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Synthesis and Characterization of Hexaaryltellurium ($TeAr_6$); The First Neutral Hexaarylated Element Compound

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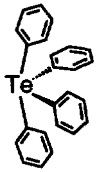
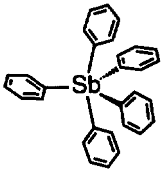
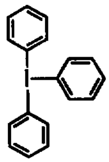
Abstract: $Te(C_6H_4\text{-}4\text{-}CF_3)_6$ **1a** was obtained by the unique one-pot reaction of $LiC_6H_4\text{-}4\text{-}CF_3$ with $TeCl_4$. The Te atom resides in the highest oxidation state (Te^{VI}) having six C—Te bonds in **1a**. Compound **1a** is extremely thermally stable and not light sensitive unlike tetraorganotellurium compounds. The X-ray crystallographic analysis of **1a** revealed a rare example of approximately T_h molecular symmetry. © 1997 Elsevier Science Ltd.

Organotellurium compounds are playing an ever-increasing role as important synthetic reagents[1] and notably attract investigation of their structure and reactivity due to its possibility for variable valency.[2] Although the early stage of organotellurium chemistry had been developed as an extension of sulfur and selenium analogues, for example chemistry of lowvalent chalcogen compounds was elaborated in the historical order of thione,[3] selone[4] and tellone,[5] chemistry of hypervalent organochalcogens[6] opened from tellurium when Wittig prepared $TePh_4$[7] in 1952. Tetraphenyltellurium having decet of electrons on tellurium valence shell could be isolated as relatively stable solid which decomposed thermally to biphenyl and diphenyltellurium by ligand coupling reaction,[8] and was found to have a distorted pseudo-trigonal-bipyramidal geometry with the axial phenyl groups bending toward the equatorial groups.[9] Intensive efforts have been recently directed toward the hypervalent organochalcogen compounds in which chalcogen atom is bonded directly to carbon substituents.[10] Wittig et al. also prepared aryl substituted hypervalent compounds of Group 15 and 17 in their high oxidation states, species like $SbPh_5$ and IPh_3.[11] For the Group 16, only few attempts have so far been made for synthesis and observation of such species bearing the highest valency state (Te^{VI}).[12]

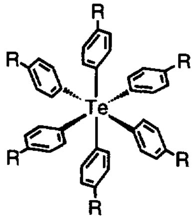






Meanwhile, there has been substantial interest in homoleptic molecules of transition metals and typical elements for some time,[13] because of their intriguing bonding nature, especially for compounds only with carbon-element bond. However, only two neutral peralkylated hexavalent transition metals are known to exist, i.e., $W(CH_3)_6$[14] and $Re(CH_3)_6$,[15] and their main group analogues had never been synthesized until recently. The successful synthesis and isolation of $Te(CH_3)_6$, i.e., the first neutral main group peralkylated compound containing six carbon-element bond was reported by Morrison and Ahmed.[16] The octahedral structure of $Te(CH_3)_6$ was determined by gas-phase electron diffraction.[17, 18]

Very recently, we reported the synthesis of a novel hypervalent tellurium, hexaaryltellurium **1**, as the first example of neutral compound comprising hexaarylated element in a preliminary form.[19] In this paper we delineate a detailed account of the one-pot synthesis of **1a**, by the reaction of the ArLi and $TeCl_4$. And X-ray crystallographic analysis and stability of the hypervalent tellurium are also described.



1a; R = CF_3
1b; R = H

RESULTS AND DISCUSSIONS

Synthesis of Hexaaryltellurium. The synthesis of $Te(C_6H_4\text{-}4\text{-}CF_3)_6$ **1a** was achieved by a one-pot reaction of $LiC_6H_4\text{-}4\text{-}CF_3$ (ArLi) and tellurium tetrachloride ($TeCl_4$) in the molar ratio 4 : 1. An ether suspension of $TeCl_4$ was added to an ether solution of ArLi, prepared by lithiation of ArBr at -78 °C. After stirring for 1.5 h at -78 °C and 3 h at room temperature, the solvent was removed and the residue was washed with hexane, water, and ethanol, and dried to afford **1a** (17%, based on tellurium). The soluble by-products were separated by preparative HPLC to give **2** and **3** (Table 1). When the reaction was quenched by 3% HCl aq. at low temperature after addition of ArLi or use of a stoichiometric quantity (6 : 1) of ArLi with $TeCl_4$, the yield of **1a** seemed to get lowered.

$$TeCl_4 + ArLi \xrightarrow[\text{temperature}]{Et_2O} TeAr_6\,\mathbf{1a} + Ar_3TeCl\,\mathbf{2} + TeAr_2\,\mathbf{3}$$

Scheme 1.

