Accepted Manuscript

Synthesis of organyltellanyl(IV) trihalides $[2-(Me_2NCH_2)C_6H_4TeX_3]$ (X = CI, Br, I) and their rare zwitterionic derivatives containing organyltellanyl(II) groups

Felipe D. da Silva, Cláudia A.D.P. Simões, Sailer S. dos Santos, Ernesto S. Lang

PII: S0022-328X(17)30035-9

DOI: 10.1016/j.jorganchem.2017.01.015

Reference: JOM 19772

To appear in: Journal of Organometallic Chemistry

Received Date: 18 November 2016

Revised Date: 20 January 2017

Accepted Date: 21 January 2017

Please cite this article as: F.D. da Silva, C.A.D.P. Simões, S.S. dos Santos, E.S. Lang, Synthesis of organyltellanyl(IV) trihalides $[2-(Me_2NCH_2)C_6H_4TeX_3]$ (X = CI, Br, I) and their rare zwitterionic derivatives containing organyltellanyl(II) groups, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.01.015.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



STATEMENT

The authors state that the article "Synthesis of organyltellanyl(IV) trihalides $[2-(Me_2NCH_2)C_6H_4TeX_3]$ (X = Cl, Br, I) and their rare zwitterionic derivatives containing organyltellanyl(II) groups" is original and unpublished and is not being considered for publication elsewhere.

Prof. Dr. Ernesto Schulz Lang Universidade Federal de Santa Maria Departamento de Química Campus – Camobi 97115-900 – SANTA MARIA (RS) - BRAZIL E-mail: eslang@quimica.ufsm.br Synthesis of organyltellanyl(IV) trihalides $[2-(Me_2NCH_2)C_6H_4TeX_3]$ (X = Cl, Br, I) and their rare zwitterionic derivatives containing organyltellanyl(II) groups

Felipe D. da Silva,^a Cláudia A. D. P. Simões,^a Sailer S. dos Santos^a and Ernesto S. Lang^{a,*}

^a Departamento de Química, Laboratório de Materiais Inorgânicos - Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil.

*Corresponding author. Tel.: (55) 55 3220 8868

E-mail address: eslang@ufsm.br

Abstract

In this article we describe the synthesis and structural characterization of a series of organyltellanyl(IV) trihalides containing the [2-((dimethylamino)methyl)phenyl] moiety $[2-(Me_2NCH_2)C_6H_4TeX_3]$ (X = Cl, Br, I), and some of its derivatives in the form of rare zwitterionic compounds with organyltellanyl(II) groups. The supramolecular structure of the different organyltellanyl halides presents considerable changes due to the nature of Te...X and X...X secondary interactions. The positive and negative charges of the zwitterionic compounds, the size of the halogens and the repulsion of the lone electron pairs around the tellurium atom were also evaluated. All compounds were characterized by single crystal X-ray diffraction, vibrational spectroscopy (FT-IR and Raman) and NMR (¹H and ¹²⁵Te) spectroscopy and elemental analysis.



Graphical synopsis:

X = Cl, Br, I

Keywords: Tellurium; Zwitterion; Organyltellanyl halides; bis[2-((dimethylamino)methyl)phenyl] ditellane;

1. Introduction

Tellurium compounds have been studied in several branches of chemistry, for example, as intermediates in organic chemistry and in materials science [1-5]. In addition, many examples of compounds containing organochalcogen groups show a variety of biological activities [6,7]. The intermediary classical metallic and non-metallic chemical behavior attributed to the tellurium atom allied to its relatively large atomic size allow the stabilization of positive or negative charges, which provides versatility in terms of suitable oxidation states and coordination numbers [8-10]. Organyltellanyl halides are good examples to show these interesting features, including species of the general formulae RTe^{II}X, RTe^{IV}X₃, R₂Te^{IV}X₂, R₃Te^{IV}X and R₅Te^{VI}X (R = alkyl, aryl; X = Cl, Br, I), and their related derivatives [11].

The solid-state structure of organyltellanyl halides indicates that they display distinct behavior and reactivity due to the supramolecular arrangements generated by the atoms attached to tellurium when secondary bonds (non-covalent interactions) are formed [12,13]. The competition of donor atoms generating intramolecular interactions *via* secondary bonds with the tellurium atom is the key to understanding the supramolecular organization of this class of compounds. These secondary bonds can be described as a *quasi*-linear three-centered system $Y-E\cdots X$, where Y-E is a covalent bond and $E\cdots X$ an interaction for which the distance is shorter than the sum of the van der Waals radii. This is a common feature of the heaviest main group elements and these

non-covalent interactions lead to a rich supramolecular structural chemistry, particularly when tellurium is the central atom, since the substituent effects influence of the interplay of Te…X and X…X contacts. Several examples demonstrate that these interactions play a central hole on the building of the crystal molecular packing as well as ionic tellurium-based species [14-16].

