

Crystal Structures and *ab Initio* Calculations of New Dicationic Telluranes (λ^4 -Tellane), $[10\text{-Te-}4(\text{C}2\text{X}2)]^{2+}$ (X = S, Se): Positively Charged Hypervalent Bonding Systems

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Abstract: The reactions of 2,6-bis[(phenylthio- or phenylseleno)methyl]phenyl phenyl telluride or the corresponding *Te*-oxide, with NOBF_4 or trifluoromethanesulfonic anhydride afforded the new telluranes, $[10\text{-Te-}4(\text{C}2\text{X}2)]^{2+}\cdot 2\text{Y}^-$ (λ^4 -tellane) (X = S or Se, Y = BF_4 or CF_3SO_3). These compounds were characterized by elemental and spectroscopic (FABMS, ^1H , ^{13}C , and ^{125}Te NMR) analyses. X-ray structure determinations revealed that the hypervalent tellurium atoms are at the center of a distorted trigonal bipyramid, with two apical sulfonio or selenonio ligands connected via transannular bonds. The Te–S distances are in the range 2.652–2.706 Å, the Te–Se distances in the range 2.759–2.807 Å, and the X–Te–X bond angles in the range 160.41–163.92°. *Ab initio* calculations indicate that the positive charges in the dications are exclusively on the three chalcogen atoms that form three-center, four-electron bonds.

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 are known.³ The majority of these compounds involve a three-center transannular interaction in a cyclic or acyclic framework as exemplified by types A and B as shown in Figure 1. However, no dicationic σ -telluranes were synthesized and isolated. We report the preparation of a new type of dicationic σ -telluranes (λ^4 -tellane), $[10\text{-Te-}4(\text{C}2\text{X}2)]^{2+}\cdot 2\text{Y}^-$ (X = S or Se, Y = BF_4 or CF_3SO_3) (**4a**, **4b**, and **6**) from the new flexible acyclic tris-chalcogenide, 2,6-bis[(phenylthio)methyl]phenyl phenyl telluride (**2a**) and 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluride (**5**), and the corresponding

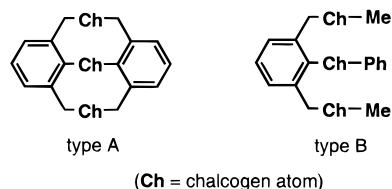


Figure 1.

telluroxide (**3**) via transannular bond formation. Single-crystal X-ray structure determinations revealed that two apical sulfonio- or selenonio ligands bond to the central tellurium atom. Also included in this article are the results of *ab initio* calculations for the tellurane dications **4b** and **6**, which reveal the charge distribution and electronic structure of the molecules.

Experimental Section

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 - and ^{13}C – ^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, 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. All melting points are uncorrected.

2,6-Bis[(phenylthio)methyl]-1-bromobenzene (1a). NaOH (0.39 g, 9.63 mmol) was added to a solution of thiophenol (1.06 g, 9.63 mmol) in ethanol (50 mL). The solution was added dropwise to a

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solution of 2,6-bis(bromomethyl)-1-bromobenzene⁴ (1.50 g, 4.38 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH_2Cl_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 2,6-bis[(phenylthio)methyl]-1-bromobenzene **1a** (1.54 g) in 88% yield. ¹H NMR (270 MHz, CDCl_3 , room temperature) δ 4.25 (s, 4H, CH_2), 7.06–7.33 (m, 13H, ArH). ¹³C NMR (68 MHz, CDCl_3 , room temperature) δ 40.5, 126.7, 126.7, 126.9, 128.9, 129.6, 130.7, 135.7, 137.8; MS (*m/z*) 402 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{BrS}_2$: C, 59.85; H, 4.27. Found: C, 59.93; H, 4.32.

2,6-Bis[(phenylthio)methyl]phenyl Phenyl Telluride (2a). *n*-BuLi (4.8 mL, 7.6 mmol, 1.59 M in *n*-hexane) was added to a dry ether (40 mL) solution of 2,6-bis[(phenylthio)methyl]-1-bromobenzene (**1a**) (3.0 g, 6.9 mmol) at -78 °C under an argon atmosphere. As the reaction proceeded the solution turned yellow. The solution was stirred for 30 min and then added to a solution of diphenyl ditelluride (1.4 g, 3.5 mmol) in dry Et_2O (32 mL) using a transfer needle at -78 °C. The resulting orange mixture was allowed to warm to room temperature overnight. After the removal of solvents, the residue was extracted with CH_2Cl_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 mixture of two compounds. These were separated by preparative liquid chromatography to afford a white solid, telluride **2a** (1.96 g) in 54% yield and the substrate (300 mg) in 10% recovery. Recrystallization of the telluride **2a** from *n*-hexane gave white crystals. Mp 55–56 °C; ¹H NMR (270 MHz, CDCl_3 , room temperature) δ 4.39 (s, 4H, CH_2), 7.11–7.41 (m, 18H, ArH). ¹³C NMR (68 MHz, CDCl_3 , room temperature) δ 45.7, 117.2, 123.8, 126.3, 127.0, 128.0, 128.6, 129.3, 129.4, 130.0, 135.2, 135.7, 144.1; ¹²⁵Te NMR (85 MHz, CDCl_3 , room temperature) δ 445.7 (relative to Me_2Te); MS (*m/z*) 528 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{S}_2\text{Te}$: C, 59.35; H, 4.21. Found: C, 59.28; H, 4.13.

