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Faculty of Chemistry and Chemical Engineering

Contributions to the chemistry of organoelement compounds of selenium, tellurium and tin.

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Abstract PhD Thesis

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Introduction

The aim of the present work was the synthesis of new organometallic compounds of elements from the main groups (Se, Te and Sn), with bidentate ligands and/or organic functional groups that possess pendant arms capable for *C,N*-chelation towards the central atom (Se and Sn). Previously it was observed that in ionic compounds as $[\text{Ph}_3\text{Te}]^+[(\text{XPPH}_2)(\text{YPPH}_2)\text{N}]^-$ (X, Y = S, O), besides the cation-anion electrostatic interactions there are established $\text{O}\cdots\text{Te}$ and $\text{S}\cdots\text{Te}$ contacts in the range of the sum of the van der Waals radii of the two elements, which lead to an increased coordination number of the tellurium atom.⁴ In the studies presented in this work the behavior of some organophosphorus ligands towards the $[\text{Ph}_3\text{Te}]^+$ cation was investigated, with regard to additional contacts that can lead to an increased coordination number at tellurium. For comparison, two triphenyltelluronium salts with organoantimony(III) anions were investigated also, which cannot establish other types of interactions with the tellurium atom than the electrostatic ones.

The studies were focused on organo-selenium, - tellurium and -tin compounds, not only for structural considerations, but also in the light of their potential applications, as mentioned further.

The chemistry of organoselenium compounds has become a field of research intensely studied in recent years due to the potential applications of these compounds in organic synthesis, biochemistry and nanomaterials with applications in microelectronics (semiconductors). Organoselenium compounds with a *N,N*-diorganobenzylamine functional group, in which the nitrogen atom of the pendant arm is capable of forming $\text{N}\rightarrow\text{Se}$ interactions, showed higher catalytic properties and antioxidant activity than those substituted with simple organic functional groups.⁵ Recently, organoselenium(II) compounds have been used in radical-initiated polymerization processes as RAFT agents (Reversible Addition Fragmentation Chain Transfer Polymerization).⁶

Organtellurium compounds have also found applications in catalysis, biology and microelectronics.⁷ Tellurium compounds have thermoelectric properties or a special electronic behavior and for this reason efforts were made to obtain single source or dual source precursors for such nanomaterials.⁸

Organotin(IV) compounds are well known for their biological activity, which is influenced by the nature of the functional groups attached to the metal atom, but also by the nature of the anionic ligands present in the molecule.⁹ The chemistry of hypervalent organotin(IV) compounds has evolved in the last years, following the synthesis and the

structural characterization in solution or in solid state of compounds containing ligands with one or more pendant arms such as 2-(Me₂NCH₂)C₆H₄ or 2,6-(Me₂NCH₂)₂C₆H₃. Tin(IV) dithiocarbamates have attracted interest as biologically active agents, as well as potential precursors for nanomaterials (tin sulfide) used in microelectronics.¹⁴

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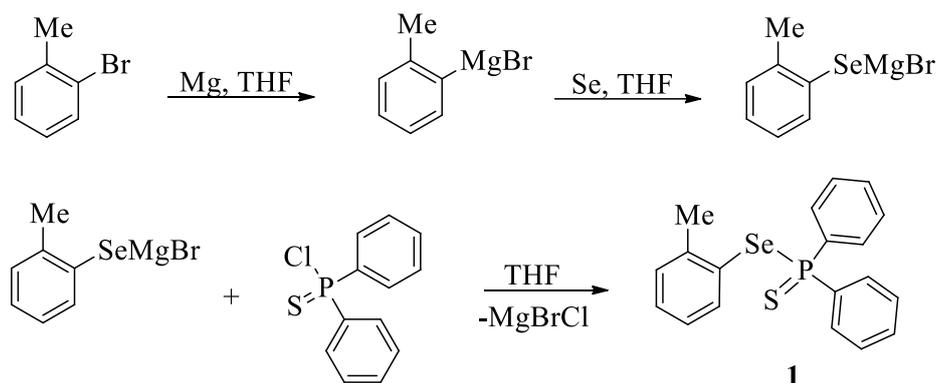
Chapter 1. Esters of diorganochalcogenoselenophosphinic acids, $\text{Ph}_2\text{P}(\text{E})\text{SeR}'$ ($\text{E} = \text{S}, \text{Se}$),

1.2. Original contributions

The aim of the present studies was the synthesis of new organophosphorus(V) compounds that contain both sulfur and selenium atoms in their structure, which could be further used as RAFT agents in polymerization reactions.

