Journal of Organometallic Chemistry 728 (2013) 38–43

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Alkoxycarbonylmethyl derivatives of tellurium: Facile synthesis and structural studies

Ashok K.S. Chauhan [a,*], Swami N. Bharti [a], Ramesh C. Srivastava [a], Ray J. Butcher [b], Andrew Duthie [c]

[a] Department of Chemistry, University of Lucknow, Lucknow 226007, India
[b] Department of Chemistry, Howard University, Washington, DC 20059, USA
[c] School of Life and Environmental Sciences, Deakin University, Geelong 3217, Australia

ARTICLE INFO

Article history:
Received 16 November 2012
Received in revised form
10 January 2013
Accepted 11 January 2013

Keywords:
Tellurium insertion
α-Tellurated ester
Functionalized organotellurium
Nucleophilic telluration
Secondary bonding interaction

ABSTRACT

Methyl and *t*-butyl esters of α-bromoacetic acid added oxidatively to elemental tellurium in the presence of sodium iodide to give high yields of crystalline bis(alkoxycarbonylmethyl)tellurium(IV) diiodides, $(ROCOCH_2)_2TeI_2$. The chloro and bromo analogs were prepared via their reduction into tellurides followed by dihalogen oxidation. Activation of the α-C_{sp3}–Br bond by ester functionality appears to be insufficient as methyl α-bromoacetate failed to add to Te(0) or aryltellurium(II) bromides. The nucleophilic substitution reaction of α-bromoesters with aryltellurolates, $ArTe^-Na^+$ (Ar = 1-$C_{10}H_7$, Np; 2,4,6-$Me_3C_6H_2$, Mes), gave (alkoxycarbonylmethyl)aryltellurides that were characterized as mixed diorganotellurium dihalides. Crystal structures of $Np(MeOCOCH_2)TeBr_2$, $Mes(MeOCOCH_2)TeBr_2$ and $Mes(t\text{-}BuOCOCH_2)TeCl_2$ show that the functionalized organic moiety, $ROCOCH_2$, behaves as a (C, O) chelating ligand. The carbonyl O atom of the ester group in these compounds is involved in a 1,4-Te⋯O secondary bonding interaction. However, the functionalized ligands in the case of $(MeOCOCH_2)_2TeI_2$ are devoid of such an interaction. Surprisingly, one of the two organic ligands in $(MeOCOCH_2)_2TeBr_2$ takes part in an intramolecular 1,4-Te⋯O interaction, the other appears to involve an intermolecular Te⋯O interaction to result in a one-dimensional array of molecules in the crystal lattice.

1. Introduction

Reactions of active metals viz. Li and Mg with functionalized organic substrates, as a route to C-metalated corresponding derivatives, are not so straightforward due to the possible nucleophilic attack of the Li/Mg–C bond on the functional group. The less electropositive element Te inserts into the C–I bond of acylmethyl- and amidomethyl iodides to afford functionalized organotellurium(IV) diiodides, $(YCH_2)_2TeI_2$ (Y = RCO–, R^1R^2NCO–). α-Carbonyl activation of the C_{sp3}–Br bond of acylmethyl- and amidomethyl bromides has also been exploited in our laboratory as a one-step synthetic protocol to get analogous dibromides, $(YCH_2)_2TeBr_2$ [1,2]. Crystallographic structure determination of more than a dozen such diorganotellurium(IV) halides revealed that the carbonyl O atom is almost invariably involved in the intramolecular 1,4-Te⋯O secondary bonding interactions (SBI), at least in the solid state [3]. The moderate oxophilicity exhibited by the tellurium atom in these compounds may be attributed to the inductive effect of the halogen atoms linked to it and its propensity to take hypervalent bond state. This appears to result in the positive polarization of the carbon atom of the Te–C bond(s), in spite of the greater electronegativity when compared to that of a tellurium atom. Taking advantage of this property, coupling reaction of bis(α-carbonylmethyl)tellurium dichlorides, $(RCOCH_2)_2TeCl_2$ with lithium nitronates $[LiC(NO_2)R^1R^2]$, which provide nucleophilic stabilized carbanions, has been devised and the coupling products $[RCOCH{=}CR^1R^2]$ isolated in high yields, though $(ROCOCH_2)_2TeCl_2$ required higher reaction temperature to afford the coupling product in modest yield [4]. The rare absence of 1,4-Te⋯O SBIs observed in case of $(PhOCOCH_2)_2TeCl_2$, [the only ester functionalized organotellurium(IV) dihalide characterized crystallographically [4]] is interesting and substantiates poor electrophilicity of Te(IV) center in it. Also, the described synthesis of $(ROCOCH_2)_2TeCl_2$, (R = Me, Ph), the only reported bis(alkoxycarbonylmethyl)tellurium(IV) dihalides, requires initial preparation of the ketene silyl acetal $[H_2C{=}C(OR)OSiMe_3]$ from the enol of the parent acetic acid ester followed by electrophilic substitution with moisture sensitive $TeCl_4$ [5]. However, different synthetic approaches in the past have been made to obtain (alkoxycarbonylmethyl)tellurium(II) derivatives analogous to well explored α-organylselenoesters. α-Alkyltelluoesters were first prepared by thermal decomposition of telluronium salts, $[R_2(ROCOCH_2)$

---

* Corresponding author. Tel.: +91 9415010762; fax: +91 522 2338531.
E-mail addresses: akschauhan2003@yahoo.co.in, akschauhan@hotmail.com (A.K.S. Chauhan), goswamiswaminath@yahoo.com (S.N. Bharti), rameshlko@yahoo.co.nz (R.C. Srivastava), rbutcher99@yahoo.com (R.J. Butcher), aduthie@deakin.edu.au (A. Duthie).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.01.010

Te]$^{+}$ Br^{-} [6,7]. Subsequent methods include reactions of organotellurium reagents, prepared *in situ*, such as $ArTe^{-}$ M^{+} (M = Li, Na) and ArTeX (X = Br, I) with α-bromoesters [8,9] and lithium enolates [10] or Reformatsky reagent, $BrZnCH_2COOR$ [11], respectively. Interestingly, 1:1 addition of PhTeBr to ethyl diazoacetate provided labile ethyl-α-bromo-α-pheyltelluroacetate [12], while the reaction of bis(triphenylstannyl)telluride with α-bromoesters provided symmetrical telluroesters, $(ROCOCH_2)_2Te$ [13]. Surprisingly, oxidative addition of α-haloesters to elemental tellurium, similar to the synthetic protocol for Reformatsky reagents, has never been observed.

