Journal of Organometallic Chemistry 728 (2013) 44–51

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Tellurium derivatives of 3-acetyl-2,5-dimethylthiophene: Synthetic and structural aspects

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ARTICLE INFO

Article history:
Received 22 October 2012
Received in revised form
21 December 2012
Accepted 27 December 2012

Keywords:
Tellurium
3-Acetyl-2,5-dimethylthiophene
Organotellurium(IV) compound
Intramolecular secondary interaction

ABSTRACT

Oxidative addition of α-bromo-3-acetyl-2,5-dimethylthiophene to elemental tellurium and aryltellurium(II) bromide provides direct routes to (2,5-dimethyl-3-thiophenoylmethyl)tellurium(IV) dibromides, $(Me_2TpnCOCH_2)_2TeBr_2$ (**1a**; $Me_2Tpn = 2,5\text{-}Me_2\text{-}3\text{-}C_4HS$) and $Ar(Me_2TpnCOCH_2)TeBr_2$ ($Ar = 1\text{-}C_{10}H_7$, Npl, **2a**; 2,4,6-$Me_3C_6H_2$, Mes, **3a**). The chloro analogs of **2a** and **3a**, $Ar(Me_2TpnCOCH_2)TeCl_2$ (Ar = Npl, **2b**; Mes, **3b**) and derivative when Ar = Anisyl (anisyl = 4-$MeOC_6H_4$, **4b**) were prepared by the condensation reaction of methyl ketone, $Me_2TpnCOCH_3$ with $NplTeCl_3$, $MesTeCl_3$ and $anisylTeCl_3$ respectively while the chloro analog of **1a**, bis(2,5-dimethyl-3-thiophenoylmethyl)tellurium(IV) dichloride, $(Me_2TpnCOCH_2)_2TeCl_2$ (**1b**) was obtained by the condensation reaction of methyl ketone, $Me_2TpnCOCH_3$ with $TeCl_4$. Metathesis of these products (**1a**–**b**, **2a**–**b**, **3a**–**b** and **4b**) with an alkali iodide affords the iodo analogs **1c**, **2c**, **3c** and **4c**. These diorganotellurium dihalides are reduced with aqueous bisulfite to diorganotellurides **1**–**4**, which can be oxidized readily with dihalogens to the desired diorganotellurium(IV) dihalides. The crystal structures of the Te(IV) compounds **1b**, **2a**, **3c** and **4b** have been studied and all the Te(IV) compounds, the carbonyl functionalized organic moiety, show intramolecular 1,4–Te···O secondary bonding interaction (SBI). In the crystal lattice of **2a**, the intermolecular Te···Br secondary bonding interactions are evident and result in a dimer. They get further associated via C–H···Br secondary interactions to form a 3D supramolecular motifs. In **1b**, **3c** and **4b** supramolecular motifs are formed through C–H···O and C–H···Cl interactions.

1. Introduction

The tellurium chemistry has been the subject of intensive research in last three decades due to the interest of several research groups in organometallic and supramolecular chemistry of organotellurium compounds [1,2] and applications of metal complexes of such compounds in catalysis [3–5]. An increase in the focus on the exploration of new organotellurium compounds has been noticed in past and as a result, various types of functionalized tellurium derivatives have also been synthesized [6–13]. Functionalization of a Te compound by incorporating the heteroaryl moiety in the backbone is also an interesting strategy. However, such compounds have not been synthesized in a large number so far.

Heteroaroylmethyltellurium derivatives may represent a class of such compounds and some compounds have already been explored. Bis(2-thiophenoylmethyl)tellurium(IV) dichloride $(TpnCOCH_2)_2TeCl_2$ ($Tpn = 2\text{-}C_4H_3S$), first compound of its type, was obtained by the reaction of $TeCl_4$ with 2-acetylthiophene [14–16] and its solid state structure was also solved by X-ray diffraction technique [17]. Its reduction resulted in bis(2-thiophenoylmethyl)telluride(II). Likewise, bis(2-benzo[b]furoylmethyl)tellurium(IV) dichloride $(BnzFuCOCH_2)_2TeCl_2$ [15] and corresponding telluride, $(BnzFuCOCH_2)_2Te$ ($BnzFu = 2\text{-}C_8H_7O$) have also been isolated.

The tellurated thiophene derivatives [18], bis(2-thiophenoylmethyl)tellurium(IV) dibromide [19] and bis(2-furoylmethyl)tellurium(IV) dibromide [20] have been synthesized recently by insertion of elemental tellurium into the Mg–C(Tpn) or by oxidative insertion of elemental tellurium into the C–Br bond of $RCOCH_2Br$.

Taking into consideration that this class can become more interesting if enriched further by exploration of new analogs, in this paper we report isolation and structural characterization including supramolecular chemistry of the (2,5-dimethyl-3-thiophenoylmethyl)tellurium(II and IV) derivatives with the aim of studying the effect of different organic moieties (naphthyl, mesityl and anisyl) and their substituents on SBI and other structural aspects. These species

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http://dx.doi.org/10.1016/j.jorganchem.2012.12.038

have been prepared under ambient conditions by (i) oxidative addition of α-bromo/iodo-2,5-dimethyl-3-acetylthiophene to elemental tellurium, (ii) electrophilic substitution of 3-acetyl-2,5-dimethylthiophene with the aryltellurium trichlorides that bear a sterically cumbersome aryl ligand bound to tellurium atom and (iii) oxidative addition of dihalogens to the tellurides to give the corresponding tellurium(IV) dihalides. The isolated products have been characterized with the help of elemental analyses and spectroscopic studies. Single crystals could also be grown for some of these newly synthesized compounds and the solid state structural studies have been made with X-ray diffraction technique in such cases.

2. Results and discussion

2.1. Synthesis and general

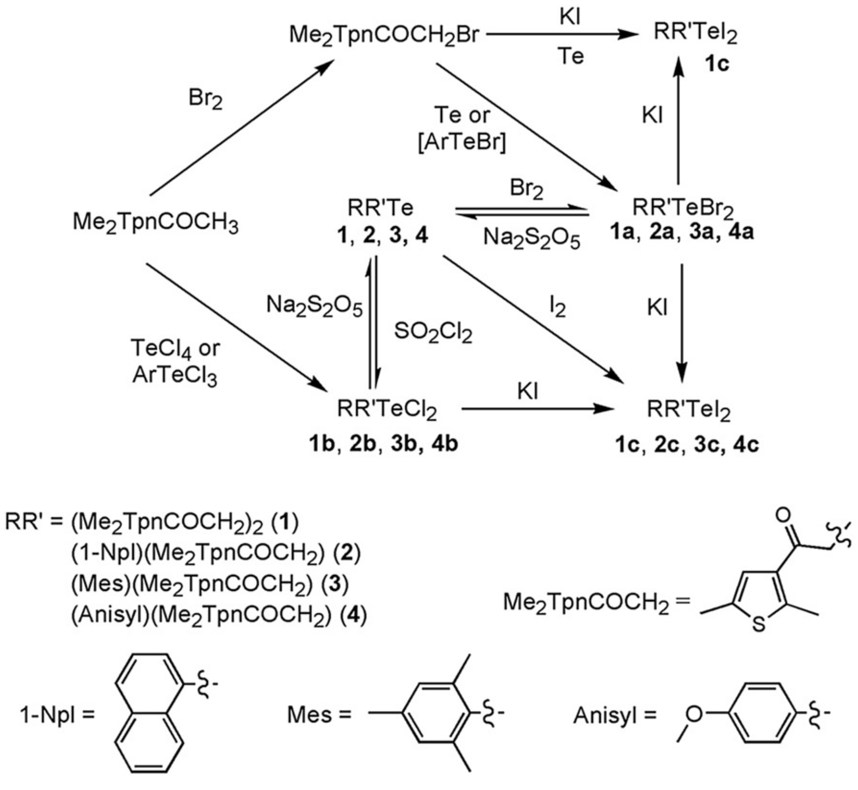
The $(Me_2TpnCOCH_2)_2TeBr_2$ (**1a**) is synthesized by the reaction of thermally unstable α-bromo-3-acetyl-2,5-dimethylthiophene with elemental tellurium at ambient temperature. When ArTeBr (prepared *in situ* from Ar_2Te_2 and Br_2; Ar = Npl, Mes) is used as a reactant instead of elemental Te in this reaction, formation of $Ar(Me_2TpnCOCH_2)TeBr_2$ (**2a** and **3a**) takes place. The chloro analogs, $(Me_2TpnCOCH_2)_2TeCl_2$ (**1b**) and $Ar(Me_2TpnCOCH_2)TeCl_2$ (**2b**–**4b**) have been obtained by electrophilic substitution of the parent ketone ($Me_2TpnCOCH_3$) with $TeCl_4$ and $ArTeCl_3$ (Ar = Npl, Mes and anisyl) respectively. Reduction of these dihalides (**1a**–**3a** and **1b**–**3b**) with $Na_2S_2O_5$ affords the corresponding tellurides (**1**–**3**) with +2 oxidation states. These tellurides (**1**–**3**) are readily oxidizable with dihalogens to afford the corresponding diorganotellurium(IV) dihalides (Scheme 1). The iodo analogs (**1c**–**4c**) have been prepared by metathesis of the corresponding bromo/chloro compounds (**1a**, **2b**, **3b**, **4b**) with alkali metal iodides. Iodo analogs of **1a** can also be prepared by oxidative addition of α-iodo-2,5-dimethyl-3-acetylthiophene to tellurium powder.

