Syntheses and Reactions of Hexavalent Organotellurium Compounds Bearing Five or Six Tellurium–Carbon Bonds

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Abstract: A variety of hexaorganotellurium compounds, $Ar_{6-n}(CH_3)_nTe$ [Ar = 4-$CF_3C_6H_4$, $n=0$ (**1a**), $n=1$ (**3a**), $n=2$ (*trans*-**4a** and *cis*-**4a**), $n=3$ (*mer*-**5a**), $n=4$ (*trans*-**6a**); Ph, $n=0$ (**1b**), $n=1$ (**3b**), $n=2$ (*trans*-**4b**); 4-$CH_3C_6H_4$, $n=0$ (**1c**), $n=1$ (**3c**), $n=2$ (*trans*-**4c**), $n=4$ (*trans*-**6c**); 4-BrC_6H_4, $n=0$ (**1d**)] and $Ar_5(R)Te$ [Ar = 4-$CF_3C_6H_4$, R = 4-$CH_3OC_6H_4$ (**8**); Ar = 4-$CF_3C_6H_4$, R = vinyl (**9**), Ar = Ph, R = vinyl (**10**), Ar = 4-$CF_3C_6H_4$, R = $PhSCH_2$ (**11**), Ar = Ph, R = $PhSCH_2$ (**12**), Ar = 4-$CF_3C_6H_4$, R = *n*Bu (**13**)] and pentaorganotellurium halides, Ar_5TeX [Ar = 4-$CF_3C_6H_4$, X = Cl (**2a**-Cl), X = Br (**2a**-Br); Ar = Ph, X = Cl (**2b**-Cl), X = Br (**2b**-Br); Ar = 4-$CH_3C_6H_4$, X = Cl (**2c**-Cl), X = Br (**2c**-Br); Ar = 4-BrC_6H_4, X = Br (**2d**-Br)] and $(4\text{-}CF_3C_6H_4)_4(CH_3)TeX$ [X = Cl (*trans*-**7a**-Cl) and X = Br (*trans*-**7a**-Br)] were synthesized by the following methods: 1) one-pot synthesis of **1a**, 2) the reaction of SO_2Cl_2 or Br_2 with $Ar_5Te^-Li^+$ generated from $TeCl_4$ or $TeBr_4$ with five equivalents of ArLi, 3) reductive cleavage of $Ar_{6-m}(CH_3)_mTe$ ($m=0$ or 2) with KC_8 followed by treatment with CH_3I, 4) valence expansion reaction from low-valent tellurium compounds by treatment with KC_8 followed by reaction with CH_3I, 5) nucleophilic substitution of $Ar_{6-y-z}(CH_3)_zTeX_{y-z}$ (X = Cl, Br, OTf; $z=0$, 1; $y=1$, 2) with organolithium reagents. The scope and limitations and some details for each method are discussed and electrophilic halogenation of the hexaorganotellurium compounds is also described.

Keywords: hypervalent anions · organotellurium compounds · tellurium

Introduction

Organotellurium compounds have been utilized in organic synthesis[1] and the structures and reactivity of dialkyltellurides, dialkyltellurium oxides, and trialkyltellurium halides have been thoroughly investigated.[2] Although considerable attention has been paid to the hypervalency of some tetraorganotellurium compounds,[3] of the hexavalent organotellurium compounds bearing more than five Te–C bonds, $(CH_3)_6Te$[4] was the only structurally characterized compound until our recent reports.[5,6] We reported several new synthetic procedures for novel types of hexavalent organotellurium compounds bearing five or six Te–C bonds; 1) first synthesis of $(4\text{-}CF_3C_6H_4)_6Te$ (**1a**) by one-pot reaction of 4-$CF_3C_6H_4Li$ and $TeCl_4$ together with synthesis of Ph_6Te (**1b**) by reaction of Ph_4TeF_2 with PhLi,[5a,b] 2) Ph_5TeCl (**2b**-Cl) and Ph_5TeBr (**2b**-Br) by the reaction of SO_2Cl_2 or Br_2, respectively, with $Ph_5Te^-Li^+$ generated from $TeCl_4$ or $TeBr_4$ with five equivalents of PhLi,[5c,d] 3) $(4\text{-}CF_3C_6H_4)_5(CH_3)Te$ (**3a**) from $(4\text{-}CF_3C_6H_4)_5Te^-K^+C_8$ by treatment with CH_3I, [5e] and 4) $(4\text{-}CH_3C_6H_4)_5(CH_3)Te$ (**3c**) from $(4\text{-}CH_3C_6H_4)_2Te$ by treatment with KC_8 followed by reaction with CH_3I.[5f] These methods recently reported by us are illustrated in Scheme 1.

However, since most of the methods were reported as communications, synthetic details, structural properties, and especially reactivities of these newly prepared hexavalent organotellurium compounds bearing five or six Te–C bonds were not included. In addition, we need to show the scope and limitations of these synthetic procedures because some are only applicable for certain substituents. Here we report the scope and details of the synthetic method for hexaorganotellurium compounds, including some new compounds. We also describe the electrophilic halogenation of these compounds to give the corresponding halides, which were

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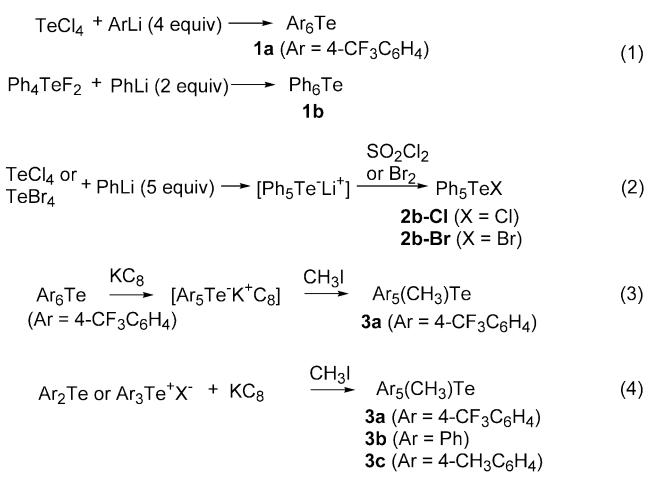
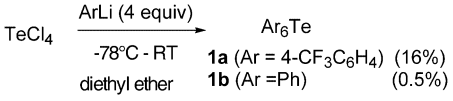


Scheme 1. Synthesis of hexavalent organotellurium compounds reported by us.

converted to new unsymmetrically substituted hexaorganotellurium compounds by organolithium reagents. Structural properties, especially X-ray structural analysis of pentaaryltellurium halides and of the corresponding pentaaryltellurium cations (square-pyramid (SP) or trigonal-bipyramid (TBP)), will be reported separately, together with the coordination behavior of the cations with some nucleophiles.

Results and Discussion

Synthesis of hexaaryltellurium compounds based on the one-pot procedure: In our previous report,[5a,b] (4-$CF_3C_6H_4)_6$Te (**1a**) was prepared by the one-pot reaction of 4-$CF_3C_6H_4$Li and $TeCl_4$ in 16% yield as shown in Scheme 2.

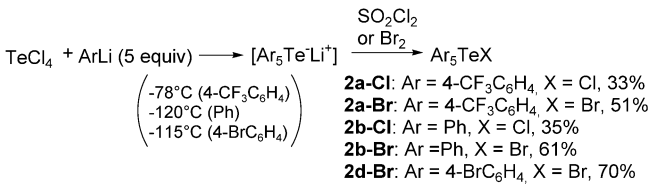


Scheme 2. One-pot synthesis of hexaaryltellurium compounds.

But Ph_6Te (**1b**) was prepared by the stepwise reaction of Ph_4TeF_2 with PhLi since the one-step procedure gave Ph_6Te in only 0.5% yield even after careful examination of the reaction conditions.

Since the possible mechanism for the formation of (4-$CF_3C_6H_4)_6$Te is a complicated multistep process, the one-pot method is applicable only for the synthesis of (4-$CF_3C_6H_4)_6$Te (**1a**).

Synthesis of Ar_5TeCl (or Ar_5TeBr) by the reaction of SO_2Cl_2 (or Br_2) with $Ar_5Te^-Li^+$: In our previous report,[5c,d] Ph_5TeCl (**2b-Cl**) and Ph_5TeBr (**2b-Br**) were prepared by halogenation of $Ph_5Te^-Li^+$, which was prepared by the reaction of five equivalents of PhLi with one equivalent of $TeCl_4$ or $TeBr_4$. The reaction should be carried out at very low temperatures (−120 °C for **2b-X**). The method can be applied to the synthesis of (4-$CF_3C_6H_4)_5$TeX (**2a-Cl** and **2a-Br**) and (4-$BrC_6H_4)_5$TeBr (**2d-Br**) as shown in Scheme 3. However, after several attempts, we found that the temperature required for efficient trapping of $Ar_5Te^-Li^+$ with the halogenating reagents was different for each substituent. That is,



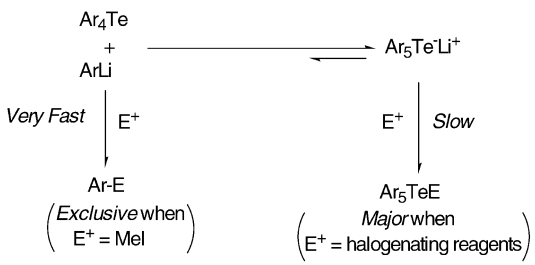
Scheme 3. Synthesis of pentaaryltellurium halides.

very low temperatures (−115 to −120 °C) are necessary for **2b** and **2d**, but a relatively high temperature (−78 °C) was applicable for **2a**.

$Ph_5Te^-Li^+$[7] was reported to be in equilibrium with the mixture of Ph_4Te and PhLi and the equilibrium is shifted to $Ph_5Te^-Li^+$ at very low temperatures (−120 °C) in THF (which solvates Li^+ efficiently). Since (4-$CF_3C_6H_4)_5Te^-Li^+$ bearing an electron-withdrawing substituent should be more stable than $Ph_5Te^-Li^+$, (4-$CF_3C_6H_4)_5Te^-Li^+$ should be the predominant species in the equilibrium even at −78 °C. In contrast, (4-$CH_3C_6H_4)_5$TeX bearing an electron-donating substituent could not be obtained by the procedure.

In addition, the reactivity of electrophiles for the reaction with the equilibrium mixture including $Ar_5Te^-Li^+$ is also crucial in the reaction. For example, the reaction of CH_3I (weaker electrophile than halogenating reagents) with the equilibrium mixture including $Ph_5Te^-Li^+$ did not give $Ph_5(CH_3)Te$ (**3b**) efficiently. Only after very careful experiments, could a 1% yield of **3b** be obtained by the reaction of $TeCl_4$ with five equivalents of PhLi followed by treatment with excess CH_3I (7.5 equivalents) at −105 °C. In the case of (4-$CF_3C_6H_4)_5Te^-Li^+$, (4-$CF_3C_6H_4)_5(CH_3)$Te was not obtained at all.

