Novel Valence Expansion Reactions Using KC_8: A New Route to Hexavalent Organotellurium Compounds from Divalent Tellurium

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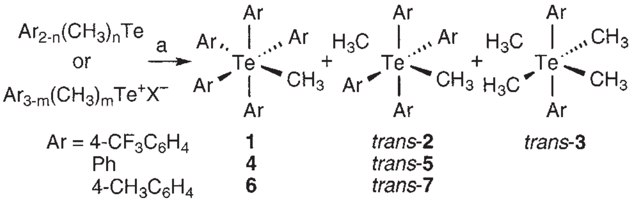
Hexavalent tellurium compounds, $Ar_5(CH_3)Te$, $Ar_4(CH_3)_2Te$, and $Ar_2(CH_3)_4Te$ ($Ar = 4\text{-}CF_3C_6H_4$, Ph, $4\text{-}CH_3C_6H_4$), were synthesized by the reaction of $Ar_{2\text{-}n}(CH_3)_nTe$ (n = 0–1) or $Ar_{3\text{-}m}(CH_3)_mTe^+X^-$ (m = 0–2) with KC_8 followed by the treatment with CH_3I.

Valence of main group element compounds are generally exalted higher by oxidizing reagents such as halogens and valence shell expansion takes place in certain cases. For example, Ph_4F_2Te was prepared by treatment of Ph_4Te with XeF_2 as an oxidant.[1] However, reactions of R_2Te or R_4Te with alkyl halides did not yield hypervalent tellurium compounds but the corresponding oniums R_3Te^+.[2] Here we report one-pot novel valence expansion reactions from $Ar_{2\text{-}n}(CH_3)_nTe(II)$ (n = 0–1) or $Ar_{3\text{-}m}(CH_3)_mTe^+X^-(IV)$ (m = 0–2) to $Ar_5(CH_3)Te(VI)$, $Ar_4(CH_3)_2Te(VI)$, and $Ar_2(CH_3)_4Te(VI)$ ($Ar = 4\text{-}CF_3C_6H_4$, Ph, $4\text{-}CH_3C_6H_4$) by use of KC_8 followed by treatment with CH_3I.

The reaction of $(4\text{-}CF_3C_6H_4)_2Te(II)$ with potassium graphite (KC_8)[3] (ca. 15 equiv) was carried out at −78 °C in THF for 5 min and the reaction mixture was treated with CH_3I (ca. 30 equiv) to afford several hexavalent tellurium compounds, that is, $(4\text{-}CF_3C_6H_4)_5(CH_3)Te$ (**1**)(4%), $(4\text{-}CF_3C_6H_4)_4(CH_3)_2Te$ (*trans*-**2**) (9%), and $(4\text{-}CF_3C_6H_4)_2(CH_3)_4Te$ (*trans*-**3**) (10%) (Scheme 1).[4–6] These hexavalent tellurium compounds are stable to atmospheric moisture and could be separated by recycling HPLC. They were characterized by spectroscopies and elemental analyses. X-ray analysis of *trans*-**2** and *trans*-**3** confirmed that these were octahedral and the two methyl groups in *trans*-**2** and the two $4\text{-}CF_3C_6H_4$ groups in *trans*-**3** were located *trans* to each other. The ORTEP drawing of *trans*-**3** is shown in Figure 1.[7]



a : 1) KC_8, THF, -78 °C, 2) CH_3I, -78 °C–rt.

Scheme 1. Synthesis of hexaorganotellurium compunds.

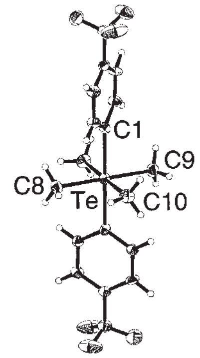


Figure 1. X-ray structure of *trans*-**3** (30% thermal ellipsoid). The structure is almost perfectly octahedral; bond angles for each *cis* group is in the range of 90 ± 0.7° and for each *trans* group is in the range of 180 ± 1.4°. Selected bond lengths (Å): Te-C(1) 2.25(1), Te-C(8) 2.19(1), Te-C(9) 2.18(1), Te-C(10) 2.18(1).

