c(#14)
R= 0.065, R$_w$= 0.072.

Bond Distances (Å)

Te(1)-N(1) 2.33(1)

Te(1)-N(2) 2.31(1)

Te(1)-C(1) 2.06(2)

Te(1)-C(9) 2.11(2)

Bond Angles (deg)

N(1)-Te(1)-N(2) 154.9(5)
N(1)-Te(1)-C(1) 77.5(6)
N(1)-Te(1)-C(9) 94.0(6)
N(2)-Te(1)-C(1) 77.4(7)
N(2)-Te(1)-C(9) 90.8(6)
C(1)-Te(1)-C(9) 100.2(6)·

Figure 2-4

B. Synthesis of the Novel Dicationic Tellurane (+Se–Te–Se+)

The telluride **6** was also oxidized by adding a solution of anhydrous CH_2Cl_2 containing $NOBF_4$ or $NOPF_6$ (2 equiv) dropwise to a solution of anhydrous CH_2Cl_2/CH_3CN containing **6** at –78 °C under an argon atmosphere. After removal of the solvent, the tellurane dication $2BF_4^-$ salt (**21a**) and $2PF_6^-$ salt (**21b**) were isolated as yellow solids.
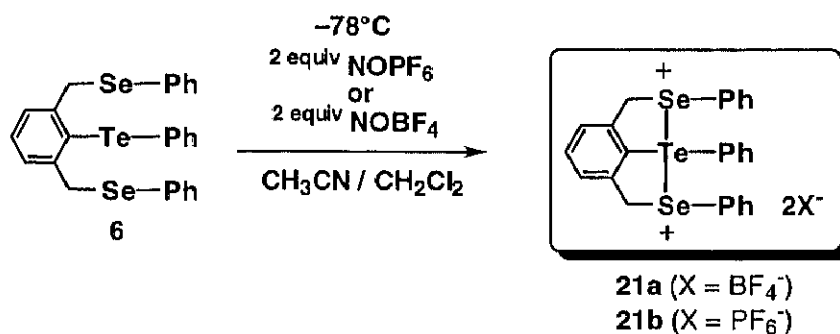
Scheme 2-10

The author also tried to synthesize the telluroxide **22** from the corresponding telluride **6** in *m*-CPBA as an oxidant in order to react with trifluoromethanesulfonic anhydride to form the corresponding dicationic tellurane $2CF_3SO_3^-$ salt **21c**. However, the pure telluroxide could not be obtained because the products are unstable and readily decompose at room temperature.
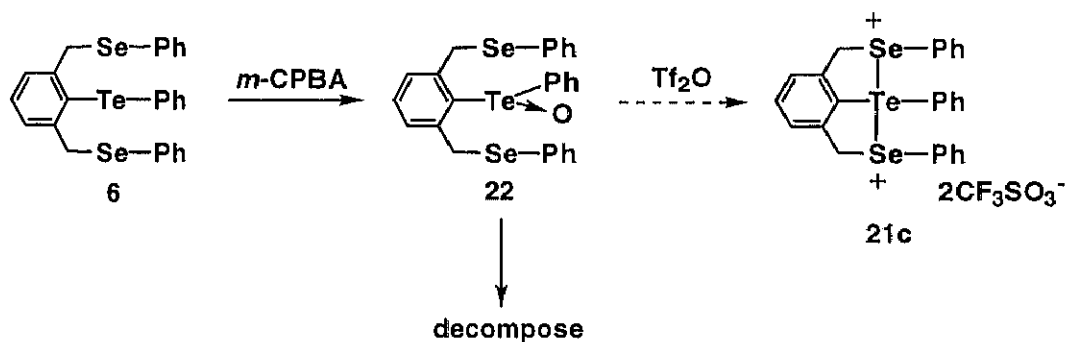
Scheme 2-11

To determine the structures of **21a**, ^1H, ^{13}C, and ^{125}Te NMR spectra were measured. The ^1H NMR spectrum of each compound when measured in CD_3CN at 20 °C exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.26, 5.23 (J = 16.0 Hz) and 4.96, 5.23 (J = 15.0 Hz) in a 1 : 1 ratio. These signals were assigned to the asymmetric bicyclic form. The ^{125}Te NMR spectrum of **21a** shows one peak at 1174.9 ppm at –40 °C with four satellite peaks due to the spin-spin coupling ($^1J_{Te-Se}$ = 443, 491 Hz) between the central tellurium and two asymmetric selenium atoms as shown in Figure 2-5. The ^{77}Se chemical shifts of **21a**

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appear at 393.6 and 462.3 ppm at −40 °C with some satellite peaks. Interestingly, each site shows four satellite peaks due to not only the spin-spin coupling ($^1J_{Se-Te}$ = 443, 491 Hz) between the selenium and tellurium atoms, but also due to the coupling ($^2J_{Se-Se}$ = 71 Hz) between selenium atoms through the tellurium atom as shown in Figure 2-5. Such an example of spin-spin coupling through a three-center four-electron bond has not been reported and is thus an addition to the very interesting behavior of hypervalent chemistry. These results indicate that compound 21a exists in the asymmetric bicycle form and supports the bond formation between the tellurium and selenium atoms.
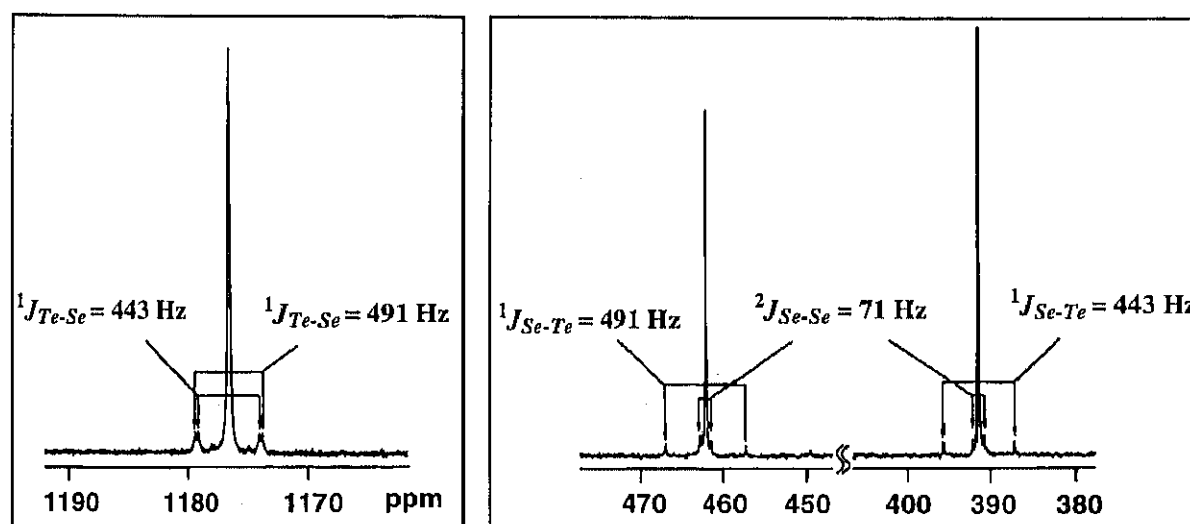

Figure 2-5

In principle, the dicationic tellurane 21 could exist as one of the following three possible stereoisomers: *cis-trans*, *trans-cis* (*dl*-pairs) and/or *trans-trans* (meso) and/or *cis-cis* (meso), as shown in Figure 2-6. The *trans-trans* isomer is expected to be the most sterically stable configuration of the dicationic telluranes. However, the NMR spectra of this compound indicate that this structure has either a *cis-trans* or *trans-cis* configuration.
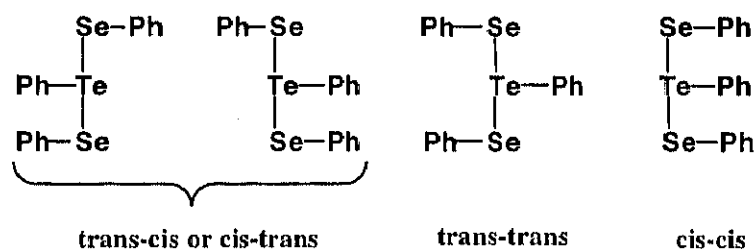

Figure 2-6

Furthermore, the elemental analysis of **21a** is consistent with the molecular formula of the corresponding dicationic tellurane and the FAB-mass spectra of **21a** show the molecular ion at m/e 620 ($M^+-2BF_4^-$).

X-ray Analysis of the Dicationic Tellurane 21a (+Se–Te–Se+)

Suitable crystals for X-ray analysis were obtained by recrystallization of **21a** from dry solutions of CD_3CN at 0 °C. The dication structure of **21a** is similar to that of **2a**. An ORTEP view of **21a** is shown in Figure 2-7. The X-ray crystal structure determination of **21a** establishes that in the solid state this compound exists only as one isomer and is the first example of a dicationic σ-tellurane with two apical selenonio ligands. In addition to the two counter anions ($2BF_4^-$) this crystal also contains one molecule of acetonitrile as a lattice solvate. The bond lengths Te(1)–Se(1) (2.759(2) Å) and Te(1)–Se(2) (2.807(2) Å) are longer than the normal Te–Se single bond (2.519 Å).[6] The bond angles Se(1)–Te(1)–Se(2) and C(1)–Te(1)–C(9) are equal to 163.93(5) ° and 99.0(5) °, respectively. Thus, the Te(1) atoms of **21a** have a distorted trigonal bipyramidal bonding geometry with two apical Te–Se bonds, two equatorial Te–C bonds and the lone-pair of electrons occupying the third equatorial position. These structural features are very similar to those observed in the normal non-charged tellurane (IV) compounds.[7] However, the ideally deviant Se(1)–Te(1)–Se(2) and C(1)–Te(1)–C(9) bond angles may not only be ascribed to the repulsive force between the lone-pair and bonding electrons, but also the effect due to the incorporation of Se(1) and Se(2) into five-membered rings. In addition, these rings are in a twist conformation, thus compensating for the distortion energy of the five-membered rings.

From the view of **21a** down the Te(1)-C(1) axis, it is seen that the phenyl rings are almost perpendicular to the Se(1)-Te(1)-Se(2) bond. Further, the angle between the cis oriented phenyl rings is only 8.0° and the distance between them 3.37-4.10 Å, indicating that π-π stacking may play an important role for the formation of this conformer in the solid phase.