2,6-Bis(methoxymethyl)phenyl Phenyl Telluride (2b). *n*-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 (**1b**)⁵ (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_2O (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_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 (silica gel; eluent, *n*-hexane- CHCl_3 , 4:1) to give a yellow oil, telluride **2b** (429 mg) in 84% yield. ¹H NMR (270 MHz, CDCl_3 , room temperature) δ 3.32 (s, 6H, CH_3O), 4.54 (s, 4H), 7.12–7.43 (m, 8H, Ar-H). ¹³C 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; ¹²⁵Te NMR (85 MHz, CDCl_3 , room temperature) δ 446.4 (relative to Me_2Te); MS (*m/z*) 372 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Te}$: C, 51.95; H, 4.90. Found: C, 51.94; H, 4.90.

2,6-Bis[(phenylthio)methyl]phenyl Phenyl Telluroxide (3). The telluride **2a** (200 mg, 0.38 mmol) was dissolved in dry MeOH (2.5 mL)- CH_2Cl_2 (2.5 mL), and the solution was cooled to 0 °C. To this *t*-BuOCl (47 μL , 0.42 mmol) was added, and the resulting solution was stirred for 5 min at 0 °C. The reaction mixture was diluted with dry CH_2Cl_2 (5 mL) and then hydrolyzed with a saturated aqueous solution of sodium bicarbonate under vigorous stirring. After 5 min the organic phase was separated, dried over anhydrous MgSO_4 , and concentrated by evaporator to give a white solid, which was recrystallized from *n*-hexane- CHCl_3 to give telluroxide **3** (170 mg) in 83% yield. Mp 155 °C; ¹H NMR (270 MHz, CDCl_3 , room temperature) δ 4.19, 4.25 (ABq, 2H, $J = 16.2$ Hz, CH_2), 4.44, 4.50 (ABq, 2H, $J = 16.2$ Hz, CH_2), 7.09–7.33 (m, 16H, ArH), 7.84–7.87 (m, 2H, ArH); ¹³C NMR (68 MHz, CDCl_3) δ 37.2, 126.3, 128.8, 129.1, 129.3, 129.9,

130.1, 130.5, 132.0, 135.5, 137.9, 138.8, 143.3; ¹²⁵Te NMR (85 MHz, CDCl_3) δ 1203.1 (relative to Me_2Te); FABMS (*m/z*) 545 ($\text{M}^+ + 3$), 542 (M^+); IR (KBr) 731 cm^{-1} (Te-O). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{OS}_2\text{Te}$: C, 57.60; H, 4.09. Found: C, 57.60; H, 4.20.

2,6-Bis[(phenylthio)methyl]phenyl Phenyl Telluranyl Bis(tetrafluoroborate) (4a). An anhydrous CH_2Cl_2 (10 mL) solution of NOBF₄ (49 mg, 0.42 mmol) was added dropwise to an anhydrous CH_2Cl_2 (20 mL) solution of telluride **2a** (100 mg, 0.19 mmol) 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, and a yellow solid, tellurane dication 2BF_4^- salt **4a** (122 mg) in 92% yield was obtained. Crystals for X-ray crystallographic analysis were grown from a CD_3CN solution. Mp 157–196 °C (dec); ¹H NMR (270 MHz, CD_3CN) δ 4.45, 5.15 (ABq, 1H, $J = 17.1$ Hz, CH_2), 4.95, 5.21 (ABq, 1H, $J = 17.3$ Hz, CH_2), 6.83–7.18 (m, 9H, ArH), 7.47 (m, 6H, ArH), 7.99–8.14 (m, 3H, ArH); ¹³C NMR (67.8 MHz, CD_3CN) δ 39.6, 40.3, 121.9, 124.3, 125.0, 128.7, 130.2, 131.0, 131.6, 132.1, 132.5, 132.9, 133.1, 134.9, 135.3, 136.3, 147.6, 148.0; ¹²⁵Te NMR (85.2 MHz, CD_3CN) δ 1327.3 (relative to Me_2Te); ¹⁹F NMR (254 MHz, CD_3CN) δ -150.7 (relative to CFCl_3); FABMS (*m/z*) 526 ($\text{M}^+ - 2\text{BF}_4^-$). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{B}_2\text{F}_8\text{S}_2\text{Te}$: C, 44.62; H, 3.17. Found: C, 44.08; H, 3.38.

