



Dedicated to Professor Mihaela Hillebrand
on the occasion of her 80th anniversary

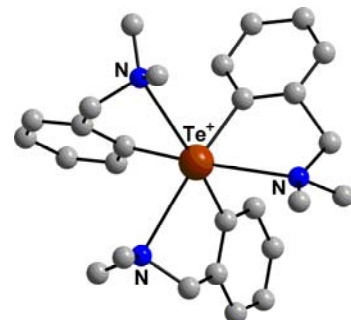
NEW HYPERCOORDINATED TRIARYLTELLURONIUM DERIVATIVES OF ORGANOPHOSPHORUS LIGANDS. SYNTHESIS AND STRUCTURAL CHARACTERIZATION

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Hypercoordinated triaryltelluronium compounds of type $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]^+\text{L}^-$ [$\text{L}^- = (\text{SPMe}_2)_2\text{N}$ (**1**), $(\text{OPPh}_2)_2\text{N}$ (**2**), $(\text{SPPH}_2)_2\text{N}$ (**3**), $(\text{SPPH}_2)\{\text{OP}(\text{OEt})_2\text{N}$ (**4**), $(\text{SPPH}_2)(\text{O}_2\text{SMe})\text{N}$ (**5**) and $\{\text{SP}(\text{OEt})_2\}(\text{O}_2\text{SC}_6\text{H}_4\text{Cl-4})\text{N}$ (**6**)] were prepared by salt metathesis reactions between $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]\text{Cl}\cdot\text{H}_2\text{O}$ and the potassium salts of the corresponding organophosphorus ligands in a 1:1 molar ratio. Multinuclear NMR spectroscopy, mass spectrometry, molar conductivity and IR spectroscopy were used to characterize the new complexes. The ^1H NMR spectra suggest for all compounds the intramolecular coordination of the nitrogen atoms from the pendant arms to tellurium in solution. For compound **3** single-crystal X-ray diffraction studies revealed strong $\text{N}\rightarrow\text{Te}$ intramolecular interactions in solid state, which result in hypercoordinated triaryltelluronium(IV) cations (14-Te-6 species) with a distorted octahedral coordination geometry around tellurium. Weak $\text{S}\cdots\text{H}$ interactions between anions and cations resulted in a 2D supramolecular network.



INTRODUCTION

In recent years organotellurium compounds stabilized by intramolecular $\text{N}\rightarrow\text{Te}$ interactions attracted an increased interest due to their recognized potential in organic synthesis, materials science and biology.¹⁻³ The tendency of tellurium to take part in secondary bonding interactions is higher than that one observed for the lighter chalcogens, selenium and sulfur. Several organic groups capable for $\text{N}\rightarrow\text{Te}$ intramolecular coordination were employed in organotellurium chemistry, either in $\text{Te}(\text{I})$, $\text{Te}(\text{II})$ or $\text{Te}(\text{IV})$ compounds, including $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ groups,^{4,5}

N,N -dimethylaminoalkyl- and pyridyl- / pyrimidyl-based ligands.⁶ Such hypercoordinated compounds attracted a considerable interest also related to their structural features, which are responsible for their improved specific properties. Triorganotellurium(IV) salts of type R_3TeX ($\text{R} = \text{aryl}$) behave in solution as 1:1 electrolytes. In solid state, such species have a strong tendency to expand the coordination sphere around tellurium beyond the octet rule by secondary bonding interactions based either on intramolecular coordination or on weak $\text{Te}\cdots$ anion contacts, thus resulting in penta- or hexacoordinated species.⁷ The $[\text{R}_3\text{Te}]^+$ cations bearing three equivalent organic groups capable for a C,N chelating behaviour, e.g. $\text{tris}[2-(2'\text{-pyridyl})\text{phenyl}]$

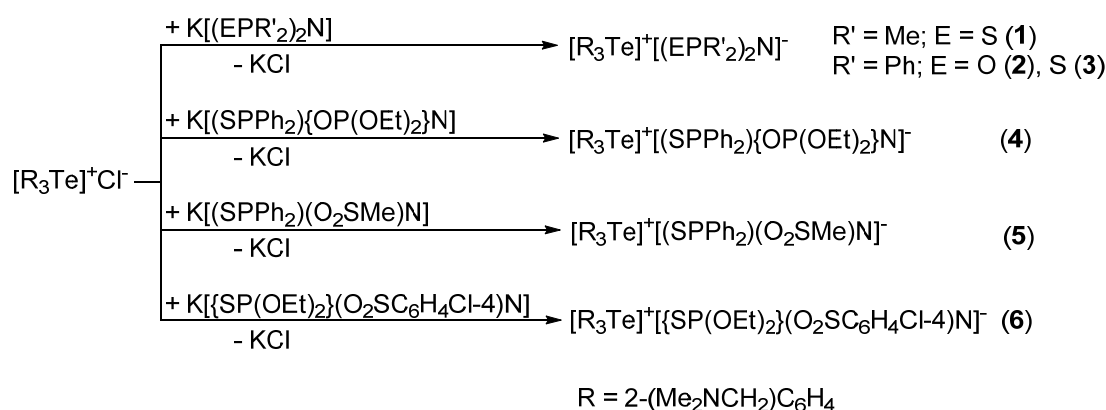
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telluronium bromide,⁸ tris(8-quinoliny)telluronium chloride,⁹ and tris(*N,N*-dimethylbenzylamino)telluronium halides,¹⁰ exhibit octahedral coordination geometries, thus enabling no further secondary bonding interactions between tellurium and X⁻ anions. By contrast, in triphenyltelluronium halides¹¹ or pseudohalides¹² the anions behave as bridging units between neighbour tellurium atoms, thus increasing the coordination number at tellurium and resulting in dimeric or polymeric associations. Organophosphorus ligands of type [R₂PX₂]⁻ or [(XPR₂)(YPR'₂)N]⁻ (R, R' = alkyl, aryl; X, Y = O, S, Se) behave as bidentate, chelating moieties towards triphenyltelluronium cations, thus resulting mostly in monomeric species.^{13,14}

