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Convenient One-Pot Synthesis and Structures of Pentaphenyltellurium Monohalides

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Summary: A novel family of organochalcogens, Ph_5TeX ($X = Cl$, Br), was readily obtained by the halogenation of Ph_5TeLi, which was prepared by reaction of 5 equiv of PhLi with 1 equiv of $TeCl_4$ or $TeBr_4$; Ph_5TeF was obtained by treating the bromide with KF. The Te atom is in the highest oxidation state, Te(VI), and is covalently bonded to the halogen atom, in contrast to the ionic bonding in $R_3Te^{IV}X$.

A large number of triorganochalcogen monohalides (chalcogenonium salts $R_3Ch^{IV}X$: Ch = S, Se, Te; X = halogens) and their pnictogen analogues (R_4Pn^VX: Pn = P, As, Sb, Bi) have found use in organic transformation[1] and in the synthesis of neutral hypervalent tetraorganochalcogens (R_4Ch^{IV}) and pentaorganopnictogens (R_5Pn^V), respectively.[2] However, little is known about compounds having the general formula $R_5Ch^{VI}X$ because a practical method for their synthesis was not available. There is a paucity of a knowledge about organochalcogen compounds in the highest oxidation state VI.[3,4] Pentaorganochalcogen monohalides, i.e., $R_5Ch^{VI}X$, are of interest since it was not known if their Ch−X bonds are covalent or ionicc, as had been discussed in the case of the Pn−X bond of R_4PnX compounds.[5] In this communication, we present a convenient and efficient route to the novel family of organochalcogens pentaphenyltellurium monohalides, Ph_5TeX (**1**: X = F (**a**), Cl (**b**), Br (**c**)), and report their X-ray structural characterization.

Ph_5TeCl (**1b**) was readily prepared by the one-pot reaction[6] of SO_2Cl_2 with Ph_5TeLi (**2**),[7] which was prepared by reaction of 5 molar equiv of PhLi with 1 equiv of $TeCl_4$ in THF at −105 °C (Scheme 1). Since

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[1] For reviews on triorganochalcogens and tetraorganopnictogens see: (a) Block, E. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Vol. II, p 761. (b) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: New York, 1986. (c) Irgolic, K. J. In *The Organic Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974; p 199. (d) Beck, P. In *Organic Phosphorus Compounds*; Kosolapoff, G. W., Maier, L., Eds.; Wiley: New York, 1972; Vol. II, p 189. (e) Akiba, K.-y.; Yamamoto, Y. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; p 761. (f) Cross, W. I.; Godfrey, S. M.; McAuliffe, C. A.; Mackie, A. G.; Pritchard, R. G. In *Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie Academic: London, 1998; p 207.

[2] For reviews see: (a) Hellwinkel, D. *Top. Curr. Chem.* **1983**, *109*, 1. (b) Bergman, J.; Engman, L.; Sidén, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. I, p 517. (c) Detty, M. R.; O'Regan, M. B. In *Tellurium-Containing Heterocycles*; Taylor, E. C., Ed.; Wiley: New York, 1994; p 425. (d) *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999.

[3] Some organochalcogen compounds having valence state VI have been synthesized by the oxidative halogenation of the corresponding chalcogen(IV) compounds: (a) Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529. (b) Alam, K.; Janzen, A. F. *J. Fluorine Chem.* **1985**, *27*, 467. (c) Sato, S.; Yamashita, T.; Horn, E.; Furukawa, N. *Organometallics* **1996**, *15*, 3526. (d) Sato, S.; Yamashita, T.; Horn, E.; Takahashi, O.; Furukawa, N. *Tetrahedron* **1997**, *53*, 12183. (e) Sato, S.; Arakawa, H.; Horn, E.; Furukawa, N. *Chem. Lett.* **1998**, 213.

