Heteroatom Chemistry
Volume 12, Number 5, 2001

Synthesis and Structure of Pentaphenyltelluronium Salts of Perchlorate and Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate: Hypervalent Onium Compounds

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Received 5 January 2001; revised 12 February 2001

ABSTRACT: *The reaction of pentaphenyltellurium chloride* **2** *with silver perchlorate afforded the pentaphenyltelluronium salt, $Ph_5Te^+ClO_4^-$, (***1b***), and treatment of* **2** *with silver triflate and sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate provided $Ph_5Te^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (1c), which were isolated as stable yellow solids. X-ray crystallographic analyses of the hypervalent telluronium salts revealed square-pyramidal geometry around the tellurium, which are rare examples for penta-substituted main group element compounds.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:380–384, 2001

INTRODUCTION

The chemistry of hypervalent organic compounds whose central element holds a decet or dodecet of electrons in the valence shell has stimulated interdisciplinary interest due to their intriguing bonding nature and reactivity [1]. For the synthesis of neutral hypervalent tetraorganochalcogens (R_4Ch^{IV}; Ch = S, Se, Te) and pentaorganopnictogens (R_5Pn^{V}; Pn = P, As, Sb, Bi), triorganochalcogenonium salts, [$R_3Ch^{IV}X$ (X = anions)] and their pnictogen analogues ($R_4Pn^{V}X$) have been used in a variety ways, respectively [2].

In contrast to the well-investigated triorganochalcogenonium salts [3], little is known about the compounds having the general formula R_5Ch^{VI+} due to the lack of suitable synthetic methods and the paucity of knowledge of organochalcogen com-

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Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture, Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research 09440218.
Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture, Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research 10740296.
Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture, Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research 11304044.
Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture, Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research 12740352.
Contract Grant Sponsor: Nishida Research Fund for Fundamental Organic Chemistry (to M.M.).

pounds bearing the highest oxidation state VI [4,5]. Very recently, we reported the first hypervalent onium compound, pentaphenyl telluronium, Ph_5Te^+ $(C_6F_5)_4B^-$ **1a** [6]. The X-ray crystallographic analysis of **1a** provided evidence for the onium to be a free hypervalent tellurium cation without any interaction with the counteranion. Despite the fact that most penta-substituted compounds are trigonal bipyramidal (*TBP*), the Ph_5Te^+ of **1a** had a square pyramidal (*SP*) geometry around the tellurium. In order to see the effect of counteranions on the structure of Ph_5Te^+, we prepared and determined the structure of pentaphenyltelluronium salts of perchlorate (ClO_4^-) **1b** and a large counteranion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) **1c**.

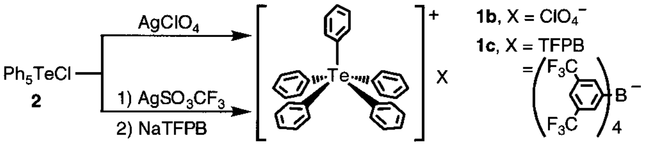
RESULTS AND DISCUSSION

Hypervalent telluronium, $Ph_5Te^+ClO_4^-$ **1b** was synthesized by the treatment of pentaphenyltellurium chloride **2** with silver perchlorate in tetrahydrofuran (THF) at −78°C (Scheme 1). After removal of the silver chloride under argon, the filtrate was evaporated and recrystallized from hexane-dichloromethane to give **1b** (98%) as a thermally stable yellow solid.

The telluronium salt having a large counteranion, Ph_5Te^+TFPB **1c** was obtained by the halogen abstraction of **2** with silver triflate in THF and anion exchange by use of sodium TFPB in dichloromethane at −78°C (Scheme 1). After filtration under argon, the filtrate was concentrated in vacuo, and recrystallized from hexane-dichloromethane to give **1c** (90%) as a thermally stable yellow solid.

The structure of **1b** was established by X-ray crystallography of a single crystal obtained by recrystallization from dichloromethane. The crystal structure is shown in Figure 1 and reveals weak coordination of an oxygen atom in the ClO_4^- to the cationic tellurium center in the Ph_5Te^+. By comparison with the typical covalent bond length of Te–O (2.11 Å), the tellurium and oxygen distance of 2.740(3) Å is long, but nevertheless shorter than the sum of the van der Walls radii (3.60 Å).

