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Solution behaviour and solid state structure of new main group (Sn, Pb, Te) compounds with organophosphorus ligands

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PhD Thesis Summary

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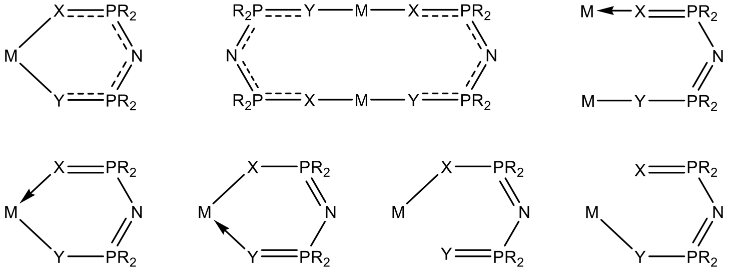
1 General introduction

Metal complexes containing inorganic (carbon-free) chelate rings are an important chapter of coordination chemistry, mainly due to the higher stability of the compounds containing chelate rings when compared to metal complexes with unidentate ligands and, also important, due to the derived applications of such species.[1]

The anions with the general formula $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se, Te) exhibit a large bite and a high flexibility. They are generally coordinated by both chalcogen atoms to the metal centre,[12] thus resulting in six-membered inorganic chelate rings ($MXYP_2N$). The coordination patterns observed in various metal complexes with dichalcogenoimidodiphosphinato ligands are displayed in **Scheme 1.1**.



Scheme 1.1 Coordination possibilities of dichalcogenoimidodiphosphinato ligands

Besides the above mentioned *monometallic biconnective* pattern, in some metal complexes also a *monometallic monoconnective* behaviour of the ligand was observed, in which only one of the two chalcogen atoms is coordinated to the metal centre. Other less common coordination patterns of these type of bidentate dichalcogenoimidodiphosphinato ligands are the *bimetallic biconnective* and the *bridging* patterns, which result in dimeric or polymeric associations, the *bimetallic triconnective* coordination, leading to twelve-membered carbon-free rings with transannular interactions, *X,N*- or *Y,N*-chelating coordination, which involves the nitrogen atom as well, *X,N,Y-monometallic triconnective* coordination pattern.

The studies reported in this work are based on the interest to investigate from structural point of view several main group organometallic complexes with tetraorganodichalcogenoimidodiphosphinato ligands and to complete with several not yet revealed important aspects the chemistry and coordination behaviour of this type of ligands. The studies are devoted to three classes of complexes:

1. Homo- and heteroleptic diorganotin(IV) complexes of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(R)Sn\{(EPPh_2)_2N\}][(EPPh_2)_2N]$ ($R = 2\text{-}(Me_2NCH_2)C_6H_4$, ${}^{n}Bu$; E = O, S, Se);

2. Di- and triorganolead(IV) complexes of types $Ph_2Pb(X)[(EPPh_2)_2N]$ (X = Cl, Br), $Ph_2Pb[(EPPh_2)_2N]_2$ and $R_3Pb[(EPPh_2)_2N]$ (R = Me, Ph; E = S, Se);

3. Triorganotelluronium(IV) complexes of type $R_nPh_{3-n}TeL$, where $R = 2\text{-}(Me_2NCH_2)C_6H_4$; n = 1-3; L = S_2PMe_2, $(XPR_2)(YPR_2')N$ (X, Y = O, S, Se; R, R' = Me, Ph, OEt) and $(SPR_2)(O_2SR')N$ (R = Ph, OEt, R' = Me, C_6H_4Me-4, C_6H_4Cl-4). The complexes with the dimethyldithiophosphinato ligand and those with ligands having a SPNSO skeleton were studied in order to see any influence on the structure of these tellurium(IV) compounds when the flexibility of the organophosphorus ligand is reduced.

This work comprises, besides the original contributions, an overview on the organotellurium, organotin and organolead complexes with dichalcogenoimidodiphosphinato ligands of type $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se; R, R' = alkyl, aryl, alkoxy, aryloxy). Considerations about the synthesis, properties, coordination behaviour and structure of selected organometallic complexes with relevance for a comparison with the compounds reported for the first time in this work are summarized in the introductory part of this thesis.

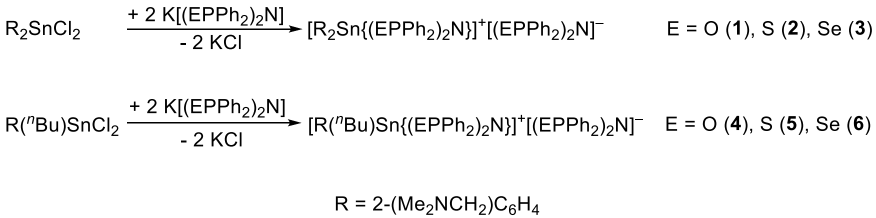
3 Original contributions

3.1 Organotin(IV) compounds

3.1.1 Results and discussion

Diorganotin(IV) compounds with organophosphorus ligands

New diorganotin(IV) complexes with chelating dichalcogenoimidodiphosphinato ligands were synthetized by reacting R_2SnCl_2 or $R(^nBu)SnCl_2$ ($R = 2\text{-}(Me_2NCH_2)C_6H_4$) with the potassium salts of the ligands in a 1:2 molar ratio, as depicted in **Scheme 3.1.1**. All the reactions were carried out in dichloromethane or in dichloromethane-methanol mixtures.



$$R_2SnCl_2 \xrightarrow[-\ 2\ KCl]{+\ 2\ K[(EPPh_2)_2N]} [R_2Sn\{(EPPh_2)_2N\}]^+[(EPPh_2)_2N]^- \qquad E = O\ (\mathbf{1}),\ S\ (\mathbf{2}),\ Se\ (\mathbf{3})$$

$$R(^nBu)SnCl_2 \xrightarrow[-\ 2\ KCl]{+\ 2\ K[(EPPh_2)_2N]} [R(^nBu)Sn\{(EPPh_2)_2N\}]^+[(EPPh_2)_2N]^- \qquad E = O\ (\mathbf{4}),\ S\ (\mathbf{5}),\ Se\ (\mathbf{6})$$

$$R = 2\text{-}(Me_2NCH_2)C_6H_4$$

Scheme 3.1.1 Synthesis of compounds **1-6**

Compounds **1-6** were isolated as microcrystalline, colourless (**1**, **2**, **4** and **5**) or yellow powders (**3** and **6**). An ionic structure of type $[RR'Sn\{(EPPh_2)_2N\}]^+[(EPPh_2)_2N]^-$ is suggested in solution by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{119}Sn and ^{77}Se as appropriate), ESI+ and ESI– mass spectrometry and molar conductivity.

The ^1H and ^{13}C NMR spectra of compounds **1-3** suggest the equivalence of the organic groups attached to tin. For derivative **1** two well resolved sharp signals were observed in the aliphatic region of the ^1H NMR spectrum, which correspond to the NCH_3 groups, while for complexes **2** and **3** very broad resonances were assigned to the methyl groups attached to the nitrogen (**Figure 3.1.1**). AB spin systems were observed for the CH_2N protons in the ^1H NMR spectra of **1-3**, thus suggesting the existence of N→Sn intramolecular interactions in solution. For the protons corresponding to tetraphenyldichalcogenoimidodiphosphinato ligands three sets of multiplet signals could be identified in a 1:1:2 integral ratio.

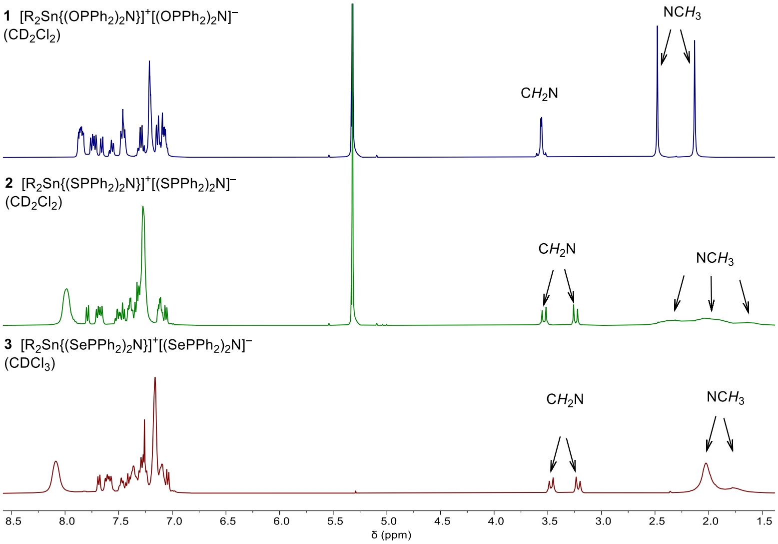


Figure 3.1.1 ^{1}H NMR spectra of compounds **1-3** (R = 2-(Me_2NCH_2)C_6H_4)

The signals with higher intensities which corresponds to the organophosphorus ligand in the ^{1}H NMR spectra of compounds **1-3** can be assigned to the free anionic ligand, while the two sets of signals with lower intensities could be assigned for two sets of non-equivalent phenyl groups attached to the phosphorus atoms in the ligand bonded to tin.

In the ^{31}P NMR spectra of the diorganotin(IV) derivatives two resonances were identified for each compound (**Figure 3.1.2**), a sharp one, accompanied by ^{119}Sn satellites in **1**, assigned to the equivalent phosphorus atoms in the ligand attached to tin, and a broad one, assigned to the two equivalent phosphorus atoms in the organophosphorus anion. In the ^{31}P NMR spectrum of **1** the two resonances are well separated, while in case of compound **2** they are very close (δ 35.7 and 37.00 ppm) and in case of compound **3** the sharp resonance signal has practically the same *δ* value (28.5 ppm) as the centre of the very broad second resonance. The presence of tin-phosphorus satellites around the sharp signal in the ^{31}P NMR spectrum of compound **1** and the equivalence of the two phosphorus atoms in the bonded ligand unit confirm the chelating coordination behaviour of the ligand attached to tin in solution. The resonance signal in the spectrum of compound **3** is surrounded by selenium satellites with a coupling constant of 490 Hz. The chemical shifts of the resonances assigned to the organophosphorus anions are close to those observed for the corresponding potassium salt.

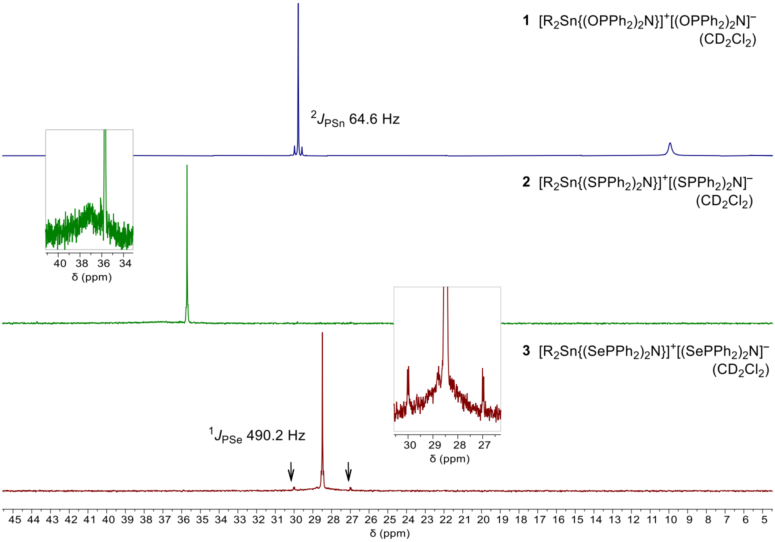


Figure 3.1.2 ^{31}P NMR spectra of compounds **1-3** (R = 2-$(Me_2NCH_2)C_6H_4$)

For compound **1** the ^{31}P-^{1}H HMQC NMR spectrum show three sets of resonances for the *ortho*-phenyl protons in the ^{1}H NMR spectrum which give couplings with the two signals in the ^{31}P NMR spectrum, consistent with the non-equivalent phenyl groups at each phosphorus in the ligand attached to tin (two multiplet resonances in a 1:1 molar ratio) and one multiplet resonance corresponding to the equivalent phenyl groups in the organophosphorus anion (**Figure 3.1.3**).