All the tellurium(IV) compounds (**1a**–**1c**, **2a**–**2c**, **3a**–**3c** and **4a**–**4c**) and tellurides **1** and **3** are sharp melting colorless to orange solids, soluble in chloroform and dichloromethane while the telluride **2** is red color oil and soluble in many organic solvents such as hexane, petroleum ether, dichloromethane and chloroform. These Te(IV) and Te(II) compounds are fairly stable as compared to the analogous 2-acetylthiophene and 2-acetylfuran tellurium derivatives [19,20].

2.2. Spectroscopic studies

Important NMR chemical shifts of all the newly synthesized compounds are listed in Table 1 for critical comparison. Methylene protons, appearing at ~4.1 ppm in the ^1H NMR spectra of Te(II) derivatives **1**–**3**, are appreciably shielded in comparison to those of corresponding Te(IV) analogs (δ 5.1–5.7 ppm) except in case of **3c** (δ 4.2 ppm). Protons of the thiophene ring along with the ring protons of naphthyl, mesityl and anisyl groups appear in the aromatic region, while the methyl protons of the thiophene and mesityl as well as methoxy proton of anisyl group have been observed in the aliphatic region. Appearance of separate signals (1:1) for the *ortho* methyls of the mesityl group in the ^1H NMR spectra of **3a**–**3c** is indicative of restricted rotation of the benzene ring about the Te–C(Mes) bond.

The ^{13}C NMR chemical shifts for the carbonyl carbon appear in the range 186–193 ppm and the methylene carbon between 58 and 70 ppm for Te(IV) derivatives and 13.6, 17.2 and 15.6 ppm in case of tellurides **1**, **2** and **3** respectively. The symmetrical (**1a**, **1b**, **1c**) and unsymmetrical diorganotellurium(IV) derivatives (**2a**–**b**, **3a**–**b**, **4b**) give rise to a single ^{125}Te NMR resonance indicating the presence of only one Te containing species in their solutions. The chemical shift for telluride **3** (δ 357 ppm) is toward higher field than those of the Te(IV) derivatives and the chemical shift for the Te(IV) derivatives are consistent with the electronegativity of the halo ligands.



Scheme 1.

Table 1
Important chemical shifts (in ppm) for 2,5-dimethyl-3-thiophenoylmethyltellurium derivatives.

	^{1}H		^{13}C			^{125}Te
	CH_2	CH_3[a]	CH_2	CH_3[a]	CO	
1b	5.12	–	58.4	–	186.7	678
1a	5.25	–	58.3	–	186.7	680
1c	–	–	58.4	–	186.7	679
2b	5.57	–	66.9	–	186.0	763
2a	5.73	–	68.3	–	186.3	694
2c	5.74	–	54.9	–	186.3	–
3b	5.49	2.33, 2.44 (*o*-Me) 2.82 (*p*-Me)	66.2	21.0 (*p*-Me) 23.6, 24.2 (*o*-Me)	186.8	783
3a	5.65	2.33, 2.45 (*o*-Me) 2.79 (*p*-Me)	65.1	21.0 (*p*-Me) 23.3, 24.8 (*o*-Me)	186.8	703
3c	4.15	2.36, 2.42 (*o*-Me) 2.66 (*p*-Me)	63.0	21.0 (*p*-Me) 23.2, 25.9 (*o*-Me)	187.1	–
4b	5.24	3.88 (*p*-OMe)	70.3	55.5 (*p*-OMe)	186.2	845
4a	5.45	3.88 (*p*-OMe)	71.2	56.4 (*p*-OMe)	186.1	–
4c	5.50	3.87 (*p*-OMe)	69.9	55.4 (*p*-OMe)	185.7	–
1	4.06	–	13.6	–	193.1	–
2	4.11	–	17.2	–	193.6	–
3	3.95	2.30(*p*-Me) 2.61(*o*-Me)	15.6	21.0 (*p*-Me) 28.1, 29.6 (*o*-Me)	193.0	357

[a] Methyl protons excluding those of methyl groups of 3-acetyl-2,5-dimethylthiophene moiety.

2.3. *Crystal structures*

The molecular structures of **1b**, **2a**, **3c** and **4b** are shown in Figs. 1–4 with selected bond parameters collected in the caption to each figure. Asymmetric units in each case consist of one independent molecule.

The central Te(IV) atom among **1b**, **2a**, **3c** and **4b** shows trigonal bipyramidal primary geometry with expected X–Te–X and C–Te–C angular distortions due to its lone pair. However, the C–Te–C angle in **3c** is appreciably widened by the presence of the sterically demanding mesityl ligand in comparison to that in **1b**, **2a** and **4b** (see Table 2).

In molecular structures of all the four diorganotellurium(IV) dihalides (**1b**, **2a**, **3c** and **4b**), the carbonyl O atom of the sole functionalized ligand is involved simultaneously in the intramolecular secondary bonding interaction to the Te(IV) center. The observed internuclear distance between O and Te atoms, which is shorter than the sum of their van der Waals radii [d(Te, O) = 2.825(2) (**1b**), 2.892(3) (**2a**), 2.837(3) (**3c**), 2.803(22) (**4b**) Å; Σr_{vdw}(Te, O) = 3.58 Å] and near linearity of the O···Te–C_{trans} triad (∠O–Te–C_{trans} measures 154.80(5)°, 149.9(1)°, 162.9(1)° and 152.2(4)° in **1b**, **2a**, **3c** and **4b** respectively) substantiate the presence of attractive 1,4–Te···O interaction. This interaction can be attributed to the overlap of a filled *p*-orbital on the O atom with the vacant σ^*(Te–C_{trans}) molecular orbital (partly responsible for such an interaction) feasible. This interaction brings the O atom in to the equatorial C1A–Te–C1B plane, reduces somewhat the tetrahedral angle Te–C1A–C2A to 105.1(1)°, 106.8(2)°, 104.0(2)° and 104.6(1)° in **1b**, **2a**, **3c** and **4b** respectively and marginally the *trans* Te–C(aryl) bond length [d(Te–C(aryl)) = 2.121(3) (**2a**), 2.147(3) (**3c**), 2.092(2) (**4b**) Å]; *cf.* 2.103 Å in α-Npl_2TeCl_2 [21], 2.108 Å in β-Npl_2TeI_2) [22] and 2.113–2.112, 2.110–2.114, 2.107–2.128 Å in $(4\text{-}(MeO)C_6H_4)_2TeX_2$ (where X = Cl, Br, I respectively) [23–25].