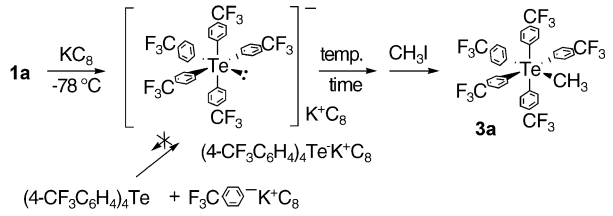
Although $Ar_5Te^-Li^+$ derivatives were known to be the predominant species in the equilibrium with Ar_4Te and ArLi, the reaction rate of the weak electrophile (CH_3I) with ArLi should be much higher than that with $Ar_5Te^-Li^+$, where a higher temperature would be necessary for the reaction to occur. On the other hand, the energy barrier of the reaction of $Ar_5Te^-Li^+$ with strong halogenating reagents such as Br_2 should be much lower, and even at low temperatures the reaction could proceed to give Ar_5TeX (**2-X**) (Scheme 4).



Scheme 4. Electrophilic trapping of lithium pentaaryltelluride, which is in equilibrium with tetraaryltellurium and aryllithium.

However, the situation was dramatically different for (4-$CF_3C_6H_4)_5Te^-K^+C_8$, which could be methylated easily by CH_3I.[5e]

Reductive cleavage of one of the Te–C bonds in (4-$CF_3C_6H_4)_6$Te and the related hexaorganotellurium compounds: formation and reactions of $Ar_5Te^-K^+C_8$: As was previously communicated,[5a,b] (4-$CF_3C_6H_4)_6$Te showed remarkable stability toward chromatographic treatment, thermolysis (up to 300 °C) or photolysis, alkyllithium reagents (MeLi, *n*BuLi, or *t*BuLi), and some strong reducing reagents (lithium naphthalenide, 4,4′-di-*tert*-butylbiphenylide, Na/K alloy, K, or Na/Hg amalgam etc.). However, we found recently that the reaction of (4-$CF_3C_6H_4)_6$Te with KC_8 proceeded smoothly even at −78 °C in THF and the expected anion (4-$CF_3C_6H_4)_5Te^-K^+C_8$ was generated quantitatively.[5c] A singlet signal ($\delta = 600$ ppm at −45 °C), which could be assigned to (4-$CF_3C_6H_4)_5Te^-K^+C_8$, was observed by ^{125}Te NMR spectroscopy. Although (4-$CF_3C_6H_4)_5(CH_3)$Te (**3a**) could not be prepared from $CF_3C_6H_4)_5Te^-Li^+$ under various conditions, **3a** was obtained quantitatively from (4-$CF_3C_6H_4)_5Te^-K^+C_8$ (Scheme 5). The yields of **3a** at various temperature implied that (4-$CF_3C_6H_4)_5Te^-K^+C_8$ could be stable up to −20 °C (Table 1).



Scheme 5. Synthesis of pentakis(4-trifluoromethyl-phenyl)methyltellurium by reduction of **1a** with KC_8 followed by treatment with CH_3I.

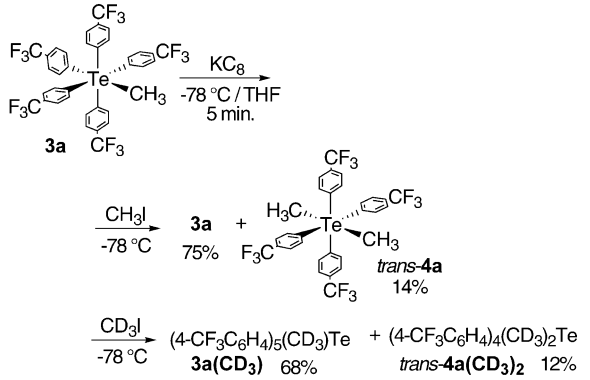
Table 1. Yields of **3a** from **1a** and KC_8.

Temp [°C]	Time [h]	**3a** [%]
−78	1	98
−45	1	98
−45	12	35
−20	1	98
0	0.5	15
RT	0.5	0[a]

[a] (4-$CF_3C_6H_4)_2$Te, (4-$CF_3C_6H_4)_2$, and 4-$CF_3C_6H_4$I were obtained.

The large difference of the reactivities between (4-$CF_3C_6H_4)_5Te^-Li^+$ and (4-$CF_3C_6H_4)_5Te^-K^+C_8$ toward CH_3I strongly indicated that (4-$CF_3C_6H_4)_5Te^-K^+C_8$ should be the exclusive species in the equilibrium with (4-$CF_3C_6H_4)_4$Te and (4-$CF_3C_6H_4$)KC_8, if any (Scheme 5). Since the potassium cation is intercalated by graphite,[8] the resultant K^+C_8 system can be regarded as a noncoordinating cation and does not aggregate. That is, typical contact-ion pairing is suppressed by intercalation of K^+ into graphite. Since (4-$CF_3C_6H_4$)KC_8 should be quite nucleophilic because of the lack of aggregation, the equilibrium between (4-$CF_3C_6H_4)_5Te^-K^+C_8$, (4-$CF_3C_6H_4)_4$Te, and (4-$CF_3C_6H_4$)KC_8 shifted toward (4-$CF_3C_6H_4)_5Te^-K^+C_8$, which became the exclusive anion.

With heteroleptic hexavalent organotellurium compounds such as (4-$CF_3C_6H_4)_5(CH_3)$Te (**3a**) having five aryl groups and one methyl group in hand, it is interesting to examine the selectivity of the Te–C (Te–Ar or Te–CH_3) bond cleavage. The reaction of **3a** with excess KC_8 was carried out at −78 °C in THF, followed by treatment with CH_3I. The products were separated and purified by recycling HPLC and the dimethyl derivative, (4-$CF_3C_6H_4)_4(CH_3)_2$Te (*trans*-**4a**), was isolated in 14% yield together with 75% recovery of **3a** (Scheme 6). Based on the NMR spectroscopic analyses, (4-



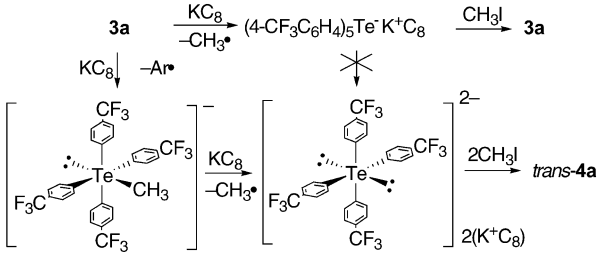
Scheme 6. Synthesis of *trans*-**4a** by reduction of **3a** with KC_8 followed by treatment with CH_3I (or CD_3I).

$CF_3C_6H_4)_4(CH_3)_2$Te was characterized as a *trans* isomer. In the ^{1}H NMR, a singlet (6H) derived from two equivalent methyl groups appeared at $\delta = 2.25$ ppm. In addition, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy showed that all of the four 4-$CF_3C_6H_4$ groups were equivalent. The structure of **4a** was further confirmed to be *trans* by X-ray analysis.[5e] The crystal structure of *trans*-**4a** revealed that it had almost perfect octahedral symmetry around the tellurium center. The ^{125}Te NMR spectrum exhibited a signal at $\delta = 272$ ppm, which was upfield shifted from the monomethyl compound **3a** ($\delta =$ 345 ppm).

Signals assigned to the *cis* isomer were not observed in the products, and isomerization of *trans*-**4a** to the corresponding *cis*-**4a** did not take place even at 230–250 °C for 1 h in the solid state. Most of *trans*-**4a** was recovered and the decomposition product, (4-$CF_3C_6H_4)_2$Te, was obtained in small amounts.

To clarify the mechanism of the reaction of (4-$CF_3C_6H_4)_5(CH_3)$Te (**3a**) with KC_8, CD_3I was used instead of CH_3I after the reduction was complete. Only deuterated compounds, (4-$CF_3C_6H_4)_5(CD_3)$Te (**3a(CD$_3$)**) (68%) and (4-$CF_3C_6H_4)_4(CD_3)_2$Te (*trans*-**4a(CD$_3$)$_2$**) (12%) with high CD_3 contents, were obtained (Scheme 6). These results showed that cleavage of the tellurium–carbon bonds took place almost quantitatively and the Te–CH_3 bond was preferentially cleaved over the five Te–Ar bonds. A plausible mechanism is shown in Scheme 7.

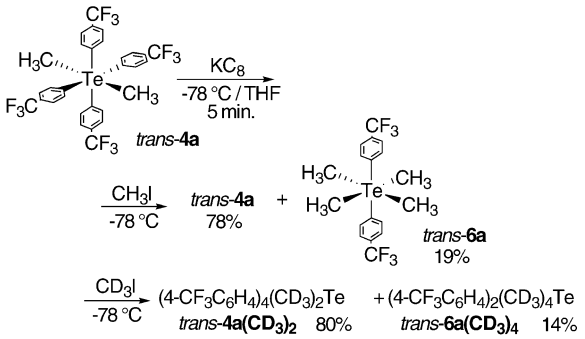
As a first step, one-electron reduction took place followed by the preferred formation of (4-$CF_3C_6H_4)_5Te^-K^+C_8$ and



Scheme 7. Possible mechanism for formation of **3a** and *trans*-**4a** in the reduction of **3a** with KC_8 followed by treatment with CH_3I.

$CH_3^{\bullet}$ over that of $(4\text{-}CF_3C_6H_4)_4(CH_3)Te^-K^+C_8$ and $(4\text{-}CF_3C_6H_4)^{\bullet}$. The selectivity (68:12) would be related to the higher stability of $(4\text{-}CF_3C_6H_4)_5Te^-K^+C_8$ over $(4\text{-}CF_3C_6H_4)_4(CH_3)Te^-K^+C_8$, which decompose to $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$. Formation of *trans*-**4a(CD$_3$)$_2$** indicated the presence of a novel species, the hypervalent 12-Te-4 dianion, $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$. ^{125}Te NMR spectra of supernatant of the reaction mixture from **3a** with KC_8 in THF at −78 °C before addition of CH_3I showed two signals at $\delta =$ 591 ppm {corresponding to $(4\text{-}CF_3C_6H_4)_5Te^-K^+C_8$ ($\delta =$ 600 ppm at −45 °C)} and $\delta = 385$. The latter higher field signal could be assigned to $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$ since **3a** and *trans*-**4a** were obtained almost quantitatively after addition of CH_3I to the solution. It should be pointed out that conversion of $(4\text{-}CF_3C_6H_4)_5Te^-K^+C_8$ to $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$ did not take place because only one of the six Te–Ar bonds in $(4\text{-}CF_3C_6H_4)_6Te$ (**1a**) was cleaved even in the excess use of KC_8 (Scheme 5).

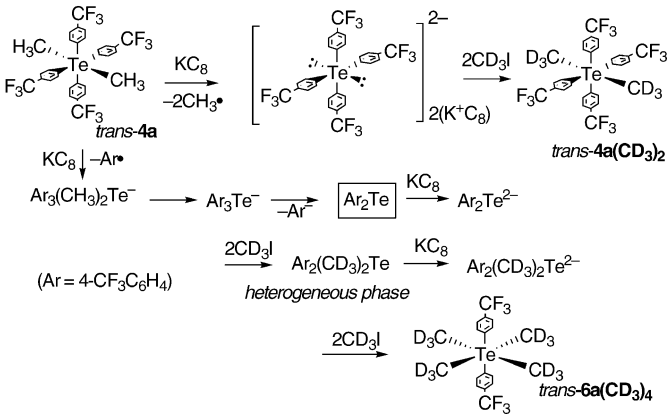
Successful synthesis of *trans*-**4a** led us to the investigation of the reductive cleavage of *trans*-**4a** with KC_8. The reaction of *trans*-**4a** with excess KC_8 was carried out at −78 °C followed by addition of CH_3I. After HPLC separation of crude products, *trans*-**4a** was recovered in 78% yield and newly formed $(4\text{-}CF_3C_6H_4)_2(CH_3)_4Te$ (*trans*-**6a**) was obtained in 19% yield (Scheme 8).