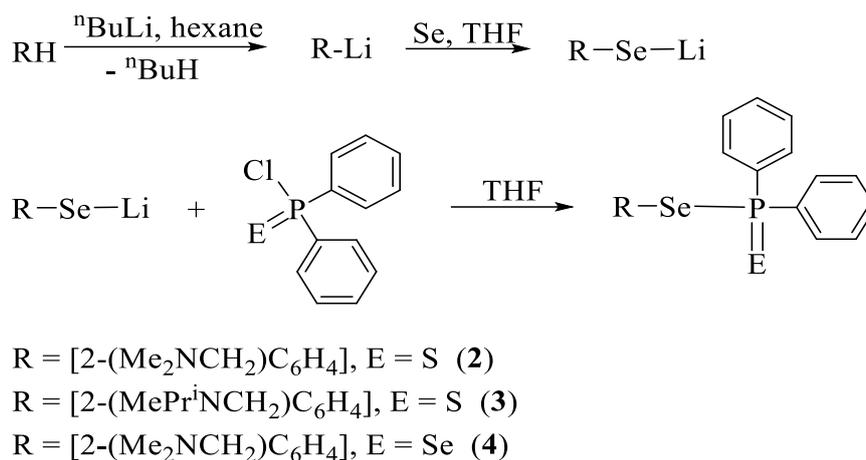
1.2.1 Synthesis

$\text{Ph}_2\text{P}(\text{S})\text{SeTol-}o$ (**1**) was prepared as presented in Scheme 1.4. Initially, the insertion of selenium into the C–Mg bond of the *in situ* generated Grignard reagent *o*-TolMgBr was performed, followed by the reaction of the *o*-TolSeMgBr with thiophosphinyl chloride, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$, thus leading to compound **1** as a slightly brown liquid.



Scheme 1.4.

Afterwards, a series of reactions were performed as presented in Scheme 1.5, in order to obtain compounds **2-4**, which contain organic functional groups with pendant arms bonded to the selenium atom. The products were isolated as white colorless or slightly yellow solids, which were characterized by multinuclear NMR spectroscopy (^1H , ^{31}P and ^{77}Se where appropriate). For compounds **1** and **2** the ^{13}C NMR spectra were also recorded.



Schema 1.5.

1.2.2. NMR spectroscopy

The ^1H NMR spectra of compounds **2** - **4** show multiplet signals in the aromatic region, characteristic for the *ortho*, *meta* and *para* protons belonging to the phenyl groups attached to the phosphorus atom and also signals corresponding to the aromatic protons belonging to the $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4]$ group. In the aliphatic region of the ^1H NMR spectra of compounds **2** and **4** singlet resonances can be observed, corresponding to the methyl protons from the NMe_2 groups; and also a singlet signal for the methylene protons in the CH_2N group. From these results, we concluded that the aliphatic region of the ^1H RMN spectra of these compounds don't provide data concerning the $\text{N} \rightarrow \text{Se}$ intramolecular coordination in solution.

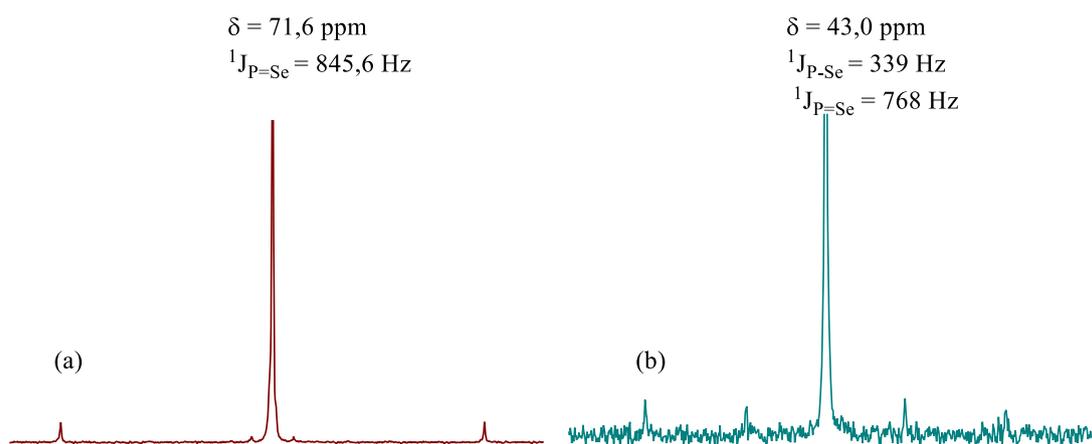


Fig. 1.3. ^{31}P NMR signals for the starting material $\text{Ph}_2\text{P(Se)Cl}$ (a) and compound **4** (b) (CDCl_3 , 121 MHz)

The ^{31}P NMR spectrum (Fig. 1.3) of compound **4** confirms the presence of single bonds between P–Se and P=Se respectively, due to the presence of two corresponding pairs of satellites.

The ^{77}Se NMR spectrum (Fig. 1.4) of compounds **1** and **2** indicate the presence of P–Se couplings, as they appear as doublets.

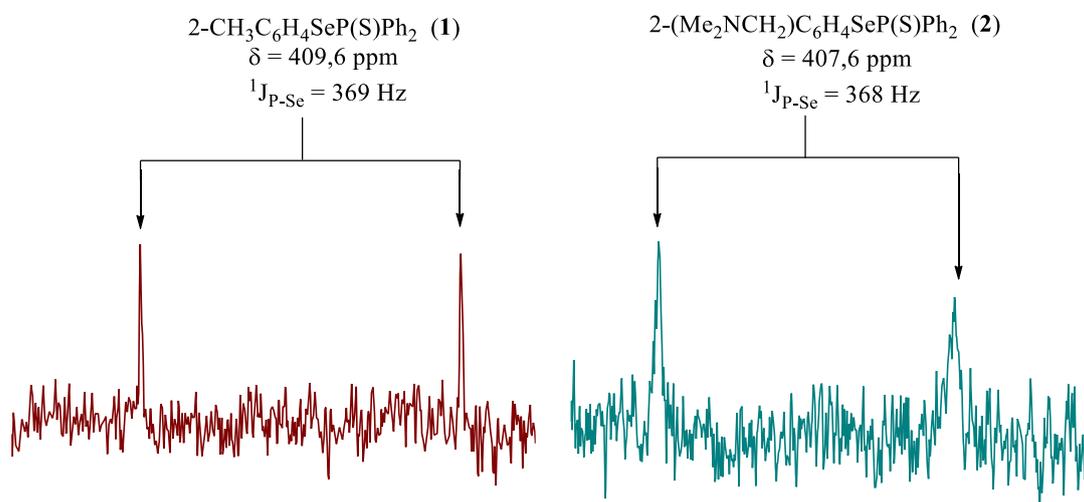


Fig. 1.4. ^{77}Se NMR resonance signals for compounds **1** (a) and **2** (b) (CDCl_3 , 58 MHz)

