

Synthesis and Characterization of a Hypervalent Tellurium Cation, Ph_5Te^+ : A Stable Nonclassical Onium Compound

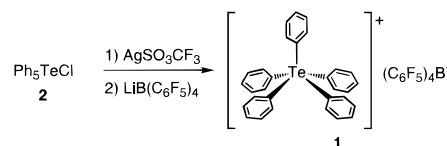
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As represented by carbocations, positively charged onium species have played important roles in both fundamental and applied chemistry.¹ During the last several years, rapid development of the synthesis and characterization of “free” group 14 element cationic compounds such as tricoordinate silyl and germyl cations in the condensed phase has occurred as the complement to carbocations.² On the other hand, a large number of onium species derived from heavier group 15–17 elements such as Ph_4P^+ , Ph_3Te^+ , and Ph_2I^+ have been known for a long time and used to prepare many neutral hypervalent compounds such as Ph_5P , Ph_4Te , and Ph_3I .³ The chemistry of hypervalent organic compounds has stimulated interdisciplinary interest due to their intriguing bonding nature and reactivity.⁴ Nonetheless, very little is known for chalcogen compounds with valence VI compared to those with valence IV, and no hexaarylated chalcogen had been described until we recently reported the synthesis of hexaaryl-telluriums as neutral compounds comprising Te^{VI} .^{5,6} Moreover, the pentaorganochalcogenonium ion, hypervalent onium species, has been a missing class of onium ions against the background of well-studied classical triorganochalcogenonium salts and pentaarylpnictogens which are isoelectronic to the hypervalent oniums.⁷ Consequently, there is a great deal of interest to explore pentasubstituted hypervalent cations, which should be essentially different from pentacoordinate carbocations, i.e., hypercarbons.⁸ Here, we present the first synthesis of a hypervalent onium

Scheme 1



compound, pentaphenyltelluronium, $\text{Ph}_5\text{Te}^+(\text{C}_6\text{F}_5)_4\text{B}^-$, **1**, and its structure and reactivity.

The synthesis of **1** was achieved by chlorine abstraction of Ph_5TeCl , **2**, which was readily prepared by chlorination of Ph_6Te , **3**, with Cl_2 in chloroform. Reaction of **2** with silver triflate followed by treatment with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in dichloromethane at -78°C gave **1** (Scheme 1). After removal of the silver chloride and lithium triflate by filtration under argon, the filtrate was concentrated in vacuo and recrystallized from hexane–dichloromethane to give pure **1** quantitatively as yellow crystals.⁹

Surprisingly, this cation is thermally stable and not moisture-sensitive both in solution and in the solid state. The molecular structure of **1** was determined by X-ray crystallographic analysis (see Figures 1 and 2).¹⁰ In the crystal, the cationic tellurium atom of **1** has five phenyl rings and is not coordinated by the counter borate anion. The distance from tellurium to the boron is well separated, 8.439(5) Å, and that to the nearest fluorine atom in the anion is 3.584(3) Å, which is longer than sum of the van der Waals radii (3.55 Å). These values are larger than those of the corresponding classical onium salt $\text{Ph}_3\text{Te}^+(\text{C}_6\text{F}_5)_4\text{B}^-$, **4**, (Te–B: 5.622(3), Te–F: 3.363(2) Å). Accordingly, it is clear that the cation in **1** is “free” in the solid state. When the Pauling’s bond index equation is applied for those distances, the result indicated almost no cation–anion interaction.¹¹

It is noteworthy that the tellurium environment of **1** is a square-pyramidal (SP) geometry which has one apical phenyl group and four propeller-like basal phenyl groups. The structure is analogous to that of Ph_5Sb .¹² Bond angles around the Te indicated that the structure has high SP character (91%) which was calculated by