According to crystal packing of these dication compounds, the chalcogen atoms of **21a** are weakly coordinated by the fluorine of BF_4^- and nitrogen of acetonitrile. The compounds **21a** have two tetrafluoroborate anions and one acetonitrile in each unit cell as shown in Figure 2-8. The chalcogen atoms making up the three-center four-electron bond have from one to three secondary bonds, and these bond lengths are within van der Waals radii of each bond (F–Te = 3.55, F–Se = 3.35, N–Te = 3.70 and N–Se = 3.50 Å).[6] These results indicate that the three chalcogen atoms of **21a** have highly positive charges.
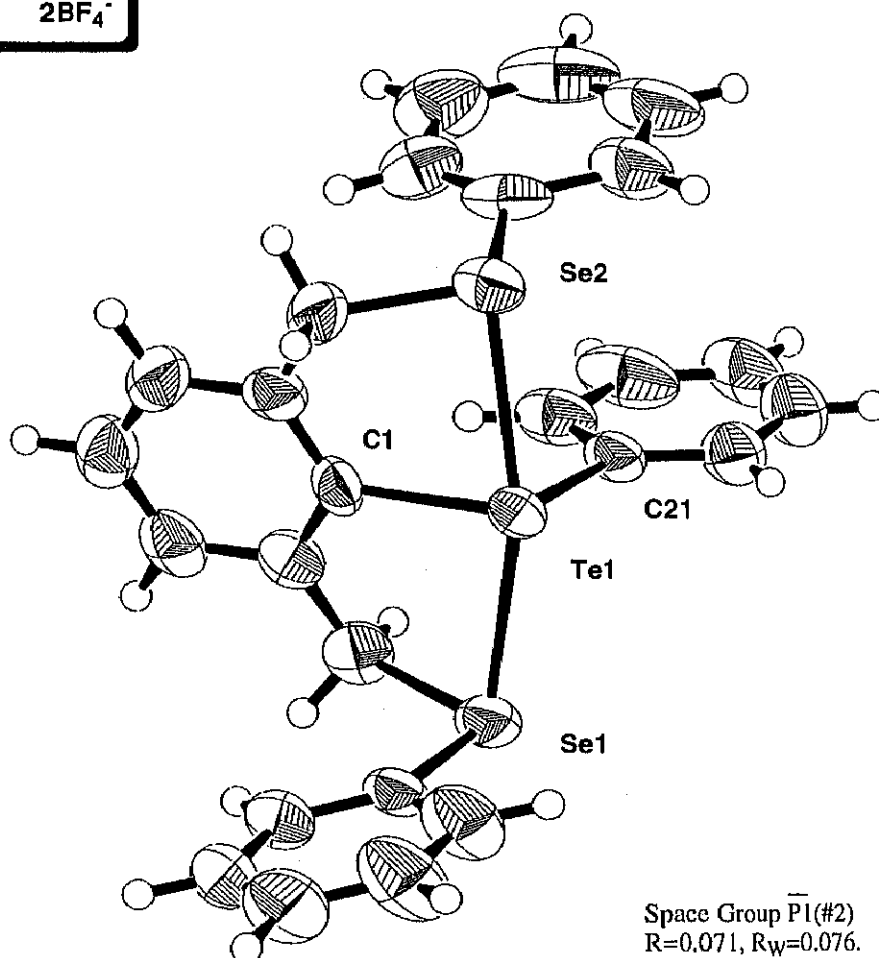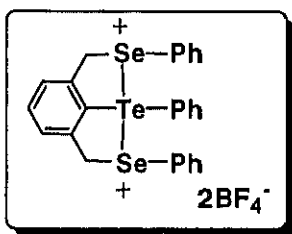
The tetrafluoroborate anions and the solvent molecule are omitted.

Space Group P1̄(#2)
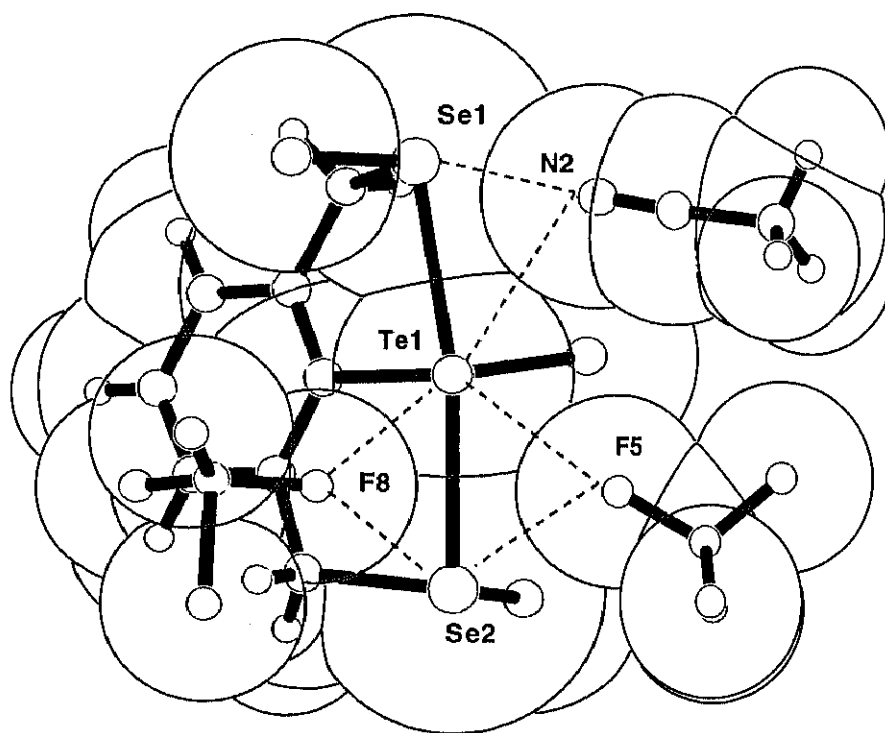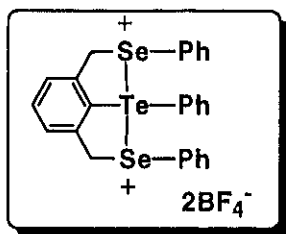R=0.071, R$_W$=0.076.

Bond Distances (Å)

Te(1)-Se(1) 2.759(2)
Te(1)-Se(2) 2.808(2)
Te(1)-C(1)   2.17(1)
Te(1)-C(21) 2.12(2)

Bond Angles (deg)

Se(1)-Te(1)-Se(2) 163.92(6)
Se(1)-Te(1)-C(21) 88.6(3)
Se(1)-Te(1)-C(1)   81.8(3)
Se(2)-Te(1)-C(21) 90.5(3)
Se(2)-Te(1)-C(1)   82.5(3)
C(1)-Te(1)-C(21)   99.0(6)

Figure 2-7

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For clarity only the chalcogen bonded carbon atoms of the phenyl rings are shown.

Sum of van der Walls Radii (Å)		Intermolecular Contacts (Å)	
Se-N	3.5	Se(1)-N(2)	3.20(3)
Se-F	3.35	Te(1)-N(2)	3.54(2)
Te-F	3.55	Te(1)-F(5)	3.11(1)
Te-N	3.70	Se(1)-F(5)	3.33(1)
		Te(1)-F(8)	3.00(2)
		Se(2)-F(8)	3.30(2)

Figure 2-8

C. Synthesis of the Novel Dicationic Tellurane (+Se–Te–O+)

Furthermore, the telluride **11** was oxidized with $NOBF_4$ by the same method as the telluride **6**. After removal of the solvent, the tellurane dication $2BF_4^-$ salt **23** was isolated as yellow solid. This dicationic tellurane **23** has interesting structure, because the three chalcogen atoms, making 3c-4e bond, are all different.
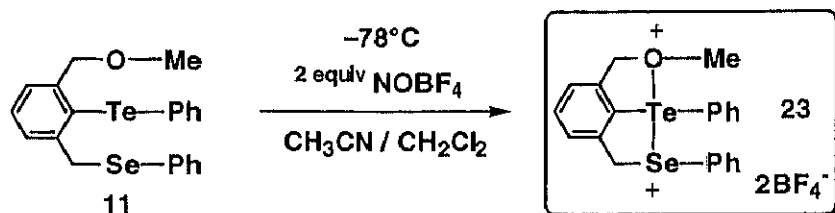
Scheme 2-12

The ^1H NMR spectrum of **23** when measured in CD_3CN at 20 °C exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.65, 5.02 ($J = 14.0$ Hz) and 5.37, 5.53 ($J = 16.0$ Hz) in a 1 : 1 ratio as the dicationic tellurane **21**. And the signal of the methyl protons is observed at δ 3.52, which is downshifted compared with the telluride **11** (δ 3.30). This downshift indicates that the oxygen of the methoxy group connects to the cationic tellurium atom. The ^{125}Te NMR spectrum of **23** show one peak at δ 1374.9 at 20 °C with two satellite peaks due to the spin-spin coupling ($^1J_{Te-Se} = 374$ Hz) between the central tellurium atom as shown in Figure 2-9. And the ^{77}Se chemical shifts of **23** appear at δ 481.3 at 20 °C with two satellite peaks due to the spin-spin coupling ($^1J_{Te-Se} = 374$ Hz). These results indicate that compound **23** exists in the asymmetric bicyclic form and supports the bond formation between the tellurium and selenium atom.
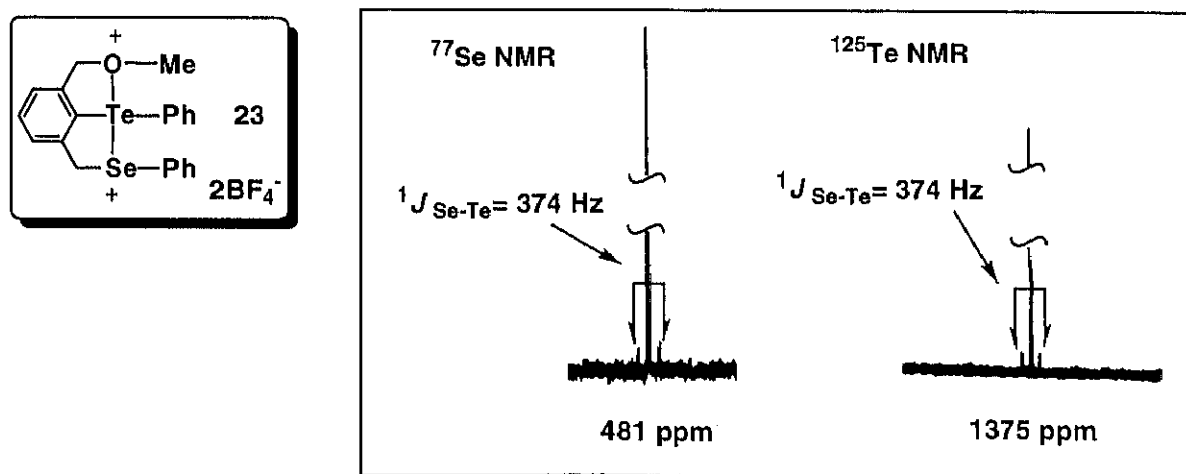
Figure 2-9