Recrystallization of **1c** yielded yellow crystals suitable for X-ray crystallographic analysis, which was realized only by the slow evaporation of saturated acetonitrile solution in a glove box. In the crystal, the cationic tellurium atom of **1c** is weakly coordinated by the nitrogen of a MeCN molecule derived from the recrystallization solvent (Figure 2). The distance from the tellurium to the nitrogen is 2.865(4) Å, which is much longer than the covalent bond length (2.07 Å) but shorter than the sum of the van der Walls radii (3.70 Å), and the TFPB is well separated. This solvent inclusion and coordination would be attributable to the large counteranion, which provides a space between the Ph_5Te^+ and TFPB.



SCHEME 1

Although the *SP* structure is quite rare in main group element chemistry [7], the free tellurium cation in **1a** shows the *SP* structure in the solid state. In the case of **1b** and **1c**, bond angles around the Te indicated that the structures have also high *SP* character (89 and 91%, respectively), which were calculated by the dihedral angle method [8]. The tellurium-apical carbon bonds (**1b**, 2.125(4); **1c**, 2.125(4) Å) are shorter than the four basal carbon bond lengths (**1b**, 2.184(4)–2.214(4), **1c**, 2.174(4)–2.201(4) Å), and these apical bond shortenings are known to be a characteristic phenomenon in the *SP* structure [7]. Thus, it is apparent that the counteranion has no significant effect on the structure of Ph_5Te^+ in the solid state. All the C–Te bond lengths in **1b** and **1c** are shorter than those of neutral Ph_6Te (av. 2.228 Å) [5a] due to cationic attractive interaction between the tellurium and five carbon ligands.

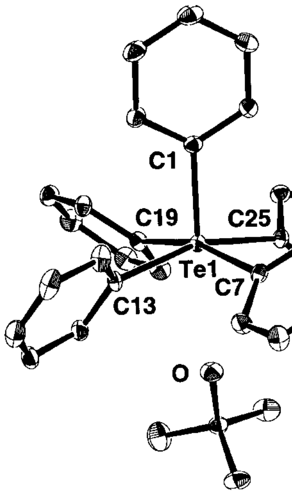


FIGURE 1 Molecular structure of **1b** (thermal ellipsoids with 30% probability). Selected bond lengths (Å): Te1–C1, 2.120(4); Te1–C7, 2.203(4); Te1–C13, 2.190(4); Te1–C19, 2.214(4); Te1–C25, 2.184(4); Te1–O, 2.740(3). Selected bond angles (deg): C1–Te1–C7, 98.7(1); C1–Te1–C13, 97.6(2); C1–Te1–C19, 97.2(2); C1–Te1–C25, 101.6(2); C7–Te1–C13, 87.2(1); C7–Te1–C19, 164.0(2); C7–Te1–C25, 88.1(1); C13–Te1–C19, 90.1(1); C13–Te1–C25, 160.6(2); C19–Te1–C25, 89.3(1).

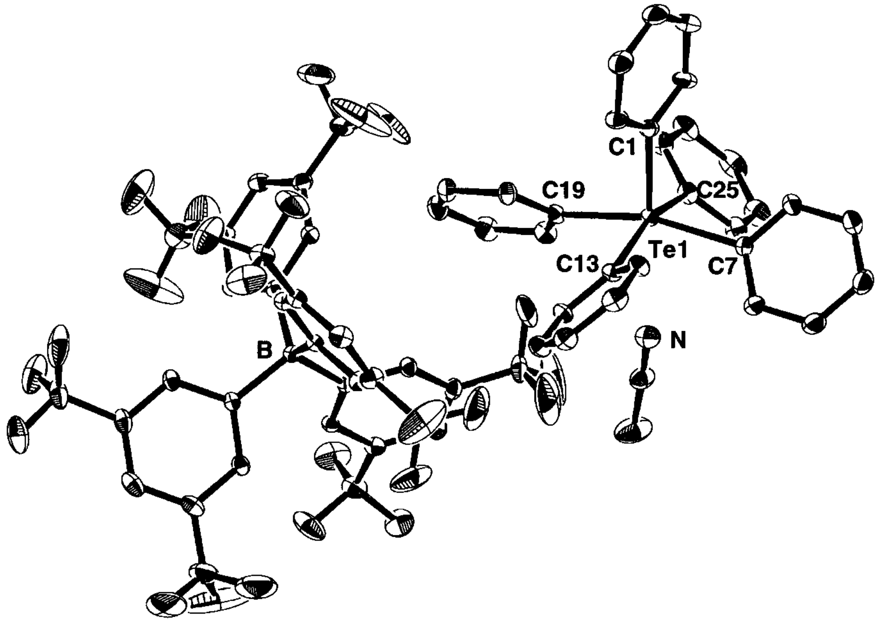


FIGURE 2 Molecular structure of **1c**·MeCN (thermal ellipsoids with 30% probability). Selected bond lengths (Å): Te1–C1, 2.125(4); Te1–C7, 2.199(4); Te1–C13, 2.174(4); Te1–C19, 2.201(4); Te1–C25, 2.180(4); Te1–N, 2.865(4). Selected bond angles (deg): C1–Te1–C7, 97.8(1); C1–Te1–C13, 98.9(2); C1–Te1–C19, 98.6(1); C1–Te1–C25, 100.2(2); C7–Te1–C13, 88.7(1); C7–Te1–C19, 163.6(2); C7–Te1–C25, 88.6(1); C13–Te1–C19, 89.0(1); C13–Te1–C25, 161.0(2); C19–Te1–C25, 88.3(1).