[4] We have recently reported the synthesis of novel hypervalent tellurium(VI) species, the hexaaryltellurium species Ar_6Te ($Ar = C_6H_4$-4-CF_3, C_6H_5), as the first neutral hexaarylated element[4a,b] and the pentaphenyltellurium cation, $Ph_5Te^+(C_6F_5)_4B^-$, as the nonclassical onium compound:[4c] (a) Minoura, M.; Sagami, T.; Akiba, K.-y.; Modrakowski, C.; Sudau, A.; Seppelt, K.; Wallenhauer, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2660; *Angew. Chem.* **1996**, *108*, 2827. (b) Minoura, M.; Sagami, T.; Miyasato, M.; Akiba, K.-y. *Tetrahedron* **1997**, *53*, 12195. (c) Minoura, M.; Mukuda, T.; Sagami, T.; Akiba, K.-y. *J. Am. Chem. Soc.* **1999**, *121*, 10852.

[5] The compounds having general formula R_4PnX have been characterized as two structural forms, i.e., with either a covalent or an ionic character in the Pn−X bond. This depends on Pn and X. For examples see: (a) Goel, R. G. *Can. J. Chem.* **1969**, *47*, 4607. (b) Richardson, J. F.; Ball, J. M.; Boorman, P. M. *Acta Crystallogr.* **1986**, *C42*, 1271. (c) Sowerby, D. B. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; p 26. (d) Baker, L.-J.; Rickard, C. E. F.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 2895.

[6] Preparation of **1c**: a solution of 4 equiv of PhLi (1.8 M solution in cyclohexane/ether, 22.2 mL, 40.0 mmol) in THF (20 mL) was added to a solution of $TeBr_4$ (4.47 g, 10.0 mmol) in THF (30 mL) at −78 °C. After the mixture was stirred for 2.0 h at −78 °C, an additional 1 equiv of PhLi (5.56 mL, 10.0 mmol) was added to the mixture at −105 °C. To the reaction mixture was added Br_2 (2.4 g, 15.0 mmol) after the end of addition of the fifth PhLi. The color of the solution changed from yellow to orange. The mixture was well stirred for 10 min at −105 °C and for 2 h at room temperature. The solvent was removed in vacuo, and the residue was washed with acetonitrile and recrystallized from CH_2Cl_2/hexane to afford **1c** (3.81 g, 6.4 mmol, 64% based on tellurium). Preparative HPLC separation (LC-908, Japan Analytical Industry, with 1,2-dichloroethane as solvent) of acetonitrile-soluble byproducts gave Ph_3TeBr (1.23 g, 2.8 mmol, 28%) and small amounts of Ph_6Te,[4a] Ph_2Te, and Ph_2TeBr_2. Chloride **1b** (2.48 g, 4.5 mmol, 45%) was prepared in a manner similar to that for **1c** from $TeCl_4$ (2.69 g, 10.0 mmol) and SO_2Cl_2 (1.35 g, 10.0 mmol). Although we previously synthesized **1b** by the reaction of Ph_6Te with Cl_2(gas),[4c] the quantity that could be prepared was not satisfactory because of the large amount of the difficult to prepare Ph_6Te[4a] which was needed. **1b**: pale yellow plates; mp 216 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, 8H, $J = 7.3$ Hz), 7.34 (t, 4H, $J = 7.3$ Hz), 7.56 (d, 8H, $J = 7.8$ Hz), 7.39 (t, 2H, $J = 7.3$ Hz), 7.49(t, 1H, $J = 7.3$ Hz), 7.79 (d, 2H, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.7(d), 129.2 (d), 130.7 (d), 131.9 (d), 133.4 (d), 134.2 (d), 134.8 (s), 154.4 (s). ^{125}Te NMR (126 MHz, $CDCl_3$, Me_2Te): δ 533.9. Anal. Calcd for $C_{30}H_{25}TeCl$: C, 65.68; H, 4.59. Found: C, 65.98; H, 4.32. **1c**: yellow plates; mp 217 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, 8H, $J = 7.3$ Hz), 7.35 (t, 4H, $J = 7.3$ Hz), 7.41 (t, 2H, $J = 7.3$ Hz), 7.50 (t, 1H, $J = 7.3$ Hz), 7.77 (d, 8H, $J = 7.3$ Hz), 7.80 (d, 2H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.6 (d), 129.1 (d), 129.2 (d), 130.7 (d), 133.3 (d), 133.5 (s), 134.0 (d), 153.7 (s). ^{125}Te NMR (126 MHz, $CDCl_3$, Me_2Te): δ 541.0. Anal. Calcd for $C_{30}H_{25}TeBr$: C, 60.76; H, 4.25. Found: C, 60.87; H, 4.38.

