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Tetrahydrofuran Ring Opening and Unexpected Oxidation of The Furyl Ring in The Reaction of Bis(2-furyl)ditelluride with Iodine and Triphenylphosphine

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Abstract

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The reaction of bis(2-furyl) ditelluride Fu_2Te_2 (1) with iodine in diethyl ether under ambient conditions expectedly yields FuTeI (2). The *in situ* reaction of 2 with triphenylphosphine affords Ph₃PTe(Fu)I (3), which was characterized in the solid state by single crystal X-ray crystallography. The crystal structure of 3 shows linear P – Te – I backbone and T-shaped coordination around the tellurium atom. In the solid lattice, 3 exists as discrete molecules, which are lined together by a H···I hydrogen bonding network. There is no evidence of the secondary bonding Te···I or I···I interactions, which are typical for many tellurium-iodine compounds. When this two-step reaction of Fu₂Te₂ with I₂ and PPh₃ is carried out in tetrahydrofuran, a mixture of products is obtained. The main products, which were identified by single-crystal X-ray crystallography, are {Ph₃P(C₄H₅O₂)}₂[TeI₄] (4), {Ph₃P(CH₂)₄PPh₃}[TeI₄]·2CH₂Cl₂ (5·2CH₂Cl₂), Fu₂Te (6), (CH₂)₄Tel₂ (7), Ph₃PO, and elemental tellurium. The formation of the products has been discussed in terms of THF ring opening, abstraction of tellurium by PPh₃, and the conversion of the furyl ring in FuTeI into a lactone ring due to the presence of atmospheric moisture.

1. Introduction

Diaryl ditellurides R₂Te₂ react with iodine (I₂) forming aryltellurenyl iodides RTeI which have been used as intermediary compounds for the formation of different type of organotellurium compounds containing tellurium iodine bonds [1-16]. A multitude of compounds with varying structural features have been characterized and in addition to conventional covalent bonds, the description of bonding in these compounds necessitates the use of concepts like hypervalence, multicenter bonding, chargetransfer interactions, secondary bonding, as well as hydrogen bonding. As a consequence, in the solid state the discrete molecules often form supramolecular lattices and even 1D, 2D, and 3D polymeric networks.

Decomposition or rearrangement reactions are often observed upon solidification of aryltellurenyl halogenides [3,16-19]. A common pathway in aryltellurenyl(II) halides involves migration of the organic substituents and the formation of diaryltellurium dihalides and elemental tellurium [3,20]. Only a few compounds have been observed, which retain their initial solution stoichiometry in the crystalline state [3,4,15]. Even in these cases the monomeric species are often associated into larger frameworks, as exemplified by the X-ray structure of PhTeI, which consists of cyclic tetrameric Ph₄Te₄I₄ molecules [3,4]. Smaller molecular units can, however, be stabilized in the solid state by bulky aryl groups, as observed 2,6-dimesitylphenyltellurenyl iodide 2,3,5,6in $2,6-(\text{mes})_2C_6H_3\text{TeI}$ [11] and tetramethylphenyltellurenyl iodide (tmp)TeI [15]. Both show dimeric solid-state structures with Te…Te, Te…I, interactions. Sterically demanding and I…I 2,4,6-tri-terteven more butylphenyltellurenyl iodide exhibits only discrete molecules without Te…Te, Te…I, or I…I intermolecular contacts [21].

The reactions of diorganyl ditellurides with halogens also yield mixed-valence aryltellurenyl halides RX_2TeTeR [11]. The removal of the organyl group from RTeI also leads to the formation of tetraiodidotellurate(II) and hexaiodidotellurate(IV) ions [13,15], and addition of second halide yields $[RTeX_2]^-$ [7,10,12,15]. Polyiodides are formed when an excess of iodine is used in the reactions, as exemplified by $(PyH)[tmpTeI_3(I_3)]$ and $(PyH)_3[dmephTeI_2(I_2)]_2(I_3)$ (dmeph = 2,6-dimethylphenyl) [10,11,13-16]. The phenyltellurenyl iodide has also been stabilized by the addition of the Lewis base Ph₃P into the diethylether solution of PhTeI [4]. This reaction yields quantitatively Ph₃PTe(Ph)I.

Tellurium tetrahalogenides react both as Lewis bases and Lewis acids. There are several examples of adducts where tellurium tetrahalides have acted both as acceptors and as donors (see ref. 22, and references therein). Chalcogen tetrahalogenides undergo spontaneous redox reactions with neutral Lewis bases [23,24] and the reductive power of P(III) towards the Se and Te centers has been recently recognized [24]. In the case of tellurium tetrachloride, the reaction with triphenylphosphine in an inert atmosphere has been shown to yield [Ph₃PCl]₂[TeCl₆] and Te(0) [24] as well as Ph₃PCl₂ and Te(0) [25] or TeCl₂, Te(0), and Ph₃PO [26]. In ambient conditions, [Ph₃PCl]⁺ reacts with the formation of Ph₃PO [23, 26]. These reactions indicate redox processes, in which phosphorus is oxidized from P(III) to P(V) and tellurium is reduced. The reduction of the Group 16 elements to the elemental form in the presence of two electron donors has been reported to be partially responsible for the limited information of coordination of the electron-rich Lewis base to a Group 16 element center [24,27].