Scheme 8. Synthesis of *trans*-**6a** by reduction of *trans*-**4a** with KC_8 followed by treatment with CH_3I (or CD_3I).

The characterization of *trans*-**6a** was performed by spectroscopic methods and elemental analyses. X-ray analysis of *trans*-**6a** confirmed the octahedral structure, which was similar to that of *trans*-**4a**. The two $4\text{-}CF_3C_6H_4$ groups in *trans*-**6a** were located *trans* to each other.[5f]

CD_3I was also used instead of CH_3I to elucidate the mechanism of formation of the unexpected product, *trans*-**6a**. Deuterated compounds, $(4\text{-}CF_3C_6H_4)_4(CD_3)_2Te$ (*trans*-**4a(CD$_3$)$_2$**) and $(4\text{-}CF_3C_6H_4)_2(CD_3)_4Te$ (*trans*-**6a(CD$_3$)$_4$**), were obtained in similar yields (80:14) to the reaction with CH_3I and their CD_3 contents were almost quantitative (Scheme 8). High CD_3 contents of *trans*-**6a(CD$_3$)$_4$** implied that the quantitative cleavage of all Te–CH_3 bonds in *trans*-**4a** had occurred. ^{125}Te NMR of the reaction mixture before addition of CH_3I at −78 °C showed that the signal at $\delta =$ 385 ppm attributed to $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$ was dominant, but assignments for other many detectable signals were unsuccessful. This complicated multi-step mechanism (Scheme 9) will be considered below.

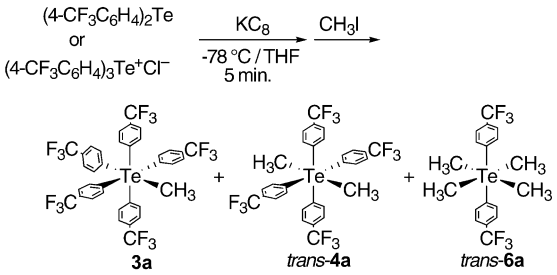


Scheme 9. Possible mechanism for formation of *trans*-**4a(CD$_3$)$_2$** and *trans*-**6a(CD$_3$)$_4$** in the reduction of *trans*-**4a** with KC_8 followed by treatment with CD_3I.

In this hypothetical mechanism, when the two Te–CH_3 bonds bonds were cleaved, $(4\text{-}CF_3C_6H_4)_4Te^{2-}(K^+C_8)_2$ would be generated as discussed in Scheme 7 and was trapped with CH_3I to give *trans*-**4a**. Since *trans*-**4a** was the predominant product, this reaction should be the main pathway. Since $Ar_3(CH_3)_2Te^-$ generated by cleavage of the tellurium–aryl bond would be less stable than Ar_5Te^-, continuous cleavage took place to give corresponding divalent species such as Ar_2Te. Then KC_8 transferred electrons to Ar_2Te to form the dianion species, Ar_2Te^{2-}, followed by reactions with electrophilic reagents and KC_8 successively. Since the hypothetical mechanism indicated a possible new method for generation of hexaorganotellurium compounds from divalent organotellurium, the reaction of KC_8 with Ar_2Te and other low-valent organotellurium compounds are examined.[5f]

Valence expansion reactions from low valent organotellurium compounds to hexaorganotellurium compounds: The reaction of $(4\text{-}CF_3C_6H_4)_2Te$ with excess KC_8 proposed above was separately carried out at −78 °C in THF for 5 min followed by treatment with CH_3I. Fortunately, we could obtain hexavalent tellurium compounds, **3a** (4%), *trans*-**4a** (9%), and *trans*-**6a** (10%) as expected (Scheme 10).

This novel valence expansion reaction could be carried out from other various lower valent tellurium compounds



Scheme 10. Synthesis of hexaorganotellurium from lower valent organotellurium compounds.

such as $(4\text{-}CF_3C_6H_4)_3Te^+Cl^-$, and the results are summarized in Table 2. It should be noted that CH_3K[9] or $PhCH_2K$[10] could be used instead of KC_8, showing that CH_3K or $PhCH_2K$ acted as electron-donating reagents similar to KC_8 in these systems.

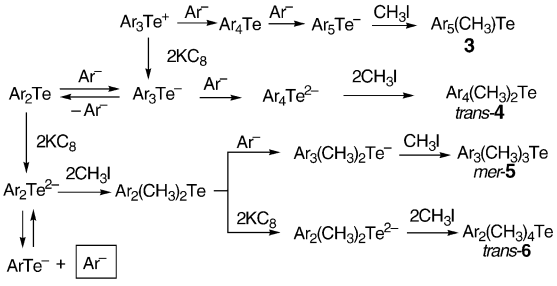
Table 2. Yields of the reaction of organotellurium compounds with KC_8 (15 equivalents) or CH_3K (2 equivalents) or $PhCH_2K$ (1 equivalent) after treatment with CH_3I (30 equivalents).

Starting material	Reagents	Yields [%, based on Te]		
		3a	*trans*-**4a**	*trans*-**6a**
$(4\text{-}CF_3C_6H_4)_2Te$	KC_8	4	9	10
	CH_3K	no	11	no
	$PhCH_2K$	no	13	no
$(4\text{-}CF_3C_6H_4)(CH_3)Te$	KC_8	no	no	4
$(4\text{-}CF_3C_6H_4)_3Te^+Cl^-$	KC_8	21	7	7
	CH_3K	16	6	no
$(4\text{-}CF_3C_6H_4)_2(CH_3)Te^+CF_3SO_3^-$	KC_8	no	31	4
$(4\text{-}CF_3C_6H_4)(CH_3)_2Te^+I^-$	KC_8	no	no	16
		3b	*trans*-**4b**	*trans*-**6b**
$Ph_3Te^+Br^-$[a]	KC_8	19	12	no
		3c	*trans*-**4c**	*trans*-**6c**
$(4\text{-}CH_3C_6H_4)_3Te^+Cl^-$[b]	KC_8	36	0.2	6

[a] C_6H_5I (4 equivalents) was added. [b] $4\text{-}CH_3C_6H_4I$ (4 equivalents) was added.

A possible mechanism is illustrated in Scheme 11 although the detailed reaction mechanism is not yet clear.

To clarify the mechanism, the effects of the amount of reagents (KC_8 and CH_3I) on the product yields were investigated in the reaction of $(4\text{-}CF_3C_6H_4)_2Te$ (Table 3).



Scheme 11. Possible mechanism for the formation of hexavalent organotellurium compounds in the reduction of low valent organotellurium compounds with KC_8 followed by treatment with CH_3I.

Table 3. Effects of equivalents of the reagents (KC_8 and CH_3I) on the products and the yields in the reaction of $(4\text{-}CF_3C_6H_4)_2Te$.

Equivalents		Yields [%, based on Te]			
KC_8	CH_3I	**3a**	*trans*-**4a**	*trans*-**6a**	
1	8	–	–	–	$(4\text{-}CF_3C_6H_4)_2Te$ recovered
5	8	–	21	–	$(4\text{-}CF_3C_6H_4)_2Te$ 38 % $(4\text{-}CF_3C_6H_4)(CH_3)$ Te 27 %
10	11	–	31	–	
15	30	4	9	10	

When an equimolar amount of KC_8 to $(4\text{-}CF_3C_6H_4)_2Te$ was used, no hexaorganotellurium compounds were obtained, but instead the starting material was recovered. In the case where five equivalents of KC_8 were used, *trans*-**4a** along with the starting $(4\text{-}CF_3C_6H_4)_2Te$ and $(4\text{-}CF_3C_6H_4)(CH_3)Te$, which implied the generation of $(4\text{-}CF_3C_6H_4)Te^-$, were obtained. These results strongly indicated the formation of $ArTe^-$ and Ar^- as was proposed in the mechanism of Scheme 11. By comparison of the results from ten equivalents of KC_8 with those from fifteen equivalents of KC_8, it could be confirmed that when more KC_8 was used, the electron transfer from KC_8 was greater, which in turn effected the cleavage of Ar^-, and the the yields of methylated products increased (Table 3).

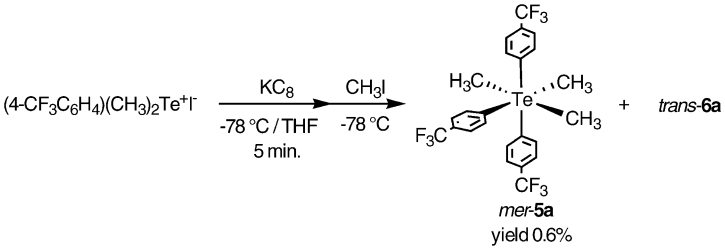
Based on this mechanism, the aryl anion derived from the equilibrium between Ar_2Te^{2-} and $ArTe^-$ should behave as a key intermediate since an aryl source is needed to provide hexavalent compounds having more aryl ligands than the starting material, for example, **3a** or *trans*-**4a**. To examine the effect of equivalents of added aryl halides on the yields of the products, four equivalents of $4\text{-}CF_3C_6H_4Br$ were added to a mixture of $(4\text{-}CF_3C_6H_4)_2Te$ and excess KC_8 (Table 4). As expected, the yields of *trans*-**4a** (27 %) were

Table 4. Effects of equivalents of $4\text{-}CF_3C_6H_4Br$ on the products and yields in the reaction of $(4\text{-}CF_3C_6H_4)_2Te$ with KC_8.

Equivalents	Yields [%, based on Te]		
$4\text{-}CF_3C_6H_4Br$	**3a**	*trans*-**4a**	*trans*-**6a**
2	4	9	10
4	–	27	9
6	–	26	6

increased in comparison with the results of two equivalents of the bromide, and the sum of the yields for hexavalent compounds also improved from 23 % to 36 %. Although addition of six equivalents of $4\text{-}CF_3C_6H_4Br$ did not give better results (26 % of *trans*-**4a** and 6 % of *trans*-**6a**), these results showed that the addition of aryl halides was effective and that the corresponding aryl anion played an important role in the reaction.

Based on the possible mechanism in Scheme 11, the formation of the trimethyl derivative, $(4\text{-}CF_3C_6H_4)_3(CH_3)_3Te$ (**5a**), should be possible. To isolate **5a**, we made efforts to optimize the reaction conditions and finally **5a** was obtained though in very small amount (ca. 0.6 %) in a larger scale reaction of $(4\text{-}CF_3C_6H_4)(CH_3)_2Te^+I^-$ together with *trans*-**6a** (10 %; Scheme 12).



Scheme 12. Formation of *mer*-**5a** in the reaction of (4-$CF_3C_6H_4)(CH_3)_2Te^+I^-$ with KC_8.