Table 1. Yields of **1a** by the Reaction of ArLi with Tellurium Tetrachloride.

				Product yields / %[a]		
entry	ArLi (eq)	temperature °C	quencher	**1 a**	**2**	**3**
1[b]	4	-78 — 25	—	16.7	35.7	34.1
2	4	-78	3% HCl aq	9.7	42.5	36.7
3	6	-78 — 25	—	6.9	13.2	55.2

a; Yields are based on tellurium. b; Biaryl **7** was also obtained as a by-product in 8.3% yield based on Ar group.

The reaction certainly involves valence expansion at tellurium and is obviously multi-steps. Probable course of the formation of **1a** is intriguing (Scheme 2). In the first stage of the reaction, $TeAr_4$ **4** and Cl_2TeAr_2 **5** are formed in situ, then a disproportionation reaction occurs between **4** and **5** to give Cl_2TeAr_4 **6** and $TeAr_2$ **3**. $TeAr_6$ **1a** is most likely formed by the succeeding reaction of **6** with ArLi during warming of the reaction mixture to room temperature. The other product Ar_3TeCl **2** is produced by the reaction of 3 molar ArLi with $TeCl_4$ just before formation of **4** and/or seems to be formed by the decomposition of **4**. Although the $TePh_6$ was prepared from F_2TePh_4 with PhLi by us,[19] the proposed mechanism is still not clear at present because we could not obtain Cl_2TeAr_4 **6** in the present one-pot process.

$$
\begin{array}{lcll}
\mathrm{TeCl_4} + \mathrm{3ArLi} & \longrightarrow & \mathrm{Ar_3TeCl}\ \mathbf{2} & + \mathrm{3LiCl} \\
\mathbf{2} + \mathrm{ArLi} & \longrightarrow & \mathrm{TeAr_4}\ \mathbf{4} & + \mathrm{LiCl} \\
\mathrm{TeCl_4} + \mathrm{2ArLi} & \longrightarrow & \mathrm{Cl_2TeAr_2}\ \mathbf{5} & + \mathrm{2LiCl} \\
\mathbf{4} + \mathbf{5} & \xrightarrow{\text{disproportionation}} & \mathrm{Cl_2TeAr_4}\ \mathbf{6} & + \mathrm{TeAr_2}\mathbf{3} \\
\mathbf{6} + \mathrm{2ArLi} & \longrightarrow & \mathbf{1a} & + \mathrm{2LiCl} \\
\hline
\mathrm{2TeCl_4} + \mathrm{8ArLi} & \longrightarrow & \mathrm{TeAr_6}\ \mathbf{1a} + \mathrm{TeAr_2}\mathbf{3} & + \mathrm{8LiCl}
\end{array}
$$

Scheme 2.

Spectroscopic and structural properties of 1a. The ^1H and ^{19}F NMR spectra of **1a** show two doublets and one singlet, respectively, consistent with the symmetric structure. In the ^{13}C NMR of **1a**, the ipso carbons resonate at 152.1 ppm and the coupling constant is $^1J_{C\text{-}Te} = 42$ Hz. The chemical shift is significantly downfield and the coupling constant is very much smaller compared with $TeAr_2$ **3** (119.9 ppm, 288 Hz) and the reported values for other organotellurium compounds.[20] The ^{125}Te NMR spectrum of **1a** (467 ppm) exhibits an upfield resonance in comparison to $Te(C_6H_5)_4$ (509 ppm) and diaryltelluride **3** (727 ppm).