As the case of the dicationic tellurane **21**, the dication **23** could exist as one of the following three possible stereoisomers: *cis-trans*, *trans-cis* and/or *trans-trans* and/or *cis-cis*, as shown in Figure 2-10. These stereoisomers are more complicated when compared with those of **21** because the three chalcogen atoms, making 3c-4e bond, are all different. However, the ^{1}H, ^{13}C and ^{125}Te NMR spectra of **23** indicate that this structure has either a *cis-trans* or *trans-cis* configuration as the case of **21**.
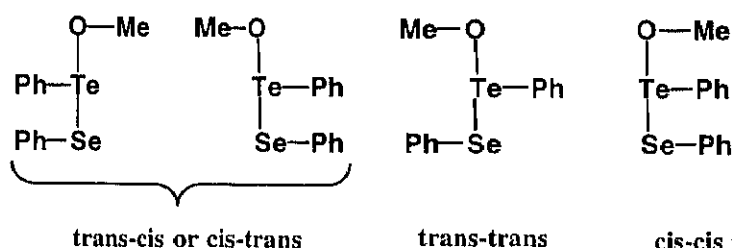

Figure 2-10

D. Synthesis of Other Dicationic Telluranes

The telluride **10** was also oxidized by adding a solution of NOBF$_4$, only to give complex mixtures (Scheme 2-13). This result depends on the instability of the dicationic tellurane having two apical oxonium atoms. In the case of selenium centered hypervalent dications, the dicationic selenurane with two oxonium atoms was only detectable and not isolated although the dicationic selenurane with two selenonium atoms was stable to moisture as reported.[8]
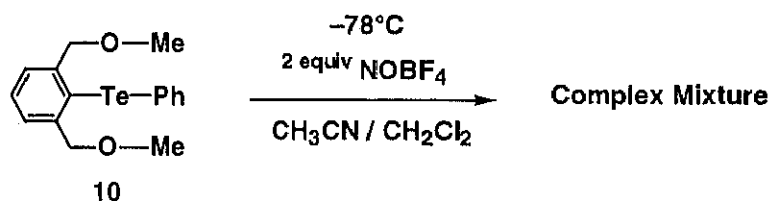
Scheme 2-13

When the telluride **10** was treated with concd D$_2$SO$_4$, a dark red solution was obtained. And the ^{1}H and ^{125}Te NMR spectra of the solution changed slowly during two months. Finally those spectra indicate formation of the dicationic tellurane **24** as shown in Scheme 2-14. The ^{1}H NMR spectrum of **24** exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.70, 4.81 (*J* = 13.0 Hz) and 5.03, 5.15 (*J* = 13.0 Hz) in a 1 : 1 ratio as the dicationic telluranes **21** and **23**. The ^{125}Te NMR spectrum of **24** shows one peak at δ 1369.0.

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Scheme 2-14

The telluride **17** was also oxidized by adding a solution of NOBF$_4$ to form the new dicationic tellurane having sulfonio ligands (Scheme 2-15). After removal of the solvent, the tellurane dication 2BF$_4^-$ salt (**25a**) was isolated as a white solid. In the ^{1}H NMR spectrum of **25a**, the peaks in aliphatic region were rather complicated and this result indicates that the dicationic tellurane **25a** has stereoisomers in solution. The ^{125}Te NMR spectrum of **25a** also shows two peaks at δ 1191.4 and δ 1169.8. So the dicationic tellurane **25a** is estimated to exist as two stereoisomers, *cis-trans* (*trans-cis*) and *trans-trans*.
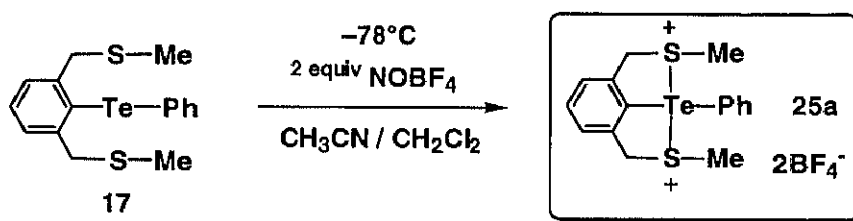
Scheme 2-15

Recently, Balenkova *et al.* reported the oxidative properties of Tf$_2$O.[9] They described that the mechanistic scheme of the reaction path of dialkyl sulfide to dialkyl sulfoxide by the reaction with Tf$_2$O as shown in Scheme 2-16. In this reaction, Tf$_2$O works as an oxidizing reagent although it is an acid anhydride. Furukawa's group already applied this method to the preparation of several dications[8].
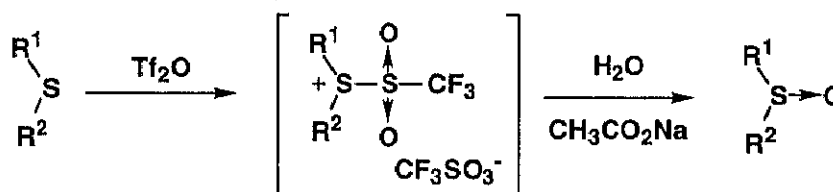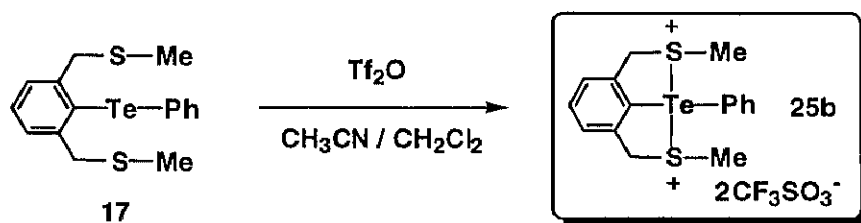

Scheme 2-16

The telluride **17** was treated with Tf$_2$O to form the corresponding dicationic tellurane 2CF$_3$SO$_3^-$ salt (**25b**). After removal of the solvent, the tellurane dication **25b** was isolated as a white solid. The ^{1}H NMR spectrum of **25b** shows almost the same pattern as **25a** and the ^{125}Te NMR spectrum of **25b** also shows two peaks at δ 1172.9 and δ 1201.0. So this dicationic tellurane **25b** is also estimated to exist as two stereoisomers, *cis-trans* (*trans-cis*) and *trans-trans*.

In the case of each dicationic telluranes **25a** and **25b**, recrystallization could not give the single stereoisomer. It is very interesting to compare this result with the dicationic tellurane **2** having two phenyl groups instead of two methyl groups, because it exists as one configuration both in the solution and the solid. There is no rational explanation for these results, it is supposed that π–π interaction of the phenyl groups might be effective in the case of the dicationic tellurane **2**.

X-ray crytallographic analysis is necessary to determine the configuration of **25**, but all attempts to get the single crystals were failed.

Scheme 2-17

Attempt to Synthesize the Spiro Dicationic Tellurane

In order to make a spiro-type dicationic tellurane, bis[2-(phenylthio)methyl]phenyl telluride **19** was readily oxidized by adding a solution of NOBF$_4$ (2 equiv) at -78 °C under an argon atmosphere. However, the reaction gave only complex mixture and no spiro dicationic tellurane was observed. This result is supposed to depend on the flexibility of the spiro structure.
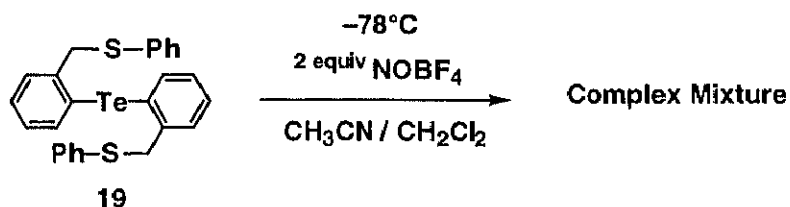

Figure 2-18

Intermolecular Dicationic Tellurane

The intermolecular dicationic tellurane was also tried to synthesize by following method. To an acetonitrile-d_3 solution of 1,5-bis[(phenylseleno)methyl]benzene 26 and diphenyl telluroxide 27, Tf_2O was added under an argon atmosphere in an NMR tube. The color of the solution changed from colorless to bright yellow which is common for the dicationic telluranes. However the ^1H and ^{125}Te NMR spectrum of the solution only showed complex signals and the corresponding dicationic tellurane was not observed. This result indicates that the transannular interaction is important to make the hypervalent Se-Te–Se bond.
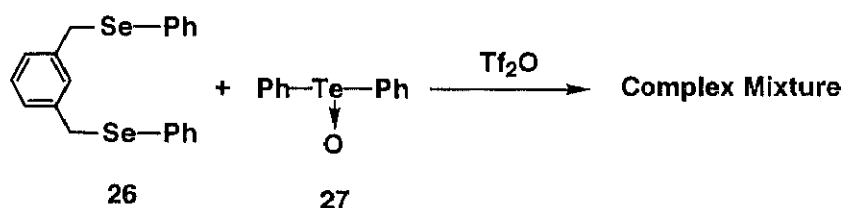
Scheme 2-19

IV. Electorochemical Studies

In order to investigate transannular interaction in the novel telluride, electrochemical studies by cyclic voltammetry (CV) were carried out. Peak potentials (E_p) of the first oxidation peak were obtained with 2 mM samples in CH_3CN-0.1 M $NaClO_4$ with a glassy carbon working electrode and Ag/AgCl in 3 M KCl as a reference electrode (scan rate 100 mV/s). The peak potentials for 6, 10, 11, 12 and 14 showed the values presented in Table 2-1. For comparison, values for the compound having a similar structure (29 and 30) and diphenyl telluride 28 observed under the same conditions are included in the table.