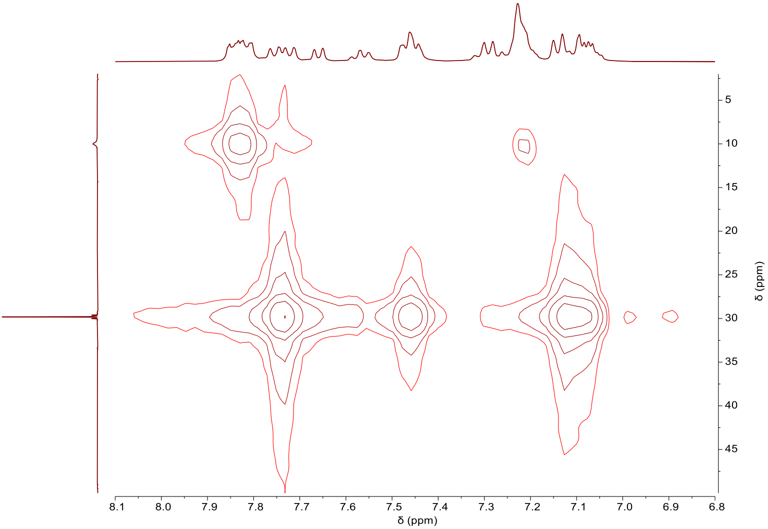


Figure 3.1.3 Details of the ^{31}P-^{1}H HMQC NMR spectrum of $[R_2Sn\{(OPPh_2)_2N\}]^+[(OPPh_2)_2N]^-$ (**1**) in CD_2Cl_2 (R = 2-(Me_2NCH_2)C_6H_4)

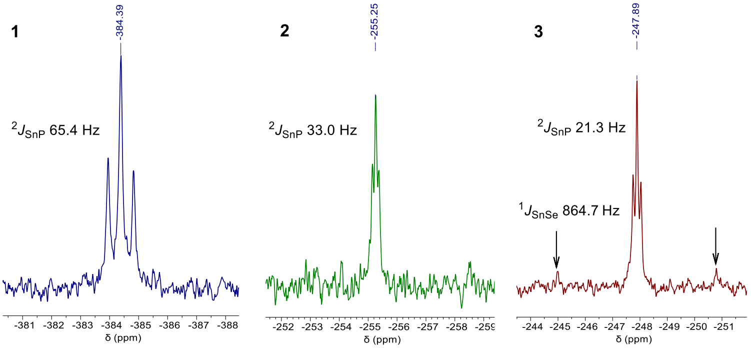


Figure 3.1.4 ^{119}Sn NMR spectra of compounds **1-3** (CD_2Cl_2)

The ^{119}Sn resonances for compounds **1-3** appear as triplets due to the ^{31}P-^{119}Sn coupling (**Figure 3.1.4**). It can be observed in the case of compound **1** that the ^{31}P-^{119}Sn coupling constants in the ^{31}P and ^{119}Sn NMR spectra are almost the same, 64.6 and 65.4 Hz, respectively. For compound **3** also the ^{77}Se-^{119}Sn coupling is visible on the ^{119}Sn NMR spectrum. The value of the chemical shifts of the resonances in the ^{119}Sn NMR spectra of **2** and **3** is close to the chemical shift for the starting $[2-(Me_2NCH_2)C_6H_4]_2SnCl_2$ (-258.4 ppm in CD_2Cl_2), thus indicating the presence of hexacoordinated tin in solution. The triplet resonance found in the ^{119}Sn NMR spectrum of **1** is shifted in comparison with the starting material and complexes **2** and **3**, but it is comparable with similar hexacoordinated diorganotin(IV) derivatives with *O*,*O*-chelating ligands (*i.e.* -365 ppm for $Me_2Sn(acac)_2$[38]).

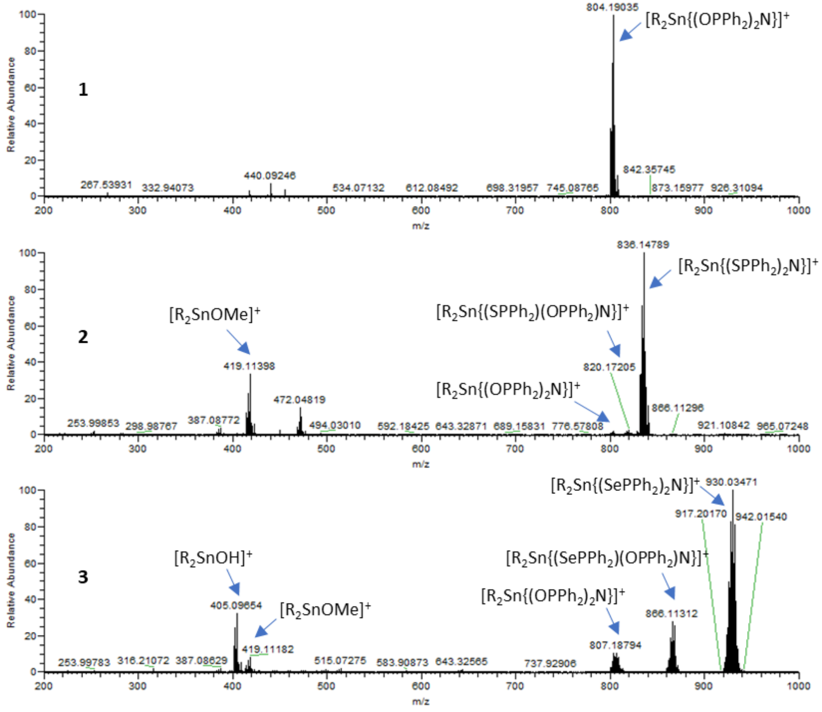


Figure 3.1.5 ESI+ mass spectra of compounds **1-3** recorded after 24 hours

The ESI+ mass spectra of compounds **1-3** show for their solutions in methanol the $[\{2-(Me_2NCH_2)C_6H_4\}_2Sn\{(EPPh_2)_2N\}]^+$ cations as base peaks. Surprisingly, compounds **2** and **3** showed a low stability in methanol, as the solution of these compounds showed in the ESI+ mass spectra recorded after 24 hours (**Figure 3.1.5**), besides the peak of the $[\{2-(Me_2NCH_2)C_6H_4\}_2Sn\{(EPPh_2)_2N\}]^+$ cation, also peaks of lower intensity for cations formed by reactions with methanol or by exchanging sulphur or selenium with oxygen, e.g. $[R_2Sn\{(OPPh_2)(EPPh_2)N\}]^+$, $[R_2Sn\{(OPPh_2)_2N\}]^+$, $[R_2SnOMe]^+$ and $[R_2SnOH]^+$ (R = 2-(Me_2NCH_2)C_6H_4, E = S, Se). The ESI– mass spectra of **1-3** show as base peaks only the $[(EPPh_2)_2N]^-$ anion for each diorganotin(IV) complex.

For the R(^{n}Bu)Sn(IV) derivatives **4-6** (R = 2-(Me_2NCH_2)C_6H_4) in the multinuclear (^{1}H, ^{13}C, ^{31}P, ^{77}Se (for **6**) and ^{119}Sn) NMR spectra broad resonances can be observed, thus suggesting a dynamic behaviour in solution. All the expected resonances could be assigned in the aliphatic region, both in the ^{1}H and the ^{13}C NMR spectra, but in the aromatic region some of the signals are overlapped.

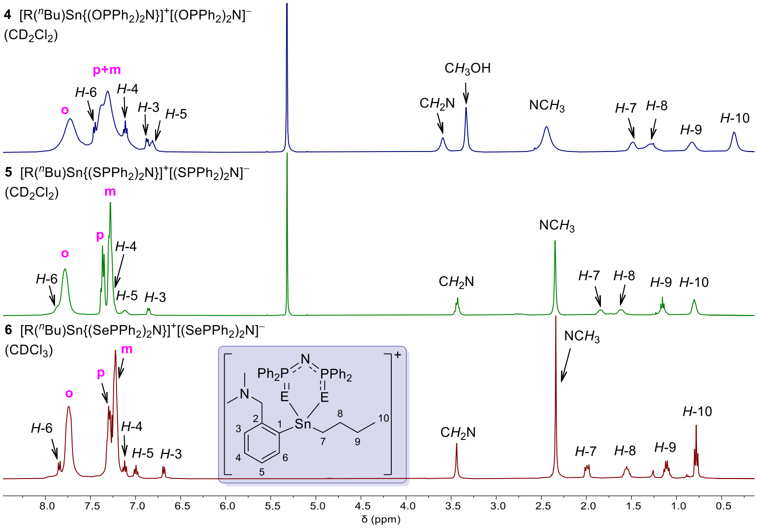


Figure 3.1.6 ^{1}H NMR spectra of compounds **4-6** (R = 2-(Me_2NCH_2)C_6H_4)

By contrast with compounds **1-3**, in the aliphatic region of the ^{1}H NMR spectra of **4-6** recorded at room temperature (**Figure 3.1.6**) there is no evidence for the intramolecular coordination of the nitrogen to tin, as just slightly broad singlet resonances were observed for the methylene and methyl protons in the pendant arms.

In the ^{31}P NMR spectra of **4-5** two broad signals were observed, while in the ^{31}P NMR spectrum of **6** just one broad resonance is present. It is possible that the signal corresponding to the phosphorus atoms in the cation is overlapped with the signal for the phosphorus atoms in the anion, as appeared also in the case of compound **3**.

In the ^{77}Se NMR spectra of **3** and **6** it can be observed that the chemical shift for the well resolved doublet of **3** (-72 ppm) is similar with the chemical shift of the very broad resonance in the spectrum of **6** (-76 ppm).

These compounds display one broad resonance in their ^{119}Sn NMR spectra (**Figure 3.1.7**), which are all shifted in comparison with the signal for the starting material (-101.2 ppm for $[2\text{-}(Me_2NCH_2)C_6H_4](^n Bu)SnCl_2$ in $CDCl_3$). By comparing the ^{119}Sn NMR spectra of **1-3** and **4-6**, it can be observed that the chemical shifts are of the same magnitude: -384.4, -255.3 and -247.9 ppm for **1-3** and -370.5, -213.1 and -238.1 ppm for **4-6**.