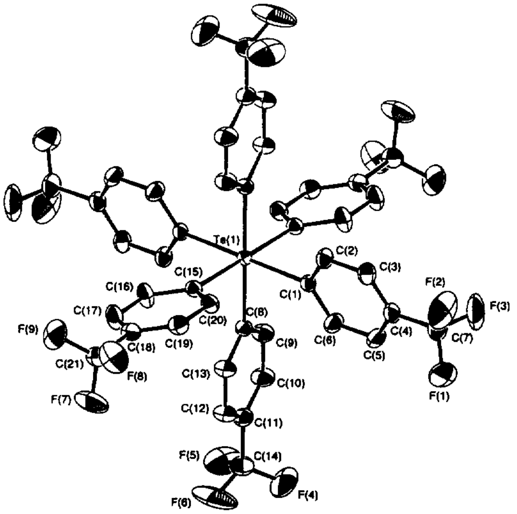


Fig. 1. ORTEP drawing of **1a** with thermal ellipsoids representing 30% probability

The molecular structure of **1a** was determined by X-ray crystallographic analysis (Figure 1 and Tables 2 and 3). The tellurium environment is very regular octahedral and the deviation of ideal bond angles of 90° and 180° are less than or equal to 1.4°. The six Te–C bond lengths (Å) of the molecule are almost identical [2.226(4)-2.240(2)], and a little longer than the average Te^{II}—$C_{aromatic}$ bond lengths (2.116 Å),[21] but comparable to the average (2.21 Å) of axial (2.29 Å) and equatorial (2.13 Å) bond lengths of tetraphenyltellurium.[9] The planes of adjacent phenyl groups are nearly perpendicular, *trans*-phenyl groups are coplanar. The molecule **1a** has approximately T_h symmetry which is not common in chemistry.[22] This peculiar symmetry seems to be favorable in terms of interligand repulsion.

Table 2. Selected Bond Lengths (Å) with e.s.d. in Parentheses for **1a**.

Te1—C1	2.229 (4)	C4—C5	1.369 (7)
Te1—C8	2.240 (2)	C4—C7	1.494 (7)
Te1—C15	2.226 (4)	C5—C6	1.382 (8)
C1—C2	1.382 (6)	F1—C7	1.304 (4)
C1—C6	1.386 (7)	F2—C7	1.304 (8)
C2—C3	1.380 (7)	F3—C7	1.339 (7)
C3—C4	1.374 (7)		

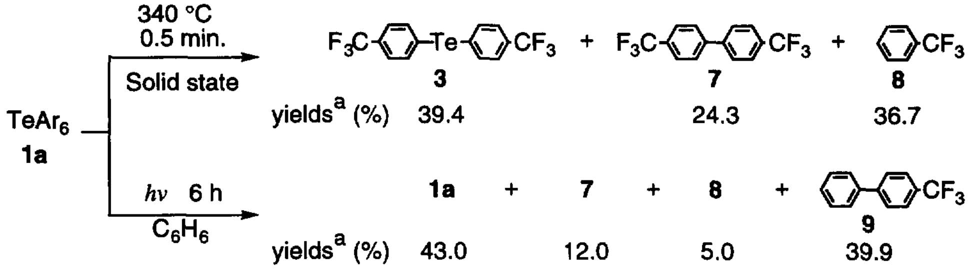
Table 3. Selected Bond Angles (degrees) with e.s.d. in Parentheses for **1a**.

C1—Te1—C15	91.4 (2)	C1—C6—C5	120.5 (5)
C1—Te1—C8	88.9 (1)	C3—C4—C7	120.9 (4)
C8—Te1—C15	88.8 (1)	C5—C4—C7	119.5 (5)
C2—C1—Te1	121.8 (3)	C4—C7—F1	112.8 (4)
C6—C1—Te1	120.0 (3)	C4—C7—F2	112.8 (4)
C2—C1—C6	118.1 (4)	C4—C7—F3	112.9 (5)
C1—C2—C3	121.2 (4)	F1—C7—F2	109.5 (5)
C2—C3—C4	119.9 (4)	F1—C7—F3	103.3 (4)
C3—C4—C5	119.6 (5)	F2—C7—F3	104.8 (4)
C4—C5—C6	120.6 (6)		

Stability of 1a. $TeAr_6$ **1a** is thermally extremely stable compound without any perceptible decomposition in the refluxing solution (THF, benzene, *n*-butyl ether) for 6 h or directly heating the solid under the melting point. In contrast to the thermal behavior of $TePh_4$ which undergoes ligand coupling reaction easily to give $TePh_2$ and biphenyl, the thermolysis of **1a** required at 350 °C for 30 sec in a sealed tube to obtain decomposition products **3**, **7**,[23] and **8** (Scheme 3).