In the above context, it has been envisaged in the present investigation to examine the potential of alkoxycarbonyl functionality in the activation of α-C_{sp3}–X (X = I, Br) bond to insert elemental tellurium and to determine the bonding mode of the organic ligands in the resulting bis(alkoxycarbonylmethyl)tellurium(IV) dihalides. The mixed (alkoxycarbonylmethyl)aryltellurium(IV) dihalides have also been prepared for structural comparison.

2. Results and discussion

2.1. Synthesis

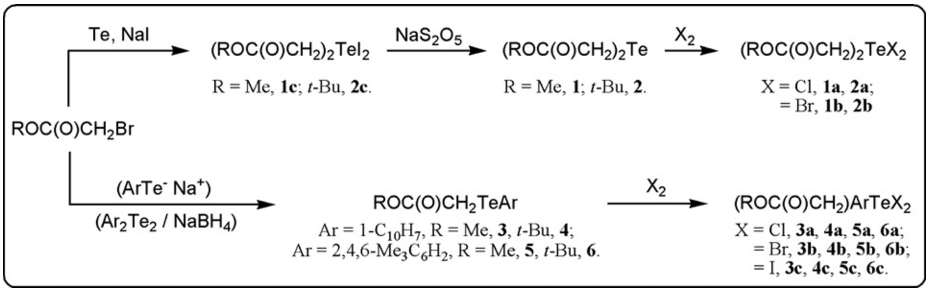
Elemental tellurium failed to react with α-bromoesters when heated together up to ~100 °C. However, when a mixture of tellurium powder, $ROCOCH_2Br$ and NaI was stirred overnight at room temperature, bis(alkoxycarbonylmethyl)tellurium(IV) diiodides, $(ROCOCH_2)_2TeI_2$ (R = Me, **1c**; *t*-Bu, **2c**) were obtained in very good yields. On reduction in a biphasic medium with $Na_2S_2O_5$, both diiodides afforded the corresponding tellurides, $(ROCOCH_2)_2Te$ as yellow liquids which were characterized as their dihalides $(ROCOCH_2)_2TeX_2$ [X = Cl (**1a**, **2a**), Br (**1b**, **2b**)] after halogenations with SO_2Cl_2 and Br_2 at 0 °C (Scheme 1). The addition of a dichloromethane solution of $MeOCOCH_2Br$ to a stirred solution of mesityltellurium(II) bromide in the same solvent (prepared *in situ* by mixing equimolar amounts of dimesityl ditelluride and Br_2) separated some elemental tellurium. Removal of the solvent from the filtrate gave a light yellow residue. The ^{1}H NMR spectrum of this compound corresponded to that of dimesityltellurium dibromide and was devoid of any signal due to tellurium-bound methylene protons.

All the six dihalides are crystalline solids fairly stable at ambient conditions and soluble in dichloromethane and chloroform. Their ^{1}H NMR spectra consist of singlets for the methylene (δ ~4.4 ppm) and alkoxy protons (δ ~3.8 ppm, Me; ~1.5 ppm, CMe_3). Compound **1a** has been prepared earlier by a different method, but the assignment of peaks is erroneous [4]. The ^{13}C chemical shifts of the methylene carbon and the ^{125}Te chemical shifts for the examined compounds appear to be sensitive to the nature of halo ligands, but the $\delta(^{13}C)$ values for the carbonyl carbons (164–166 ppm) are little affected. Compound **1b** was also prepared by the metathetical reaction between **1a** and sodium bromide. Attempts to prepare the mixed halide, $(MeOCOCH_2)_2TeClBr$ by stirring an equimolar mixture of **1a** and NaBr did not succeed, however the isolated sample showed three peaks (at 796, 775 and 748 ppm in 1:3:3 ratio) which may be assigned to $(MeOCOCH_2)_2TeCl_2$, $(MeOCOCH_2)_2TeClBr$ and $(MeOCOCH_2)_2TeBr_2$ respectively.

The nucleophilic substitution reactions of α-bromoesters, $ROCOCH_2Br$, used in the present study with aryltellurolates, $ArTe^{-}$ (Ar = 1-$C_{10}H_7$, Np; 2,4,6-$Me_3C_6H_2$, Mes) proceeded readily at room temperature to afford alkylaryltellurides, $Ar(ROCOCH_2)Te$ (Ar = Np and R = Me, **3**; *t*-Bu, **4**; Ar = Mes and R = Me, **5**; *t*-Bu, **6**) as yellow oils or low melting solid (**6**). Oxidative addition of dihalogens gave the dihalides, $Ar(ROCOCH_2)TeX_2$ (X = Cl, **3a**–**6a**; Br, **3b**–**6b**; I, **3c**–**6c**) (Scheme 1). These mixed diorganotellurium(IV) dihalides are crystalline solids stable to air and moisture, except **3c** and **5c** which decompose on standing at room temperature. In the ^{1}H NMR spectra, Te(II) compounds **4** and **6** showed a high field signal for the methylene protons ((compared to the respective dihalides), $Ar(ROCOCH_2)TeX_2$) in addition to the expected signals for aryl and *t*-butyl protons. Presence of a single resonance owing to the two *ortho* methyls of the mesityl ligand in **5** and **6** is consistent with the free rotation of the aryl moiety about the Te–C_{Mes} bond. This is, however, not so in the ^{1}H NMR spectra of the dihalides, $Mes(ROCOCH_2)TeX_2$, which show separate signals for each of the *ortho* methyls as well as for the ring protons of the aryl ligand. Magnetic inequivalence of methyl substituents of the aryl moiety among the mesityltellurium(IV) dihalides is also evident from the separate signals for the methyl carbons in their ^{13}C NMR spectra. The presence of axial halo ligands in these mesityltellurium(IV) compounds thus causes steric hindrance in the free rotation of the aryl moiety about the Te–C_{Mes} bond. There is a single peak in the ^{125}Te NMR spectra of the examined tellurium(IV) dihalides and the chemical shift values in the range 687–804 ppm appear to be more affected by the nature of the halide than that of the organic ligands.