The observed signals in ^1H and ^{19}F NMR spectra are in good agreement with the *meridional* isomer of **5a** (integral ratios for the three Ar and the three CH_3 groups were 2:1) and another possible isomer, the *facial* isomer, was not observed. The ^{125}Te NMR spectrum showed a singlet at $\delta =$ 201 ppm, which is expected for the trimethyl derivative, since the chemical shift was in between those of *trans*-**4a** ($\delta = 272$ ppm) and *trans*-**6a** ($\delta = 119$ ppm). Unfortunately, X-ray analysis of *mer*-**5a** was not successful.

These results also indicated that the unique valence expansion reactions could be applicable for the synthesis of new hexavalent tellurium compounds with mixed carbon ligands. In fact, we could obtain hexaorganotellurium species possessing 4-$CH_3C_6H_4$ ligands, which could not be prepared otherwise. The X-ray structure of (4-$CH_3C_6H_4)_4(CH_3)_2Te$ (*trans*-**4c**) is shown in Figure 1.

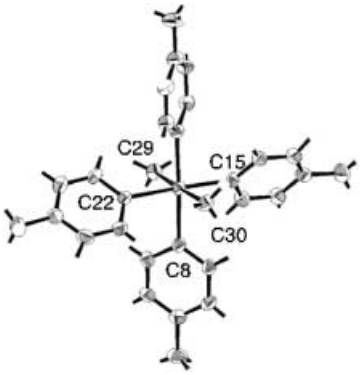
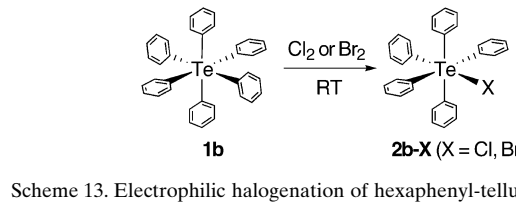


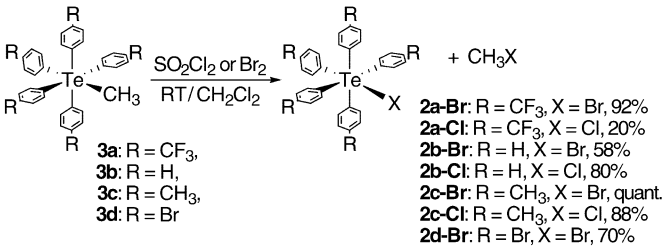
Figure 1. X-ray structure of *trans*-**4c** (30% thermal ellipsoids). Selected bond lengths [Å]: Te–C1(aryl) 2.200(2), Te–C8(aryl) 2.207(2), Te–C15(aryl) 2.201(2), Te–C22(aryl) 2.212(2), Te–C29(methyl) 2.183(2), Te–C30(methyl) 2.200(2).

Electrophilic halogenation of hexaorganotellurium compounds: The electrophilic halogenation reactions of the newly prepared hexaorganotellurium compounds is interesting because the reaction of the permethylated tellurium compound, $(CH_3)_6Te$, with Br_2 was reported to result in quantitative formation of $TeBr_4$ and CH_3Br.[4a] Although (4-$CF_3C_6H_4)_6Te$ did not react with strong halogenating reagents (Cl_2 or Br_2), Ph_6Te reacted with Cl_2 or Br_2 at room temperature to afford the corresponding monohalide, Ph_5TeX (**2b-X**) (X = Cl, Br), respectively (Scheme 13).[5d]

Interestingly, the reaction of (4-$CF_3C_6H_4)_5(CH_3)Te$ with Br_2 proceeded smoothly at room temperature within five minutes to give only (4-$CF_3C_6H_4)_5TeBr$ (**2a-Br**) in 92% yield (Scheme 14). Br_2 cleaved the Te-CH_3 bond exclusively without cleavage of the Te–Ar bond and (4-$CF_3C_6H_4)_4(CH_3)TeBr$ was not detected. Other monomethyl derivatives, **3b**, **3c**, and **3d** also reacted with excess Br_2 to



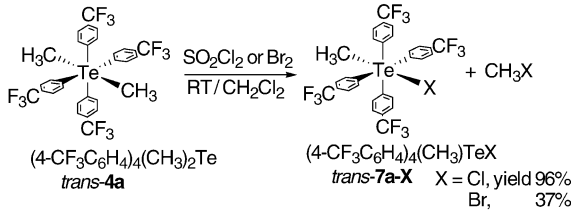
Scheme 13. Electrophilic halogenation of hexaphenyl-tellurium.



Scheme 14. Electrophilic halogenation of pentaaryl-methyltellurium to give pentaaryltellurium halide.

afford the corresponding monobromide in good yields [Ph_5TeBr (**2b-Br**: 58% yield), (4-$CH_3C_6H_4)_5TeBr$ (**2c-Br**: quantitative yield), and (4-$BrC_6H_4)_5TeBr$ (**2d-Br**: 70% yield)]. Similarly, SO_2Cl_2 also reacted with **3** to give the corresponding monochlorides [(4-$CF_3C_6H_4)_5TeCl$ (**2a-Cl**: ca. 20% yield), Ph_5TeCl (**2b-Cl**: 80% yield), (4-$CH_3C_6H_4)_5TeCl$ (**2c-Cl**: 88% yield)]. The reaction of **3a** with SO_2Cl_2 was found to be sluggish, and more than 70% of **3a** was recovered after five minutes. These results indicated that the compound having more electron-donating substituents reacted more easily.

Similary, *trans*-**4a** was reacted with Br_2 or SO_2Cl_2 to give (4-$CF_3C_6H_4)_4(CH_3)TeX$ (*trans*-**7a-X**; X = Br or Cl) in 37 or 96% isolated yield, respectively (Scheme 15). Also in this



Scheme 15. Electrophilic halogenation of tetraaryl-dimethyltellurium.

case, only one CH_3 group was cleaved to give the corresponding halide exclusively even when excess Br_2 or SO_2Cl_2 was used. Since *trans*-**7a-Br** was unstable, the isolated yield of *trans*-**7a-Br** was low. The molecular structure of *trans*-**7a-Cl** was confirmed by NMR spectroscopy and the X-ray analysis (Figure 2).

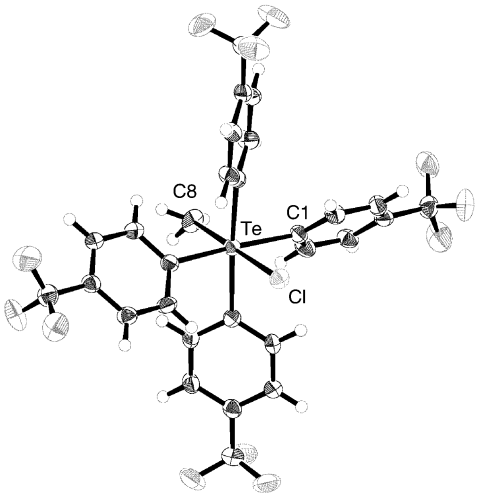
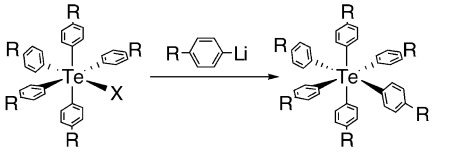


Figure 2. X-ray structure of *trans*-**7a**-Cl (30% thermal ellipsoids). Selected bond lengths [Å]: Te–C1(aryl) 2.189(2), Te–C8(methyl) 2.12(2), Te–Cl 2.539(4).

Nucleophilic reactions of Ar_5TeX with organolithium reagents: With several pentaorganotellurium halides in hand, nucleophilic substitution reaction of the halide with carbon nucleophiles was examined (Scheme 16).

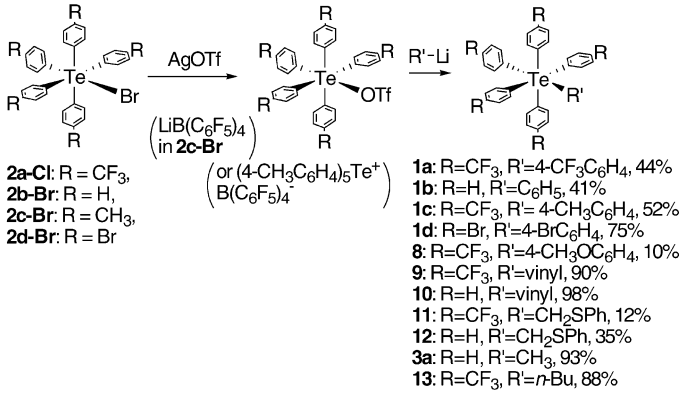


Scheme 16. Synthesis of hexaorganotellurium compounds from pentaaryltellurium halide.

However, the reactions shown in Scheme 16 were sluggish under S_N2 conditions and the reaction of Ph_5TeCl with excess PhLi in THF afforded the expected Ph_6Te in only 5% yield.

Therefore, to develop the efficient method for the nucleophilic substitution (S_N1 type), treatment of the halide with silver triflate (AgOTf: Tf = trifluoromethanesulfonyl) was carried out before addition of the nucleophile. The structures of the triflate will be discussed in a separate paper. The yields were much improved as expected in the synthesis of **1a**–**1d**, and various new unsymmetrically substituted hexaorganotellurium compounds could be prepared by the procedures (Scheme 17). ORTEP drawings of **1d** and **9** are shown in Figure 3 and 4, respectively.

Interestingly, the similar reaction of *trans*-**7a**-**Cl** by AgOTf followed by nucleophilic reaction with CH_3Li afforded *cis*-dimethyl compound (*cis*-**4a**) in 44% yield (Scheme 18). The NMR spectral data (^1H, ^{13}C, and ^{19}F) of the product were in agreement with *cis*-**4a**, which has two different 4-$CF_3C_6H_4$ groups based on its symmetry, and a ^{125}Te NMR signal appeared at the same position as its other



Scheme 17. Improved synthesis of hexaorganotellurium compounds from pentaaryltellurium triflate.

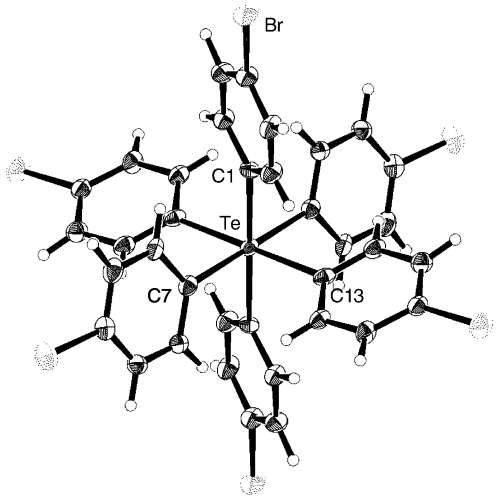


Figure 3. X-ray structure of **1d** (30% thermal ellipsoids). Selected bond lengths [Å]: Te–C1(aryl) 2.220(7), Te–C7(aryl) 2.245(8), Te–C13(aryl) 2.244(8).