In this work, we have investigated the reaction of Fu_2Te_2 [Fu = 2-furyl, C₄H₃O] (1) with an equimolar amount of I₂ in diethyl ether or in tetrahydrofuran (THF). FuTeI (2) was found to be formed in both solutions. With the treatment of the reaction solutions with Ph₃P, Ph₃PTe(Fu)I (3) was readily precipitated from the diethylether solution. In THF, however, the THF ring opening and the redox

reactions of Te(II) and P(III) took place resulting in a mixture of products. The reactions were monitored by NMR spectroscopy and the products were characterized by X-ray crystallography.

2. Experimental

2.1. General Procedures

All reactions were carried out in air using dry solvents. The solvents (Et₂O, THF) were dried over Na/benzophenone and distilled under an argon atmosphere prior to use. Ph₃P (Fluka) was dried under dynamic vacuum. I₂ (Aldrich) was stored under argon and used without further purification. Fu₂Te₂ [Fu = 2-furyl, C₄H₃O] (**1**) was prepared by modifying the method described by Engman and Cava [28]. In this work, potassium hexacyanoferrate(III) was used for the oxidation of FuTeLi [29].

2.2 Spectroscopic Methods

The ³¹P{¹H} and ¹²⁵Te NMR spectra were recorded on an Ascend 400 spectrometer operating at 161.98 and 126.34 MHz, respectively. The respective spectral widths were *ca*. 64 and 139 kHz. The pulse widths were 24.25 and 10.00 μ s, corresponding to the nuclear tip angles of 90 and 40, respectively. The ³¹P{¹H} pulse delay was 5.00 s and that for ¹²⁵Te 1.60 s. The ³¹P{¹H} accumulations contained *ca*. 250 transients. The ¹²⁵Te accumulations in the acquisition of the spectrum of FuTeI contained *ca*. 1000 transients. The ¹²⁵Te NMR spectrum of the reaction mixture of FuTeI and PPh₃ contained *ca*. 30000 transients. The spectra were recorded unlocked. 85 % H₃PO₄ and a saturated solution of Te(OH)₆ were used as external standards. The ³¹P chemical shifts were reported relative to the standard and the ¹²⁵Te chemical shifts relative to neat Me₂Te [(Me₂Te) = (H₆TeO₆) + 712] [30].

2.3. X-ray Crystallography

Diffraction data for compounds **3** –**7** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo K radiation (= 0.71073 Å). Crystal data and the details of the structure determinations are given in Table 1. The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97 [31]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the aromatic rings (C-H = 0.95 Å) and in the methylene groups (C-H = 0.99 Å). In the final refinement the calculated hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the aromatic hydrogen atoms were fixed at 1.2, and those of aliphatic hydrogen atoms at 1.5 times to that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the program. The highest peaks in the final residual electron density are near to tellurium or iodine.

(Table 1 here)

2.4. Reactions of Fu_2Te_2 with I_2 and PPh_3 in Et_2O

A solution of I_2 (133 mg, 0.52 mmol) in Et₂O (5 ml) was added to the solution of Fu₂Te₂ (1) (201 mg, 0.52 mmol) in Et₂O (20 ml) in an ethanol-liquid nitrogen bath (T = ca. -115 °C). After 20 minutes the cooling bath was removed and the reaction mixture was stirred for 1.5 h during which time it warmed to the ambient temperature and the bright red color of the solution turned dark violet due to the formation of FuTeI (2). The reaction solution was again cooled in an ethanol-liquid nitrogen bath, and

Ph₃P (269 mg, 1.03 mmol) in 5 ml of Et₂O was added dropwise into the solution. The formation of yellowish precipitate of Ph₃PTe(Fu)I (**3**) was immediately observed. After 20 minutes the bath was removed and the stirring was continued for further 45 minutes allowing the mixture to warm to the ambient temperature. The precipitate was removed by decantation and dried in an argon flow. Yield: 433 mg (72 % based on Ph₃P). Anal. Calcd. for $C_{22}H_{18}IOPTe$ **3**: C 45.26, H 3.11. Found: C 44.75, H 3.14.

2.5. Reactions of Fu_2Te_2 with I_2 and PPh_3 in THF

The reactions of $\mathbf{1}$ with I_2 and Ph_3P in THF were carried out in a similar fashion to those in Et₂O. The addition of Ph_3P to $\mathbf{2}$ resulted in the color change of the solution into reddish brown, but no precipitate was formed. Upon prolonged stirring of the mixture, the reaction vessel was coated with "metallic" grey layer of elemental tellurium.

The reaction mixture was filtered and the solvent was removed by evaporation upon which a dark, very viscose oily material was formed. Most of the material dissolved in hexane/CH₂Cl₂ (1:1), and the crystals of $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (4), $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$ (5·2CH₂Cl₂), $C_4H_8TeI_2$ (7), and Ph_3PO were grown from the mixture upon slow evaporation of the solvent. Crystals of Fu₂Te (6) were obtained upon sublimation in the cold trap.

3. Results and Discussion

3.1. General

The reaction of Fu₂Te₂ (**1**) with I₂ in Et₂O or THF afforded FuTeI (**2**) (see Scheme 1). The formation of **2** in both solutions was confirmed by the ¹²⁵Te NMR spectroscopy. A single ¹²⁵Te NMR resonance at 867 ppm or 959 ppm was observed in the Et₂O and THF solutions of **2**, respectively.