2,6-Bis[(phenylthio)methyl]phenyl Phenyl Telluranyl Bis(trifluoromethanesulfonate) (4b). $(\text{CF}_3\text{SO}_3)_2\text{O}$ (30 μL , 0.179 mmol) was added to a heterogeneous mixture of the telluroxide (**3**) (88 mg, 0.16 mmol) in dry CH_3CN (10 mL) at room temperature under an argon atmosphere. The mixture immediately turned clear yellow. After stirring for 1 h the solvent was evaporated at room temperature, and the red-brown oily residue that remained was crystallized from $\text{Et}_2\text{O}/\text{CH}_3\text{CN}$ (1:1) to give yellow crystals, tellurane dication $2\text{CF}_3\text{SO}_3^-$ salt **4b** (43 mg) in 32% yield. Crystals for X-ray crystallographic analysis were grown from a CD_3CN solution. Mp 200–205 °C (dec); ¹H NMR (270 MHz, CD_3CN) δ 4.45, 5.13 (ABq, 1H, $J = 17.7$ Hz, CH_2), 5.09, 5.24 (ABq, 1H, $J = 17.0$ Hz, CH_2), 6.87–7.50 (m, 15 H, ArH), 7.95–8.17 (m, 3H, ArH); ¹³C NMR (67.8 MHz, CD_3CN) δ 39.7, 40.7, 122.3, 122.6, 124.6, 125.3, 128.8, 130.5, 131.0, 131.6, 132.0, 132.1, 132.5, 132.8, 133.0, 135.0, 135.2, 136.2, 147.7, 148.2; ¹²⁵Te NMR (85.2 MHz, CD_3CN) δ 1330.7 (relative to Me_2Te); ¹⁹F NMR (254.0 MHz, CD_3CN) δ -80.4 (relative to CFCl_3); FABMS (*m/z*) 526 ($\text{M}^+ - 2\text{TfO}^-$). Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{F}_6\text{O}_6\text{S}_4\text{Te}$: C, 40.80; H, 2.69. Found: C, 40.46; H, 2.71.

2,6-Bis[(phenylseleno)methyl]phenyl Phenyl Telluride (5). To a dry CH_3CN (100 mL) solution of 2,6-bis[(methoxy)methyl]phenyl phenyl telluride (**2b**) (430 mg, 1.15 mmol) were added KI (1.5 g, 11.5 mmol) and AlCl_3 (2.0 g, 11.5 mmol) 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_3CN (20 mL) was added using a transfer needle. The solution was stirred overnight, and then the solvent was evaporated at room temperature. Saturated $\text{Na}_2\text{S}_2\text{O}_3$ aqueous (100 mL) was added to the residue, and the organic products extracted with ether, the organic layer was separated and dried over anhydrous MgSO_4 , and the solvent was removed. The crude product was purified by column chromatography (silica gel; eluent, *n*-hexane- CH_2Cl_2 , 4:1) to give a pale yellow oil, telluride **5** (60 mg) in 8% yield. ¹H NMR (400 MHz, CDCl_3 , room temperature) δ 4.38 (s, 4H), 7.02–7.41 (m, 18H, Ar-H); ¹³C 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; ¹²⁵Te NMR (85 MHz, CDCl_3 , room temperature) δ 428.0 ($J_{\text{Te-Se}} = 100$ Hz) (relative to Me_2Te); ⁷⁷Se NMR (51 MHz, CDCl_3 , room temperature) δ 387.3 ($J_{\text{Te-Se}} = 100$ Hz) (relative to Me_2Se); MS (*m/z*); 620 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{Se}_2\text{Te}$: C, 50.37; H, 3.58; Found: C, 50.18; H, 3.49.

2,6-Bis[(phenylseleno)methyl]phenyl Phenyl Telluranyl Bis(tetrafluoroborate) (6). An anhydrous CH_3CN (10 mL) solution of NOBF₄ (30 mg, 0.26 mmol) was added dropwise to a solution of telluride **5** (67 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (20 mL) 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 **6** (44 mg) in 51% yield.

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Table 1. X-ray Crystallographic Data for Diffraction Studies of **4a**, **4b**, and **6**

compd	4a	4b	6
formula	C ₂₈ H ₂₅ B ₂ F ₈ NS ₂ Te	C ₃₂ H ₂₈ F ₆ N ₂ O ₆ S ₄ Te	C ₂₈ H ₂₅ B ₂ F ₈ NS ₂ Te
fw	740.84	906.41	834.64
cryst syst	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> , Å	8.629(1)	12.569(1)	10.011(4)
<i>b</i> , Å	9.938(1)	16.114(1)	19.156(8)
<i>c</i> , Å	19.207(2)	9.887(1)	8.675(4)
α , deg	77.79(1)	99.66(1)	93.68(4)
β , deg	86.53(1)	104.13(1)	111.23(3)
γ , deg	86.53(1)	69.63(1)	77.31(4)
<i>V</i> , Å ³	1495.4(3)	1813.0(3)	1512(1)
<i>Z</i>	2	2	2
<i>D</i> _{calcd} , g cm ⁻³	1.645	1.66	1.83
<i>F</i> (000)	732.0	704.0	804.0
temp, °C	23 ± 1	-60 ± 1	23 ± 1
radiation (λ , Å)	Mo K α (0.710 73)	Mo K α (0.710 73)	Cu K α (1.54178)
cryst dimens, mm	0.15 × 0.40 × 0.95	0.15 × 0.30 × 1.00	0.20 × 0.20 × 0.25
μ , cm ⁻¹	12.05	11.27	111.49
scan type	ω -2 θ	200 × 200 mm plate	ω -2 θ
scan rate	2-20 deg/min	46 oscill. images	16 deg/min
scan width, deg	0.60 + 0.49 tan θ	(6 min/exposure)	0.60 + 0.49 tan θ
maxi 2 θ , deg	55.9	53.1	135.2
tot no. of rflns	7676	5281	5661
no. of unique rflns	7202	5281	5320
no. of params refined	469	461	352
rflns included	5016 (<i>I</i> > 5 σ (<i>I</i>))	5052 (<i>I</i> > 5 σ (<i>I</i>))	3799 (<i>I</i> > 3 σ (<i>I</i>))
agreement factors ^a			
<i>R</i>	0.038	0.043	0.071
<i>R</i> _w	0.041	0.048	0.076