In the crystal structure of symmetrically carbonyl functionalized diorganotellurium(IV) dichloride (**1b**) both the carbonyl functionalized organic ligands exhibit (C, O) chelating behavior and impart six-coordination to the central Te atom, similar to the molecular structures of bis(hetroaroylmethyl)tellurium(IV) dihalides [$(RCOCH_2)_2TeX_2$, R = (C_4H_3S), X = Cl; (C_4H_3O), X = Cl, Br] described earlier [17,20]. The skeletal frameworks of the organic ligands, Te–C–C(O)–C, in these compounds are invariably almost coplanar, with the equatorial C–Te–C plane and the cisoidal orientation of the ligands imparting a butterfly shape C_{2v} molecular symmetry. Due to the steric influence of the methyl groups on 2- and 5-position of the thiophene ring of organic moiety, 1,4 S···O intramolecular secondary bonding interaction are absent in these compounds. However such interactions have been reported to be present in similar compounds containing 2-acetylthiophene moiety [19]. In aryl(2,5-dimethyl-3-thiophenoylmethyl)tellurium(IV) dihalides **2a**, **3c** and **4b**, the increased values of dihedral angles between the C–Te–C plane and the mean planes of the organic ligands (Table 3) appears to be directly related with the steric demand of the aryl ligand similarly as conclusion drawn from the aryl(2-furoylmethyl)tellurium dichlorides [20].

In the crystal lattice of **1b**, the Te centers are not involved in any intermolecular interactions presumably due to the presence of sterically demanding heteroaroyl moiety ($Me_2TpnCOCH_2$–). In this case one-dimensional supramolecular array was realized due to the presence of C–H···O and C–H···Cl, H-bonding interactions (Figure S1).

In **2a** the five-coordinate central Te atom becomes accessible for intermolecular Te···Br secondary bonding interactions. The centrosymmetric zero-dimensional dimeric unit was realized via reciprocatory Te···Br1 interactions [d(Te, Br) = 3.7870(5) Å < Σ_{vdw}(Te, Br) (3.93 Å)] (Figure S2), these dimers are self-assembled, in the crystal lattice of **2a**, by means of C–H···Br secondary bonding interactions to give rise the 3D–supramolecular architecture (Figure S3). On the other hand in **3c**, steric bulk of

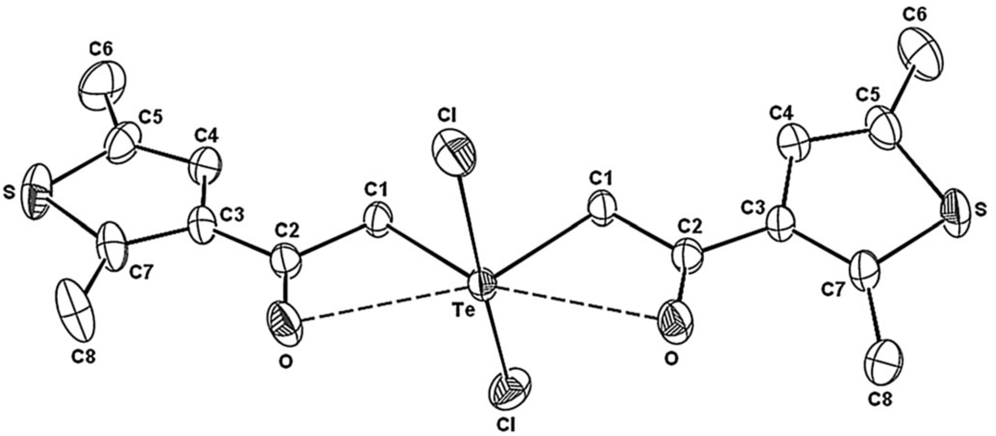


Fig. 1. Molecular structure of **1b**. Selected interatomic distances (Å) and angles (°): Te–C1 2.125(2), Te–Cl 2.4852(6), Te···O 2.825(2), C1–Te–C1 100.43(6), Cl–Te–Cl 172.83(2), O···Te–C1 154.80(5).

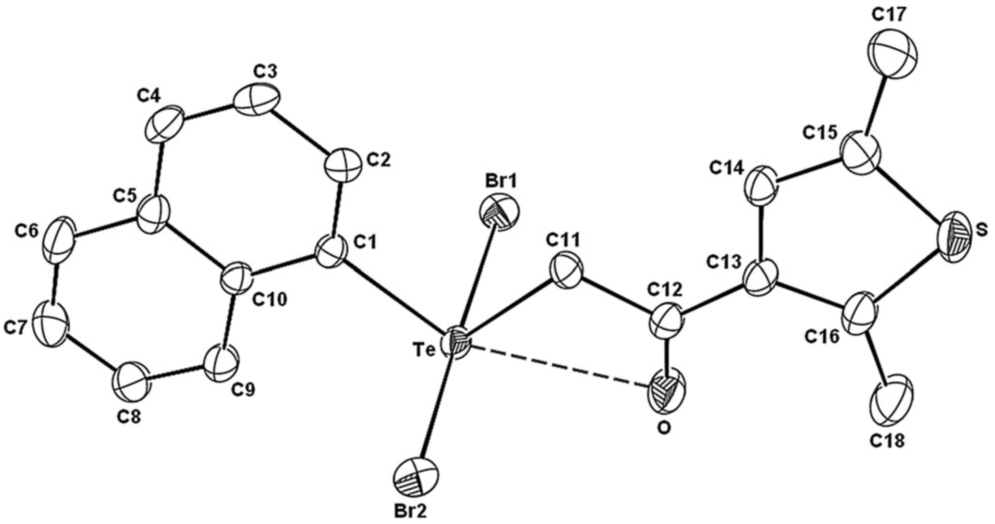


Fig. 2. Molecular structure of **2a**. Selected interatomic distances (Å) and angles (°): Te—C1 2.121(3), Te—C11 2.130(4), Te—Br1 2.7114(5), Te—Br2 2.6432(5), Te···O 2.892(3), C1—Te—C1 96.5(1), Br1—Te—Br2 176.79(2), O···Te—C1 149. 9(1).

the mesityl ligand hinders the involvement of central Te atom to enter in SBIs with the electron-rich I, O or S atoms. Molecular units in it assemble into the one-dimensional supramolecular arrays via C—H···O interactions (Figure S4). Presence of sterically cumbersome heteroaromatic Me_2Tpn moiety in **4b** appears to discourage the Te involved SBIs to take the center-stage, which paves the way for a combination of C—H···O and C—H···Cl interactions. The centrosymmetric dimeric units was formed through strong reciprocatory C—H···O interactions via C—H of $Me_2TpnCOCH_2$ — moiety and O of anisyl ligand and these dimeric units are self-assembled in the crystal lattice via (anisyl)C—H···Cl interactions to give rise the ribbons (i.e. one-dimensional supramolecular arrays) consisted of well-knit molecules (Figure S5).