During last years we were interested to investigate the competition for the coordination sphere of tellurium between the nitrogen atom in triaryltelluronium cations bearing both 2-(Me₂NCH₂)C₆H₄ and phenyl groups and the anionic ligands, as well as the possibilities to

design supramolecular architectures based on [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺ cations. We have reported previously on triaryltelluronium halides of type [R_nPh_{3-n}Te]⁺X⁻ (R = 2-(Me₂NCH₂)C₆H₄; n = 1-3; X = Cl, Br, I)¹⁰ and several triaryltelluronium salts with organophosphorus ligands of type [R_nPh_{3-n}Te]⁺L⁻ [R = 2-(Me₂NCH₂)C₆H₄; n = 1-3; L = S₂PMe₂, (SPPPh₂)₂N, (SePPh₂)₂N, (SPPPh₂)(O₂SC₆H₄Me-4)N].¹⁵

As a continuation of our work, we report here the synthesis and structural characterization of several triaryltelluronium salts of type [R₃Te]⁺L⁻ [R = 2-(Me₂NCH₂)C₆H₄; L = (SPMe₂)₂N (**1**), (OPPh₂)₂N (**2**), (SPPPh₂){OP(OEt)₂}N (**4**), (SPPPh₂)(O₂SMe)N (**5**), {SP(OEt)₂}(O₂SC₆H₄Cl-4)N (**6**)]. For the previously reported [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺[(SPPPh₂)₂N]⁻ (**3**), we present here the solid state structure determined by single-crystal X-ray diffraction.



Scheme 1 – Synthesis of compounds 1–6.

RESULTS

Compounds 1–6 were prepared by salt metathesis reactions between the triaryltelluronium chloride, [{2-(Me₂NCH₂)C₆H₄}]₃TeCl·H₂O, and the potassium salts of the corresponding organophosphorus ligands in a 1:1 molar ratio, using chloroform or methanol as solvents, as depicted in Scheme 1.

The desired compounds were isolated as microcrystalline, yellow (**1**) or colourless (**2**, **3** and **5**) species, or as yellow sticky solids (**4** and **6**). Multinuclear NMR spectroscopy (¹H, ¹³C, ³¹P and ¹²⁵Te), ESI+ and ESI- mass spectrometry, IR spectroscopy and molar conductivity were employed to characterize the new compounds. The

analytical data confirmed the expected ionic structure and the purity of the new species.

DISCUSSION

Spectroscopic characterization

For all compounds the NMR data is consistent with only one species in solution. The ¹H and ¹³C NMR spectra suggest the equivalence of the three 2-(Me₂NCH₂)C₆H₄ groups attached to tellurium. The ¹H NMR spectra show a broad singlet resonance and an AB spin system in the aliphatic region for the N(CH₃)₂ and the CH₂N protons, respectively, thus suggesting the existence of

N→Te intramolecular interactions in solution. The organophosphorus ligands show in their ^1H NMR spectra multiplet resonances, due to both proton-proton and phosphorus-proton couplings, while in the ^{13}C NMR spectra doublet resonances are determined by phosphorus-carbon couplings, e.g. the $\text{P}(\text{CH}_3)_2$ groups in compound **1** show doublet resonances at δ 1.95 ppm ($^2J_{\text{PH}} = 12.6$ Hz) in the ^1H NMR spectrum and at δ 27.06 ppm ($^1J_{\text{PC}} = 72.9$ Hz) in the ^{13}C NMR spectrum. The ^1H NMR spectra of anions containing OCH_2CH_3 groups (**4** and **6**) show triplet and quartet resonances for the CH_3 and the CH_2 protons, respectively. In the ^1H NMR spectrum of compound **5** a sharp singlet resonance was observed for the SCH_3 protons at δ 3.08 ppm. In the aromatic region of the ^1H NMR spectra, four multiplet resonances are present, corresponding to the 2-(Me_2NCH_2) C_6H_4 groups attached to tellurium and characteristic multiplet signals for the aromatic groups attached to phosphorus.

The ^{31}P NMR spectra show only one sharp singlet resonance in each case in the range δ 8.6–55.7 ppm, except compound **4**, where a doublet (δ 1.9 ppm, PO , $^2J_{\text{PP}} = 20.2$ Hz) and a broad (δ 34.1 ppm, PS) resonances are present, corresponding to the two non-equivalent phosphorus atoms in the organophosphorus anion.