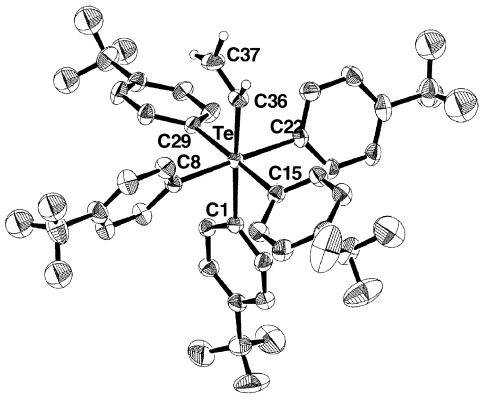
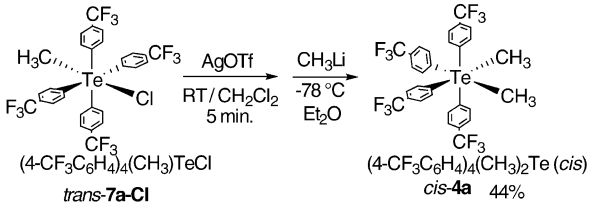


Figure 4. X-ray structure of **9** (30% thermal ellipsoids). Selected bond lengths [Å]: Te–C1(aryl) 2.238(5), Te–C8(aryl) 2.218(5), Te–C15(aryl) 2.213(5), Te–C22(aryl) 2.221(6), Te–C29(aryl) 2.221(5), Te–C36(vinyl) 2.177(5).

isomer *trans*-**4a** ($\delta = 272$ ppm). The structural characterization of *cis*-**4a** was confirmed by X-ray analysis (Figure 5). The crystals of *cis*-**4a** melted at 236 °C without decomposi-



Scheme 18. Formation of *cis*-**4a** in the reaction of CH_3Li with *trans*-**7a-OTf**.

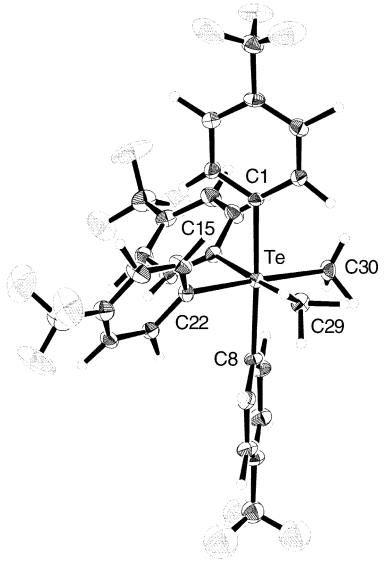


Figure 5. X-ray structure of *cis*-**4a** (30% thermal ellipsoids). Selected bond lengths [Å]: Te–C1(aryl) 2.223(5), Te–C8(aryl) 2.208(5), Te–C15(aryl) 2.218(4), Te–C22(aryl) 2.217(4), Te–C29(methyl) 2.187(4), Te–C30(methyl) 2.185(4).

tion, but the isomerization to *trans*-**4a** did not take place at all even after melting.

The reaction of *cis*-**4a** with Br_2 was carried out in a similar manner to the reaction of *trans*-**4a** with Br_2 and gave *trans*-**7a**-Br quantitatively. The possible mechanism of the isomerization will be discussed in a separate paper.

Conclusion

Herein, several new synthetic methods including nucleophilic reaction of pentaorganotellurium triflate with organolithium reagents are described together with detailed discussion on the scope and limitations of our recently reported methods for hexavalent organotellurium compounds. The triflats could be prepared by halogenation of hexaorganotellurium compounds followed by treatment with silver triflate. The results presented here show that hexavalent organotellurium compounds have provided new insights into a full picture of the nature of the hexacoordinate state of tellurium. A separate paper concerning the structures and properties of pentaorganotellurium halides which lead pentaorganotellurium cations will be presented in due course.

Experimental Section

General: Graphite powder (1–2 micron) was purchased from Aldrich Chemical Co. Elemental analyses were performed on a Perkin Elmer Model 2400. ^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 or AL-400 spectrometer. 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 a solvent. Compounds **1a**[5a,b] and **2b**[5c] were prepared by published procedures.

Synthesis of pentaaryltellurium halides: A solution of ArLi was prepared from ArBr (12.0 mmol) in diethyl ether (30 mL) and *n*BuLi (1.60 M solution in hexane, 769 mg, 12.0 mmol) at −78 °C. This solution of ArLi was added to a suspension of $TeCl_4$ (808 mg, 3.0 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred for 1.5 min at −78 °C, and then SO_2Cl_2 (405 mg, 3.0 mmol) or Br_2 (480 mg, 3.0 mmol) was added at −78 °C. The mixture was stirred for 2 h at −78 °C and was allowed to warm to room temperature. The crude products were separated by HPLC.

(4-$CF_3C_6H_4$)$_5$TeCl (2a-Cl): Yellow crystals; m.p. 242–243 °C; ^1H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.87$ (d, $^3J(H,H) = 8$ Hz, 2H), 7.75 (d, $^3J(H,H) = 8$ Hz, 2H), 7.63 (d, $^3J(H,H) = 8$ Hz, 8H), 7.57 ppm (d, $^3J(H,H) = 8$ Hz, 8H); ^1H NMR (C_6D_6, 25 °C, C_6D_5H): $\delta = 7.46$ (d, $^3J(H,H) = 8$ Hz, 8H), 7.39 (d, $^3J(H,H) = 8$ Hz, 2H), 7.15 (d, $^3J(H,H) = 8$ Hz, 8H), 7.07 ppm (d, $^3J(H,H) = 8$ Hz, 2H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.3$ (12F), −63.8 ppm (3F); ^{19}F NMR (C_6D_6, 25 °C, $CFCl_3$): $\delta = -62.6$ (12F), −63.1 ppm (3F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta =$ 157.1 (s, $^1J(C,Te) = 48$ Hz), 139.0 (s, $^1J(C,Te) = 153$ Hz), 134.4 (d), 133.6 (q, $^2J(C,F) = 33$ Hz), 133.4 (d), 132.2 (q, $^2J(C,F) = 33$ Hz), 126.7 (d), 125.3 (d), 123.5 (q, $^1J(C,F) = 272$ Hz), 123.2 ppm (q, $^1J(C,F) = 274$ Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 498.8$ ppm; elemental analysis calcd (%) for $C_{35}H_{20}ClF_{15}Te$: C 47.31, H 2.27; found: C 47.12, H 2.27.

(4-$CF_3C_6H_4$)$_5$TeBr (2a-Br): Yellow crystals; m.p. 274–275 °C; ^1H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.87$ (d, $^3J(H,H) = 8$ Hz, 2H), 7.73 (d, $^3J(H,H) = 8$ Hz, 2H), 7.63 (d, $^3J(H,H) = 8$ Hz, 8H), 7.56 ppm (d, $^3J(H,H) = 8$ Hz, 8H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.3$ (12F), −63.8 ppm (3F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 157.1$ (s, $^1J(C,Te) = 50$ Hz), 139.1 (s, $^1J(C,Te) = 158$ Hz), 134.4 (d), 133.7 (q, $^2J(C,F) = 31$ Hz), 133.4 (d), 132.2 (q, $^2J(C,F) = 33$ Hz), 126.6 (d), 125.3 (d), 123.6 (q, $^1J(C,F) = 272$ Hz), 123.3 ppm (q, $^1J(C,F) = 274$ Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 487.8$ ppm; elemental analysis calcd (%) for $C_{35}H_{20}F_{15}TeBr$: C 45.06, H 2.16; found: C 44.87, H 2.02.

Ph$_5$TeCl (2b-Cl): Yellow crystals; m.p. 215–216 °C; ^1H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.79$ (d, $^3J(H,H) = 7$ Hz, 2H), 7.56 (d, $^3J(H,H) = 7$ Hz, 8H), 7.49 (t, $^3J(H,H) = 7$ Hz, 1H), 7.39 (t, $^3J(H,H) = 7$ Hz, 2H), 7.34 (t, $^3J(H,H) = 7$ Hz, 4H), 7.23 ppm (t, $^3J(H,H) = 7$ Hz, 8H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 154.4$ (s), 134.8 (s), 134.2 (d), 133.4 (d), 131.9 (d), 130.7 (d), 129.2 (d), 127.7 ppm (d); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 533.9$ ppm; elemental analysis calcd (%) for $C_{30}H_{25}ClTe$: C 65.68, H 4.59; found: C 65.98, H 4.32.

Ph$_5$TeBr: Yellow crystals; m.p. 217 °C; ^1H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.77$ (d, $^3J(H,H) = 7$ Hz, 2H), 7.57 (d, $^3J(H,H) = 7$ Hz, 8H), 7.51 (d, $^3J(H,H) = 7$ Hz, 1H), 7.32–7.45 (m, 6H), 7.23 ppm (t, $^3J(H,H) = 7$ Hz, 8H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 153.7$ (s), 134.0 (d), 133.5 (s), 133.3 (d), 130.7 (d), 129.2 (d), 129.1 (d), 127.6 ppm (d); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 548.4$ ppm; elemental analysis calcd (%) for $C_{30}H_{25}BrTe$: C 60.76, H 4.249; found: C 60.87, H 4.38.

(4-BrC_6H_4)$_5$TeBr (2d-Br): Pale yellow needles; m.p. 220 °C (decomp); ^1H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.34$ (d, $^3J(H,H) = 9$ Hz, 8H), 7.38 (d, $^3J(H,H) = 9$ Hz, 8H), 7.55 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 124.5$ (s), 126.2 (s), 130.8 (d), 131.7 (s), 132.7 (d), 134.1 (d), 135.2 (d), 151.9 ppm (s, $^1J(C,Te) = 34$ Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 512$ ppm; elemental analysis calcd (%) for $C_{30}H_{20}Br_6Te$: C 36.49, H 2.04; found: C 36.71, H 2.01.

General procedure for the reduction with KC_8 and reductive cleavage of a Te–C bond in 1a: Potassium graphite (KC_8) was freshly prepared before every experiment. Graphite powder was added into a two- or three-necked round-bottomed flask with a stirring bar and dried well in vacuo with heating (using a heat gun), then the vessel was purged with

argon. Potassium cut into small pieces was rinsed with hexane and added to the graphite. The mixture was well stirred magnetically with heating, then preparation of KC_8 was confirmed by the observation of a brown colored powder. A solution of **1a** (1.55 g, 1.55 mmol) in THF (30 mL) was added to KC_8 (3.1 equivalents) at −78 °C. After 1 h of stirring, CH_3I (1.00 mL, 16.1 mmol) was added. The mixture was filtered through a Celite pad (graphite powder was removed) and volatile materials were evaporated under reduced pressure. Recycling HPLC gave 1.32 g (97.9 %) of **3a**.

(4-$CF_3C_6H_4$)$_5$(CH_3)Te (3a): Colorless needles; m.p. 258–259 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.35 (s, 3H), 7.45 (d, ^3J(H,H) = 8 Hz, 8H), 7.52 (d, ^3J(H,H) = 8 Hz, 8H), 7.54 (d, ^3J(H,H) = 8 Hz, 2H), 7.67 ppm (d, ^3J(H,H) = 8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): δ = −63.1 (12F), −63.3 ppm (3F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 33.8 (q, ^1J(C,Te) = 8 Hz, 12 Hz), 123.8 (q, ^1J(C,F) = 273 Hz), 123.8 (q, ^1J(C,F) = 273 Hz), 124.9 (d), 125.2 (d), 131.1 (q, ^2J(C,F) = 33 Hz), 131.2 (q, ^2J(C,F) = 33 Hz), 133.1 (d), 133.7 (d), 153.9 (s, ^1J(C,Te) = 21 Hz), 157.2 ppm (s, ^1J(C,Te) = 64 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 345 ppm; elemental analysis calcd (%) for $C_{36}H_{23}F_{15}Te$: C 49.81, H 2.67; found: C 49.62, H 2.41.

