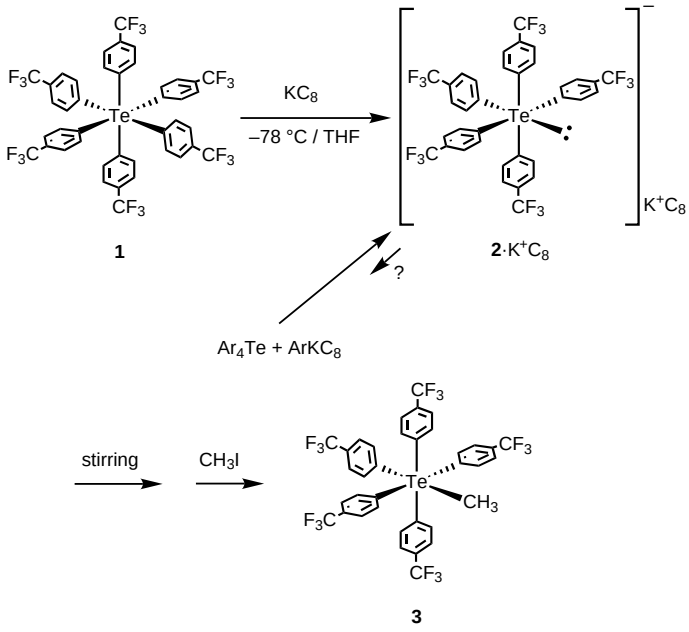
Cleavage of Tellurium–Carbon Bonds of Hexavalent Organotellurium Compounds by Potassium Graphite**

Masataka Miyasato, Mao Minoura, and Kin-ya Akiba*

Recently, we reported on the synthesis of the hexaaryltellurium compounds Ar_6Te (**1**: Ar = 4-$CF_3C_6H_4$) and Ph_6Te,[1] the first neutral hexaarylated compounds.[2] These hexaaryl compounds are stable to atmospheric moisture and are inert to nucleophiles such as alkyllithium reagents. Here we report that one of the Te–C bonds of **1** is readily cleaved by potassium graphite (KC_8)[3] to afford $Ar_5Te^-K^+C_8$ (**2**·K^+C_8) (Scheme 1). The reaction of **2**·K^+C_8 with CH_3I gave quantitatively Ar_5TeCH_3 (**3**), which could not be obtained from $Ar_5Te^-Li^+$.[4]

We tried to reduce **1** with lithium or sodium–naphthalenide, lithium 4,4′-di-*tert*-butylbiphenylide, Na amalgam, NaK alloy, and K under various conditions, but **1** was recovered quantitatively in all cases. However, in the reaction of **1** with KC_8[3] the expected **2**·K^+C_8 was generated even at −78 °C in THF. By ^{125}Te NMR spectroscopy, a singlet ($\delta = 600$ at −45 °C) was observed. The ^{125}Te NMR chemical shift in THF was comparable to that of $Ar_5Te^-Li^+$ (**2**·Li^+, $\delta = 588$), which was prepared from Ar_4Te ($\delta = 505$)[5] and ArLi. A remarkable difference between **2**·Li^+ and **2**·K^+C_8 was noted, however, when **2**·Li^+ or **2**·K^+C_8 was treated with CH_3I. Although Ar_5TeCH_3 (**3**) was not obtained at all from **2**·Li^+ under various conditions, **3** was obtained quantitatively from **2**·K^+C_8 up to −20 °C (Scheme 1 and Table 1). The remarkable reactivity of **2**·K^+C_8 is presumably attributable to the intercalation of the potassium cation in graphite. Since $Ph_5Te^-Li^+$[4a] was reported to be in an equilibrium with Ph_4Te and PhLi, the failure of **2**·Li^+ to react with CH_3I could be due to a much higher rate of the reaction of ArLi (in the equilibrium) with CH_3I than with **2**·Li^+ (Curtin–Hammett situation[6]). Therefore, the quantitative formation of **3** from **2**·K^+C_8 strongly indicated that **2**·K^+C_8 should be the exclusive species, if any, in the equilibrium with Ar_4Te and $ArKC_8$. Since the potassium cation is intercalated by graphite,[3] the resulting K^+C_8 is a weakly coordinating cation and would not tend to aggregate. That is, typical ion pairing is suppressed by intercalation of K^+ in graphite. Since $ArKC_8$ should be unstable because of the lack of aggregation, the equilibrium between **2**·K^+C_8, Ar_4Te, and $ArKC_8$ shifts toward **2**·K^+C_8, which becomes the exclusive anion. To our knowledge such a unique effect of graphite has not been noted so far, although the importance of graphite has been reported for some reactions.[3a,c] In fact, no **3** was obtained by the reaction of CH_3I with $Ar_5Te^-K^+$ (**2**·K^+), which was prepared from Ar_5TeX (X = Cl, Br)[7] and potassium without graphite. Although weakly coordinating anions have recently attracted extensive interest,[8] weakly coordinating cations have not been reported, apart from complexation of metal cations by crown ethers or cryptands. The present K^+C_8 system can be regarded as a new weakly coordinating cation.