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12 (+718 mV[a])

[a]Reversible.
[b]Pseudo-reversible
[c]Irreversible.

PhSe / MeO

6 (+623 mV[b]) 11 (+680 mV[b])

0.1 M NaClO$_4$;
potential vs, Ag / AgCl
saturated KCl
reference; scan rate 100
mV/s

PhSe
Me$_2$N—TePh
PhSe
Me$_2$N

14 (+370 mV[c])

MeO
—TePh
MeO
10 (+878 mV[c])

Ph-Te-Ph
28 (+900 mV[c])

Me$_2$N

Me$_2$N
29 (+982 mV[c])

PhSe

PhSe
30(+1136 mV[c])

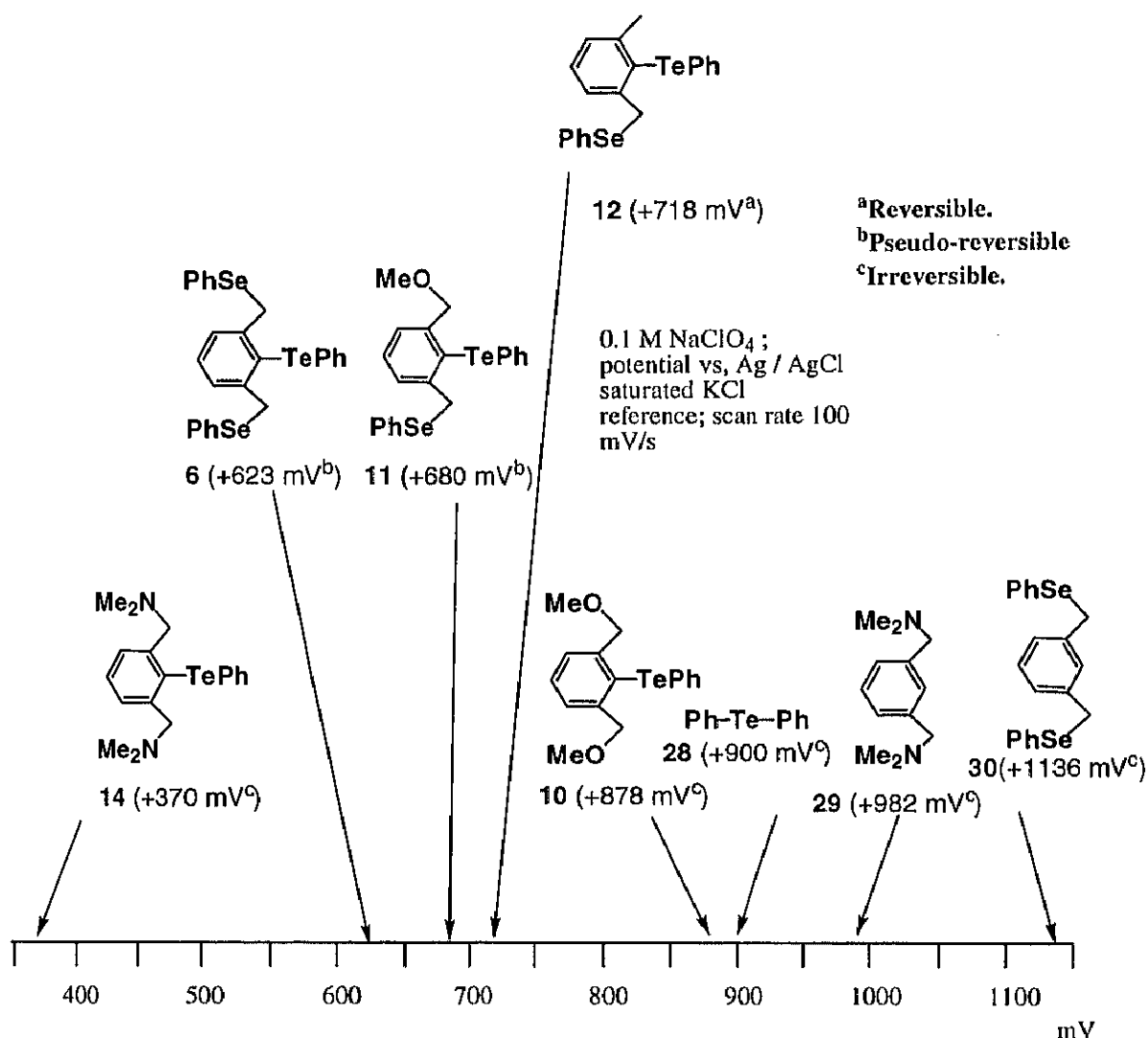| 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 |

mV

Table 2-1

Normally, the oxidations of tellurides are irreversible as observed for diphenyl telluride (Ph–Te–Ph), since the cation radicals of heteroatoms having alkyl or aryl groups in general will deprotonate or react with nucleophiles, leading to short lifetimes of these species and irreversible oxidation waves. However, it is noted that the tellurides 6 and 11 show pseudo-reversible behavior, and therefore should be stabilized by introduction of phenyl seleno-methyl ligand. And the existence of an interaction between the three chalcogen atoms in 6, 10, 11, 12 or 14 was apparent, because 182 ~ 530 mV reduction in the oxidation potentials was observed when 14 (370 mV), 6 (623 mV), 11 (680 mV), or 12 (718 mV) was compared with diphenyl telluride (Ph–Te–Ph) (900 mV). The cyclic voltammograms of 6 and 11 are shown in Figure 2-11.
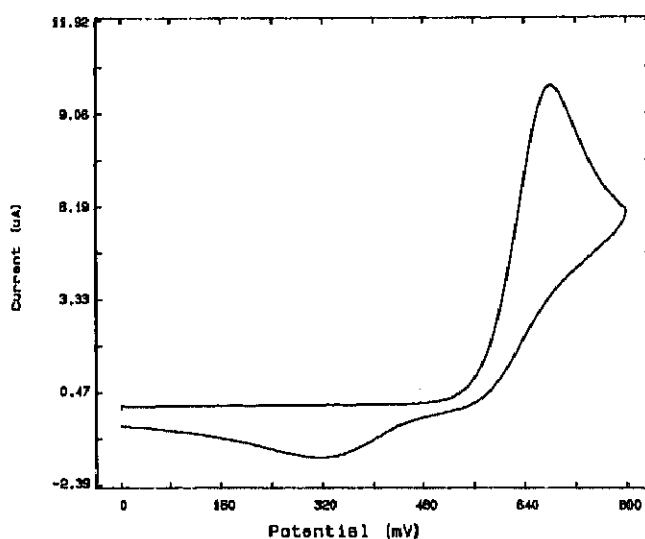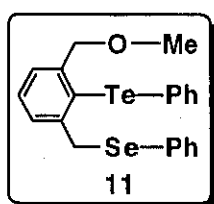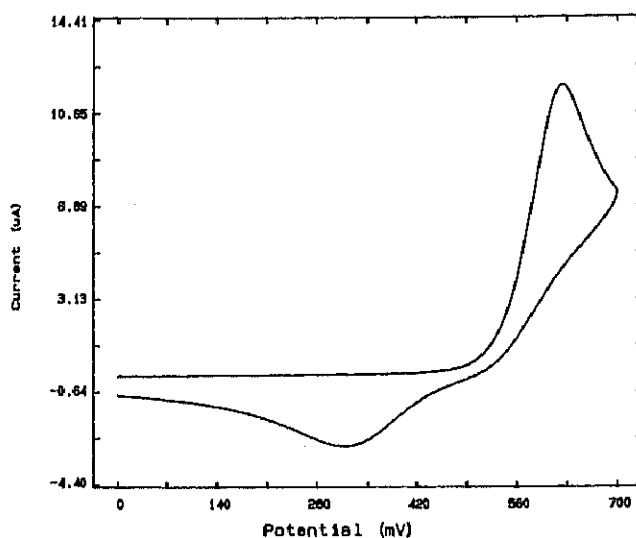
58
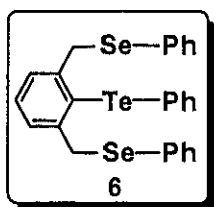
Figure 2-11

In the electrochemical sense, compounds 6 and 11 show pseudo-reversible and not reversible behavior, since the anodic wave peak and cathodic wave peak are separated by more than 60 mV. However, the gap between the two peaks may be due to the conformational changes in the compounds which are accompanied by the redox process. The energy required for these conformational changes is not accounted for in the definition of electrochemical reversibility. In addition, multi-cycle experiments showed that the cyclic voltammograms after one and five scans were almost identical in both cases. Therefore, the voltammograms observed may actually reflect reversible behavior as shown in Scheme 2-20.

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X= N(Me)$_2$, SePh, OMe.
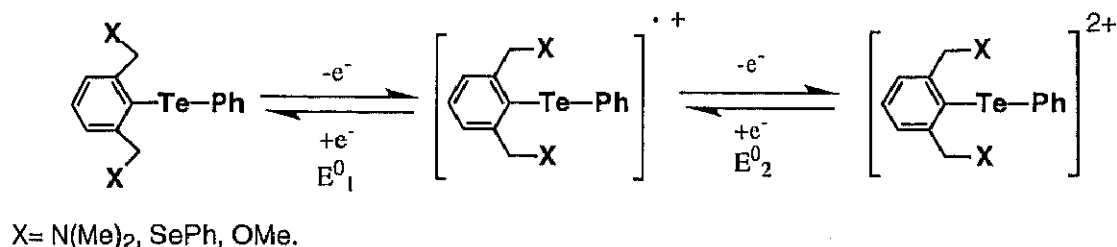
Scheme 2-20

Interestingly, the result of multi-cycle experiments revealed that the telluride **12** gives a reversible wave with peak potential of 718 mV as shown in Figure 2-12. Only this telluride shows reversible wave while the other "tris-chalcogenides" show pseudo-reversible behavior. It is supposed that the difference should be depending on their structure. The telluride **12** has only two chalcogen atoms, so the conformational change should be easily compared with "tris-chalcogenides" such as **6**, **11** and **14**.
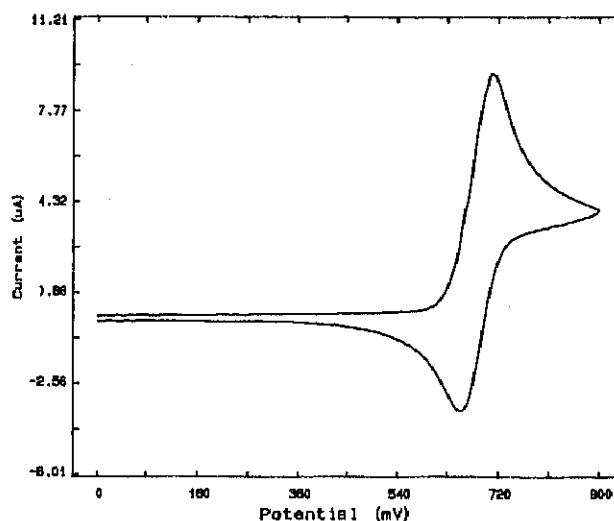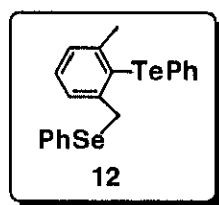
Figure 2-12

In addition, the electrochemical properties of the dicationic telluranes **21b** and **20** are also examined. The voltammogram of the dicationic tellurane **21b** is shown in Figure 2-13. On the reverse sweep a cathodic wave appeared at a peak potential of 233 mV which is also irreversible and is due to the reduction of the dicationic tellurane **21b**. An anodic wave appears at a peak of 631 mV which is due to the oxidation of the telluride **6**. This peak oxidation potential consists with the voltammogram of the telluride **6**, whose peak oxidation potential is 623 mV.

