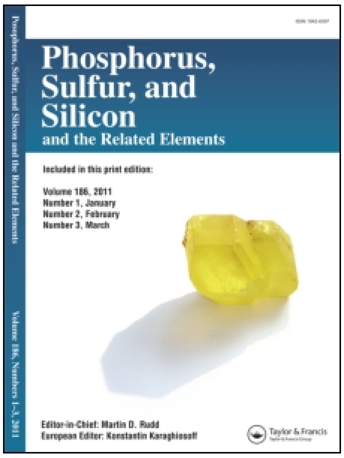

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SYNTHESIS OF TELLURIUM CENTERED NOVEL HYPERVALENT DICATIONS

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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–Te–4(C2X2)]$^{2+}\bullet 2Y^-$ (λ^4-tellane) (X = S or Se, Y = BF_4 or CF_3SO_3). 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. *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.

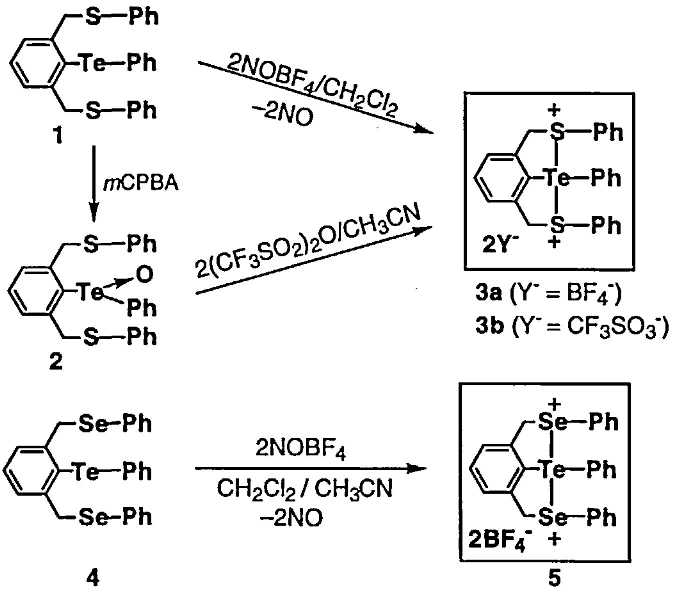
Keywords: hypervalent dication; tellurane; transannular interaction

Syntheses and Characterization

Diaryl telluride derivatives **1** and **4** were readily oxidized by adding a solution of anhydrous CH_2Cl_2 containing $NOBF_4$ (2 equiv) dropwise to a solution of anhydrous CH_2Cl_2/CH_3CN containing **1** or **4** at –78 °C under an argon atmosphere. After removal of the solvent, the tellurane dication $2BF_4^-$ salts **3a** and **5** were isolated in 92% and 51% yield, as yellow solids, respectively.

Treating the corresponding telluroxide **2** with trifluoromethanesulfonic anhydride [$(CF_3SO_2)_2O$; 1 equiv] in dry CH_3CN under an argon at 0 °C resulted in its conversion to the yellow tellurane dication $2CF_3SO_3^-$ salt, **3b**.

SCHEME 1



In order to determine the molecular structures of **3a**, **3b**, and **5**, ^1H, ^{13}C, ^{77}Se, 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 4.95, 5.21 (J = 17.3 Hz) and δ 4.45, 5.15 (J = 17.1 Hz); δ 4.45, 5.13 (J = 17.7 Hz) and δ 5.09, 5.24 (J = 17.0 Hz); and δ 4.26, 5.23 (J = 16.0 Hz) and 4.96, 5.23 (J = 15.0 Hz) in a 1 : 1 ratio, respectively. These signals were assigned to the asymmetric bicyclic form. The ^{125}Te NMR spectra of **3a** and **3b** show only a single peak at 1327.3 and 1330.7 ppm, respectively. However, the ^{125}Te NMR spectrum of **5** shows one peak at 1174.9 ppm at –40 °C with four satellite peaks due to the spin-spin coupling ($^1J_{Te\text{-}Se}$ = 443, 491 Hz) between the central tellurium and two asymmetric selenium atoms. The ^{77}Se chemical shifts of **5** 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

$^1J_{Se\text{-}Te}$ = 443, 491 Hz) between the selenium and tellurium atoms, but also due to the coupling ($^2J_{Se\text{-}Se}$ = 71 Hz) between selenium atoms hrough the tellurium atom. Such an example of spin-spin coupling hrough a three-center four-electron bond has not been reported and is hus an addition to the very interesting behavior of hypervalent chemistry. These results indicate that compound **2** also exists in the asymmetric bicyclic form and supports the bond formation between the tellurium and elenium atoms.

n principle, the dications **3a**, **3b**, and **5** 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). The *trans-trans* isomer s expected to be the most sterically stable configuration of the dicationic elluranes. However, the NMR spectra of these compounds indicate that hese structures have either a *cis-trans* or *trans-cis* configuration.

The X-ray crystal structure determination of **3a**, **3b**, and **5** establishes hat in the solid state these compounds exists only as one isomer. The favored stereoisomer has the *trans-cis* or *cis-trans* conformation, which is n agreement with the NMR results. ORTEP views of **3a** and **5** are shown in Figure 1.

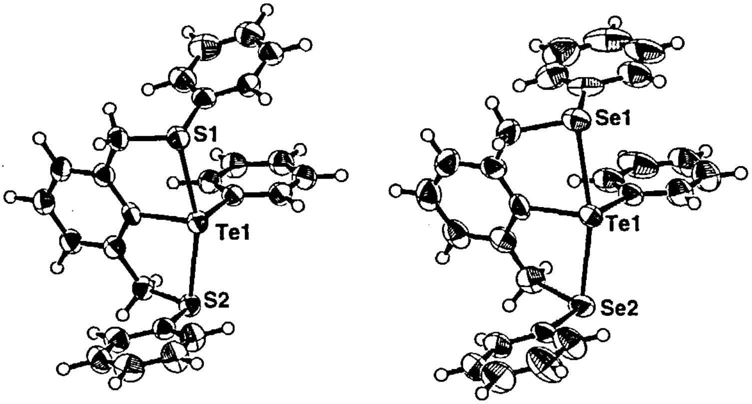


FIGURE 1. ORTEP view of 3a and 5

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 **3b** and **5**. The calculations were carried out at the RHF/3-21G$^{(*)}$ level. The atomic charges were evaluated by the natural population analysis. The charge distributions and various electronic properties in the two dications are summarized in Table 1.

Table 1. Comparison of the Electronic Structures of Dications **3b** (X = S) and **5** (X = Se)

quantity	atom or bond	**3b** (X = S)	**5** (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.

The atomic charges of Te(1), S(1), and S(2) in **3b** were calculated to be +1.600, +0.483, and +0.495, respectively. 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 the case of **5**, the Te(1) atom is less positively charged than in **3b** and the positive charges on Se(1) and Se(2) are larger than those of the sulfur atoms in **3b**, simply reflecting the fact that the electronegativity of selenium is smaller than that of sulfur.

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.

References

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