2.2. Crystal structures

The crystal structures determined by single-crystal diffraction for $(MeOCOCH_2)_2TeBr_2$, **1b**, $(MeOCOCH_2)_2TeI_2$, **1c**, $Np(MeOCOCH_2)TeBr_2$, **3b**, and $Mes(MeOCOCH_2)TeBr_2$, **5b**, are unambiguous while *t*-butyl group in case of $Mes(t\text{-}BuOCOCH_2)TeCl_2$, **6a**, is two-fold disordered. The ORTEP views of the molecular structures showing the atom numbering are presented in Figs. 1–5. Hydrogen atoms are omitted for clarity. The selected bond lengths and angles are summarized in Table 1 and crystallographic data together with the structure refinement details are given in Table 2. All of these compounds exhibit putative see-saw geometry to the C_2TeX_2 core, characterized by a hypervalent quasi-linear X–Te–X fragment. The planarity of the skeletal frameworks of the alkoxycarbonylmethyl ligands ($_{methylene}C$–C(O)O–C_{alkyl}) is another common feature of these ester-functionalized organotellurium(IV) dihalides. Despite the similarity of the primary geometry around the Te(IV) atom in these



Scheme 1. Synthetic routes and interconversion reactions.

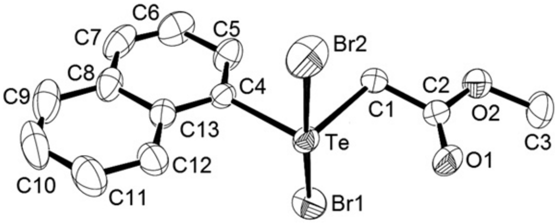


Fig. 1. ORTEP view of **3b** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

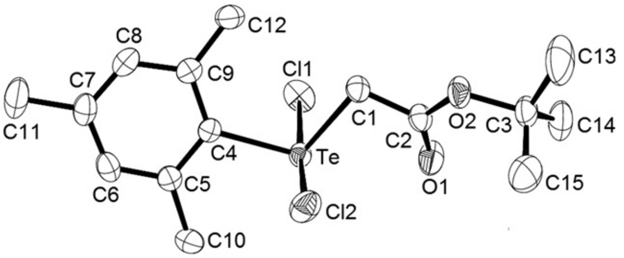


Fig. 3. ORTEP view of **6a** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

compounds, they crystallized in different space groups. The diversity of space groups among these alkoxycarbonylmethyltellurium(IV) dihalides suggests that the packing of these compounds is sensitive to the nature of the ligands attached to the central atom.

Asymmetric units in the crystal structures of **3b** and **6a** each consist of one molecule, but two in case of **5b**. The molecular structure in these mixed-diorganotellurium(IV) halides is characterized by the presence of the functionalized ligand in (C,O) chelating mode involving intramolecular 1,4-Te···O secondary bonding interaction (Figs. 1–3).

The attractive interaction between the carbonyl O atom of the ester group and central Te(IV) atom results in a significantly shorter interatomic distance [d(Te,O), (Å) = 2.979(3), **3b**; 3.074(3), 2.995(3), **5b**; 2.938(1), **6a**] in comparison to the sum of their van der Waal radii [Σr_{vdw}(Te, O) = 3.58 Å]. The functionalized ligand orients itself to become nearly coplanar with the C–Te–C plane [interplanar angle, (°) = 11.8(2), **3b**; 37.2(2), 30.8(1), **5b**; 22.4(4), **6a**] and the O atom lies almost in the equatorial plane [distance of O atom from the equatorial plane, (Å) = −0.377(4), **3b**; 0.347(3), −0.491(4), **5b**; 0.220(1), **6a**] and occupies a position nearly trans to the Te–C_{aryl} bond [∠O···Te–C_{aryl}, (°) = 150.9(2), **3b**; 157.2(1), 157.3(1), **5b**; 160.4(1), **6a**]. Formation of the four-member chelate ring causes angular distortion at the tellurium-bound C atom of the alkoxycarbonylmethyl ligand, as a consequence the measure of ∠Te–C_{sp3}–C_{carbonyl} in these compounds [106.7(3)°, **3b**; 104.7(3)°, 104.7(2)°, **5b**; 105.0(1)°, **6a**] is smaller to the ideal value of 109.5°. The propensity of central Te(IV) atom to increase its coordination number thus imparts an octahedral environment including its lone pair around it, at least in the crystalline state of the alkoxycarbonylaryltellurium(IV) compounds. Besides, the steric demand of an aryl ligand in these compounds widens the equatorial angle [∠C–Te–C, (°) = 99.7(2), **3b**; 107.6(1), 108.0(1), **5b**; 108.0(1), **6a**; *cf.* 96(3)°, the average value for a C_2TeX_2 core [14]] and makes the Te(IV) atom inaccessible for the ubiquitous intermolecular Te···X interactions.

The ligational behavior of the functionalized organic ligands in $(MeOCOCH_2)_2TeI_2$, **1c** is however exceptional. The asymmetric unit in the crystal lattice comprises of half a molecule and unlike the (C,O) chelating mode exhibited by acylmethyl and amidomethyl ligands among analogous compounds, $(RCOCH_2)_2TeX_2$ [1,3,15,16] and $(R_2NCOCH_2)_2TeX_2$ [2], the C-bonded ester functionalized ligands in **1c** are devoid of any intramolecular Te···O interactions as observed earlier in the case of $(PhCOCH_2)_2TeCl_2$ [5]. The skeletal plane of each organic ligand is skewed away from the equatorial plane of the central Te atom and becomes nearly orthogonal to it [dihedral angles = 65.1(1)°] (Fig. 4).