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(9) Characterization of **1**: mp 139–140 °C; ¹H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.8$ Hz, 10H, *ortho*), 7.47 (t, $J = 7.8$ Hz, 10H, *meta*), 7.61 (t, $J = 7.8$ Hz, 5H, *para*); ¹³C NMR (100 MHz, CDCl_3) δ 124 (B-*ipso*), 133.0 (Te-*para*), 132.3 (Te-*ortho*), 130.7 (Te-*meta*), 136.2 (d, ¹J_{CF} = 244.5 Hz, B-*meta*), 138.1 (d, ¹J_{CF} = 246.4 Hz, B-*para*), 140.4 (Te-*ipso*), 148.2 (d, ¹J_{CF} = 240.8 Hz, B-*ortho*); ¹²⁵Te NMR (126 MHz, CDCl_3) δ 659.0; ¹⁹F NMR (376 MHz, CDCl_3) δ -133.1 (*ortho*), -163.7 (*para*), -167.3 (*meta*); ¹¹B NMR (128 MHz, CDCl_3) δ -16.7; UV–visible spectra (CH_2Cl_2) λ_{max} (ε) 235 (36, 000), 275 (7, 500), 315 (2, 100).

(10) Crystal data for **1**: $\text{C}_{54}\text{H}_{25}\text{BF}_{20}\text{Te}$, monoclinic, $P2_1/n$, $a = 16.9860(4)$ Å, $b = 16.0790(6)$ Å, $c = 17.2840(6)$ Å, $\beta = 91.565(2)^\circ$, $V = 4718.8(2)$ Å³, $Z = 4$, D_{calc} = 1.678 g cm⁻³. Data were collected at 190 K on a MAC Science DIP2030 imaging plate with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved using the teXsan (Rigaku) system, and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. The final $R = 0.064$ ($R_w = 0.105$) and GOF = 1.14 for 6442 observed reflections (685 parameters) with $I > 3.00\sigma(I)$.

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(6) For hypervalent organochalcogen reviews, see: Lunazzi, L.; Martin, J. C. In *Organic Sulfur Chemistry*; Bernardi, F., Ciszmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; pp 408–483; Bergman, J.; Engman, L.; Sidén, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, pp 517–558; Dettly, M. R.; O’Regan, M. B. In *Tellurium-Containing Heterocycles*; Taylor, E. C., Ed.; John Wiley & Sons: New York, 1994; pp 425–490; Furukawa, N.; Sato, S. In *Rodd’s Chemistry of Carbon Compounds*; Sainsbury, M., Ed.; Elsevier: Amsterdam, 1996; Vol. IIIA, pp 469–520.

(7) The term of hyper- or peronium ions concerning positively charged hepta- or pentacoordinate chalcogen species have been suggested by Musher. However, those species have never been isolated or characterized. [Musher, J. I. *Ann. N.Y. Acad. Sci.* **1972**, *192*, 52–59; Hellwinkel, D. *Ann. N.Y. Acad. Sci.* **1972**, *192*, 158–166.] According to IUPAC rules, R_5Te^+ is named λ^6 -tellanylum, and we call this hypervalent telluronium in this report.

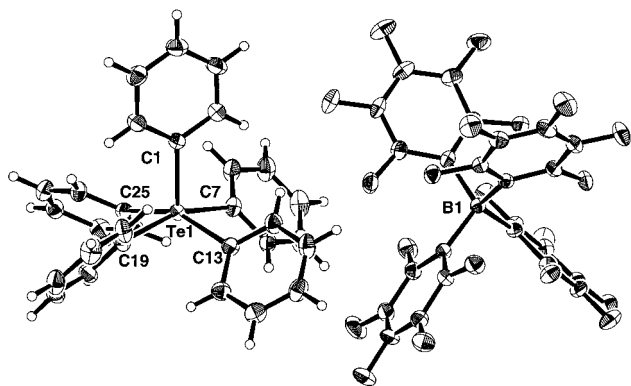


Figure 1. Molecular structure of **1** (thermal ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg): Te1–C1, 2.101(5); Te1–C7, 2.195(5); Te1–C13, 2.208(5); Te1–C19, 2.196(5); Te1–C25, 2.205(5); C1–Te1–C7, 99.2(2); C1–Te1–C13, 103.5(2); C1–Te1–C19, 99.1(2); C1–Te1–C25, 101.8(2); C7–Te1–C13, 88.4(2); C7–Te1–C19, 161.7(2); C7–Te1–C25, 87.8(2); C13–Te1–C19, 86.8(2); C13–Te1–C25, 154.6(2); C19–Te1–C25, 88.9(2).