The ^{125}Te NMR spectra show singlet resonances in the range δ 749.5–755.1 ppm, characteristic for the triorganotelluronium cations. The small range of the chemical shifts for these compounds suggests that no other type of interactions, except the electrostatic ones, are established between cations and anions in solution.

For all compounds the ESI+ and ESI \square high resolution mass spectra show as base peak the $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]^+$ cation and the corresponding organophosphorus anion, respectively, thus confirming the identity of the investigated species.

The molar conductivity of compounds **1–6** was measured in 10^{-4} M MeOH solutions and are in the range of 156–267 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. These values are of a similar magnitude as that found for $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]^+\text{Cl}^-$ ($\Lambda_{\text{M}} = 203$ $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) and they are in accordance with their behaviour as 1:1 electrolytes.

In the IR spectra of compounds **1–6** strong absorption bands were observed in the range 1171–1248 cm^{-1} , characteristic for the asymmetric vibrations $\nu_{\text{as}}(\text{P}_2\text{N})$. These values differ from those corresponding to the free acids and are close to the

values found for the starting potassium salts.^{16,17} No absorption bands characteristic for $\nu(\text{NH})$ (around 2700–2600 cm^{-1}) or $\nu_{\text{as}}(\text{P}_2\text{NH})$ (around 950–900 cm^{-1}) were observed, thus indicating that the organophosphorus ligands are deprotonated.

X-Ray diffraction studies

The structure of $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]^+[(\text{SPPH}_2)_2\text{N}]^-$ (**3**) was determined by single-crystal X-ray diffraction. A thermal ellipsoids representation of the cation-anion assembly of this compound is depicted in Figure 1 and selected interatomic distances and angles are given in Table 1.

Compound **3** crystallizes in the $P2_1$ space group. The 2-(Me_2NCH_2) C_6H_4 groups in the cation behave as C,N chelating ligands towards tellurium, thus resulting in a 14-Te-6 hypervalent species.¹⁸ The nitrogen-tellurium interatomic distances are in the range 2.73–2.87 Å, well below the sum of the van der Waals radii of the two elements [$\Sigma r_{\text{vdW}}(\text{N},\text{Te}) = 3.75$ Å¹⁹]. These strong secondary N→Te intramolecular interactions resulted in a distorted octahedral coordination geometry around the tellurium atom, with N–Te–C angles in the range 165.6(2)–167.9(11)°. The N→Te interactions induce planar chirality to each of the three NC_3Te five-membered rings, which are not planar, but folded about the imaginary $\text{Te}\dots\text{CH}_2$ axes. As a consequence, the crystal contains a racemic mixture of $S_{\text{N}2}, S_{\text{N}3}, R_{\text{N}4}$ -**3** and $R_{\text{N}2}, R_{\text{N}3}, S_{\text{N}4}$ -**3** isomers.²⁰ The three N→Te interactions prevents any further $\text{S}\dots\text{Te}$ contacts between cations and anions in **3**, as those evidenced in $\text{Ph}_3\text{Te}[(\text{SPPH}_2)_2\text{N}]$.¹³ The two phosphorus-sulfur and the two phosphorus-nitrogen interatomic distances in the organophosphorus anion are only slightly different [P–S 1.957(3) and 1.964(3) Å and P–N 1.584(4) and 1.590(4) Å] and are consistent with delocalization of the π electrons over the SPNPS skeleton, cf. P=S 1.937(1)/1.950(1) Å and P \square N 1.672(2)/1.683(2) Å in the free acid $(\text{SPPH}_2)_2\text{NH}^{21}$ vs P \square S 2.0568(13) Å and P=N 1.557(3) Å in $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Te}-\text{S}-\text{PPh}_2=\text{N}-\text{PPh}_2=\text{S}$.²²

Both sulfur atoms in the anion are involved in weak $\text{S}\dots\text{H}$ contacts [$\text{S1}\dots\text{H3}$ 2.96 Å, $\text{S1}\dots\text{H4}$ 3.01 Å, $\text{S2}\dots\text{H27}$ 2.85 Å; cf. $\Sigma r_{\text{vdW}}(\text{H},\text{S}) = 3.05$ Å¹⁹] with hydrogens in the organic groups attached to tellurium, thus joining neighbour cations and anions in a 2D layer (Figure 2).

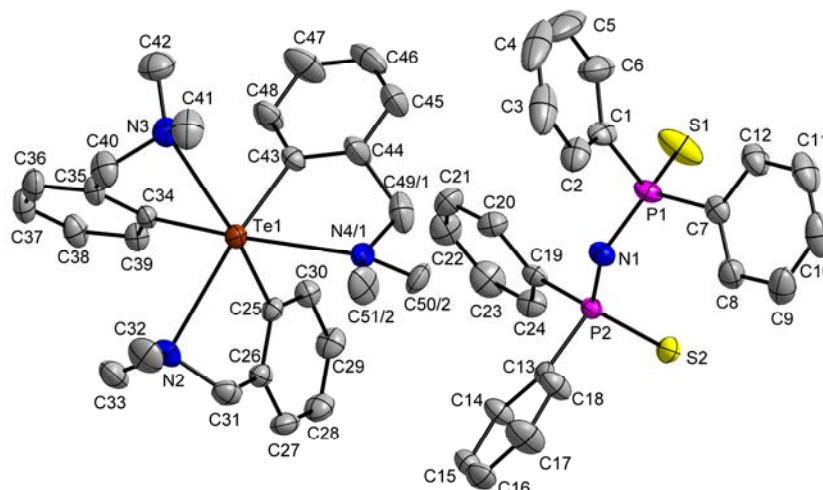


Fig. 1 – Thermal ellipsoids representation at 30% probability of a pair of $S_{N2}, S_{N3}, R_{N4}-[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_3\text{Te}]^+$ cation and $[(\text{SPPPh}_2)_2\text{N}]^-$ anion in the crystal of **3**. Hydrogen atoms are omitted for clarity.