(4-$CF_3C_6H_4$)$_4$(CH_3)$_2$Te (4a): Colorless cubes, m.p. 275–276 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.25 (s, 6H), 7.40 (d, ^3J(H,H) = 8 Hz, 8H), 7.52 ppm (d, ^3J(H,H) = 8H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): δ = −63.1 ppm (s, 12F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 30.9 (q, ^1J(C,Te) = 13 Hz), 124.0 (q, ^1J(C,F) = 273 Hz), 124.7 (d), 130.6 (q, ^2J(C,F) = 33 Hz), 132.7 (d), 160.3 ppm (s, ^1J(C,Te) = 105 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 272 ppm; elemental analysis calcd (%) for $C_{30}H_{22}F_{12}Te$: C 48.82, H 3.00; found: C 48.71, H 2.91.

(4-$CF_3C_6H_4$)$_3$(CH_3)$_3$Te (*mer*-5a): A solution of (4-$CF_3C_6H_4$)(CH_3)$_2$Te$^+$I$^-$ (4.30 g, 10.0 mmol) in THF (200 mL) was added to KC_8 (11.6 equiv) at −78 °C. After 5 min of stirring, CH_3I (12.5 mL, 201 mmol) was added. Recycling HPLC gave *trans*-**4a** (t_R = 58 min, 48.7 mg, 0.0660 mmol, 0.660 %), *trans*-**6a** (t_R = 64 min, 477 mg, 0.998 mmol, 9.98 %), and *mer*-**5a** (t_R = 63 min, 37.3 mg, 0.0613 mmol, ca. 0.6 %). *mer*-**5a**: colorless plates, m.p. 219–220 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.06 (s, 3H), 2.07 (s, 6H), 7.32 (d, ^3J(H,H) = 8 Hz, 2H), 7.45 (d, ^3J(H,H) = 8 Hz, 2H), 7.56 (d, ^3J(H,H) = 8 Hz, 4H), 7.62 ppm (d, ^3J(H,H) = 8 Hz, 4H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): δ = −62.9 (s, 3F), −63.0 ppm (s, 6F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 33.5 (q), 33.7 (q), 124.0 (q, ^1J(C,F) = 273 Hz), 124.0 (q, ^1J(C,F) = 273 Hz), 124.3 (d), 124.7 (d), 130.0 (q, ^2J(C,F) = 33 Hz), 130.0 (q, ^2J(C,F) = 33 Hz), 131.5 (d), 132.1 (d), 162.2 (s), 162.9 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 201 ppm; elemental analysis calcd (%) for $C_{24}H_{21}F_9Te$: C 47.41, H 3.48; found: C 47.66, H 3.58.

(4-$CF_3C_6H_4$)$_2$(CH_3)$_4$Te (*trans*-6a): A solution of *trans*-**4a** (0.0384 g, 0.0520 mmol) in THF (5 mL)was added to KC_8 (43 equiv) at −78 °C. After the mixture had been stirred for 5 min, CH_3I (0.30 mL, 4.82 mmol) was added. Recycling HPLC gave *trans*-**4a** (30.0 mg; 78.2 %) and *trans*-**6a** (4.8 mg; 19.3 %). *trans*-**6a**: Colorless cubes, m.p. 223–224 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 1.88 (s, 12H), 7.64 (d, ^3J(H,H) = 8 Hz, 4H), 7.85 ppm (d, ^3J(H,H) = 8 Hz, 4H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): δ = −63.0 ppm (s, 6F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 36.3 (q, ^1J(C,Te) = 7 Hz), 124.2 (q, ^1J(C,F) = 273 Hz), 124.9 (d), 129.6 (q, ^1J(C,F) = 33 Hz), 130.5 (d), 165.9 ppm (s, ^1J(C,Te) = 173 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 119 ppm; elemental analysis calcd (%) for $C_{30}H_{22}F_{12}Te$: C 45.29, H 4.22; found: C 45.29, H 4.23.

Ph_4(CH_3)$_2$Te (*trans*-4b): A solution of $Ph_3Te^+Br^-$ (0.220 g, 0.501 mmol) and PhI (0.230 mL, 2.06 mmol) in THF (30 mL) was added to KC_8 (20.0 equiv) at −100 °C. After the mixture had been stirred for 1 min, CH_3I (1.30 mL, 20.9 mmol) was added. Recycling HPLC gave **3b** (50.6 mg, 0.0958 mmol, 19.1 %) and *trans*-**4b** (27.3 mg, 0.0586 mmol, 11.7 %). *trans*-**4b**: Colorless needles, m.p. 246–247 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.14 (s, 6H), 7.20 (t, ^3J(H,H) = 7 Hz, 8H), 7.28 (t, ^3J(H,H) = 7 Hz, 4H), 7.32 ppm (d, ^3J(H,H) = 7 Hz, 8H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 29.5 (q, ^1J(C,Te) = 17 Hz), 127.1 (d), 127.5 (d), 132.6 (d), 157.5 ppm (s, ^1J(C,Te) = 75 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 274 ppm; elemental analysis calcd (%) for $C_{26}H_{26}Te$: C 67.00, H 5.62; found: C 66.73, H 5.35.

(4-$CH_3C_6H_4$)$_5$(CH_3)Te (3c), (4-$CH_3C_6H_4$)$_4$(CH_3)$_2$Te (*trans*-4c), and (4-$CH_3C_6H_4$)$_2$(CH_3)$_4$Te (*trans*-6c): A solution of (4-$CH_3C_6H_4$)$_3$Te$^+$Cl$^-$ (2.18 g, 5.00 mmol) and 4-$CH_3C_6H_4$I (4.36 g, 20.0 mmol) in THF (150 mL) was added to KC_8 (15.3 equivalents) at −115 °C. After the mixture had been stirred for 5 min, CH_3I (10.0 mL, 161 mmol) was added. Recycling HPLC gave **3c** (t_R = 68 min, 1.13 g, 1.89 mmol, 36.3 %), *trans*-**4c** (t_R = 71 min, 6.4 mg, 0.0123 mmol, 0.245 %), and *trans*-**6c** (t_R = 71 min, 102 mg, 0.277 mmol, 5.54 %). **3c**: Colorless plates, m.p. 226–227 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.16 (s, 3H), 2.24 (s, 3H), 2.31 (s, 12H), 6.95 (d, ^3J(H,H) = 8 Hz, 2H), 6.97 (d, ^3J(H,H) = 8 Hz, 8H), 7.27 (d, ^3J(H,H) = 8 Hz, 8H), 7.50 ppm (d, ^3J(H,H) = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 21.0 (q), 21.1 (q), 33.0 (q, ^1J(C,Te) = 12 Hz), 127.7 (d), 127.9 (d), 133.1 (d), 133.7 (d), 137.0 (s), 137.1 (s), 148.5 (s, ^1J(C,Te) = 17 Hz), 151.9 ppm (s, ^1J(C,Te) = 50 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 341 ppm; elemental analysis calcd (%) for $C_{36}H_{38}Te$: C 72.27, H 6.40; found: C 72.02, H 6.60. *trans*-**4c**: Colorless needles, m.p. 272–273 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.07 (s, 6H), 2.33 (s, 12H), 7.00 (d, ^3J(H,H) = 8 Hz, 8H), 7.20 ppm (d, ^3J(H,H) = 8 Hz, 8H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 21.3 (q), 29.7 (q, ^1J(C,Te) = 15 Hz), 127.7 (d), 132.6 (d), 136.9 (s), 154.5 ppm (s, ^1J(C,Te) = 70 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 266 ppm; elemental analysis calcd (%) for $C_{30}H_{34}Te$: C 69.00, H 6.56; found: C 68.72, H 6.58. *trans*-**6c**: Colorless plates, M.p. 213–214 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 1.82 (s, 12H), 2.36 (s, 6H), 7.19 (d, ^3J(H,H) = 8 Hz, 4H), 7.63 ppm (d, ^3J(H,H) = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 21.3 (q), 35.5 (q, ^1J(C,Te) = 7 Hz), 128.4 (d), 129.9 (d), 136.7 (s), 159.8 ppm (s, ^1J(C,Te) = 126 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 113 ppm; elemental analysis calcd (%) for $C_{18}H_{26}Te$: C 58.43, H 7.08; found: C 58.20, H 7.29.

General procedures for bromination of hexaaryltellurium to give pentaarylbromotellurium (2-Br): Br_2 (5 drops, ca. 2.0 mmol) was added to a solution of **3** (0.2 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the mixture had been stirred for 3 h, volatile materials were evaporated. The crude product was almost pure **2-Br**. The spectra of **2a-Br** and **2b-Br** were identical to those described above.

(4-$CH_3C_6H_4$)$_5$TeBr (2c-Br): Yellow needles, m.p. 211–212 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.33 (s, 15H), 7.03 (d, ^3J(H,H) = 8 Hz, 10H), 7.47 ppm (d, ^3J(H,H) = 8 Hz, 10H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 21.1 (q), 128.2 (d), 133.2 (d), 139.2 (d), 150.7 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 536 ppm.

General procedures for chlorination of hexaaryltellurium to give pentaarylchlorotellurium (2-Cl): SO_2Cl_2 (10 drops, ca. 2.0 mmol) was added to a solution of **3** (0.1 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the mixture had been stirred for 5 min, volatile materials were removed in vacuo. The spectra of **2a-Cl** and **2b-Cl** were identical with those described above. (4-$CH_3C_6H_4$)$_5$TeBr (**2c-Cl**): Yellow needles, m.p. 180–181 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.33 (s, 15H), 7.02 (d, ^3J(H,H) = 8 Hz, 10H), 7.43 ppm (d, ^3J(H,H) = 8 Hz, 10H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 21.2 (q), 128.3 (d), 133.4 (d), 139.1 (d), 151.3 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 536 ppm.

(4-$CF_3C_6H_4$)$_4$(CH_3)TeBr (*trans*-7a-Br): Br_2 (5 drops, ca. 2.0 mmol) was added to a solution of *trans*-**4a** (0.148 g, 0.201 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the mixture had been stirred for 3 h, volatile materials were evaporated. Crude products were almost pure *trans*-**7a-Br**. Recycling HPLC gave *trans*-**7a-Br** (0.059 g, 0.074 mmol, 37 %); yellow plates, m.p. 119–120 °C (decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 2.61 (s, 3H), 7.56 ppm (s, 16H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): δ = −63.2 ppm (s, 12F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): δ = 19.1 (q, ^1J(C,Te) = 70 Hz), 123.4 (q, ^1J(C,F) = 273 Hz), 125.0 (d), 131.9 (q, ^2J(C,F) = 33 Hz), 131.9 (d), 158.0 ppm (s, ^1J(C,Te) = 42 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2$Te): δ = 399 ppm. Br_2 (3 drops, ca. 1.2 mmol) was added to a solution of *cis*-**4a** (0.074 g, 0.100 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the mixture had been stirred for 5 min, volatile materials were evaporated. Crude products were almost pure *trans*-**7a-Br**.

