

DOI:10.1002/ejic.201402294

# A Facile Route for Stabilizing Highly Reactive ArTeCl Species Through the Formation of T-Shaped Tellurenyl Chloride Adducts: *quasi*-Planar Zwitterionic [HPy\*]TeCl<sub>2</sub> and [HPm\*]TeCl<sub>2</sub>; Py\* = 2-pyridyl, Pm\* = 2-(4,6-dimethyl)pyrimidyl

## Victor N. Khrustalev, \*<sup>[a]</sup> Zhanna V. Matsulevich,<sup>[b]</sup> Julia M. Lukiyanova,<sup>[b]</sup> Rinat R. Aysin,<sup>[a]</sup> Alexander S. Peregudov,<sup>[a]</sup> Larissa A. Leites,<sup>[a]</sup> and Alexander V. Borisov<sup>[b]</sup>

Keywords: Tellurium / Multinuclear NMR spectroscopy / IR spectroscopy / Raman spectroscopy / X-ray diffraction / Quantum chemistry

Two new stable T-shaped tellurenyl chloride adducts, viz., [HPy\*]TeCl<sub>2</sub> (1) and [HPm\*]TeCl<sub>2</sub> (2) [Py\* = 2-pyridyl, Pm\* = 2-(4,6-dimethyl)pyrimidyl], act as close chemical analogs of highly unstable monomeric Py\*TeCl and Pm\*TeCl. The *quasi*-planar zwitterionic structures of 1 and 2 have been studied by experimental (X-ray diffraction, multinuclear NMR, IR and Raman spectroscopy) and theoretical (DFT and QTAIM) methods. Thus, a novel facile route to stabilize highly reactive  $Ar^{*}TeCl$  species ( $Ar^{*} = N$ -functionalized aryl) by the addition of a hydrochloric acid molecule has been demonstrated.

### Introduction

Recently, we reported a new possibility for stabilizing highly reactive organoselenenyl(II) chlorides by *N*-functionalization of an organyl substituent and the subsequent addition of a hydrochloric acid molecule.<sup>[1]</sup> It is well-known that organotellurenyl(II) chlorides are even less stable than the related organoselenenyl(II) chlorides. This fact prompted us to apply the same approach to organotellurenyl(II) chlorides containing an *N*-functionalized aryl substituent. The main purpose of the present investigation was to expand this new stabilization route found for synthetically important RSeCl species to their tellurium congeners.

To this end, we treated di(2-pyridyl) ditelluride<sup>[2]</sup> and bis(4,6-dimethyl-2-pyrimidyl) ditelluride<sup>[3]</sup> with sulfuryl chloride in dichloromethane at room temperature to prepare the desired T-shaped aryltellurenyl(II) dichlorides **1** and **2** (Scheme 1).

These reactions proceed through the formation of the corresponding transient [ArTeCl] aryltellurenyl chlorides to which a hydrochloric acid molecule, detached from the  $CH_2Cl_2$  solvent, then adds. Similar properties of dichloro-



Scheme 1. Reaction of di(2-pyridyl) ditelluride or bis(4,6-dimethyl-2-pyrimidyl) ditelluride with sulfuryl chloride.

methane have been observed previously.<sup>[4]</sup> As expected, the aryltellurenyl(II) dichlorides **1** and **2** obtained are quite stable both in solution and the solid state. Their structures and properties were further investigated in detail by different experimental and theoretical methods.

#### **Results and Discussion**

Complexes 1 and 2 are orange substances and are quite stable both in solution and the solid state at room temperature in air. They are highly soluble in dimethyl sulfoxide (DMSO), poorly soluble in dichloromethane and chloroform, and insoluble in apolar solvents. They gave satisfactory microanalytical and NMR spectroscopic data.

X-ray diffraction analyses of **1** and **2** were undertaken to establish their nature. The analyses revealed that both **1** and **2** attain the 10-E-3 T-shaped hypervalent chalcogen adduct

 <sup>[</sup>a] A. N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Str., Moscow, 119991, Russian Federation E-mail: vkh@xray.ineos.ac.ru www.ineos.ac.ru

<sup>[</sup>b] R. E. Alekseev Nizhny Novgorod State Technical University, Minin St., 24, Nizhny Novgorod, 603950 Russian Federation

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402294.



configurations. The molecular structures of 1 and 2 along with the atomic numbering schemes and selected geometric parameters are shown in Figure 1 and Figure 2.