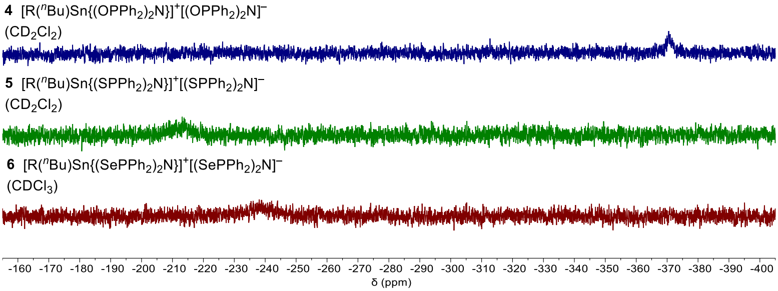


Figure 3.1.7 ^{119}Sn NMR spectra of compounds **4-6** ($R = 2\text{-}(Me_2NCH_2)C_6H_4$)

The ESI+ mass spectra of freshly prepared solutions in methanol of **4-6** show as base peak the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^n Bu)Sn\{(EPPh_2)_2N\}]^+$ cations, while the ESI– mass spectra show as base peak the $[(EPPh_2)_2N]^-$ anions, respectively (E = O, S, Se). Similarly with compounds **2** and **3**, in the ESI+ mass spectra of **5** and **6** peaks suggesting reactions with MeOH were observed after 24 hours, *i.e.* $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^n Bu)SnOH]^+$ in **5**, [{2-

$(Me_2NCH_2)C_6H_4\}(^nBu)SnOMe]^+$ and $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^nBu)SnOH]^+$ in **6**, thus suggesting the instability of these complexes in methanol.

For all compounds the molar conductivity was determined for freshly prepared solutions in methanol (10^{-4} M solutions). The molar conductivity values were observed in the range 84-174 $S{\cdot}cm^2{\cdot}mol^{-1}$, thus confirming the ionic structure of the diorganotin(IV) complexes **1-6** and their behaviour as 1:1 electrolytes.[68]

The absence of stretching vibrations in the IR spectra of **1-3** and **5**, in the regions 950-900 and 2700-2600 cm^{-1}, characteristic for the $\nu_{as}(P_2NH)$ vibration, suggest the presence of the deprotonated form of the ligands in these complexes.[12] In addition, strong absorption bands can be assigned to the asymmetric $\nu_{as}(P_2N)$ stretching vibration in the region 1250-1200 cm^{-1}.

Solid state structures

For the homoleptic diorganotin(IV) complexes **2** and **3** the solid state structures were determined by single crystal X-ray diffraction. The discrete $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sn\{(EPPh_2)_2N\}]^+$ cation and the $[(SPPh_2)_2N]^-$ anion in the crystal of **2** are displayed on **Figure 3.1.8**.

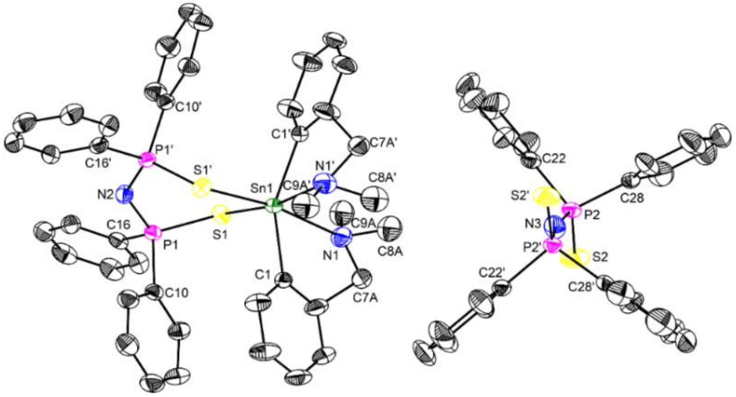
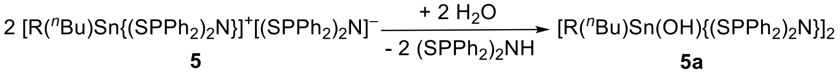


Figure 3.1.8 Ortep-like representation with 30% probability ellipsoids of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sn\{(SPPh_2)_2N\}]^+[(SPPh_2)_2N]^-$ in the crystal of **2**. Hydrogen atoms are omitted for clarity. Symmetry equivalent atoms (*x*, *y*, -*z*) are given by “prime”.

A distorted octahedral environment was found for the tin(IV) atom in the two compounds, which have similar structures. Both aryl groups attached to tin behave as *C,N*-chelating moieties, and for one organophosphorus ligand an *E,E*-bidentate coordination behaviour was observed (E = S, Se), thus resulting in *12-Sn-6* hypercoordinated cationic species in each compound.[69] The N→Sn interatomic distances are 2.594 Å in **2** and 2.610 Å in **3**, much shorter than the sum of the van der Waals radii of the nitrogen and tin (Σr_{vdW}(N,Sn) 4.08 Å[53]) and in the range found for other organotin(IV) compounds bearing such organic groups (2.39-3.52 Å[70–74]).

In the organophosphorus ligands coordinated to the tin atom the phosphorus-chalcogen interatomic distances are between the values corresponding to double and single bonds. In the counter ion the phosphorus-chalcogen bonds are better described as double bonds. The phosphorus-nitrogen interatomic distances suggest delocalization of the π electrons on the P–N–P fragment. The six-membered SnS_2P_2N and $SnSe_2P_2N$ rings in the cations have boat conformations with S1/Se1 and P1' in apices.

The attempts to obtain single crystals for compounds **4-6** were unsuccessful, but the solid state structure of the hydrolysis product $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^{n}Bu)Sn(OH)\{(EPPh_2)_2N\}]_2$ (**5a**), which was formed during the crystallization of **5** from a MeOH/hexane mixture, was determined instead. The hydrolysis product was formed probably according to the process depicted in **Scheme 3.1.2**.



$$2\,[R(^{n}Bu)Sn\{(SPPh_2)_2N\}]^{+}[(SPPh_2)_2N]^{-} \xrightarrow[-\,2\,(SPPh_2)_2NH]{+\,2\,H_2O} [R(^{n}Bu)Sn(OH)\{(SPPh_2)_2N\}]_2$$

5 **5a**

Scheme 3.1.2 Formation of the hydrolysis product **5a** (R = $2\text{-}(Me_2NCH_2)C_6H_4$)

The thermal ellipsoids representation of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^{n}Bu)Sn(OH)\{(SPPh_2)_2N\}]_2$ in the crystal of **5a** is depicted in **Figure 3.1.9**. Compound **5a** has no more an ionic structure and the organophosphorus ligand presents a monodentate coordination behaviour.

Similarly with the structures of **2** and **3**, the 2-(Me_2NCH_2)C_6H_4 group in **5a** behaves as a *C,N*-chelating moiety, with the N–Sn bond length of 2.489(8) Å, smaller than in the previously presented solid state structures for **2** and **3**. The Sn1–S1 bond (2.747(2) Å) is longer than the tin-sulphur interatomic distances in the crystal of compounds **2** and **3**. The second sulphur atom in **5a** is no longer in the coordination sphere of tin, while the S2–Sn1 interatomic distance is 4.51 Å, greater than $\Sigma r_{vdW}(Sn,S) = 4.31$ Å.[53] The molecules are associated in dimeric units by bridging OH groups (Sn1–O1 2.101(5) Å and Sn1–O1' 2.157(5) Å), thus a *12-Sn-6* hypercoordinated species is formed. Each tin atom has a distorted octahedral coordination geometry. The central Sn_2O_2 core is planar and both the 2-(Me_2NCH_2)C_6H_4 groups and the $(Ph_2PS)_2N^-$ ligands are placed *trans* each other with respect to the planar Sn_2O_2 core. The intramolecular N→Sn coordination determines planar chirality in each molecule and, as a consequence, the dimers consist of R_{N1} and S_{N1} isomers.

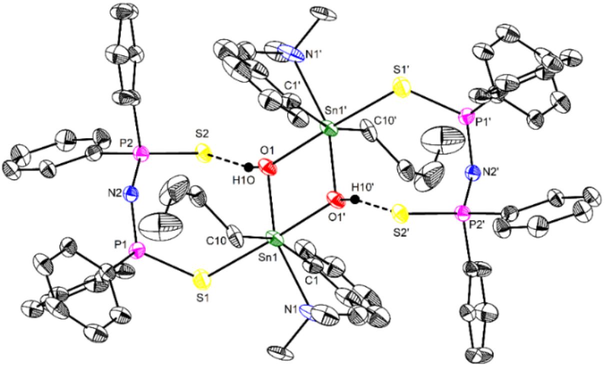


Figure 3.1.9 Thermal ellipsoids (30% probability) representation of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^nBu)Sn(OH)\{(SPPh_2)_2N\}]_2$ in the crystal of **5a**. Hydrogen atoms are omitted for clarity. Symmetry equivalent atoms (*1-x, 1-y, -z*) are given by "prime".

3.1.2 Conclusions

- Three homoleptic and three heteroleptic diorganotin(IV) complexes of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(R)Sn\{(EPPh_2)_2N\}]^+[(EPPh_2)_2N]^-$ (R = 2-

$(Me_2NCH_2)C_6H_4$, E = O (**1**), S (**2**), Se (**3**); R = ^{n}Bu, E = O (**4**), S (**5**), Se (**6**)) were synthetized and their identity and structure were assigned by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, ^{77}Se and ^{119}Sn), mass spectrometry, molar conductivity and IR spectroscopy.

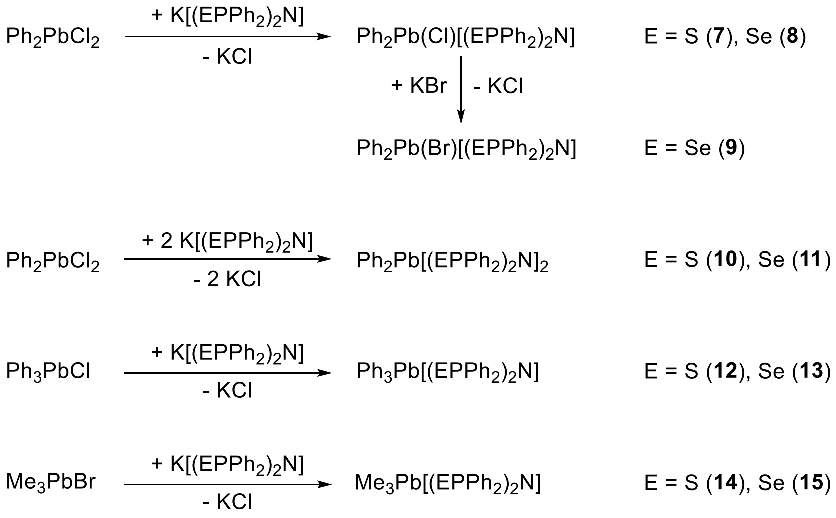
- Compounds **1-6** present an ionic behaviour in solution, with one organophosphorus ligand coordinated to tin in a bidentate fashion, thus resulting cations of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(R)Sn\{(EPPh_2)_2N\}]^+$, while the other ligand remains as a $[(EPPh_2)_2N]^-$ counter ion in solution.
- The presence of an AB spin system for the CH_2N protons in the ^{1}H NMR spectra of compounds **1-3** suggests the intramolecular N→Sn coordination of both pendant arms in the equivalent $2\text{-}(Me_2NCH_2)C_6H_4$ groups, while in the spectra of derivatives **4-6** no such evidence for intramolecular coordination in solution was observed.
- In the aromatic region of the ^{1}H NMR spectra of **1**-**3** resonances corresponding to three types of phenyl groups were identified in a 1:1:2 ratio of integrals, thus suggesting non-equivalent phenyl groups attached to each of the two equivalent phosphorus atoms in the ligand bonded to tin.
- For the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^nBu)Sn\{(EPPh_2)_2N\}]^+[(EPPh_2)_2N]^-$ derivatives **4-6** in all the NMR spectra broad resonances were observed at room temperature, thus suggesting a dynamic behaviour in solution.
- Single crystal X-ray diffraction studies revealed an octahedral environment about the tin atom in the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sn\{(EPPh_2)_2N\}]^+$ (E = S (**2**), Se (**3**)) cations, which can be described as *12-Sn-6* hypercoordinated species.
- The attempts to grow single crystals of **5** resulted in the hydrolysis product $[\{2\text{-}(Me_2NCH_2)C_6H_4\}(^nBu)Sn(OH)\{(EPPh_2)_2N\}]_2$ (**5a**) for which the solid state structure revealed a monodentate behaviour of the dithioimidodiphosphinato ligand and a dimeric association through bridging OH groups, thus resulting in a *12-Sn-6* hypercoordinated species.

