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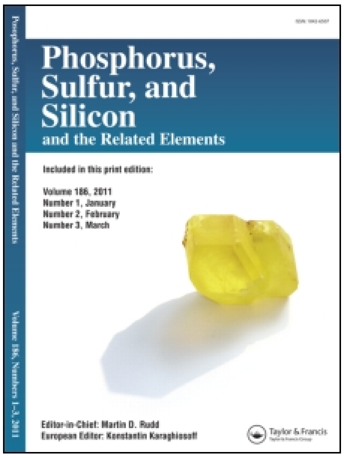

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NEW ASPECTS OF HYPERVALENT TELLURIUM COMPOUNDS

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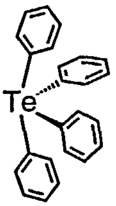
$Te(C_6H_4\text{-}4\text{-}CF_3)_6$ **1a** was obtained by the unique one-pot reaction of $LiC_6H_4\text{-}4\text{-}CF_3$ with $TeCl_4$, where oxidation of Te(IV) to Te(VI) occurred. Compound **1a** is extremely thermally stable and not light sensitive unlike tetraorganotellurium compounds. Thermolysis and some reactions of **1a** are described. $ClTe(C_6H_4\text{-}4\text{-}CF_3)_5$, synthesized by chlorination of $LiTe(C_6H_4\text{-}4\text{-}CF_3)_5$, reacted with $LiC_6H_4\text{-}4\text{-}CF_3$ to give **1a**. Bond dissociation energies of $Te(CH_3)_n$ (n = 2, 4, 6) were calculated in order to explain the stability of Te(VI) compounds.

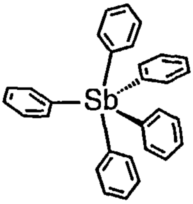
Keywords: organotellurium (VI); hypervalent; octahedral structure: thermal stability; bond dissociation energy

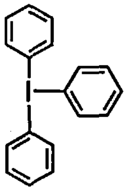
INTRODUCTION

The chemistry of hypervalent molecules of heavier typical elements has been studied extensively in recent years because of their intriguing bonding nature, scince they appear to violate the traditional octet rule by expanding the valence of the central p-block elements which located after third low of Groups 15–17 of the periodic table.

Fifty years ago, hypervalent organic compounds of Group 15 and 17 elements in their high oxidation states, species like $SbPh_5$ and IPh_3, have been reported by Wittig et al.[1] For Group 16 elements, although the early stage of organotellurium chemistry[2] had been developed as an extension of sulfur and selenium analogues, chemistry of hypervalent organochalcogens[3] commenced from tellurium when Wittig prepared $TePh_4$[4] 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,[5] and was found to have a distorted pseudo trigonalbipyramidal geometry with the axial phenyl groups bending toward the equatorial groups.[6] Intensive efforts have been recently directed toward the hypervalent organochalcogen compounds in which chalcogen atom is bonded directly to carbon substituents.[7] However considerable attention has been shown for those tetrasubstituted hypervalent organochalcogens, although chalcogens are known to expand into own oxidation state VI, only few attempts have so far been made for synthesis and observation of such species bearing the highest valency state.[8]

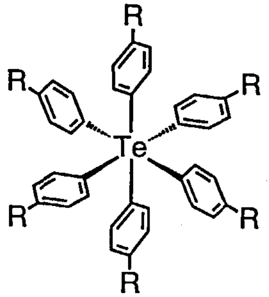






Meanwhile, there has been substantial interest in homoleptic molecules of transition metals and typical elements for some time,[9] because of their intriguing bonding nature, especially for compounds only with carbon-element bonds. However, only two neutral peralkylated hexavalent transition metals are known to exist, i.e., $W(CH_3)_6$[10] and $Re(CH_3)_6$,[11] 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.[12] The octahedral structure of $Te(CH_3)_6$ was determined by gas-phase electron diffraction.[13, 14]

Very recently, we reported the synthesis of a novel hypervalent tellurium, hexaaryltellurium **1**, as the first example of neutral compound comprising hexaarylated element.[15] In this paper, we present (i) a detailed account of the one-pot synthesis of **1a**, by the reaction of the ArLi (Ar = C_6H_4-4-CF_3) and $TeCl_4$, (ii) synthesis of monochloropentaaryltellurium, $ClTeAr_5$ **2**, which would rationalize the formation of $TeAr_6$, (iii) X-ray crystallographic analysis of both **1a** and **2**, (iv) stability of **1a**, and (v) results of theoretical consideration for hypervalent organotellurium.



