

Chapter 3

First Synthesis and Characterization of Stable Sulfenium Ion Salts and Tellurenum Monoxide Dimer Stabilized by the Coordination of Nitrogen Atoms

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I. Introduction

Recently, van Koten and co-workers have discovered that the potentially tridentate ligand $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]^-$ (type A) is very useful for the stabilization of unusual oxidation states and for the isolation of reactive intermediates. This ligand is widely used to isolate unstable species (for example, trivalent silicon cation R_3Si^+), and a number of studies have already been reported.¹⁾ Some examples are shown in Figure 3-1.

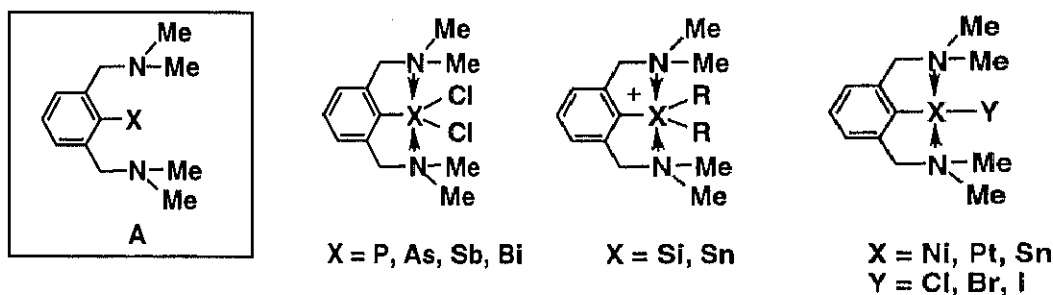
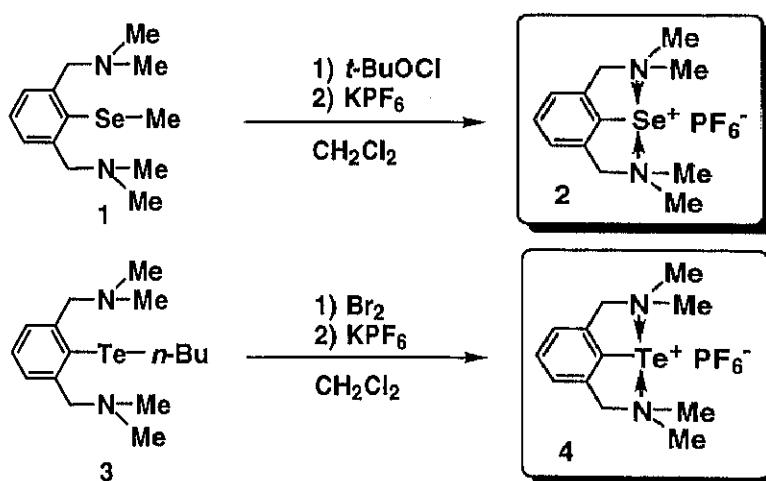


Figure 3-1

The selenenium and tellurenum ions **2** and **4** were prepared by using the coordination of the neighboring two amino groups of the ligand.²⁾ These ions were synthesized from the corresponding selenide or telluride by oxidizing with *t*-BuOCl or Br_2 as shown in Scheme 3-1. The crystal structure of the selenenium ion was determined by X-ray diffraction analysis. The X-ray data reveal the existence of the almost linear N–Se–N bond (161.9°). And there are short intramolecular Se–N contacts of 2.154 and 2.180 Å, which are remarkably shorter than the sum of the van der Waals radii (3.5 Å) of the two elements.



Scheme 3-1

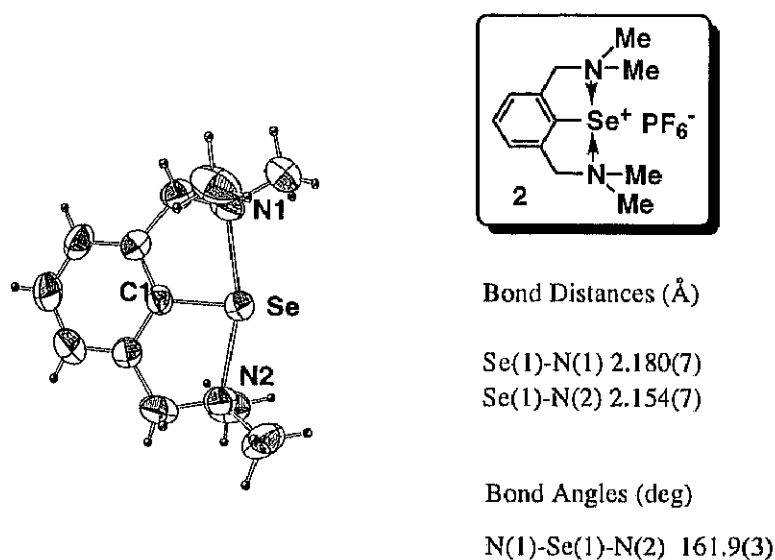


Figure 3-2

As described in Chapter 1, sulfenium ion species are known to be unstable and highly reactive as a strong electrophilic reagent. Therefore, these species have neither been directly detected, nor isolated as a 'free' cation. The studies of sulfenium ion are rather old among those of the sulfur compounds having positive charges.³⁾ The two approaches focusing preparation of sulfenium ion species have been reported. The former is the heterolysis of the S-X bond of the precursors which contain rather weak sulfur-X bond (X = carbon and heteroatoms),⁴⁾ The latter is the anodic oxidation of various disulfides using the electrochemical method.⁵⁾ Although the formation of sulfenium ions has been proposed in many studies, it is controversial whether the corresponding cations exist or not. Because their reactivity would not readily allow their existence as free cations. To date, there is no report concerning the actual structure of the sulfenium ions.

The author tried to isolate the sulfenium ions and their oxides by applying the ligand, [2,6-(Me₂NCH₂)₂C₆H₃]⁺ (type A). The selenonium and tellurenum ions, their analogous species of selenium and tellurium, and their oxides were also investigated.

II. Synthesis and Characterization of the Sulfenium Ions

A. Synthesis of the Sulfenium Ions

At first, the author tried to synthesize the sulfenium ion via the corresponding sulfide. 2,6-Bis(dimethylamoniomethyl)-1-thiomethylbenzene was prepared from the direct lithiation of 1,3-bis(dimethylamoniomethyl)benzene **5**. The sulfide **6** was treated with *t*-BuOCl to produce the sulfenium ion **7**. However the yield of the sulfenium ion **7** is only 1%, which is too low to get larger amount of the compound.

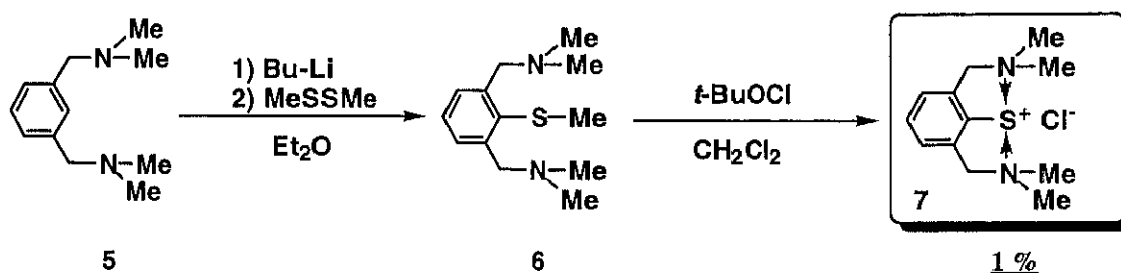
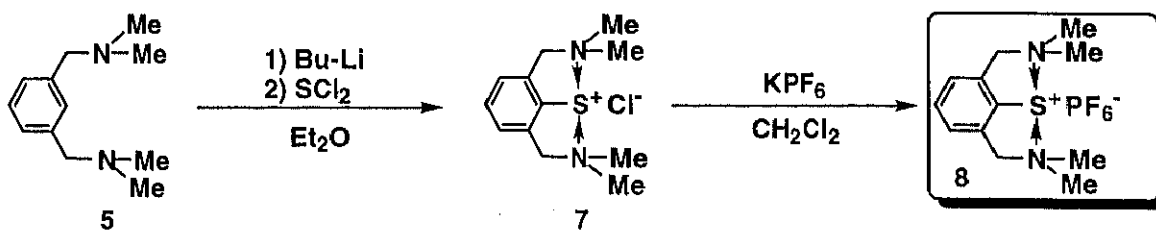


Figure 3-2

So another method was attempted to synthesize the sulfenium ion. 1,3-Bis(dimethylamoniomethyl)benzene **5** was easily lithiated by *n*-BuLi in anhydrous ether at room temperature under an argon atmosphere to prepare 1,3-bis(dimethylamoniomethyl)-2-lithiobenzene in situ. The ether solution of lithiated compound was added dropwise to 1 molar equiv of sulfur dichloride (SCl₂) in dry ether. After the removal of the solvent at room temperature, the corresponding sulfenium chloride **7** having Cl⁻ as the counter anion was isolated as stable yellow needle crystals in 20% yield.