1.2.3. Single crystal X-ray diffraction studies

Structure of compound $[2-(\text{Me}^i\text{PrN}(\text{H}^+)\text{CH}_2)\text{C}_6\text{H}_5][\text{Ph}_2\text{P}(\text{S})\text{O}]^-$ (**3a**).

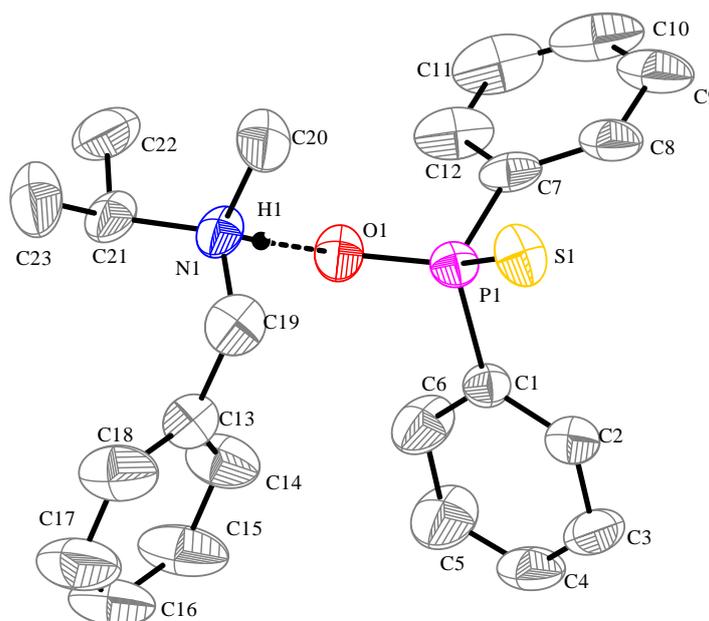


Fig. 1.9. The molecular structure of compound **3a**. Hydrogen atoms are not shown for clarity. Thermal ellipsoids are shown with 30% probability.

The coordination geometry around the P and N atoms is distorted tetrahedral. Between the two ions formed by hydrolysis, the protonated amine [(MeⁱPrN(H⁺)CH₂)C₆H₅] and Ph₂P(S)O⁻, besides the cation-anion electrostatic interactions, hydrogen bonds are also formed with the interatomic distance H⁺⋯O = 1.647(3) Å having an intermediate value between Σr_{vdW}(H,O) (2.75 Å) and Σr_{cov}(H,O) (1.12 Å).²⁰

1.3. Conclusions

- The organophosphorus compounds **1-4** were successfully synthesized and they could be used as RAFT agents. The synthesis of compound **1** has been performed using organomagnesium derivatives, while the synthesis of compounds **2-4** has been performed by an *ortho*-lithiation reaction, followed by insertion of selenium into the C-Li bond and subsequent reaction with diphenylthio/seleno phosphinyl chloride.
- All syntheses were performed in argon due to the instability of the compounds in atmospheric conditions.
- The compounds were characterized by ¹H, ¹³C, ³¹P and ⁷⁷Se NMR spectroscopy. The ¹H and ¹³C NMR spectra show specific resonances for the expected chemical structures and they do not suggest any N→Se intramolecular coordination.
- Together with compound **3**, the derivative **3a** formed by decomposition and hydrolysis was also isolated.
- Compound **3a** was characterized in solid state by single crystal X-ray diffraction and its ionic structure was evidenced.

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Mass spectrometry

The mass spectra are consistent with the ionic structure of these compounds. In the case of all studied compounds, the ESI+ mass spectra showed the corresponding base peak for $[\text{Ph}_3\text{Te}]^+$ cation with a m/z value of 361.02, while the ESI- spectra showed peaks corresponding to the organophosphorus anions.

Molar conductivity

The molar conductivity of the compounds in DMSO was found to be lower than in the case of the starting material Ph_3TeCl ($\Lambda_M = 79.9 \text{ S}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$), which in turn is also lower than that of KCl completely dissociated in water (0.01 M solution, $\Lambda_M = 141 \text{ S}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$)³⁷⁻³⁹ and consistent with 1:1 electrolytes. These behavior suggests an incomplete dissociation and the existence of $\text{Te}\cdots\text{Cl}$ interactions in the case of Ph_3TeCl ,⁴⁰ and $\text{Te}\cdots\text{O/S}$ interactions respectively in the case of the investigated compounds.