$$^a R = \sum |F_oI - |F_cI|| / \sum |F_oI|; R_w = [\sum w(|F_oI - |F_cI|^2) / \sum w F_o^2]^{1/2}.$$

Mp 201-204 °C (dec); ¹H NMR (270 MHz, CD₃CN, -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); ¹³C NMR (68 MHz, CD₃CN, 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; ¹²⁵Te NMR (85 MHz, CD₃CN, -40 °C) δ 1174.9 (*J*_{Te-Se} = 443, 491 Hz) (relative to Me₂Te); ⁷⁷Se NMR (51 MHz, CD₃CN, -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 Me₂Se); ¹⁹F NMR (254 MHz, CD₃CN, room temperature) δ -159 (BF₄⁻) (relative to CFCl₃); MS (*m/z*): 620 (M⁺ - 2BF₄⁻); HRMS: calcd for C₂₆H₂₂Se₂Te (M⁺ - 2BF₄⁻) 352.0922, found 352.0920.

Crystal Structure Determination of the Dicationic Telluranes 4a, 4b and 6. All crystals analyzed were mounted on top of a glass fiber, and their respective X-ray data were collected using either a four-circle diffractometer or an imaging plate area detector. The crystallographic details are given in Table 1. Non-hydrogen atoms were modeled anisotropically using neutral atom scattering factors. The hydrogen atoms were added to the respective carbon atoms assuming either a tetrahedral or planar geometry with the C-H distances equal to 0.97 or 1.08 Å. All structures were refined on *F* by full-matrix least-squares techniques. The neutral atom scattering factors used in the refinements were taken from Cromer and Waber⁶ and corrected for anomalous dispersion⁷ using the *f'* and *f''* values determined by Creagh and McAuley.⁸ The teXsan⁹ crystallographic software package was used for the refinement and geometrical calculations and molecular graphics. All calculations were done on a Indy work station.

(i) **Compound 4a.** Data were collected at 23 ± 1 °C for a yellow platelike crystal using an Enraf-Nonius CAD4 diffractometer with

graphite monochromated Mo K α radiation. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range 9.00 < 2 θ < 18.00 °. The intensities of 7202 reflections were corrected for Lp effects, absorption (DIFABS:¹⁰ correction range 0.68-1.00), and crystal decay (5.8%). The structure was solved by direct methods¹¹ and expanded using difference Fourier syntheses. In the final cycle of full-matrix least-squares all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to the respective carbon atoms at calculated positions, and subsequently their coordinates were refined but their isotropic B's were fixed. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.75 and -0.81 e/Å³, respectively.

(ii) **Compound 4b.** Data were collected at -60 ± 1 °C for a yellow platelike crystal using a Rigaku RAXIS II imaging plate area detector with graphite monochromated Mo-K α radiation. The unit cell parameters were determined from a least-squares treatment of 30 reflections in the range 9.00 < 2 θ < 18.00 °. The intensities of 5281 reflections were corrected for Lp effects and secondary extinction (coefficient = 1.84225e-06). The structure was solved by the heavy-atom Patterson method¹² and expanded using difference Fourier syntheses. In the final cycle of full-matrix least-squares all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to the respective carbon atoms at calculated positions but not refined. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.53 and -1.69 e/Å³, respectively.

(iii) **Compound 6.** Data were collected at 13 ± 1 °C for a colorless prismatic crystal using a Rigaku AFC7S four-circle diffractometer with graphite monochromated Cu-K α radiation. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles

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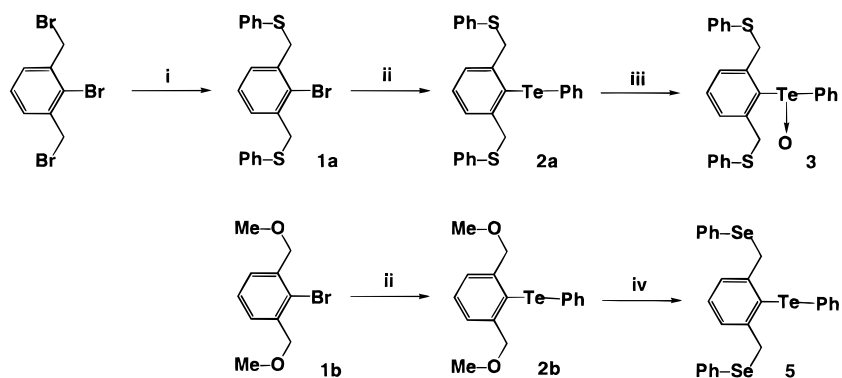
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Scheme 1^a