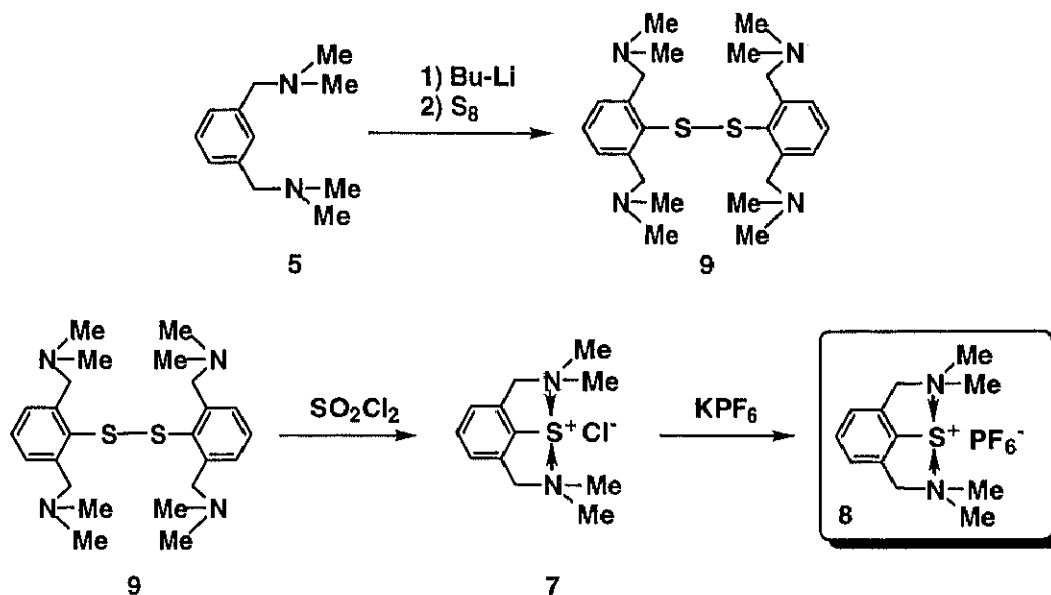
Furthermore, the product **7** was treated with potassium hexafluorophosphate (KPF₆) in CH₂Cl₂ to afford the 2,6-[bis(dimethylamoniomethyl)phenyl]sulfenium hexafluorophosphate **8** in 56% yield as shown in Scheme 3-3. The products **7** and **8** were identified by ¹H, ¹³C, ¹⁹F, and ³¹P NMR, mass spectroscopy, and elemental analysis.



Scheme 3-3

It is also possible to get the sulfenium ion from the corresponding disulfide **9** as shown in

Scheme 3-4. The disulfide **9** was treated with the sulfuryl chloride (SO_2Cl_2) to produce the sulfenium ion **7** quantitatively. The anion exchange with KPF_6 also gave the sulfenium ion **8**.



Scheme 3-4

The ^1H NMR signals of benzylic and four methyl protons in **8**, measured in CDCl_3 at room temperature, appear at 4.31 ppm and at 2.96 ppm as two sets of singlet in a 4 : 6 ratio, respectively. These chemical shifts of **8** were lower field than those of 1,3-bis(dimethylamoniomethyl)-2-methylthiobenzene **6**. These results indicate that each amino groups coordinate to the cationic sulfur. And two singlet peaks indicate that four methyl groups and four methylene protons are chemically equivalent respectively. Lowering the temperature of the NMR sample resulted in giving the same spectrum. By considering this result, it is supposed that there is an equilibrium as shown in Figure 3-3, and the activation energy of the equilibrium should be very low. Indeed, the *ab initio* calculation result of the sulfenium ion, using RHF / 3-21G(*), evaluates the activation energy of the equilibrium as 1.3 kcal mol $^{-1}$. This value is coincident with the NMR result. And the ^1H NMR spectrum of **7**, measured in CDCl_3 at room temperature, exhibits almost same signals as **8**, and no significant difference of chemical shift was observed.

The proton-decoupled ^{31}P and ^{19}F signals of **8** appeared at -145.4 ppm as the septet and -73.5 ppm as the doublet due to a spin-spin coupling between the phosphorus and fluorine nuclei ($^1J_{\text{P-F}} = 707$ Hz) which is derived from PF_6^- counter anion. Each compounds **7** and **8** were characterized by the signals excepted counter anion from their parent peaks in their EI-MS spectra. In addition, **7** and **8** were also identified by elemental analysis.

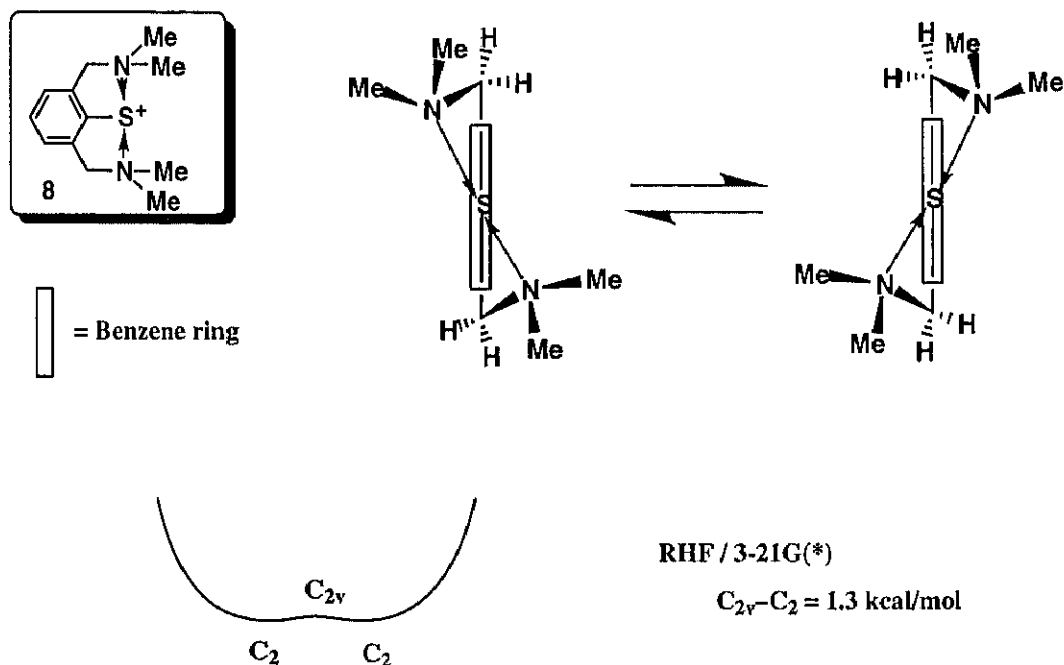
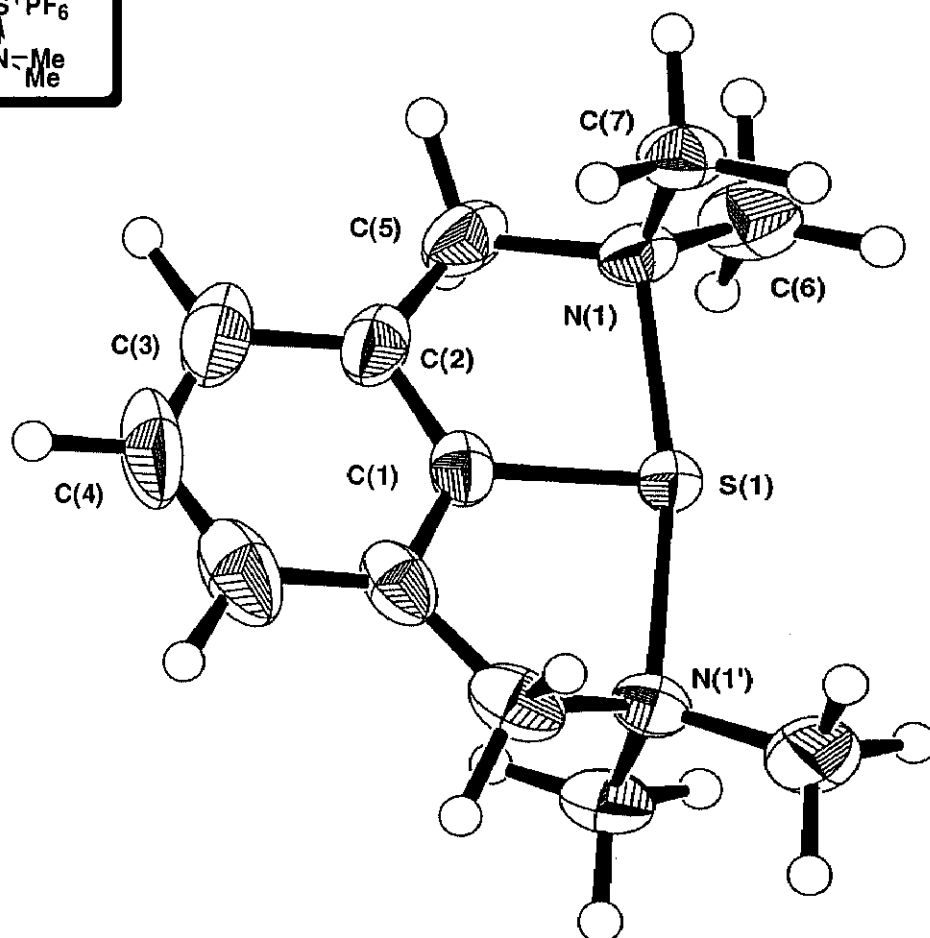
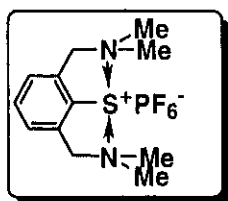


Figure 3-3

B. X-ray Crystallographic Analysis of the Sulfenium Ion

Furthermore, the structure of sulfenium ion **8** in solid state was determined by X-ray diffraction method. An ORTEP view of **8** is shown in Figure 3-4. In the solid state, the two neighboring amino nitrogens coordinate directly to the sulfur atom. Each bond lengths between the sulfur and each nitrogen atoms exhibited are 2.064 Å, which are slightly longer than a single covalent bond (1.74 Å)⁶⁾ between sulfur and nitrogen atoms. This result indicates the notion that the dimethylamino groups coordinate weakly to the central sulfur atom. The angle of N(1)–S(1)–N(1'), 168.5° is much distorted from linear arrangement, which is expected for the apical bond in hypervalent compounds generally. The sum of the angles around the sulfur atom is closely 360°, which indicate that the C(1), S(1), N(1) and N(2) are located co-planary. The counter anion, PF₆⁻, is independent of the cationic part of the sulfenium cation and not located within the sum of van der Waals radii between the sulfur and fluorine atoms (2.20 Å).⁶⁾ The tricyclo ring on the sulfur and nitrogen atoms is distorted and the dihedral angle between the planes making by N–S–N bond and benzene ring exhibited is 14.1(1)° as shown in Figure 3-5.