And these facts indicate that an anodic peak for the telluride **6** and cathodic peak for the dicationic tellurane **21b** seem to be resulted via the two electron transfer process.
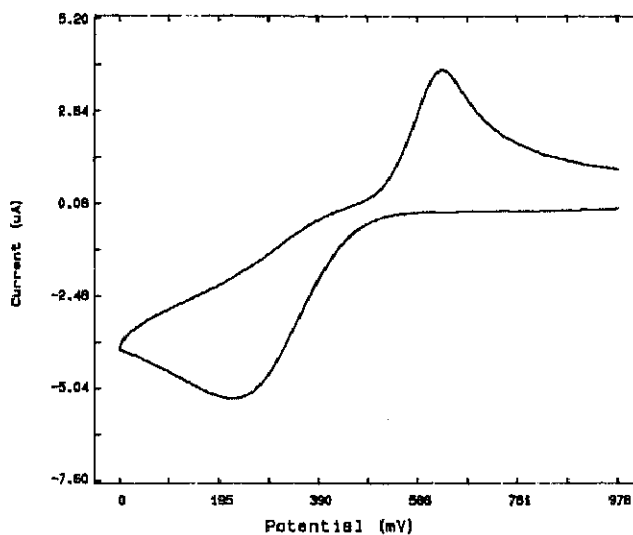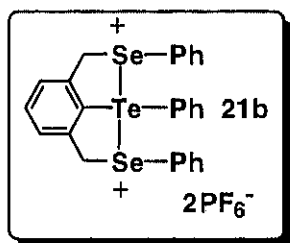
Figure 2-13

The voltammogram of the dicationic tellurane **20** is also shown in Figure 2-14. On the reverse sweep a cathodic wave appeared at a peak potential of −310 mV, which is also irreversible and is due to the reduction of the dicationic tellurane **20**. This peak reduction potential is relatively low, and this result is connected with the stability of the dicationic tellurane **20**. And an anodic wave appears at a broad peak around 300 mV, which is due to the oxidation of the telluride **14**.

Figure 2-14

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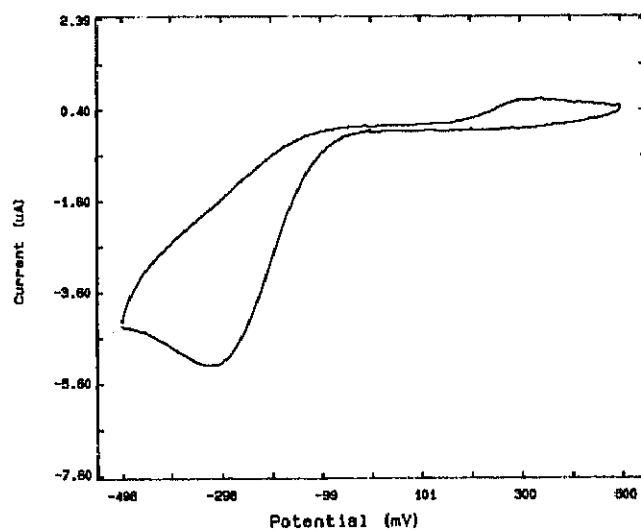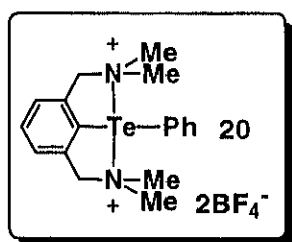
V. Theoretical Calculations

In order to understand the electronic structure of the dicationic σ-telluranes, single point *ab initio* calculations were carried out using the crystal structures of **20** and **21**. The calculations were carried out at the RHF/3-21G(*) level. The atomic charges were evaluated by the natural population analysis;[10] this method is particularly more suitable than the traditional Mulliken population analysis for hypervalent species which have strongly polar bonds.[11] The charge distributions in the two dications are shown in Figure 2-16 and 2-17 and various electronic properties are summarized in Table 2-2. The theoretical calculation results of the dicationic tellurane (+S–Te–S+), although it was already reported[12], is also shown here for comparison (Figure 2-15).
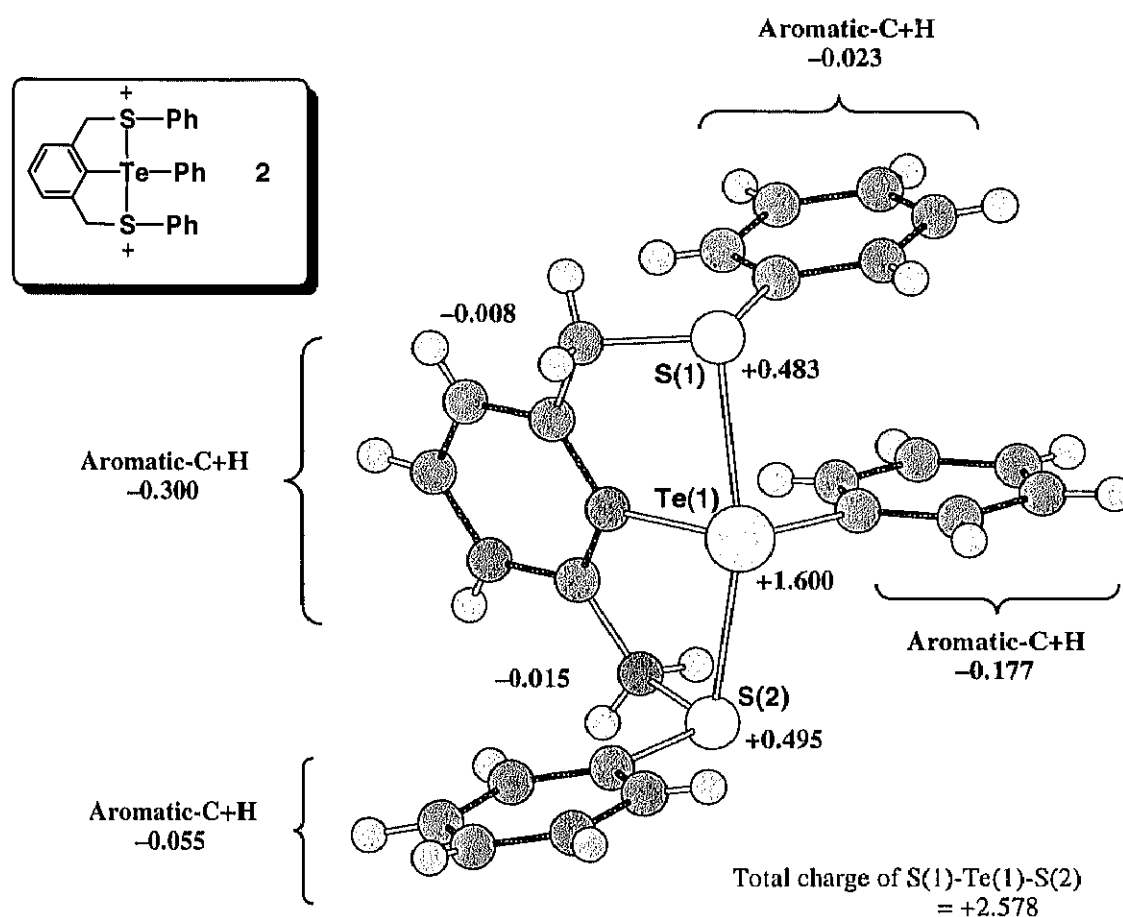
Figure 2-15[12]

A. The Dicationic Tellurane (+Se–Te–Se+) 21

The atomic charges of Te(1), Se(1), and Se(2) in **21** were calculated to be +1.422, +0.615, and +0.602, respectively. Thus, the total positive charge of +2.639 is located exclusively on the three chalcogen atoms of hypervalent bonding system. The charge is larger than two due to the

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polarization of Te–C and Se–C bonds. In addition, the hypervalent apical bonds seem to be polarized as is normally observed in hypervalent molecules, since the positive charges of Se(1) and Se(2) are substantially smaller than one (the charge of the sulfur atom in the trimethylsulfonium cation is calculated to be +0.98 by the same method of calculation). In 21, the Te(1) atom is less positively charged than in 2 and the positive charges on Se(1) and Se(2) are larger than those of the sulfur atoms in 2, simply reflecting the fact that the electronegativity of selenium is smaller than that of sulfur.