Beckmann explored extensively the total or partial hydrolysis of organyltellanyl halides to obtain telluroxane compounds [17]. The oxidation of the telluroxane cluster $(8-Me_2NC_{10}H_6Te)_6O_8(OH)_2$ or the diarylditellane (8- $Me_2NC_{10}H_6Te)_2$ hydrogen peroxide (H_2O_2) using provided bis(aryl)ditelluronic acid [8-(Me₂NC₁₀H₆)Te(O)(OH)₂]₂(O) [18]. Some of these compounds can be considered ampholytes because these molecules contain both acidic and basic groups [17]. Similarly, zwitterionic compounds containing tellurium have also been described in the literature, but just a few examples are known. Bergman and co-workers related the synthesis and crystal structure elucidation of a 2-oxazolinyltetrachlorotellurolate obtained by cyclofuncionalization of N-acetyldiallylamine with tellurium tetrachloride [19]. Whitmire and co-workers published the synthesis and characterization of the carbide cubane cluster $[Fe_3(CO)_9Te_4(\mu_3-CTeBr_4)]$ with an unusual tetrahedral CTe₄ unit [20]. Oilunkaniemi and co-workers related the reaction involving the treatment of triphenylphosphane with tellurium tetrabromide in tetrahydrofuran, for the preparation and structural characterization of new tellurium halides. The reaction unexpectedly leaded to the opening of the

tetrahydrofuran ring and the formation of Ph₃PO(CH₂)₄TeBr₄ [21]. Richards and co-workers prepared the compound $[[{N(C_6H_3'Pr_2-$ 2,6C(Me) $_2$ CH]TeCl₄] in good yields starting from the corresponding lithium β -diketiminato salt and characterized it in the solid state by X-ray crystallography [22]. Lappert and co-workers treated TeCl₄ with a mixture of single equivalent portions of $2,6^{-i}Pr_2(C_6H_3)NH_2$ and $H[\{N(C_6H_3)^{i}Pr_2$ produce $[Cl_4Te(C_6H_2-iPr_2-3,5-NH_3-4)(thf)_2]$ $2,6)C(H)_{2}CPh$ to [23]. Khrustalev and co-workers prepared [HPymTeCl₂] and $[H^{o}PyTeCl_{2}]$ (Pym = 2-(4,6-dimethyl)pyrimidyl; o Py = 2-pyridyl) to demonstrate a facile route for the stabilization of highly reactive $Ar^{*}TeCl$ species ($Ar^{*} = N$ -functionalized aryl) through the addition of a hydrogen chloride molecule [24].

More recently, we studied the reactions of $({}^{p}PyTe)_{2}$ (${}^{p}Py = 4$ -pyridyl) with HCl, CH₃I, CH₃I/I₂, I₂/(Ph₃Te)I and CoCl₂·6H₂O to prepare the zwitterionic compounds [H^{*p*}PyTeCl₂], [Me^{*p*}PyTeI₂] and [Me^{*p*}PyTeI₄] and the coordination polymer [Co(${}^{p}PyTe)_{2}Cl_{2}$]_n, in order to explore the reactivity and coordination modes of the 4-pyridyl-tellanyl groups [25]. The protonated or methylated nitrogen provided the cationic moiety - and the oxidative addition of halogen atoms to tellurium provided the proper Te^{II} or Te^{IV} anionic unit. Despite the interesting structural properties presented by this class of compounds and also their zwitterionic derivatives, they remain until now little explored.

In this context, in this article we describe the synthesis and structural characterization of a series of new Te,N-based molecules containing [2-((dimethylamino)methyl)phenyl]tellanyl (DmapTe) moieties.

2. Results and Discussion

Scheme 1 summarizes our attempts to obtain zwitterionic species containing the [2-(dimethylamino)methyl)phenyl]tellanyl group.

Insert Scheme 1

The reactions of DmapHgCl (1) with tellurium tetrachloride in dioxane followed by the addition of a hydrohalic acid (in the case of the bromine derivative) afforded the organyltellanyl(IV) trihalides 2 (DmapTeCl₃) and 3 (DmapTeBr₃) (see Figure 1 and Figure 2).