^a (i) PhSNa/EtOH/0 °C; (ii) *n*-BuLi/Et₂O/-78 °C, PhTeTePh; (iii) *t*-BuOCl/MeOH-CH₂Cl₂/0 °C; (iv) KI/AlCl₃/CH₃CN/room temperature, PhSeNa.

of 20 reflections in the range $33.2 < 2\theta < 36.4^\circ$. The intensities of 5320 reflections were corrected for Lp effects and absorption (DIFABS;¹⁰ correction range 0.42–1.00). The structure was solved by direct methods,¹¹ expanded using difference Fourier syntheses, and refined on *F* by full-matrix least-squares techniques. In the final cycle of full-matrix least-squares all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to the respective carbon atoms at calculated positions but not refined. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 1.74 and $-1.44 \text{ e}/\text{\AA}^3$,³ respectively.

Electrochemical Study. Peak potentials of the first oxidation peak were determined at a glassy carbon electrode with 2 mM samples in dry CH₃CN–0.1 M NaClO₄ vs Ag/AgCl in 3 M KCl, 100 mV/s scan rate.

Ab Initio Calculations. *Ab initio* single-point calculations of the dication were carried out on a HP735/125 workstation using Spartan version 3.1.¹³ The X-ray molecular structures of **4b** and **6** 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.¹⁴

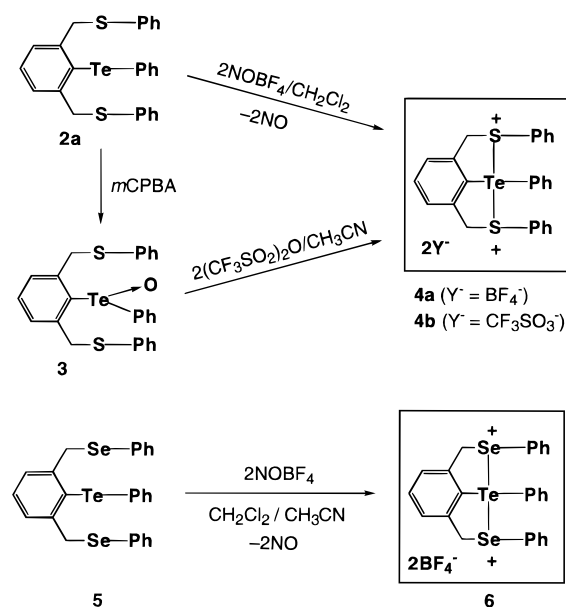
Results and Discussion

Syntheses and Characterization. The compounds **2a**, **3**, and **5** were synthesized as shown in Scheme 1 and characterized by various spectroscopies and elemental analyses. Interestingly, the ⁷⁷Se and ¹²⁵Te NMR spectra of compound **5** show satellite peaks between the selenium and tellurium atoms although there are no Se–Te bonds. The coupling constant ($J_{\text{Se-Te}}$) is 100 Hz. 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.

The existence of an interaction between the three chalcogen atoms in **2a** or **5** was apparent from cyclic voltammetry studies, because 234 or 277 mV reduction in the oxidation potentials was observed when **2a** (666 mV) or **5** (623 mV) was compared with diphenyl telluride (Ph–Te–Ph) (900 mV). In contrast to diphenyl telluride which showed an irreversible oxidation wave, both **2a** and **5** exhibited pseudoreversible behavior, indicating a stabilizing effect by the introduction of the two phenylthio- or phenylselenomethyl ligands. Compounds **2a** and **5** were readily oxidized by, for example, adding a solution of anhydrous CH₂Cl₂ containing NOBF₄ (2 equiv) dropwise to a solution of anhydrous CH₂Cl₂/CH₃CN containing **2a** or **5** at -78°C under an argon atmosphere. After removal of the solvent, the tellurane dication 2BF₄[−] salts (**4a**) and (**6**) were isolated in 92% and 51% yield, as yellow solids, respectively.

Treating the corresponding telluroxide **3** with trifluoromethanesulfonic anhydride [(CF₃SO₂)₂O; 1 equiv] in dry CH₃CN under

Scheme 2



argon at 0 °C resulted in its conversion to the yellow tellurane dication 2CF₃SO₃[−] salt, **4b**. We also tried to synthesize the telluroxide from the corresponding telluride **5** in the *m*-CPBA as an oxidant to mimic the above reaction. However, we could not obtain the pure telluroxide because the products are unstable and readily decompose at room temperature.

Subsequent crystallization from an ether–CH₃CN solution gave yellow crystals of **4a**, **4b**, and **6**, as shown in Scheme 2.