Absence of intramolecular Te···O interactions in the crystalline state of **1c** paves the way for intermolecular Te···I interactions. Each central Te(IV) atom in the self assembly acquires coordination number 6 (excluding its lone pair) via reciprocatory intermolecular Te···I interactions [d(Te, I) = 3.655 Å, *cf.* Σr_{vdw}(Te, I) = 4.04 Å; ∠I···Te–C_{trans} = 166.9°] with two adjacent molecules. A folded ribbon like supramolecular architecture thus becomes evident in the solid state of this compound (Fig. S1). Although the intermolecular Te···I linkages are longer compared to the primary Te–I bonds [d(Te, I) = 2.895(1) Å], all the angles around Te atom in the TeC_2I_4 moiety are quite close to the ideal value of 90°. The two iodine atoms drawn from the adjacent molecules that lie in the domain of the lone pair on the central Te(IV) atom in each molecule, subtend an angle even smaller than the angle opposite to it [∠I···Te···I = 90.8(1)°, ∠C–Te–C = 94.8(1)°]. It may be concluded that the self assembly via intermolecular Te···I interactions in the crystalline state of this compound, ignores the Te(IV) lone pair stereochemical activity, if any. The crystal structure of its bromo analog, $(MeOCOCH_2)_2TeBr_2$, **1b** is interestingly somewhat different (Fig. 5). While one of the organic ligands takes part in the intramolecular 1,4-Te···O interaction, the other is devoid of it. The chelated organic ligand orients its plane suitably to become almost coplanar with the C–Te–C plane [interplanar angle = 16.9(1)°] and its carbonyl O atom lies nearly trans to the other Te–C bond [∠O1A···Te–C1B_{trans} = 145.5(1)°] at a distance of 3.003(3) Å from the Te(IV) center which is significantly shorter to the value of Σr_{vdw}(Te, O). A comparison of the Te–C_{sp3}–C_{carbonyl} angular measures for the two C-bonded ligands in this compound [106.6(3)° versus 112.8(3)°] suggests a significant contraction at the methylene C atom of the chelated ligand owing to the attractive non

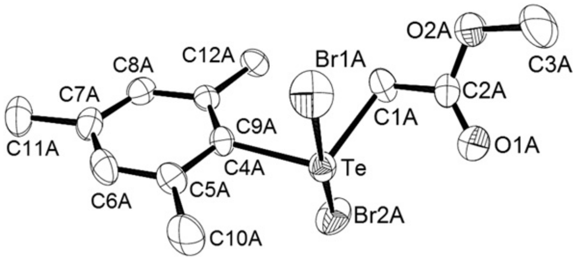


Fig. 2. ORTEP view of **5b** (molecule 1) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

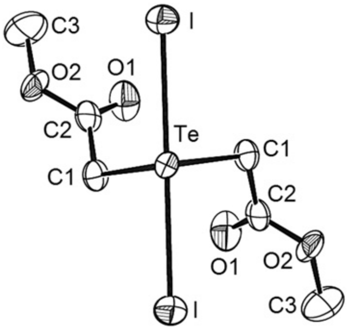


Fig. 4. ORTEP view of **1c** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

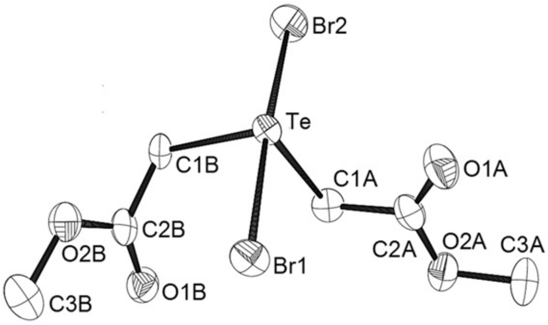


Fig. 5. ORTEP view of **1b** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

bonded Te···O interaction. The skeletal plane of the second C-bonded methoxycarbonylmethyl moiety in the solid state of this compound is almost orthogonal to the C–Te–C plane [dihedral angle = 67.1(2)°]. The central Te atom in this molecule is accessible and invokes intermolecular Te··· Br^i SBI as supramolecular motif [d(Te, Br^i) = 3.562(1) Å, *cf.* Σr_{vdw}(Te, Br) = 3.93 Å; Br^i···Te–C1A$_{\mathrm{trans}}$ = 163.0(1)°; $i = x - 1/2, -y + 3/2, z - 1/2$]. This interaction interlinks two rows of molecules in the crystal lattice in a gear-teeth fashion. The carbonyl O atom of the organic ligand (devoid of intramolecular Te···O interaction) from an adjacent molecule also approaches the central Te(IV) atom so that the interatomic distance is smaller [d(Te,O1B^{ii}) = 3.512(4) Å, O1B^{ii}···Te–C1A$_{\mathrm{trans}}$ = 129.7(1)°; $ii = x + 1/2, -y + 3/2, z - 1/2$], though marginally, compared to Σr_{vdw}(Te, O) value and may be said to account for a weak intermolecular Te···O SBI on the distance versus strength criteria (Fig. S2).

3. Conclusion

The potential of an ester group to activate the α-C$_{sp3}$–Br bond to insert Te(0) and afford ester-functionalized organotellurium derivatives is poor compared to an acyl or amido group. However, stirring at room temperature of a mixture of an alkyl ester of α-bromoacetic acid, sodium iodide and tellurium powder provides a convenient synthetic route to obtain the desired organotellurium compounds. The delicate balance between the electronic factors and crystal forces appear to direct the bonding mode of the alkoxycarbonylmethyl ligands in the solid state. The secondary bonding interactions involving Te(IV) atom with a lone pair, appear to ignore the VSEPR rules at least in the crystalline state of the functionalized organotellurium(IV) halides.

4. Experimental

4.1. General procedures

Preparative work was performed under dry nitrogen. All solvents were purified and dried before use. Methyl and *t*-butyl esters of bromoacetic acid (synthesis grade) were procured from Merck, Germany and used as such. Bis(1-naphthyl)ditelluride and dimesitylditellurides were prepared by the reported method [17,18]. Melting points were recorded in capillary tubes and are uncorrected. ^{1}H NMR (300.13 MHz) spectra were recorded on a Bruker DRX300 spectrometer and ^{13}C{^{1}H} (100.54 MHz) and ^{125}Te{^{1}H} (126.19 MHz) NMR spectra on a JEOL Eclipse Plus 400 NMR spectrometer. CDCl$_3$was used as NMR solvent and the reported ^{1}H and ^{13}C chemical shifts in ppm are against Me$_4$Si while the ^{125}Te chemical shifts are against Me$_2$Te. C, H analyses were carried out using a Carlo Erba 1108 analyzer.