The addition of Ph_3P into the Et_2O solution of **2** leads to a rapid formation of $Ph_3PTe(Fu)I$ (**3**) (see Scheme 1). The product could be isolated in a good yield and identified by the determination of the crystal structure. The reaction proceeded in a similar fashion to that reported previously for diphenylditelluride [4]. The ${}^{31}P{}^{1}H$ NMR spectrum of the reaction solution showed two distinct, rather broad resonances at approximately -7 and 25 ppm. The resonance at -7 ppm was assigned to $Ph_3PTe(Fu)I$ (**3**) and that at 25 ppm to Ph_3PO .

(Scheme 1 here)

In THF, the reaction of FuTeI (2) and PPh₃ proceeded in a more complicated manner. The formation of **3** between FuTeI and PPh₃ was not observed, but the reaction seemed to involve the ring opening of the solvent together with redox processes involving tellurium. The reaction afforded a mixture of $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (4), $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]$ (5), Fu_2Te (6), $(CH_2)_4TeI_2$ (7), Ph_3PO , and Te(0). The compounds were identified by X-ray crystallography. The crystal structures of 4 and 5 are described below (see Section 3.3), that of 7 has been reported previously [23], and there are several reports of the crystal structure determinations of Ph_3PO [32-38].

The reaction of **2** with PPh₃ in THF was also monitored with both ${}^{31}P{}^{1}H$ and ${}^{125}Te$ NMR spectroscopy. At the initial stages of the reaction, the ${}^{31}P{}^{1}H$ NMR spectrum showed relatively broad

resonance at -(18-20) ppm. It is likely to be due to Ph₃PI₂, the formation of which in the early stages of the reaction seems quite reasonable [39,40]. With increasing reaction time, this resonance shifted downfield and its intensity decreased. At the same time, new resonances at 11.7 ppm, 25 ppm and 32-28 ppm were observed. Their intensities increased upon prolonged stirring of the reaction solution.

Since we have identified two of the end products in the reaction of **2** and PPh₃ as **4** and **5**, it is reasonable to assume that the initially formed Ph₃PI₂ is converted to phosphonium and tetraiodidotellurate ions consuming more I₂ relative to PPh₃ resulting in the formal increase of the Ph₃P:I₂ molar ratio and consequently leads to a downfield shift of the high field resonance. This dependence of the chemical shift on the Ph₃P:I₂ molar ratio has been suggested also earlier [39,40]. Since also elemental tellurium is formed in the reaction, the formation of the [TeI₄]²⁻ anion finds support from its related preparations from Te, I₂, and Γ [41-43].

The ³¹P chemical shift of Ph₃PO has been reported at 45 – 25 ppm depending on the solvent, concentration, and the moisture content among other things [39,44]. Therefore a resonance, which has been observed in the region 32-28 ppm in different reaction batches, is assigned to Ph₃PO. The resonances at 25 ppm and 11.7 are assigned to the $\{Ph_3P(C4H_5O_2)\}^+$ cation in **4** and the $\{Ph_3P(CH_2)_4PPh_3\}^{2+}$ cation in (**5**), respectively.

Upon prolonged stirring, the main resonances in the ¹²⁵Te spectrum of the reaction mixture were observed at 870 and 376 ppm. The resonance at 376 ppm was assigned to Fu₂Te (**6**). The related Th₂Te (Th = 2-thienyl, C₄H₃S) has been reported to exhibit the ¹²⁵Te resonance at 408 ppm [45]. The resonance at 870 ppm was assigned to C₄H₈TeI₂ (**7**). This compound has been reported to show the ¹²⁵Te chemical shift at 929 ppm in DMSO [46]. Its formation in the reaction was confirmed by the unit cell measurements of the crystals isolated from the reaction mixtures.

3.2. The crystal structure of $Ph_3PTe(Fu)I(3)$

Suitable crystals of **3** for the X-ray structure analysis were obtained by recrystallization of the isolated compound from toluene. The molecular structure of **3** is shown in Figure 1 together with the numbering of the atoms and the selected bond lengths and angles.

(Figure 1 here)

The lattice of Ph₃PTe(Fu)I (**3**) consists of discrete molecules. The P – Te – I fragment is nearly linear displaying a bond angle of $176.80(7)^{\circ}$. The P – Te – C bond angle is $90.3(3)^{\circ}$. The T-shaped coordination of tellurium indicates two stereochemically active lone pairs as a consequence of charge-transfer interaction between tellurium and iodine atoms. For ionic [Ph₃P(R)Te]⁺T, a bent P – E – I (E = chalcogen) linkage would be expected, as observed in [(Me₃N)₃PSePh]I (C – Se – P angle of 94.1(3)^o) [47]. The Te – I bond length in **3** is 3.1174(15) Å. It is longer than the Te – I single bond (sum of the covalent radii for tellurium and iodine is 2.70 Å [48]). The Te – I bond length in **3** is, however, comparable to that in Ph₃PTe(Ph)I [3.0930(9) Å][4]. Consistently, the P – Te bond lengths in **3** and Ph₃PTe(Ph)I are identical {2.561(3) and 2.568(2) Å [4], respectively}. The Te – C bond length in **3** is quite normal.

The discrete $Ph_3PTe(Fu)I$ molecules are linked together by a three-dimensional H···I and H···Te network as shown in Figure 2. The shortest H···I contacts span a range 3.1563(9)-3.2849(10) Å and the shortest Te⁻⁻H contact is 3.2323(9) Å.