To determine the structures of **4a**, **4b**, and **6**, ¹H, ¹³C, and ¹²⁵Te NMR spectra were measured. The ¹H NMR spectrum of each compound when measured in CD₃CN at 20 °C exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.95, 5.21 ($J = 17.3 \text{ Hz}$) and δ 4.45, 5.15 ($J = 17.1 \text{ Hz}$); δ 4.45, 5.13 ($J = 17.7 \text{ Hz}$) and δ 5.09, 5.24 ($J = 17.0 \text{ Hz}$); and δ 4.26, 5.23 ($J = 16.0 \text{ Hz}$) and 4.96, 5.23 ($J = 15.0 \text{ Hz}$) in a 1:1 ratio, respectively. These signals were assigned to the asymmetric bicyclic form. The ¹²⁵Te NMR spectra of **4a** and **4b** show only a single peak at 1327.3 and 1330.7 ppm, respectively. However, the ¹²⁵Te NMR spectrum of **6** shows one peak at 1174.9 ppm at -40°C with four satellite peaks due to the spin–spin coupling ($^1J_{\text{Te-Se}} = 443, 491 \text{ Hz}$) between the central tellurium and two asymmetric selenium atoms as shown in Figure 2. The ⁷⁷Se chemical shifts of **6** 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

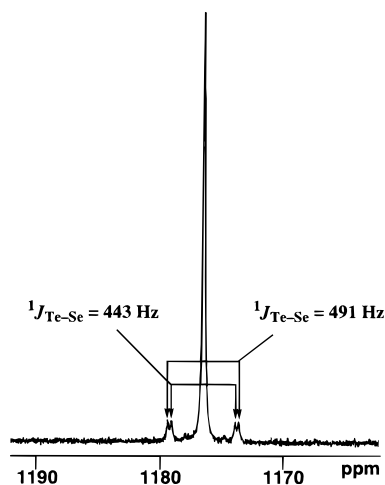


Figure 2. ^{125}Te NMR spectrum of **6**.

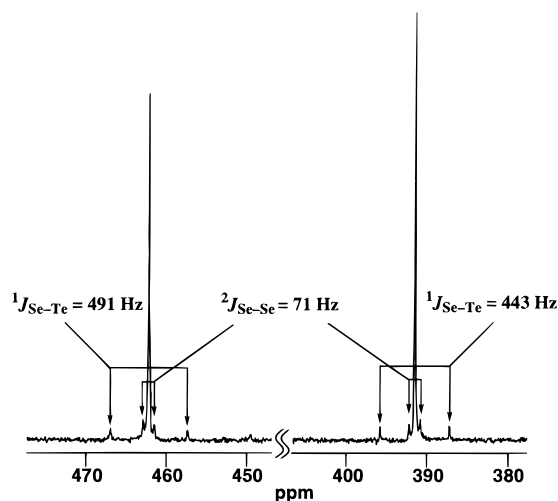


Figure 3. ^{77}Se NMR spectrum of **6**.

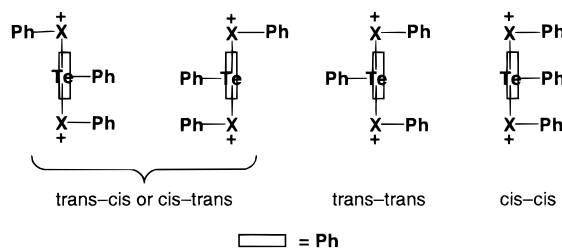
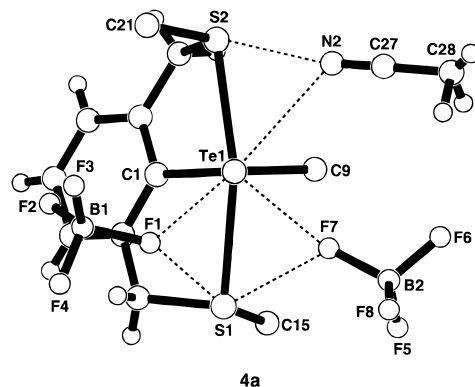


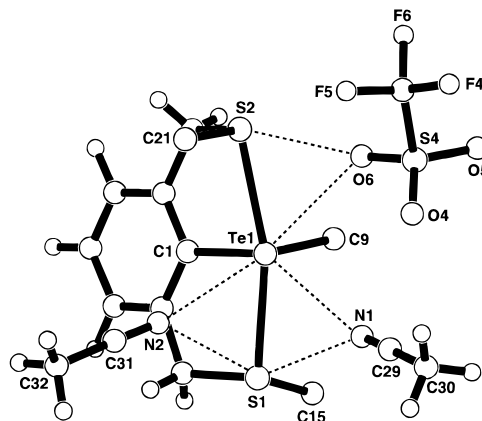
Figure 4. Isomers of **4** ($X = \text{S}$) and **6** ($X = \text{Se}$).

only the spin–spin coupling ($^1J_{\text{Se-Te}} = 443, 491 \text{ Hz}$) between the selenium and tellurium atoms but also due to the coupling ($^2J_{\text{Se-Se}} = 71 \text{ Hz}$) between selenium atoms through the tellurium atom as shown in Figure 3. 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 **5** also exists in the asymmetric bicycle form and support the bond formation between the tellurium and selenium atoms.