The third example of this series, compund **5** (DmapTeI₃) (see Figure 3), was obtained from the reaction of bis[2-((dimethylamino)methyl)phenyl]ditellane – (DmapTe)₂ – and three equivalents of diiodine in tetrahydrofuran. The synthesis of **2** and **3** has been previously described in the literature [26] and the structure of **3** is reported for the first time in this study. However, an alternative and easier procedure for the synthesis of **2** and **3** is described herein. The supposed Te^{II} precursor for the synthesis of these two compounds previously reported in the literature [26] could not be identified. The reactions to obtain **2**, **3** and **5** were also carried out in the presence of HX (X = Cl, Br,

I). Although the reactions occurred in the presence of the corresponding hydrohalic acids, the expected zwitterionic species HDmapTe^{IV}X₄, could not identified. A previously reported evaluation of the coordination be compounds containing the [2-((dimethylamino)methyl)phenyl] group identified a conformational preference for the intra-coordinated form [27-28]. The molecular structures of the obtained compounds present Te-N bond distances of 2.406(3) Å – 2, 2.434(3) Å – 3 and 2.458(4) Å/2.492(4) Å – 5 indicating that the nitrogen atom of each compound is not protonated. The IR spectra of DmapTeX₃ species do not exhibit bands in the region of 2700 cm⁻¹ -2800 cm^{-1} , corresponding to v(N–H), which confirms the absence of N–H bonds. We can suggest that the preference for the structure containing the N---Te interaction in the specie $[2-(Me_2NCH_2)C_6H_4]TeX_3$ instead of the expected zwitterionic species $[2-(Me_2HNCH_2)C_6H_4]TeX_4)$ is due the chelate effect. This assumption is supported by the previously occurring Te^{IV}–N interactions in the chemical structure of the precursors 2, 3 and 5, due to the preference for interaction between hard-hard centers. The resulting five-membered ring formed by the hard-hard Te^{IV}–N interactions is possibly the most stable specie available in the reaction milieu.

The tellurium geometry in these compounds is similar to a seesaw considering only the covalent bonds of Te–C and Te–X (see Table 1 to compare the bond lengths of the compounds 2, 3 and 5). However, if we consider the Te…N intramolecular interaction and the Te…X interaction in the

supramolecular structure, the geometry of the central atom can be classified as a square pyramidal for **2** and distorted octahedral arrangement for **3** and **5** $(Te1\cdotsBr2' = 3.5646(6)Å; C3-Te1-Br2' = 172.81(10)^{\circ}$ for **3**; Te1 \cdots I3' = $3.7889(4)Å, Te2\cdots$ I6'' = $3.6862(6)Å; C3-Te1\cdots$ I3' = $170.82(9)^{\circ}, C13-Te2\cdots$ I6' = $174.14(15)^{\circ}$).

Insert Figure 1

Insert Figure 2

Compounds 2, 3 and 5 present very similar molecular structures but their supramolecular constructions are quite different. The molecules of 2 are connected by Te…Cl interactions (d = 3.7419(9) Å) building a zig-zag chain along the crystallographic *a* axis (Figure 1). The molecules of 3 are connected by Te…Br (d = 3.5645(6) Å) interactions leading to a pseudo-dimeric structure (Figure 2), with no other significant interactions. Compound 5 presents a multi-sided supramolecular structure where firstly the molecules are connected by Te…I (3.6862(6) Å) interactions building a pseudo-dimeric structure and these dimeric units are connected by I…I (3.8440(6) Å and 3.9098(5) Å) assembling layers parallel to the *ac* crystallographic planes (Figure 3).

Insert Figure 3

The zwitterionic [2-((dimethylammonium)methyl)phenyl]tellanyl(II) dihalides (6-8) – HDmapTeX₂ – (see Scheme 1) were synthesized from the reaction of $(DmapTe)_2$ in the presence of hydrochloric acid (for 6), hydrobromic acid (for 7) in dichloromethane and hydriodic acid plus one equivalent of diiodine in acetonitrile (for 8). The isostructural compounds 6and 7 are shown in Figure 4 and compound 8 can be seen in Figure 5. The reactions of $(DmapTe)_2$ with HX (X = Cl, Br, I) generate the expected zwitterionic species HDmapTeX₂ (Scheme 1). The formation of the N-H bond is confirmed by the presence of v(N-H) in the IR spectra, indicated by the bands at 2712 cm⁻¹ (6), 2733 cm⁻¹ (7) and 2696-2725 cm⁻¹ (8). Overall, these compounds are neutral molecules with simultaneous positive and negative charges in different groups ("inner salts"). The negative charge is located on the tellurium dihalide moiety and the positive charge on the nitrogen atom of the ammonium group. This different chemical behavior in comparision to the DmapTeX₃ molecules can be related to the presence of the Te^{II} atom in the zwitterionic species. The Te^{II} centers behave as Lewis acids softer than the Te^{IV} ones. Indeed, our results showed that Te^{II} centers can interact more efficiently with the softer halogenide ions rather than with the

harder nitrogen-based donors, leaving the amino group free to interact with the H^+ ion from the acidic milieu. This feature was crucial to the obtainment of the rare zwitterionic compounds.