(4-$CF_3C_6H_4$)$_4$(CH_3)TeCl (*trans*-7a-Cl): SO_2Cl_2 (10 drops, ca. 2.0 mmol) was added to a solution of *trans*-**4a** (0.0736 g, 0.0997 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the mixture had been stirred for 5 min, volatile materials were removed in vacuo to give the desired *trans*-**7a-Cl** (0.0726 g, 0.0957 mmol, 96.0 %); colorless needles, m.p. 233–234 °C

(decomp); ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.58$ (s, 3H), 7.56 ppm (s, 16H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.2$ ppm (s, 12F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 19.8$ (q, ^1J(C,Te) = 86 Hz), 123.6 (q, ^1J(C,F) = 273 Hz), 125.2 (d), 131.9 (q, ^2J(C,F) = 33 Hz), 132.2 (d), 158.8 ppm (s, ^1J(C,Te) = 57 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 409$ ppm; elemental analysis calcd (%) for $C_{29}H_{19}ClF_{12}Te$: C 45.92, H 2.52; found: C 45.72, H 2.35.

General procedures for nucleophilic substitution of the halide in pentaorganotellurium halide with organolithium reagents by triflate: THF (25 mL) was added to a mixture of $AgSO_3CF_3$ (0.537 g, 2.09 mmol) and pentaorganotellurium halide (1.20 mmol) at room temperature and the reaction mixture was stirred for 10 min. After evaporation of THF in vacuo, CH_2Cl_2 (25 mL) was added. Precipitated AgCl was filtered off from the reaction mixture under an argon atmosphere, and CH_2Cl_2 was evaporated from the filtrate. Et_2O (50 mL) was added to the condensed reaction mixture followed by addition of organolithium reagent (15 mmol) at −90 °C. The reaction mixture was allowed to warm to room temperature and the solvent was removed. Products were washed with NH_4Cl (aq).

(4-BrC$_6$H$_4$)$_6$Te (1d): Colorless plates, m.p. >300 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 6.85$ (d, ^3J(H,H) = 9 Hz, 12H), 7.35 ppm (d, ^3J(H,H) = 9 Hz, 12H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 123.9$ (s), 131.6 (d), 134.6 (d), 147.3 ppm (s, ^1J(C,Te) = 37 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 476$ ppm.

(4-CF$_3$C$_6$H$_4$)$_5$(4-MeOC$_6$H$_4$)Te (8): Colorless crystals; m.p. >290 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.52$ (d, ^3J(H,H) = 9 Hz, 2H), 7.49 (d, ^3J(H,H) = 9 Hz, 8H), 7.12 (d, ^3J(H,H) = 9 Hz, 8H), 7.10 (d, ^3J(H,H) = 9 Hz, 2H), 6.83 (d, ^3J(H,H) = 9 Hz, 2H), 6.77 (d, ^3J(H,H) = 9 Hz, 2H), 3.79 ppm (s, 3H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.1$ (s, 12F), −63.3 ppm (s, 3F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 159.6$ (s), 153.2 (s), 153.0 (s), 152.9 (s), 134.6 (q, ^2J(C,F) = 42 Hz), 134.4 (q, ^2J(C,F) = 42 Hz), 134.3 (d), 133.5 (d), 133.4 (d), 125.7 (q, ^1J(C,F) = 289 Hz), 125.6 (q, ^1J(C,F) = 289 Hz), 125.6 (d), 125.5 (d), 125.4 (d), 55.3 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 469.9$ ppm; elemental analysis calcd (%) for $C_{37}H_{23}F_{15}Te + 1/2\,H_2O$: C 49.97, H 2.72; found: C 50.02, H 2.54.

(4-CF$_3$C$_6$H$_4$)$_5$(CH=CH$_2$)Te (9): Colorless needles; m.p. 214–215 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.53$ (d, ^3J(H,H) = 8 Hz, 2H), 7.51 (d, ^3J(H,H) = 8 Hz, 8H), 7.41 (d, ^3J(H,H) = 8 Hz, 2H), 7.35 (d, ^3J(H,H) = 8 Hz, 8H), 6.80 (dd, ^3J(H,H) = 11 Hz, 18 Hz, 1H), 6.39 (d, ^3J(H,H) = 11 Hz, 1H), 5.38 ppm (d, ^3J(H,H) = 18 Hz, 1H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 153.9$ (s, ^1J(C,Te) = 49 Hz), 151.6 (s, ^1J(C,Te) = 25 Hz), 133.6 (d), 132.9 (d), 131.5 (q, ^2J(C,F) = 32 Hz), 131.3 (q, ^2J(C,F) = 32 Hz), 129.6 (d), 125.6 (d), 125.5 (d), 125.1 (d), 123.7 (q, ^1J(C,F) = 271 Hz), 123.6 ppm (q, ^1J(C,F) = 271 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 420.3$ ppm; elemental analysis calcd (%) for $C_{37}H_{23}F_{15}Te + 1/2\,H_2O$: C 49.97, H 2.72; found: C 50.02, H 2.54.

Ph$_5$(CH=CH$_2$)Te (10): Colorless needles; m.p. 239–240 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.30$–7.45 (m, 1H), 7.38 (d, ^3J(H,H) = 8 Hz, 2H), 7.30 (t, ^3J(H,H) = 8 Hz, 8H), 7.19 (t, ^3J(H,H) = 8 Hz, 4H), 7.15–7.22 (m, 2H), 7.07 (d, ^3J(H,H) = 8 Hz, 8H), 6.85 (dd, ^3J(H,H) = 11 Hz, 19 Hz, 1H), 6.27 (d, ^3J(H,H) = 11 Hz, 1H), 5.32 ppm (d, ^3J(H,H) = 19 Hz, 1H). ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 154.2$ (s, ^1J(C,Te) = 53 Hz), 151.6 (s, ^1J(C,Te) = 37 Hz), 150.1 (d), 149.8 (d), 133.6 (d), 133.2 (d), 128.3 (d), 128.1 (d), 127.5 (d), 127.3 ppm (d); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 429.5$; elemental analysis calcd (%) for $C_{32}H_{28}Te + 1/2\,H_20$: C 69.98, H 5.32; found: C 69.88, H 5.13.

(4-CF$_3$C$_6$H$_4$)$_5$(CH$_2$SPh)Te (11): Red solid; m.p. 152–153 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.77$ (d, ^3J(H,H) = 7 Hz, 2H), 7.72 (d, ^3J(H,H) = 7 Hz, 2H), 7.6–7.7 (m, 5H), 7.68 (d, ^3J(H,H) = 7 Hz, 8H), 7.46 (d, ^3J(H,H) = 7 Hz, 8H), 3.55 ppm (s, 2H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.0$ (s, 12F), −63.4 ppm (s, 3F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 152.2$ (s), 150.6 (s), 140.8 (s), 133.6 (d), 133.2 (d), 131.0 (q, ^2J(C,F) = 30 Hz), 130.4 (q, ^2J(C,F) = 30 Hz), 130.1 (d), 125.9 (d), 125.8 (d), 125.7 (d), 123.3 (q, ^1J(C,F) = 270 Hz), 123.0 (q, ^1J(C,F) = 270 Hz), 122.5 (d), 47.0 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 420.7$ ppm; elemental analysis calcd (%) for $C_{42}H_{27}F_{15}STe$: C 51.6, H 2.78; found: C 49.9, H 2.67.

Ph$_5$(CH$_2$SPh)Te (12): Colorless crystals; m.p. 164–165 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.46$ (d, ^3J(H,H) = 7 Hz, 2H), 7.42 (d, ^3J(H,H) = 7 Hz, 8H), 7.36–7.39 (m, 2H), 7.33 (t, ^3J(H,H) = 7 Hz, 4H), 7.24 (t, ^3J(H,H) = 7 Hz, 8H), 7.14–7.20 (m, 4H), 7.08 (t, ^3J(H,H) = 7 Hz, 2H), 3.76 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 151.9$ (s), 148.1 (s), 140.1 (s), 135.0 (d), 134.4 (d), 133.1 (d), 131.7 (d), 130.5 (d), 128.4 (d), 127.8 (d), 125.0 (d), 122.2 (d), 46.5 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 403.7$ ppm; elemental analysis calcd (%) for $C_{37}H_{32}STe$: C 69.84, H 5.06; found: C 70.14, H 5.00.

Ph$_5$(nBu)Te (13): Colorless crystals; m.p. 130–131 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 7.27$ (d, ^3J(H,H) = 7 Hz, 2H), 7.22 (d, ^3J(H,H) = 7 Hz, 8H), 7.22 (t, ^3J(H,H) = 7 Hz, 2H), 7.15 (t, ^3J(H,H) = 7 Hz, 1H), 7.11 (t, ^3J(H,H) = 7 Hz, 8H), 7.04 (t, ^3J(H,H) = 7 Hz, 4H), 2.84 (t, ^3J(H,H) = 9 Hz, 2H), 1.41 (tt, ^3J(H,H) = 7 Hz, 9 Hz, 2H), 1.25 (tq, ^3J(H,H) = 7 Hz, 2H), 0.78 ppm (t, ^3J(H,H) = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 152.7$ (s), 151.6 (s), 133.6 (d), 132.9 (d), 128.3 (d), 127.9 (d), 127.8 (d), 127.5 (d), 50.1 (s), 30.9 (s), 24.7 (s), 13.6 ppm (s); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 401.9$ ppm; elemental analysis calcd (%) for $C_{42}H_{27}F_{15}Te + 3$ benzene: C 60.32, H 3.79; found: C 59.98, H 3.55.

(4-CF$_3$C$_6$H$_4$)$_4$(CH$_3$)$_2$Te (*cis*-4a): Colorless plates; m.p. 236–237 °C; ^{1}H NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.19$ (s, 6H), 7.46 (d, ^3J(H,H) = 8 Hz, 4H), 7.52 (d, ^3J(H,H) = 8 Hz, 4H), 7.53 (d, ^3J(H,H) = 8 Hz, 4H), 7.56 ppm (d, ^3J(H,H) = 8 Hz, 4H); ^{19}F NMR ($CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.0$ (s, 6F), −63.1 ppm (s, 6F); ^{13}C NMR ($CDCl_3$, 25 °C, $CHCl_3$): $\delta = 34.5$ (q, ^1J(C,Te) = 9 Hz), 123.8 (q, ^1J(C,F) = 273 Hz), 123.9 (q, ^1J(C,F) = 273 Hz), 124.6 (d), 124.7 (d), 130.4 (q, ^2J(C,F) = 33 Hz), 130.5 (q, ^2J(C,F) = 33 Hz), 132.7 (d), 132.8 (d), 159.6 (s, ^1J(C,Te) = 87 Hz), 160.0 ppm (s, ^1J(C,Te) = 25 Hz); ^{125}Te NMR ($CDCl_3$, 25 °C, $(CH_3)_2Te$): $\delta = 272$ ppm; elemental analysis calcd (%) for $C_{30}H_{22}F_{12}Te$: C 48.82, H 3.00; found: C 48.65, H 2.82.