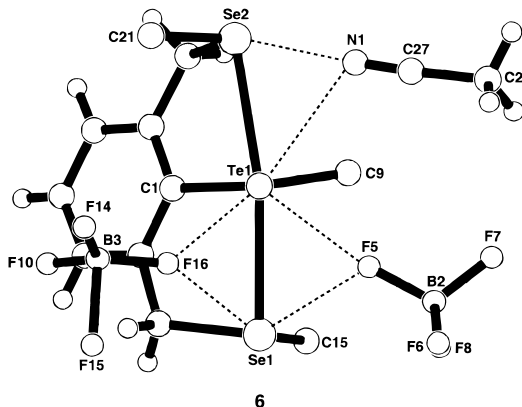
In principle, the dications **4a**, **4b**, and **6** could exist as one of the following three possible stereoisomers: *cis-trans*, *trans-cis* (*dl*-pairs), and/or *trans-trans* (meso) and/or *cis-cis* (meso), as shown in Figure 4. The *trans-trans* isomer is expected to be the most sterically stable configuration of the dicationic telluranes. However, the NMR spectra of these compounds indicate that these structures have either a *cis-trans* or *trans-cis* configuration. Furthermore, the elemental analyses of **4a**,



4a



4b



6

Figure 5. A ball and stick view of **4a**, **4b**, and **6**. For clarity, the three phenyl rings on chalcogen atoms were omitted.

4b, and **6** are consistent with the molecular formula of the corresponding dicationic tellurane, and the FAB-mass spectra of **4a**, **4b**, and **6** show the molecular ion at m/e 526 ($M^+ - 2 \text{ counteranions}$) and m/e 620 ($M^+ - 2\text{BF}_4^-$), respectively.

X-ray Crystallographic Analyses. Suitable crystals for X-ray analysis were obtained by recrystallization of **4a** and **4b** from dry solutions of CD_3CN at 0°C . The dication structure of **4b** is similar to that of **4a**. A ball and stick view of **4a** and **4b** is shown in Figure 5. The X-ray crystal structure determination of **4a** 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 sulfonio ligands. Crystals of **4a** and **4b** contain not only two counteranions (2BF_4^- or 2TfO^- , respectively) but also one molecule of acetonitrile as a lattice solvate. The favored stereoisomer has the *trans-cis* or *cis-trans* conformation, which is in agreement with the NMR results. The respective bond lengths $\text{Te}(1)\text{-S}(1)$ (2.706(1) and 2.652-

(1) Å) and Te(1)–S(2) (2.661(1) and 2.654(1) Å) are longer than the normal Te–S single bond (2.36 Å).¹⁵ The bond angles S(1)–Te(1)–S(2) and C(1)–Te(1)–C(9) are equal to 160.4(4)°, 162.54(5)° and 98.5(2)°, 95.5(2)°, respectively. Thus, the Te(1) atoms of **4a** and **4b** 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. These structural features are very similar to those observed in the normal noncharged tellurane(IV) compounds.¹⁶

Suitable crystals for X-ray analysis were obtained by recrystallization of **6** from dry solutions of $\text{CD}_3\text{CN}/\text{Et}_2\text{O}$ at 0 °C. The X-ray crystal structure determination of **6** establishes that in the solid state it also exists only in the *trans-cis* or *cis-trans* conformation and is the first example of a dicationic σ -tellurane with two apical selenonio ligands as shown in Figure 5. In addition to the two counteranions (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).¹⁵ 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. The Te(1) of **6** has the same configuration as that of compounds **4a** and **4b**.

According to crystal packing of these dication compounds, the chalcogen atoms of **4a**, **4b**, and **6** are weakly coordinated by the fluorine of BF_4^- or oxygen of CF_3SO_3^- and nitrogen of acetonitrile. The compounds **4a** and **6** have two tetrafluoroborate anions and one acetonitrile, and **4b** has one triflate anion and two acetonitrile molecules in each unit cell as shown in Figure 5. 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–S = 3.20, F–Se = 3.35, O–Te = 3.60, O–S = 3.25, O–Se = 3.40, N–Te = 3.70, N–S = 3.35, and N–Se = 3.50 Å).¹⁶ These results indicate that the three chalcogen atoms of **4a**, **4b**, and **6** have highly positive charges. In summary, the crystal structures of **4a**, **4b**, and **6** are very similar as shown in Table 2.

Theoretical Calculations. To understand the electronic structure of the dicationic σ -telluranes, single point *ab initio* calculations were carried out using the crystal structures of **4b** and **6**. The calculations were carried out at the RHF/3-21G(*) level. The atomic charges were evaluated by the natural population analysis;¹⁴ this method is particularly more suitable than the traditional Mulliken population analysis for hypervalent species which have strongly polar bonds.¹⁷ The charge distributions in the two dications are shown in Figure 6, and various electronic properties are summarized in Table 3.

The atomic charges of Te(1), S(1), and S(2) in **4b** were calculated to be +1.600, +0.483, and +0.495, respectively.