Figure 1. Molecular structure of 1. Thermal ellipsoids are shown at the 50% probability level. The dashed line corresponds to the intramolecular N1–H1····Cl2 hydrogen bond. Selected bond lengths [Å] and angles [°]: Te1–Cl1 2.5207(7), Te1–Cl2 2.6106(7), Te1–C2 2.140(3), N1–C2 1.352(3), N1–C6 1.350(4), C2–C3 1.391(4), Cl1–Te1–Cl2 177.29(2), Cl1–Te1–C2 90.26(7), Cl2–Te1–C2 87.13(7), Te1–C2–N1 118.3(2), Te1–C2–C3 124.3(2), N1–C2–C3 117.4(2).



Figure 2. Molecular structure of **2**. Thermal ellipsoids are shown at the 50% probability level. The dashed line corresponds to the intramolecular N1–H1···Cl2 hydrogen bond. Selected bond lengths [Å] and angles [°]: Te1–Cl1 2.4641(9), Te1–Cl2 2.6684(10), Te1–C2 2.138(3), N1–C2 1.346(5), N1–C6 1.347(4), C2–N3 1.318(4), N3–C4 1.351(5), Cl1–Te1–Cl2 175.40(3), Cl1–Te1–C2 90.51(10), Cl2–Te1–C2 86.38(10), Te1–C2–N1 117.5(2), Te1–C2–N3 121.4(3), N1–C2–N3 121.1(3).

Both structures are essentially zwitterionic, a negative charge resides on the TeCl<sub>2</sub> moiety and a positive charge is delocalized over the heteroarene system. The C–Te distances of 2.140(3) Å in 1 and 2.138(3) Å in 2 are characteristic of single bonds [cf. previously reported lengths of C=Te double bonds are 2.042(3)–2.087(3) Å].<sup>[5]</sup> The N1–C2 and N1–C6 bond lengths in both compounds are equal due to the aromaticity of the cyclic systems.

The virtually linear Cl–Te–Cl moieties in 1 [177.29(2)°] and 2 [175.40(3)°] lie almost in the heteroaryl planes [displacements of 4.7(1) and 9.3(2)° for 1 and 2, respectively]. Similar to the structure of benzothiazole-2-selone-dichloride,<sup>[1]</sup> the *quasi*-planar conformations observed for 1 and 2 can be explained by the absence of steric hindrance (a bulky substituent in the 3-position of the aromatic six-membered ring) inhibiting the formation of a strong intramolecular N1–H1···Cl2 hydrogen bond [N···Cl 3.008(3) Å, H···Cl 2.24(4) Å, N–H···Cl 144(3)° for 1 and N···Cl 2.988(3) Å, H···Cl 2.24 Å, N–H···Cl 139° for 2]. The formation of the intramolecular N1–H1···Cl2 hydrogen bond leads to a decrease in the Cl2–Te1–C2 bond angle in comparison with the Cl1–Te1–C2 angle [87.13(7) vs. 90.26(7)° for 1 and 86.38(10) vs. 90.51(10)° for 2, respectively].

Noticeably, the *quasi*-planar conformation of T-shaped tellurenyl chloride adducts can be stabilized not only by strong intramolecular but also by strong intermolecular interactions, as observed in the case of zwitterionic [HPy\*]

TeCl<sub>2</sub> (Py\* = 4-pyridyl).<sup>[6]</sup> It is noteworthy that, in contrast to **1** and **2**, the T-shaped adduct [HPy\*]TeCl<sub>2</sub> was obtained by the direct reaction of di(4-pyridyl) ditelluride with HCl.

The Cl2 atoms in both 1 and 2 are also involved in the intermolecular secondary Te--Cl interactions [Te1---Cl2  $(-x, -\frac{1}{2} + v, \frac{1}{2} - z)$  3.4744(7) Å for 1 and Te1···Cl2 (-x, 1 y, 1 - z) 3.4602(10) Å for 2]. Thus, the tellurium atoms in both 1 and 2 adopt a distorted square-planar coordination. Due to the intermolecular Te····Cl interactions, molecules of 1 form chains along the crystallographic b axis, whereas molecules 2 form almost planar centrosymmetric dimers. As a result of intramolecular and intermolecular interactions, the TeCl<sub>2</sub> moieties in 1 and 2 have asymmetric geometries with the Te-Cl2 bonds [2.6106(7) Å in 1 and 2.6684(10) Å in 2] being longer than the Te-Cl1 bonds [2.5207(7) Å in 1 and 2.4641(9) Å in 2]. The mean values of the two Te-Cl bond lengths in 1 [2.5657(7) Å] and 2 [2.5663(10) Å] are significantly larger than those in the twocoordinate supermesityl-tellurenyl(II) chloride 2,4,6 $tBu_{3}C_{6}H_{2}TeCl [2.384(1) Å].^{[7]}$ 