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

RESULTS AND DISCUSSIONS

One-Pot Synthesis of Hexaaryltellurium 1a.

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 diaryltelluride **3** and triaryltelluronium chloride **4** (Table 1). When the reaction was quenched by 3% HCl aq. at low temperature after addition of ArLi or a stoichiometric quantity (6 : 1) of ArLi was used with $TeCl_4$, the yield of **1a** seemed to get lowered.

The reaction certainly involves valence expansion at tellurium and is obviously multi-steps. Probable course of the formation of **1a** is intriguing (Scheme 2). Three probable courses are proposed. In each course, the formation of $TeAr_4$ **5** seems vital in the initial stage of the reaction. Disproportionation reactions are proposed to be essential to generate Te(VI) species in each course (Scheme 2. c, g, i). In course A, disproportionation reaction (c) occurs between **5** and Cl_2TeAr_2 **6** to give Cl_2TeAr_4 **7** and $TeAr_2$ **3**. $TeAr_6$ **1a** is most likely formed by the succeeding reaction of **7** with ArLi through $ClTeAr_5$ **2** during warming of the reaction mixture to room temperature. Disproportionation reaction of $LiTeAr_5$ **8**, which is produced by the reaction of ArLi with $TeAr_4$, is proposed in the course B-(g), that is, with Cl_2TeAr_2 **6** to give $ClTeAr_5$ **2** and $TeAr_2$ **3**. In course C, disproportionation reaction (i) takes place between **8** and $ClTeAr_3$ **4** afford **1a** and **3**. Actually, **2** was obtained when the reaction mixture was quenched at low temperature (Table 1, entry 3).

$$TeCl_4 + ArLi \xrightarrow[\text{temperature}]{Et_2O} \begin{array}{l} TeAr_6\ \mathbf{1a} + TeAr_2\ \mathbf{3} + \\ ClTeAr_3\ \mathbf{4} + ClTeAr_5\ \mathbf{2} \end{array}$$

Scheme 1.

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

entry	ArLi (eq)	temperature °C	Product yields / %[a]			
			1a	3	4	2
1[b]	4	-78 — 25	16.7	35.7	34.1	—
2	6	-78 — 25	6.9	13.2	55.2	—
3[c]	4	-78	9.7	42.5	36.7	5.5

a; Yields are based on tellurium. b; Biaryl was also obtained as a by-product in 8.3% yield based on Ar group. c; Reaction mixture was quenched by 3% HCl aq. at -78 °C.

$$2TeCl_4 + 8ArLi \xrightarrow[-8LiCl]{} TeAr_6\ \mathbf{1a} + TeAr_2\ \mathbf{3}$$

Probable Course A

$$\begin{array}{llr}
TeCl_4 + 4ArLi \xrightarrow[-4LiCl]{} & TeAr_4\ \mathbf{5} & \text{(a)} \\
TeCl_4 + 2ArLi \xrightarrow[-2LiCl]{} & Cl_2TeAr_2\ \mathbf{6} & \text{(b)} \\
\mathbf{5} + \mathbf{6} \xrightarrow{\text{disproportionation}} & Cl_2TeAr_4\ \mathbf{7} + TeAr_2\ \mathbf{3} & \text{(c)} \\
\mathbf{7} + ArLi \xrightarrow[-LiCl]{} & ClTeAr_5\ \mathbf{2} & \text{(d)} \\
\mathbf{2} + ArLi \xrightarrow[-LiCl]{} & TeAr_6\ \mathbf{1a} & \text{(e)}
\end{array}$$