Insert Figure 4

Insert Figure 5

The molecular compounds 6, 7 and 8 can be considered structurally very similar, exhibiting a "T"-shaped coordination geometry for the tellurium atom. The variations in the C-Te-X and X-Te-X angles (Table 1) can be attributed mainly to the different sizes of the halogen atoms. Also, the increase in the atom size generates a regular variation of the torsion angle C-C-Te-X = 75.758(147) (6), 78.547(239) (7) and 84.971(262) (8). Each structure presents asymmetric X–Te–X bond distances with the longest Te–X distances belonging to the halogen atom associated with a non-classical hydrogen bond. The supramolecular assemblies of compounds 6 and 7 formed by Te $\cdot\cdot\cdot$ X interactions in a zigzag format along the crystallographic b axis are very similar. In contrast to 6 and 7, the molecules of 8 are associated by double Te…I secondary bonds (3.7524(7) Å) to build up pseudo-dimeric structures. The pseudo-dimeric structures are connected by I…I interactions (4.0782(4) Å) forming a chain along the crystallographic c axis. Further details on the bond distances and angles of these compounds are given in Table 1.

4. Conclusions

A systematic series of organyltellanyl(IV) trihalides containing the [2-((dimethylamino)methyl)phenyl] moiety $[2-(Me_2NCH_2)(C_6H_4)TeX_3]$ (X = Cl, Br, I), and some of its derivatives in the form of zwitterionic compounds with organyltellanyl(II) groups have been synthesized. The structural characterization of this two series of Te,N-based molecules allowed us to show many different structural arrangements. The existence of positive and negative charges inside the zwitterionic compounds seems to be not relevant for the building of this arrangement. The oxidation states, the influence of the size of the halogens, the repulsion of lone electron pairs around the tellurium atom and the steric hindrance of the free electron pairs in the opposite position to the tellurium-halogen interaction can be considered the main driving factors for the building of the observed structural arrangements. The Te···X (X = Cl, Br) intramolecular interactions strongly indicated the direction of the assembly of the supramolecular structure for compounds 2, 3, 6 and 7. The presence of iodide in compounds 5 and 8 added the I...I interactions as an important extra driving force in the assembly of the supramolecular structures. A better understanding and control of the synthesis

and behaviors of this series of compounds will aid in the planning of the design and properties of new compounds under development [29-32].

5. Experimental Section

5.1. General

Solvents and standard reagents were obtained commercially from Sigma-Aldrich and used with standard further purification [33]. Bis[2-((dimethylamino)methyl)phenyl]ditellane and [2-((dimethylamino)methyl)phenyl]mercury(II) chloride were prepared following procedures described in the literature [34, 35].

Procedures to obtain 1-5 and 8 were carried out under argon and all compounds were crystallized in open atmosphere.

Elemental analysis (CHN) was carried out with a VARIO EL analyzer (Elementar Analysensysteme GmbH) at São Paulo University, Brazil. Infrared spectra were collected using a Bruker Tensor 27 mid-IR spectrometer (400 – 4000 cm⁻¹) and a Shimadzu IR Prestige 21 spectrometer and Raman spectra were obtained on a Bruker MultiRAM (1064 nm laser, 50 – 3500 cm⁻¹). NMR spectra were recorded on Bruker Avance III NMR spectrometers at 600.22 MHz (for ¹H) and 126.24 MHz (for ¹²⁵Te) in [D₆]DMSO. Chemical shifts in the ¹H NMR spectra were indirectly referenced to TMS by the solvent signals. Chemical shifts in the ¹²⁵Te NMR spectra were measured with (PhTe)₂ as an external standard (δ = 420.8 ppm) and referenced to Me₂Te [36].