Many light sensitive compounds are known in organotellurium, however, photolysis (100 W, Hg arc) of **1a** in THF at 20 °C for 6 h could not effect decomposition and **1a** is quite stable. In a benzene solution of **1a**, the photolysis proceeded, but very slowly, to give decomposition products along with unchanged **1a**. Moreover, **1a** was inert toward halogenating agents (XeF_2, SO_2Cl_2, Br_2) at room temperature for several hours although most organotellurium compounds including $TeMe_6$ react with these halogenating agents easily. Attempted lithiation of **1a** by equimolar RLi (R = Me, *n*-Bu, *t*-Bu) was failed showing the stability of **1a** even toward strong nucleophiles. The high stability described above may reflect the equivalence of the six hypervalent bonds around the tellurium.

$TeAr_6$ **1a** represents an interesting and unique opportunity to the study of hypervalency of tellurium. While this work is still in its infancy, progress in this rapidly growing field will contribute to understanding some of the most interesting aspects of modern hypervalent chemistry.



a; Yields are calculated based on the aryl group.

Scheme 3.

EXPERIMENTAL

Melting points were recorded using a capillary sealed under argon atmosphere on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed on Parkin Elmer Model 2400. IR spectra (KBr disk) were recorded on a Jasco FT/IR-7300 spectrometer. Raman spectra were recorded on a JEOL JRS-400D spectrophotometer. UV-vis spectra were taken with a Shimadzu UV-2200 UV-vis spectrometer. ^1H (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{125}Te (126 MHz) NMR spectra were measured with a JEOL EX-400 spectrometer. Chemical shifts of ^1H and ^{13}C NMR were reported in ppm downfield from tetramethylsilane or a residual solvent as an internal standard, and $CFCl_3$ and Me_2Te for an external standard of ^{19}F and ^{125}Te NMR, respectively. Mass spectra were obtained with a JEOL JMS-SX102A spectrometer at an ionization potential of 70 eV. Preparative gel permeation liquid chromatography (HPLC) was performed by LC-908 equipped with JAIGEL-1H and -2H columns (Japan Analytical Industry) with 1,2-dichloroethane as solvent.

Synthesis of Hexaaryltellurium 1a: A solution of LiC_6H_4-4-CF_3 was prepared from BrC_6H_4-4-CF_3 (9.90 g 44.0 mmol) in ether (60 mL) and *n*-BuLi (1.60 M solution in hexane, 27.5 mL, 44.0 mmol) at -78 °C. The mixture was warmed to room temperature and stirred for 1 h. At -78 °C a suspension of $TeCl_4$ (2.69 g 10.0 mmol) in ether (60 mL) cooled to -78 °C was added through a Teflon tube within 30 min. After stirring for 1.5 h at -78 °C and further stirring for additional 3 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with hexane, water, and ethanol and dried to afford **1a** (1.67 g, 1.67 mmol 16.7% based on tellurium) after recrystallization from dichloromethane. Preparative HPLC separation of hexane, water, and ethanol-soluble products gave **2** (2.13 g, 3.57 mmol, 35.7%), **3** (1.42 g, 3.41 mmol, 34.1%), and bis[4-(trifluoromethyl)phenyl] (1.06 g, 3.65 mmol, 8.3% based on BrC_6H_4-4-CF_3). Results under the other conditions and products yields are listed in Table 1.

Hexakis[4-(trifluoromethyl)phenyl]tellurium (1a): colorless plates, m.p. 328-330 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.3 Hz), 7.55 (d, J = 8.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.7(q, $^1J_{CF}$ = 272 Hz), 125.8(d), 131.9(q, $^2J_{CF}$ = 33 Hz), 133.5(d), 152.1(s); ^{13}C (100 MHz, [D_8]THF): δ 126.1(q, $^1J_{CF}$ = 273 Hz), 125.8(d), 133.4(q, $^2J_{CF}$ = 33 Hz), 136.0(d), 154.7(s, $^1J_{CTe}$ = 42 Hz); ^{125}Te NMR (126 MHz, [D_8]THF, Me_2Te): δ 467.3; IR (KBr) 3075(w), 2356(w), 1926(w), 1598(m), 1390(m), 1326(s), 1274(m), 1032(s), 1008(m), 957(m), 846(w), 825(s), 773(s), 631(w), 595(m), 498(m), 408(m) cm^{-1}; Raman (solid, Ar-ion) 1600(m), 1560(w), 1490(w), 1395(w), 1330(m), 1205(w), 1080(m), 1040(m), 1025(w), 998(w), 835(m), 780(s), 730(w), 650(s), 595(w), 500(w), 395(m), 345(m), 240(m), 140(vs) cm^{-1}; UV λ_{max} (acetonitrile) 212(log ε 4.78), 265(sh, 3.97), 275(sh, 3.82) nm; MS (70eV, EI): m/z (%) 858(13) $[Te(C_6H_4\text{-}4\text{-}CF_3)_5^+]$, 565(100)$[Te(C_6H_4\text{-}4\text{-}CF_3)_3^+]$, 154(10)$[(C_6H_4\text{-}4\text{-}CF_3)_2^+]$. Found: C, 50.83; H, 2.32%. Calcd for $C_{42}H_{24}F_{18}Te$: C, 50.54; H, 2.42%.