(Figure 2 here)

3.3. The crystal structures of $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (4) and $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]^2CH_2Cl_2$ (5·2CH₂Cl₂)

The molecular structures of **4** and $5 \cdot 2 CH_2 Cl_2$ are shown in Figure 3. The selected bond parameters in the $[TeI_4]^{2-}$ anion are shown in Table 2. All bond lengths and angles involving the cations are normal.

(Figure 3 here)

(Table 2 here)

The $[TeI_4]^{2-}$ anion in both salts shows an approximate square-planar coordination geometry. The Te-I bond lengths in **4** and **5** span a very narrow range of 2.9348(11)-2.9795(4) Å and the I-Te-I bond angles show a range 88.43(1)-91.570(10) °. The metrical parameters in $[TeI_4]^{2-}$ ions are consistent with those reported for $[(Et_3PO)_2H]_2[TeI_4]$ [49], $[Co(en)_3][TeI_4](I)$ [13], $(C_{10}H_8S_8)_4[TeI_4]$ [50], and $(Et_4N)_2[TeI_4]$ [40].

The cation of the compound seems to have only little effect on the geometry of the anions and in the lattice the anions generally occupy the voids between bulky cations. The coordination polyhedra of tellurium atom is usually completed to trigonal bipyramidal or to octahedron by intermolecular secondary interactions but in the case of $[TeI_4]^{2-}$ ions these kind of intermolecular interactions are generally absent [14,40,48,49], which is also the case in **4** and **5**·2CH₂Cl₂. Only weak hydrogen bonds connecting cations and anions have been previously observed [13]. In both salts the cations and anions are linked together with weak H···I hydrogen bonds of 3.0000(1) - 3.0225(6) Å, as shown in Figure 4. In addition, there are two symmetry-related Te···H hydrogen bonds of 2.7759(8) Å in **4**. The cations are also linked together by hydrogen bonds to the ketone oxygen atoms. The O···H contacts are 2.385(4) and 2.416(4) Å.

(Figure 4 here)

3.4. The crystal structure of $Fu_2Te(6)$

The molecular structure of Fu₂Te (**6**) is shown in Figure 5 together with selected bond parameters. The lengths of the Te-C bonds of 2.0836(4)-2.0847(4) Å in molecular Fu₂Te (**6**) are close to single bond lengths and agree well with those in the related bis(2-thienyl) telluride Th₂Te [2.082(12)-2.103(10) Å] [51]. The Fu₂Te molecules are linked together into columns by a bifurcated H···O hydrogen bonding network with two pairs of H···O contacts [2.6957(5)-3.1722(6) Å and 2.8017(7)-3.4188(8) Å], as shown in Figure 6. The tellurium atoms of the neighbouring molecules also show Te···Te secondary bonding interactions of 3.9733(11) Å. While Th₂Te is not isomorphic with **6**, its lattice shows similar features exhibiting bifurcated hydrogen bonds and Te···Te secondary bonding interactions.

(Figure 5 here)

(Figure 6 here)

3.5. The pathway of the reaction of FuTeI and PPh_3 in the THF solution

FuTeI (2) reacts with triphenylphosphine in THF and forms an oily reaction mixture. The crystallization by using the 1:1 solution of hexane and CH_2Cl_2 affords $\{Ph_3P(CH_2)_4PPh_3\}$ [TeI₄]·2CH₂Cl₂ (5·2CH₂Cl₂), (CH₂)₄TeI₂ (7), and Ph₃PO indicating that the THF ring opening plays a significant role in the reaction (see Scheme 1). The formation of 5 resembles that of zwitterionic $Ph_3PO(CH_2)_4TeBr_4$ from Ph_3P and $TeBr_4$ in THF [52]. The THF ring opening and the formation of 7 have previously been observed also in the reaction of Ph_3P and TeI_4 [23]. The THF,

dioxane, and thioxane ring opening reactions have recently been reviewed, expanded, and discussed in terms of reactivity of frustrated Lewis pairs [53]. Furthermore, bimetallic sodium–magnesium and sodium-magnese bases lead to the ring fragmentation of tetrahydrofuran with subsequent capture of the fragments in a number of crystalline complexes [54].

Ph₃PBr₂ has been reported to react with THF to afford Ph₃PO and BrCH₂(CH₂)₂CH₂Br [55]. Since the reaction of BrCH₂(CH₂)₂CH₂Br with Ph₃P has been reported to yield $\{Ph_3P(CH_2)_4PPh_3\}^{2+}$ [56], the presence of $\{Ph_3P(CH_2)_4PPh_3\}^{2+}$ in 5·2CH₂Cl₂ can readily be rationalized to be due to the formation of ICH₂(CH₂)₂CH₂I during the reaction of FuTeI with Ph₃P in THF. This species has also been suggested to be an intermediate in the formation of (CH₂)₄TeI₂ (7) upon treating TeI₄ with PPh₃ [23].