5.2. X-ray Structure Determinations

A Bruker CCD X8 Kappa APEX II diffractometer operated using graphite monochromator and Mo-K α radiation ($\lambda = 0.71073$ Å) was used for the X-ray structure analysis. The structures were solved by direct methods with SHELXS and refined with SHELXL with anisotropic displacement parameters for all non-hydrogen atoms [37]. The idealized positions of the hydrogen atoms bonded to carbon atoms were calculated and treated with the "riding model" option of SHELXL. The positions of hydrogen atoms bonded to nitrogen atoms were located on the final Fourier maps and refined with isotropic displacement parameters. More information on the structure determinations is given in Table S1.

The supplementary crystallographic data (CCDC 1516033-1516038) for compounds **2**, **3** and **5–8** can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of DmapHgCl (1) [35]

A solution of *n*-butyl-lithium (60 mL 2 M - 120 mmol) in hexane was syringed into a solution of *N*,*N*-dimethylbenzylamine (13.5 g, 100 mmol) in diethyl ether (100 mL) at -78 °C. After stirring for 8 h, mercury(II) chloride

(27.2 g, 100 mmol) in THF (10 mL) was added to the reaction and the mixture was stirred overnight. The extraction was carried out with petroleum ether. The solvent was reduced under high-vacuum and **1** crystallized in a freezer.

Yield: 33.3 g – 90% based on *N*,*N*-dimethylbenzylamine. Properties: white crystalline substance; m.p.: 77 °C; Raman (cm⁻¹): 322; 208; 196; 171; 115; 86. Elem. anal. calcd. for C₉H₁₂NClHg (370.24): C, 29.20; H, 3.27; N, 3.78; Found: C, 28.9; H, 3.11; N, 3.82.

Synthesis of $DmapTeCl_3$ (2)

Compound **2** was obtained when tellurium tetrachloride (0,084 g, 0.312 mmol) was added to a solution of DmapHgCl (0.115 g, 0.312 mmol) in dioxane (30 mL). The reaction was stirred for 5 h at reflux temperature, the solvent was removed by rotaevaporation and the product was recrystallized from methanol.

Yield: 0.083 g - 73% based on **1**. Properties: pale yellow crystalline substance; m.p.: 181.2 °C; FT-IR (KBr, cm⁻¹): 2930.21; 1952.86; 1460.67; 1104.82; 765.60; 473.45; Raman (cm⁻¹): 361; 287; 250; 146; 101. Elem. anal. calcd. for C₉H₁₂NCl₃Te (368.16): C, 29.36, H, 3.29; N, 3.80. Found: C, 29.47, H, 3.29; N, 3.70.

Synthesis of $DmapTeBr_3$ (3)

Hydrobromic acid (5 mL) was added dropwise to a solution of **2** (0.736 g, 2 mmol) in methanol (20 mL). Crystals of **3** were formed from slow evaporation of the reaction mixture.

Yield: 0.712 g - 71% based on **2**. Properties: gold-yellow crystalline substance; m.p.: decomposition at 200 °C; FT-IR (KBr, cm⁻¹): 2901.63; 1631.16; 1457.74; 1095.31; 751.88; 465.77; Raman (cm⁻¹): 273; 250; 178; 151. Elem. anal. calcd. for C₉H₁₂NBr₃Te (501.51): C, 21.55; H, 2.41; N, 2.79; Found: C, 21.73, H, 2.61; N = 2.93.

Synthesis of $(DmapTe)_2$ (4) [34]

A solution of *n*-butyl-lithium (60 mL - 2 M in hexane - 120 mmol) was syringed into a solution of *N*,*N*-dimethylbenzylamine (13.52 g, 100 mmol) in diethyl ether (100 mL). The reaction was cooled with an ice-bath and elemental tellurium (12.76 g, 100 mmol) was added in small portions. After stirring for 5 h at room temperature, the solution was placed into a beaker with water (10 mL) and oxygen was bubbled for 1 h. Compound **4** was extracted with diethyl ether and recrystallized from methanol to yield a pale yellow solid.

Yield: 17.01 g, 65% based on tellurium. Properties: pale yellow crystalline substance; m.p.: 86 °C; NMR (600 MHz, $[D_6]DMSO$, $(CH_3)_4Si$, 298K): ¹H: δ (ppm) = 2.24 (s, CH₃), 3.53 (s, CH₂), 7.04 (t, *J* = 9 Hz), 7.11 (d, *J* = 6.6 Hz),

7.16 (t, J = 7.8 Hz), 7.87 (d, J = 7.8 Hz). ¹²⁵Te: δ (ppm) = 345.29. FT-IR (KBr, cm⁻¹): 3056.72; 2941.66; 2770.03; 1580.55; 1177.26; 1148.39; 748.50.