Table 1

Selected interatomic distances (Å) and angles (°) for $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_3\text{Te}]^+[(\text{SPPPh}_2)_2\text{N}]^-$ (**3**)

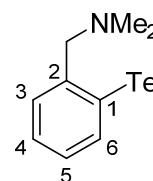
Te1–C25	2.127(6)	C25–Te1–C34	96.3(2)	N2–Te1–C25	71.9(2)
Te1–C34	2.135(5)	C25–Te1–C43	94.6(2)	N2–Te1–C34	79.7(2)
Te1–C43	2.136(6)	C34–Te1–C43	97.3(2)	N2–Te1–C43	165.6(2)
Te1–N2	2.77			N2–Te1–N3	108.1(2)
Te1–N3	2.84			N2–Te1–N4/1	107.2(9)
Te1–N4/1	2.73			[N2–Te1–N4/2]	[112.8(9)]
[Te1–N4/2]	[2.87]	N3–Te1–C25	165.9(2)	N4/1–Te1–C25	77.0(9)
		N3–Te1–C34	70.1(2)	N4/1–Te1–C34	167.9(11)
		N3–Te1–C43	83.8(2)	N4/1–Te1–C43	73.5(10)
		N3–Te1–N4/1	115.6(10)	[N4/2–Te1–C25]	[83.3(9)]
		[N3–Te1–N4/2]	[108.9(10)]	[N4/2–Te1–C34]	[166.5(12)]
				[N4/2–Te1–C43]	[69.3(11)]
S1–P1	1.957(3)	P1–N1–P2	132.2(3)		
S2–P2	1.964(3)	N1–P1–S1	121.16(18)		
P1–N1	1.584(4)	N1–P2–S2	120.07(19)		
P2–N1	1.590(4)				

EXPERIMENTAL

Solvents were dried and distilled prior to use. The starting materials were prepared according to literature procedures: $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_3\text{Te}]\text{Cl}\cdot\text{H}_2\text{O}$,¹⁰ $\text{K}[(\text{SPMe}_2)_2\text{N}]$,²³ $\text{K}[(\text{OPPh}_2)_2\text{N}]$,²⁴ $\text{K}[(\text{SPPPh}_2)_2\text{N}]$,²⁵ $\text{K}[(\text{SPPPh}_2)\{\text{OP}(\text{OEt})_2\}\text{N}]$,²⁶ $\text{K}[(\text{SPPPh}_2)(\text{O}_2\text{SMe})\text{N}]$,¹⁷ $\text{K}[\{\text{SP}(\text{OEt})_2\}(\text{O}_2\text{SC}_6\text{H}_4\text{Cl-4})\text{N}]$.²⁷ Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Infrared spectra were recorded in the range 4000–550 cm^{-1} on a Bruker Vektor 22 FTIR spectrometer as KBr pellets (for compounds **1–3** and **5**) or on a Jasco FTIR-610 machine in the range 4000–500 cm^{-1} (for compounds **4** and **6**). Molar conductivity of 10^{-4} M MeOH solutions was measured with a TDS Meter CON 510 instrument. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{125}\text{Te}\{^1\text{H}\}$ NMR spectra were recorded on a BRUKER Avance III 400 instrument (^1H 400.13 MHz, ^{13}C 100.61 MHz, ^{31}P 161.98 MHz, ^{125}Te 126.24 MHz) or a BRUKER Avance III 600 instrument (^1H 600.13 MHz, ^{13}C 150.90 MHz). The ^1H and ^{13}C chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl_3 : ^1H - δ 7.26; ^{13}C - δ 77.16

ppm). The ^1H and ^{13}C resonances were assigned using 2D experiments (COSY, HSQC and HMBC), according to the numbering shown in Scheme 2.

For the $^{31}\text{P}\{^1\text{H}\}$ and $^{125}\text{Te}\{^1\text{H}\}$ NMR spectra the chemical shifts are reported in δ units (ppm) relative to H_3PO_4 85% and Me_2Te , respectively. The NMR spectra were processed using the MestReNova software.²⁸ ESI+ and ESI– high resolution mass spectra were recorded on a Thermo Scientific LTQ-Orbitrap XL spectrometer equipped with a standard ESI/APCI source. The mass spectra were processed with Thermo Xcalibur software.²⁹



Scheme 2 – Numbering scheme for NMR assignments in compounds **1–6**.