Scheme 1. Reaction of Ar_6Te (**1**) to give **3** via **2**·K^+C_8.

Table 1. Yield of **3** in the reaction of Ar_6Te with KC_8, followed by reaction with CH_3I.

T [°C]	t [h]	Yield of **3** [%]
−78	1	98
−45	1	98
	12	35
−20	1	98
0	0.5	15
20	0.5	0[a]

[a] Products were Ar_2Te, Ar_2, and ArI.

With pentaarylmonomethyltellurium **3** in hand, the selective cleavage of the two different tellurium–carbon bonds, namely, Te–Ar and Te–CH_3, was of interest. The reaction of **3** with excess KC_8 at −78 °C, followed by addition of CH_3I, gave $Ar_4Te(CH_3)_2$ (*trans*-**4**) in 14% yield, and 75% of **3** was recovered (Scheme 2). X-ray analysis of *trans*-**4**[9] confirmed the *trans* arrangement of the two methyl groups (Figure 1).

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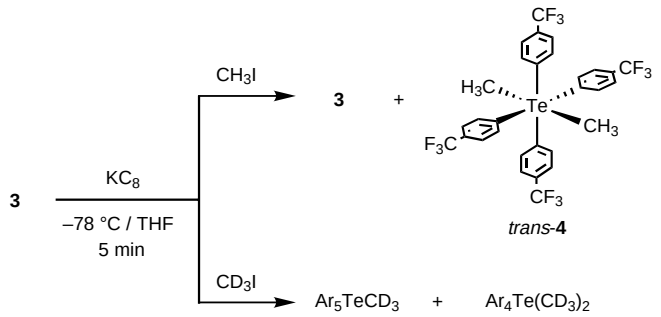


Scheme 2. Reaction of Ar_5TeCH_3 (**3**) with KC_8, followed by reaction with CH_3I or CD_3I.

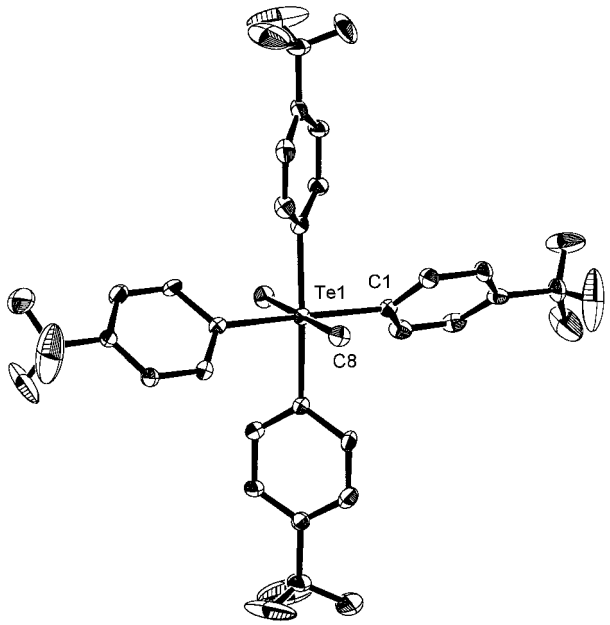
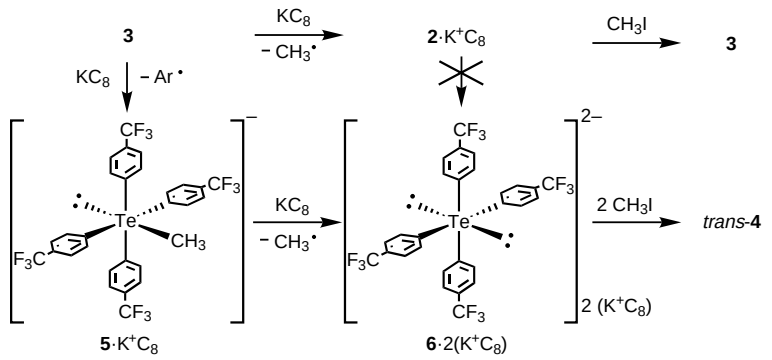


Figure 1. Crystal structure (30% thermal ellipsoids) of *trans*-**4**. Selected bond lengths [Å]: Te-C1 2.205(5), Te-C8 2.182(8).