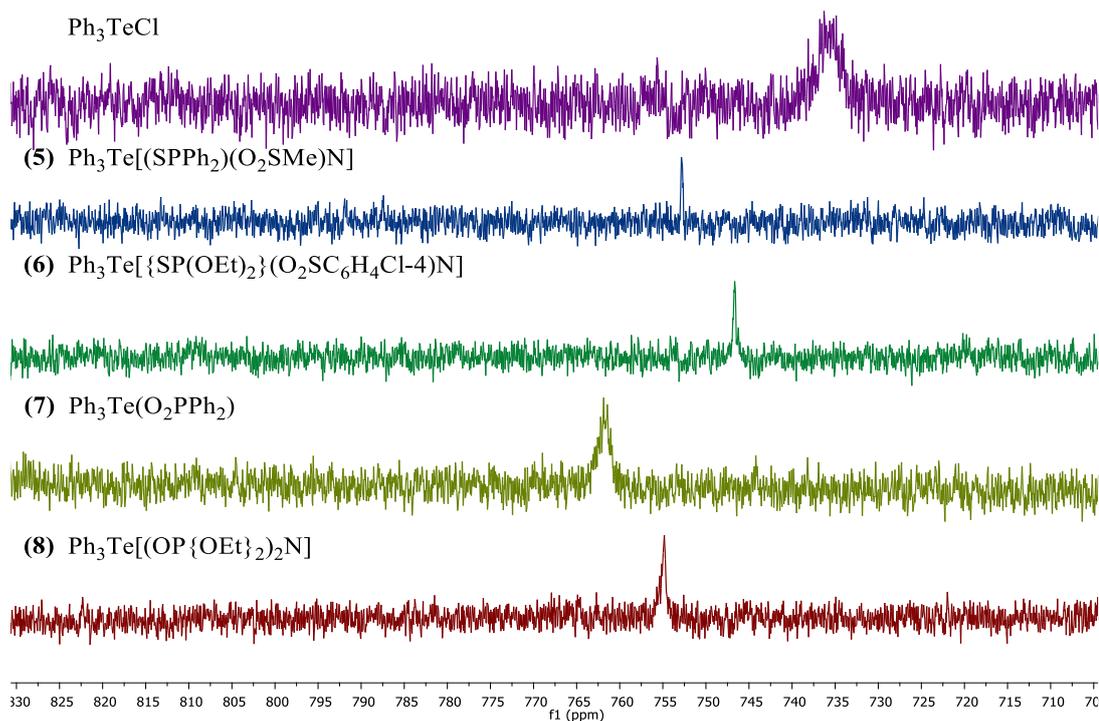


Fig. 2.10. ¹²⁵Te NMR spectra for compounds **5 – 8** (CDCl₃, 126.33 MHz)

2.2.1.3. Single-crystal X-ray diffraction studies

The molecular structure of compound 7·Ph₂P(O)OH structure

The $[\text{Ph}_2\text{PO}_2]^-$ anion and the free acid $\text{Ph}_2\text{P}(\text{O})\text{OH}$ interact with the tellurium atom through the oxygen atoms, which together with the three C–Te bonds, determine a distorted

square pyramidal coordination geometry around the tellurium atom, with one phenyl group in apical position.

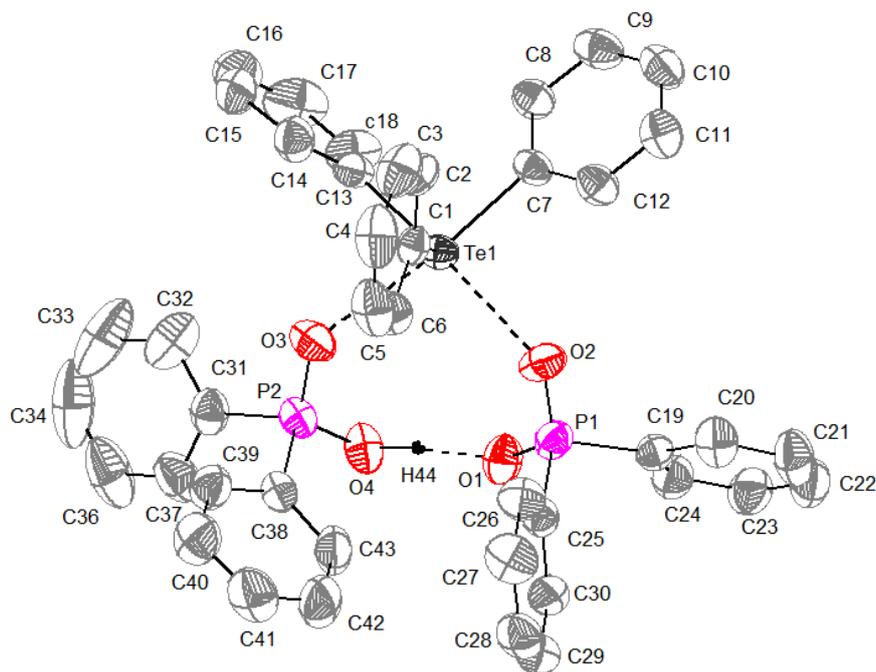
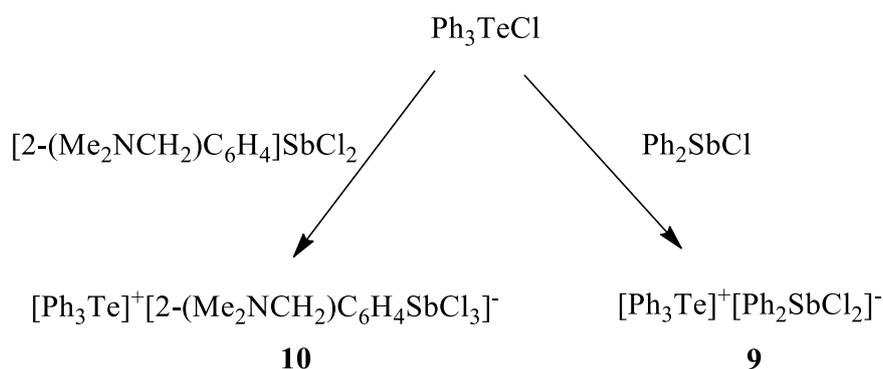