2.4. Conclusion

A strategy involving oxidative addition of α-bromo-3-acetyl-2,5-dimethylthiophene to elemental tellurium and aryltellurium(II) bromide has been used as a direct synthetic route to obtain (2,5-dimethyl-3-thiophenoylmethyl)tellurium(IV) dibromides (**1a**–**3a**). The corresponding dichlorides can be obtained by the condensation of an appropriate tellurium(IV) chlorides ($TeCl_4$ or $ArTeCl_3$) with the parent methyl ketone ($Me_2TpnCOCH_3$). These tellurium(IV) compounds have been converted to corresponding Te(II) compounds by reduction with aqueous sodium metabisulfite solution. The structural aspects of these newly synthesized compounds have been studied to explore the supramolecular chemistry. The 2,5-dimethyl-3-thiophenoylmethyl moiety among the all Te(IV) compounds (**1b**, **2a**, **3c** & **4b**) act as (C, O) chelating ligand and in (2,5-dimethyl-3-thiophenoylmethyl)aryltellurium(IV) dihalides, the central Te atom is five-coordinate even in the presence of a bulky aryl ligand.

3. Experimental

3.1. General procedures

All solvents were purified and dried before use. Te powder was purchased from Sigma Aldrich (USA). The 3-acetyl-2,5-dimethylthiophene required as a precursor for the synthesis of the α-bromo-3-acetyl-2,5-dimethylthiophene has been procured from Aldrich (USA). 1-Naphthyl, mesityl and anisyltellurium trichlorides were

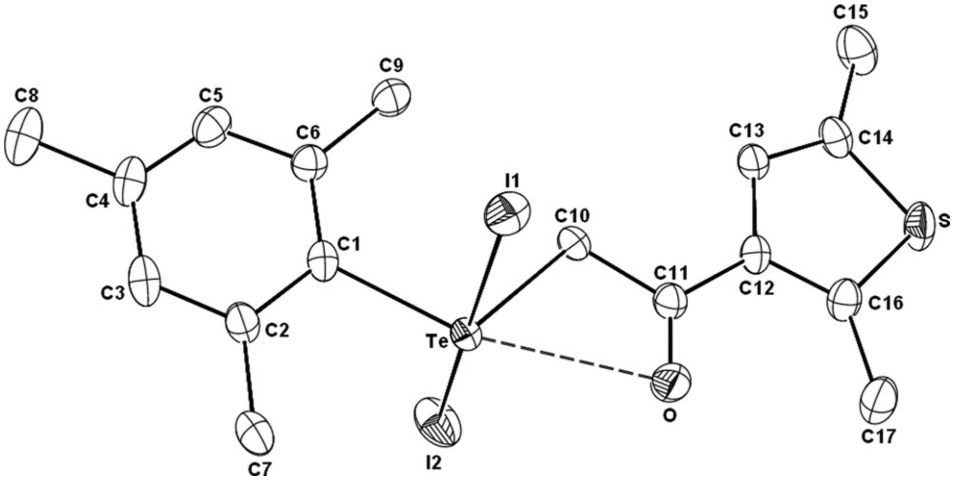


Fig. 3. Molecular structure of **3c**. Selected interatomic distances (Å) and angles (°): Te—C1 2.147(3), Te—C10 2.150(3), Te—I1 2.9291(3), Te—I2 2.9073(4), Te···O 2.837(3), C1—Te—C10 108.5(1), I1—Te—I2 173.93(1), O···Te—C1 162.9(1).

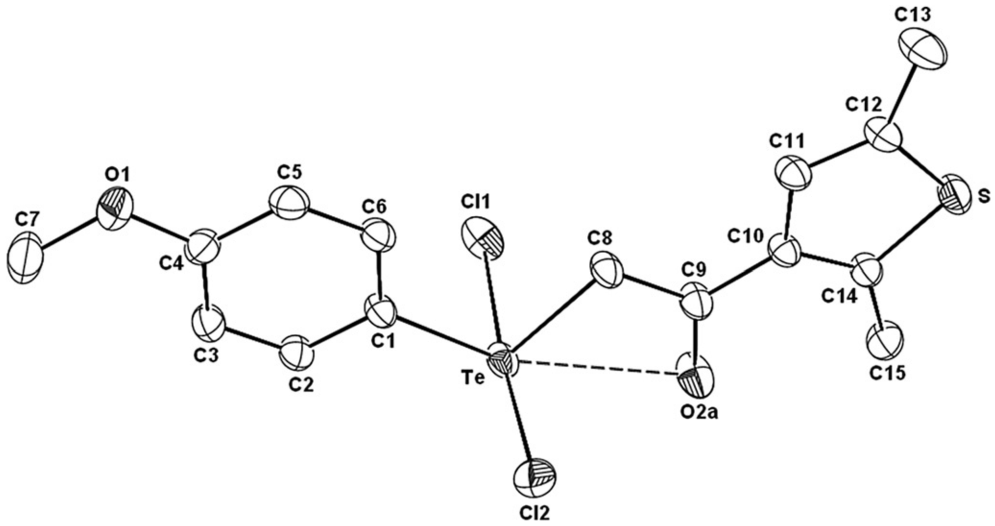


Fig. 4. Molecular structure of **4b**. Selected interatomic distances (Å) and angles (°): Te–C1 2.092(23), Te–C8 2.129(2), Te–Cl1 2.5111(7), Te–Cl2 2.5394(7), Te···O2a 2.803(22), C1–Te–C8 99.71(8), Cl1–Te–Cl2 173.11(2), O2a···Te–C1 152.2(4).

prepared by the chlorination of their corresponding ditellurides with SO_2Cl_2. Melting points were recorded in capillary tubes and are uncorrected. ^1H NMR spectra were recorded at 300.13 MHz in $CDCl_3$ on a Bruker DRX300 spectrometer using Me_4Si as the internal standard. $^{13}C\{^1H\}$ (100.54 MHz) and $^{125}Te\{^1H\}$ (126.19 MHz) NMR spectra were recorded on a JEOL Eclipse Plus 400 NMR spectrometer, using Me_4Si and Me_2Te respectively as internal standards. Spectra for compound **2b** were obtained in 1:1 $CDCl_3$/DMSO-d_6 solution, spectra for compounds **2c**, **4c** and **4a** were recorded in DMSO-d_6 while $CDCl_3$ was used as a solvent for all other. Microanalyses were carried out using a Carlo Erba 1108 analyzer.

3.2. Syntheses

3.2.1. Synthesis of α-bromo-3-acetyl-2,5-dimethylthiophene

Bromine (1.03 mL, 20 mmol) solution in 10 mL glacial acetic acid was added slowly over a period of 2 h from a pressure equalizing dropping funnel to a solution of 2,5-dimethy-3-acetylthiophene (2.84 mL, 20 mmol) in glacial acetic acid (~20 mL) with constant stirring. During addition, the color of solution changed from brown to darker. After the addition was complete, the reaction mixture was stirred further for 3 h and then poured into a beaker containing crushed ice. A colorless semi-solid got settled at the bottom, which was washed with water (6 × 20 mL) and extracted with ~50 mL diethyl ether. The solvent was removed at reduced pressure to obtain a residual liquid which was cooled overnight in a deep-freezer and colorless lachrymatory crystals of α-bromo-3-acetyl-2,5-dimethylthiophene were afforded after 48 h. Yield: 4.1 g (88%). M.p.: 47–49 °C. ^1H NMR: δ 2.43 (3H, s, CH_3), 2.69 (3H, s, CH_3), 4.26 (2H, s, CH_2), 7.01 (1H, s, thiophene ring) ppm.