The five-membered lactone ring in the {Ph₃P(C₄H₅O₂)}⁺ cation of **4** can originate either from THF or from the furyl group of the reactant bis(2-furyl) ditelluride **1**. It has been reported that triphenylphosphine is oxidized to triphenylphosphine oxide in the presence of metallic catalyst in airsaturated THF under nitrogen atmosphere [57]. After the oxidation, THF reacts to form butyrolactol and butyrolactone. Butyrolactone can also be formed by the reaction of THF with molecular oxygen in the presence of a metallic catalyst or a radical initiator [58-69]. The yield of γ -butyrolactone in the reactions varies from trace amounts to almost quantitative. γ -Butyrolactone, however, doesn't readily react at the 4-position although fluorination at the 4- or 5-position has been reported [70]. Ab initio molecular orbital calculations have shown that the relative electron densities at 3-, 4-, and 5-positions of the γ -butyrolactone ring are 3 \approx 4 \gg 5 [70]. This indicates that the nucleophilic attack of Ph₃P should most readily take place at the 5-position of the γ -butyrolactone, which is generally the position, at which the butyrolactone ring is attacked. This is inconsistent with our observation of the formation of {Ph₃P(C₄H₅O₂)}⁺ cation, where triphenylphosphine is attached at the 4-position.

The formation of the $C_4H_5O_2$ ring, which is bound to the phosphorus atom of triphenyl phosphine at the position 4, can be rationalized by the oxidation of the furyl group of **1**, as shown in Scheme 2. When Ph_3P is added into the reaction mixture containing **2**, part of it abstracts tellurium with the formation of unstable Ph_3PTe , which will be converted in ambient atmosphere into Ph_3PO and elemental tellurium. Another product is 2-furyl iodide. It can be expected to react with moisture in air resulting in the removal of HI and the formation of 2-furyl hydroxide. Due to keto-enol equilibrium it can also exist as a ketone. In this form the carbon in position 4 is slightly electron-deficient and can be conceived to undergo a reaction with a nucleophile such as Ph_3P . The final cation is formed with the reaction of a H^+ , which was formed upon removal of HI from 2-furyl iodide.

The abstraction of tellurium by Ph_3P may also explain the formation of $Fu_2Te(6)$ during the reaction.

(Scheme 2 here)

4. Conclusions

The reaction of Fu₂Te₂ (**1**) with iodine yields FuTeI (**2**), which was treated *in situ* with PPh₃. The products in the reaction of Ph₃P with FuTeI depend on the solvent. In Et₂O, the reaction affords Ph₃PTe(Fu)I (**2**). When the reaction of **2** and Ph₃P is carried out in THF, no evidence of the formation of Ph₃PTe(Fu)I is observed. The reaction yields a mixture of products comprising $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (**4**), $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]$ (**5**), Fu₂Te (**6**), $(CH_2)_4TeI_2$ (**7**), Ph₃PO, and elemental tellurium. The formation of the $\{Ph_3P(C_4H_5O_2)\}^+$ cation can be explained by the abstraction of tellurium from **2** followed by the reaction of the resulting 2-furyl iodide with atmospheric moisture and Ph₃P. Compounds **5** and **7** are formed as a consequence of THF ring opening reactions induced by

triphenylphoshine. The reaction products were identified and characterized by single-crystal X-ray crystallography and the reactions were monitored by ${}^{31}P{}^{1}H$ and ${}^{125}Te$ NMR spectroscopy.

Appendix A. Supplementary data

CCDC 943627-943630 contain the supplementary crystallographic data for **3-6**. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

nP

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6. References

- [1] O. Vikane, Acta Chem. Scand. A 29 (1975) 787-793.
- [2] E. Schulz Lang, U. Abram, J. Strähle, Z. Anorg. Allg. Chem. 623 (1997) 1968-1972.
- [3] E. Schulz Lang, R.M. Fernandes Jr., E.T. Silveira, U. Abram, E.M. Vázquez-López, Z. Anorg.
 Allg. Chem. 625 (1999) 1401-1404.
- [4] P.D. Boyle, W.I. Cross, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarwar, J.M. Sheffield, Angew. Chem. Int. Ed. 39 (2000) 1796-1798.

- [5] G.N. Ledesma, E. Schulz Lang, E.M. Vázquez-López, U. Abram, Inorg. Chem. Commun. 7 (2004) 478-480.
- [6] E. Schulz Lang, G. Manzoni de Oliveira, G.A. Casagrande, J. Organomet. Chem. 691 (2006) 59-64.
- [7] G. Manzoni de Oliveira, E. Faoro E. Schulz Lang, G.A. Casagrande, Z. Anorg. Allg. Chem. 632 (2006) 659-663.
- [8] E. Schulz Lang, G.N. Ledesma, U. Abram, M. Vega-Teijido, I. Caracelli, J. Zukerman-Schpector,
 Z. Kristallogr. 221 (2006), 166-172.
- [9] E. Schulz Lang, G.A. Casagrande, G. Manzoni de Oliveira, G.N. Ledesma, S.S. Lemos, E.E. Castellano, U. Abram, Eur. J. Inorg. Chem. (2006) 958-964.
- [10] E. Faoro, G. Manzoni de Oliveira, E. Schulz Lang, J. Organomet. Chem. 691 (2006) 5867-5872.
- [11] J. Beckmann, M. Hesse, H. Poleschner, K. Seppelt, Angew. Chem. 46 (2007) 8277-8280.
- [12] E. Faoro, G. Manzoni de Oliveira, E. Schulz Lang, J. Organomet. Chem. 694 (2009) 1557-1561.
- [13] E. Faoro, G. Manzoni de Oliveira, E. Schulz Lang, Polyhedron 28 (2009) 63-68.
- [14] G. Manzoni de Oliveira, E. Faoro, E. Schulz Lang, Inorg. Chem. 48 (2009) 4607-4609.
- [15] E. Faoro, G. Manzoni de Oliveira, E. Schulz Lang, C.B. Pereira, J. Organomet. Chem. 695 (2010) 1480-1486.
- [16] E. Faoro, G. Manzoni de Oliveira, E. Schulz Lang, C.B. Pereira, J. Organomet. Chem. 696 (2011) 2438-2444.
- [17] R.T. Mahdi, J.D. Miller, J. Chem. Soc. Dalton Trans. (1983) 1071-1074.
- [18] N.W. Alcock, W.D. Harrison, J. Chem. Soc. Dalton Trans. (1984) 869-875.
- [19] J.V. Comasseto, R.E. Barrientos-Astigarraga, Aldrichimica Acta 33 (2000) 66-78.
- [20] W.L. Dorn, A. Knöchel, P. Schulz, G. Klar, Z. Naturforsch., Teil B 31 (1976) 1043-1047.
- [21] T.M. Klapötke, B. Krumm, I. Schwab, Acta Crystallogr. Sect. C 61 (2005) 04045-04046.