Fig. 2.13. The molecular structure of compound **7·Ph₂P(O)OH**. The hydrogen atoms are not shown for clarity. Thermal ellipsoids are shown with 50% probability.

2.2.2. Compounds with anionic organoantimony(III) ligands

2.2.2.1. Synthesis

Ionic compounds containing organoantimony anions were also synthesized (Scheme 2.14).



Scheme 2.14.

Compounds **9** and **10** were characterized by NMR spectroscopy (¹H, ¹³C and ¹²⁵Te), mass spectrometry and molar conductivity.

2.3. Conclusions

- The synthesis of triphenyltelluronium compounds **5 – 8** was performed by salt metathesis reactions between Ph_3TeCl and the potassium salts of the corresponding organophosphorus acids.
- Compounds **9** and **10** were prepared by transferring the Cl^- anion from Ph_3TeCl to Ph_2SbCl , and to $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{SbCl}_2$ respectively, so that the coordination number of the antimony atom increases with one unit.
- All synthesized compounds were characterized by ^1H , ^{13}C , ^{31}P and ^{125}Te NMR.
- The ^1H and ^{13}C NMR spectra of compound **10** do not indicate the existence of any $\text{N} \rightarrow \text{Sb}$ intramolecular interaction.
- The ^{31}P and ^{125}Te NMR spectra showed only one singlet signal in all the studied compounds, with the exception of compound $\text{Ph}_3\text{Te}[(\text{OP}\{\text{OEt}\}_2)_2\text{N}]$ (**8**), for which the ^{31}P NMR spectrum showed two signals in a 1:1 ratio of intensity, which suggest the non-equivalent nature of the two phosphorus atoms, probably due to $\text{O} \cdots \text{Te}$ interactions established between the $[\text{Ph}_3\text{Te}]^+$ cation with one of the oxygen atoms bonded to the phosphorus atom in the organophosphorus ligand.
- Molar conductivity values obtained in DMSO suggest ionic structures corresponding to 1:1 electrolytes for compounds with organoantimony anions, while for compounds with organophosphorus ligands the significantly lower values indicate weak interactions between Te and the ligand in the range of the sum of the van der Waals radii for Te and oxygen, in addition to the electrostatic ones.
- ESI- mass spectra are consistent with the ionic structure of these compounds. In the ESI+ mass spectra the base peak has a m/z value of 361.02, corresponding to the $[\text{Ph}_3\text{Te}]^+$ cation, while the ESI- mass spectra showed base peaks corresponding to the organophosphorus anions (**5 – 8**), and the organoantimony(III) anions (**9** and **10**).
- The molecular structure obtained by single crystal X-ray diffraction for compound $\text{Ph}_3\text{Te}[\text{O}_2\text{PPh}_2] \cdot \text{Ph}_2\text{P}(\text{O})\text{OH}$ (**7**·**Ph₂P(O)OH**) showed strong $\text{Te} \cdots \text{O}$ interactions between the triphenyltelluronium cation, the Ph_2PO_2^- anion and the free acid $\text{Ph}_2\text{PO}_2\text{H}$. The monodentate nature of the two ligands towards the tellurium atom generates the distorted square pyramidal coordination geometry.

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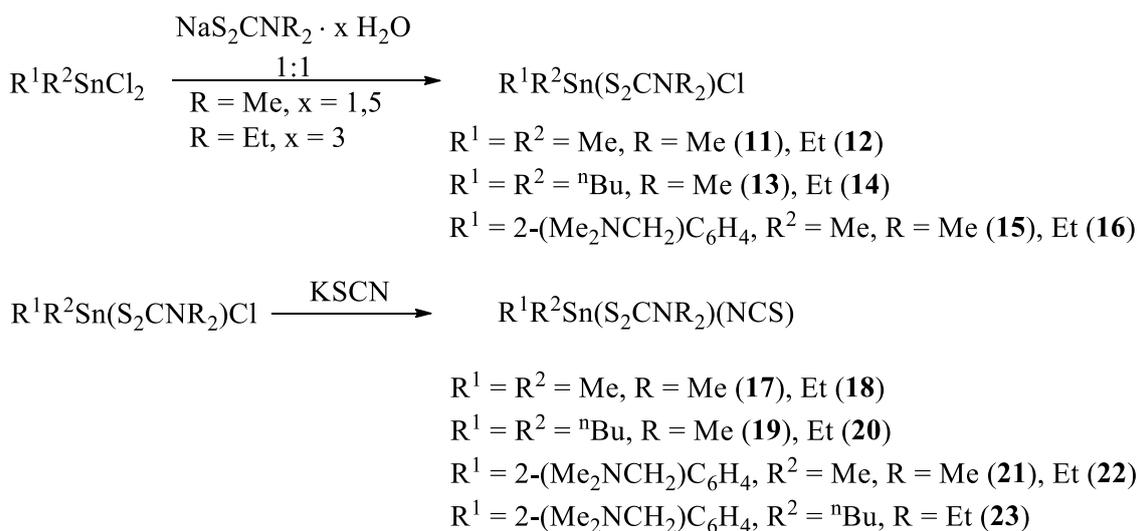
Chapter 3. Hypercoordinated diorganotin (IV) compounds

3.2. Original contributions

This chapter presents the contributions of this work to the chemistry of organotin(IV) compounds with dithiocarbamate and thiocyanato ligands.