The Mulliken bond orders of Te(1)–Se(1) and Te(1)–Se(2) in 21 are 0.587 and 0.556, which are almost equal to the maximum value (0.5) attainable by the three-center four-electron (3c–4e) bond model using only an sp basis set.[14] The Te(1)–S(1) and Te(1)–S(2) bond orders of 2 are somewhat smaller. The total 5d-orbital population of tellurium is small (about 0.03) in 21, the d orbitals are not primarily concerned with the Te–Se bonds. The Mulliken valency values, about 3 and 2.6 for the tellurium and selenium atoms, respectively, are consistent with the resonance as shown in Scheme 2-21.
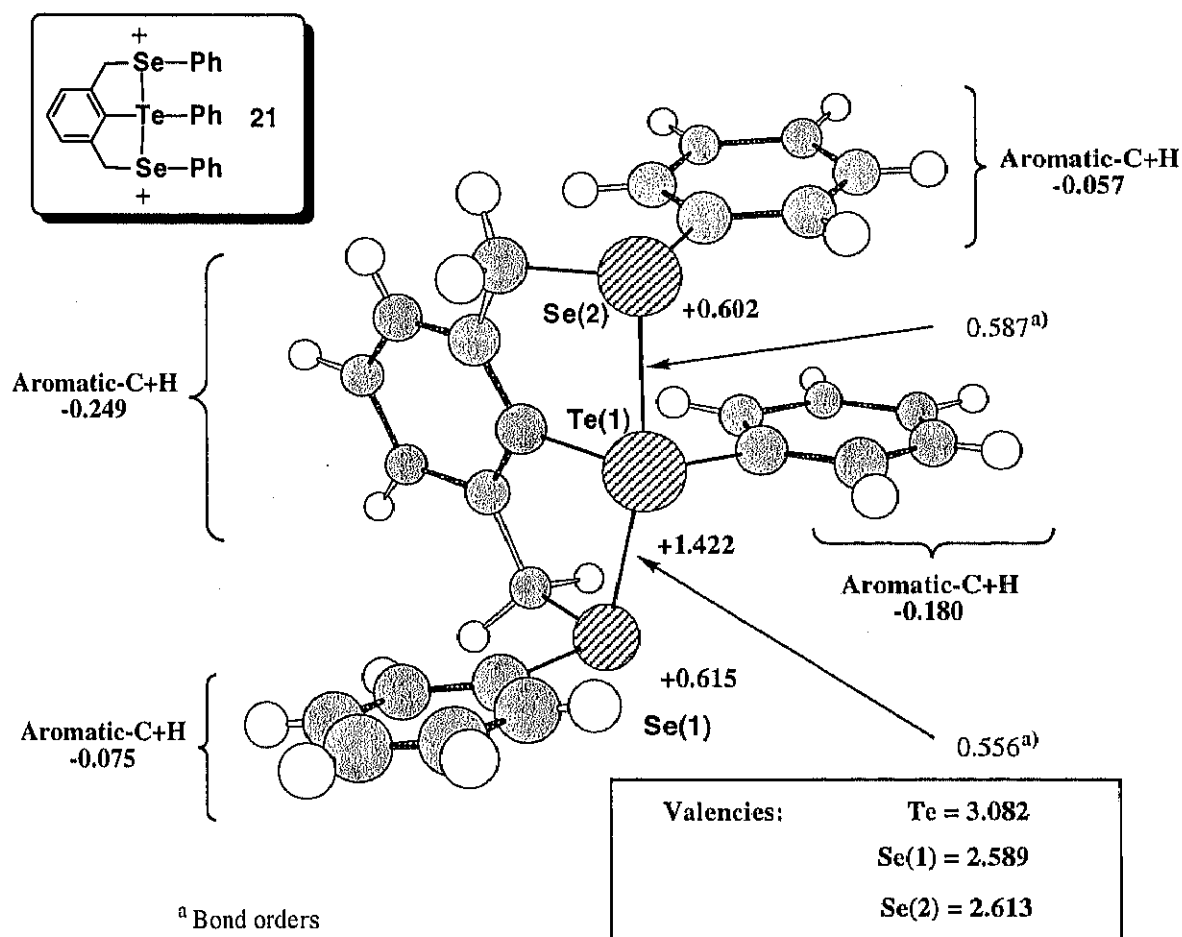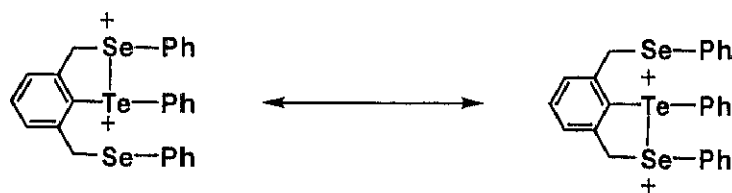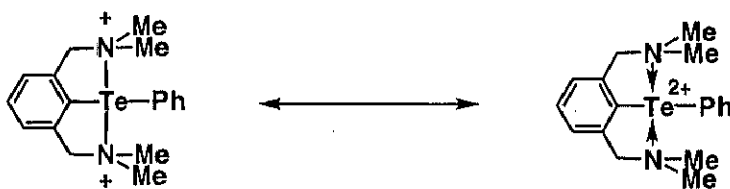

Figure 2-16

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Scheme 2-21

As shown in Figure 2-16, the positive charges are not delocalized onto the phenyl ring systems. This can be explained by the following molecular orbital consideration. Delocalization of the positive charges implies that electrons are pulled into the hypervalent bond and this would require that electrons are placed in the antibonding molecular orbital which is unfavorable.

The counter ion and solvent molecules were not included in the *ab initio* calculations. It should be noted, however, that the positive charges are exclusively carried by the three chalcogen atoms without the presence of counter ions; further charge localization induced by counter ions is not expected. Charge transfer interaction is also possible, but its amount is expected not to be large judging from the interatomic distances between the dication and counter ions. Therefore, the author thought that the charge distributions calculated for the isolated dications are not so different from those in crystals and in solutions, and that the interactions between the dication and counter ions are essentially electrostatic.

B. The Dicationic Tellurane (+N–Te–N+) 20

The calculation result of the dicationic tellurane **20** is different from that of **21**. The atomic charges of Te(1), N(1), and N(2) in **20** were calculated to be +1.898, –0.634, and –0.650, respectively. Thus, the sum of the positive charge on the three chalcogen atoms of hypervalent bonding system is +0.614 which is very small value compared with those of **20**. And the charge of the tellurium atom, +1.898, is nearly equal to the total charge of the molecule, +2.0. This result indicates that the positive charges are localized in the tellurium atom. Considering these results, the dicationic tellurane **20** should be represented by following resonance structure (Scheme 2-22).

Scheme 2-22
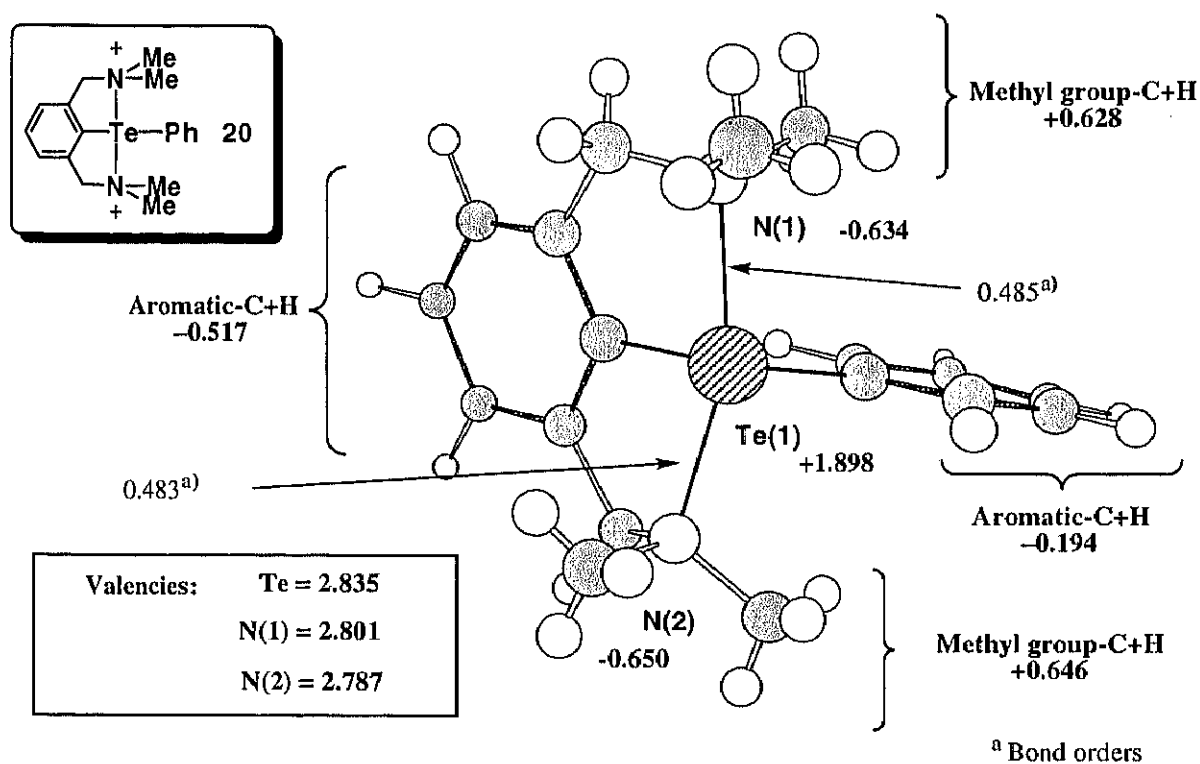
Figure 2-17

quantity	atom or bond	21a (X = Se)	20 (X = N)
atomic charge[a]	Te	+1.422	+1.898
	X(1)	+0.602	−0.634
	X(2)	+0.615	−0.650
bond order[b]	Te−X(1)	0.556	0.485
	Te−X(2)	0.587	0.483
valency[b]	Te	3.082	2.835
	X(1)	2.589	2.801
	X(2)	2.613	2.787
5d occupancy[a]	Te	0.033	0.022

[a] Natural population analysis. [b] Mulliken values.

Table 2-2

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VII. Conclusion

In conclusion, the chemical properties and preparation of a new type of dicationic σ-telluranes (λ^4-tellane), $[10-Te-4]^{2+}$ salts from the new flexible acyclic tris-chalcogenides via transannular bond formation were studied. Single crystal X-ray structure determinations revealed that two apical amino- and selenonio ligands bond to the central tellurium atom via transannular bond formation. Furthermore, the computational results show that the dicationic tellurane **21** contains a positively charged hypervalent bond, which accordingly can be characterized as an electron rich three atom center bonding system (3c–4e) with positively charged atoms.