Table 1. Yields of the reaction of organotellurium compounds with KC_8 (CH_3K, $PhCH_2K$) after treatment with CH_3I

Starting Material	Reagent	Yields (%, based on Te)		
		1	*trans*-**2**	*trans*-**3**
$(4\text{-}CF_3C_6H_4)_2Te$	A	4	9	10
	B	no	11	no
	C	no	13	no
$(4\text{-}CF_3C_6H_4)(CH_3)Te$	A	no	no	4
$(4\text{-}CF_3C_6H_4)_3Te^+Cl^-$	A	21	7	7
	B	16	6	no
$(4\text{-}CF_3C_6H_4)_2(CH_3)Te^+CF_3SO_3^-$	A	no	31	4
$(4\text{-}CF_3C_6H_4)(CH_3)_2Te^+I^-$	A	no	no	16
		4	*trans*-**5**	
$Ph_3Te^+Br^-$ [a]	A	19	12	
		6	*trans*-**7**	
$(4\text{-}CH_3C_6H_4)_3Te^+Cl^-$ [b]	A	36	7	

A; KC_8 (15 equiv), B; CH_3K (2 equiv), C; $PhCH_2K$ (1 equiv). CH_3I (30 equiv) was used. no; not obtained.
[a]C_6H_5I (4 equiv) was added. [b]$4\text{-}CH_3C_6H_4I$ (4 equiv) was added.

The reaction of $(4\text{-}CF_3C_6H_4)_3Te^+Cl^-$ with KC_8 followed by treatment with CH_3I afforded a similar mixture of the hexavalent tellurium compounds (**1**: 21%, *trans*-**2**: 7%, and *trans*-**3**: 7%) (Table 1). When $(4\text{-}CF_3C_6H_4)(CH_3)Te$, $(4\text{-}CF_3C_6H_4)_2(CH_3)Te^+OTf^-$, and $(4\text{-}CF_3C_6H_4)(CH_3)_2Te^+I^-$ were used instead of homoleptic materials as mentioned above, i.e., $(4\text{-}CF_3C_6H_4)_2Te$ and $(4\text{-}CF_3C_6H_4)_3Te^+Cl^-$, monomethylated **1** was not obtained at all but di- and tetramethylated compounds (*trans*-**2** and *trans*-**3**) were obtained with increased yields. For example, *trans*-**2** (31%) and *trans*-**3** (4%) were obtained from $(4\text{-}CF_3C_6H_4)_2(CH_3)Te^+OTf^-$ and only *trans*-**3** was obtained from

$(4\text{-}CF_3C_6H_4)(CH_3)_2Te^+I^-$ and $(4\text{-}CF_3C_6H_4)(CH_3)Te$ in low yields. These results clearly indicate that the unique valence expansion took place by electron transfer from KC_8 and was applicable for the synthesis of new hexavalent tellurium compounds with mixed carbon ligands. In fact, $Ph_{6\text{-}n}(CH_3)_nTe$ (n = 1, **4**;[8] n = 2, *trans*-**5**[9]) and $(4\text{-}CH_3C_6H_4)_{6\text{-}n}(CH_3)_nTe$ (n = 1, **6**;[10] n = 2, *trans*-**7**) were obtained from $Ph_3Te^+Br^-$ and $(4\text{-}CH_3C_6H_4)_3Te^+Cl^-$ as shown in Table 1.

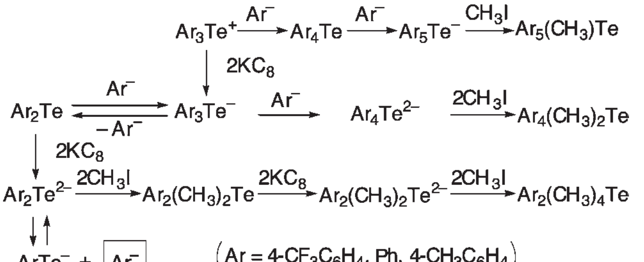
Instead of KC_8, CH_3K[11] or $PhCH_2K$[12] could be used for the reaction (Table 1), and *trans*-**2** was obtained from $(4\text{-}CF_3C_6H_4)_2Te$ even by the use of $PhCH_2K$. Therefore, $PhCH_2K$ and CH_3K should behave as an electron donor similar to KC_8.

In order to elucidate the mechanism of the reaction, we examined the effects of the equivalents of the reagents of KC_8 and CH_3I in the reaction with $(4\text{-}CF_3C_6H_4)_2Te$ on the yield of hexavalent tellurium compounds. These results are shown in Table 2. The generation of $(4\text{-}CF_3C_6H_4)Te^-$ was suggested by the formation of $(4\text{-}CF_3C_6H_4)(CH_3)Te$ in the initial stage of the reaction (entry 2 in Table 2). By use of a large excess of KC_8 the number of the Te-Ar bond clevaged increased. The ^{125}Te NMR of the reaction mixture from $(4\text{-}CF_3C_6H_4)_2Te$ and a large excess of KC_8 at −78 °C before the addition of CH_3I showed a signal at δ 360 ppm, which can be assigned as that for a dianion $(4\text{-}CF_3C_6H_4)_4Te^{2-}\cdot 2(K^+C_8)$, generated independently by the reaction of $(4\text{-}CF_3C_6H_4)_5(CH_3)Te$ with KC_8.[5] The signal at δ 362 ppm was also observed in the reaction of $(4\text{-}CF_3C_6H_4)_2Te$ with CH_3K before the addition of CH_3I, therefore, it is confirmed that CH_3K acts as an electron donor. The detailed reaction mechanism is not clear yet but a possible mechanism is illustrated in Scheme 2.