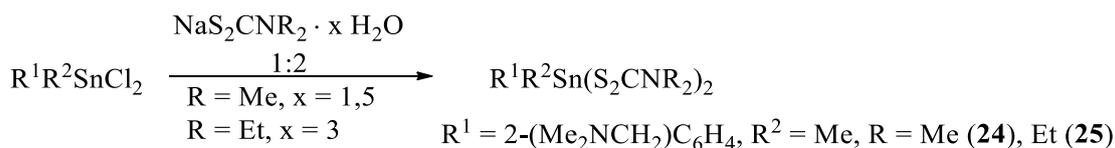
3.2.1. Synthesis of the organotin(IV) complexes

New organotin(IV) complexes were prepared as presented in Schemes 3.4 and 3.5. The organotin complexes **17** – **23** were obtained by salt metathesis reactions, in two-steps (Scheme 3.4). Diorganotin(IV) dichlorides were treated with sodium diorganodithiocarbamates in a 1:1 molar ratio, thus obtaining compounds **11** – **16**, which were further reacted with KSCN to give compounds **17** – **23**.



Scheme 3.4.

Compounds **24** and **25** were prepared by reacting the diorganotin(IV) dichlorides with sodium diorganodithiocarbamates in a 1:2 molar ratio (Scheme 3.5).



Scheme 3.5.

The compounds were isolated as colorless microcrystalline solids, with the exception of compounds **13**, **14**, **19**, **20** and **23**, substituted with ⁿBu groups, which were isolated as oils.

The obtained compounds were investigated by NMR spectroscopy, mass spectrometry and also IR spectroscopy for the solid compounds. For some of the obtained compounds, the molecular structures were determined by single crystal X-ray diffraction.

The ¹H and ¹³C NMR resonances corresponding to the organic groups bonded to the tin atom are accompanied by ¹H – ^{117/119}Sn and ¹³C – ^{117/119}Sn satellites, respectively. Based on the coupling constants obtained from the NMR spectra of the compounds substituted with two aliphatic groups, the C–Sn–C angle was calculated in solution and a coordination geometry was proposed for the studied compounds. For compounds with two alkyl groups attached to the tin atom, a trigonal bipyramidal coordination geometry was proposed, with both substituents in equatorial position. For compounds **17** and **18**, the C–Sn–C angle value calculated in solution is similar to the one determined in solid state by single crystal X-ray diffraction.

In Fig. 3.18 are presented the ^1H and ^{13}C NMR resonances for compound **17**, accompanied by the characteristic satellites.

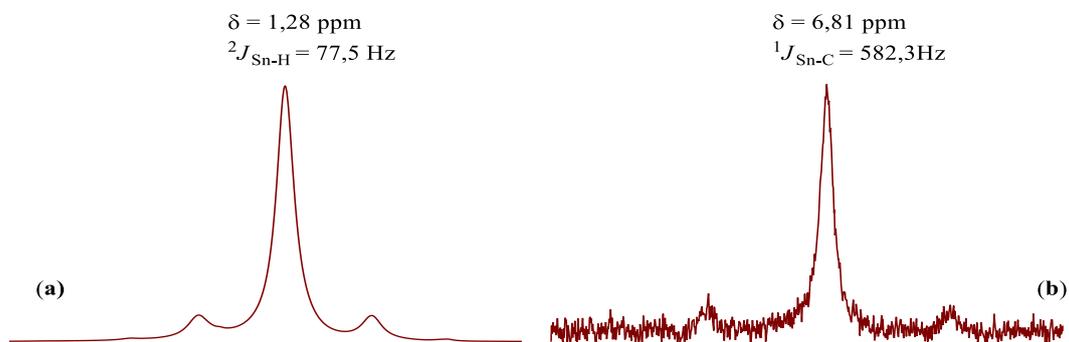


Fig. 3.18. ^1H NMR (a) and ^{13}C NMR (b) resonances for the Me_2Sn group in the spectra of compound **17** (CDCl_3)

Mass spectrometry

ESI+ mass spectra recorded for compounds **11** – **16** in methanol showed a maximum intensity peak (100 %) at m/z values corresponding to $[\text{M}-\text{Cl}]^+$ ions. For compounds **17** – **23** the base peak (100 %) was observed for the $[\text{M}-\text{NCS}]^+$ ions.

IR spectrometry

IR spectra of compounds with SCN^- ligands showed very intense $\nu(\text{CN})$ bands around 2050 cm^{-1} and $\nu(\text{CS})$ bands in the $754 - 798\text{ cm}^{-1}$ interval, supporting the isothiocyanate behavior of the SCN^- ligand in solid state³⁴, which can also be observed in the molecular structures of compounds **17**, **18** and **22** determined by single-crystal X-ray diffraction.