4.2. Syntheses

4.2.1. Syntheses of bis(alkoxycarbonylmethyl)tellurium diiodides

A typical experiment is described. Te powder (1.3 g, 10 mmol), 2-bromomethylacetate (2.0 mL, 21.6 mmol) and sodium iodide (3.0 g, 20 mmol) were stirred together for 72 h at room temperature (the reaction is complete in 4–5 h when stirred at moderate temperature ~40–50 °C). The resulting red colored paste was dissolved in diethyl ether and filtered. The filtrate was freed of solvent and the residue triturated with petroleum ether (40–60 °C). The red solid obtained was filtered and recrystallized from dichloromethane to give **1c**. Yield: 4.75 g (90%). M.p.: 72 °C. Anal. Calc. for $C_6H_{10}O_4TeI_2$ (527.55): C, 13.66; H, 1.91. Found: C, 13.76; H, 1.84. ^{1}H NMR: δ 3.88 (s, 6H, CH$_3$O), 4.48 (s, 4H, CH$_2$) ppm. ^{13}C{^{1}H} NMR: δ 41.0 (CH$_3$), 54.0 (CH$_2$), 166.4 (CO) ppm. ^{125}Te{^{1}H} NMR: δ 687 ppm.

The use of *t*-butyl ester of bromoacetic acid in the synthesis described above gave red crystals of **2c**. Yield: 5.2 g (86%). M.p.: 93 °C. Anal. Calc. for $C_{12}H_{22}O_4TeI_2$ (611.71): C, 23.56; H, 3.63. Found: C, 23.88; H 3.91. ^{1}H NMR: δ 1.54 (s, 18H, *t*-Bu), 4.39 (s, 4H, CH$_2$) ppm. ^{13}C{^{1}H} NMR: δ 28.0 (CH$_3$), 43.2 (CH$_2$), 85.6 (quaternary C), 164.8(CO) ppm. ^{125}Te{^{1}H} NMR: δ 655 ppm.

4.2.2. Syntheses of bis(alkoxycarbonylmethyl)tellurium dibromides and dichlorides

The bromo and chloro analogs of **1c** and **2c** were prepared by their reduction to the respective bis(alkoxycarbonylmethyl)tellurides followed by oxidative halogenations with Br$_2$ and SO$_2$Cl$_2$. In a typical experiment, an aqueous solution of sodium metabisulphite (0.19 g, 1.0 mmol) was added slowly under stirring to a dichloromethane solution of 0.528 g (1.00 mmol) of the compound **1c**. The organic layer was separated within 15 min and washed thrice with water and passed over a bed of anhydrous sodium sulfate. The filtrate was freed from the solvent to give yellow oily telluride, **1**. Addition of a solution of SO$_2$Cl$_2$ (0.12 mL, 1.5 mmol) in *n*-hexane (~10 mL) to a cooled (0 °C) light yellow solution of **1** in the same solvent (20 mL) under stirring precipitated a white solid which was filtered and recrystallized from dichloromethane to give analytically pure **1a**. Yield: 0.28 g (80%). M.p.: 60 °C (lit. 50–55 °C [4]). Anal. Calc. for $C_6H_{10}O_4TeCl_2$ (344.65): C, 20.91; H, 2.92. Found: C, 20.78; H, 2.85. ^{1}H NMR: δ 3.87 (s, 6H, OCH$_3$), 4.42 (s, 4H,

Table 1
Selected interatomic distances (Å) and bond angles (°) of **1b**, **1c**, **3b**, **5b**, and **6a**.

Parameter	**1b**	**1c**	**3b**	**5b**	**6a**
Te–C$_{\mathrm{alkyl}}$(C1/C1A, C1B)	2.129(5)	2.158(1)	2.137(4)	2.148(3), 2.138(3)	2.127(1)
Te–C$_{\mathrm{alkyl}}$ (C1/1B) or Te–C$_{\mathrm{aryl}}$(C4/C4A, C4B)	2.154(4)	2.158(1)	2.115(4)	2.131(3), 2.119(3)	2.125(1)
C$_{\mathrm{alkyl}}$–Te–C$_{\mathrm{aryl}}$	93.2(2)	94.8(2)	99.7(2)	107.6(1), 108.0(1)	108.02(6)
Te–X1	2.655(1)	2.895(1)	2.705(1)	2.693(1), 2.698(1)	2.503(1)
Te–X2	2.670(1)	2.895(1)	2.628(1)	2.644(1), 2.634(1)	2.512(1)
X1–Te–X2	175.15(2)	176.50(2)	173.30(2)	173.92(2), 174.34(2)	171.43(2)
Te···O1 (O1A, O1B) (<3.58)	3.003(3)	–	2.979(3)	3.074(3), 2.995(3)	2.938(1)
O1 (O1A, O1B)···Te–C$_{\mathrm{trans}}$	145.5(1)	–	150.9(2)	157.2(1), 157.3(1)	145.5(1)

Table 2
Crystal data and structure refinement details of **1b**, **1c**, **3b**, **5b**, and **6a**.