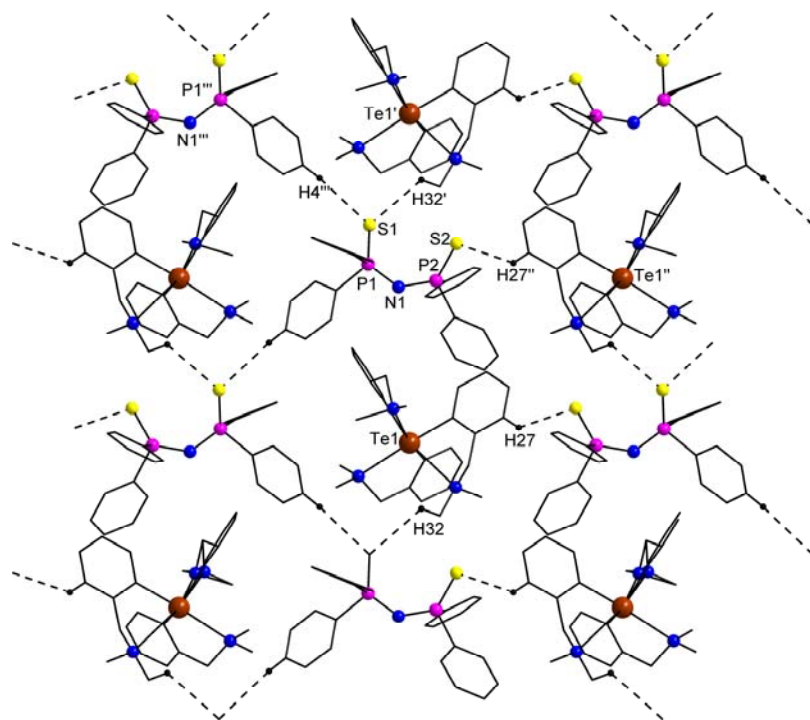


Fig. 2 – View along axis a of a 2D layer in the crystal of **3** (only hydrogen atoms involved in intermolecular contacts are shown): S1...H32' 2.958(2) Å, S1...H4'' 3.011(2) Å, S2...H27'' 2.846(2) Å. Symmetry equivalent positions $x, l+y, z; l-x, l/2+y, -z$ and $l-x, l/2+y, l-z$ are given by “prime”, “second” and “tert”, respectively.

Synthesis of $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+[(\text{SPMe}_2)_2\text{N}]^-$ (**1**)

$\text{K}[(\text{SPMe}_2)_2\text{N}]$ (0.16 g, 0.7 mmol) and $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}\text{Cl}\cdot\text{H}_2\text{O}$ (0.39 g, 0.7 mmol) were mixed in CHCl_3 (15 mL). The reaction mixture was left under stirring for 1 h, then KCl was filtered off. The solvent was removed under vacuum and the resulted yellowish solid was washed with hexane. Yield: 0.45 g (92%). M.p.: 108 °C. ^1H NMR (CDCl_3 , 400.13 MHz): δ 1.95 (d, 12H, PCH_3 , $^2J_{\text{PH}} = 12.6$ Hz), 1.95 (s, v.br., 18H, NCH_3), AB spin system with δ_A 3.34 and δ_B 3.88 (6H, CH_2N , $^2J_{\text{HH}} = 14.2$ Hz), 7.10 (d, 3H, C_6H_4 , $H-6$, $^3J_{\text{HH}} = 7.5$ Hz), 7.30 (t, 3H, C_6H_4 , $H-5$, $^3J_{\text{HH}} = 7.4$ Hz), 7.38 (d, 3H, C_6H_4 , $H-3$, $^3J_{\text{HH}} = 7.2$ Hz), 7.48 (t, 3H, C_6H_4 , $H-4$, $^3J_{\text{HH}} = 7.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.90 MHz): δ : 27.06 (d, PCH_3 , $^1J_{\text{PC}} = 72.9$ Hz), 44.40 (s, br, NCH_3), 63.85 (s, CH_2N), 127.43 (s, C_6H_4 , $C-2$), 129.51 (s, C_6H_4 , $C-5$), 130.46 (s, C_6H_4 , $C-3$), 131.80 (s, C_6H_4 , $C-4$), 134.54 (s, C_6H_4 , $C-6$), 141.36 (s, C_6H_4 , $C-1$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.98 MHz): δ 50.8 (s). $^{125}\text{Te}\{^1\text{H}\}$ NMR (CDCl_3 , 126.24 MHz): δ 749.5 (s). HRMS (ESI+, MeCN), m/z (%): calcd. for $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+$ 532.1966, found 532.1937 (100); HRMS (ESI-, MeOH), m/z (%): calcd. for $[(\text{SPMe}_2)_2\text{N}]^-$ 199.9881, found 199.9892 (100). Selected IR data (ν , cm^{-1}): 2833m, 1473s, 1286m, 1205s, 1172s, 1021m, 932s, 903s, 843s, 771vs.