We have demonstrated by means of <sup>77</sup>Se NMR spectroscopy that, for the planar benzothiazole-2-selenenyl dichloride in DMSO solution, propeller-like free rotation of the SeCl<sub>2</sub> moiety around the C–Se bond takes place due to the cleavage of the intramolecular hydrogen bond.<sup>[1]</sup> Assuming that an analogous dynamic process could occur in solutions of **1** and **2**, we performed variable-temperature <sup>125</sup>Te NMR investigations of **1** in [D<sub>6</sub>]DMSO/CD<sub>2</sub>Cl<sub>2</sub> solution. The <sup>125</sup>Te NMR spectra recorded at 298 and 253 K exhibit a single signal at  $\delta$  = 1296 ppm and 1284 ppm, respectively, with the low-temperature signal demonstrating a characteristic upfield shift (see Supporting Information).

Remarkably, the tellurium signal, substantially broadened at 298 K ( $\Delta v_{1/2} = 220$  Hz), becomes twice as narrow at 253 K ( $\Delta v_{1/2} = 110$  Hz). This observation unambiguously proves the presence of the propeller-like dynamic process in the solution of **1**, which can be frozen out on temperature decrease and, consequently, clearly confirms the zwitterionic nature of **1** and **2** with the ordinary character of the central C–Te bonds. The calculated values of the rotational barriers (at the M05–2x level) are 10.2 kcalmol<sup>-1</sup> and 11.0 kcalmol<sup>-1</sup> for **1** and **2**, respectively (see Supporting Information).

Of particular interest is the manifestation in the IR spectrum of the strong intramolecular N–H···Cl hydrogen bond. The IR spectra of pyridinium salts with strong ( $\Delta H \approx 10$ – 11 kcalmol<sup>-1</sup>) interionic N<sup>+</sup>–H···B<sup>-</sup> hydrogen bonds were studied and discussed by Iogansen and coworkers.<sup>[8,9]</sup> Estimation of the H-bond strengths in 1 and 2 based on AIM results (see Supporting Information) yield values of 10.9 and 12.7 kcalmol<sup>-1</sup>, respectively. These values are very close or even higher than those reported in refs.<sup>[8,9]</sup> Thus, we could expect that the H-bonds in 1 and 2 should manifest themselves in the IR spectra similarly. Indeed, the patterns observed in the IR spectra of 1 and 2 strongly resemble that for the pyridinium salt of CHCl<sub>2</sub>COOH with  $\Delta H =$ 10.3 kcalmol<sup>-1</sup>.<sup>[9]</sup> In the region below 2000 cm<sup>-1</sup>, the spectra exhibit a very broad and intense continuum of a compli-



cated contour observed as a background under a series of narrow skeletal bands. In the spectrum of **2** (Figure 3), this background has three broad "sub-maxima" due to Fermiresonance perturbations. Such a pattern is typical of strong hydrogen bonds.<sup>[9]</sup> Naturally, as described in ref.,<sup>[8,9]</sup> this broad continuum, corresponding to the vNH perturbed by H-bond formation is absent in the Raman spectra.



Figure 3. IR spectrum of solid 2.

The presence, in **1** and **2**, of the intramolecular H-bond closing the five-membered ring involving one Cl atom, makes the two Te–Cl bonds inequivalent and thus leads to a change in the vibrational mechanics of the  $\nu$ TeCl stretches compared, for example, with those of Me<sub>2</sub>TeCl<sub>2</sub> ( $\nu$ <sup>s</sup>TeCl = 248 cm<sup>-1</sup>,  $\nu$ <sup>as</sup>TeCl = 281 cm<sup>-1</sup>).<sup>[10]</sup>