	1b	**1c**	**3b**	**5b**	**6a**
Empirical formula	$C_6H_{10}Br_2O_4Te$	$C_6H_{10}I_2O_4Te$	$C_{13}H_{12}Br_2O_2Te$	$C_{12}H_{16}Br_2O_2Te$	$C_{15}H_{22}Cl_2O_2Te$
Formula mass (g mol^{-1})	433.56	527.54	487.65	479.67	432.83
Temperature (K)	123(2)	110(2)	295(2)	295(2)	295(2)
Wavelenth, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Crystal size (mm^3)	0.85 × 0.45 × 0.11	0.47 × 0.44 × 0.32	0.48 × 0.44 × 0.15	0.53 × 0.21 × 0.18	0.55 × 0.22 × 0.17
Space group	$P\,2_1/n$	$C\,2/c$	$P\,-1$	$P\,2_1/n$	$P\,b\,c\,a$
a (Å)	6.6483(2)	19.2748(9)	7.2466(5)	11.1424(4)	9.9930(3)
b (Å)	19.1797(6)	9.2967(5)	9.4560(5)	9.2479(3)	17.8639(6)
c (Å)	9.4488(5)	6.9406(3)	12.4268(5)	30.9878(13)	20.6867(5)
α (°)	90	90	72.137(4)	90	90
β (°)	106.836(4)	93.080(4)	77.153(4)	99.124(4)	90
γ (°)	90	90	70.577(5)	90	90
V ($Å^3$)	1153.19(7)	1241.90(10)	757.46(7)	3152.70(19)	3692.86(19)
Z	4	4	2	8	8
ρ_{calcd} (Mg m^{-3})	2.497	2.821	2.138	2.021	1.557
μ (Mo$K\alpha$, mm^{-1})	9.492	7.352	7.230	6.946	1.899
$F(000)$	800	944	456	1808	1712
h, k, l ranges collected	$-6 \leq h \leq 10$ $-26 \leq k \leq 29$ $-14 \leq l \leq 10$	$-21 \leq h \leq 26$ $-11 \leq k \leq 9$ $-9 \leq l \leq 9$	$-10 \leq h \leq 9$ $-12 \leq k \leq 14$ $-14 \leq l \leq 18$	$-16 \leq \mathrm{h} \leq 13$ $-12 \leq k \leq 13$ $-44 \leq \mathrm{l} \leq 43$	$-15 \leq \mathrm{h} \leq 14$ $-18 \leq k \leq 25$ $-26 \leq \mathrm{l} \leq 30$
Reflection collected	7235	3062	9110	28,479	19,592
Independent reflections	3780[R(int) = 0.0399]	1447 [R(int) = 0.0215]	4978 [R(int) = 0.0356]	10,558 [R(int) = 0.0525]	6236 [R(int) = 0.0321]
θ range (°)	5.17 to 32.75	4.75 to 29.39	5.15 to 32.76	5.04 to 32.80	5.07 to 32.66
Completeness to θ_{max} (%)	98.7	98.9	99.0	98.7	99.1
Absorption correction	Analytical	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.338, 0.027	1.00000, 0.57455	1.00000, 0.15936	1.00000, 0.23326	1.00000, 0.72057
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3780/0/121	1447/0/62	4978/0/165	10,558/0/316	6236/0/201
Goodness of fit on F^2	1.033	0.983	0.917	0.860	0.919
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0441$, $wR2 = 0.0906$	$R1 = 0.0242$, $wR2 = 0.0545$	$R1 = 0.0493$, $wR2 = 0.1120$	$R1 = 0.0411$, $wR2 = 0.0688$	$R1 = 0.0326$, $wR2 = 0.0694$
R indices (all data)	$R1 = 0.0613$, $wR2 = 0.0992$	$R1 = 0.0333$, $wR2 = 0.0563$	$R1 = 0.0875$, $wR2 = 0.1225$	$R1 = 0.1223$, $wR2 = 0.0800$	$R1 = 0.0727$, $wR2 = 0.0761$
Largest diff peak/hole (e $Å^{-3}$)	2.751/−2.300	0.999/−0.852	1.503/−1.876	0.962/−0.755	0.622/−0.476

CH_2) ppm. **2a**: yield: 86%. M.p.: 120 °C. Anal. Calc. for $C_{12}H_{22}O_4TeCl_2$ (428.81): C, 33.61; H, 5.17. Found: C, 33.58; H, 4.93. ^{1}H NMR: δ 1.53 (s, 18H, t-Bu), 4.32 (s, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: δ 27.9 (CH_3), 49.7 (CH_2), 85.3 (quaternary C), 164.7 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 793 ppm.

1b: yield: 72%. M.p.: 61 °C. Anal. Calc. for $C_6H_{10}O_4TeBr_2$ (433.55): C, 16.62; H, 2.32. Found: C, 16.38; H, 2.35. ^{1}H NMR: δ 3.88 (s, 6H, CH_3O), 4.52 (s, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: δ 44.9 (OCH_3), 53.8 (CH_2), 166.3 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 748 ppm. **2b**: yield: 80%. M.p.: 105 °C. Anal. Calc. for $C_{12}H_{22}O_4TeBr_2$ (517.71): C, 27.84; H, 4.28. Found: C, 27.58; H, 4.12. ^{1}H NMR: δ 1.54 (s, 18H, t-Bu), 4.41 (s, 4H, CH_2) ppm.

4.2.3. *Metathetical reactions of **1a** and **2a** with sodium bromide*

Compounds **1b** and **2b** were also obtained by the halide exchange reaction between **1a** or **2a** and NaBr. A solution of **1a** (0.70 g 2.0 mmol) in dichloromethane (20 mL) was stirred with sodium bromide (0.50 g, 4.9 mmol) for 6 h. The sodium halides were removed by filtration. Concentration of the filtrate and addition of petroleum ether (40–60 °C) afforded 0.73 g (84%) of **1b** as a light yellow solid, which when recrystallized from chloroform gave yellow crystals. Compound **2b** was obtained similarly.

Attempts to prepare a pure sample of mixed halide, $(MeOCOCH_2)_2TeClBr$ by stirring **1a** with NaBr in 1:1 molar ratio were unsuccessful, though ^{125}Te NMR of the isolated sample showed three signals at 796, 748 and 775 (~1:3:3) ppm which may be assigned to **1a**, **1b** and the mixed halide respectively.