3.2 Organolead(IV) compounds

3.2.1 Results and discussion

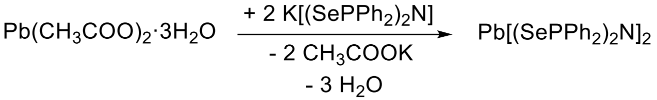
Di- and triorganolead(IV) compounds with organophosphorus ligands

New diorgano- and triorganolead(IV) compounds were prepared by reacting Ph_2PbCl_2, Ph_3PbCl or Me_3PbBr with the corresponding potassium salts of the tetraorganodichalcogenoimidodiphosphinato ligands in a 1:1 or 1:2 molar ratio, as depicted in **Scheme 3.2.1**. The reactions were carried out in dichloromethane or chloroform and the desired products were obtained in good yields.



Scheme 3.2.1 Synthesis of compounds **7-15**

The redistribution product $Pb[(SePPh_2)_2N]_2$ (**16**) resulted during the procedures used for the isolation of $Me_3Pb[(SePPh_2)_2N]$ (**15**). It was subsequently synthetized by employing a literature procedure[10] based on the reaction of an aqueous solution of lead acetate trihydrate with $K[(SePPh_2)_2N]$, in methanol (**Scheme 3.2.2**).

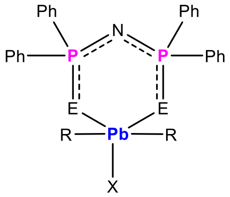


$$Pb(CH_3COO)_2\cdot 3H_2O \xrightarrow[\substack{-\ 2\ CH_3COOK \\ -\ 3\ H_2O}]{+\ 2\ K[(SePPh_2)_2N]} Pb[(SePPh_2)_2N]_2 \qquad (\mathbf{16})$$

Scheme 3.2.2 Synthesis of compound **16**

The desired compounds were isolated as microcrystalline, yellowish (**7**, **11**, **13**, **14**, **15**, **16**), light orange (**8**, **9**) or colourless species (**10**, **12**). All the products were characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, ^{209}Pb and ^{77}Se as appropriate) and APCI+ mass spectrometry.

The assignments of the ^{1}H and ^{13}C chemical shifts on the figures were made according to **Scheme 3.2.3**. The proton or carbon atoms from the phenyl groups attached to lead are depicted with blue (***i***, ***o***, ***m***, ***p***) and those from the phenyl groups bonded to the phosphorus atoms are noted with magenta (***i***, ***o***, ***m***, ***p***).



Scheme 3.2.3 Scheme for NMR assignments of compounds **7-15**

The NMR spectra of the obtained organolead(IV) complexes are consistent with the formation of only one major product in solution. The ^{1}H and ^{13}C NMR spectra of compounds **7-15** suggest the equivalence of the two or three phenyl or methyl groups attached to lead and also the equivalence of the four phenyl groups bonded to the phosphorus atoms.

The ^{1}H NMR spectra of compounds **7-9** are very similar, showing the expected resonances for the phenyl groups attached to the lead and to the phosphorus atoms, respectively. Thus, in the aromatic region of the ^{1}H NMR spectra (**Figure 3.2.1**) for the compounds of type $Ph_2Pb(X)[(EPPh_2)_2N]$ (**7-9**), four multiplet resonance signals can be observed, three resonances belonging to the aromatic protons of the phenyl groups being partially overlapped. The doublet resonance signals for the *ortho* protons of the phenyl groups attached to lead are surrounded by lead satellites.

In the case of the compounds of type $Ph_2Pb[(EPPh_2)_2N]_2$ (**10-11**) the ^{1}H NMR spectra (**Figure 3.2.1**) present six multiplet resonances with the expected multiplicities due to ^{1}H-^{1}H and ^{1}H-^{31}P couplings, corresponding to the protons attached to the phenyl groups. The doublet resonance signals corresponding to the *ortho* protons of the phenyl groups bonded to lead in **10-11** are more deshielded comparing to the resonances corresponding to the same protons in compounds **7-9**. The $^{3}J_{HPb}$ coupling constants have higher values in the ^{1}H NMR spectra of compounds **10-11**, $^{3}J_{HPb}$ 206.4 and 203.7 Hz, comparing to those observed for compounds **7-9**, 177.0, 170.5 and 171.2 Hz, respectively.

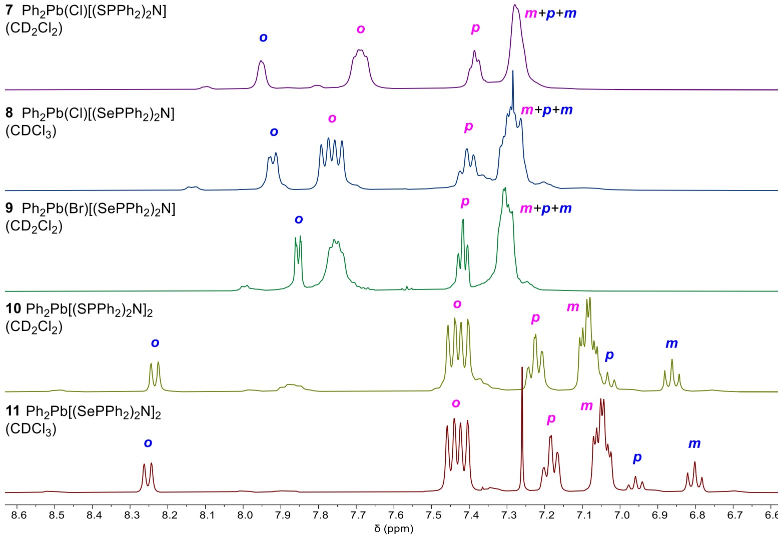


Figure 3.2.1 Aromatic region of the ^{1}H NMR spectra of compounds **7-11**

In the ^{31}P NMR spectra of compounds **7-11** singlet resonance signals can be observed, which indicate the equivalence in solution of the two phosphorus atoms in the organophosporus ligand. The ^{31}P chemical shifts in the ^{31}P NMR spectra are congruent with the presence of the deprotonated form of the organophosphorus ligand. Selenium satellites are accompanying the signals in the spectra of selenium containing complexes, with phosphorus-selenium coupling constants of 527.3, 525.3 and 580.4 Hz for compounds **8**, **9** and **11**, respectively.

The ^{77}Se NMR spectra of compounds **8** and **9** show doublet resonance signals at -17.6 and 33.1 ppm, with coupling constants of 570.6 and 534.8 Hz, respectively, due to the coupling with phosphorus. The presence of only one resonance signal in each of these spectra are showing the equivalence of the two chalcogen atoms in the organophosphorus ligand and suggest the bidentate, chelating behaviour in solution. The chemical shifts in the ^{77}Se NMR spectra are again consistent with the deprotonated form of the ligand.

The chemical shifts in the ^{207}Pb NMR spectra of compounds **7-10** have different values comparing to the chemical shift for the starting dichloride, Ph_2PbCl_2. Generally, the increase of the lead coordination number is followed by the increase of nuclear shielding of ^{207}Pb nucleus in the ^{207}Pb NMR spectra.[77,78] This tendency can be observed in the case of compounds **7-10**. The magnitude of the chemical shifts for compounds **7-9** indicates the existence of five-coordinate complexes in solution, while the chemical shift in ^{207}Pb NMR spectrum of compound **10** is characteristic to a six-coordinate lead(IV) compound. Thus, it can be concluded that the chelating ligands in these complexes have a bidentate coordination behaviour in solution.

The aliphatic region of the ^{1}H NMR spectra of the $Me_3Pb(IV)$ derivatives (**Figure 3.2.2**) show singlet resonances for the methyl protons surrounded by lead satellites. In the aromatic region two sets of multiplet signals can be observed, the resonances corresponding to the protons in the *meta* and *para* positions being overlapped.

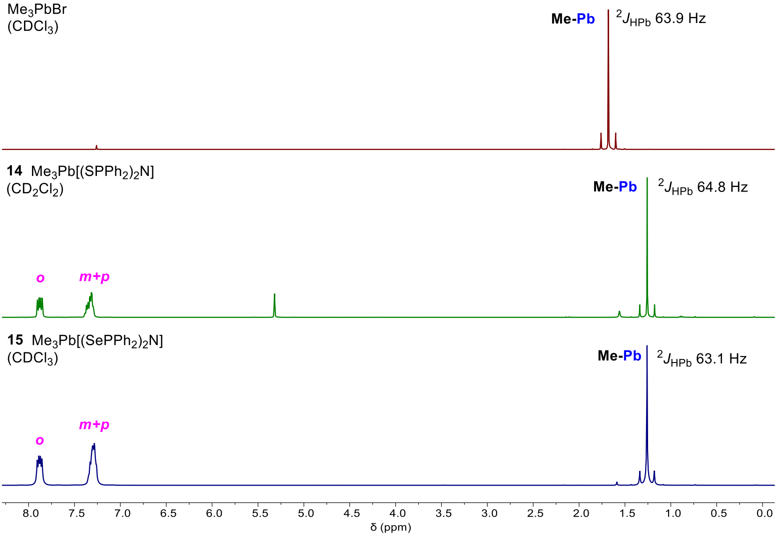


Figure 3.2.2 ^{1}H NMR spectra of compounds **14-15** and Me_3PbBr

In the ^{31}P NMR spectra of the triphenyl- and trimethyllead(IV) derivatives **12-15** singlet resonances were observed, indicating the equivalence of the two phosphorus atoms in each compound. For compound **14** a broad resonance of high intensity is observed in the ^{31}P NMR spectrum.

In the ^{77}Se NMR spectrum of $Ph_3Pb[(SePPh_2)_2N]$ a very broad resonance was detected at -62.3 ppm and for $Me_3Pb[(SePPh_2)_2N]$ a well resolved doublet resonance can be observed with a chemical shift of -72.4 ppm (**Figure 3.2.3**).

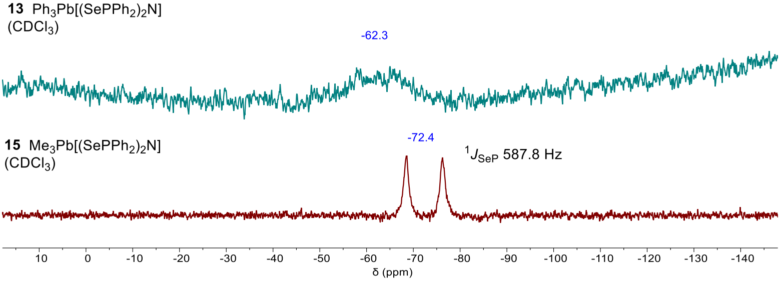


Figure 3.2.3 ^{77}Se NMR resonances in the spectra of compounds **13** and **15**

The range of the chemical shifts in the ^{207}Pb NMR spectra of compounds **12-15** (**Figure 3.2.4**) is specific for five-coordinate triorganolead(IV) complexes. Thus, an isobidentate coordination behaviour of the dichalcogenoimidodiphosphinato ligands can be predicted in solution.