- [22] B. Krebs, F.-P. Ahlers, Adv. Inorg. Chem. 35 (1990) 235-317.
- [23] S.M. Närhi, R. Oilunkaniemi, R.S. Laitinen, M. Ahlgren, Inorg. Chem. 43 (2004) 3742-3750.
- [24] J.L. Dutton, R. Tabeshi, M.C. Jennings, A.J. Lough, P.J. Ragogna, Inorg. Chem. 46 (2007) 8594-8602.
- [25] F.J. Berry, N. Gunduz, M. Roshani, B.C. Smith, Commun. Fac. Sci. Univ. Ankara, Ser. B, 22B (1975) 21-23.
- [26] M. Albeck, S. Shaik, J. Chem. Soc. Perkin Trans. 1 (1975) 1223-1229.
- [27] J.L. Dutton, P.J. Ragogna, Inorg. Chem. 48 (2009) 1722-1730.
- [28] L. Engman, M.P. Cava, Organometallics 1 (1982) 470-473.
- [29] K. Y. Jen, M. P. Cava, J. Org. Chem. 48 (1983) 1449-1451.
- [30] M.J. Collins, G.J. Schrobilgen, Inorg. Chem. 24 (1985) 2608-2614.
- [31] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467–473; ibid. A64 (2008) 112–122.
- [32] G. Bandoli, G. Bartolozzo, D.A. Clemente, U. Croatto, C. Panattoni, J. Chem. Soc. A (1970) 2778-2780.
- [33] A.I. Gusev, N.G. Bokii, N.N. Afonina, T.V. Timofeeva, A.E. Kalinin, Yu.T. Struchkov, Zh. Strukt. Khim. 14 (1973) 116-125.
- [34] G. Ruban, V. Zabel, Cryst. Struct. Commun. 5 (1976) 671-677.
- [35] C.P. Brock, W.B. Schweizer, J.D. Dunitz, J. Am. Chem. Soc. 107 (1985) 6964-6970.
- [36] A.L. Spek, Acta Crystallogr. Sect. C 43 (1987) 1233-1235.
- [37] K.A. Al-Farhan, J. Crystallogr. Spectrosc. Res. 22 (1992) 687-689.
- [38] J.A. Thomas, T.A. Hamor, Acta Crystallogr. Sect. C 49 (1993) 355-357.
- [39] P. Deplano, S.M. Godfrey, F. Isaia, C.A. McAuliffe, M.L. Mercuri, E.F. Trogu, Chem. Ber./Recueil 130 (1997) 299-305.

- [40] N. Bricklebank, S.M. Godfrey, A.G. Mackie, C.A. McAuliffe, R.G. Pritchard, P.J. Kobryn, J. Chem. Soc. Dalton Trans. (1993) 101-103.
- [41] S. Pohl, W. Saak, B. Krebs, Z. Naturforsch., Teil B 40 (1985) 251-257.
- [42] P.C. Srivastava, H.G. Schmidt, H.W. Roesky, Z. Naturforsch., Teil B 50 (1995) 695-696.
- [43] P.C. Srivastava, S. Bajpai, Synth. React. Inorg. Metal-Org. Chem. 29 (1999) 1793-1804.
- [44] G.E. Maciel, R.V. James, Inorg. Chem. 3 (1964) 1650-1651.
- [45] M.J. Poropudas, L. Vigo, R. Oilunkaniemi, R.S. Laitinen, Heteroatom Chem. 22 (2011) 348-357.
- [46] A.Z. Al-Rubaie, H.A.Y. Alshirayda, P. Granger, S. Chapelle, J. Organomet. Chem. 287 (1985) 321-327.
- [47] S.M. Godfrey, R.T.A. Ollerenshaw, R.G. Pritchard, C.L. Richards, J. Chem. Soc. Dalton Trans. (2001) 508-509.
- [48] J. Emsley, The Elements, third ed., Oxford University Press, New York, 1998.
- [49] J. Konu, T. Chivers, Dalton Trans. (2006) 3941-3946.
- [50] M. Fujiwara, N. Tajima, T. Imakubo, M. Tamura, R. Kato, J. Solid State Chem. 168 (2002) 396-407.
- [51] G. Bandoli, J. Bergman, K.J. Irgolic, A. Grassi, G.C. Pappalardo, Z. Naturforsch., Teil B, 40 (1985) 1157-1160.
- [52] S.M. Kunnari, R. Oilunkaniemi, R.S. Laitinen, M. Ahlgren, J. Chem. Soc., Dalton Trans. (2001) 3417-3418.
- [53] B. Birkmann, T. Voss, S. J. Geier, M. Ullrich, G. Kehr, G. Erker, D.W. Stephan, Organometallics 29 (2010) 5310-5319.
- [54] R.E. Mulvey, V.L. Blair, W. Clegg, A.R. Kennedy, J. Klett, L. Russo, Nature Chem. 2 (2010) 588-591.
- [55] A.G. Anderson Jr., F.J. Freenor, J. Org. Chem. 37 (1972) 626-630.