3.2.2. Syntheses of symmetrical diorganotellurium derivatives

Compound **1a**: Freshly ground tellurium powder (0.50 g, 3.94 mmol) and α-bromo-3-acetyl-2,5-dimethylthiophene (1.84 g, 7.89 mmol) were stirred together at room temperature for 72 h. A thick paste was formed, that was washed with diethyl ether (4 × 10 mL) to remove excess of unreacted bromo compound. The desired product **1a** was extracted with dichloromethane (50 mL) and the extract was passed through a small silica column. After that the solvent was reduced to about 5 mL by distillation and 15 mL of petroleum ether (40–60 °C) was added to obtain a white precipitate which was recrystallized from dichloromethane to give **1a** as pale yellow rectangular crystals. Yield: 1.6 g (54%). M.p.: 167 °C. Anal. Calc. for $C_{16}H_{18}O_2S_2TeBr_2$ (593.85): C, 32.36; H, 3.06. Found: C, 32.23; H, 2.98. ^1H NMR: δ 2.44 (s, 6H, CH_3Tpn), 2.74 (s, 6H, CH_3Tpn), 5.25 (s, 4H, CH_2), 7.00 (s, 2H, ring proton) ppm. $^{13}C\{^1H\}$ NMR: δ 14.9 (CH_3), 16.3 (CH_3), 58.3 (CH_2), 126.2, 132.2, 136.4, 151.8 (ring carbons), 186.7 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 680 ppm.

Table 2
Important bond angles (°) and distances (Å) in compounds **1b**, **2a**, **3c** & **4b**.

	C–Te–C	Te–C–C	O···Te–C_{trans}	Te···O	Te–C(Ar)
1b	100.43(6)	105.1(1)	154.80(5)	2.825(2)	–
2a	96.5(1)	106.8 (2)	149.9(1)	2.892(3)	2.121(3)
3c	108.5(1)	104.0(2)	162.9(1)	2.837(3)	2.147(3)
4b	99.71(8)	104.6(1)	152.2(4)	2.803(22)	2.092(23)

Compound **1**: A solution of **1a** (0.30 g, 0.51 mmol) in dichloromethane (25 mL) was stirred with an aqueous solution of $Na_2S_2O_5$ (0.10 g, 0.53 mmol in 25 mL distilled water) for 1 h at 0 °C. The yellow organic layer was separated, washed with water (4 × 20 mL), and passed through anhydrous Na_2SO_4. The solvent was reduced under vacuum at room temperature to about ~2 mL. Diethyl ether (5 mL) was added and the solution was kept in a deepfreezer overnight affording yellow needles of **1**. Yield: 0.17 g (78%). M.p.: 115 °C. Anal. Calc. for $C_{16}H_{18}O_2S_2Te$ (434.04): C, 44.27; H, 4.18. Found: C, 44.14; H, 4.09. ^1H NMR: δ 2.40 (s, 6H, CH_3Tpn), 2.66 (s, 6H, CH_3Tpn), 4.06 (s, 4H, CH_2), 6.96 (s, 2H, ring proton) ppm. $^{13}C\{^1H\}$ NMR: δ 14.9 (CH_3), 16.1 (CH_3), 13.6 (CH_2), 126.3, 133.2, 135.1, 148.8 (ring carbons), 193.1 (CO) ppm.

Compound **1b**: Addition of a solution of SO_2Cl_2 (0.12 mL, 1.5 mmol) in dichloromethane (5 mL) to a cooled light yellow solution of **1** (0.22 g, 0.50 mmol) in the same solvent (20 mL) resulted in the precipitation of **1b** as a white solid that was collected by filtration. Recrystallization from dichloromethane gave **1b** as white needles. Yield: 0.23 g (91%). M.p.: 174–175 °C dec. Anal. Calc. for

Table 3
Interplanar angles, τ (°) among 3-heteroaroylmethyltellurium derivatives.

2,5-Dimethyl-3-thiophenoyl methyltellurium derivative	τ_1[a]	τ_2[b]
1b	14.74(5)	–
2a	4.63(8)	8.2(1)
3c	5.8(1)	10.8(1)
4b	2.13(5)	2.16(5)

[a] τ_1 = angle between the equatorial plane C–Te–C and mean plane of skeletal atoms of the heteroaroyl moiety.

[b] τ_2 = angle between the equatorial plane C–Te–C and mean plane of ring atoms of the aryl ligand.

$C_{16}H_{18}O_2S_2TeCl_2$ (504.95): C, 38.06; H, 3.59. Found: C, 38.11; H, 3.47. ^{1}H NMR: δ 2.43 (s, 6H, CH_3Tpn), 2.74 (s, 6H, CH_3Tpn), 5.12 (s, 4H, CH_2), 6.99 (s, 2H, ring proton) ppm. $^{13}C\{^1H\}$ NMR: δ 14.95 (CH_3), 16.4 (CH_3), 58.4 (CH_2), 126.1, 132.2, 136.4, 151.9 (ring carbons), 186.7 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 678 ppm.

Compound **1b** was also prepared by condensation of $TeCl_4$ (0.54 g, 2.0 mmol) with 3-acetyl-2,5-dimethylthiophene (0.57 mL, 5.0 mmol) in refluxing chloroform (15 mL) for 5 h. The color of the solution changed from yellow to black as HCl evolved. Chloroform (20 mL) was added and the solution passed through a small silica column. Reduction of solvent upto 5 mL by distillation, followed by cooling, gave **1b** as colorless solid which was recrystallized from dichloromethane to give colorless needle shape crystals. Yield: 0.45 g (45%). M.p.: 174–175 °C dec.

Compound **1c**: An iodine (0.08 g, 0.3 mmol) solution in 20 mL petroleum ether (40–60 °C) was added to a cold solution of **1** (0.109 g, 0.25 mmol) in 2 mL dichloromethane at 0 °C under stirring. After 15 min, the precipitated solid was filtered and recrystallized from dichloromethane to obtain **1c** as deep orange hexagonal crystals. Yield: 0.162 g (94%). M.p.: 154 °C. Anal. Calc. for $C_{16}H_{18}O_2S_2TeI_2$ (687.85): C, 27.94; H, 2.64. Found: C, 27.69; H, 2.59. $^{13}C\{^1H\}$ NMR: δ 14.95 (CH_3), 16.4 (CH_3), 58.4 (CH_2), 126.1, 132.2, 136.4, 151.9 (ring carbons), 186.7 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 679 ppm.

Compound **1c** was also obtained when tellurium powder (0.13 g, 1.0 mmol) and α-iodo-2,5-dimethyl-3-acetylthiophene [prepared by stirring α-bromo-2,5-dimethyl-3-acetylthiophene (0.47 g, 2.0 mmol) with KI (0.35 g, 2.1 mmol) in 1 mL acetone for 1 h] were stirred together at room temperature for 2 h. An orange paste containing the desired product (**1c**) formed. The **1c** was extracted with dichloromethane (20 mL), passed through a small silica column and the solvent reduced to ~2 mL by distillation. Addition of 10 mL petroleum ether (40–60 °C) and cooling afforded **1c** as an orange solid. Yield: 0.47 g (68% with respect to Te). M.p.: 154 °C.

Alternatively **1c** was prepared from a solution of **1a** (0.30 g, 0.51 mmol) in dichloromethane (15 mL), stirred with KI (0.33 g, 2.0 mmol) for 4 h. Potassium halides were removed by filtration and excess solvent was removed by distillation. An orange solid settled on cooling which was recrystallized from chloroform to give deep orange crystals of **1c**. Yield: 0.25 g (73% with respect to **1a**). M.p.: 154 °C.