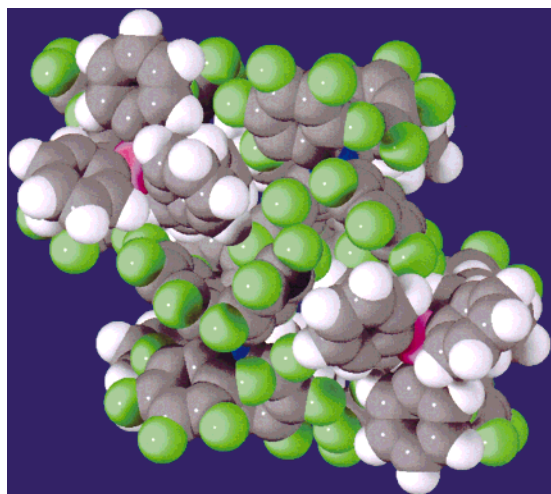
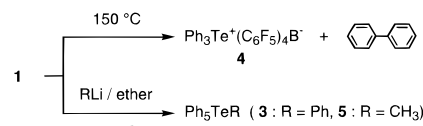


Figure 2. Space-filling representation of the unit cell of **1** down the crystallographic *c* axis. Color code: Te, red; C, gray; H, white; B, blue; F, green.

the dihedral angle method.¹³ The tellurium-apical carbon bond length (2.101(5) Å) is significantly shorter than the four basal carbon bond lengths (2.195(5)–2.208(5) Å). All of the C–Te bond lengths in **1** are shorter than those of neutral **3** (2.228 Å)⁵ and this may be explained by cationic attractive interaction between the tellurium and five carbon ligands.

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Scheme 2



In solution, the ¹²⁵Te NMR spectrum of **1** exhibits upfield shift (659.0 ppm) in comparison with that of Ph₃Te⁺ (**4**, 753.0 ppm). This is consistent with the trend in chemical shift for these series Ph₂Te (688 ppm), Ph₄Te (509 ppm),¹⁴ and Ph₆Te (**3**, 493 ppm), which shows that the shift to higher fields is induced by the increase of oxidation state and the decrease in the number of lone-pair electrons on the tellurium. In the ¹H and ¹³C NMR spectra of **1**, only one set of phenyl groups could be observed even at –70 °C in CDCl₃. This is due to rapid Berry pseudorotation with a small energy difference between SP and TBP structures, as is usually the case for pentaorgano-element compounds.¹⁵ Therefore this suggests the possibility that Ph₅Te⁺ would have an SP structure in the solid-state induced by lattice control.

Hypervalent compounds, such as Ph₅Sb and Ph₄Te, are known to decompose thermally by ligand-coupling reactions to give the corresponding reductively eliminated products, i.e., Ph₃Sb and Ph₂Te, respectively.¹⁶ Although Ph₆Te, **3**, and Ph₃Te⁺, **4**, are quite stable up to the melting points, thermolysis of **1** proceeds at 150 °C in the solid state to give **4** quantitatively along with biphenyl (~80%) and a small amount of benzene. The reaction of **1** with phenyllithium or methyllithium proceeded at the cationic tellurium center and afforded the corresponding neutral hexaorganotellurium, **3**, or Ph₅TeMe, **5**, quantitatively (Scheme 2). Thus, **1** can be regarded as a useful source of hexavalent organotellurium compounds.

In view of the long-known existence and widespread use of onium compounds, the easy synthesis and great stabilities of the hitherto unknown hypervalent onium species will provide new chemistry.

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Supporting Information Available: Characterization and X-ray crystallographic details with positional parameters, bond lengths and angles, and ORTEP drawings for **1**, **2**, **4**, and **5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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