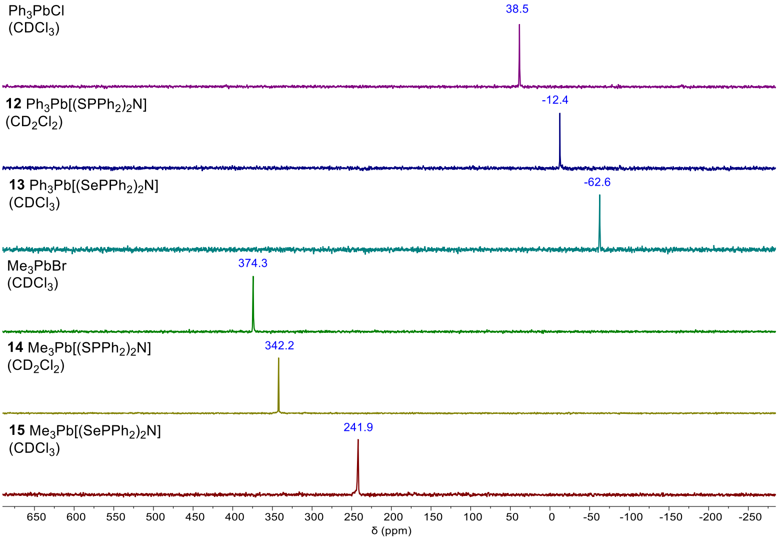


Figure 3.2.4 ^{207}Pb NMR spectra of compounds **12-15** and the corresponding starting materials

For three compounds variable low temperature ^{1}H and ^{31}P NMR spectra were recorded in deuterated dichloromethane (**Figure 3.2.5**). In the ^{31}P NMR spectra of $Ph_2Pb(Cl)[(SePPh_2)_2N]$ and $Me_3Pb[(SePPh_2)_2N]$ no significant changes could be observed at -78 or -70 °C, respectively, just a broadening of the singlet resonances with the decrease of the temperature, which indicate a very fast fluxional process in solution. In the case of $Ph_3Pb[(SePPh_2)_2N]$ (**13**) the sharp singlet resonance observed in the ^{31}P NMR spectrum recorded at room temperature splits in two broad resonances at -78 °C. A free enthalpy of 10.06 kcal/mol was calculated[79] at the coalescence temperature of -45 °C for the dynamic process suffered by compound **13**.

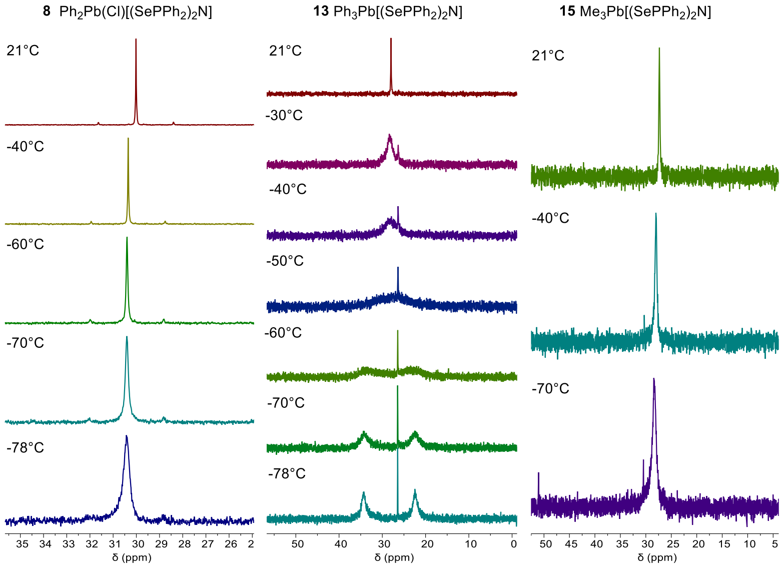
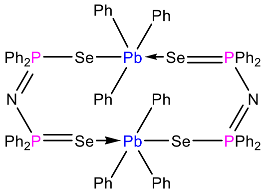


Figure 3.2.5 VT ^{31}P NMR spectra of compounds **8**, **13** and **15** in CD_2Cl_2

For a better elucidation of the structure of compound **13** in solution, diffusion-molecular weight (D-MW) analysis was performed in C_6D_6. The experimental molecular weight obtained for $[Ph_3Pb\{(SePPh_2)_2N\}]_n$ is 1916.05 g/mol. This value corresponds to the molecular weight of the dimer $[Ph_3Pb\{(SePPh_2)_2N\}]_2$ (expected MW 1961.68 g/mol), with an error of 2.3%.

Based on these results (VT NMR and diffusion NMR) a dimeric structure for compound **13** is proposed with two non-equivalent phosphorus atoms (**Scheme 3.2.4**). The diselenoimidodiphosphinato ligand acts as a bimetallic biconnective unit, with an unisobidentate coordination to the two Ph_3Pb fragments.



Scheme 3.2.4 Proposed dimeric structure for compound **13** in solution

The organolead(IV) complexes with organophosphorus ligands described in this chapter exhibit low stability and endure decomposition on standing in air or in solution. The decomposition processes in solution for some of the selenium containing compounds were monitored by using ^{1}H, ^{31}P and ^{207}Pb NMR spectroscopy and mass spectrometry, and some decomposition products could be identified.

The NMR spectra of the freshly prepared samples are consistent with the formation of the desired products. To investigate the decomposition pathways the samples were monitored during a range of time by NMR spectroscopy. A higher stability of the organolead(IV) derivatives was observed for the NMR samples prepared in CD_2Cl_2 in comparison to the samples in $CDCl_3$. This might be due to the presence of the hydrogen chloride in deuterated chloroform.

The decomposition of the selenium containing trimethyllead(IV) derivative could be easily monitored also by ^{1}H NMR spectroscopy. In the ^{1}H spectra recorded by time for compound **15** the formation of Me_4Pb and the alkylation product of the organophosphorus ligand could be detected (**Figure 3.2.6**). The presence of the decomposition products in the NMR tube is confirmed also by the ^{31}P, ^{77}Se and ^{207}Pb NMR spectra. In the ^{31}P NMR spectrum (**Figure 3.2.7**), besides the two doublets for $(MeSePPh_2)(SePPh_2)N$[75] (δ = 22.5 ppm, MeSeP, $^{2}J_{PP}$ 7.3 Hz, $^{1}J_{PSe}$ 406.4 Hz and δ = 35.0 ppm, SeP, $^{2}J_{PP}$ 5.9 Hz, $^{1}J_{PSe}$ 707.2 Hz), a singlet resonance surrounded by selenium satellites was observed at a chemical shift δ = 29.7 ppm ($^{1}J_{PSe}$ 567.8 Hz), which corresponds to $Pb[(SePPh_2)_2N]_2$.[10]

In the ^{77}Se NMR spectrum of the freshly prepared sample of compound **15** a doublet resonance was observed at -73.5 ppm ($^{1}J_{SeP}$ 585.2 Hz), but in the spectrum recorded after nine days for the same sample this signal was no more detected and three other doublets appeared at the δ chemical shifts of -146.4 and 140.8 ppm, corresponding to the methylated organophosphorus ligand ($^{1}J_{SeP}$ 707.5 and 405.8 Hz, respectively), and at -17.2 ppm for the lead(II) derivative ($^{1}J_{SeP}$

561.8 Hz). Two signals are present in the ^{207}Pb NMR spectrum after decomposition of $Me_3Pb[(SePPh_2)_2N]$, one at the chemical shift δ = 6.5 ppm, which is assigned to Me_4Pb, and the second one at 1753.2 ppm corresponding to $Pb[(SePPh_2)_2N]_2$.

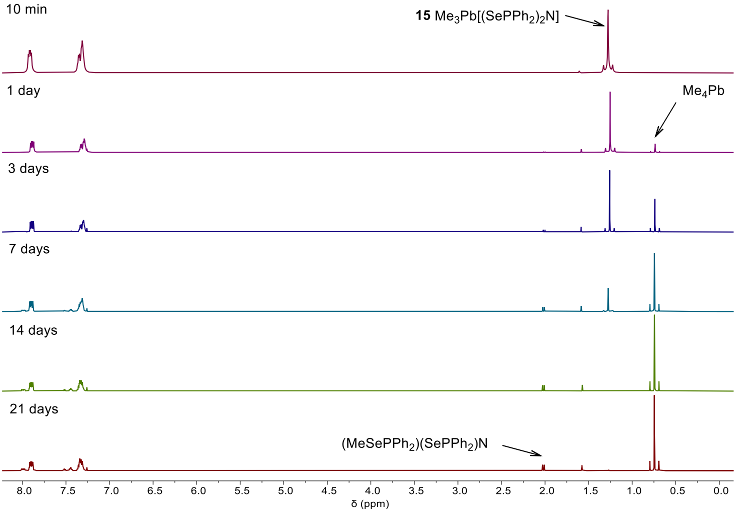


Figure 3.2.6 Time dependent ^{1}H NMR spectra of **15** in $CDCl_3$

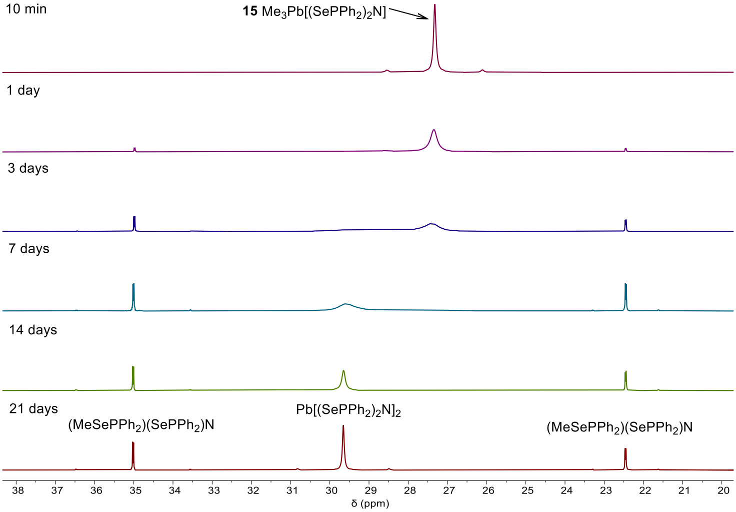


Figure 3.2.7 Time dependent ^{31}P NMR spectra of **15** in $CDCl_3$

Solid state structures

The molecular structures of $Ph_2Pb(Br)[(SePPh_2)_2N]$ (**9**) and $Ph_2Pb[(SePPh_2)_2N]_2$ (**13a**) were determined by single crystal X-ray diffraction. The single crystals suitable for investigation were obtained by slow diffusion using dichloromethane/hexane and chloroform/hexane mixtures for compounds **9** and **13a**, respectively. Complex **13a** was obtained as a redistribution product during the crystallization of the triphenyllead(IV) derivative **13**. The proposed redistribution process of $Ph_3Pb[(SePPh_2)_2N]$ (**13**) based also on the NMR studies is depicted on **Scheme 3.2.5**.

$$\underset{\mathbf{13}}{2\ Ph_3Pb[(SePPh_2)N]} \longrightarrow Ph_4Pb + \underset{\mathbf{13a}}{Ph_2Pb[(SePPh_2)_2N]_2}$$

Scheme 3.2.5 Redistribution process of complex **13**

The ORTEP representation of the molecular structure of compounds **9** and **13a** are shown on **Figure 3.2.8** and **Figure 3.2.9**.