The vTeCl region 240–300 cm<sup>-1</sup> in the Raman spectra of solid 1 and 2 is given in Figure 4. Three lines can be observed in this region for 1. The NCA results show that the most intense line at 260 cm<sup>-1</sup> is a mixed mode with significant contribution from the symmetrical stretch of the TeCl<sub>2</sub> moiety ( $v^{s}$ TeCl<sub>2</sub>), the line at 270 cm<sup>-1</sup> involves mostly the free Te–Cl bond stretch (vTeCl<sub>free</sub>), and the line at 246 cm<sup>-1</sup> corresponds to a deformational mode which is complex in origin. The vTeCl<sub>H-bond</sub> coordinate contributes mostly to the mode at 185 cm<sup>-1</sup> which shows itself as a strong Raman line. The vibrational mode Eigenvectors of molecule 2 are slightly different. As for 1, the vTeCl<sub>H-bond</sub> vibration is a Raman line at 184 cm<sup>-1</sup>. However, the line corresponding to the vTeCl<sub>free</sub> appears as a doublet 289/282 cm<sup>-1</sup>, probably



Figure 4. Raman spectra of solid 1 (red) and 2 (blue).

due to crystal-field splitting, whereas the weak lines at 222 and  $232 \text{ cm}^{-1}$  belong to various deformational modes.

For benzothiazole-2-selone dichloride, the structure of which is very similar to those of 1 and 2, some contribution of a "carbene-Lewis acid" resonance form, leading to a partial Se-C bond doubling, was suggested.<sup>[1]</sup> To elucidate the contribution from the analogous resonance form into the total structure of 1 and 2, the population and  $QTAIM^{[11]}$ analyses at the DFT level with the M05-2X functional were performed. It is easy to see from Figure 5 that the lone pair of the Te atom acts as a  $\pi$  donor towards the empty p orbital of the carbon atom (the corresponding molecular orbital is the HOMO for both 1 and 2). The HOMO involves a 67–68% contribution from the p orbital of the Te atom, 20-25% from the p orbitals of the two chlorine atoms, and only 1-2% from that of the C2 atom. Therefore, the contributions from the "carbene-Lewis acid" resonance form and, as a consequence, the  $\pi$  component in the Te–C interaction are negligible. Thus the rotational barrier around the Te-C bond is determined only by the strength of the intramolecular N-H····Cl hydrogen bond.



Figure 5. Representations of the HOMO of the planar complexes 1 (left) and 2 (right) as calculated at the M05-2X/6-311++G(d,p),cc-pVTZ-pp level.

Moreover, we have observed that the dimeric solid bis-(2-pyridyltellurenyl chloride) [2-PyTeCl]<sub>2</sub> reported by us previously<sup>[12]</sup> is fully converted into 1*H*-pyridine-2-tellurenyl(II) dichloride **1** in dichloromethane solution over 120 h. Evidently, in dichloromethane solution, the dimeric [2-Py-TeCl]<sub>2</sub> dissociates into the transient [2-PyTeCl] monomers to which a hydrochloric acid molecule, detached from the solvent, then adds (Scheme 2). Hence, in dichloromethane solution, the T-shaped adduct [HPy]TeCl<sub>2</sub> rather than the dimer [2-PyTeCl]<sub>2</sub> built up by the intermolecular dative Te $\leftarrow$ N interactions occurs as the energetically favorable stabilized form of 2-pyridyltellurenyl chloride.



Scheme 2. Transformation of dimeric 2-pyridyltellurenyl chloride to compound 1 by reaction with dichloromethane.

It is interesting to note that the dimeric stabilized form was not observed by us for 4,6-dimethyl-2-pyrimidyltellurenyl chloride apparently due to the steric reasons. The DFT quantum-chemical calculations show that the change in the



Gibbs' free energy for the 4,6-dimethyl-2-pyrimidyltellurenyl chloride dimerization reaction is positive and equal to +3.37 kcal mol<sup>-1</sup> whereas, in the case of the 2-pyridyltellurenyl chloride, the analogous value is negative and equal to -11.64 kcal mol<sup>-1</sup> (for details, see Supporting Information).

The reactivity of 1 and 2 towards alkenes was also studied, namely styrene and norbornene. In acetonitrile, similar to 2-pyridyltellurenyl chloride,<sup>[13]</sup> the reactions proceeded smoothly at 20 °C affording heterocyclization products 3-6 (Scheme 3).



Scheme 3. Reactions of  ${\bf 1}$  and  ${\bf 2}$  with alkenes in acetonitrile solutions.

The formation of 3-6 can be considered as the polar [3+2] cycloaddition of tellurenyl chlorides to double bonds. The corresponding hetarenetellurenyl chlorides are apparently generated in situ upon the dissociation of 1 and 2 with the abstraction of hydrochloric acid.