[7] Ph_5TeLi has been described. (a) Wittig, G.; Fritz, H. *Liebigs Ann. Chem.* **1952**, *577*, 39. (b) Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus, Sulfur, Silicon Relat Elem.* **1992**, *67*, 83 (Proc. 6th Int. Conf. on the Chemistry of Selenium and Tellurium, Osaka, Japan).

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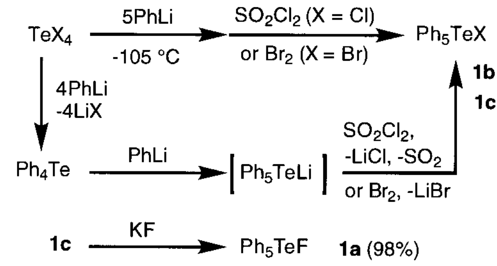
Scheme 1



the in situ formation of **2** in the one-pot reaction involves the intermediate generation of Ph_4Te (**3**), the temperature was maintained at −78 °C for 2 h after the addition of 4 molar equiv of PhLi to $TeCl_4$ to allow **3** to form. Subsequently, the fifth equivalent of PhLi to form **2** was added at −105 °C. After the addition of 1 molar equivalent of SO_2Cl_2, stirring was continued for 10 min at −105 °C and 1 h at ambient temperature. The reaction mixture was concentrated in vacuo, and the residue was washed with acetonitrile and recrystallized from CH_2Cl_2/hexane to afford **1b** as pale yellow crystals in 45% yield. Bromide **1c** was similarly prepared by reaction of 5 equiv of PhLi with 1 equiv of $TeBr_4$, followed by addition of Br_2 (1 equiv). It was isolated as pale yellow crystals (64%). Ph_5TeF (**1a**) was obtained quantitatively by treating **1c** with KF in THF.[8] Compounds **1a**−**c** are thermally very stable and are not sensitive to light, oxygen, or moisture.[9]

Molecular structures of **1a**−**c** were determined by X-ray crystallographic analysis at −143 °C.[10] In the solid states of **1a**−**c**, two crystallographically unique molecules were present. There are no short intermolecular contacts involving the tellurium and halogen; therefore, the R_5TeX compounds are monomeric. In contrast, many R_3TeX compounds either exist as dimers or involve secondary bonding in the solid state.[11] The geometry around the tellurium in **1a**−**c** is slightly distorted octahedral. The distortion may be due to the fact that the halogen atoms in **1a**−**c** are smaller than the phenyl groups. Ph_6Te, in contrast, is perfectly octahedral.[4a] The ORTEP drawing clearly shows that the Te−F bond (2.019 Å on avarage of two independent molecules) in **1a** is a covalent bond where the sum of the covalent radii is 2.09 Å (Figure 1). Tellurium−halogen bonds in **1b** (average 2.607 Å) and **1c** (average 2.761 Å) are slightly longer than the sum of covalent radii of Te and the respective X. However, the Te−X distances are much shorter than the sum of the van der Waals radii. Thus, they also involve covalent bonding. In contrast, the Te−Cl bond in Ph_3TeCl has been shown to be ionic.[11a]