Tris[4-(trifluoromethyl)phenyl]tellurium chloride (2): colorless plates; m.p.>300 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.94(d, J = 8.3 Hz), 7.69(d, J = 8.3 Hz); ^{19}F NMR(376 MHz, $CDCl_3$): δ -63.8; ^{13}C NMR(100 MHz, $CDCl_3$): δ 123.1(q, $^1J_{CF}$ = 272 Hz), 127.0(s), 132.7(s), 133.7(q, $^2J_{CF}$ = 33 Hz), 135.8(s); ^{125}Te NMR(126 MHz, $CDCl_3$): δ 730.8. MS (EI 70eV): m/z (%) 565(100) $[Te(C_6H_4\text{-}CF_3)_3^+]$. Found: C, 42.39; H, 2.23%. Calcd for $C_{21}H_{12}F_9ClTe$: C, 42.15; H, 2.02%.

Bis[4-(trifluoromethyl)phenyl]tellurium (3)[24]: yellow needles, m.p. 52-53 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.48(d, J =8.3 Hz), 7.79(d, J =8.3 Hz); ^{19}F NMR(376 MHz, $CDCl_3$): δ -63.4; ^{13}C NMR(100 MHz, $CDCl_3$): δ 119.9(s, $^1J_{CTe}$ = 288 Hz), 124.0(q, $^1J_{CF}$ = 272 Hz), 126.3(s), 130.4(q, $^2J_{CF}$ = 33 Hz), 138.0(s); ^{125}Te NMR(126 MHz, $CDCl_3$): δ 715.3. MS (EI 70eV): m/z (%) 420(45)$[Te(C_6H_4\text{-}CF_3)_2^+]$, 145(100)$(C_6H_4\text{-}CF_3^+)$.

X-ray Crystallographic Analysis of 1a: The diffraction-quality single crystals of **1a** were obtained by the slow evaporation of a saturated solution in chloroform at room temperature. The intensity data (2θ = 3-55°) were collected on a Mac Science MXC3 diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å), and an absorption correction was applied. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4462 observed reflections [$I > 3.00\sigma(I)$] and 319 variable parameters with $R(R_w)$ = 0.040(0.046), GOF = 2.87; residual electron density (electrons Å^{-3}) min = -0.81, max = 0.98. Crystal data for **1a**; $C_{42}H_{24}F_{18}Te$, M = 998.2, triclinic, space group $P\bar{1}$, a = 9.210(2) Å, b = 11.200(2) Å, c = 11.245(2) Å, α = 96.05(1)°, β = 114.18(1)°, γ = 105.72(1)°, V = 987.2(3) Å^3, Z = 1, $\rho_{calcd.}$ = 1.68 gcm^{-3}, μ = 7.78 cm^{-1}, F(000) = 490, Crystal dimensions = 0.40 x 0.30 x 0.15 mm^3. The final values of selected bond lengths and angles are listed in Tables 2 and 3. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ(UK), on quoting the full journal citation.

Thermolysis of 1a. $TeAr_6$ **1a** (50.0 mg, 0.050 mmol) in a sealed Pyrex tube (1 mm diameter and 0.1 mm wall) was heated at 350 °C (sand bath) for 30 sec. To the cooled reaction mixture was added $CDCl_3$ and a ^{19}F NMR spectrum of the solution was taken. The peak area (-65 — -62 ppm) was integrated to determine the product distribution by comparison with authentic samples. The results are shown in Scheme 3.

Photolysis of 1a. A benzene solution (75 ml) of **1a** (50.0 mg, 0.050 mmol) in a Pyrex tube (50 mm diameter and 1 mm wall) was photolyzed by a medium pressure 100 W Hg lamp at 20 °C for 6 h. The product distribution was determined by integrating the peak area of aryl groups in ^{19}F NMR by comparison with authentic samples and the results are shown in Scheme 3.

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