This X-ray data clearly indicate that the significant interactions exist between the sulfur and nitrogen atoms in the solid state. However, it is not defined what sorts of interaction, pseudo-hypervalent bond (pseudo-3c-4e bond) or ion-dipole electrostatic interaction exists.



The hexafluorophosphate ion is omitted.

Space Group C2/c(#15)
R=0.037, R_w=0.034.

Bond Distances (Å)

S(1)-N(1) 2.063(1)
S(1)-C(1) 1.758(2)

Bond Angles (deg)

N(1)-S(1)-N(1') 168.54(9)
N(1)-S(1)-C(1) 84.27(5)
S(1)-N(1)-C(5) 105.5(1)
S(1)-N(1)-C(6) 106.1(1)
S(1)-N(1)-C(7) 109.3(1)

Figure 3-4

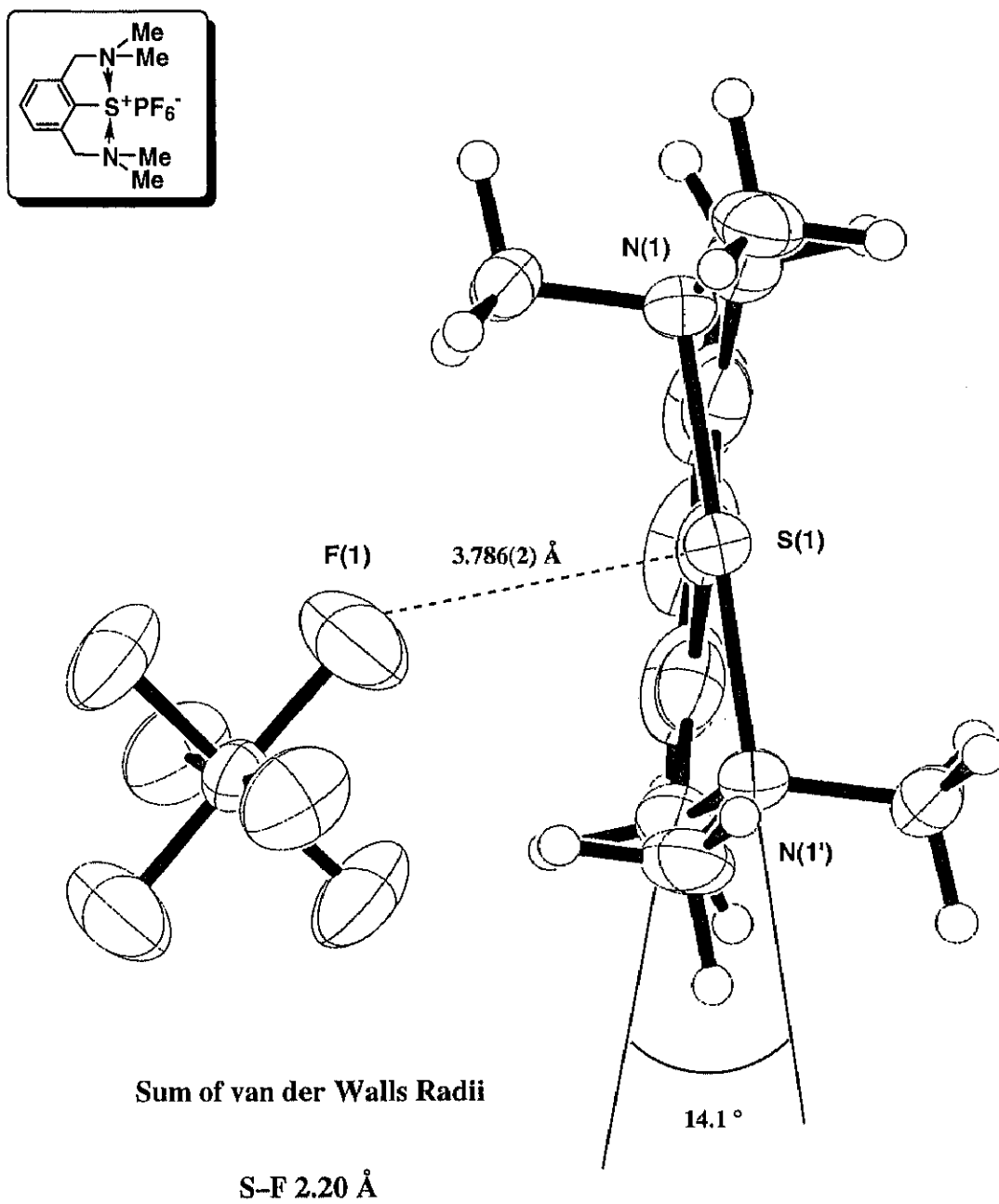


Figure 3-5

C. *ab initio* Calculations of the Sulfenium Ion

In order to understand the electronic structure of the sulfenium ion species single-point *ab initio* calculations were carried out using the crystal structure coordinates of **8**. The charge on the S atom in **8** was calculated to be +0.550 and the two nitrogen atoms are negatively charged as shown in Table 3-1. The Mulliken and Löwdin bond orders of S(1)-N(1) of **8** are 0.379 and 0.539, respectively. These results indicate that the N-S-N bond has a three-center four-electron (3c-4e) hypervalent bonding system. The sulfur atom formally possesses ten valence electrons, the two S-N bonds being strongly polarized toward the nitrogen atoms. Finally the author noticed that the total 3d orbital population evaluated by the natural population analysis is very small (0.025) indicating that the d orbitals are not primarily concerned with the 3c-4e bond in agreement with the current view of hypervalent species.

Atoms or Group	Charge (e)	Bonds	Bind Orders
S(1)	+0.550	S(1)-N(1)	0.379 (Mulliken)
N(1)	-0.535		0.539 (Löwdin)
C(1)	-0.235	S(1)-C(1)	0.945 (Mulliken)
C(2)	-0.057		1.067 (Löwdin)
C(3)	-0.146		
C(4)	-0.106		
C(5)	-0.160		
C(6)	-0.271		
C(7)	-0.302		
Benzene ring ^a	-0.196		
H(CH ₂)	+0.219 ^b		
H(CH ₃)	+0.192 ^b		

^a Six carbons plus three hydrogens. ^b Averaged values.

Table 3-1

Furthermore, an *ab initio* calculation of the simplified sulfenium ion **10** using the 3-21G(*) basis set was carried out. The optimized structure of the sulfenium ion is shown in Figure 3-6. The calculated structure is reasonably in agreement with the structure determined by X-ray crystallographic analysis of the sulfenium ion **8**.

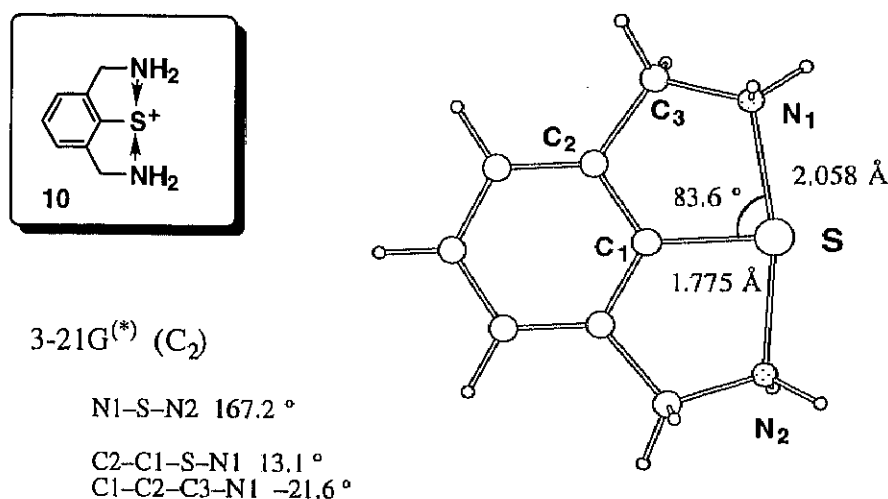


Figure 3-6

D. Reactivity of the Sulfenium Ion

As described in Chapter 1, sulfenium ions or sulfenium halides are known to be very reactive species and they easily react with alkenes or acetylenes to give the addition products. So the sulfenium ion **8** was treated with some reagents in order to clarify the reactivity of it.

At first, the sulfenium ion was treated with *trans*-stilbene, but the reaction did not proceed at all. This result may be attributed to that the reactive HOMO orbital that is a vacant p orbital of the sulfur atom is blocked by lone pairs of the two nitrogen atoms (Figure 3-7).

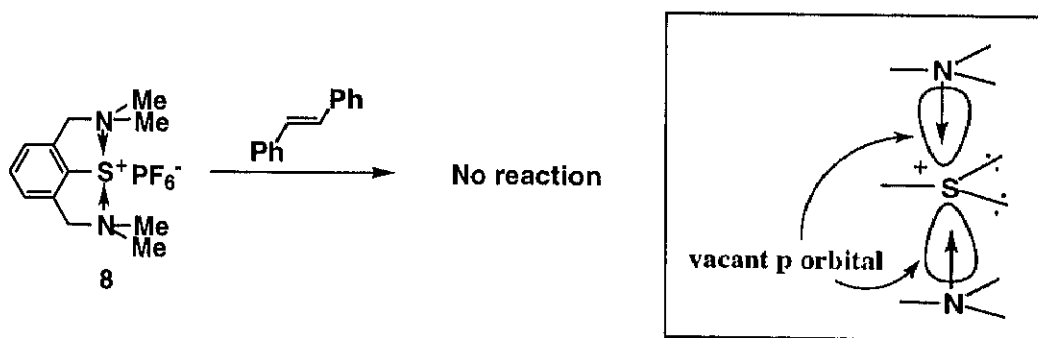
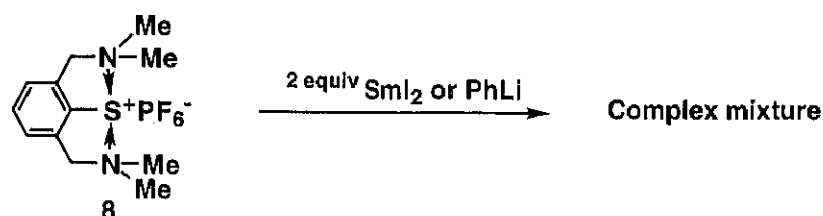


Figure 3-7

The sulfenium ion **8** was also treated with samarium (II) iodide to reduce the sulfur atom to the thiolate ion. Samarium (II) iodide is widely used as a one electron reducing reagent. However the reaction only gave a complex mixture and no corresponding thiol was isolated.