3.2.3. Syntheses of unsymmetrical diorganotellurium dichlorides

Compound **2b**: A mixture of 1-naphthyltellurium trichloride (0.5 g, 1.39 mmol) and 3-acetyl-2,5-dimethylthiophene (0.4 mL, 2.8 mmol) was stirred together at room temperature under a flow of dry nitrogen for 8 h. The resulting paste was washed with cold diethyl ether (5 × 10 mL), dissolved in dichloromethane (50 mL) and passed through a short silica column. The solvent was reduced to 10 mL and petroleum ether (40–60 °C) added to afford **2b** as a cream color solid, which was recrystallized from dichloromethane to give pale yellow rectangular crystals. Yield: 0.58 g (88%). M.p.: 180 °C. Anal. Calc. for $C_{18}H_{16}OSTeCl_2$ (478.89): C, 45.14; H, 3.37. Found: C, 45.00; H, 3.24. ^{1}H NMR: δ 2.45 (s, 3H, CH_3Tpn), 2.80 (s, 3H, CH_3Tpn), 5.57 (s, 2H, CH_2), 7.08 (s, 1H, thiophene ring), 7.61–8.25 (m, 7H, Npl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 13.3 (CH_3), 14.6 (CH_3), 66.9 (CH_2), 125.1, 125.5, 125.6, 125.9, 126.4, 127.7, 130.1, 130.7, 130.8, 131.8, 132.3, 132.6, 134.3, 149.6 (aromatic carbons), 186.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 763 ppm.

Compound **3b**: It has been synthesized by reaction of mesityltellurium trichloride (0.5 g, 1.42 mmol) and 3-acetyl-2,5-dimethylthiophene (0.4 mL, 2.8 mmol) using a similar procedure as used for **2b**. Recrystallization from dichloromethane afforded rectangular colorless crystals of the compound on slow evaporation. Yield: 0.48 g (72%). M.p.: 152 °C. Anal. Calc. for $C_{17}H_{20}OSTeCl_2$ (470.91): C, 43.36; H, 4.28. Found: C, 43.35; H, 4.21. ^{1}H NMR: δ 2.33 (s, 3H, *p*-Me), 2.44 (s, 3H, CH_3Tpn), 2.75, 2.76 (2 s, 6H, *o*-Me), 2.82 (s, 3H, CH_3Tpn), 5.49 (s, 2H, CH_2), 6.99 (s, 1H, *m*-H mesityl ring), 7.01 (s, 1H, thiophene ring), 7.05 (s, 1H, *m*-H mesityl ring) ppm. $^{13}C\{^1H\}$ NMR: δ 14.9 (CH_3), 16.4 (CH_3), 21.0 (*p*-Me), 23.6 (*o*-Me), 24.2 (*o*-Me), 66.2 (CH_2), 125.9, 130.3, 131.5, 132.4, 134.5, 136.4, 140.2, 141.1, 142.2, 151.9 (aromatic carbons), 186.8 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 783 ppm.

Compound **4b**: It was synthesized by reacting anisyltellurium trichloride (0.5 g, 1.47 mmol) with 3-acetyl-2,5-dimethylthiophene (0.4 mL, 2.8 mmol) in a similar method as used in case of **2b** and **3b**. Its recrystallization from chloroform gave rectangular colorless crystals on slow evaporation. Yield: 0.56 g (83%). M.p.: 142 °C. Anal. Calc. for $C_{15}H_{16}O_2STeCl_2$ (458.86): C, 39.26; H, 3.51. Found: C, 39.23; H, 3.57. ^{1}H NMR: δ 2.41 (s, 3H, CH_3Tpn), 2.75 (s, 3H, CH_3Tpn), 3.88 (s, 3H, *p*-OMe), 5.24 (s, 2H, CH_2), 6.94 (s, 1H, thiophene ring), 7.06, 7.08 (d, 2H, *o*-aryl), 8.13, 8.16 (d, 2H, *m*-aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 14.9 (CH_3), 16.4 (CH_3), 55.5 (*p*-OMe), 70.3 (CH_2), 115.6, 118.2, 126.1, 132.1, 135.8, 136.3, 152.0, 162.2 (aromatic carbons), 186.2 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 845 ppm.

3.2.4. Reduction of *2b*, *3b* to *2*, *3*

Compound **2**: A solution of **2b** (0.24 g, 0.50 mmol) in dichloromethane (20 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.09 g, 0.47 mmol) for 20 min. The yellow organic layer was separated, washed with water (4 × 20 mL) and passed through anhydrous Na_2SO_4. The solvent was reduced to ~1 mL by distillation and the solution was cooled to 0 °C after addition of 5 mL of hexane in order to achieve the precipitation of unreacted **2b** which is removed by filtration. The filtrate was left till the complete evaporation of volatiles to obtain the **2** as red oil. Yield: 0.14 g (69%). ^{1}H NMR: δ 2.15 (s, 3H, CH_3Tpn), 2.55 (s, 3H, CH_3Tpn), 4.11 (s, 2H, CH_2), 6.40 (s, 1H, thiophene ring), 7.00–8.27 (m, 7H, Npl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 15.2 (CH_3), 16.4 (CH_3), 17.2 (CH_2), 116.1, 126.6, 126.7, 126.8, 127.5, 129.3, 130.9, 133.2, 133.8, 134.2, 134.9, 136.8, 141.8, 148.8 (aromatic carbons), 193.6 (CO) ppm.

Likewise, **3** was obtained as yellow crystals from **3b** (0.23 g, 0.50 mmol) and $Na_2S_2O_5$ (0.09 g, 0.47 mmol). Yield: 0.15 g (75%). M.p.: 54 °C. Anal. Calc. for $C_{17}H_{20}OSTe$ (400.01): C, 51.04; H, 5.04. Found: C, 50.95; H, 5.21. ^{1}H NMR: δ 2.30 (s, 3H, *p*-Me), 2.61 (s, 6H, *o*-Me), 2.76 (s, 6H, CH_3Tpn), 3.95 (s, 2H, CH_2), 6.49 (s, 1H, thiophene ring), 6.95 (s, 2H, *m*-H mesityl ring) ppm. $^{13}C\{^1H\}$ NMR: δ 14.9 (CH_3), 15.6 (CH_2), 15.8 (CH_3), 21.0 (*p*-Me), 28.1 (*o*-Me), 29.6 (*o*-Me), 117.1, 126.2, 127.2, 133.5, 134.3, 139.6, 145.8, 148.2 (aromatic carbons), 193.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 357 ppm.

3.2.5. Oxidative addition reactions of *2*, *3* with dihalogens

Compound **2a**: Bromine (0.03 mL, 0.50 mmol) in hexane (10 mL) was added dropwise at room temperature to a stirred solution of **2** (0.20 g, 0.50 mmol) in the same solvent (~10 mL). A yellow solid began to separate instantly and the mixture was stirred for another 15 min to complete the reaction. The solid was filtered and dissolved in dichloromethane. The solution was passed through a short silica column, concentrated and kept for slow evaporation to afford **2a** as yellow crystals. Yield: 0.19 g (94%). M.p.: 173 °C. Anal. Calc. for $C_{18}H_{16}OSTeBr_2$ (567.79): C, 38.08; H, 2.84. Found: C, 38.05; H, 2.78. ^{1}H NMR: δ 2.46 (s, 3H, CH_3Tpn), 2.80 (s, 3H, CH_3Tpn), 5.73 (s, 2H, CH_2), 7.10 (s, 1H, thiophene ring), 7.59–8.24 (m, 7H, Npl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 14.98 (CH_3), 16.5 (CH_3), 68.3 (CH_2), 126.1, 126.6, 126.9, 127.4, 128.2, 129.5, 129.6, 131.9, 132.0, 132.6, 133.6, 134.3, 136.6, 152.6 (aromatic carbons), 186.3 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 694 ppm.

Likewise, **3a** was obtained as yellow crystals from **3** (0.20 g, 0.50 mmol) and Br_2 (0.03 mL, 0.50 mmol). Yield: 0.17 g (81%).