When CD_3I was used instead of CH_3I, Ar_5TeCD_3 (68% yield) and $Ar_4Te(CD_3)_2$ (12% yield) were obtained. These results showed that cleavage of the Te–C bonds took place almost quantitatively and the Te–CH_3 bond was cleaved in preference to the five Te–Ar bonds. This unexpected selectivity can be explained as shown in Scheme 3. As a first step one-electron reduction took place, followed by formation of Ar_5Te^- ($\mathbf{2}\cdot K^+C_8$) and $CH_3^\bullet$ rather than $Ar_4TeCH_3^-$ ($\mathbf{5}\cdot K^+C_8$) and $Ar^\bullet$. The selectivity could be related to the higher stability of $\mathbf{2}\cdot K^+C_8$ relative to that of $\mathbf{5}\cdot K^+C_8$. Formation of $Ar_4Te(CD_3)_2$ suggested the presence of the novel hypervalent dianion Ar_4Te^{2-} [$\mathbf{6}\cdot 2(K^+C_8)$]. In the ^{125}Te NMR of the supernatant of the reaction mixture from **3** with KC_8 in THF at $-78\,^\circ C$ before addition of CH_3I, two signals were observed at $\delta = 591$ ($\mathbf{2}\cdot K^+C_8$: $\delta = 600$ at $-45\,^\circ C$) and $\delta = 385$. The latter high-field signal could be assigned to $\mathbf{6}\cdot 2(K^+C_8)$, since **3** and **4** were obtained quantitatively after addition of CH_3I to the solution. Note that conversion of $\mathbf{2}\cdot K^+C_8$ to $\mathbf{6}\cdot 2(K^+C_8)$ did not take place, because only one of the six tellurium–aryl bonds in **1** was cleaved even with an excess of KC_8 (Scheme 1).



Scheme 3. Possible mechanism for formation of **3** and *trans*-**4**.

Experimental Section

$\mathbf{2}\cdot K^+C_8$ and **3**: A solution of **1** in THF (30 mL) (1.55 g, 1.55 mmol) was added to freshly prepared potassium graphite (KC_8: K 0.187 g, 4.76 mmol; C 0.361 g, 30.1 mmol) at $-78\,^\circ C$. After 1 h of stirring, CH_3I (1.00 mL, 16.1 mmol) was added at the same temperature, and the reaction mixture was allowed to warm to room temperature. Graphite powder was filtered off and the solvent and excess CH_3I were removed in vacuo. Recycling HPLC gave 1.32 g (97.9%) of **3**: colorless needles, m.p. 258–259 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.35$ (s, 3H; CH_3), 7.45 (d, $^3J(H,H) = 8$ Hz, 8H; *cis*-2-H), 7.52 (d, $^3J(H,H) = 8$ Hz, 8H; *cis*-3-H), 7.54 (d, $^3J(H,H) = 8$ Hz, 2H; *trans*-2-H), 7.67 (d, $^3J(H,H) = 8$ Hz, 2H; *trans*-3-H); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.1$ (12F; *cis*-CF_3), -63.3 (3F; *trans*-CF_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 33.8$ (q, $^1J(C,Te) = 12$ Hz; CH_3), 123.8 (q, $^1J(C,F) = 273$ Hz; *cis*- and *trans*-CF_3), 124.9 (d; *cis*-3-C), 125.2 (d; *trans*-3-C), 131.1 (q, $^2J(C,F) = 33$ Hz; *cis*-4-C), 131.2 (q, $^2J(C,F) = 33$ Hz; *trans*-4-C), 133.1 (d; *trans*-2-C), 133.7 (d; *cis*-2-C), 153.9 (s, $^1J(C,Te) = 21$ Hz; *trans*-1-C), 157.2 (s, $^1J(C,Te) = 64$ Hz; *cis*-1-C); ^{125}Te NMR (126 MHz, $CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 345$; elemental analysis (%) calcd for $C_{36}H_{23}F_{15}Te$: C 49.81, H 2.67; found: C 49.62, H 2.41.

trans-**4**: A solution of **3** (0.712 g, 0.820 mmol) in THF (20 mL) was added to freshly prepared potassium graphite (KC_8: K 0.239 g, 6.11 mmol; C 0.364 g, 30.3 mmol) at $-78\,^\circ C$. After 5 min of stirring, CH_3I (0.75 mL, 12.0 mmol) was added at the same temperature, and the reaction mixture was allowed to warm to room temperature. Graphite powder was filtered off, and the solvent and excess CH_3I were removed in vacuo. Recycling HPLC gave 530 mg (74.5%) of **3** and 82.8 mg (13.7%) of *trans*-**4**: colorless cubes, m.p. 275–276 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.25$ (s, 6H; CH_3), 7.40 (d, $^3J(H,H) = 8$ Hz, 8H; 2-H), 7.52 (d, $^3J(H,H) = 8$ Hz, 8H; 3-H); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.1$; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 30.9$ (q, $^1J(C,Te) = 13$ Hz; CH_3), 124.0 (q, $^1J(C,F) = 273$ Hz; CF_3), 124.7 (d; 3-C), 130.6 (q, $^1J(C,F) = 33$ Hz; 4-C), 132.7 (d; 2-C), 160.3 (s, $^1J(C,Te) = 105$ Hz; 1-C); ^{125}Te NMR (126 MHz, $CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 272$; elemental analysis (%) calcd for $C_{30}H_{22}F_{12}Te$: C 48.82, H 3.00; found: C 48.71, H 2.91.