Table 2. Effects of the equivalents of the reagents (KC_8 and CH_3I) in the reaction with $(4\text{-}CF_3C_6H_4)_2Te$

Equivalents		Yields (%, based on Te)			
KC_8	CH_3I	1	*trans*-2	*trans*-3	
1	8	no	no	no	$(4\text{-}CF_3C_6H_4)_2Te$ recovered
5	5	no	21	no	$(4\text{-}CF_3C_6H_4)_2Te$ 38% $(4\text{-}CF_3C_6H_4)(CH_3)Te$ 27%
10	11	no	31	no	
15	30	4	9	10	

no; not obtained



Scheme 2. Possible mechanism.

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Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 75th birthday.

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4 General procedure; A THF solution of $Ar_{2\text{-}n}(CH_3)_nTe$ or $Ar_{3\text{-}m}(CH_3)_mTe^+X^-$ (Ar: $4\text{-}CF_3C_6H_4$, Ph, $4\text{-}CH_3C_6H_4$) {aryl halide was also added in some cases (see Table 1)} was added to freshly prepared KC_8 (ca. 15 equiv) at −78 °C. After 5 min of stirring, CH_3I (ca. 30 equiv) was added at the same temperature, and the reaction mixture was allowed to warm to room temperature. Graphite powder was filtered off, and volatile materials were evaporated. Hexavalent oraganotellurium species could be isolated by recycling HPLC (Japan Analytical Industry LC-908, 1,2-dichloroethane as an eluent). The yields are summarized in Table 1.

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6 *trans*-**3**; mp. 224 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.88 (s, 12H), 7.64 (d, 4H, $J = 8.3$ Hz), 7.85 (d, 4H, $J = 8.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 36.3 (q, $^1J_{CTe} = 7.1$ Hz), 124.2 (q, $^1J_{CF} = 272$ Hz), 124.9 (d), 129.6 (q, $^2J_{CF} = 33$ Hz), 130.5 (d), 165.9 (s, $^1J_{CTe} = 173$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ −63.0; ^{125}Te NMR [126 MHz, $CDCl_3$, 25 °C, $(CH_3)_2Te$] δ 119.

7 Data were collected at 200 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares. Crystal data for *trans*-**3**: monoclinic system, space group $C2/c$ (no. 15), $a = 12.1390(8)$ Å, $b = 18.359(1)$ Å, $c = 9.4980(5)$ Å, $\beta = 118.067(4)°$, $V = 1867.8(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.70$ g cm^{-3}. $R = 0.0654$ (Rw = 0.1305) for 1925 observed reflections (116 parameters) with $I > 3\sigma(I)$. Goodness of fit = 1.311

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9 *trans*-**5**; mp. 246 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.14 (s, 6H), 7.20 (t, 8H, $J = 6.8$ Hz), 7.28 (t, 4H, $J = 6.8$ Hz), 7.32 (d, 8H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 29.5 (q, $^1J_{CTe} = 16.6$ Hz), 127.1 (d), 127.5 (d), 132.6 (d), 157.5 (s, $^1J_{CTe} = 74.6$ Hz); ^{125}Te NMR [126 MHz, $CDCl_3$, 25 °C, $(CH_3)_2Te$] δ 274.

10 **6**; mp. 226 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.16 (s, 3H), 2.24 (s, 3H), 2.31 (s, 12H), 6.95 (d, 2H, $J = 7.8$ Hz), 6.97 (d, 8H, $J = 7.8$ Hz), 7.27 (d, 8H, $J = 7.8$ Hz), 7.50 (d, 2H, $J = 7.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.0 (q), 21.1 (q), 33.0 (q, $^1J_{CTe} = 12.4$ Hz), 127.7 (d), 127.9 (d), 133.1 (d), 133.7 (d), 137.0 (s), 137.1 (s), 148.5 (s, $^1J_{CTe} = 16.6$ Hz), 151.9 (s, $^1J_{CTe} = 49.8$ Hz); ^{125}Te NMR [126 MHz, $CDCl_3$, 25 °C, $(CH_3)_2Te$] δ 341.

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