Compounds **2-6** were prepared similarly:

$[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+[(\text{OPPh}_2)_2\text{N}]^-$ (**2**), from $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}\text{Cl}\cdot\text{H}_2\text{O}$ (0.31 g, 0.5 mmol) and $\text{K}[(\text{OPPh}_2)_2\text{N}]$ (0.24 g, 0.5 mmol), in MeOH (15 mL). The solvent was removed in vacuum and CHCl_3 (15 mL) was added. The title compound resulted as a colourless powder. Yield: 0.40 g (80%). M.p.: 80 °C. ^1H NMR (CDCl_3 , 400.13 MHz): δ 1.83 (s, v.br, 18H, NCH_3), AB spin system with δ_A 3.24 and δ_B 3.76 (6H, CH_2N , $^2J_{\text{HH}} = 14.2$ Hz), 3.88 (s, br, 2H, H_2O), 7.04-7.08 (m, 3H, C_6H_4 , $H-6$ + 12H, PC_6H_5 - $meta+para$), 7.24 (t, 3H, C_6H_4 , $H-5$, $^3J_{\text{HH}} = 7.4$ Hz), 7.32 (d,

3H, C_6H_4 , $H-3$, $^3J_{\text{HH}} = 7.3$ Hz), 7.43 (t, 3H, C_6H_4 , $H-4$, $^3J_{\text{HH}} = 7.4$ Hz), 7.89 (m, 8H, PC_6H_5 - $ortho$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz): δ 44.29 (s, br, NCH_3), 63.68 (s, CH_2N), 127.11 (m, PC_6H_5 - $meta$), 127.57 (s, C_6H_4 , $C-2$), 128.45 (s, PC_6H_5 - $para$), 129.34 (s, C_6H_4 , $C-5$), 130.45 (s, C_6H_4 , $C-3$), 131.70 (s, C_6H_4 , $C-4$), 131.82 (m, PC_6H_5 - $ortho$), 134.46 (s, C_6H_4 , $C-6$), 141.45 (s, C_6H_4 , $C-1$), 141.48 (d, PC_6H_5 - $ipso$, $^1J_{\text{CP}} = 131.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.98 MHz): δ 8.6 (s). $^{125}\text{Te}\{^1\text{H}\}$ NMR (CDCl_3 , 126.24 MHz, 21 °C): δ 753.9 (s). HRMS (ESI+, MeOH), m/z (%): calcd. for $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+$ 532.19660, found 532.19849 (100); HRMS (ESI-, MeCN), m/z (%): calcd. for $[(\text{OPPh}_2)_2\text{N}]^-$ 416.09638, found 416.10394 (100). Selected IR data (ν , cm^{-1}): 3302m,br, 2833m, 1473s, 1436s, 1246s, 1151s, 1117s, 1021m, 844s, 751s, 720s, 697vs.

$[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+[(\text{SPPPh}_2)_2\text{N}]^-$ (**3**),¹⁰ from $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}\text{Cl}\cdot\text{H}_2\text{O}$ (0.30 g, 0.5 mmol) and $\text{K}[(\text{SPPPh}_2)_2\text{N}]$ (0.25 g, 0.5 mmol). Selected IR data (ν , cm^{-1}): 2829m, 1435m, 1205s, 1171s, 1100m, 1020m, 845m, 754s, 706vs.

$[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}^+[(\text{SPPPh}_2)\{\text{OP}(\text{OEt})_2\}\text{N}]^-$ (**4**), from $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}\}\text{Cl}\cdot\text{H}_2\text{O}$ (0.065 g, 0.11 mmol) in CHCl_3 (15 mL) and $\text{K}[(\text{SPPPh}_2)\{\text{OP}(\text{OEt})_2\}\text{N}]$ (0.045 g, 0.11 mmol) in CHCl_3 (15 mL), as a yellow, sticky solid. Yield: 0.098 g (99%). ^1H NMR (CDCl_3 , 400.13 MHz): δ 1.11 (t, 6H, OCH_2CH_3 , $^3J_{\text{HH}} = 7.0$ Hz), 1.96 (v.br, 18H, NCH_3), AB spin system with δ_A 3.36 and δ_B 3.91 (6H, CH_2N , $^2J_{\text{HH}} = 14.2$ Hz), 3.97 (q, 4H, OCH_2CH_3 , $^3J_{\text{HH}} = 6.7$ Hz), 7.12 (d, 3H, C_6H_4 , $H-6$, $^3J_{\text{HH}} = 7.6$ Hz), 7.21 (m, 6H, PC_6H_5 - $meta+para$), 7.31 (t, 3H, C_6H_4 , $H-5$, $^3J_{\text{HH}} = 7.4$ Hz), 7.40 (d, 3H, C_6H_4 , $H-3$, $^3J_{\text{HH}} = 7.3$ Hz), 7.50 (t, 3H, C_6H_4 , $H-4$, $^3J_{\text{HH}} = 7.4$ Hz), 8.11 (dd, 4H, PC_6H_5 - $ortho$, $^3J_{\text{PH}} = 13.3$, $^3J_{\text{HH}} = 6.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz): δ 16.54 (d, OCH_2CH_3 , $^3J_{\text{PC}} = 8.0$ Hz), 44.54 (s, br, NCH_3), 61.19 (d, OCH_2CH_3 , $^2J_{\text{PC}} = 5.6$ Hz), 63.90 (s, CH_2N), 127.31 (d, PC_6H_5 - $meta$, $^3J_{\text{PC}} = 12.8$ Hz),