Expermental

General procedure. All NMR spectra were obtained with a JEOL LMN-EX-270 or a Bruker ARX-400 spectrometer. Each chemical shift was determined by two dimensional shift correlation (^{1}H–^{1}H–COSY) spectra. Mass spectra were taken with a Shimazu QP-2000 and a JEOL JMX SX102 mass spectrometer, and IR spectra with a JASCO FT/IR-300F spectrometer. For cyclic voltammetry measurements, a Cypress Systems Inc. CS–1090 computer-controlled electroanalytical system was used. The X-ray crystallographic analyses were performed on an Enraf-Nonius CAD4 diffractometer, a Rigaku AFC7S diffractometer and a Rigaku RAXIS II imaging plate area detector. All solvents and reagents were dried and purified according to standard methods. Elemental analyses were carried out by the Chemical Analytical Center at the University of Tsukuba.

***Ab Initio* calculations.** *Ab initio* single-point calculations of the dications were carried out on a HP735/125 workstation using Spartan version 3.1[14]. The X-ray molecular structures of **20** and **21a** were used. The RHF method was employed with the 3-21G(*) basis set which includes d polarization functions on sulfur, selenium, and tellurium atoms. The atomic charges were calculated by the natural population analysis[10].

Synthesis of 2,6-bis(methoxymethyl)phenyl phenyl telluride 10

BuLi (0.86 mL, 1.38 mmol, 1.60 M in *n*-hexane) was added to a dry ether (20 mL) solution of 2,6-bis(methoxymethyl)phenyl bromide **9** (337 mg, 1.38 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of diphenyl ditelluride (662 mg, 1.62 mmol) in dry Et$_2$O (20 mL) using a transfer needle under the

same conditions. The resulting orange mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, *n*-hexane-CHCl$_3$, 4 : 1) to give a yellow oil, telluride **2b** (429 mg) in 84% yield.
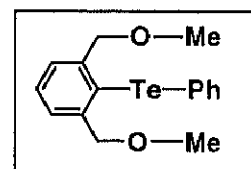
2,6-Bis(methoxymethyl)phenyl phenyl telluride 10

^{1}H NMR (270 MHz, CDCl$_3$, room temperature) δ 3.32 (s, 6H, CH$_3$O), 4.54 (s, 4H), 7.12–7.43 (m, 8H, Ar-H). ^{13}C NMR (68 MHz, CDCl$_3$, room temperature) δ 58.0, 116.6, 119.6, 127.1, 127.3, 129.3, 129.4, 135.7, 144.0; ^{125}Te NMR (85 MHz, CDCl$_3$, room temperature) δ 446.4 (relative to Me$_2$Te); MS (m/z) 372 (M$^+$); Anal. Calcd for C$_{16}$H$_{18}$O$_2$Te: C, 51.95; H, 4.90. Found: C, 51.94; H, 4.90.

Synthesis of 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluride 6 and [2-methoxymethyl-6-(phenylseleno)methyl]phenyl phenyl telluride 11

To a dry CH$_3$CN (100 mL) solution of 2,6-bis[(methoxy)methyl]phenyl phenyl telluride **10** (430 mg, 1.15 mmol), KI (1.5 g, 11.5 mmol) and AlCl$_3$ (2.0 g, 11.5 mmol) were added at room temperature under an argon atmosphere. The solution was stirred for 10 h and then a mixture of NaBH$_4$ (65 mg, 1.72 mmol) and diphenyl diselenide (430 mg, 1.37 mmol) in CH$_3$CN (10 mL) was added using a transfer needle. The solution was stirred overnight and then the solvent was evaporated at room temperature. Saturated Na$_2$S$_2$O$_3$ aq. (100 mL) was added to the residue and the organic

products extracted with ether, the organic layer was separated, dried over anhydrous MgSO$_4$ and the solvent was removed. The crude product was purified by column chromatography (silica gel; eluent, n-hexane-CH$_2$Cl$_2$, 4 : 1) to give a pale yellow oil, telluride **5** (60 mg) in 8% yield.
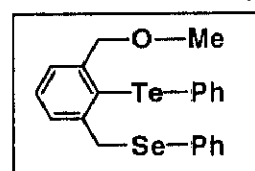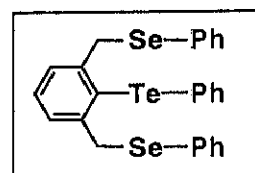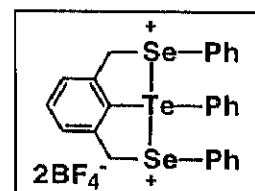
2,6-Bis[(phenylseleno)methyl]phenyl phenyl telluride 6

^{1}H NMR (400 MHz, CDCl$_3$, room temperature) δ 4.38 (s, 4H), 7.02–7.41 (m, 18H, Ar-H); ^{13}C NMR (100 MHz, CDCl$_3$, room temperature) δ 40.0, 117.2, 123.0, 127.0, 127.4, 127.7, 128.9, 129.5, 130.2, 134.0, 134.8, 146.1; ^{125}Te NMR (85 MHz, CDCl$_3$, room temperature) δ 428.0 (J_{Te-Se} = 100 Hz) (relative to Me$_2$Te); ^{77}Se NMR (51 MHz, CDCl$_3$, room temperature) δ 387.3 (J_{Te-Se} = 100 Hz) (relative to Me$_2$Se); MS (m/z); 620 (M$^+$); Anal. Calcd for C$_{26}$H$_{22}$Se$_2$Te: C, 50.37; H, 3.58; Found: C, 50.18; H, 3.49.

[2-Methoxymethyl-6-(phenylseleno)methyl]phenyl phenyl telluride 11

^{1}H NMR (270 MHz, CDCl$_3$, r.t.) δ 3.30 (s, 3H), 4.43 (s, 2H), 4.53 (s, 2H), 7.02-7.43 (m, 13H, Ar-H); ^{13}C NMR (67.8 MHz, CDCl$_3$, r.t.) δ 39.8, 58.1, 116.8, 120.7, 126.3, 127.0, 127.4, 128.2, 128.9, 129.3, 129.4, 130.3, 133.9, 135.2, 144.9, 145.1; ^{125}Te NMR (85.2 MHz, CDCl$_3$, r.t.) δ 430 (J_{Te-Se} =121 Hz); ^{77}Se NMR (51.4 MHz, CDCl$_3$, r.t.) δ 385 (J_{Te-Se} =121 Hz); EIMS (m/z); 496 (M$^+$); Anal. Calcd for C$_{21}$H$_{20}$OSeTe: C, 50.96; H, 4.07; Found: C, 50.69; H, 3.96.

Synthesis of 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 21a

An anhydrous CH$_3$CN (10 mL) solution of NOBF$_4$ (30 mg, 0.26 mmol) was added dropwise to a solution of telluride **6** (67 mg, 0.11 mmol) in anhydrous CH$_2$Cl$_2$ (20mL) at –78 °C under an argon atmosphere. The resulting solution turned yellow. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the

solvents were evaporated at room temperature and recrystallization from CH_2Cl_2, CH_3CN and ether gave yellow crystals of tellurane dication $2BF_4^-$ salt **21a** (44 mg) in 51% yield.

2,6-Bis[(phenylseleno)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 21a

mp 201–204 °C (dec); ^1H NMR (270 MHz, CD_3CN, –40 °C) δ 4.37, 5.23 (ABq, J = 17 Hz, 2H), 5.01, 5.25 (ABq, J = 16 Hz, 2H), 6.7 – 8.12 (m,18H, Ar-H); ^{13}C NMR (68 MHz, CD_3CN, room temperature) δ 38.1, 38.4, 119.8, 125.1, 129.1, 129.6, 130.3, 131.3, 131.8, 132.1, 132.2, 132.4, 133.0, 133.9, 134.5, 134.7, 135.8, 147.7, 148.3; ^{125}Te NMR (85 MHz, CD_3CN, –40 °C) δ 1174.9 (J_{Te-Se} = 443, 491 Hz) (relative to Me_2Te); ^{77}Se NMR (51 MHz, CD_3CN, –40 °C) δ 393.6 (J_{Se-Te} = 443 Hz, J_{Se-Se} = 71 Hz), 462.3 (J_{Se-Te} = 491 Hz, J_{Se-Se} = 71 Hz) (relative to Me_2Se); ^{19}F NMR (254 MHz, CD_3CN, room temperature) δ -159 (BF_4^-) (relative to $CFCl_3$); MS (m/z); 620 ($M^+-2BF_4^-$); HRMS: calcd for $C_{26}H_{22}Se_2Te$ ($M^+-2BF_4^-$) 352.0922, found 352.0920.

Synthesis of [2-methoxymethyl-6-(phenylseleno)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 23

An anhydrous CH_3CN (10 mL) solution of $NOBF_4$ (36 mg, 0.31 mmol) was added dropwise to a solution of telluride **11** (63 mg, 0.13 mmol) in anhydrous CH_2Cl_2 (20mL) at –78 °C under an argon atmosphere. The resulting solution turned yellow. When the addition was completed, the NO gas was removed under vac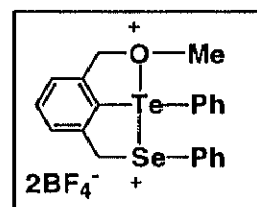uum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH_2Cl_2, CH_3CN and ether gave yellow crystals of tellurane dication $2BF_4^-$ salt **23** (75 mg) in 85% yield.

[2-Methoxymethyl-6-(phenylseleno)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 23

mp 155-157 °C (decomp.); ^1H NMR (270 MHz, CD_3CN, r.t.) δ 3.52 (s, 3H), 4.62 and 5.02 (ABq, J=14 Hz, 2H), 5.53 and 5.37 (ABq, J=16 Hz, 2H), 6.96-8.05 (m,13H, Ar-H); ^{13}C NMR (67.8 MHz, CD_3CN, r.t.) δ 42.0, 60.8, 72.5, 119.9, 122.1, 125.0, 127.8, 130.3, 130.8, 130.9, 131.4, 132.8, 133.4, 134.3, 134.5, 143.6, 146.6; ^{125}Te NMR (85.2 MHz, CD_3CN, r.t.) δ 1375 (J_{Te-Se} =374 Hz); ^{77}Se NMR (51.4 MHz, CD_3CN, r.t.) δ 481 (J_{Te-Se} =374 Hz); ^{19}F NMR (254 MHz, CD_3CN, r.t.) δ 149.9; EI-MS (m/z); 496 ($M^+-2BF_4^-$).