M.p.: 145 °C. Anal. Calc. for $C_{17}H_{20}OSTeBr_2$ (559.81): C, 36.47; H, 3.60. Found: C, 36.35; H, 3.78. ^1H NMR: δ 2.33 (s, 3H, *p*-Me), 2.45 (s, 3H, CH_3Tpn), 2.73, 2.76 (2 s, 6H, *o*-Me), 2.79 (s, 3H, CH_3Tpn), 5.65 (s, 2H, CH_2), 6.97 (s, 1H, *m*-H mesityl ring), 7.01 (s, 1H, thiophene ring), 7.04 (s, 1H, *m*-H mesityl ring) ppm. $^{13}C\{^1H\}$ NMR: δ 14.95 (CH_3), 16.4 (CH_3), 21.0 (*p*-Me), 23.3 (*o*-Me), 24.8 (*o*-Me), 65.1 (CH_2), 125.8, 130.4, 131.1, 131.5, 132.2, 136.4, 139.8, 141.2, 142.1, 152.0 (aromatic carbons), 186.8 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 703 ppm.

Compound **4a**: A solution of **4b** (0.23 g, 0.50 mmol) in dichloromethane (25 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.09 g, 0.47 mmol) for 30 min. The yellow organic layer was separated, washed with water (4 × 20 mL) and passed through anhydrous Na_2SO_4. The solvent was reduced to ~1 mL and the solution was cooled to 0 °C after addition of 5 mL of hexane to remove the precipitate, so formed, of unreacted **4b** by filtration. In the filtrate, Br_2 (0.03 mL, 0.50 mmol) solution in hexane (5 mL) was added and stirred for 15 min to obtain the **4a** as a solid which was filtered, dissolved in dichloromethane, passed through a short silica column and kept for crystallization to afford **4a** as yellow crystals. Yield: 0.17 g (62%). M.p.: 142 °C dec. Anal. Anal. Calc. for $C_{15}H_{16}O_2STeBr_2$ (547.76): C, 32.89; H, 2.94. Found: C, 32.78; H, 2.87. ^1H NMR: δ 2.42 (s, 3H, CH_3Tpn), 2.76 (s, 3H, CH_3Tpn), 3.88 (s, 3H, *p*-OMe), 5.45 (s, 2H, CH_2), 6.97 (s, 1H, thiophene ring), 7.02, 7.05 (d, 2H, *o*-aryl), 8.11, 8.14 (d, 2H, *m*-aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 15.1 (CH_3), 16.4 (CH_3), 56.4 (*p*-OMe), 71.2 (CH_2), 115.4, 118.1, 126.2, 132.3, 134.9, 136.6, 152.0, 161.5 (aromatic carbons), 186.1 (CO) ppm.

3.2.6. *Metathetical reactions of **2b**, **3b**, **4b** with KI*

Compound **2c**: A solution of **2b** (0.24 g, 0.50 mmol) in dichloromethane (25 mL) was stirred with KI (0.33 g, 2.0 mmol) for 7 h. The potassium chloride formed as a byproduct and excess of KI were removed by filtration. The filtrate was passed through a short silica column. Petroleum ether (40–60 °C) was added to the solution after reduction of the solvent to give orange **2c** which was recrystallized from chloroform and red rectangular crystals were obtained. Yield: 0.31 g (94%). M.p.: 135–136 °C. Anal. Calc. for $C_{18}H_{16}OSTeI_2$ (661.79): C, 32.67; H, 2.44. Found: C, 32.59; H, 2.51. ^1H NMR: δ 2.46 (s, 3H, CH_3Tpn), 2.80 (s, 3H, CH_3Tpn), 5.74 (s, 2H, CH_2), 7.11 (s, 1H, thiophene ring), 7.53–8.20 (m, 7H, Npl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 15.4 (CH_3), 16.6 (CH_3), 55.2 (CH_2), 120.1, 127.1, 127.4, 127.6, 128.0, 129.4, 130.9, 133.2, 133.7, 136.2, 136.5, 137.1, 144.7, 150.7 (aromatic carbons), 186.6 (CO) ppm.

Compound **3c** was prepared in a similar way used for the metathesis of **3b** (0.24 g, 0.50 mmol) with KI (0.33 g, 2.0 mmol) as orange crystals. Yield: 0.24 g (73%). M.p.: 108 °C. Anal. Calc. for $C_{17}H_{20}OSTeI_2$ (653.81): C, 31.23; H, 3.08. Found: C, 31.15; H, 3.01. ^1H NMR: δ 2.36 (s, 3H, *p*-Me), 2.42 (s, 3H, CH_3Tpn), 2.66 (s, 3H, CH_3Tpn), 2.77 (s, 6H, *o*-Me), 4.15 (s, 2H, CH_2), 7.00 (s, 2H, *m*-H mesityl ring), 7.02 (s, 1H, thiophene ring) ppm. $^{13}C\{^1H\}$ NMR: δ 15.01 (CH_3), 16.3 (CH_3), 21.0 (*p*-Me), 23.2 (*o*-Me), 25.9 (*o*-Me), 63.0 (CH_2), 125.8, 127.2, 130.7, 131.7, 132.2, 136.5, 139.3, 141.9, 147.1, 152.0 (aromatic carbons), 187.1 (CO) ppm.

Compound **4c** was also prepared using similar procedure as in case of **2c** and **3c** by metathesis of **4b** (0.23 g, 0.50 mmol) with NaI (0.30 g, 2.0 mmol) or KI (0.33 g, 2.0 mmol) as orange crystals of **4c**. Yield: 0.24 g (75%). M.p.: 134 °C. Anal. Calc. for $C_{15}H_{16}O_2STeI_2$ (641.76): C, 28.07; H, 2.51. Found: C, 28.13; H, 2.47. ^1H NMR: δ 2.43 (s, 3H, CH_3Tpn), 2.75 (s, 3H, CH_3Tpn), 3.87 (s, 3H, *p*-OMe), 5.50 (s, 2H, CH_2), 6.94 (s, 1H, thiophene ring), 6.99 (d, 2H, *o*-aryl), 8.06 (d, 2H, *m*-aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 14.6 (CH_3), 15.8 (CH_3), 55.4 (*p*-OMe), 69.9 (CH_2), 114.5, 126.2, 132.3, 134.7, 136.2, 143.4, 149.9, 159.4 (aromatic carbons), 185.7 (CO) ppm.

Table 4
Crystal data and structure refinement details for 1b, 2a, 3c and 4b.