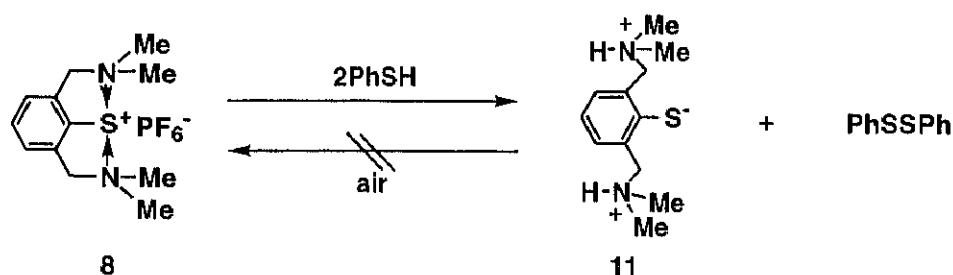
As a nucleophile, phenyl lithium was also reacted with the sulfenium ion **8**. If the phenyl anion attacked to the cationic sulfur atom, the corresponding sulfide should be obtained. However only complex mixture was produced from the reaction and the corresponding sulfide was not isolated (Scheme 3-5).



Scheme 3-5

In conclusion, the sulfenium ion **8** has very low reactivity compared with 'naked' sulfenium ion. This nature of the sulfenium ion **8** should be due to the stabilization of the neighboring two nitrogen atoms.

The sulfenium ion was also reacted with 2 equiv of thiophenol to reduce the sulfur atom. The reaction proceeded smoothly and gave diphenyl disulfide quantitatively, which was characterized by TLC. And the sulfenium ion was reduced to the corresponding thiolate ion **11** having two ammonium groups. This thiolate ion **11** is stable to the oxygen of the air although the corresponding selenolate ion, getting from the selenenium ion **2** with 2 equivs of thiophenol, is easily oxidized by the air. This difference depends on the reduction potential of the central chalcogen atoms.



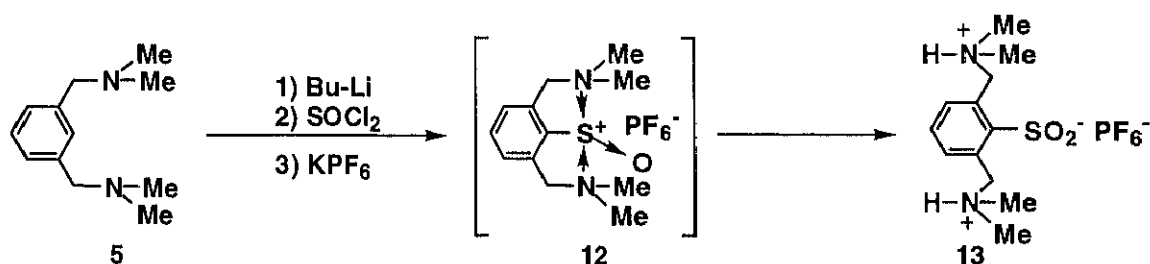
Scheme 3-6

III. Sulfenium Ion Derivatives

Formally the sulfenium ion **8** has two lone pairs perpendicular to the vacant p orbital as shown in Figure 3-7. It is possible to replace these lone pairs with oxygen atoms in principle. So the author tried to synthesize the sulfenium mono- and dioxide ion by following methods.

2,6-Bis(dimethylamoniomethyl)-1-thiomethylbenzene was prepared from the direct lithiation of 1,3-bis(dimethylamoniomethyl)benzene **5**. The ether solution of lithiated compound was

added dropwise to 1 molar equiv of thionyl chloride (SOCl_2) in dry ether. After the removal of the solvent at room temperature, the residue was treated with potassium hexafluorophosphate (KPF_6) in CH_2Cl_2 to afford the sulfenium monoxide ion **12** as shown in Scheme 3-7. However only the sulfinate ion **13**, having two ammonium groups, was obtained as colorless crystals. The sulfenium monoxide ion **12** seems to be unstable to moisture because the oxygen atom directly connected to the sulfur atom that makes the sulfur atom more electronegative. The sulfinate ion is supposed to be produced from the hydrolysis of the sulfenium monoxide ion.



Scheme 3-7

Finally the structure of the sulfinate ion **13** was determined by X-ray crystallographic analysis. The structure without the counter anion is shown in Figure 3-8. The nitrogen atoms are located far from the central sulfur atom and there is no interaction between the two atoms.

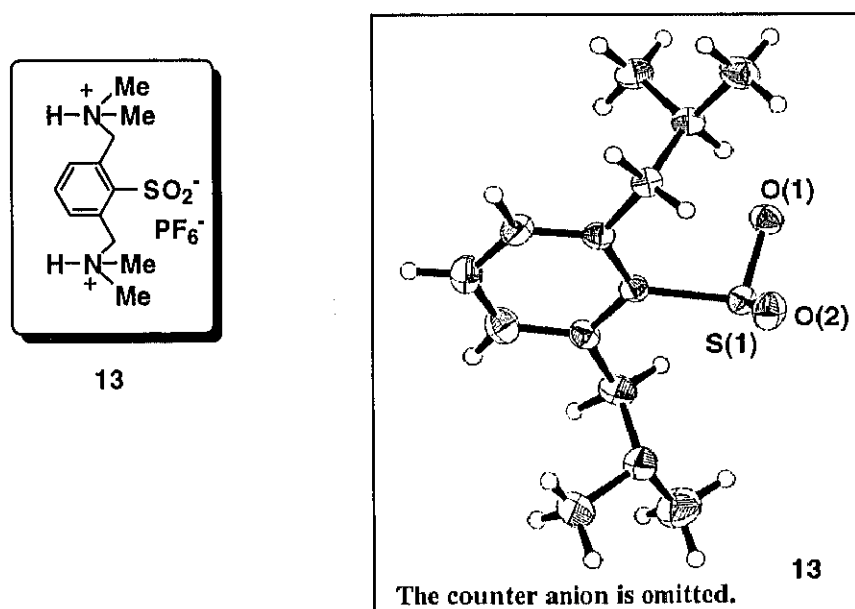
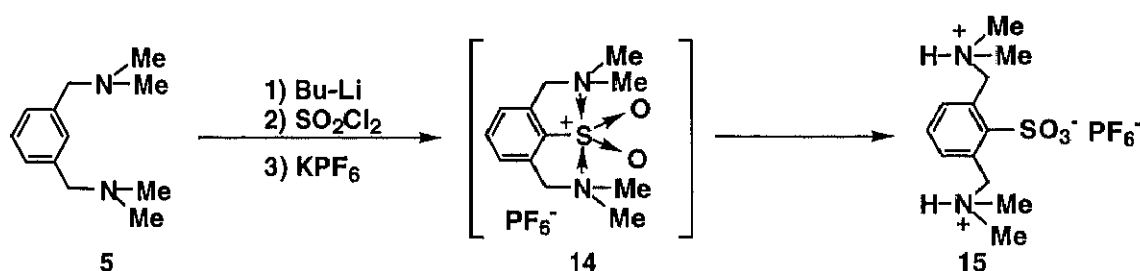


Figure 3-8

2,6-Bis(dimethylamoniomethyl)-1-thiomethylbenzene was also treated with sulfuryl chloride (SO_2Cl_2) to produce the sulfenium dioxide ion **14**. After the removal of the solvent at room temperature, the residue was treated with potassium hexafluorophosphate (KPF_6) in CH_2Cl_2 to afford the sulfenium dioxide ion **14** as shown in Scheme 3-8. However, likewise the case of the sulfenium monoxide ion, only hydrated sulfonate ion **15** was obtained and the sulfenium dioxide ion was not detected. This result indicates the notion that the sulfenium dioxide ion also seems to be unstable to moisture because the two oxygen atoms are directly connected to the sulfur atom, that makes the sulfur atom more electronegative.



Scheme 3-8

The structure of the hydrated sulfonate ion **15** was also determined by X-ray crystallographic analysis. The structure without the counter anion is shown in Figure 3-9. The nitrogen atoms are also located far from the central sulfur atom and there is no interaction between the two atoms.