Synthesis of $DmapTeI_3$ (5)

Diiodine (0.145 g, 0.572 mmol) was added to a solution of **4** (0.100 g, 0.190 mmol) in THF (20 mL). The mixture was stirred for 3 h and the solution was filtered. After two days dark red crystals were obtained by slow evaporation of the solvent.

Yield: 0.161 g, 66% based on **4**. Properties: dark red crystalline substance; m.p.: 161.2 °C; FT-IR (KBr, cm⁻¹): 2893.78; 1581.54; 1403.03; 1094.09; 1020.89; 751.63; 457.63; Raman (cm⁻¹): 164.3; 145.9; 107.8. Elem. anal. calcd. for C₉H₁₂NTeI₃ (642.51): C, 16.82, H, 1.88; N, 2.18; Found: C, 16.92, H, 1.91; N, 2.13.

Synthesis of $HDmapTeCl_2$ (6)

A solution of **4** (1.05 g, 2 mmol) in dichloromethane (5 mL) was over-layered by 37% hydrochloric acid (6 mL). After 24 h, yellow crystals were formed at the interface of the solutions.

Yield: 0.76 g, 57% based on **4**. Properties: yellow crystalline substance; m.p.: 158 °C; FT-IR (KBr, cm⁻¹): 3026.04; 2712.46; 1580.65; 1453.39; 1105.73; 771.40; 761.08; 452.73; Raman (cm⁻¹): 343; 257; 234. Elem. anal. calcd. for

C₉H₁₃NCl₂Te (333.71): C, 32.39, H, 3.93; N, 4.20; Found: C, 32.5; H, 4.20; N, 4.07.

Synthesis of $HDmapTeBr_2$ (7)

A solution of **4** (1.05 g, 2 mmol) in dichloromethane (5 mL) was over-layered by 48% hydrobromic acid (6 mL). After 24 h, orange crystals were formed at the interface of the solutions.

Yield: 1.03 g, 61% based on **4**. Properties: orange crystalline substance; m.p.: 191.6 °C; FT-IR (KBr, cm⁻¹): 2965.76; 2733.75; 1580.50; 759.96; Raman (cm⁻¹): 233.8; 164.9; 137.1. Elem. anal. calcd. for C₉H₁₃N Br₂Te (422.61): C, 25.58; H, 3.10; N, 3.31; Found: C, 25.5, H, 3.40; N, 3.10.

Synthesis of $HDmapTeI_2(\mathbf{8})$

Diiodine (0.025 g, 0.01 mmol) in THF (15 mL) was added to a solution of 4 (0.052 g, 0.01 mmol) in THF (5 mL). The reaction was stirred at -10 °C for 1 h to form DmapTeI *in situ* and then 57 % hydriodic acid (5 mL) was added to the mixture.

Yield: 0.042 g, 43% based on 4. Properties: dark red crystalline substance.
m.p.: 137 °C; FT-IR (KBr, cm⁻¹): 2955.33; 2934.29; 2725.15; 1578.34;
756.03; Raman (cm⁻¹): 224; 108. Elem. anal. Calcd. for C₉H₁₃NI₂Te (516.62):
C, 20.92; H, 2.54; N, 2.71 %; Found: C, 20.71; H, 2.60; N, 2.48.

Acknowledgments

This work was supported by funding from CAPES, CNPq and FAPERGS.

References

[1] J. S. S. Neto, D. F. Back, G. Zeni, Eur. J. Org. Chem. (2015) 1583–
1590.

[2] B. Tirloni, C. N. Cechin, G. F. Razera, M. B. Pereira, G. M. de

Oliveira, E. S. Lang, Z. Anorg. Allg. Chem. 642 (2016) 239–245.

[3] H. P. Nayek, H. Niedermeyer, S. Dehnen, Dalton Trans. (2009) 4208–4212.

[4] F. A. Devillanova, W.-W. du Mont, Handbook of ChalcogenChemistry New Perspectives in Sulfur, Selenium and Tellurium, 2nd Edition,RSC Publishing, 2013.

[5] A. F. Cozzolino, P. J. W. Elder, I. Vargas-Baca, Coord. Chem. Rev. 255 (2011) 1426–1438.

[6] C. W. Nogueira, J. B. T. Rocha, Arch. Toxicol. 85 (2011) 1313 –1359.

[7] C. W. Nogueira, G. Zeni, J. B. T. Rocha, Chem. Rev. 104 (2004) 6255–6285.

[8] T.-P. Lin, F. P. Gabbaï, Angew. Chem. Int. Ed. 52 (2013) 3864 – 3868.