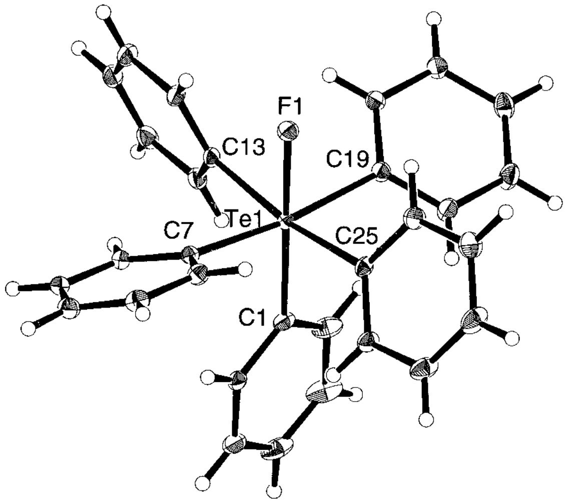


Figure 1. ORTEP drawing of **1a** with thermal ellipsoids representing 50% probability. Selected bond lengths (Å) and angles (deg) (one of the two independent molecules in the unit cell is shown in brackets): Te1−F1, 2.011(2) [2.027(1)]; Te1−C1, 2.171(2) [2.155(2)]; Te1−C7, 2.185(2) [2.177(2)]; Te1−C13, 2.177(2) [2.177(2)]; Te1−C19, 2.174(2) [2.183(2)]; Te1−C25, 2.167(2) [2.176(2)]; F1−Te1−C1, 177.94(7) [179.05(7)]; F1−Te1−C7, 84.37(7) [86.34(7)]; F1−Te1−C13, 85.73(7) [83.96(7)]; F1−Te1−C19, 85.66(7) [85.40(7)]; F1−Te1−C25, 85.69(7) [84.14(6)].

It is interesting to note that the Te−C1 (trans to X) bond length (**1a**, 2.163 Å; **1b**, 2.175 Å; **1c**, 2.183 Å; average of two independent molecules) is definitely shorter than Te−C7,13,19,25 (cis to X) bonds (**1a**, 2.177 Å; **1b**, 2.196 Å; **1c**, 2.208 Å; average of two independent molecules). The differences in the cis and trans bond lengths can be ascribed to the change of trans influence, which may be attributed to the electron-withdrawing character of the halogen, forming an unsymmetrical hypervalent bond in C1−Te−X. As compared with the

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(8) Synthesis of **1a**: to a suspension of KF (1.30 mmol, 75.5 mg) in THF (10 mL) was added Ph_5TeBr (0.50 mmol, 289 mg) in THF (30 mL) at room temperature. After 4 h of stirring, the reaction mixture was filtered and the filtrate was concentrated. The resulting product was purified by the preparative HPLC (the same conditions as in ref 6) to give **1a** (263 mg, 0.49 mmol, 99%). **1a**: colorless needles; mp 224 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, 8H, $J = 7.3$ Hz), 7.29 (t, 4H, $J = 7.3$ Hz), 7.39 (d, 8H, $J = 6.8$ Hz), 7.41 (t, 2H, $J = 7.3$ Hz), 7.48 (t, 1H, $J = 7.3$ Hz), 7.66 (d, 2H, $J = 6.8$ Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −41.96 ($^1J_{^{125}Te-F} = 1379$ Hz, $^1J_{^{123}Te-F} = 1143$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.8 (d), 128.7 (d), 128.9 (d), 130.4 (d), 133.1 (d), 134.4 (d), 136.1 (d, $^2J_{C-F} = 57$ Hz), 151.9 (d, $^1J_{C-Te} = 75.4$ Hz, $^2J_{C-F} = 14.7$ Hz). ^{125}Te NMR (126 MHz, $CDCl_3$, Me_2Te): δ 549.5 (d, $J = 1379$ Hz). Anal. Calcd for $C_{30}H_{25}TeF{\cdot}0.5CHCl_3$: C, 61.90; H, 4.34. Found: C, 61.89; H 4.38. (The analytical sample was obtained by recrystallization from chroloform.)

(9) Corresponding divalent tellurenyl harides ($PhTe^{II}X$) are known to be unstable compounds: Sonoda, N.; Ogawa, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Rappoport, Z., Patai, S., Eds.; Wiley: New York, 1986; Vol. 1, p 619. Petragnani, N. In *Tellurium in Organic Chemistry*; Academic: New York, 1994.