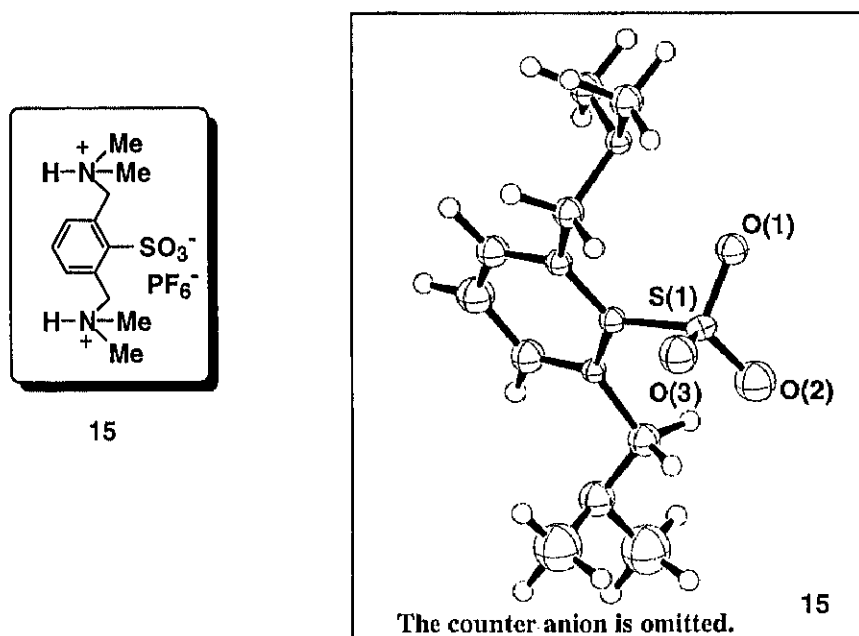
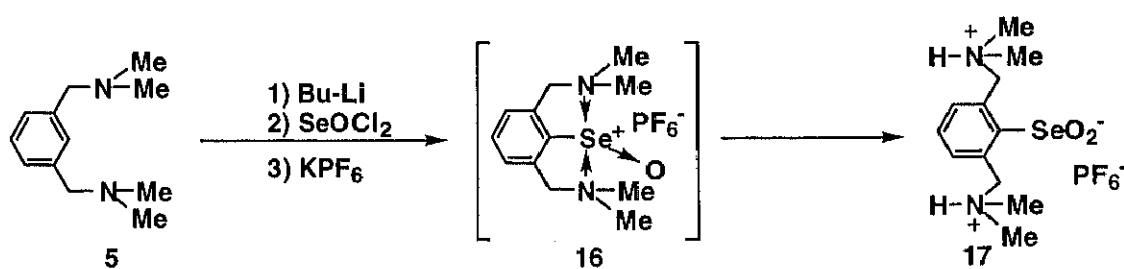


Figure 3-9

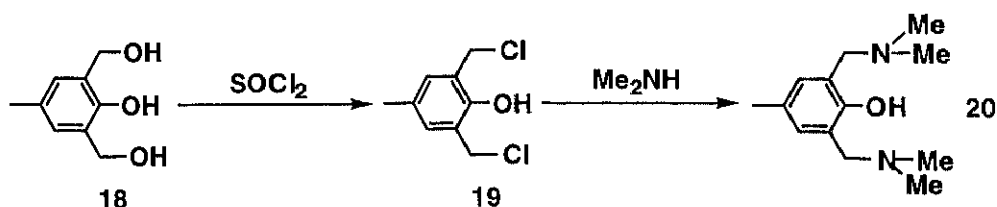
The selenenium monoxide ion **16**, one of the selenenium ion derivatives, was tried to synthesize by the method shown in Scheme 3-9. 2,6-Bis(dimethylamoniomethyl)-1-lithiobenzene was treated with selenium oxychloride (SeOCl_2) to produce the selenenium monoxide ion **16**. After the removal of the solvent at room temperature, the residue was treated with potassium hexafluorophosphate (KPF_6) in CH_2Cl_2 to afford selenenium monoxide ion **16**. However, likewise the case of the sulfur analogues, only hydrated seleninate ion **17** was obtained and the selenenium monoxide ion was not detected. This result indicates that the selenenium monoxide ion also seems to be unstable to moisture because the oxygen atom makes the selenium atom electronegative by connecting directly.



Scheme 3-9

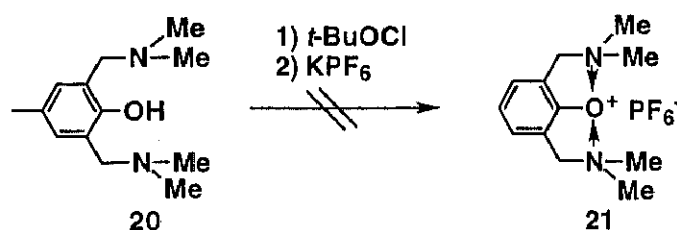
Theoretically, it is possible to suppose the mono-coordinated oxygen cation species, which is an oxygen analogue of sulfenium ion. To the best of the author's knowledge, there is no report about the mono-coordinated oxygen cation species until today. As applying the strategy of the sulfenium ion **8**, the author tried to synthesize the mono-coordinated oxygen cation **21** by following method.

At first, 2,6-bis(dimethylamoniomethyl)-4-methylphenol **20** was prepared as a precursor for the mono-coordinated oxygen cation **21** shown in Scheme 3-10. Commercially available 2,6-bis(hydroxymethyl)-4-methylphenol **18** was converted to 2,6-bis(chloromethyl)-4-methylphenol **19** by adding thionyl chloride (SOCl_2). Then the bis-chloride **19** was treated with dimethylamine (Me_2NH) to afford the phenol **20**.



Scheme 3-10

The phenol **20** was reacted with *t*-BuOCl to form the mono-coordinated oxygen cation. However only a complex mixture was obtained and the mono-coordinated oxygen cation was not observed. This result should depend on the nature of the oxygen atom, which doesn't make any hypervalent compound containing 3c-4e bond.

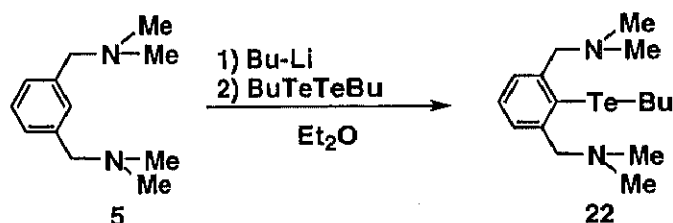


Scheme 3-11

IV. Synthesis and Characterization of the Tellurenum Monoxide Dimer

A. Synthesis of the Tellurenum Monoxide Dimer

In order to synthesize the dicationic tellurane **23** having *n*-Bu group, 2,6-[bis(dimethylamino)methyl] phenyl *n*-butyl telluride **22** was synthesized by the method shown in Scheme 3-12. 1,3-Bis(dimethylamoniomethyl)benzene **5** was easily lithiated by *n*-BuLi to prepare 2,6-bis(dimethylamoniomethyl)-1-lithiobenzene in situ. The solution of lithiated compound was added to di-*n*-butyl ditelluride (*n*-BuTeTe*n*-Bu) to form the telluride **22**.



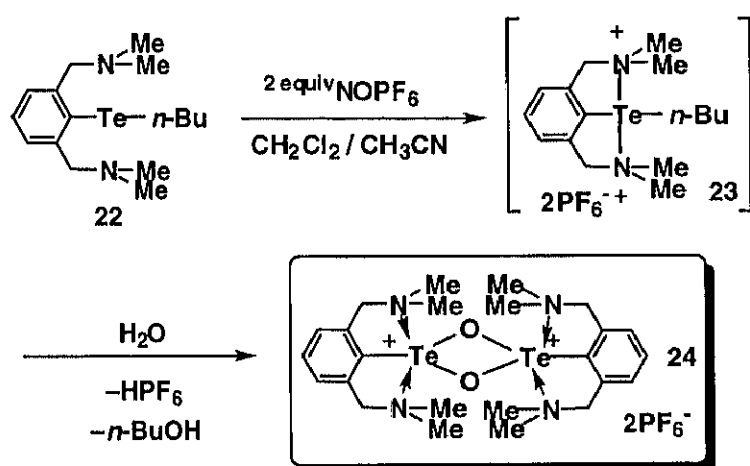
Scheme 3-12

The telluride **22** was oxidized by adding two equiv of NOPF₆ to obtain the corresponding dicationic tellurane. After removal of the solvent, a pale yellow solid was left and ¹H and ¹²⁵Te NMR measurement of the products indicated that the dicationic σ-tellurane **23** was produced. But the purification of the product at anhydrous condition is difficult. The crude product was treated at open air condition. Recrystallization of the crude product from acetonitrile gave pale yellow crystals.

In the ¹H NMR of the crystals, measured in CD₃CN at room temperature, there is no signal from *n*-butyl group, indicating clearly that dealkylation was occurred during treatment. The ¹H NMR signals of benzylic and four methyl protons appear at 4.31 ppm and at 2.96 ppm as a

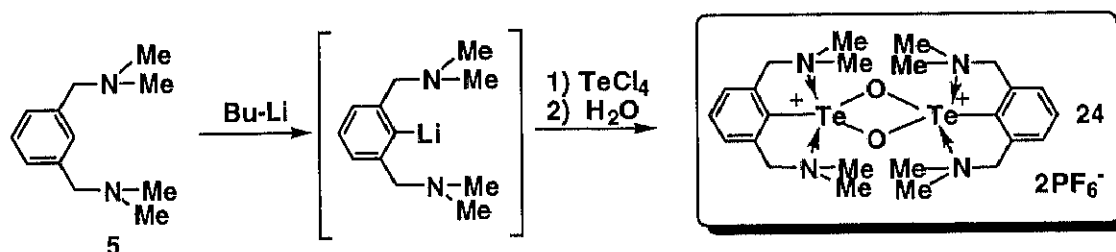
singlet, respectively. These chemical shifts were observed at lower field than those of the telluride **22**. The ^{125}Te NMR spectrum also showed a significant downfield shift at δ 1948 from the peak (δ 287) of telluride **22**. Furthermore, the elemental analysis of the crystals is consistent with molecular formula of the corresponding tellurenum ion monoxide. But EI mass spectrum shows a molecular ion at m/e 321, which is not enough one oxygen atom to the corresponding tellurium monoxide.

The structure of the crystals was determined by X-ray diffraction method finally. It was clarified that the dicationic tellurane was converted to the tellurenum monoxide dimer **24**, in which the two tellurium atoms and the two oxygen atoms makes four membered ring.



Scheme 3-13

The tellurenum monoxide dimer **24** was also synthesized by the method shown in Scheme 3-14. 2,6-Bis(dimethylamino)-1-lithiobenzene, which was generated in situ, was treated with tellurium tetrachloride (TeCl_4) and treatment with water gave the tellurenum monoxide dimer **24**.