- [56] J.-C. Chang, W.-Y. Ho, I-W. Sun, Y.-K. Chou, H.-H. Hsieh, T.-Y. Wu, S.-S. Liang, Polyhedron 29 (2010) 2976-2984.
- [57] R.F. Moreira, E.Y. Tshuva, S.J. Lippard, Inorg. Chem. 43 (2004) 4427-4434.
- [58] M. Aresta, C. Fragale, E. Quaranta, I. Tommasi, J. Chem. Soc. Chem. Commun. (1992) 315-317.
- [59] M. Sommovigo, H. Alper, J. Mol. Catal. 88 (1994) 151-158.
- [60] P. Li, H. Alper, J. Mol. Catal. 72 (1992) 143-152.
- [61] T. Akindele, K.-I. Yamada, K. Tomioka, Acc. Chem. Res. 42 (2009) 345-355.
- [62] Y. Yamamoto, K.-i. Yamada, K. Tomioka, Tetrahedron Letters 45 (2004) 795-797.
- [63] M.T. Reetz, K. Töllner, Tetrahedron Letters 36(52) (1995) 9461-9464.
- [64] R.C. Luckay, X. Sheng, C.E. Strasser, H.G. Raubenheimer, D.A. Safin, M.G. Babashkina, A. Klein, New J. Chem. 34 (2010) 2865-2840.
- [65] M. Salavati-Niasari, Inorg. Chem. Commun. 9 (2006) 628-633.
- [66] M. Salavati-Niasari, N. Mir, J. Incl. Phenom. Macrocycl. Chem. 59 (2007) 223-230.
- [67] M.T. Hay, S.J. Geib, D.A. Pettner, Polyhedron 28 (2009) 2183-2186.
- [68] T. Straub, A.M.P. Koskinen, Inorg. Chem. Commun. 5 (2002) 1052-1055.
- [69] R.F. Moreira, E.Y. Tshuva, S.J. Lippard, Inorg. Chem. 43 (2004) 4427-4434.
- [70] Y. Sasaki, R. Ebara, N. Nanbu, M. Takehara, M. Ue, J. Fluorine Chem. 108 (2001) 117-120.

Table 1. Details of the structure determinations of $Ph_3PTe(Fu)I(3)$, $\{PPh_3(C_4H_5O_2)\}_2[TeI_4](4)$, $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$ (5·2CH₂Cl₂), and Fu₂Te (6).

	3	4	$5 \cdot 2 C H_2 C l_2$	6
formula	C ₂₂ H ₁₈ OPTeI	C44H40O4P2Te I4	$C_{42}H_{42}Cl_4I_4P_2Te$	$C_8H_6O_2Te$
fw	583.83	1329.90	1385.70	261.73
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_{1}/c$	<i>P</i> -1	$P2_{1}/c$	$P2_{1}/c$
<i>a</i> , Å	9.975(2)	9.6853(19)	9.7152(2)	5.4735(11)
b, Å	24.234(5)	10.682(2)	22.6322(4)	18.758(4)
<i>c</i> , Å	9.0769(18)	11.774(2)	11.2653(3)	8.1454(16)
, deg		84.56(3)	~	
, deg	105.95(3)	76.86(3)	106.0150(10)	93.07(3)
, deg		75.92(3)		
V	2109.8(7)	1149.7(4)	2380.46(10)	835.1(3)
Ζ	4	1	2	4
<i>T</i> (K)	120(2)	120(2)	120(2)	120(2)
calcd, g cm 3	1.838	1.921	1.933	2.082
(MoK), mm 1	2.957	3.441	3.539	3.506
<i>F</i> (000)	1112	630	1312	488
crystal size (mm ³)	$0.10\times0.10\times0.05$	0.25 x 0.25 x 0.25	0.10 x 0.10 x 0.05	$0.40 \times 0.20 \times 0.20$
	C			

θ range (°)	3.17 - 25.00	3.12 - 26.00	1.80 -26.00	3.32 - 25.99
reflns collected	8103	18026	24427	3562
unique reflns	3633	4458	4656	1588
Parameters	146	250	241	101
Goodness-of-fit on F^{2a}	1.119	1.154	1.043	1.124
R _{int}	0.0779	0.0358	0.0391	0.0988
$R_1^{\ b}$	0.0637	0.0305	0.0390	0.0491
wR_2^{b}	0.1189	0.0877	0.0872	0.1335
R_1 (all data) ^{<i>c</i>}	0.0969	0.0366	0.0562	0.0584
wR_2 (all data) ^c	0.1346	0.0877	0.0926	0.1395
Largest diff. peak and	0.011, 1.062	1.075. 1.122	1 425, 1 250	1 205. 1 276
hole (e $Å^3$)	0.911; -1.062	1.873, -1.132	1.423, -1.350	1.203, -1.370
completeness	98.0 %	98.8 %	100.0 %	96.9 %

^{*a*} Goof = { $\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)$ }^{*b*} (*n* = number of reflections, *p* = total number of parameters refined). ^{*b*} $I \ge 2$ (*I*).