Probable Course B

$$TeCl_4 + 4ArLi \xrightarrow[-4LiCl]{} TeAr_4\ \mathbf{5} \qquad (a)$$

$$TeCl_4 + 2ArLi \xrightarrow[-2LiCl]{} Cl_2TeAr_2\mathbf{6} \qquad (b)$$

$$\mathbf{5} + ArLi \xrightarrow{} LiTeAr_5\mathbf{8} \qquad (f)$$

$$\mathbf{6} + \mathbf{8} \xrightarrow[-LiCl]{disproportionation} ClTeAr_5\ \mathbf{2} + TeAr_2\ \mathbf{3} \qquad (g)$$

$$\mathbf{2} + ArLi \xrightarrow[-LiCl]{} TeAr_6\ \mathbf{1a} \qquad (e)$$

Probable Course C

$$TeCl_4 + 4ArLi \xrightarrow[-4LiCl]{} TeAr_4\ \mathbf{5} \qquad (a)$$

$$TeCl_4 + 3ArLi \xrightarrow[-3LiCl]{} ClTeAr_3\mathbf{4} \qquad (h)$$

$$\mathbf{5} + ArLi \xrightarrow{} LiTeAr_5\mathbf{8} \qquad (f)$$

$$\mathbf{4} + \mathbf{8} \xrightarrow[-LiCl]{disproportionation} TeAr_6\ \mathbf{1a} + TeAr_2\ \mathbf{3} \qquad (i)$$

Scheme 2.

These results prompted us to attempt the alternative synthesis of $TeAr_6$ by the reaction of isolated $ClTeAr_5$ with ArLi and also to attempt to show the generation of $LiTeAr_5$ **8** *in situ* (*vide infra*). The other product $ClTeAr_3$ **4** can surely be produced by the reaction of 3 molar ArLi with $TeCl_4$ just before formation of **5**.

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.[16] The ^{125}Te NMR spectrum of **1a** (467 ppm) exhibits an upfield resonance in comparison to $Te(C_6H_5)_4$ (509 ppm) and $TeAr_2$ **3** (727 ppm).

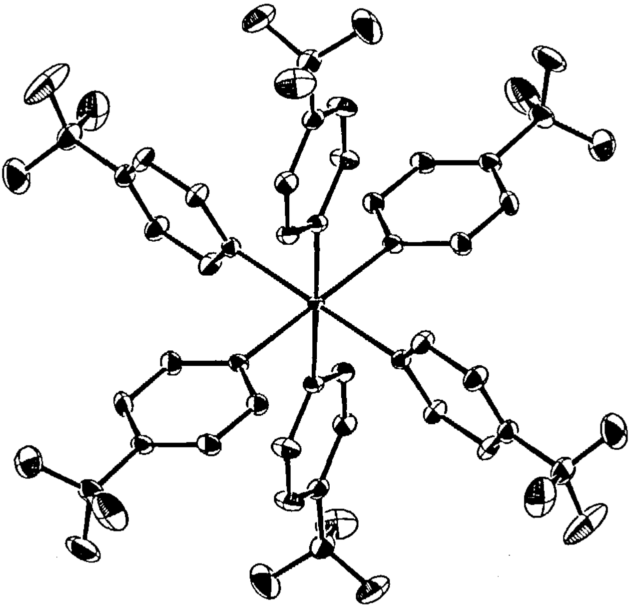
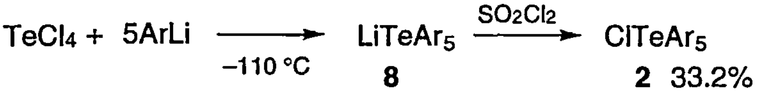


Fig. 1. ORTEP drawing of **1a** with thermal ellipsoids representing 30% probability

The molecular structure of **1a** was determined by X-ray crystallographic analysis (Figure 1). 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),[17] but comparable to the average (2.21 Å) of axial (2.29 Å) and equatorial (2.13 Å) bond lengths of tetraphenyltellurium.[6] 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.[18] This peculiar symmetry seems to be favorable in terms of interligand repulsion.