Scheme 3-14

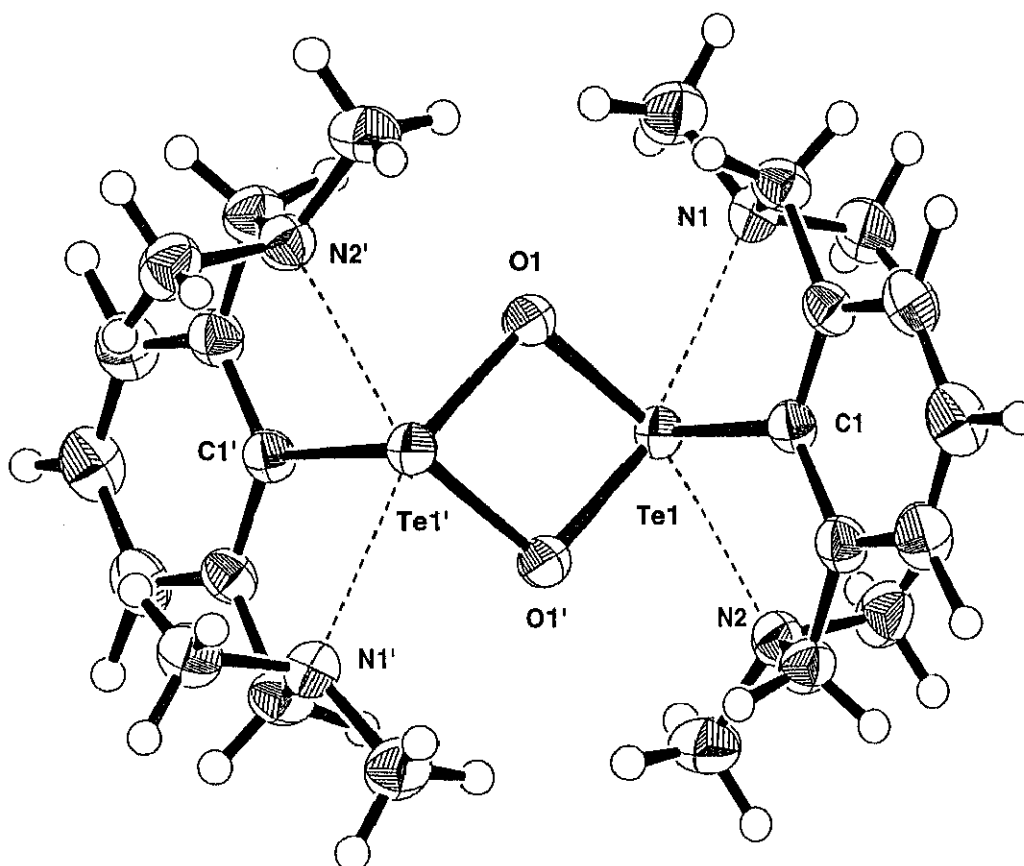
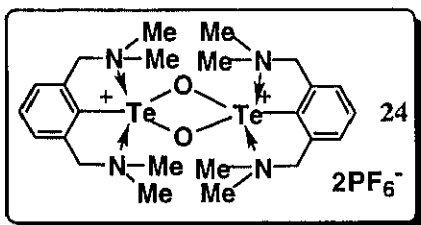
B. X-ray crystallographic analysis of the Tellurenum Monoxide Dimer

An ORTEP view of **24** is shown in Figure 3-10. Apparently, tellurenum monoxide makes a μ -oxo dimer structure, by bridging the central tellurium atoms and the two oxygen atoms. Dimer structure is commonly observed in organotellurium compounds and there are many reports about their structures.⁷⁾

Although there is no bonding interaction between nitrogen and tellurium atoms formally, the two neighboring amino nitrogen atoms direct toward the tellurium atoms. This means that two nitrogen atoms coordinate to the cationic central tellurium atom to stabilize the ion. And the angle of N-Te-N 124.7(2) is much distorted from linear arrangement. Each bond lengths between the tellurium and two nitrogen atoms are 2.475 and 2.486 Å, which are longer than a single covalent bond (2.02 Å) between tellurium and nitrogen atoms. The two tellurium atoms have a distorted octahedral coordination with the two *cis*-bridging atoms (O1 and O2), the two nitrogen atoms (N1 and N2), and one carbon atom. One lone electron pair takes part in the rest of the tellurium atoms.

Two oxygen atoms and two tellurium atoms make a four membered ring, so the distance of two tellurium atoms (3.12 Å) is shorter than the sum of van der Waals radii (4.40 Å) shown in Figure 3-11. The distance of central tellurium and oxygen is 1.987(4)-1.997(4) Å, which are significantly shorter than the single covalent bond distance (2.101 Å) of these two atoms. In our laboratory, a similar compound, tellurane *Te*-oxide dimer **25**, was synthesized and the structure was determined by X-ray crystallographic analysis. The structure of **25** is also shown in Figure 3-11 for comparison. In the structure of **25**, the distances between the tellurium atoms and the oxygen atoms are about 2.0 Å.

And the plane, which consists of these two tellurium and two oxygen, is almost perpendicular (95.8°) to the two phenyl rings, which makes two phenyl rings almost parallel each other.



The hexafluorophosphate ions are omitted.

Space Group $P2_1/c$ (#14)
 $R=0.040$, $R_w=0.052$.

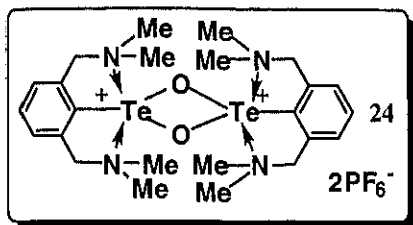
Bond Distances (\AA)

Te(1)-N(1) 2.486(6)
 Te(1)-N(2) 2.475(5)
 Te(1)-O(1) 1.987(4)
 Te(1)-O(1') 1.997(4)

Bond Angles (deg)

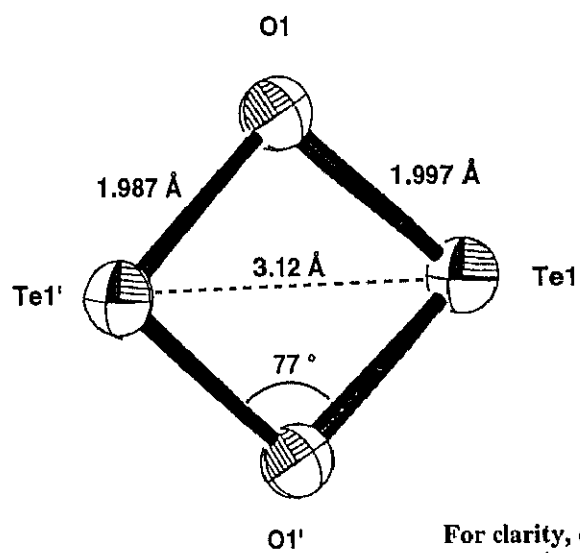
N(1)-Te(1)-N(2) 124.7(2)
 O(1)-Te(1)-O(1') 77.0(2)
 Te(1)-O(1)-Te(1') 103.0(2)
 C(1)-Te(1)-O(1) 95.8(2)

Figure 3-10



Sum of van der Waals radii (Te-Te) 4.40 \AA

Te-Te single bond distance of $(\text{PhTe})_2$ 2.71 \AA



For clarity, only the tellurium and oxygen atoms are shown

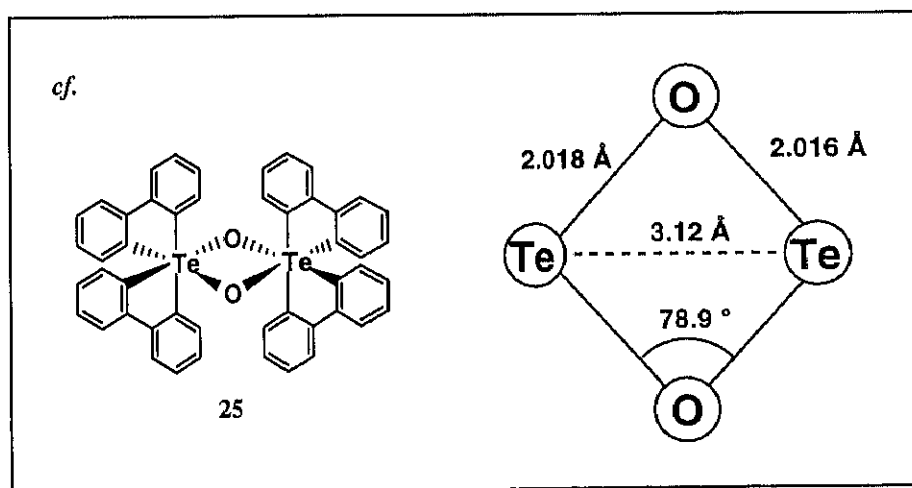


Figure 3-11

V. Conclusion

In conclusion, the remarkably stable sulfenium ion salts were prepared by using the coordination of two neighboring nitrogen atoms. A single crystal X-ray structure determination revealed that the two amino groups coordinate directly to the cationic sulfur atom, and that the counter ion, PF_6^- , is independent of the cationic part of the sulfenium ion.

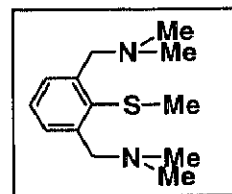
And the tellurenum ion monoxide was obtained as a dimer by oxidation of the corresponding telluride with two neighboring nitrogen atoms. The solid state structure of the dimer was determined by X-ray crystallographic analysis.

Experimental

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 (^1H - ^1H -COSY) spectra. Mass spectra were taken with a Shimadzu 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. 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.

Synthesis of 2,6-[bis(dimethylamino)methyl]-1-thiomethylbenzene 6

BuLi (3.9 mL, 6.2 mmol, 1.60 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene **5** (1 g, 5.2 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then added to a solution of dimethyl disulfide (0.6 mL, 6.2 mmol) in dry Et_2O (100 mL) using a transfer needle at -78°C . The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_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 (N-H silica gel; eluent, hexane-EtOAc, 4 : 1) to give a colorless oil, 2,6-[bis(dimethylamino)methyl]-1-thiomethylbenzene **6** (850 mg) in 70% yield.