[9] V. K. Jain, R. S. Chauhan, Coord. Chem. Rev. 306 (2016) 270–301.

[10] R. S. Chauhan, G. Kedarnath, A. Wadawale, A. L. Rheingold, A.
Muñoz-Castro, R. Arratia-Perez, V. K. Jain, Organometallics 31 (2012)
1743–1750.

[11] G. M. de Oliveira, E. Faoro, E. S. Lang, Inorg. Chem. 48 (2009) 4607–4609.

[12] J. Zukerman-Spector, I. Haiduc, Phosphorus Sulfur Silicon Relat. Elem.171 (2001) 171–175.

[13] I. Haiduc, F. T. Edelmann, Supramolecular Organometallic Chemistry, Wiley-VCH, Germany, 1999.

[14] G. A. Casagrande, E. S. Lang, B. Tirloni, R. A. Burrow, G. M. de Oliveira, S. S. Lemos, Z. Anorg. Allg. Chem. 632 (2006) 893–896.

[15] E. Faoro, G. M. de Oliveira, E. S. Lang, C. B. Pereira, J. Organomet.Chem. 696 (2011) 2438–2444.

[16] S. S. dos Santos, E. S. Lang, R. A. Burrow, J. Braz. Chem. Soc. 17(2006) 1566–1570.

[17] J. D. Woollins, R. S. Laitinen, Selenium and Tellurium Chemistry -From Small Molecules to Biomolecules and Materials (Chapter 7,

Organotelluroxanes, J. Beckmann, P. Finke - pp 168–174) Springer–Verlag Berlin Heidelberg, 2011.

[18] J. Beckmann, J. Bolsinger, A. Duthie, P. Finke, Organometallics 31(2012) 289–293.

[19] J. Bergman, J. Siden, K. Maartmann-Moe, Tetrahedron 40 (1984) 1607–1610.

[20] J. R. Eveland, K. H. Whitmire, Angew. Chem. Int. Ed. in Engl. 36 (1997) 1193–1194.

[21] S. M. Kunnari, R. Oilunkaniemi, R. S. Laitinen, M. J. Ahlgrén, J. Chem. Soc., Dalton Trans. (2001) 3417–3418.

[22] A. F. Gushwa, J. G. Karlin, R. A. Fleischer, A. F. J. Richards, J. Organomet. Chem. 691 (2006) 5069–5073.

[23] P. B. Hitchcock, M. F. Lappert, G. Li, Inorg. Chim. Acta 362 (2009) 3982–3986.

[24] V. N. Khrustalev, Z. V. Matsulevich, J. M. Lukiyanova, R. R. Aysin,A. S. Peregudov, L. A. Leites, A. V. Borisov, Eur. J. Inorg. Chem. (2014)3582–3586.

[25] S. S. dos Santos, B. N. Cabral, U. Abram, E. S. Lang, J. Organomet.Chem. 723 (2013) 115–121.

[26] H. B. Singh, N. Sudha, A. A. West, T. A. Hamor, J. Chem. Soc. Dalton Trans. (1990) 907–913.

[27] K. Ortner, L. Hilditch, J. R. Dilworth, U. Abram, Inorg. Chem. Comm.1 (1998) 469–471.

[28] S. Kolay, N. Ghavale, A. Wadawale, D. Dasa, V. K. Jain, Phosphorus Sulfur Silicon Relat. Elem. 188 (2013) 1449–1461.

[29] R. Cargnelutti, A. Hagenbach, U. Abramb, R. A. Burrow, E. Schulz Lang, Polyhedron 96 (2015) 33–37.

[30] R. Cargnelutti, F. D. da Silva, U. Abram, E. S. Lang, New J. Chem. 39 (2015) 7948–7953.

[31] R. Cargnelutti, E. S. Lang, R. F. Schumacher, Tetrahedron Lett. 56 (2015) 5218–5222.

[32] B. Tirloni, C. N. Cechin, G. F. Razera, M. B. Pereira, G. N. M de Oliveira, E. S. Lang, Z. Anorg. Allg. Chem. 642 (2016) 239–245.

[33] D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, 3^a ed., Pergamon Press, Oxford, EUA, 1988.

[34] R. Kaur, H. B. Singh, R. J. Butcher, Organometallics, 14 (1995) 4755– 4763.

[35] A. F. M. J. van der Ploeg, C. E. M. van der Kolk, G. van Koten, J.Organomet. Chem., 212 (1981) 283–290.