In summary, a novel facile route for stabilizing highly reactive Ar\*TeCl species (Ar\* = nitrogen-containing aryl) by hydrochloric acid addition has been demonstrated, exemplified by two new T-shaped tellurenyl chloride adducts, viz. 1H-pyridine-2-tellurenyl-dichloride and 4,6-dimethyl-1H-pyrimidine-2-tellurenyl-dichloride. Their quasi-planar zwitterionic structures with strong intramolecular N-H···Cl hydrogen bonds have been evidenced by experimental (single-crystal X-ray diffraction, multinuclear NMR, vibrational spectroscopy) and theoretical (DFT and QTAIM) methods. Due to this structure, the studied heteroaryl tellurenyl dichlorides react with alkenes in a similar manner to the corresponding monomeric tellurenyl chlorides affording the same cycloaddition products. The described approach to difficult-to-obtain, extremely unstable organotellurenyl chlorides opens alluring prospects in the synthesis and study of low-valent chalcogen compounds.

## **Experimental Section**

**General Methods:** All manipulations were carried out in air. The commercially available solvents were purified by conventional methods and distilled immediately prior to use. NMR spectra were recorded on Bruker AVANCE-600 (<sup>1</sup>H and <sup>13</sup>C) and AVANCE-400 (<sup>125</sup>Te) NMR spectrometers at 600.22 MHz (for <sup>1</sup>H), 150.93 MHz (for <sup>13</sup>C) and 126.24 MHz (for <sup>125</sup>Te) in [D<sub>6</sub>]DMSO. Chemical

shifts in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were indirectly referenced to TMS by the solvent signals. The assignment of the signals in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra was performed by 2D COSY, HSQC and HMBC techniques on the basis of the Bruker standard software library. Chemical shifts in the <sup>125</sup>Te NMR spectra were measured with  $Ph_2Te_2$  as an external standard ( $\delta$  = 420.8 ppm<sup>[14]</sup>) and referenced to Me<sub>2</sub>Te. The accuracy of chemical shift measurements is  $\pm 0.01$  ppm (for <sup>1</sup>H),  $\pm 0.05$  ppm (for <sup>13</sup>C) and  $\pm 0.1$  ppm (for <sup>125</sup>Te). The Raman spectra in the region 100-4000 cm<sup>-1</sup> were recorded for the solid samples by using a LabRAM 300 Jobin-Yvon laser Raman spectrometer with an exciting He-Ne laser line of 632.8 nm at 1 mW power. IR spectra were recorded on a Nicolet Magna IR-750 FTIR spectrometer in KBr pellets in the region 400–4000 cm<sup>-1</sup>. The chemical analyses were performed by using a Carlo Erba EA1108 CHNS-O analyzer. All calculations were performed with the Gaussian 03 program at the DFT level of theory using the PBE, PBE0 and M05-2X functionals with the aug-cc-pVTZ-pp and 6-311++G(d,p) basis sets for Te and all other atoms, respectively. (For details, see Supporting Information).

1H-Pyridine-2-tellurenyl Dichloride (1): (A) A solution of SO<sub>2</sub>Cl<sub>2</sub> (0.27 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added to a solution of di(2-pyridyl) ditelluride (0.82 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at room temperature. After 120 h, the solvent was evaporated in vacuo. The precipitate contained 1.1 g (100%) of an orange crystalline product, m.p. 195–197 °C. (b) Pyridine-2-tellurenyl chloride<sup>[11]</sup> (0.12 g, 0.5 mmol) was dissolved in CH2Cl2 (100 mL) at room temperature. After 120 h, the solvent was evaporated in vacuo. The precipitate contained 0.138 g (100%) of an orange crystalline product, m.p. 195-197 °C. C5H5Cl2NTe (277.60): calcd. C 21.62, H 1.80, N 10.11; found C 21.57, H 1.99, N 10.22. <sup>1</sup>H NMR (600 MHz,  $[D_6]DMSO, Me_4Si, 298 K$ ):  $\delta = 7.86$  (t, J = 7.2 Hz, 1 H, 5-H), 8.32  $(d_t, J = 7.8, J = 1.8 \text{ Hz}, 1 \text{ H}, 4\text{-H}), 8.70 (d, J = 8.4 \text{ Hz}, 1 \text{ H}, 3\text{-H}),$ 8.79 (dd, J = 6.0, J = 1.2 Hz, 1 H, 6-H) ppm. <sup>13</sup>C NMR (150 MHz,  $[D_6]DMSO, Me_4Si, 298 K$ :  $\delta = 125.6 [^4J_{13C,125Te} = 163 Hz, C5],$ 137.5  $[{}^{2}J_{13C,125Te} = 177 \text{ Hz}, \text{ C3}], 142.9 [{}^{1}J_{13C,125Te} = 517 \text{ Hz}, \text{ C2}],$ 144.0  $[{}^{3}J_{13C,125Te} = 197 \text{ Hz}, \text{ C6}], 144.7 [{}^{3}J_{13C,125Te} = 161 \text{ Hz},$ C4] ppm. <sup>125</sup>Te NMR (126 MHz, [D<sub>6</sub>]DMSO, Ph<sub>2</sub>Te<sub>2</sub>, 298 K):  $\delta$  = 1282 ppm.