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[5] Spectral data of Ar_4Te: ^1H NMR (400 MHz, C_6D_6, 25 °C, C_6D_5H): $\delta =$ 7.12 (d, $^3J(H,H) = 8$ Hz, 8H; 2-H), 7.26 (d, $^3J(H,H) = 8$ Hz, 8H; 3-H); ^{19}F NMR (376 MHz, C_6D_6, 25 °C, $CFCl_3$): $\delta = -62.7$; ^{13}C NMR (100 MHz, C_6D_6, 25 °C, C_6D_6): $\delta = 124.6$ (q, $^1J(C,F) = 273$ Hz; CF_3), 125.8 (d; 3-C), 130.9 (q, $^1J(C,F) = 33$ Hz; 4-C), 133.5 (d; 2-C), 152.3 (s, $^1J(C,Te) = 230$ Hz; 1-C); ^{125}Te NMR (126 MHz, C_6D_6, 25 °C, $(CH_3)_2Te$): $\delta = 490$; M. Minoura, M. Miyasato, K.-y. Akiba, unpublished results.

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[9] Crystal data for *trans*-**4**: cubic, space group $P\bar{4}3n$ (no. 218), $a =$ 16.9860(2) Å, $V = 4900.87(9)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.50$ g cm^{-3}; $R = 0.0599$ ($Rw = 0.1041$) for 973 observed reflections (99 parameters) with $I > 3\sigma(I)$; GOF = 1.417. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159924. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Data were collected at 200 K on a Mac Science DIP2030 imaging plate with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by autoindexing several images in each data set separately with the program DENZO (Mac Science). 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 by using the teXsan (Rigaku) system and refined by full-matrix least-squares methods.

Highly Sensitive Novel Biosensor Based on an Immobilized *lac* Repressor**

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Sequence-specific interactions of proteins with DNA are central to all aspects of the utilization of genetic information in any organism. The lactose repressor of *E. coli* served as a paradigm for such interactions even before the chemical structure of the interacting partners was elucidated.[1] The *lac* repressor protein recognizes the *lac* operator, a particular region of base pairs in the chromosome of *E. coli* and binds to it tightly with a dissociation constant of 10^{-11}–10^{-13} M.[2] Site-specific recognition of DNA by the *lac* repressor is interrupted by an inducer, such as lactose, to allow the production of the enzymes necessary for the utilization of this carbon source.[3] A major conformational change in the *lac* repressor structure takes place as the result of inducer binding.[4, 5] The majority of inducers that bind to the *lac* repressor are galactose derivatives, such as isopropyl-D-thiogalactoside (IPTG), *o*-nitrophenyl-D-galactoside (ONPG), and 1,6-allolactose.[6] Other sugars like *o*-nitrophenylfucoside (ONPF) also bind strongly to the *lac* repressor.[7]

Capacitance measurements have been successfully used as a basis for the construction of biosensors for sensitive detection of the human chorionic gonadotropin (HCG) hormone, by immobilization of antibodies on the electrode surface.[8] Heavy metals can also be detected, with heavy metal binding proteins as recognition elements.[9, 10] The capacitive transduction principle has now been used for the development of a biosensor to monitor inducer molecules or DNA, through the use of a repressor protein as the biological recognition element.

Biosensors prepared by immobilizing the *lac* repressor protein on a gold surface modified with thioctic acid have been used in the experimental set-up presented schematically, along with the detection principle in Figure 1. The specificity of *lac* repressor based biosensors for operator DNA was tested by injections of plasmid p310 DNA, two linearized plasmid DNAs, and genomic DNA. Plasmid p310 DNA (2455 base pairs (bp) in length) was constructed by cloning a 24 bp fragment that contains the *lac* ideal operator into the *Nhe*I site of plasmid pEE4. One linearized plasmid DNA was obtained by digestion of the plasmid p310 DNA with *Eco*RI, and the target *lac* operator (the second linearized plasmid DNA) was excised as an 84 bp fragment by cutting with *Eco*RI and *Hind*III.

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