In solution, the ^{125}Te NMR spectrum of **1b** (δ = 659.3 ppm) and **1c** (659.9 ppm) in $CDCl_3$ showed almost identical chemical shift with the **1a** (659.0 ppm). In the ^{1}H and ^{13}C NMR spectra of **1b** and **1c**, only one set of phenyl group could be observed even at -70°C. This is consistent with rapid Berry pseudorotation that contains *SP* and *TBP* structures, as generally shown in the spectrum of pentaorgano element compounds. It seems reasonable to suppose that the previously mentioned observed coordination of the oxygen and the nitrogen in the solid state of **1b** and **1c** are very weak.

It is important to address the question on the relative stabilities of the *SP* and *TBP* structures for understanding the fluxional nature of the pentaorganotellurium cation. Hence we performed density functional theory (DFT) calculations on $(H_3C)_5Te^+$ as a model compound [9]. Both of the *TBP* and *SP* structures of $(H_3C)_5Te^+$ were optimized, and *SP* was found to be a transition state for Berry pseudorotation (Figure 3). This transition state lies only 2.2 kcal/mol above the *TBP* ground state. Therefore, this suggests the possibility that the Ph_5Te^+ would have an *SP* structure in the solid state induced by lattice control. However, there is still the possibility that the structure of the ground state of Ph_5Te^+ would be *SP*, but this will be addressed in the near future. In solution, on the other hand, the tellurium cation undergoes very rapid stereoisomerization via Berry pseudorotation. These results agree with the experimental findings.

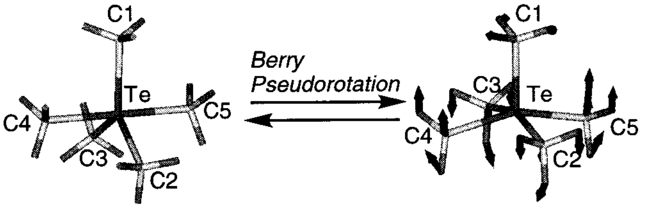


FIGURE 3 Optimized *TBP* (left) and *SP* (right) geometries of $(H_3C)_5Te^+$. The arrows in *SP* structure indicate the calculated pseudorotational motion. The important bond parameters are as follows. In TBP: Te–C1, 2.154 Å; Te–C4, 2.189 Å; C1–Te–C2, 120.0°, C4–Te–C5, 180.0°. In SP: Te–C1, 2.114 Å; Te–C3, 2.189 Å; C1–Te–C2, 101.4°, C4–Te–C5, 157.6°.

Further investigation of the physical and chemical properties of **1b** and **1c**, as well as the synthesis of other hypervalent telluroniums, is currently in progress.

EXPERIMENTAL

All manipulations were carried out under an argon atmosphere in a glove box. Solvents were dried by standard methods and freshly distilled prior to use.

Melting points were recorded using a capillary tube sealed under argon atmosphere on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed on a Parkin Elmer Model 2400. NMR spectra were measured at 25°C with a JEOL EX-400 spectrometer. ^{1}H (400 MHz), ^{11}B (128 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{125}Te (126 MHz). Chemical shifts of ^{1}H and ^{13}C NMR were reported in ppm downfield from tetramethylsilane or a residual solvent as an internal standard, and $BF_3 \cdot Et_2O$, $CFCl_3$, and Me_2Te were used for an external standard for ^{11}B, ^{19}F, and ^{125}Te NMR resonances, respectively.