**4,6-Dimethyl-1***H***-pyrimidine-2-tellurenyl Dichloride (2):** A solution of SO<sub>2</sub>Cl<sub>2</sub> (0.0675 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to a solution of bis(4,6-dimethyl-2-pyrimidyl) ditelluride<sup>[3]</sup> (0.234 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at room temperature. After 1 h the solvent was evaporated in vacuo. The precipitate contained 0.3 g (100%) of an orange powder product, m.p. 155–157 °C. C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>Te (306.64): calcd. C 23.53, H 2.61, N 9.15; found C 23.23, H 2.73, N 9.25. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Me<sub>4</sub>Si, 298 K):  $\delta$  = 2.75 (s, 6 H, 2CH<sub>3</sub>), 7.20 (s, 1 H, 4-H) ppm. <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Me<sub>4</sub>Si, 298 K):  $\delta$  = 22.7 [br, 2CH<sub>3</sub>, C7, C8], 118.1 [CH, C5], 119.7 [v.br, 2C(CH<sub>3</sub>), C4, C6], 159.4 [C(Te), C2] ppm.

**Reactions of 1 and 2 with Alkenes (General Procedure):** A solution of unsaturated compound (1 mmol) in acetonitrile (20 mL) was added to a solution of tellurenyl dichloride (1 mmol) in acetonitrile (20 mL) at 20 °C with stirring. After 48 h at 20 °C, the solvent was evaporated in vacuo. Compounds **3–6** were obtained after recrystallization of the crude products from dichloromethane.

**3-Phenyl-2,3-dihydro[1,3]tellurazolo[3,2-***a***]pyridine-4-ium Chloride (3): The yield of yellow crystals was 97%, m.p. 172–174 °C. C\_{13}H\_{12}CINTe (345.30): calcd. C 45.22, H 3.50; found C 45.11, H 3.45. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO, Me<sub>4</sub>Si, 298 K): \delta = 3.80 (dd, J = 10.3, J = 7.3 Hz, 1 H, 2-H), 4.28 (dd, J = 10.3, J = 7.3 Hz, 1 H, 2-H), 7.40 (m, 2 H, Ph), 7.48** 

3585



(m, 3 H, Ph), 7.78 (dd, J = 7.3, J = 5.9 Hz, 1 H, 6-H), 8.32 (t, J = 7.3 Hz, 1 H, 7-H), 8.42 (d, J = 7.3 Hz, 1 H, 8-H), 8.52 (d, J = 5.9 Hz, 1 H, 5-H) ppm.

**5,7-Dimethyl-3-phenyl-2,3-dihydro[1,3]tellurazolo[3,2-***a***]pyrimidine-<b>4-ium Chloride (4):** The yield of yellow crystals was 75%, m.p. 122– 124 °C.  $C_{14}H_{15}CIN_{2}Te$  (374.34): calcd. C 44.92, H 4.04; found C 44.87, H 4.01. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO, Me<sub>4</sub>Si, 298 K):  $\delta$ = 2.53 and 2.63 (s, 6 H, 2CH<sub>3</sub>); 3.19 (d, J = 11.7 Hz, 1 H, 2-H); 4.80 (dd, J = 11.7, J = 7.3 Hz, 1 H, 2-H); 6.75 (d, J = 7.3 Hz, 1 H, 3-H); 7.20 (m, 2 H, Ph); 7.42 (m, 3 H, Ph); 7.64 (s, 1 H, 6-H) ppm.