4.2.4. *Syntheses of aryl(alkoxycarbonylmethyl)tellurides*

In a typical experiment, a solution of bis(1-naphthyl)ditelluride (0.51 g, 1.0 mmol) in dry THF (20 mL) was cooled to 0 °C in a two neck 100 mL round bottom flask under a flow of dry nitrogen. t-Butyl ester of 2-bromoacetic acid (0.45 mL, 2.7 mmol) was added with stirring, followed by slow addition of a 5% aqueous solution of sodium borohydride until the red color of the ditelluride faded. The mixture was stirred at room temperature for a further 5 h. The compound was extracted with dichloromethane (50 mL), washed with distilled water (3 × 50 mL) and dried over anhydrous sodium sulfate. The solvent was removed completely under reduced pressure to result in a light orange oil of (1-naphthyl)(t-butoxycarbonylmethyl)telluride, **4**. The product was added to a silica column, eluted with n-hexane to wash out the unreacted ditelluride and then with dichloromethane to obtain the purified product. Yield: 0. 61 g (81%); ^{1}H NMR: δ 1.26 (s, 9H, t-Bu), 3.47 (s, 2H, CH_2), 8.26–7.30 (m, 7H, aryl protons).

The other aryl(alkoxycarbonylmethyl)tellurides, **3**, **5** and **6** were prepared similarly. These tellurides are liquids at ambient temperature, except **6** which is a low melting solid (M.p.: 33–34 °C).

5: yield: 81%; ^{1}H NMR: δ 2.29 (s, 3H, p-CH_3), 2.62 (s, 6H, o-CH_3), 3.38 (s, 2H, CH_2); 3.52 (s, 3H, OCH_3), 6.99 (s, 2H, m-aryl protons) ppm.

6: yield: 86%; ^{1}H NMR: δ 1.67 (s, 9H, t-Bu), 2.28 (s, 3H, p-CH_3), 2.63 (s, 6H, o-CH_3), 3.31 (s, 2H, CH_2); 6.97 (s, 2H, m-aryl protons) ppm.

The oxidative halogenations of the mixed diorganotellurides (**3**–**6**) using SO_2Cl_2, Br_2 and I_2 by the procedure described above in

Section 4.2.2 gave the corresponding white chlorides, yellow bromides and red iodides as stable crystalline solids, except **3c** and **5c** which decompose on standing at room temperature.

3a: yield: 80%. M.p.: 121–122 °C. Anal. Calc. for $C_{13}H_{12}O_2TeCl_2$ (398.74): C, 39.16; H, 3.03. Found: C, 39.36; H, 3.18. ^1H NMR: δ 3.93 (s, 3H, CH_3O), 4.76 (s, 2H, CH_2), 7.60–8.21 (m, 7H, aryl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 51.9 (OCH_3), 54.0 (CH_2), 126.5, 126.6, 127.4, 128.3, 129.5, 131.5, 131.8, 132.9, 134.3, 134.8 (aryl carbons), 166.2 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 774 ppm.

3b: yield: 85%. M.p.: 139 °C. Anal. Calc. for $C_{13}H_{12}O_2TeBr_2$ (487.64): C, 32.02; H, 2.48. Found: C, 31.86; H, 2.60. ^1H NMR: δ 3.96 (s, 3H, CH_3O), 4.89 (s, 2H, CH_2), 7.62–8.18 (m, 7H, aryl protons) ppm. $^{13}C\{^1H\}$ NMR: δ 50.2 (OCH_3), 54.2 (CH_2), 126.5, 126.8, 127.5, 128.3, 129.5, 131.0, 131.4, 132.3, 132.8, 134.3 (aryl carbons), 166.3 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 713 ppm.

4a: yield: 85%. M.p.: 106 °C. Anal. Calc. for $C_{16}H_{18}O_2TeCl_2$ (440.82): C, 43.59; H, 4.12. Found: C, 44.05; H, 3.97. ^1H NMR: δ 1.59 (s, 9H, *t*-Bu), 4.72 (s, 2H, CH_2), 7.59–8.14 (m, 7H, aryl protons) ppm. $^{13}C\{^1H\}$ NMR in 4:1 $CDCl_3$:DMSO-d_6: δ 26.8 (CH_3), 53.2 (CH_2), 56.0 (quaternary C), 125.6, 125.8, 126.1, 126.9, 128.3, 130.5, 131.4, 131.5, 133.0, 133.9 (aryl carbons), 167.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 792 ppm.

4b: yield: 88%. M.p.: 126 °C. Anal. Calc. for $C_{16}H_{18}O_2TeBr_2$ (529.72): C, 36.28; H, 3.42. Found: C, 35.93; H, 3.22. ^1H NMR: δ 1.63 (s, 9H, *t*-Bu), 4.82 (s, 2H, CH_2), 7.53–8.09 (m, 7H, aryl protons) ppm.

4c: yield: 84%. M.p.: 109 °C. Anal. Calc. for $C_{16}H_{18}O_2TeI_2$ (623.72): C, 30.81; H, 2.91. Found: C, 30.06; H, 2.82. ^1H NMR: δ 1.61 (s, 9H, *t*-Bu), 4.85 (s, 2H, CH_2), 7.58–8.11 (m, 7H, aryl protons) ppm.

5a: yield: 85%; M.p.: 122–123 °C. Anal. Calc. for $C_{12}H_{16}O_2TeCl_2$ (390.76): C, 36.88; H, 4.13. Found: C, 36.70; H, 3.98. ^1H NMR: δ 2.31 (s, 3H, *p*-CH_3), 2.69 (s, 3H, *o*-CH_3), 2.79 (s, 3H, *o*-CH_3), 3.91 (s, 3H, OCH_3), 4.83 (s, 2H, CH_2), 6.98 (s, 1H, *m*-proton), 7.03 (s, 1H, *m*-proton) ppm. $^{13}C\{^1H\}$ NMR: δ 20.9, 23.3, 23.4 (mesityl methyl carbons), 51.7 (OCH_3), 53.9 (CH_2), 130.4, 131.7, 135.4, 139.5, 141.0, 142.4 (mesityl ring carbons), 166.6 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 798 ppm.

5b: yield: 83%. M.p.: 106–108 °C. Anal. Calc. for $C_{12}H_{16}O_2TeBr_2$ (479.66): C, 30.05; H, 3.36. Found: C, 29.82; H 3.10. ^1H NMR: δ 2.32 (s, 3H, *p*-CH_3), 2.66 (s, 3H, *o*-CH_3), 2.76 (s, 3H, *o*-CH_3), 3.92 (s, 3H, OCH_3), 4.97 (s, 2H, CH_2), 6.96 (s, 1H, *m*-proton), 7.02 (s, 1H, *m*-proton) ppm. $^{13}C\{^1H\}$ NMR: δ 21.0, 23.2, 24.0 (mesityl methyl carbons), 50.7 (OCH_3), 54.1 (CH_2), 130.5, 131.8, 132.2, 139.2, 141.2, 142.4 (mesityl ring carbons), 166.6 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 721 ppm.