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Table 2. Selected Bond Distances (Å) and Angles (deg) with ESD's in Parentheses for **4a**, **4b**, and **6a**

	4a (X = S)	4b (X = S)	6 (X = Se)
Te(1)–X(1)	2.706(1)	2.652(1)	2.807(2)
Te(1)–X(2)	2.661(1)	2.654(1)	2.759(2)
Te(1)–C(1)	2.114(4)	2.108(5)	2.17(1)
Te(1)–C(9)	2.096(5)	2.118(5)	1.92(1)
X(1)–C(7)	1.798(6)	1.800(6)	1.96(1)
X(1)–C(15)	1.779(5)	1.775(6)	1.94(1)
X(2)–C(8)	1.808(6)	1.793(6)	1.98(1)
X(2)–C(21)	1.785(5)	1.782(5)	1.92(1)
X(1)–Te(1)–X(2)	160.41(4)	162.54(5)	163.93(5)
X(1)–Te(1)–C(1)	80.1(1)	81.7(1)	82.4(4)
X(1)–Te(1)–C(9)	90.4(1)	93.3(1)	90.5(3)
X(2)–Te(1)–C(1)	80.5(1)	81.1(1)	81.9(4)
X(2)–Te(1)–C(9)	89.6(1)	91.2(1)	88.6(3)
C(1)–Te(1)–C(9)	98.5(2)	95.5(2)	99.0(5)
Te(1)–X(1)–C(7)	91.4(2)	95.6(2)	87.2(4)
Te(1)–X(1)–C(15)	105.5(2)	106.7(2)	102.9(4)
Te(1)–X(2)–C(8)	92.8(2)	95.0(2)	88.7(4)
Te(1)–X(2)–C(21)	99.1(1)	92.0(2)	96.3(4)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

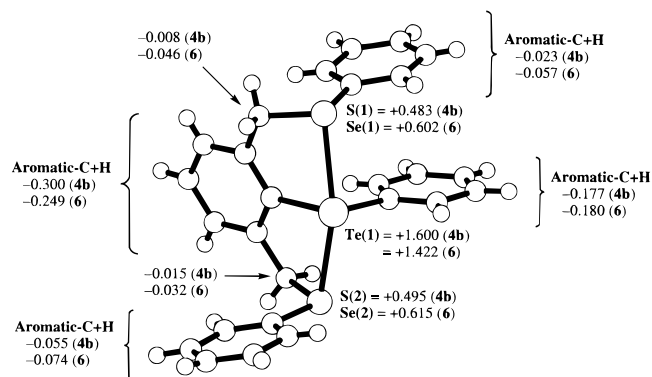


Figure 6. The charge distribution (natural population analysis) in the tellurane dications **4b** and **6**.

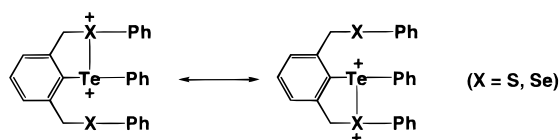
Table 3. Comparison of the Electronic Structures of Dications **4b** (X = S) and **6** (X = Se)

quantity	atom or bond	4b (X = S)	6 (X = Se)
atomic charge ^a	Te	+1.600	+1.422
	X(1)	+0.483	+0.602
	X(2)	+0.495	+0.615
bond order ^b	Te–X(1)	0.501	0.556
	Te–X(2)	0.501	0.587
valency ^b	Te	3.02	3.08
	X(1)	2.43	2.59
	X(2)	2.43	2.61
5d occupancy ^a	Te	0.034	0.033

^a Natural population analysis. ^b Mulliken values.

Thus, the total positive charge of +2.578 is located exclusively on the three chalcogen atoms of hypervalent bonding system. The charge is larger than two due to the polarization of Te–C and S–C bonds. In addition, the hypervalent apical bonds seem to be polarized as is normally observed in hypervalent molecules, since the positive charges of S(1) and S(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 **6**, the Te(1) atom is less positively charged than in **4b**, and the positive charges on Se(1) and Se(2) are larger than those of the sulfur atoms in **4b**, simply reflecting the fact that the electronegativity of selenium is smaller than that of sulfur.

Scheme 3



The Mulliken bond orders of Te(1)–S(1) and Te(1)–S(2) in **4b** are 0.501, which is 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.¹⁸ The Te(1)–Se(1) and Te(1)–Se(2) bond orders of **6** are somewhat larger. The total 5d-orbital population of tellurium is small (about 0.03) both in **4b** and in **6**, and the d orbitals are not primarily concerned with the Te–S and Te–Se bonds. The Mulliken valency values, about 3, 2.4, and 2.6 for the tellurium, sulfur, and selenium atoms, respectively, are consistent with the resonance as shown in Scheme 3.

As shown in Figure 6, 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 counterion 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 counterions; further charge localization induced by counterions 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 counterions. Therefore, we think that the charge distributions calculated for the isolated dications are not so dif-

ferent from those in crystals and in solutions and that the interactions between the dication and counterions are essentially electrostatic.

Conclusions

In conclusion, the chemical properties and preparation of a new type of dicationic σ -telluranes (λ^4 -tellane), $[10\text{-Te-4}]^{2+}$ salts from the new flexible acyclic tris-chalcogenide via transannular bond formation were studied. Single crystal X-ray structure determinations revealed that two apical sulfonio- or selenonio ligands bond to the central tellurium atom via transannular bond formation. Furthermore, the computational results show that the dicationic telluranes contain 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. Further studies on the characterization of hypervalent chalcogenurane dications are in progress.

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Supporting Information Available: Detailed crystallographic data, positional and thermal parameters, and bond distances and angles of **4a**, **4b**, and **6** (56 pages). See any current masthead page for ordering and Internet access instructions.

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