Thermal behavior

The thermal behavior of compounds **17**, **18** and **25** was investigated by thermogravimetric analysis. The experiments were carried in non-isothermal conditions, within a temperature range of $20 - 1000^\circ\text{C}$, with a heating rate of $10^\circ\text{C}/\text{min.}$, in air.

3.2.3. Single-crystal X-ray diffraction studies

The molecular structures for compounds **17**, **18**, **22** and **25** were determined by single crystal X-ray diffraction.

The molecular structure of compound **17** is presented in Fig. 3.26.

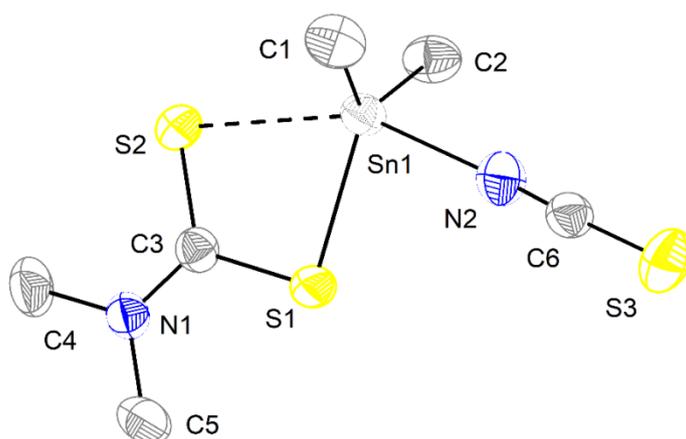


Fig. 3.26. Molecular structure of $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)(\text{NCS})$ (**17**). Hydrogen atoms not shown for clarity. Thermal ellipsoids are shown with 30% probability.

The coordination geometry around the Sn atom was found to be that of a distorted trigonal bipyramid and it is determined in the equatorial plan by the two carbon atoms C1 and C2, corresponding to the methyl groups bonded to tin and the S1 atom corresponding to the dimethyldithiocarbamate group, while the axial positions are occupied by the S2 and N2 atoms of the isothiocyanate ligand ($\text{S2-Sn1-N2 } 152,63(12)^\circ$).

In the packing of the crystal the molecules are associated in *zig-zag* polymeric chains by bridging of the NCS^- ligand ($\text{NCS}\cdots\text{Sn } 4.02 \text{ \AA}$ vs. $\Sigma r_{\text{vdW}}(\text{S},\text{Sn}) 4.05 \text{ \AA}^{15}$) (Fig. 3.27).

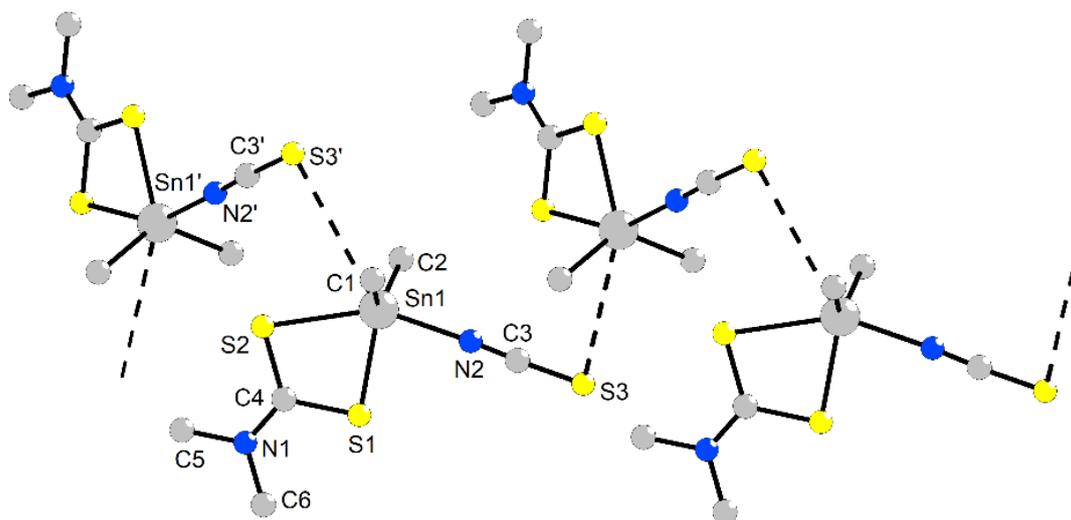


Fig. 3.27. Polymeric association in $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)(\text{NCS})$ (**17**)

The molecular structure of compound **22** is presented in Fig. 3.30. The coordination geometry around the tin atom was found to be distorted octahedral and it is determined by the

bidentate behavior of the dithiocarbamato ligand, the *C,N* chelating behavior of the [2-(Me₂NCH₂)C₆H₄] group and the two monodentate ligands, the methyl group and isothiocyanate group respectively. A strong N→Sn intramolecular interaction was observed, the interatomic distance having a value of 2.55(3) Å.