Synthesis and Structure of $ClTeAr_5$ 2

Pentaorganotellurium(VI) had never been synthesized, although the quenched reaction mixture of above mentioned one-pot process (table 2, entry 3) was found to contain $ClTeAr_5$ **2** (5.5%). We could obtain **2** in pure form as the first example of hexavalent organotellurium bearing five tellurium-carbon bonds and one halogen ligand. The isolation of **2** required a careful perseverance due to small quantity of **2** in the mixture. In connection with our program investigating the chemistry of novel hypervalent organotelluriums, we had an occasion to prepare **2** via direct chlorination of $LiTeAr_5$ **8** with SO_2Cl_2 as following. $ClTeAr_5$ **2** was synthesized by the reaction of SO_2Cl_2 with $LiTeAr_5$ **8** generated from 5 molar of ArLi with $TeCl_4$ at -110 °C in Et_2O. The reaction mixture was purified by preparative HPLC to give **2** as pale yellow crystals in 33% yield (Scheme 3).



$$TeCl_4 + 5ArLi \xrightarrow[-110\,°C]{} \underset{\mathbf{8}}{LiTeAr_5} \xrightarrow{SO_2Cl_2} \underset{\mathbf{2}\ \ 33.2\%}{ClTeAr_5}$$

Scheme 3.

Although tellurenyl harides (ArTeX, X = halogen) are known to be unstable, isolated $ClTeAr_5$ **2** is thermally very stable. The X-ray crystallographic analysis of **2** indicates the slightly distorted octahedral geometry around the Te atom, which was caused by the smaller chlorine atom in **2** on the tellurium than Ar group in $TeAr_6$ **1a** (Figure 2). The Te-C (*trans* to Cl) bond length (2.175 Å) is shorter than Te-C (*cis* to Cl) bonds (av. 2.198 ± 0.01 Å). In contrast to Te-X bond in telluronium salt (Ar_3TeX) which has been shown as ionic bond, the Te-Cl bond in **2** is covalent bond where the bond length is 2.564 Å.

An attractive mechanism for the formation of $TeAr_6$ **1a** in the one-pot synthesis, proposed mechanism [Scheme 2-(e)] was supported by the fact that the reaction of isolated $ClTeAr_5$ **2** with an equimolar amount of ArLi in Et_2O afforded **1a** in 10% yield.

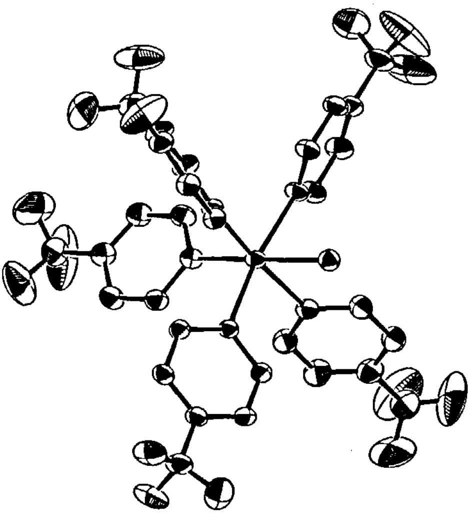
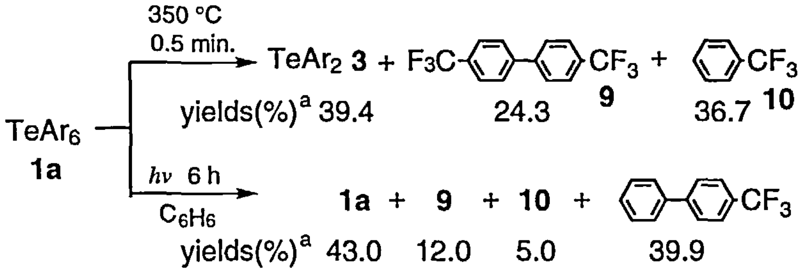


Fig. 2. ORTEP drawing of **2** with thermal ellipsoids representing 30% probability

Stability of $TeAr_6$ 1a

$TeAr_6$ **1a** is an extremely thermally 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 as high temperature as 350 °C for 30 sec in a sealed tube to afford decomposition products **3**, **9**, and **10** (Scheme 3).

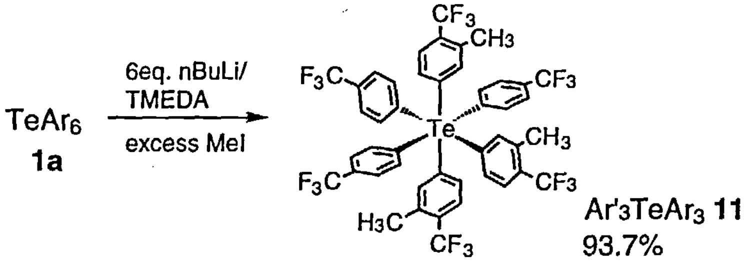


a; Yields are calculated based on the aryl group.