6a: yield: 85%. M.p.: 104–105 °C. Anal. Calc. for $C_{15}H_{22}O_2TeCl_2$ (432.84): C, 41.62; H, 5.12. Found: C, 41.34; H 5.28. ^1H NMR: δ 1.57 (s, 9H, *t*-Bu), 2.32 (s, 3H, *p*-CH_3), 2.67 (s, 3H, *o*-CH_3), 2.79 (s, 3H, *o*-CH_3), 4.76 (s, 2H, CH_2), 6.98 (s, 1H, *m*-proton), 7.02 (s, 1H, *m*-proton) ppm. $^{13}C\{^1H\}$ NMR: δ 21.0, 23.4, 23.5 (mesityl methyl carbons), 27.9 (*t*-Bu), 54.0 (CH_2), 85.3 (quaternary C), 130.3, 131.6, 135.4, 139.7, 141.1, 142.3 (mesityl ring carbons), 165.0 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 804 ppm.

6b: yield: 86%. M.p.: 125–126 °C. Anal. Calc. for $C_{15}H_{22}O_2TeBr_2$ (521.74): C, 34.53; H, 4.25. Found: C, 34.28; H, 4.07. ^1H NMR: δ 1.58 (s, 9H, *t*-Bu), 2.30 (s, 3H, *p*-CH_3), 2.52 (s, 3H, *o*-CH_3), 2.64 (s, 3H, *o*-CH_3), 4.91 (s, 2H, CH_2), 6.91 (s, 1H, *m*-proton), 6.98 (s, 1H, *m*-proton) ppm.

6c: yield: 84%. M.p.: 101 °C. Anal. Calc. for $C_{15}H_{22}O_2TeI_2$ (615.74): C, 29.26; H, 3.60. Found: C 28.98, H 3.82; ^1H NMR: δ 1.58 (s, 9H, *t*-Bu), 2.32 (s, 3H, *p*-CH_3), 2.63 (s, 3H, *o*-CH_3), 2.76 (s, 3H, *o*-CH_3), 4.90 (s, 2H, CH_2), 6.96 (s, 1H, *m*-proton), 7.01 (s, 1H, *m*-proton) ppm.

4.3. Crystallography

Single crystals suitable for X-ray diffraction measurements were grown by slow evaporation of dichloromethane solutions of **1b**, **1c**, **3b**, **5b** and **6a** at ambient temperature. 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 CrysAlisPro171.NET program from Oxford Diffraction Ltd. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 [19]. 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 1. In **6a**, methyl groups of t-butyl fragment are disordered over two conformations and each conformer was refined with occupancy factors which summed to one. The ORTEP figures (omitting H atoms for clarity and showing 50% probability displacement ellipsoids) were generated using the WinGX 2002 platform [20].

Acknowledgments

Financial assistance by the Department of Science and Technology, Government of India, New Delhi, is gratefully acknowledged. The authors are thankful to the Head, Department of Chemistry, University of Lucknow, for providing laboratory facilities and the Sophisticated Analytical Instrument Facility (SAIF) at C.D.R.I., Lucknow, for ^1H NMR and C, H analyses.

Appendix A. Supplementary material

CCDC 921596–921600 contain the supplementary crystallographic data for **1b**, **1c**, **3b**, **5b** and **6a** respectively. 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.2013.01.010.

References

[1] A.K.S. Chauhan, A. Kumar, R.C. Srivastava, R.J. Butcher, J. Organomet. Chem. 658 (2002) 169–175.
[2] S. Misra, A.K.S. Chauhan, P. Singh, R.C. Srivastava, A. Duthie, R.J. Butcher, Dalton Trans. 39 (2010) 2637–3643.
[3] A.K.S. Chauhan, P. Singh, R.C. Srivastava, R.J. Butcher, A. Duthie, J. Organomet. Chem. 695 (2010) 2118–2125. and references therein.
[4] R. Tamura, H. Shimizu, N. Ono, N. Azuma, H. Suzuki, Organometallics 11 (1992) 954–958.
[5] I.D. Sadekov, A.A. Maksimenko, B.B. Rivkin, Zh. Org. Khim. 14 (1978) 874.
[6] M.P. Bafle, C.A. Chaplin, H. Phillips, J. Chem. Soc. (1938) 341–347.
[7] M.P. Bafle, K.N. Nandi, J. Chem. Soc. (1941) 70–72.
[8] L. Engman, Organometallics 5 (1986) 427–431.
[9] L.A. Silks III, J.D. Odom, R.B. Dunlap, Synth. Commun. 21 (1991) 1105–1119.
[10] T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai, N. Sonoda, Synthesis (1987) 1096–1097.
[11] Y. Ho, Z. Huang, X. Huang, Synth. Commun. 19 (1989) 1625–1629.
[12] M.J. Dabdoub, P.G. Guerrero Jr., J. Organomet. Chem. 460 (1993) 31–37.
[13] C.-J. Li, D.N. Harpp, Sulf. Lett. 13 (1991) 139–142.
[14] F.H. Allen, O. Kennard, Chem. Des. Automat. News 8 (1993) 31–37.
[15] A.K.S. Chauhan, P. Singh, A. Kumar, R.C. Srivastava, R.J. Butcher, A. Duthie, Organometallics 26 (2007) 1955–1959.
[16] A.K.S. Chauhan, P. Singh, R.C. Srivastava, A. Duthie, A. Voda, Dalton Trans. (2008) 4023–4028.
[17] M.R. Detty, B.J. Murray, D.L. Smith, N. Zumbulyadis, J. Am. Chem. Soc. 105 (1983) 875–882.
[18] M. Akiba, M.V. Lakshmikantham, K.-Y. Jen, M.P. Cava, J. Org. Chem. 49 (1984) 4819–4821.
[19] G.M. Sheldrick, SHELXL-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), 2008.
[20] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.