X-ray structural analysis of 1d, *cis*-4a, *trans*-4c, *trans*-7a-Cl, and 9: CCDC-212473 (**1d**), CCDC-212475 (*cis*-**4a**), CCDC-212476 (*trans*-**4c**), CCDC-212478 (*trans*-**7a-Cl**), and CCDC-212479 (and **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk). A summary of the important data from the X-ray structure determinations is given in Table 5. Data were collected at 150 K on a Mac Science DIP2030 imaging plate equipped 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 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 structures were solved by using the teXsan system and refined by full-matrix least-squares. The programs (DENZO and SCALEPACK) are available from Mac Science Co. Z Otwinowski, University of Texas, Southwestern Medical Center. The program teXsan is available from Rigaku Co.

[1] a) N. Petragnani, *Tellurium in Organic Synthesis*, Academic Press, New York, **1994**; b) N. Petragnani, J. V. Comasseto, *Synthesis* **1991**, 793–812; c) N. Petragnani, J. V. Comasseto, *Synthesis* **1991**, 897–919; d) L. Engman, *Acc. Chem. Res.* **1985**, *18*, 274–279; e) F. S. Guziec, Jr., L. J. Guziec, in *Comprehensive Organic Functional Group Transformations, Vol. 3* (Ed.: G. Pattenden, A. R. Katritzky, O. Meth-Cohn, C. W. Rees), Pergamon, Oxford, **1995**, pp 381–401.

[2] a) K. Y. Irgolic in *Houben-Weyl, Methods of Organic Chemistry, Vol.* E 12b (Ed.: D. Klamann), Thieme, Stuttgart, **1990**; b) T. Chivers, *J. Chem. Soc. Dalton Trans.* **1996**, 1185–1194; c) F. S. Guziec, Jr., in *The Chemistry of Organic Selenium and Tellurium Compounds, Vol. 2* (Ed.: S. Patai), Wiley, New York, **1987**, pp 217–273.

[3] a) G. Wittig, H. Fritz, *Justus Liebigs Ann. Chem.* **1952**, *577*, 39–46; b) D. H. R. Barton, S. A. Glover, S. V. Ley, *J. Chem. Soc. Chem. Commun.* **1977**, 266–267; c) S. A. Glover, *J. Chem. Soc. Perkin Trans. 1* **1980**, 1338–1344; d) C. S. Smith, J.-S. Lee, D. D. Titus, R. F. Ziolo, *Organometallics* **1982**, *1*, 350–354; e) C. H. W. Jones, R. D. Sharma, *J. Organomet. Chem.* **1987**, *318-337*, 115–121; f) D. Hellwinkel, G. Fahrbach, *Tetrahedron Lett.* **1965**, *23*, 1823–1827; g) D. Hellwinkel, G. Fahrbach, *Chem. Ber.* **1968**, *101*, 574–584; h) D. Hellwinkel, G. Fahrbach, *Justus Liebigs Ann. Chem.* **1968**, *712*, 1–20; i) D. Hellwinkel, *Ann. N. Y. Acad. Sci.* **1972**, *192*, 158–166; j) S. Ogawa, S. Sato, T. Erata, N. Furukawa, *Tetrahedron Lett.* **1992**, *33*,

Table 5. Crystallographic data for **1d**, *cis*-**4a**, *trans*-**4c**, *trans*-**7a-Cl**, and **9**.

Compound	**1d**	*cis*-**4a**	*trans*-**4c**	*trans*-**7a-Cl**	**9**
formula	$C_{36}H_{24}Br_6Te$	$C_{30}H_{22}F_{12}Te$	$C_{30}H_{34}Te$	$C_{29}H_{19}ClF_{12}Te$	$C_{37}H_{23}F_{15}Te$
molecular weight	1063.61	738.08	522.20	758.50	880.16
crystal system	triclinic	triclinic	monoclinic	tetragonal	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P21/n$	$P4nc$	$P21/n$
crystal dimensions [mm]	$0.25\times0.25\times0.20$	$0.45\times0.35\times0.15$	$0.50\times0.40\times0.15$	$0.30\times0.20\times0.15$	$0.35\times0.20\times0.15$
color	colorless	colorless	colorless	colorless	Colorless
habit	plate	plate	plate	plate	Plate
a [Å]	8.8090(5)	11.3390(4)	10.1390(2)	12.1140(3)	11.3410(3)
b [Å]	10.3350(6)	12.3720(5)	19.4320(5)	12.1140(3)	18.3810(6)
c [Å]	10.6080(8)	12.6680(5)	13.3370(2)	9.5460(3)	17.090(4)
α [°]	73.533(3)	72.540(2)	90	90	90
β [°]	77.535(3)	88.201(2)	104.740(1)	90	91.788(2)
γ [°]	67.508(3)	62.302(2)	90	90	90
V [Å^3]	849.39(10)	1488.7(1)	2541.19(8)	1400.87(4)	3562.3(1)
Z	1	2	4	2	4
ρ_{calcd} [g cm^{-3}]	2.079	1.646	1.365	1.798	1.641
μ[cm^{-1}]	7.979	1.093	1.185	1.256	0.940
F(000)	502	724	1024	740	1728
$Mo_{K\alpha}$ radiation [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
temp [K]	190	200	190	200	273
2θ max [°]	56.1	56.1	56	–	–
data collected	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,\ \pm k,\ +l$	$+h,\ +k,\pm l$
total data collected, obsd	3326, 2664($I>3\sigma(I)$)	6503, 6045($I>3\sigma(I)$)	5774, 5628($I>3\sigma(I)$)	1025, 859($I>3\sigma(I)$)	7949, 6707($I>3\sigma(I)$)
no. of parameters refined	196	380	280	100	469
R, R_w, goodness of fit (obs)	0.0743, 0.1180, 1.290	0.0648, 0.0984, 1.228	0.0471, 0.0844, 1.340	0.0316, 0.0466, 0.936	0.0749, 0.1246, 1.420
max shift in final cycle	0.0008	0.0015	0.0008	0.0291	0.0530
final diff map, max [e Å^{-3}]	1.11	1.19	0.63	0.35	1.27

1915–1918; k) S. Sato, N. Kondo, N. Furukawa, *Organometallics* **1994**, *13*, 3393–3395; l) S. Sato, N. Furukawa, *Tetrahedron Lett.* **1995**, *36*, 2803–2806; m) K.-y. Akiba, *Chemistry of Hypervalent Compounds* (Ed.: K.-y. Akiba), Wiley-VCH, New York, **1999**.

[4] a) L. Ahmed, J. A. Morrison, *J. Am. Chem. Soc.* **1990**, *112*, 7411–7413; b) A. Haaland, H. P. Verne, H. V. Volden, J. A. Morrison, *J. Am. Chem. Soc.* **1995**, *117*, 7554–7555; c) J. E. Fowler, T. P. Hamilton, H. F. Schaefer III, *J. Am. Chem. Soc.* **1993**, *115*, 4155–4158; d) J. E. Fowler, H. F. Schaefer III, K. N. Raymond, *Inorg. Chem.* **1996**, *35*, 279–281.

[5] a) M. Minoura, T. Sagami, K.-y. Akiba, C. Modrakowski, A. Sudau, K. Seppelt, S. Wallenhauer, *Angew. Chem.* **1996**, *108*, 2827–2829; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2660–2662; b) M. Minoura, T. Sagami, M. Miyasato, K.-y. Akiba, *Tetrahedron* **1997**, *53*, 12195–12202; c) M. Minoura, T. Sagami, K.-y. Akiba, *Organometallics* **2001**, *20*, 2437–2439; d) M. Minoura, T. Mukuda, T. Sagami, K.-y. Akiba, *J. Am. Chem. Soc.* **1999**, *121*, 10852–10853; e) M. Miyasato, M. Minoura, K.-y. Akiba, *Angew. Chem.* **2001**, *113*, 2746–2748; *Angew. Chem. Int. Ed.* **2001**, *40*, 2674–2676; f) M. Miyasato, M. Minoura, Y. Yamamoto, K.-y. Akiba, *Chem. Lett.* **2002**, 288–289.

[6] Furukawa and co-workers reported the synthesis of (biphenyl)$_3$Te (S. Sato, T. Tanaka, E. Horn, N. Furukawa, in *abstract of 74th annual meeting of the Chemical Society of Japan* **1998**, 2C229). For other hexavalent organotellurium compounds bearing less than four Te–C bonds; see a) R. S. Michalak, J. C. Martin, *J. Am. Chem. Soc.* **1982**, *104*, 1683–1692; b) R. S. Michalak, S. R. Wilson, J. C. Martin, *J. Am. Chem. Soc.* **1984**, *106*, 7529–7539; c) K. Alam, A. F. Janzen, *J. Fluorine Chem.* **1985**, *27*, 467–469; d) A. S. Secco, K. Alam, B. J. Blackburn, A. F. Janzen, *Inorg. Chem.* **1986**, *25*, 2125–2129; e) A. F. Janzen, K. Alam, M. Jang, B. J. Blackburn, A. S. Secco, *Can. J. Chem.* **1988**, *66*, 1308–1312; f) S. Sato, T. Yamashita, E. Horn, N. Furukawa, *Organometallics* **1996**, *15*, 3256–3258; g) S. Sato, T. Yamashita, E. Horn, O. Takahashi, N. Furukawa, M. Yokoyama, K. Yamaguchi, *Tetrahedron* **1997**, *53*, 12183–12194; h) S. Sato, H. Ameta, E. Horn, O. Takahashi, N. Furukawa, *J. Am. Chem. Soc.* **1997**, *119*, 12374–12375; i) N. Furukawa, S. Sato, in *Chemistry of Hypervalent Compounds* (Ed.: K.-y. Akiba), Wiley-VCH: New York, **1999**.

[7] For $Ph_5Te^-Li^+$ by reaction of Ph_4Te with PhLi, see; a) H. J. Reich, D. P. Green, N. H. Phillips, J. P. Borst, I. L. Reich, *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 83–97; b) G. Wittig, H. Fritz, *Justus Liebigs Ann. Chem.* **1952**, *577*, 39–46; for $R_5Te^-Li^+$, see; c) D. Hellwinkel, G. Fahrbach, *Chem. Ber.* **1968**, *101*, 574–584; d) D. Hellwinkel, *Ann. N. Y. Acad. Sci.* **1972**, *192*, 158–166.

[8] For example, see; a) A. Fürstner, *Angew. Chem.* **1993**, *105*, 171; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 164–189; b) R. Csuk, B. I. Glanzer, A. Fürstner, *Adv. Organomet. Chem.* **1988**, *28*, 85–137; c) D. Savoia, C. Trombini, A. Umani-Ronchi, *Pure Appl. Chem.* **1985**, *57*, 1887–1896; d) H. Selig, L. B. Ebert, *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 281–327; e) J.-M. Lalancette, G. Rollin, P. Dumas, *Can. J. Chem.* **1972**, *50*, 3058–3062.

[9] a) E. Weiss, G. Sauermann, *Angew. Chem.* **1968**, *80*, 123; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 133–134; b) E. Weiss, G. Sauermann, *Chem. Ber.* **1970**, *103*, 265–271; c) C. Eaborn, P. B. Hitchcock, K. Izod, A. J. Jaggar, J. D. Smith, *Organometallics* **1994**, *13*, 753–754.

[10] a) M. Schlosser, J. Hartmann, *Angew. Chem.* **1973**, *85*, 544; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 508–509; b) M. Schlosser, *Pure Appl. Chem.* **1988**, *60*, 1627–1634.

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