*exo-cis*-9-Tellurium-3-azoniatetracyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>]tetradeca-3(8),4,6-triene Chloride (5): The yield of yellow crystals was 95%, m.p. 230–232 °C.  $C_{12}H_{14}$ CINTe (335.30): calcd. C 42.99, H 4.21; found C 42.88, H 4.15. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO, Me<sub>4</sub>Si, 298 K):  $\delta = 1.34$  (d, J = 10.8 Hz, 1 H,  $H_{syn}$ 14), 1.39 (m, 1 H, 12-H), 1.52 (m, 1 H, 12-H), 1.68 (d, J = 10.8 Hz, 1 H,  $H_{anti}$ 14), 1.71 (m, 2 H, 13-H), 2.61 (s, 1 H, 11-H), 2.82 (s, 1 H, 1-H), 4.12 (d, J= 8.4 Hz, 1 H, 10-H), 5.32 (d, J = 8.4 Hz, 1 H, 2-H), 7.70 (dd, J= 7.5, J = 6.2 Hz, 1 H, 5-H), 8.01 (dd, J = 8.0, J = 7.5 Hz, 1 H, 6-H), 8.20 (d, J = 8.0 Hz, 1 H, 7-H), 8.93 (d, J = 6.2 Hz, 1 H, 4-H) ppm. <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Me<sub>4</sub>Si, 298 K):  $\delta = 25.71$ (C12), 29.41 (C13), 31.84 (C14), 32.84 (C10), 45.97 (C11), 48.16 (C1), 82.78 (C2), 123.99 (C5), 132.61 (C7), 141.45 (C6), 145.22 (C4) ppm.

*exo-cis*-4,6-Dimethyl-9-tellurium-3-azonia-7-azatetracyclo-[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>]tetradeca-3(8),4,6-triene Chloride (6): The yield of yellow crystals was 79%, m.p. 136–138 °C.  $C_{13}H_{17}CIN_2Te$  (364.34): calcd. C 42.86, H 4.70; found C 42.78, H 4.62. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO, Me<sub>4</sub>Si, 298 K):  $\delta$  = 1.40 (m, 1 H, 12-H), 1.47 (d, *J* = 11.0 Hz, 1 H, H<sub>syn</sub>14), 1.60 (m, 1 H, 12-H), 1.81 (m, 2 H, 13-H), 2.10 (d, *J* = 11.0 Hz, 1 H, H<sub>anti</sub>14), 2.52 and 2.75 (s, 6 H, 2CH<sub>3</sub>), 2.61 (s, 1 H, 11-H), 2.71 (s, 1 H, 1-H), 4.30 (d, *J* = 8.8 Hz, 1 H, 10-H), 5.22 (d, *J* = 8.8 Hz, 1 H, 2-H), 7.58 (s, 1 H, 5-H) ppm.

**Crystal Data for 1 at 100 K:**  $C_5H_5NCl_2Te$  ( $M_r = 277.60$ ), monoclinic, space group  $P2_1/c$ , a = 12.0195(9) Å, b = 7.0071(5) Å, c = 9.5895(7) Å,  $\beta = 104.071(1)^\circ$ , V = 783.41(10) Å<sup>3</sup>, Z = 4,  $\rho_{calcd.} = 2.354$  g cm<sup>-3</sup>,  $\mu = 4.389$  mm<sup>-1</sup>, Bruker SMART APEX-II CCD diffractometer, graphite monochromator,  $\lambda$ (Mo- $K_{\alpha}$ ) = 0.71073 Å. A total of 9643 reflections were collected in the  $\theta$  range of 1.75–30.00° with 2274 being unique ( $R_{int} = 0.0375$ ). A semi-empirical absorption correction was applied based on the intensities of equivalent reflections ( $T_{min} = 0.353$ ,  $T_{max} = 0.668$ ). Least-squares refinement on 85 parameters converged normally with  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0380 (2151 reflections),  $wR_2$  (all data) = 0.1039, GOF = 1.001.

**Crystal Data for 2 at 100 K:**  $C_6H_8N_2Cl_2Te$  ( $M_r = 306.64$ ), monoclinic, space group  $P2_1/n$ , a = 6.5102(6) Å, b = 12.6556(12) Å, c = 11.8465(11) Å,  $\beta = 97.857(2)^\circ$ , V = 966.88(16) Å<sup>3</sup>, Z = 4,  $\rho_{calcd.} = 2.107$  gcm<sup>-3</sup>,  $\mu = 3.570$  mm<sup>-1</sup>, Bruker SMART APEX-II CCD diffractometer, graphite monochromator,  $\lambda$ (Mo- $K_a$ ) = 0.71073 Å. A total of 10218 reflections were collected in the  $\theta$  range of 2.37–27.96° with 2320 being unique ( $R_{int} = 0.0441$ ). A semi-empirical absorption correction was applied based on the intensities of equivalent reflections ( $T_{min} = 0.507$ ,  $T_{max} = 0.635$ ). Least-squares refinement on 102 parameters converged normally with  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0280 (1908 reflections),  $wR_2$  (all data) = 0.0584, GOF = 1.002.