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 reagents (XeF_2, SO_2Cl_2, Br_2) at room temperature for several hours although most organotellurium compounds including $TeMe_6$ react with these halogenating reagents easily.

Attempted lithiation of **1a** by equimolar RLi (R = Me, *n*-Bu, *t*-Bu) failed showing the stability of **1a** even toward strong nucleophiles. So functionalization of the benzene ring was attempted under severe conditions. By the reaction of $TeAr_6$ with 6 equiv of *n*-BuLi followed by addition of excess MeI, functionalized hexaaryltellurium Ar'_3TeAr_3 (Ar' = 3-CH_3-4-$CF_3C_6H_3$) **11** with the methyl group in three aromatic rings was obtained. Surprisingly, six C-Te bonds in $TeAr_6$ were intact during this reaction, the X-ray structural analysis showed octahedral geometry around the Te^{VI} in **11**.



Scheme 4.

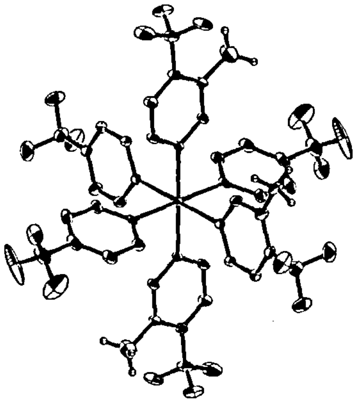


Fig. 3. ORTEP drawing of **11** with thermal ellipsoids representing 30% probability

Theoretical Consideration for Stability of $TeAr_6$

The change of the bond dissociation energies in each oxidation state of tellurium is still uncertain, although the hypervalent property of organotelluriums has been frequently discussed in the literature. The bond dissociation energy of a series of organotelluriums, $TeMe_n$ (n = 2, 4, 6), was estimated systematically in order to understand high stability of tellurium–carbon bond in $TeAr_6$.

Ab initio calculations were performed on all molecules considered in this section using 6-31G** for C and H and ECP basis sets of [21/21/1*] for Te. All energy calculations were carried out QCISD(T) at MP2 geometries and the results are shown in Table 2.

The tellurium–carbon bond dissociation energies of di-, tetra-, and hexaorganotelluriums were estimated according to the following equation:

$$Te(CH_3)_n \longrightarrow Te(CH_3)_{n-1} + \cdot CH3 \qquad n = 2, 4, 6$$

Table 2. Calculated bond lengths and bond dissociation energies of $Te(CH_3)_n$

	Te–C bond length (Å)	QCISD(T) BDE (kcal/mol)
$Te(CH_3)_2$	2.15 [2.142(5)]	55.8
$Te(CH_3)_4$	2.25 (apical) [2.265(9)] 2.15 (equatorial) [2.140(8)]	42.0
$Te(CH_3)_6$	2.18 [2.19(3)]	63.1

Values in brackets are experimental values. see reference [14]

Surprisingly, despite of the hypervalent bond, the Te–C bond in $TeMe_6$ is stronger than normal covalent bond in $TeMe_2$ and the order of stability expected from the bond dissociation energy is $TeMe_4 < TeMe_2 < TeMe_6$. The results agree with experimental findings.

It is noteworthy that 5s orbital coefficients in Te–C bond calculated from NBO analysis for $TeMe_n$ (n = 2, 4, 6) are followings, i. e., for C-Te^{II}, Te^{IV}, and Te^{VI} are 0.33, 0.28 (for apical), and 0.41, respectively. These values imply that the 5s orbital contribution strengthen the Te–C bond, and the order of the values is consistent with bond dissociation energy of those of $TeMe_n$.

The extremely high stability of $TeAr_6$ **1a** even compared to $TeMe_6$ is thought to reflect a kind of through bond conjugation of π-electrons across the hypervalent Te–C bonds based on octahedral geometry around the tellurium (VI).

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