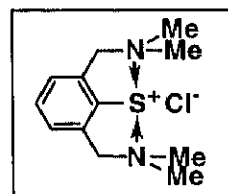


2,6-[Bis(dimethylamino)methyl]-1-thiomethylbenzene 6

^1H NMR (400 MHz, CDCl_3 , r.t.) δ 2.34 (s, 12H), 3.81 (s, 4H), 7.32-7.46 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3 , r.t.) δ 20.1, 45.5, 62.2, 128.1, 128.7, 135.9, 143.3; EIMS (m/z); 238 (M^+).

Synthesis of 2,6-[bis(dimethylamino)methyl]phenyl sulfenium chloride 7 (Method A)

To a solution of 2,6-[bis(dimethylamino)methyl]-1-thiomethylbenzene **5** (511 mg, 2.15 mmol) in 5 mL of anhydrous MeOH, *t*-BuOCl (0.4 mL, 2.6 mmol) was added at 0°C under an Ar atmosphere and the mixture was stirred for overnight. Then the solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave the crude product, and recrystallization from CH_2Cl_2 gave colorless crystals, the sulfenium ion **7** (6 mg) in 1% yield.

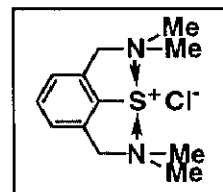


2,6-[Bis(dimethylamino)methyl]phenyl sulfenium chloride **7**

mp 130–133°C; ^1H NMR (400 MHz, CD_3CN , r.t.) δ 2.96 (s, 12H), 4.31 (s, 4H), 7.26–7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN , r.t.) δ 47.9, 62.3, 125.4, 128.1, 130.1, 134.0; EIMS (m/z); 223 ($\text{M}^+ - \text{Cl}^-$); Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_1\text{N}_2\text{S}_1(\text{H}_2\text{O})_2$: C, 48.88; H, 7.86; N 9.50; Found: C, 49.12; H, 7.93; N, 9.40.

Synthesis of 2,6-[bis(dimethylamino)methyl]phenyl sulfenium chloride **7** (Method B)

BuLi (2.4 mL, 3.8 mmol, 1.58 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene **5** (618 mg, 3.22 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then added to a solution of sulfur chloride (640 mg, 6.21 mmol) in dry Et_2O (100 mL) using a transfer needle at -78°C .



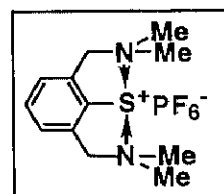
The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (N–H silica gel; eluent, CHCl_3 -MeOH, 10 : 1) to give a colorless crystals, the sulfenium ion **7** (167 mg) in 20% yield.

2,6-[Bis(dimethylamino)methyl]phenyl sulfenium chloride **7**

mp 130–133°C; ^1H NMR (400 MHz, CD_3CN , r.t.) δ 2.96 (s, 12H), 4.31 (s, 4H), 7.26–7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN , r.t.) δ 47.9, 62.3, 125.4, 128.1, 130.1, 134.0; EIMS (m/z); 223 ($\text{M}^+ - \text{Cl}^-$); Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_1\text{N}_2\text{S}_1(\text{H}_2\text{O})_2$: C, 48.88; H, 7.86; N 9.50; Found: C, 49.12; H, 7.93; N, 9.40.

Synthesis of 2,6-[bis(dimethylamino)methyl]phenyl sulfenium hexafluorophosphate **8**

To a solution of 2,6-[bis(dimethylamino)methyl]phenyl sulfenium chloride **7** (100 mg, 0.39 mmol) in 20 mL of anhydrous CH_2Cl_2 , a powder of KPF_6 (718 mg, 3.9 mmol) was added at room temperature and the mixture was stirred overnight. After white precipitates were filtered, the filtrate was purified by column chromatography (N–H silica gel; eluent, CHCl_3 -MeOH, 10 : 1) to give the colorless crystals of the sulfenium hexafluorophosphate **8** (114 mg) in 80% yield.

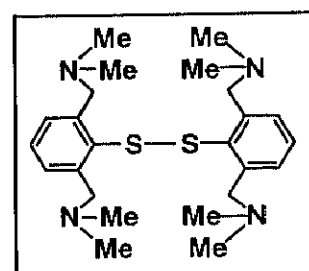


2,6-[Bis(dimethylamino)methyl]phenyl sulfenium hexafluorophosphate 8

mp 168–170°C; ^1H NMR (400 MHz, CD_3CN , r.t.) δ 2.86 (s, 12H), 4.11 (s, 4H), 7.26–7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN , r.t.) δ 47.8, 62.3, 125.3, 128.1, 128.7, 129.9; ^{19}F NMR (254 MHz, CD_3CN , r.t.) δ –73.5 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); ^{31}P NMR (109 MHz, CD_3CN , r.t.) δ –145.4 (sept, $J_{\text{P-F}} = 707$ Hz, PF_6^-); EIMS (m/z); 223 ($\text{M}^+ - \text{PF}_6^-$); Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{F}_6\text{N}_2\text{P}_1\text{S}_1$: C, 39.13; H, 5.20; N 7.61; Found: C, 39.68; H, 5.32; N, 7.54.

Synthesis of the disulfide 9

BuLi (13 mL, 19.9 mmol, 1.53 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene 5 (3.2 g, 16.7 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then S_8 (4.3 g, 134 mmol) was added to the solution at –78°C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_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 (N–H silica gel; eluent, hexane–EtOAc, 4 : 1) to give a colorless oil, the disulfide 9 (800 mg) in 20% yield.

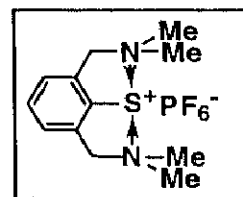


Disulfide 9

^1H NMR (400 MHz, CDCl_3 , r.t.) δ 2.23 (s, 12H), 3.41 (s, 4H), 7.32–7.46 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3 , r.t.) δ 20.1, 45.5, 62.2, 128.1, 128.7, 135.9, 143.3; EIMS (m/z); 446 (M^+).

Synthesis of 2,6-[bis(dimethylamino)methyl]phenyl sulfenium hexafluorophosphate 8 (Method C)

To a solution of the sulfide 9 (273 mg, 0.61 mmol) in 20 ml of anhydrous CH_2Cl_2 , SO_2Cl_2 (73 μL , 0.7 mmol) was added at 0 °C under an argon atmosphere and the mixture was stirred overnight. Then a powder of KPF_6 (718 mg, 3.9 mmol) was added at room temperature and the mixture was stirred for 6 hours. After white precipitates were filtered, the filtrate was purified by column chromatography (N–H silica gel; eluent, CHCl_3 –MeOH, 10 : 1) to give the colorless crystals of the sulfenium hexafluorophosphate 8 (28 mg) in 6% yield.



2,6-[Bis(dimethylamino)methyl]phenyl sulfenium hexafluorophosphate 8

mp 168–170°C; ^1H NMR (400 MHz, CD_3CN , r.t.) δ 2.86 (s, 12H), 4.11 (s, 4H), 7.26–7.27 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN , r.t.) δ 47.8, 62.3, 125.3, 128.1, 128.7, 129.9; ^{19}F NMR (254 MHz, CD_3CN , r.t.) δ –73.5 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); ^{31}P NMR (109 MHz, CD_3CN ,

r.t.) δ -145.4 (sept, $J_{\text{P-F}} = 707$ Hz, PF_6^-); EIMS (m/z); 223 ($\text{M}^+ - \text{PF}_6^-$); Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{F}_6\text{N}_2\text{P}_1\text{S}_1$: C, 39.13; H, 5.20; N 7.61; Found: C, 39.68; H, 5.32; N, 7.54.

Reaction of the sulfenium ion 8 with *trans*-stilbene

To a solution of the sulfenium ion 8 (10 mg, 0.03 mmol) in 0.5 ml of anhydrous CD_3CN , *trans*-stilbene (5.86 mg, 0.03 mmol) was added at 0 °C. The ^1H NMR spectrum of this solution only showed those of the mixture, the sulfenium ion and *trans*-stilbene.

Reaction of the sulfenium ion 8 with samarium (II) iodide (SmI_2)

To a solution of the sulfenium ion 8 (58 mg, 0.18 mmol) in 20 ml of anhydrous THF, a THF solution of samarium (II) iodide (4.0 mL, 0.4 mmol, 0.1 M in THF) was added 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_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave a pale yellow oil. However, the ^1H NMR spectrum of the oil was very complicated and any pure product was not isolated by column chromatography (N-H silica gel; eluent, hexane- CHCl_3 , 10 : 1).

Reaction of the sulfenium ion 8 with phenyl lithium (PhLi)

To a solution of the sulfenium ion 8 (27 mg, 0.07 mmol) in 20 ml of anhydrous THF, a solution of phenyl lithium (48 μL , 0.09 mmol, 1.8 M in cyclohexane-diethyl ether) was added at -78 °C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave a pale yellow oil. However, the ^1H NMR spectrum of the oil was very complicated and any pure product was not isolated by column chromatography (N-H silica gel; eluent, hexane- CHCl_3 , 10 : 1).

Reaction of the sulfenium ion 8 with thiophenol (PhSH)

To a solution of the sulfenium ion 8 (12 mg, 0.03 mmol) in 0.5 ml of CD_3CN , thiophenol (4.0 μL , 0.04 mmol) was added at 0 °C under an argon atmosphere. The ^1H NMR spectrum of this solution indicated the formation of the thiolate ion having two ammonium groups.