CCDC-980195 (for 1) and CCDC-980196 (for 2) 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.

**Supporting Information** (see footnote on the first page of this article): Full crystal data, NMR, Raman and IR spectra and details of the quantum-chemical calculations.

## Acknowledgments

The authors thank the Russian Foundation for Basic Research (grant number 14-03-00914) and the Russian Academy of Sciences in the framework of the program "Theoretical and experimental study of chemical bonding and mechanisms of chemical reactions and processes" for financial support of this work. Dr. Y. V. Zubavichus is thanked for fruitful discussions.

- V. N. Khrustalev, Sh. R. Ismaylova, R. R. Aysin, Zn. V. Matsulevich, V. K. Osmanov, A. S. Peregudov, A. V. Borisov, *Eur. J. Inorg. Chem.* 2012, 5456–5460.
- [2] K. K. Bhasin, V. Arora, T. M. Klapotke, M.-J. Crawford, Eur. J. Inorg. Chem. 2004, 4781–4788.
- [3] A. V. Borisov, Zn. V. Matsulevich, V. K. Osmanov, G. N. Borisova, A. O. Chizhov, G. Z. Mammadova, A. M. Maharramov, R. R. Aysin, V. N. Khrustalev, *Russ. Chem. Bull.* 2013, 62, 2245–2249 (*Russ. Chem. Bull. Int. Ed.* 2013, 62, in press).
- [4] a) L. Engman, A. Wojton, B. J. Oleksyn, J. Sliwinski, *Phosphorus Sulfur Silicon Relat. Elem.* 2004, 179, 285–292; b) S. Kumar, H. B. Singh, G. Wolmershauser, J. Organomet. Chem. 2005, 690, 3149–3153.
- [5] a) N. Kuhn, G. Henkel, T. Kratz, *Chem. Ber.* 1993, *126*, 2047–2049; b) A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* 1997, *119*, 12742–12749; c) G. M. Li, R. A. Zingaro, M. Segi, J. H. Reibenspies, T. Nakajima, *Organometallics* 1997, *16*, 756–762; d) Y. Mutoch, T. Murai, S. Yamago, *J. Organomet. Chem.* 2007, *692*, 129–135; e) S. T. Manjare, S. Sharma, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.* 2012, *717*, 61–74; f) R. Thirumoorthi, T. Chivers, *Polyhedron* 2013, *53*, 230–234.
- [6] S. S. dos Santos, B. N. Cabral, U. Abram, E. S. Lang, J. Organomet. Chem. 2013, 723, 115–121.
- [7] J. Beckmann, S. Heitz, M. Hesse, *Inorg. Chem.* 2007, 46, 3275– 3282.
- [8] A. V. Iogansen, S. A. Kiselev, B. V. Rassadin, A. A. Samoilenko, J. Struct. Chem. 1976, 17, 546–552.
- [9] A. V. Iogansen, Spectrochim. Acta Part A 1999, 55, 1585–1612.
- [10] A. V. Iogansen, in: *Vodorodnya svyaz'* (Hydrogen Bond) (Ed.: N. D. Sokolov), Nauka, Moscow, **1981**, p. 118 [in Russian].
- [11] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, UK, **1990**.
- [12] A. V. Borisov, Zh. V. Matsulevich, G. K. Fukin, E. V. Baranov, *Russ. Chem. Bull. Int. Ed.* **2010**, *59*, 581–583.
- [13] a) A. V. Borisov, Zh. V. Matsulevich, *Chem. Heterocycl. Compd.* 2009, 45, 884–885; b) A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, V. I. Naumov, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, V. V. Kachala, *Russ. Chem. Bull.* 2012, 61, 91–94.
- [14] P. Granger, S. Chapelle, W. R. McWhinnie, A. Al-Rubaie, J. Organomet. Chem. 1981, 220, 149–158.

Received: April 9, 2014 Published Online: June 26, 2014