127.81 (s, C₆H₄, C-2), 128.98 (s, br, PC₆H₅-*para*), 129.42 (s, C₆H₄, C-5), 130.55 (s, C₆H₄, C-3), 131.49 (d, PC₆H₅-*ortho*), ²J_{PC} = 11.1 Hz), 131.74 (s, C₆H₄, C-4), 134.59 (s, C₆H₄, C-6), 141.68 (s, C₆H₄, C-1), 142.98 (d, PC₆H₅-*ipso*, ¹J_{PC} = 112.3 Hz). ³¹P{¹H} NMR (CDCl₃, 161.98 MHz): δ 1.9 (d, PO, ²J_{PP} = 20.2 Hz), 34.1 (s, br, PS). ¹²⁵Te{¹H} NMR (CDCl₃, 126.24 MHz): δ 754.7 (s). HRMS (ESI+, MeOH), *m/z* (%): calcd. for [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺ 532.1966, found 532.1948 (100); HRMS (ESI-, MeOH), *m/z* (%): calcd. for [(SPPPh₂)₂OP(OEt)₂N⁻] 368.0634, found 368.0654 (100). Selected IR data (ν, cm⁻¹): 2833w, 2360w, 1456m, 1246m, 1173m, 1020s, 949w, 841s, 770vs.

[{2-(Me₂NCH₂)C₆H₄}]₃Te⁺[(SPPPh₂)(O₂SMe)N]⁻ (**5**), from [{2-(Me₂NCH₂)C₆H₄}]₃TeCl·H₂O (0.069 g, 0.12 mmol) and K[(SPPPh₂)(O₂SMe)N] (0.042 g, 0.12 mmol) in MeOH (20 mL). After 17 h the solvent was removed in vacuum. To the obtained precipitate dichloromethane was added (5 mL). KCl was removed by filtration and the viscous oil, resulted after removing dichloromethane at reduced pressure, was washed several times with hexane, when the title compound was isolated as a colourless powder. Yield: 0.09 g (90%). M.p.: 75 °C. ¹H NMR (CDCl₃, 400.13 MHz): δ 1.92 (s, v.br, 18H, NCH₃), 3.08 (s, 3H, SCH₃), AB spin system with δ_A 3.33 and δ_B 3.90 (6H, CH₂N, ²J_{HH} = 14.2 Hz), 7.12 (d, 3H, C₆H₄, H-6, ³J_{HH} = 7.6 Hz), 7.23-7.25 (m, 6H, PC₆H₅-*meta+para*), 7.31 (t, 3H, C₆H₄, H-5, ³J_{HH} = 7.3 Hz), 7.39 (d, 3H, C₆H₄, H-3, ³J_{HH} = 7.3 Hz), 7.49 (t, 3H, C₆H₄, H-4, ³J_{HH} = 7.4 Hz), 8.09 (ddd, 4H, PC₆H₅-*ortho*, ³J_{PH} = 13.3, ³J_{HH} = 7.7, ⁴J_{HH} = 2.1 Hz). ¹³C{¹H} NMR (CDCl₃, 100.61 MHz): δ 44.09 (s, SCH₃), 44.51 (s, br, NCH₃), 63.90 (s, CH₂N), 127.45 (d, PC₆H₅-*meta*, ³J_{PC} = 12.8 Hz), 127.88 (s, C₆H₄, C-2), 129.29 (d, PC₆H₅-*para*, ⁴J_{PC} = 2.9 Hz), 129.41 (s, C₆H₄, C-5), 130.53 (s, C₆H₄, C-3), 131.54 (d, PC₆H₅-*ortho*, ²J_{PC} = 10.8 Hz), 131.73 (s, C₆H₄, C-4), 134.61 (s, C₆H₄, C-6), 141.18 (d, PC₆H₅-*ipso*, ¹J_{PC} = 107.1 Hz), 141.74 (s, C₆H₄, C-1). ³¹P{¹H} NMR (CDCl₃, 161.98 MHz): δ 37.5 (s). ¹²⁵Te{¹H} NMR (CDCl₃, 126.24 MHz): δ 755.1 (s). HRMS (ESI+, MeOH), *m/z* (%): calcd. for [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺ 532.1966, found 532.1945 (100); HRMS (ESI-, MeOH), *m/z* (%): calcd. for [(SPPPh₂)(O₂SMe)N]⁻ 310.01198, found 310.01382 (100). Selected IR data (ν, cm⁻¹): 2830w, 1473m, 1436m, 1246s, 1129vs, 1103s, 1020w, 845m, 808s, 752s, 708s, 604m.