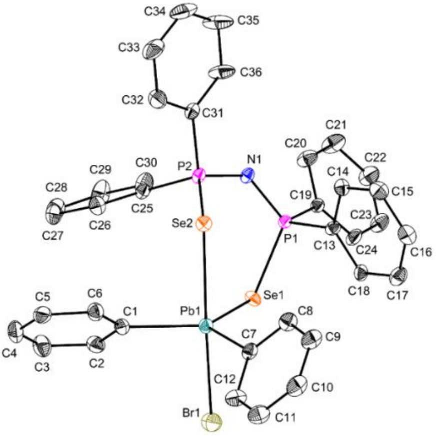


Figure 3.2.8 ORTEP diagram for $Ph_2Pb(Br)[(SePPh_2)_2N]$ (**9**). The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In both compounds the diselenoimidodiphosphinato ligands act as monometallic biconnective units which form six membered $PbSe_2P_2N$ rings. The phosphorus-selenium and the lead-selenium bond lengths in the structure of $Ph_2Pb(Br)[(SePPh_2)_2N]$ (**9**) are different, the organophosphorus ligand has an asymmetric coordination. Regarding the phosphorus-nitrogen bonds, they are just slightly different (1.585(5)/1.598(5) Å), the bond lengths are shorter than the single bonds in the corresponding free acid and between the single and double bonds in the corresponding methylated ligand. We can conclude that the π electrons are delocalized only on the PNP fragment in this compound. The coordination geometry around the five-coordinated lead atom in the structure of **9** is distorted trigonal bipyramidal with the bromine and the coordinated selenium atom in the axial positions.

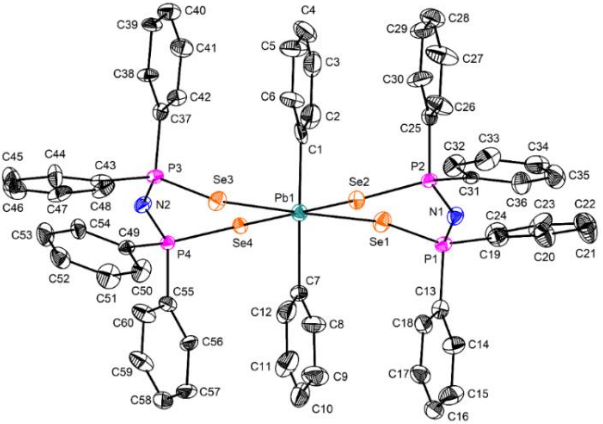


Figure 3.2.9 ORTEP diagram for $Ph_2Pb[(SePPh_2)_2N]_2$ (**13a**). The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In the molecular structure of **13a** (**Figure 3.2.9**) the phosphorus-selenium bond lengths within a coordinated ligand unit are almost the same and are between the length of the single and double bonds. Thus, a delocalization of the π-electrons on the SePNPSe skeleton is suggested, which is confirmed also by the lengths of the phosphorus-nitrogen bonds and, which are also intermediate between the single and double bonds. The length of the phosphorus-lead bonds is just slightly different, thus showing an isobidentate coordination behaviour of the diselenoimidodiphosphinato ligands. The coordination geometry around the lead atom is distorted octahedral, with the two phenyl groups in the axial positions and the four selenium atoms from the chelating bidentate ligand placed on the equatorial positions.

Single crystals of **15a** resulted during the attempts to grow crystals of the trimethyllead(IV) derivative **15**. The molecular structure of **15a** is displayed in **Figure 3.2.10**. The presence of decomposition products in solution, namely tetramethyllead, the lead(II) derivative $Pb[(SePPh_2)_2N]_2$ and the methylated ligand (**Scheme 3.2.6**), was confirmed by NMR studies.

$$\underset{\textbf{15}}{3\ Me_3Pb[(SePPh_2)N]} \longrightarrow 2\ Me_4Pb + \underset{\textbf{15a}}{Pb[(SePPh_2)_2N]_2} + (MeSePPh_2)(SePPh_2)N$$

Scheme 3.2.6 Redistribution process of complex **15**

Comparing the bond lengths within a ligand unit, a partial delocalization is suggested on the PNP skeleton, and the ligand bonded asymmetrically to the metal centre, similarly to compound **9**. The coordination geometry around the lead atom can be described as a distorted octahedron if the lead··· $\pi(Ph_{centroid})$ interactions of 3.384 Å with a phenyl group from each ligand unit are considered.

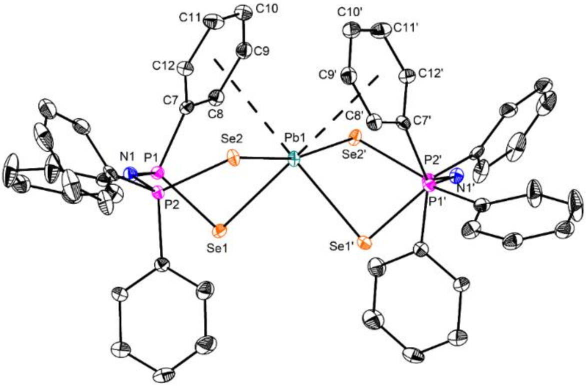


Figure 3.2.10 ORTEP diagram for $Pb[(SePPh_2)_2N]_2$ (**15a**). The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

3.2.2 Conclusions

- The reactions of Ph_2PbCl_2, Ph_3PbCl and Me_3PbBr with $K[(EPPh_2)_2N]$ (E = S, Se), using 1:1 and 1:2 molar ratios, have been investigated.
- In compounds **8**, **13** and **15** the $[(SePPh_2)_2N]^-$ ligands present a dynamic behaviour in solution, which might be determined by the fast exchange between the coordination of the two chalcogen atoms.
- Diffusion-molecular weight analysis for $Ph_3Pb[(SePPh_2)_2N]$ (**13**) shows a dimeric structure in solution for this compound.
- A low temperature ^{31}P NMR experiment showed for compound **13** non-equivalent phosphorus atoms in the $[(SePPh_2)_2N]$ ligand and a free enthalpy of 10.06 kcal/mol was calculated for the exchange process between single and double bonded selenium to phosphorus in the ligand attached to lead.
- Formation of unexpected species should be considered due to high tendency for redistribution and/or redox processes. The APCI+ mass spectra of compounds **7-16** indicate that fast rearrangement and/or decomposition processes took place in spectrometer, much faster than it was observed in a time dependent ^1H and ^{31}P NMR experiment.
- The mass spectra of $Me_3Pb[(SePPh_2)_2N]$ confirm the alkylation process which was observed also in the time-depending NMR experiments. In both NMR (^1H and ^{31}P) and APCI+ mass spectra was identified the methylated product $(MeSePPh_2)(SePPh_2)N$.
- The single crystal X-ray diffraction studies revealed a distorted trigonal bipyramidal and a distorted octahedral coordination geometry about lead in compounds $Ph_2Pb(Br)[(SePPh_2)_2N]$ (**9**) and $Ph_2Pb[(SePPh_2)_2N]_2$ (**13a**), respectively.
- A distorted octahedral environment was found in $Pb[(SePPh_2)_2N]_2$ (**15a**), where the coordination sphere at lead is completed by two intramolecular lead··· $\pi(Ph_{centroid})$ interactions.

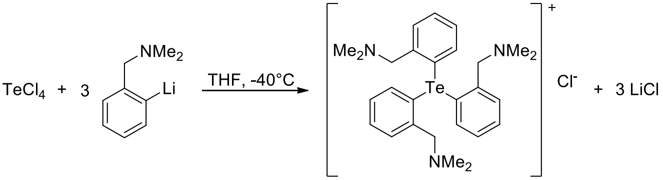
3.3 Organotellurium(IV) compounds

3.3.1 Results and discussion

Triorganotellurium(IV) halides and pseudohalides

The new triorganotelluronium(IV) compounds $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+X^-$ (X = F, Cl, Br, I, SCN, OCN) were prepared not only to investigate their structure, but also to be further used as starting materials for the complexes with organophosphorus ligands.

The triorganotelluronium(IV) chloride $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+Cl^-\cdot H_2O$ (**17**) was obtained in the reaction of $TeCl_4$ with the organolithium derivative $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ in a 1:4 molar ratio (25% excess of the RLi reagent), in THF, under inert atmosphere of argon (**Scheme 3.3.1**). The triorganotelluronium(IV) compound resulted as a precipitate in THF. The use of such an excess of organolithium reagent proved to favour the formation of the triorganotelluronium(IV) compound **17** and not the derivative corresponding to the used stoichiometry, namely $[2\text{-}(Me_2NCH_2)C_6H_4]_4Te$.

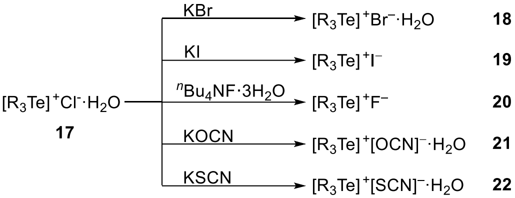


Scheme 3.3.1 Synthesis of compound **17**

The related bromide, iodide, fluoride, cyanate and thiocyanate were prepared by halogen exchange reactions, when **17** was treated with KBr, KI, $^{n}Bu_4NF\cdot 3H_2O$, KOCN or KSCN, respectively (**Scheme 3.3.2**). The reactions were carried out in a mixture of dichloromethane/water for compounds **18** and **19**, in THF for compound **20** and in methanol for compounds **21** and **22**.

Compounds **17-22** were isolated as crystalline, air-stable solids with a good solubility in polar solvents. ESI+ mass spectrometry and multinuclear (^{1}H,

^{13}C, ^{125}Te) NMR spectroscopy was employed for their characterization. In addition, compound **19** was characterized also by ESI– MS and compound **20** also by ^{19}F NMR. The spectral data were in accordance with the expected composition for each compound and they revealed the existence of only one species in solution.



Scheme 3.3.2 Synthesis of compounds **18-22** (R = $2\text{-}(Me_2NCH_2)C_6H_4$)

The room temperature ^{1}H and ^{13}C NMR spectra of compounds **17-22** present characteristic resonances for the organic groups attached to tellurium and suggest the equivalence of the three organic groups in solution. The aliphatic region of the ^{1}H NMR spectra suggest the existence of N→Te intramolecular interactions in solution, showing in each case an AB spin system for the CH_2N protons. The presence of a very broad resonance in the ^{1}H and ^{13}C NMR spectra of each compound suggests the dynamic behaviour of the CH_3 groups in solution at room temperature.

For the chloride **17** the low temperature NMR spectra (**Figure 3.3.1**) show that the three organic groups attached to tellurium remain equivalent until -30°C. The broad resonances observed in both the ^{1}H and the ^{13}C NMR spectra were resolved into two singlets for the no more equivalent CH_3 groups attached to nitrogen in each pendant arm, thus showing the existence of intramolecular N→Te interactions at low temperature.