(10) Single crystals suitable for the X-ray diffraction study were obtained from a solution (**1a**, chloroform; **1b** and **1c**, dichloromethane) of the compound at room temperature. Crystal data for **1a**: $C_{30}H_{25}FTe{\cdot}0.5CHCl_3$, $M = 591.81$, monoclinic, $P2_1/a$, $a = 20.0890(4)$ Å, $b = 13.5060(2)$ Å, $c = 20.5750(4)$ Å, $b = 114.718(1)°$, $V = 5071.0(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.550$ g cm^{-3}. $R = 0.043$ ($R_w = 0.072$) and GOF = 1.303 for 10 448 observed reflections (614 parameters, $I > 3.00\sigma(I)$). Crystal data for **1b**: $C_{30}H_{25}ClTe$, $M = 548.58$, monoclinic, $P2_1/c$, $a = 17.1760(3)$ Å, $b = 13.7300(3)$ Å, $c = 20.6260(4)$ Å, $\beta = 99.737(1)°$, $V = 4794.1(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.520$ g cm^{-3}. $R = 0.045$ ($R_w = 0.090$) and GOF = 1.663 for 9515 observed reflections (578 prameters, $I > 3.00\sigma(I)$). Crystal data for **1c**: $C_{30}H_{25}BrTe$, $M = 593.03$, monoclinic, $P2_1/c$, $a = 17.2750(2)$ Å, $b = 13.8990(3)$ Å, $c = 20.9340(4)$ Å, $\beta = 99.939(1)°$, $V = 4950.9(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.591$ g cm^{-3}. $R = 0.0719$ ($R_w = 0.1241$) and GOF = 1.497 for 9459 observed reflections (578 parameters, $I > 3.00\sigma(I)$). All data were collected at 130 K on a MAC Science DIP2030 imaging plate with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ 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. Full crystallographic information are given in the Supporting Information.

(11) (a) Ziolo, R. F.; Extine, M. *Inorg. Chem.* **1980**, *19*, 2964. (b) McWhinnie, W. R.; Mallaki, J. *Polyhedron* **1982**, *1*, 13. (c) Collins, M. J.; Ripmeester, J. A.; Sawyer, J. F. *J. Am. Chem. Soc.* **1988**, *110*, 8583. (d) Silvestru, A.; Haiduc, I.; Toscano, R. A.; Breunig, H. J. *Polyhedron* **1995**, *14*, 2047. (e) Shimizu, T.; Urakubo, T.; Jin, P.; Kondo, M.; Kitagawa, S.; Kamigata, N. *J. Organomet. Chem.* **1997**, *539*, 171.

(12) The parameters of the covalent [and van der Waals] radii (in Å: Te, 1.37 [2.20]; F, 0.72 [1.35]; Cl, 0.99 [1.80]; Br, 1.14 [1.95]) were taken from: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

averaged Te−C bond lengths in Ph_6Te (2.228 Å), the shrinkage of the Te−C bond lengths in **1a**−**c** was a function of X, becoming longer as the halogen became larger and decreased in electron-withdrawing power.

In solution, the ^{125}Te NMR resonances of **1a** (δ 550), **1b** (δ 534), and **1c** (δ 541) are shifted to lower fields relative to Ph_6Te (δ 493). In the case of **1a**, the resonance appears as a doublet with a large coupling constant of ^{125}Te−^{19}F ($^1J_{Te-F} = 1379$ Hz). In contrast, the ^{125}Te NMR signal of Ph_3TeF has been observed without Te−F coupling (ionic).[11b] The ^{1}H and ^{13}C NMR spectra of **1a**−**c** show two sets of phenyl groups in a 1:4 ratio which are assignable as the trans and cis phenyl with regard to X, respectively, which indicate that the Te−X bond in **1** is covalent in solution.

Further investigation of the physical and chemical properties of **1** as well as the application of the one-pot synthesis to the other hypervalent chalcogens is currently in progress.

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Supporting Information Available: X-ray crystallographic details, including tables of positional parameters and bond lengths and angles and ORTEP drawings for **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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