Synthesis of Telluronium **1b**

To a THF solution (10 mL) of Ph_5TeCl **2** [6] (137.25 mg, 0.250 mmol) maintained at −78°C was added $AgClO_4$ (57.2 mg, 0.250 mmol). After stirring of the mixture for 1 hour at −78°C, warming it to room temperature, further stirring was continued for another 2 hours. The reaction mixture was filtered and the filtrate evaporated in vacuo to give **1b** (150 mg, 98%) after recrystallization from CH_2Cl_2-hexane. **1b**: yellow plates; m.p. 166–167°C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.38 (d J = 7.8 Hz, 10H), 7.49 (t, J = 7.8 Hz, 10H), 7.50 (t, J = 7.8 Hz, 5H); ^{13}C NMR ($CDCl_3$) δ 129.2 (Te-*meta*), 131.3 (Te-*ortho*), 133.5 (Te-*para*), 143.6 (Te-*ipso*); ^{125}Te NMR ($CDCl_3$) δ 659.3. Anal. Calcd for $C_{30}H_{25}O_4ClTe$: C, 58.82; H, 4.11. Found: C, 58.57; H, 4.00.

X-Ray Data Collection for **1b**

A single crystal of **1b** was obtained by the slow evaporation of its saturated solution in dichlorometane at room temperature in a glove box. Data were collected at 150 K on a MAC Science DIP2030 imaging plate with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved using the teXsan (Rigaku) system, and all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. The final cycle of full-matrix least-squares refinement was based on 2754 observed reflections [$I > 3.00\sigma(I)$, where I is the observed reflection intensity] and 326 variable parameters and converged with the unweighted and weighted agreement factors equal to R = 0.030 and R_w = 0.041 and GOF = 1.09. Crystal data for **1b**: $C_{30}H_{25}O_4ClTe$, monoclinic, $P2_1$, a = 8.8650(3) Å, b = 17.2140(4) Å, c = 9.3870(5) Å, β = 116.800(2)°, V = 1278.61(7) Å^3, Z = 2, D_{calcd} = 1.591 g cm^{-3}. Atomic coordinates, bond lengths and angles, and other important parameters will be deposited at the Cambridge Crystallographic Data Center.

Synthesis of Telluronium **1c**

To a THF solution (10 mL) of **2** (54.9 mg, 0.100 mmol) at −78°C was added AgOTf (25.8 mg, 0.102 mmol). After stirring of the mixture for 1 hour at −78°C, and then warming to room temperature, further stirring was continued for another 2 hours. After removal of the AgCl by filtration under argon, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), and was added to a CH_2Cl_2 suspension (10 mL) of NaTFPB (88.6 mg, 0.100 mmol) at room temperature. After having been stirred for 2 hours, the reaction mixture was filtered and the filtrate was evaporated in vacuo to give **1c** (124 mg, 90%) after recrystallization from CH_2Cl_2-hexane. **1c**: yellow plates; m.p. 139–140°C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.30 (d, J = 7.8 Hz, 10H), 7.43 (t, J = 7.8 Hz, 10H), 7.47 (s, 4H), 7.55 (t, J = 7.8 Hz, 5H), 7.69 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 117.4 (TFPB-*para*), 124.4 (q, $^{1}J_{CF}$ = 272.8 Hz, TFPB-CF_3), 128.8 (q, $^{2}J_{CF}$ = 31.5 Hz, TFPB-*meta*), 130.7 (Te-*meta*), 132.2 (Te-*ortho*), 133.0 (Te-*para*), 134.7 (TFPB-*ortho*), 140.1 (Te-*ipso*), 161.6 (q, $^{1}J_{CB}$ = 49.7 Hz, TFPB-*ipso*); ^{11}B NMR ($CDCl_3$) δ −6.6; ^{19}F NMR ($CDCl_3$) δ −62.9; ^{125}Te NMR ($CDCl_3$) δ 659.9. Anal. Calcd for $C_{62}H_{37}BF_{24}Te$: C, 54.11; H, 2.71. Found: C, 53.87; H, 3.07.

X-Ray Data Collection of **1c**

A single crystal of **1c** was obtained by the slow evaporation of its saturated solution in acetonitrile at room temperature in a glove box. Data were collected at 190 K on a MAC Science DIP2030 imaging plate with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved using the teXsan (Rigaku) system, and all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. The final cycle of full-matrix least-squares refinement was based on 11190 observed reflections [$I > 3.00\sigma(I)$] and 821 variable parameters and converged with the unweighted and weighted agreement factors equal to R = 0.067 and R_w = 0.112 and GOF = 1.31. Crystal data for **1c**·MeCN: $C_{64}H_{40}BNF_{24}Te$, triclinic, $P1$, a = 13.1320(3) Å, b = 13.2180(4) Å, c = 19.0990(5) Å, α = 72.679(1)°, β = 78.962(2)°, γ = 88.198(2)°, V = 3105.1(1) Å^3, Z = 2, D_{calcd} = 1.516 g cm^{-3}. Atomic coordinates, bond lengths and angles, and other important parameters will be deposited at the Cambridge Crystallographic Data Center.

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