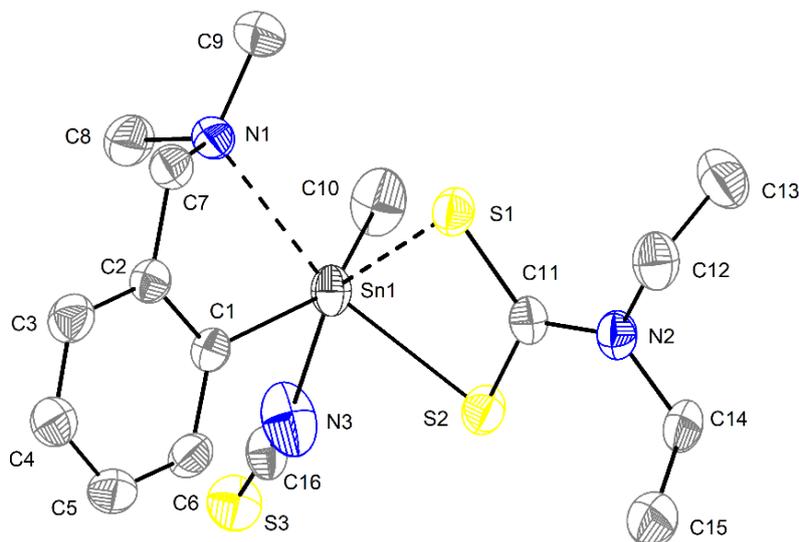


Fig. 3.30. Molecular structure of [2-(Me₂NCH₂)C₆H₄]MeSn(S₂CNEt₂)(NCS) (**22**). Hydrogen atoms not shown for clarity. Thermal ellipsoids are shown with 30% probability.

3.3. Conclusions

- Compounds **11** – **16** of the type R¹R²Sn(S₂CNR₂)Cl were obtained by reacting diorganotin(IV) dichlorides with sodium diorganodithiocarbamates in a 1:1 molar ratio.
- The treatment of compounds **11** – **16** with KSCN in a 1:1 molar ratio led to complexes **17** – **23**, of the type R¹R²Sn(S₂CNR₂)(NCS).
- Compounds **24** and **25**, R¹R²Sn(S₂CNR₂)₂ were obtained by reacting diorganotin(IV) dichlorides with sodium diorganodithiocarbamates in a 1:2 molar ratio.
- The prepared compounds were characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ¹¹⁹Sn). For compounds containing aryl groups with pendant arms, the ¹H and ¹³C NMR spectra do not suggest any N→Sn intramolecular coordination in solution. For the Me₂NCH₂ groups in compounds **21** – **23**, broad singlet signals were observed in the NMR spectra recorded at room temperature, thus suggesting that either these groups do not coordinate to the tin atom, or they are involved in a rapid fluxional process.
- The ¹H and the ¹³C NMR spectra for compounds **11** – **14** and **17** – **20**, with aliphatic groups bonded to the tin atom, showed the corresponding resonance signals

accompanied by $^1\text{H} - ^{119}\text{Sn}$ and $^{13}\text{C} - ^{119}\text{Sn}$ satellites, respectively. The C–Sn–C angle could be calculated based on the $^1\text{H} - ^{119}\text{Sn}$ and $^{13}\text{C} - ^{119}\text{Sn}$ coupling constants and a distorted trigonal bipyramidal coordination geometry could be attributed for these compounds in solution.

- The methyl and the ethyl groups found in the dithiocarbamate ligands were found to be equivalent at room temperature for all the compounds, with a single set of characteristic signals in the ^1H and ^{13}C NMR spectra, suggesting the bidentate behavior of these ligands in solution. For compound **25**, while the two dithiocarbamate groups are equivalent, the protons corresponding to the CH_2CH_3 groups are diastereotopic and showed two multiplet resonances (ABX_3 system) in the ^1H NMR spectrum at room temperature.

- The ^{119}Sn NMR spectra presented a single singlet signal for every studied compound, so that it does not suggest an isothiocyanato behavior of the SCN^- ligand.

- The IR spectra recorded for compounds containing the SCN^- ligand showed a very intense band at approx. 2050 cm^{-1} assigned to $\nu(\text{CN})$ stretching vibration and a band in the $754 - 798\text{ cm}^{-1}$ region corresponding to the $\nu(\text{CS})$, suggesting the isothiocyanato behavior of the SCN^- ligand in solid state.

- The mass spectra (ESI+) recorded for compounds **11 – 16** revealed a base peak with a m/z value (100%) corresponding to $[\text{M-Cl}]^+$, and for compounds **17 – 23** a m/z (100%) value corresponding to $[\text{M-SCN}]^+$.

- The molecular structures for compounds **17, 18, 22** and **25** were determined by single crystal X-ray diffraction studies. Distorted trigonal bipyramidal coordination geometry was found around the tin atom for compounds **17** and **18**. A closer look in the packing of the crystal revealed that the molecules are associated by NCS bridging groups between the tin atoms, thus forming polymeric chains.

- A distorted octahedral coordination geometry was found for compounds **22** and **25**; the coordination number of the tin atom increased to 6 in compound **22** and 7 in compound **25**, due to the *C,N* chelating behavior of the $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ group, by strong $\text{N} \rightarrow \text{Sn}$ intramolecular interactions.

- The dithiocarbamate ligand behaves as a bidentate ligand in all the investigated compounds, both in solution and in solid state.

- The thermal behavior of compounds **17, 18** and **25** was investigated by thermogravimetric analysis, the obtained curves indicating a continuous loss of mass in the temperature range of $150 - 350^\circ\text{C}$ through consecutive endothermic and exothermic processes.

The final products can be assimilated with SnS₂ and SnO₂, comparable with the existing literature data for other organotin(IV) dithiocarbamates.

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