Based on the VT ^{1}H NMR spectra a free enthalpy $\Delta G = 13.13$ kcal/mol was calculated[79] at the coalescence temperature of 10 °C for the dynamic process suffered by the $N(CH_3)_2$ protons.

For each compound a sharp resonance signal was observed in the ^{125}Te NMR spectrum, at δ values characteristic for triorganotelluronium cations, *i.e.* in the range 750–757 ppm. The very close values of the resonances indicate that the nature of the anion does not influence the behaviour of the cation. There are no interactions between the cations and the anions in solution. The ^{19}F NMR spectrum of compound **20** presents a sharp singlet resonance at –152.6 ppm which is shifted compared to the corresponding resonance signal of the starting material (–124.1 ppm for ^{n}Bu$_4$NF·3H$_2$O in CDCl$_3$).

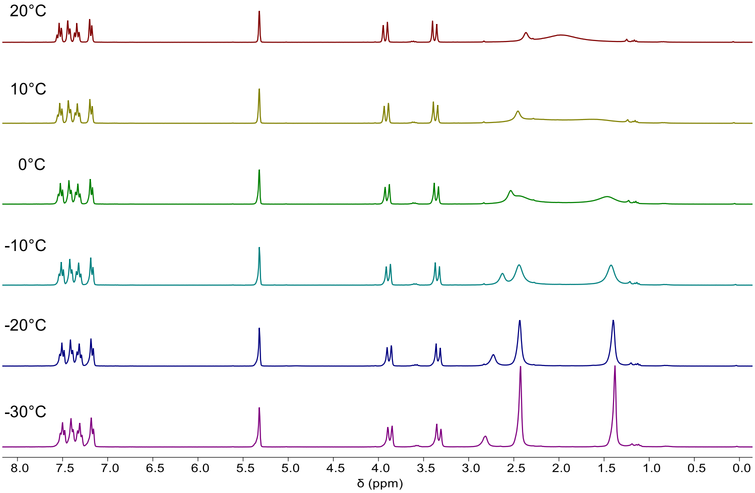


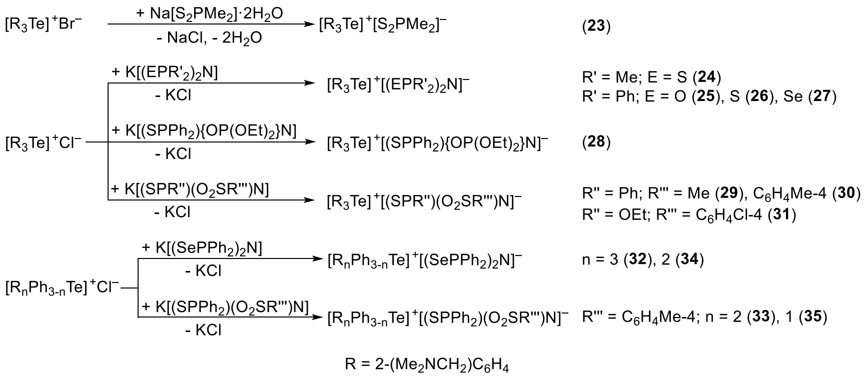
Figure 3.3.1 VT ^{1}H NMR spectra of compound **17** in CD$_2$Cl$_2$

The ESI+ mass spectra of compounds **17-22** show only one peak at the *m/z* value 532.20, corresponding to the cation [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_3$Te$^+$] present in each compound. For compound **19** the ESI– mass spectrum presents the peak corresponding to I$^–$ at *m/z* 126.91.

In the IR spectra of compounds **21** and **22** the characteristic vibration bands for OCN$^–$ and SCN$^–$ groups were observed. A broad absorption band at 1628 cm^{-1} is present in the IR spectrum of **21**, which corresponds to the symmetric vibration of the C=O bond. A very sharp and strong absorption band at 2048 cm^{-1} indicate the presence of the isothiocyanato group in compound **22**.

Triorganotellurium(IV) compounds with organophosphorus ligands

Several triorganotelluronium(IV) compounds bearing organophosphorus ligands, namely $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+L^-$ (L = S_2PMe_2 (**23**), $(SPMe_2)_2N$ (**24**), $(OPPh_2)_2N$ (**25**), $(SPPh_2)_2N$ (**26**), $(SePPh_2)_2N$ (**27**), $(SPPh_2)\{OP(OEt)_2\}N$ (**28**), $(SPPh_2)(O_2SMe)N$ (**29**), $(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$ (**30**), $\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N$ (**31**)), $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2PhTe]^+L^-$ (L = $(SePPh_2)_2N$ (**32**), $(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$ (**33**)) and $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Ph_2Te]^+L^-$ (L = $(SePPh_2)_2N$ (**34**), $(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$ (**35**)) were obtained by salt metathesis reactions between the triaryltelluronium halides $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_nPh_{3\text{-}n}Te]^+X^-$ (n = 1-3, X = Cl, Br) and the alkali metal salt of the appropriate organophosphorus acid in a 1:1 molar ratio (**Scheme 3.3.3**), using methylene dichloride, chloroform, or methanol as solvents.



Scheme 3.3.3 Synthesis of compounds **23-35**

These ionic compounds were isolated as microcrystalline, colourless (**23**, **25**, **26**, **29**, **30**, **33** and **35**) or yellow (**24**, **27**, **32** and **34**) species or as viscous oils (**28**, **31**). Multinuclear NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{125}Te and ^{77}Se as appropriate), ESI mass spectrometry and IR spectroscopy were used to characterize the synthetized new compounds. The analytical data confirmed the expected composition of the desired compounds.

The NMR data confirmed the existence of only one species in solution. The ^{1}H and ^{13}C NMR spectra showed that the 2-(Me$_2$NCH$_2$)C$_6$H$_4$ groups attached to tellurium (three in **23-31** and two in **32** and **33**) are equivalent. The aliphatic region of the ^{1}H NMR spectra of the compounds bearing two or three 2-(Me$_2$NCH$_2$)C$_6$H$_4$ groups show a broad singlet resonance and an AB spin system for the N(CH_3)$_2$ and the CH_2N protons, respectively, which indicate that the nitrogen atom in the pendant arm is intramolecularly coordinated to tellurium. The ^{1}H NMR spectra of compounds **34** and **35** show two sharp resonances for the N(CH_3)$_2$ and the CH_2N protons in the pendant arm, which suggest either no intramolecular N→Te interaction, or a very fast dynamic process comprising several steps (decoordination, inversion at nitrogen and recoordination to tellurium) which cannot be observed at the room temperature NMR time scale.[82]

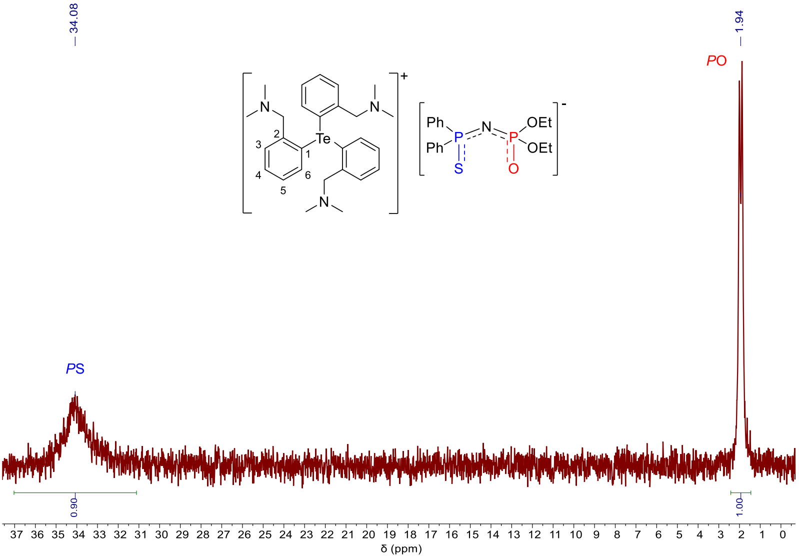


Figure 3.3.2 ^{31}P NMR spectrum of compound **28** in CDCl$_3$

The ^{31}P NMR spectra show only one singlet resonance in each case (excepting compound **28**), which demonstrate the equivalence of the two phosphorus atoms in solution. In compound **28** two non-equivalent phosphorus atoms are present and the two resonance signals in the ^{31}P NMR spectrum can be observed at 1.9 ppm (d, *P*O, $^{2}J_{PP}$ 20.2 Hz) and at 34.1 ppm (br, *P*S) (**Figure 3.3.2**).

In the ^{77}Se NMR spectra of compounds **27**, **32** and **34** (**Figure 3.3.3**) a doublet resonance is observed in each case, at -11.9, -82.9 and -35.7 ppm, with P-Se coupling constants of 664.9, 657.9 and 652.3 Hz, respectively, thus showing the equivalence of the two selenium atoms in the tetraphenyldiselenoimidodiphosphinato ligands.

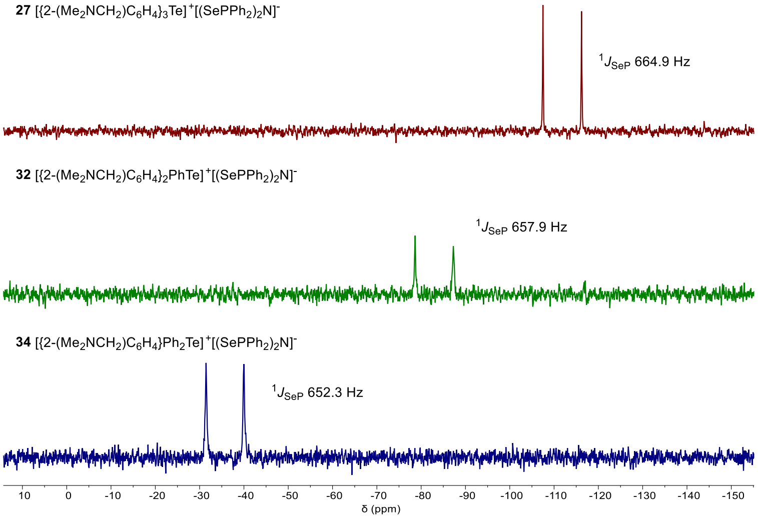


Figure 3.3.3 ^{77}Se NMR spectra of compounds **27**, **32** and **34** in $CDCl_3$

The ^{125}Te NMR spectra show singlet resonances in the range 744.7-767.2 ppm, characteristic for the triorganotelluronium cations. In the case of compounds **23-31**, containing the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+$ cation, the chemical shifts of the signals in the ^{125}Te NMR spectra are not very much influenced by the nature of the anions. The small range of the chemical shifts for these compounds (749.5-756.2 ppm) are consistent with the absence of any other type of interactions between the cations and the anions in solution, except the electrostatic forces. For compounds **32-35** the ^{125}Te NMR spectra show differences in the chemical shifts of the ^{125}Te NMR resonances when comparing to the chemical shifts of the resonances for the starting materials in two cases: a difference of 8.4 ppm for $[R_2PhTe]^+[(SPPh_2)(O_2SC_6H_4Me\text{-}4)N]^-$ (**33**) and 15.7 ppm for $[RPh_2Te]^+[(SePPh_2)_2N]^-$ (**34**) (**Figure 3.3.4**). The differences in the chemical shifts in the ^{125}Te NMR spectra may suggest some degree of interaction between the chalcogen (O, S, Se) attached to phosphorus atoms and tellurium also in solution, as it was observed by single crystal X-ray diffraction for compound **34**, where Se···Te interactions are present.