The thiolate ion 11

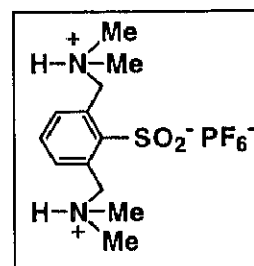
^1H NMR (400 MHz, CD_3CN , r.t.) δ 2.72 (s, 12H), 4.22 (s, 4H), 7.26-7.27 (m, 3H, Ar-H);

Reaction of 2,6-[bis(dimethylamino)methyl]-1-lithiobenzene with thionyl chloride (SOCl₂)

BuLi (1.2 mL, 1.8 mmol, 1.53 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene **5** (283 mg, 1.47 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then added to a solution of thionyl chloride (1.3 g, 14.7 mmol) in dry Et₂O (100 mL) using a transfer needle at -78°C. The resulting 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 (N-H silica gel; eluent, CHCl₃-MeOH, 10 : 1) to give a colorless crystals, the sulfinate ion **13** (152 mg) in 27% yield.

The sulfinate ion **13**

mp 85–87°C; ¹H NMR (270 MHz, CD₃CN, 50 °C) δ 2.46 (s, 12H), 4.22 (s, 4H), 7.21–7.27 (m, 3H, Ar-H); ¹³C NMR (100 MHz, CD₃CN, r.t.) δ 44.1, 60.1, 126.1, 129.3, 132.6, 155.7; IR (cm⁻¹) 1025 (S–O).

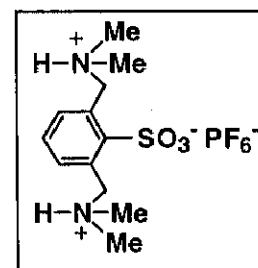


Reaction of 2,6-[bis(dimethylamino)methyl]-1-lithiobenzene with sulfonyl chloride (SO₂Cl₂)

BuLi (2.3 mL, 3.5 mmol, 1.53 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene **5** (552 mg, 2.88 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then added to a solution of sulfonyl chloride (2.9 mL, 28.8 mmol) in dry Et₂O (100 mL) using a transfer needle at -78°C. The resulting 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 (N-H silica gel; eluent, CHCl₃-MeOH, 10 : 1) to give a colorless crystals, the sulfonate ion **15** (234 mg) in 20% yield.

The sulfonate ion **15**

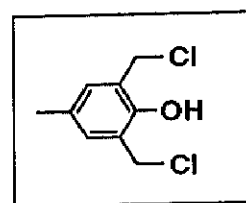
mp 236–238°C; ¹H NMR (270 MHz, CD₃CN, r.t.) δ 2.63 (s, 12H), 4.30 (s, 4H), 7.24 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.51 (d, *J* = 7.5 Hz, 2H, Ar-H); ¹³C NMR (100 MHz, CD₃CN, r.t.) δ 44.5, 61.8, 129.5, 132.6, 132.6, 144.9; ¹⁹F NMR (254 MHz, CD₃CN, r.t.) δ -72.5 (d, *J*_{P-F} = 714 Hz, PF₆⁻); IR (cm⁻¹) 1029 (S–O); EIMS (*m/z*); 272 (M⁺–HPF₆).



Synthesis of 2,6-[bis(chloromethyl)]-4-methyl-phenol

To a solution of 2,6-[bis(hydroxymethyl)]-4-methyl-phenol **18** (2.0 g, 12 mmol) in 50 mL of anhydrous CH₂Cl₂, thionyl chloride (SOCl₂, 2.0 mL, 14 mmol) was added at 0 °C under an Ar

atmosphere and the mixture was stirred for overnight. Then the solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave the crude product, and recrystallization from CH_2Cl_2 gave colorless crystals, 2,6-[bis(chloromethyl)]-4-methylphenol **19** (2.4 g) in 99% yield.

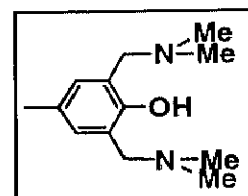


2,6-[Bis(chloromethyl)]-4-methylphenol **19**

mp 74–76°C; ^1H NMR (400 MHz, CDCl_3 , r.t.) δ 2.28 (s, 3H, Me), 4.66 (s, 4H), 5.53 (s, 1H, OH), 7.09–7.26 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3 , r.t.) δ 20.3, 42.5, 124.6, 130.5, 131.6, 151.0; EIMS (m/z); 206 (M^+).

Synthesis of 2,6-[bis(dimethylaminomethyl)]-4-methylphenol **20**

To a solution of 2,6-[bis(chloromethyl)]-4-methylphenol **19** (2.0 g, 12 mmol) in 50 ml of CH_2Cl_2 , 100 mL of dimethylamine solution (50 %) was added at 0 °C and the mixture was stirred for overnight. Then the solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave the colorless oil, 2,6-[bis(dimethylaminomethyl)]-4-methylphenol **20** (1.27 g) in 60% yield.



2,6-[Bis(dimethylaminomethyl)]-4-methylphenol **20**

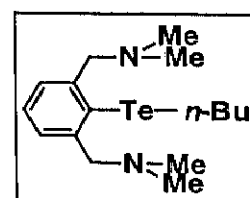
^1H NMR (270 MHz, CDCl_3 , r.t.) δ 2.24 (s, 3H, Me), 2.32 (s, 12H, Me), 3.55 (s, 4H), 6.86–7.26 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3 , r.t.) δ 20.4, 44.7, 60.1, 122.5, 127.4, 129.6, 154.4; EIMS (m/z); 222 (M^+).

Reaction of 2,6-[bis(dimethylaminomethyl)]-4-methylphenol **20** with *t*-BuOCl

To a solution of 2,6-[bis(dimethylaminomethyl)]-4-methylphenol **20** (260 mg, 1.17 mmol) in 20 ml of anhydrous MeOH, *t*-BuOCl (0.2 mL, 1.4 mmol) was added at 0 °C under an Ar atmosphere and the mixture was stirred for overnight. Then the solvents were evaporated, and the residue was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , and removal of the solvent at room temperature gave a pale yellow oil. However, the ^1H NMR spectrum of the oil was very complicated and any pure product was not isolated by column chromatography (N–H silica gel; eluent, hexane- CHCl_3 , 10 : 1).

Synthesis of 2,6-bis(dimethylamino)methylphenyl *n*-butyl telluride **22**

BuLi (2.4 mL, 3.8 mmol, 1.58 M in *n*-hexane) was added to a dry ether (100 mL) solution of 2,6-bis(dimethylaminomethyl)benzene **5** (618 mg, 3.22 mmol) at room temperature under an argon atmosphere. The solution



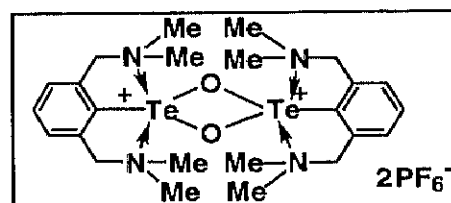
was stirred for 1 day and then added to a solution of *n*-butyl ditelluride (910 mg, 2.46 mmol) in dry Et₂O (100 mL) using a transfer needle at -78°C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with Et₂O. The organic layer was dried over anhydrous MgSO₄, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (N-H silica gel; eluent, hexane-CHCl₃, 10 : 1) to give a yellow oil, the telluride **22** (560 mg) in 60% yield.

2,6-[Bis(dimethylamino)methyl]phenyl *n*-butyl telluride **22**

¹H NMR (400 MHz, CDCl₃, r.t.) δ 0.85 (t, *J* = 7.2 Hz, 3H, Me), 1.24–1.40 (m, 2H, CH₂), 1.56–1.69 (m, 2H, CH₂), 2.20 (s, 12H, NMe), 2.55 (t, *J* = 7.2 Hz, 2H, CH₂), 3.60 (s, 4H), 7.16–7.32 (m, 3H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, r.t.) δ 9.1, 13.4, 25.2, 33.8, 44.7, 68.5, 122.9, 127.2, 127.4, 144.9; ¹²⁵Te NMR (126 MHz, CDCl₃, r.t.) δ 287.2; EIMS (*m/z*); 379 (*M*⁺).

Synthesis of the tellurenum monoxide dimer **24 (Method A)**

An anhydrous CH₃CN (10 mL) solution of NOPF₆ (112 mg, 0.64 mmol) was added dropwise to a solution of the telluride **22** (200 mg, 0.53 mmol) in anhydrous CH₂Cl₂ (20 mL) at -78 °C under an argon atmosphere. 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 CH₂Cl₂, CH₃CN and ether gave colorless crystals of the tellurenum monoxide dimer **24** (44 mg) in 20% yield.



Synthesis of the tellurenum monoxide dimer **24 (Method B)**

BuLi (11 mL, 17 mmol, 1.55 M in *n*-hexane) was added to a dry ether (100 mL) solution of 1,5-bis(dimethylaminomethyl)benzene **5** (3.0 g, 15.6 mmol) at room temperature under an argon atmosphere. The solution was stirred for 1 day and then added to a solution of tellurium tetrachloride (5.0 g, 18.5 mmol) in dry Et₂O (100 mL) using a transfer needle at -78°C. The resulting 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 (N-H silica gel; eluent, CHCl₃-MeOH, 10 : 1) to give colorless crystals, the tellurenum monoxide dimer **24** (287 mg) in 4% yield.

Tellurenum monoxide dimer 24

mp 179–180 °C (decomp.); ^1H NMR (270 MHz, CD_3CN , -40°C) δ 2.98 (s, 24H, Me), 4.03 (s, 8H), 7.33–7.37 (m, 6H, Ar-H); ^{13}C NMR (67.8 MHz, CD_3CN , -40°C) δ 50.6, 67.1, 101.0, 127.1, 129.8, 138.6; ^{125}Te NMR (126 MHz, CD_3CN , r.t.) δ 1948.6 (relative to Me_2Te); ^{19}F NMR (254 MHz, CD_3CN) δ -73.5 (d, $J_{\text{P-F}} = 707$ Hz, relative to CFCl_3); Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{F}_{12}\text{N}_4\text{O}_2\text{P}_2\text{Te}_2$: C, 30.04; H, 3.99; N, 5.84; Found: C, 30.18; H, 3.82; N, 5.44.

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