	1b	**2a**	**3c**	**4b**
Empirical formula	$C_{16}H_{18}Cl_2O_2S_2$ Te	$C_{18}H_{16}Br_2OSTe$	$C_{17}H_{20}I_2OSTe$	$C_{15}H_{16}Cl_2O_2STe$
Formula mass (g mol^{-1})	504.92	567.79	653.79	458.84
Temperature (K)	295(2)	295(2)	295(2)	295(2)
Wavelength, λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Crystal size (mm^3)	0.52 × 0.26 × 0.10	0.51 × 0.32 × 0.25	0.47 × 0.43 × 0.35	0.41 × 0.38 × 0.24
Space group	P c c n	P −1	P 1 21/n 1	P −1
a (Å)	15.4652(5)	9.2753(4)	7.5175(2)	8.1440(3)
b (Å)	13.8512(6)	9.8603(4)	18.6185(4)	8.9352(3)
c (Å)	9.5644(2)	10.7574(5)	15.0694(3)	12.1090(5)
α (deg)	90	83.515(3)	90	81.050(3)
β (deg)	90	86.702(4)	94.471(2)	87.973(3)
γ (deg)	90	80.082(4)	90	88.726(3)
V ($Å^3$)	2048.82(12)	962.21(7)	2102.76(9)	869.75(6)
Z	4	2	4	2
ρ_{calcd} (Mg m^{-3})	1.637	1.960	2.065	1.752
Absorption coefficient (mm^{-1})	1.921	5.808	4.450	2.137
F(000)	992	540	1216	448
h, *k*, *l* ranges collected	−12 → 24 −10 → 22 −15 → 15	−14 → 11 −14 → 14 −16 → 16	−6 → 11 −26 → 28 −20 → 22	−12 → 12 −13 → 13 −18 → 16
Reflection collected	10,844	12,231	17,079	11,235
Independent reflections	4229 [*R*(int) = 0.0279]	6338 [*R*(int) = 0.0374]	7081 [*R*(int) = 0.0305]	5739 [*R*(int) = 0.0225]
θ range (°)	5.01–34.98	5.14–32.73	5.07–32.75	5.10–32.76
Completeness to θ_{max} (%)	99.1	98.8	99.2	99.2
Absorption correction	Semi-empirical from equivalents			
Max., min. transmission	1.00000, 0.55270	1.00000, 0.38024	1.00000, 0.74890	1.00000, 0.68858
Refinement method	Full-matrix least-squares on F2			
Data/restraints/parameters	4229/0/107	6338/0/211	7081/0/204	5739/0/198
Goodness of fit on F^2	0.907	0.835	0.900	0.979
Final *R* indices ($I > 2\sigma(I)$)	*R*1 = 0.0295, *wR*2 = 0.0688	*R*1 = 0.0413, *wR*2 = 0.0774	*R*1 = 0.0354, *wR*2 = 0.0637	*R*1 = 0.0310, *wR*2 = 0.0673
R indices (all data)	*R*1 = 0.0560, wR2 = 0.0759	*R*1 = 0.0968, wR2 = 0.0853	*R*1 = 0.0805, wR2 = 0.0709	*R*1 = 0.0517, wR2 = 0.0718
Largest diff peak/hole (e $Å^{-3}$)	0.786/−0.536	1.172/−1.026	1.096/−0.821	1.100/−0.514
Extinction coefficient	–	–	–	0.0036(9)

3.2.7. *Alternative procedures for synthesis of **2a** and **3a***

To a solution of ArTeBr [prepared *in situ* by mixing dichloromethane solutions of Npl_2Te_2 (0.51 g, 1.0 mmol) or Mes_2Te_2 (0.49 g, 1.0 mmol) and Br_2 (0.05 mL, 1.0 mmol) at room temperature], α-bromo-2,5-dimethyl-3-acetylthiophene (0.47 g, 2.0 mmol) was added at room temperature under stirring. The reaction mixture was stirred for 24 h at room temperature and filtered to remove a black residue. The dark brown filtrate was passed through a small silica column, concentrated and an equal volume of petroleum ether (60–80 °C) added. Yellow crystals separated on overnight cooling in a refrigerator. Yield: **2a**, 0.88 g (79%); **3a** 0.83 g (73%).

3.3. *Crystallography*

Single crystals suitable for X-ray crystallography were grown by slow evaporation of dichloromethane solutions of **1b**, **2a**, **3c** and **4b**. Intensity data were collected on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated Mo-Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.34d program. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 [26]. Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to non-hydrogen atoms. Hydrogen atoms attached to carbon were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal data and structure refinement details are given in Table 4. The molecular structures are depicted in Figs. 1–4, showing 30% (**1b**, **2a**, **3c**, **4b**) probability displacement ellipsoids, omitting H atoms for clarity, and captioned with the geometrical parameters relevant to the primary geometry were generated using the program ORTEP-3 version 2.02 [27].

Acknowledgments

Financial assistance by the Department of Science and Technology, Government of India, New Delhi, is gratefully acknowledged. P.S. thanks Council of Scientific and Industrial Research (India) for the award of Senior Research Fellowship.

Appendix A. Supplementary material

CCDC 871504, 871505, 871506 and 871507 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.12.038.

References

[1] I. Haiduc, J. Zukerman-Schpector, Phosphorus, Sulfur Silicon Relat. Elem. 171 (2001) 171–185.
[2] A.F. Cozzolino, P.J.W. Elder, I. Vargas-Baca, Coord. Chem. Rev. 255 (2011) 1426–1438.
[3] A. Kumar, M. Agarwal, A.K. Singh, J. Organomet. Chem. 693 (2008) 3533–3545.
[4] A. Kumar, M. Agarwal, A.K. Singh, Inorg. Chim. Acta 362 (2009) 3208–3218.
[5] A. Kumar, G.K. Rao, A.K. Singh, RSC Adv. 2 (2012) 12552–12574.
[6] P.C. Srivastava, A. Sinha, S. Bajpai, H.G. Schmidt, M. Noltemeyer, J. Organomet. Chem. 575 (1999) 261–268.
[7] A.K.S. Chauhan, A. Kumar, R.C. Srivastava, R.J. Butcher, J. Organomet. Chem. 658 (2002) 169–175.
[8] A.K.S. Chauhana, Anamika, A. Kumar, R.C. Srivastava, R.J. Butcher, J. Organomet. Chem. 690 (2005) 313–321.
[9] V. Chandrasekhar, A. Kumar, J. Organomet. Chem. 694 (2009) 2628–2635.
[10] S.K. Tripathi, U. Patel, D. Roy, R.B. Sunoj, H.B. Singh, G. Wolmershäuser, R.J. Butcher, J. Org. Chem. 70 (2005) 9237–9247.
[11] V. Chandrasekhar, A. Kumar, M.D. Pandey, J. Organomet. Chem. 695 (2010) 74–81.
[12] K. Selvakumar, H.B. Singh, N. Goel, U.P. Singh, Organometallics 30 (2011) 3892–3896.
[13] S. Misra, A.K.S. Chauhan, P. Singh, R.C. Srivastava, A. Duthie, R.J. Butcher, Dalton Trans. 39 (2010) 2637–2643.
[14] H.J. Gysling, H.R. Luss, S.A. Gardner, J. Organomet. Chem. 184 (1980) 417–431.
[15] L. Engman, Organometallics 5 (1986) 427–431.
[16] A. Ishii, J. Nakayama, Y. Horikawa, M. Hoshino, Sulfur Lett. 10 (1989) 71–77.
[17] J. Zukerman-Schpector, R.L. Camillo, I. Caracelli, J. Comasseto, L.O.R. Cunha, Rev. Roumaine de Chim. 47 (2003) 1021–1025.
[18] A.K.S. Chauhan, P. Singh, R.C. Srivastava, R.J. Butcher, A. Duthie, Inorg. Chim. Acta 376 (2011) 80–86.
[19] A.K.S. Chauhan, P. Singh, R.C. Srivastava, R.J. Butcher, A. Duthie, J. Organomet. Chem. 695 (2010) 2532–2539.
[20] A.K.S. Chauhan, P. Singh, R.C. Srivastava, R.J. Butcher, A. Duthie, J. Organomet. Chem. 696 (2011) 3649–3656.
[21] J. Farran, A. Alvarez-Lorena, J.F. Pinella, G. Germain, L. Torres-Castellanos, Z. Kristallogr. 210 (1995) 65.
[22] E.S. Lang, R.M. Fernandes Junior, E.T. Silveira, U. Abram, E.M. Vázquez-López, Z. Anorg. Allg. Chem. 625 (1999) 1401–1404.
[23] R.K. Chadha, J.E. Drake, Acta Crystallogr. C40 (1984) 1349–1352.
[24] J. Farran, A. Alvarez-Larena, J.F. Piniella, Acta Crystallogr. C51 (1995) 639–641.
[25] J. Farran, A. Alvarez-Larena, M.V. Capparelli, J.F. Piniella, G. Germain, L. Torres-Castellanos, Acta Crystallogr. C54 (1998) 995–1000.
[26] SHELXL-97 G.M. Sheldrick, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), 2008.
[27] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.