[{2-(Me₂NCH₂)C₆H₄}]₃Te⁺[[SP(OEt)₂](O₂SC₆H₄Cl-4)N]⁻ (**6**), from [{2-(Me₂NCH₂)C₆H₄}]₃TeCl·H₂O (0.137 g, 0.23 mmol) and K[[SP(OEt)₂](O₂SC₆H₄Cl-4)N] (0.089 g, 0.23 mmol), in CHCl₃ (25 mL), as a yellowish, sticky solid, after washing with diethyl ether and pentane. Yield: 0.135 g (66%). ¹H NMR (CDCl₃, 400.13 MHz): δ 1.17 (t, 6H, OCH₂CH₃, ³J_{HH} = 7.1 Hz), 1.96 (br, 18H, NCH₃), AB spin system with δ_A 3.37 and δ_B 3.92 (6H, CH₂N, ²J_{HH} = 14.2 Hz), 4.01 (dq, 4H, OCH₂CH₃, ³J_{PH} = ³J_{HH} = 7.1 Hz), 7.13 (d, 3H, C₆H₄, H-6, ³J_{HH} = 7.6 Hz), 7.22 (d, 2H, SC₆H₄-*meta*, ³J_{HH} = 8.5 Hz), 7.32 (t, 3H, C₆H₄, H-5, ³J_{HH} = 7.3 Hz), 7.41 (d, 3H, C₆H₄, H-3, ³J_{HH} = 7.3 Hz), 7.51 (t, 3H, C₆H₄, H-4, ³J_{HH} = 7.4 Hz), 7.99 (d, 2H, SC₆H₄-*ortho*, ³J_{HH} = 8.5 Hz). ¹³C{¹H} NMR (CDCl₃, 100.61 MHz): δ 16.19 (d, OCH₂CH₃, ²J_{PC} = 8.9 Hz), 44.55 (s, br, NCH₃), 61.61 (d, OCH₂CH₃, ¹J_{PC} = 6.0 Hz), 63.89 (s, CH₂N), 127.55 (s, SC₆H₄-*meta*), 127.73 (s, C₆H₄, C-2), 128.65 (s, SC₆H₄-*ortho*), 129.46 (s, C₆H₄, C-5), 130.54 (s, C₆H₄, C-3), 131.77 (s, C₆H₄, C-4), 134.59 (s, C₆H₄, C-6), 134.90 (s, SC₆H₄-*para*), 141.61 (s, C₆H₄, C-1), 146.53 (s, SC₆H₄-*ipso*). ³¹P{¹H} NMR (CDCl₃, 161.98 MHz): δ 55.7 (s). ¹²⁵Te{¹H} NMR (CDCl₃, 126.24 MHz): δ 754.2 (s). HRMS (ESI+, MeOH), *m/z* (%): calcd. for [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺

532.1966, found 532.1948 (100); HRMS (ESI-, MeOH), *m/z* (%): calcd. for [[SP(OEt)₂](O₂SC₆H₄Cl-4)N]⁻ 341.9785, found 341.9808 (100). Selected IR data (ν, cm⁻¹): 2831w, 2360w, 1458w, 1248m, 1165m, 1134m, 1028s, 945m, 841s, 753s, 729vs.

Crystal structure determination

X-ray quality single-crystals of [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺[(SPPPh₂)₂N]⁻ (**3**) were obtained from a mixture of chloroform/n-hexane (1:3, v:v). The details of the crystal structure determination and refinement are given in Table 2. Data were collected at room temperature on a Bruker SMART APEX CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The atoms in the pendant arm CH₂N(4)Me₂ are disordered over two positions with a 0.55:0.45 ratio. The structures were refined with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. The structure was solved by the SHELXL-2016/4 crystallographic software package.³⁰ Intermolecular interactions/contacts were found with PLATON.³¹ The drawings were created with the Diamond program.³²

CONCLUSIONS

Six triaryltelluronium salts of type [{2-(Me₂NCH₂)C₆H₄}]₃Te⁺L⁻ [L = (SPMe₂)₂N, (OPPh₂)₂N, (SPPPh₂)₂N, (SPPPh₂){OP(OEt)₂}, (SPPPh₂)(O₂SMe)N, {SP(OEt)₂}(O₂SC₆H₄Cl-4)N] were prepared and structurally characterized. The three 2-(Me₂NCH₂)C₆H₄ groups are equivalent in solution and they behave as *C,N*-chelating ligands towards tellurium, with intramolecularly coordinated 2-(Me₂NCH₂) pendant arms, as it was evidenced by room temperature ¹H NMR. The single-crystal X-ray diffraction studies revealed strong intramolecular N→Te coordination in solid state in compound **3**, thus resulting in a *14-Te-6* hypercoordinated species. No further secondary interactions are evidenced for the tellurium atoms, but a 2D supramolecular architecture is formed through weak H⋯S contacts in the crystal lattice.

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Supplementary material

CCDC 2041242 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2

Crystal data and structure refinement for $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_3\text{Te}]^+[(\text{SPPPh}_2)_2\text{N}]^-$ (3)

Empirical formula	$\text{C}_{51}\text{H}_{56}\text{N}_4\text{P}_2\text{S}_2\text{Te}$
Formula weight, g/mol	978.65
Temperature, K	293
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a , Å	9.4924(11)
b , Å	13.7055(16)
c , Å	18.566(2)
α , °	90
β , °	97.215(2)
γ , °	90
Volume, Å ³	2396.3(5)
Z	2
Density (calculated), g/cm ³	1.356
Absorption coefficient, mm ⁻¹	0.813
F(000)	1008
Crystal size, mm	0.13 × 0.30 × 0.56
Theta range for data collection, °	1.9 to 25.0
Reflections collected / unique data	23156 / 8453
R(int)	0.041
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8453 / 1 / 585
Goodness-of-fit on F ²	0.968
Final R indices [I > 2sigma(I)]	R1 = 0.0343, wR2 = 0.0657
R indices (all data)	R1 = 0.0389, wR2 = 0.0670
Largest diff. peak and hole, e/Å ³	-0.25 and 0.82

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