Synthesis of 2,6-[bis(dimethylamino)methyl]phenyl phenyl telluride 14

BuLi (8.9 mL, 14 mmol, 1.60 M in n-hexane) was added to a dry ether (100 mL) solution of 2,6-bis(dimethylaminomethyl)phenyl bromide **13** (3.2 g, 12 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of diphenyl ditelluride (4.8 g, 12

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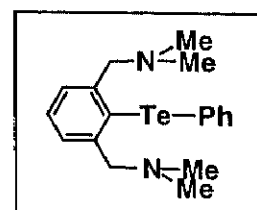
mmol) in dry Et$_2$O (100 mL) using a transfer needle under the same conditions. The resulting orange mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, CHCl$_3$-MeOH,10 : 1) to give a yellow oil, telluride **14** (544 mg) in 12% yield.

2,6-[Bis(dimethylamino)methyl]phenyl phenyl telluride 14

^{1}H NMR (400 MHz, CDCl$_3$, r.t.) δ 2.10 (s, 12H), 3.36 (s, 4H), 7.06-7.51 (m, 8H, Ar-H); ^{13}C NMR (100 MHz, CDCl$_3$, r.t.) δ 44.4, 67.8, 122.1, 124.7, 126.5, 127.4, 127.6, 128.9, 136.2, 144.3; ^{125}Te NMR (126 MHz, CDCl$_3$, r.t.) δ 515; EIMS (m/z); 398 (M$^+$). Anal. Calcd for C$_{13}$H$_{24}$N$_2$Te: C, 54.60; H, 6.11; N, 7.07; Found: C, 54.32; H, 5.90; N, 6.78.

Synthesis of 2,6-bis(dimethylaminomethyl)phenyl phenyl telluranyl bis(tetrafluoroborate) 20

An anhydrous CH$_3$CN (10 mL) solution of NOBF$_4$ (65 mg, 0.56 mmol) was added dropwise to a solution of telluride **14** (100 mg, 0.25 mmol) in anhydrous CH$_2$Cl$_2$ (20mL) at -78 °C under an argon atmosphere. The resulting solution turned yellow. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH$_2$Cl$_2$, CH$_3$CN and ether gave colorless crystals of tellurane dication 2BF$_4^-$ salt **20** (44 mg) in 20% yield.
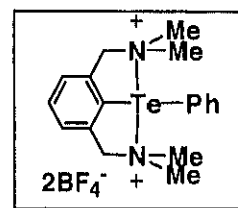

2,6-Bis(dimethylaminomethyl)phenyl phenyl telluranyl bis(tetrafluoroborate) 20

mp 197-199 °C (decomp.); ^{1}H NMR (270 MHz, CD$_3$CN, -40°C) δ 2.31 (s, 6H, Me), 3.11 (s, 6H, Me), 4.19 and 4.39 (ABq, J=16 Hz, 4H), 6.99-7.01 (m, 1H, Ar-H),7.58-8.35 (m, 7H, Ar-H); ^{13}C NMR (67.8 MHz, CD$_3$CN, -40°C) δ 48.1, 48.2, 63.2, 122.9, 129.1, 132.3, 132.5, 136.0, 136.3, 137.1, 143.4; ^{125}Te NMR (126 MHz, CD$_3$CN, r.t.) δ 1335.3 (relative to Me$_2$Te); ^{19}F NMR (254 MHz, CD$_3$CN) δ -151 (BF$_3^-$, relative to CFCl$_3$); EIMS (m/z); 398 (M$^+$-2BF$_4^-$); Anal. Calcd for C$_{13}$H$_{24}$B$_2$F$_8$N$_2$Te: C, 37.96; H, 4.25; N, 4.92; Found: C, 37.95; H, 4.24; N, 4.94.

Synthesis of 2,6-bis(methylthiomethyl)bromobenzene 16

To the solution of 2,6-bis(bromomethyl)bromobenzene **8** (1.96 g, 5.73 mmol) in CHCl$_3$, a solution of sodium thiomethoxide (930 mg, 13.3 mmol) at 0 °C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous

MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was
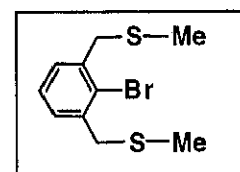
subjected to column chromatography (silica gel; eluent, *n*-hexane-CHCl₃, 4 : 1) to give a colorless crystals, **16** (1.90 g) in 98% yield.

2,6-Bis(methylthiomethyl)bromobenzene 16

mp 55–57 °C; ¹H NMR (400 MHz, CDCl₃, room temperature) δ 2.07 (s, 6H), 3.86 (s, 4H), 7.24–7.26 (m, 3H, Ar-H). ¹³C NMR (68 MHz, CDCl₃, room temperature) δ 15.3, 39.4, 126.1, 126.8, 129.4, 129.5, 138.6; EIMS (m/z) 276 (M⁺).

Synthesis of 2,6-bis[(methylthio)methyl]phenyl phenyl telluride 17

t-BuLi (5.0 mL, 7.7 mmol, 1.54 M in *n*-hexane) was added to a dry
THF (100 mL) solution of 2,6-bis(methylthiomethyl)phenyl bromide **16**
(1.45 g, 5.23 mmol) at –78 °C under an argon atmosphere. The solution
was stirred for 30 min and then added to a solution of diphenyl ditelluride

(662 mg, 1.62 mmol) in dry THF (20 mL) using a transfer needle under
the same conditions. The resulting orange mixture was allowed to warm to room temperature
overnight. The solvents were evaporated, and the residue was extracted with CH₂Cl₂. The
organic layer was dried over anhydrous MgSO₄, and removal of the solvent at room temperature
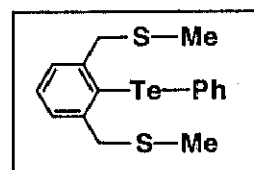gave the crude product, which was subjected to column chromatography (silica gel; eluent, *n*-hexane-CHCl₃, 4 : 1) to give a yellow oil, telluride **17** (163 mg) in 10% yield.
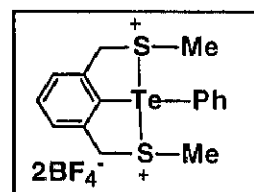
2,6-Bis[methylthio)methyl]phenyl phenyl telluride 17

¹H NMR (270 MHz, CDCl₃, room temperature) δ 1.96 (s, 6H), 3.96 (s, 4H), 7.10–7.39 (m, 8H, Ar-H). ¹³C NMR (68 MHz, CDCl₃, room temperature) δ 15.2, 45.0, 123.8, 127.0, 127.9, 129.0, 129.1, 129.5, 135.1, 145.2; ¹²⁵Te NMR (85 MHz, CDCl₃, room temperature) δ 448.2 (relative to Me₂Te); EIMS (m/z) 404 (M⁺).

Synthesis of 2,6-bis[(methylthio)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 25a

An anhydrous CH₃CN (10 mL) solution of NOBF₄ (350 mg, 2.99
mmol) was added dropwise to a solution of telluride **17** (500 mg, 1.24
mmol) in anhydrous CH₂Cl₂ (20mL) at –78 ° C under an argon
atmosphere. The resulting solution turned yellow. When the addition
was completed, the NO gas was removed under vacuum. After stirring

overnight, the solvents were evaporated at room temperature and recrystallization from CH₃CN
gave colorless crystals of tellurane dication 2BF₄⁻ salt **25a** (44 mg) in 20% yield.

2,6-Bis[(methylthio)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) 25a (Mixture of two isomers)

mp 191–193 °C (decomp.); ^{1}H NMR (400 MHz, CD$_3$CN, r.t.) δ 2.00 (s, 3H, Me), 2.64 (s, 3H, Me), 2.91 (s, 6H, Me), 4.28–4.75 (m, 8H), 6.99–7.01 (m, 1H, Ar-H),7.59–8.06 (m, 7H, Ar-H); ^{125}Te NMR (126 MHz, CD$_3$CN, r.t.) δ 1191.4, 1169.8 (relative to Me$_2$Te); EIMS (m/z); 404 (M$^+$–2BF$_4^-$); Anal. Calcd for C$_{16}$H$_{18}$B$_2$F$_8$S$_2$Te: C, 33.38; H, 3.15; Found: C, 33.06; H, 3.22.

Synthesis of the telluride 19

KOH (115 mg, 2.05 mmol) was added to a solution of thiophenol (210 mg, 1.91 mmol) in ethanol (50 mL). The solution was added dropwise to a solution of bis(2-bromomethylphenyl)tellurium dibromide (293 mg, 0.46 mmol) in CH$_2$Cl$_2$ (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH$_2$Cl$_2$ and the organic layer was dried over anhydrous MgSO$_4$. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, n-hexane-CHCl$_3$, 4 : 1) to give a colorless oil of the telluride 19 (137 mg) in 56% yield.
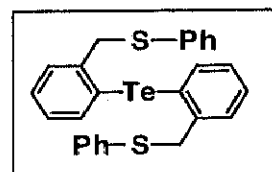
Bis[2-(phenylthio)methyl]phenyl telluride 19

^{1}H NMR (270 MHz, CDCl$_3$, room temperature) δ 4.30 (s, 4H, CH$_2$), 6.97–7.61 (m, 18H, ArH). ^{13}C NMR (68 MHz, CDCl$_3$, room temperature) δ 44.4, 121.8, 126.8, 128.2, 128.3, 128.9, 130.0, 130.6, 135.5, 139.9, 141.4; ^{125}Te NMR (126 MHz, CD$_3$CN, r.t.) δ 507.3 (relative to Me$_2$Te); EIMS (m/z) 528 (M$^+$).

Reaction of the telluride 19 with nitrosyl tetrafluoroborate.

To a solution of the telluride 19 (135 mg, 0.26 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL) was added dropwise a solution of nitrosyl tetrafluoroborate (NOBF$_4$; 72 mg, 0.62 mmol) in anhydrous CH$_3$CN (10 mL) at –78 °C under an argon atmosphere. The resulting solution turned yellow. After 30 min stirring, the NO gas evolved from the reaction was removed by using reduced pressure. The mixture was stirred overnight and after evaporation of the solvent in vacuum, a yellow residue remained. All attempts to crystallize the residue using ether-CH$_3$CN-CH$_2$Cl$_2$ at temperatures in the range –50 ~ 0 °C failed. The ^{1}H, ^{13}C and ^{125}Te NMR of the residue was complicated and the dicatonic tellurane was not detected.

Cyclic Voltammetry.

Voltammograms were obtained with 2 mM samples in anhydrous acetonitrile -0.1 M NaClO4 with a glassy carbon working electrode, a platinum counter electrode and Ag/AgCl in 3M KCl as a reference electrode.

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