[36] P. Granger, S. Chapelle, W. R. McWhinnie, A. Al-Rubaie, J.Organomet. Chem. 220 (1981) 149–158.

[37] G. M. Sheldrick, Acta Cryst. A64 (2008) 112–122.

Captions for schemes, tables and figures.

Scheme 1. Schematic representation of the reactions of [2-((dimethylamino)methyl)phenyl]mercury chloride and bis[2-((dimethylamino)methyl)phenyl]ditellane to obtain the series DmapTeX₃ and HDmapTeX₂ (Dmap = 2-((dimethylamino)methyl)phenyl and X = Cl, Br, I).

Figure 1: Supramolecular structure of **2** assembled by Te···Cl interactions along the *a* crystallographic axis. Symmetry transformation to generate equivalent atoms: (') -0.5+x, -0.5-y, 1-z; ('') 0.5+x, -0.5+y, 1-z.

Figure 2: Compound **3** monomeric units connected by Te…Br interactions forming a pseudo-dimeric structure. Symmetry transformation to generate equivalent atoms: (') 1-x, 2-y, -z.

Figure 3: Supramolecular structure of **5** assembled by Te…I and I…I interactions forming layers parallel to the *ac* crystallographic plane.

Figure 4: Arrangement of compound **6** and **7** formed by Te…X (X = Cl, Br) interactions in a zigzag format along the crystallographic *b* axis. Symmetry transformation to generate equivalent atoms: (') 2-x, -0.5+y, 1.5-z.

Figure 5: Supramolecular structure of **8**. The molecules of **8** are associated by double Te^{...}I secondary bonds to build up pseudo-dimeric units that are connected by I^{...}I interactions along the crystallographic *c* axis. Symmetry transformation to generate equivalent atoms: (') x, y, 1+z; (") 2-x, -y, -z.

Table 1. Selected bond distances (Å) and angles (°) of compounds 2, 3 and 5-8.



Figure 1







Figure 5



Graphical synopsis:



2	3	5	6	7	8
Te1-Cl1 2.5337(9)	Te1-Br1 2.5966(5)	Te-1-I1 2.8898(4)	Te1-Cl1 2.7021(6)	Te1-Br1 2.6791(4)	Te1-I1 3.0782(3)
Te1-Cl2 2.4500(9)	Te1-Br2 2.6477(5)	Te1-I2 2.8184(4)	Te1-Cl2 2.5183(6)	Te1-Br2 2.8422(4)	Te1-I2 2.8692(3)
Te1-Cl3 2.4662(9)	Te1-Br3 2.7072(6)	Te1-I3 3.0149(4)	C1-Te1-Cl2 87.71(5)	C1-Te1-Br1 87.97(7)	C1-Te1-I1 84.40(8)
Te1-N1 2.406(3)	Te1-N1 2.434(3)	Te1-N1 2.458(4)	C1-Te1-Cl1 85.19(5)	C1-Te1-Br2 86.16(7)	C1-Te1-I2 87.71(8)
Te1-C7 2.114(2)	Te1-C3 2.116(3)	Te1-C3 2.133(4)	N1…Cl1 3.1007(2)	N1…Br2 3.2720(2)	N1-I1 3.4926(2)
Cl1-Te1-Cl2 90.18(4)	Br1-Te1-Br2 88.48(2)	I1-Te1-I2 89.05(1)	N1…H…Cl1 174.19(1)	N1…H…Br2 170.00(2)	N1…H…I1 172.01(1)
Cl2-Te1-Cl3 88.23(4)	Br3-Te1-Br2 174.95(1)	I2-Te1-I3 86.31(1)	Cl2-Te1-Cl1 172.80(1)	Br2-Te1-Br1 173.89(1)	I2-Te1-I1 172.03(1)
Cl1-Te1-Cl3 172.46(3)	Br1-Te1-Br3 89.38(1)	I1-Te1-I3 174.13(1)	7		
N1-Te1-Cl2 167.03(6)	N1-Te1-Br2 94.66(8)	N1-Te1-I2 172.50(8)			
C7-Te1-Cl1 85.64(8)	C3-Te1-Br1 95.36(10)	C3-Te1-I1 88.42(11)			
		R CER			

Table 1. Selected bond distances (Å) and angles (°) of compounds 2, 3 and 5-8.

Structural characterization of a new series of Te,N-based molecules containing [2-(*N*,*N*-dimethyl)benzylamine]tellanyl (DmbaTe) moieties.

Rare zwitterionic derivatives containing organyltellanyl(II) groups.

The supramolecular structure of the different organyltellanyl halides.

Chilling and a second