^c $R_1 = [||F_0| - |F_c||]/[||F_0|], wR_2 = \{[w(F_0^2 - F_c^2)^2]/[w(F_0^2)^2]\}^{\frac{1}{2}}.$

Table 2. Selected bond lengths (Å) and angles (°) in the $[TeI_4]^{2-}$ anions in $\{PPh_3(C_4H_5O_2)[TeI_4]$ (4) and $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$ (5·2CH₂Cl₂)

	4	5	
Te1-I1	2.9348(11)	2.9795(4)	
Te1-I2	2.9494(8)	2.9606(4)	
11 T 1 10	01 20/2)	00 405(10)	
11 - 1 e 1 - 12	91.28(3)	88.425(10)	
$11-1e1-11^{\circ}$	180.0	180.0	
$11 - 1e1 - 12^{a}$ 12 To1 12 ^a	88.72(3)	91.575(10)	
12-101-12	180.0	180.0	
^{<i>a</i>} Symmetry operation	ons: 4 : 1- <i>x</i> , - <i>y</i> , - <i>z</i> . 5 : 1- <i>x</i> , 1- <i>y</i> ,	1-z	
0			

Figure Captions

Figure 1. The crystal structure of Ph₃PTe(Fu)I (**3**) indicating the numbering of the atoms. The anisotropic displacement parameters have been drawn at 50 % probability level. Selected bond lengths (Å) and angles (°): Te1-II 3.1174(15), Te1-PI 2.561(3), Te1-CI 2.092(10), P1-C111 1.802(11), P1-C121 1.801(11), P1-C131 1.793(11); I1-Te1-PI 176.80(7), I1-Te1-CI 89.4(3), P1-Te1-CI 90.3(3), Te1-P1-C111 115.8(4), Te1-P1-C121 117.0(4), Te1-P1-C131 101.1(4), C111-P1-C121 104.4(5), C111-P1-C131 109.4(5), C121-P1-C131 108.9(5).

Figure 2. The linking of the discrete $Ph_3PTe(Fu)I(3)$ molecules by $H\cdots I$ and $H\cdots Te$ hydrogen bonds. The van der Waals' radii of hydrogen, tellurium, and iodine have been superimposed to emphasize these interactions. The tetrahedra around the phosphorus centers have been indicated for clarity.

Figure 3. The crystal structures of (a) $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (4) and (b) $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$ (5·2CH₂Cl₂) indicating the numbering of the atoms. The anisotropic displacement parameters have been drawn at 50 % probability level.

Figure 4. The H···I and H···Te hydrogen bonding networks in (a) (a) $\{Ph_3P(C_4H_5O_2)\}_2[TeI_4]$ (4) and (b) $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$ (5·2CH₂Cl₂). The van der Waals' radii of hydrogen, tellurium, and iodine for the relevant interactions have been superimposed to emphasize these interactions. The solvent molecules have been omitted and the tetrahedra around the phosphorus centers have been indicated for clarity.

Figure 5. The crystal structure of Fu_2Te (6) indicating the numbering of the atoms. The anisotropic displacement parameters have been drawn at 50 % probability level. Selected bond lengths (Å) and angles (°): Te1-C11 2.084(5), Te1-C21 2.085(5); C11-Te1-C21 96.9(2).

Figure 6. The H···O hydrogen bonds and the Te···Te secondary bonding interactions in Fu_2Te (6). The van der Waals' radii of hydrogen, oxygen, and tellurium have been superimposed to emphasize these interactions.

Scheme 1. The reactions of Fu_2Te_2 (Fu = 2-furyl, C₄H₃O) with iodine and triphenyl phosphine in Et₂O and THF.

Scheme 2. A possible pathway to the formation of $\{Ph_3P(C_4H_5O_2)\}^+$ from Fu₂Te₂.

n

Crystallographic information of **3-6** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 943627-943630, Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int.code + 44(1223)336-033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>].





Figure 2











Figure 6



Scheme 1



Table of Contents Entry

Tetrahydrofuran Ring Opening and Unexpected Oxidation of The Furyl Ring in The Reaction of Bis(2-furyl)ditelluride with Iodine and Triphenylphosphine

Sari M. Närhi, Kaisa Malo, Raija Oilunkaniemi, Risto S. Laitinen

The reaction of bis(2-furyl) ditelluride Fu_2Te_2 with iodine and Ph_3P yields a mixture of products. The main products are $\{PPh_3(C_4H_5O_2)\}_2[TeI_4]$, $\{Ph_3P(CH_2)_4PPh_3\}[TeI_4]\cdot 2CH_2Cl_2$, Fu_2Te , $(CH_2)_4TeI_2$, Ph_3PO , and Te indicating THF ring opening, abstraction of tellurium by PPh₃, and the conversion of the furyl ring in FuTeI into a lactone ring.

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