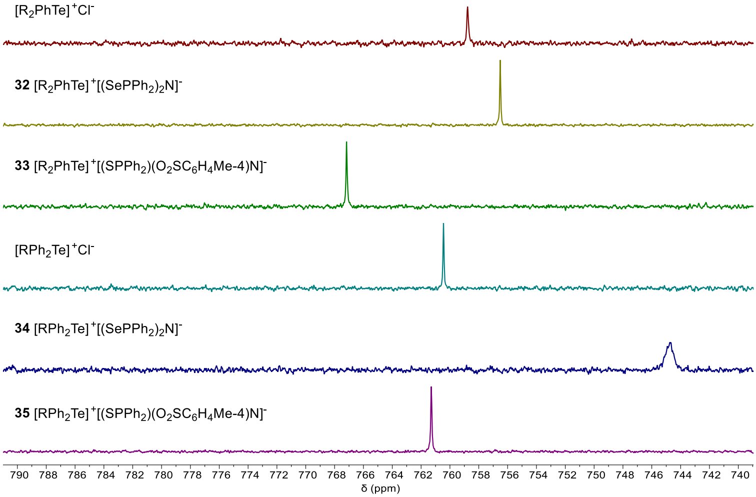


Figure 3.3.4 ^{125}Te NMR spectra of compounds **32-35** and the corresponding starting materials in $CDCl_3$ (R = $2\text{-}(Me_2NCH_2)C_6H_4$)

ESI+ and ESI– high resolution mass spectra show for all compounds as base peak the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_nPh_{3\text{-}n}Te]^+$ cation and the corresponding organophosphorus anion, respectively, thus confirming the identity of the investigated species.

Compounds **24–31** showed molar conductivities in the range 156-267 $S\cdot cm^2\cdot mol^{-1}$ for their 10^{-4} M MeOH solutions, similarly with the value determined for the chloride **17** ($\Lambda_M = 203$ $S\cdot cm^2\cdot mol^{-1}$), thus confirming their behaviour as 1:1 electrolyte.

Solid state structures

The triaryltelluronium(IV) species of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_nPh_{3-n}Te]^+X^-$ (n = 1-3, X = halogen, pseudohalogen or organophosphorus ligand) investigated in this work exhibit an ionic nature. The crystal structures for compounds **17**, **26**, **27**, **30** and **34** were established by single crystal X-ray diffraction. The single crystals of compound **17** contain a water molecule, as was observed in the ^{1}H NMR spectra also.

In all the investigated crystals the $2\text{-}(Me_2NCH_2)C_6H_4$ groups act as *C,N*-chelating moieties, thus resulting in hypercoordinated triorganotelluronium species: *14-Te-6* in **17**, **26**, **27** and **30** and *10-Te-4* in **34**.[69,84] As a result, in compounds with three $2\text{-}(Me_2NCH_2)C_6H_4$ groups bearing a pendant arm involved in intramolecular N→Te coordination, a distorted octahedral coordination geometry is established around the tellurium atom. In compound **34**, containing only one $2\text{-}(Me_2NCH_2)C_6H_4$ group and two phenyl groups, the coordination geometry of tellurium is a distorted see-saw.

Compound **17** crystallizes in the chiral space group *R*3 (trigonal) and, as a consequence, the investigated crystal contains only one isomer. The cation in compound **17** contains three $2\text{-}(Me_2NCH_2)C_6H_4$ substituents attached to tellurium and all three nitrogen atoms from the pendant arms participate to intramolecular N→Te interactions of 2.813(6) Å.

Compound **26** (**Figure 3.3.5**) crystalizes in the $P2_1$ space group. The coordination geometry around the tellurium atom in the cation is distorted octahedral due to the strong secondary intramolecular N→Te interactions. The N–Te bond lengths are in the range 2.73(6)-2.837(6) Å, well below the sum of the van der Waals radii of the two elements (Σr_{vdW}(N,Te) 3.65 Å[53]).

The anionic nature of the organophosporus ligand should be a consequence of the steric effects determined by the bulky cation. There are no S···Te interactions. The phosphorus-sulphur (1.957(2) and 1.964(3) Å) and the phosphorus-nitrogen (1.584(4) and 1.590(4) Å) interatomic distances suggest delocalization of the π electrons over the SPNPS skeleton.

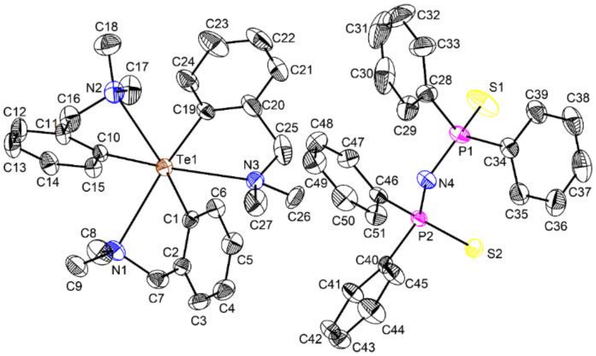


Figure 3.3.5 Thermal ellipsoids (30% probability) representation of a pair of S_{N2},S_{N3},R_{N4}-[{2-(Me_2NCH_2)C_6H_4}$_3$Te]$^+$ cation and [($SPPh_2$)$_2$N]$^-$anion in the crystal of **26**. Hydrogen atoms are omitted for clarity.

In compound **30** a *syn* conformation can be assigned to the SPNSC skeleton, with a S–P···S–C dihedral angle of 66.54°. No O···Te or S···Te interactions were observed in the crystal of **30** (**Figure 3.3.6**), but weak H···O contacts contributed to the formation of cation-anion pairs. Further inter-ionic H···S contacts (H14···S1’ 2.685(2) Å) are also present.

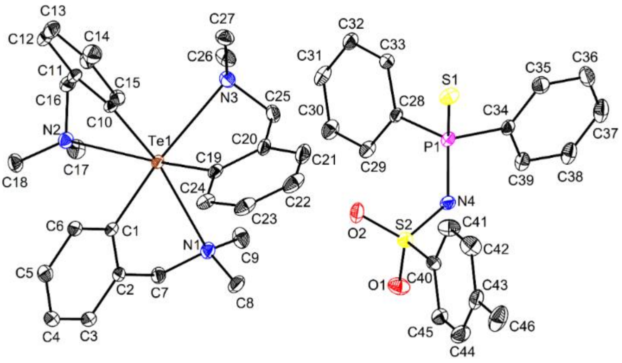


Figure 3.3.6 Thermal ellipsoids (30% probability) representation of a pair of pS_{N1},pS_{N2},pS_{N3}-[{2-(Me_2NCH_2)C_6H_4}$_3$Te]$^+$ cation and [($SPPh_2$)($O_2SC_6H_4CH_3$-4)N]$^-$ anion in **30**. Hydrogen atoms are omitted for clarity.

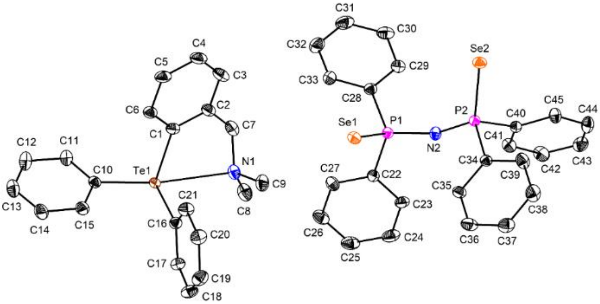


Figure 3.3.7 Thermal ellipsoids (50% probability) representation of a pair of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Ph_2Te]^+$ cation and $[(SePPh_2)_2N]^-$ anion in **34**. Hydrogen atoms are omitted for clarity.

In compound **34** (**Figure 3.3.7**), besides the electrostatic cation-anion forces, secondary Se···Te interactions are also present, thus resulting in a chelating unisobidentate coordination behaviour of the ligand. Due to the intramolecular N→Te coordination and the additional Se···Te interactions, tellurium becomes hexacoordinated. The behaviour of the diselenoimidodiphosphinato ligand in compound **34** is similar with that one in compound **27**, the two phosphorus-selenium and phosphorus-nitrogen interatomic distances are equivalent and they have values intermediate between the single and the double bonds.

3.3.2 Conclusions

- Six triorganotelluronium halides and pseudohalides of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+X^-$ (X = Cl (**17**), Br (**18**), I (**19**), F (**20**), OCN (**21**), SCN (**22**)) were prepared and structurally characterized.
- The ^1H and the $^{13}C\{H\}$ NMR spectra of **17-22** suggest the equivalence of the three $2\text{-}(Me_2NCH_2)C_6H_4$ groups in cations, and also gave evidence for the presence of N→Te intramolecular interactions in solution.
- The ESI+ mass spectra of **17-22** support the ionic nature in solution of the complexes containing $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+$ cations.

- The single crystal X-ray diffraction studies revealed intramolecular N→Te interactions in **17**, consistent with hypercoordinated triorganotelluronium cations.
- Thirteen triaryltelluronium complexes of type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_nPh_{3-n}Te]^+L^-$ (n = 1–3, L = S_2PMe_2, $(XPR_2)(YPR_2')N$ (X, Y = O, S, Se; R, R' = Me, Ph, OEt) and $(SPR_2)(O_2SR')N$ (R = Ph, OEt, R' = Me, C_6H_4Me-4, C_6H_4Cl-4) were prepared and structurally characterized in solution by multinuclear NMR spectroscopy, mass spectrometry and molar conductivity, and in solid state by IR spectroscopy and single crystal X-ray diffraction.
- For compounds **23-35**, the room temperature ^1H and ^{13}C NMR spectra suggested the equivalence of the aryl groups attached to tellurium.
- In the case of complexes in which the tellurium in the cation is bearing three or two aryl groups with pendant arms (**23-33**) the ^1H NMR spectra suggest the existence of N→Te intramolecular interactions in solution, while for compounds bearing only one $2\text{-}(Me_2NCH_2)C_6H_4$ group no evidence was found for such interactions in solution.
- A 1:1 electrolyte behaviour is suggested by the molar conductivities of the homoleptic triaryltelluronium complexes with organophosphorus ligands (**24-31**) in 10^{-4} M methanol solutions. The ESI+ and ESI– mass spectra confirm the ionic nature of all triorganotellurium(IV) derivatives, as for each compound the peaks corresponding to the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_nPh_{3-n}Te]^+$ cation and the anionic ligand, respectively, were found as base peaks.
- The single crystal X-ray diffraction studies on compounds **26**, **27**, **30** and **34** revealed intramolecular N→Te interactions, consistent with hypercoordinated triaryltelluronium cations. Only in the structure of compound **34** was observed the interaction of the chalcogen atom in the organophosphorus ligand with tellurium.

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5 List of relevant publications

1. *Experimental evidence for hypercoordination in triorganotelluronium halides with 2-(Me_2NCH_2)C_6H_4 groups*, A. Beleagă, **E. Denes**, C. Silvestru, A. Silvestru, *New. J. Chem.*, **2019**, *43*, 11585-11595.
https://doi.org/10.1039/C9NJ02530H, Impact Factor 2019: 3.288

2. *Hypercoordinated triorganotellurium(IV) derivatives of chalcogen-centred organophosphorus ligands*, **E. Denes**, A. Beleagă, A. Silvestru, *Inorg. Chim. Acta*, **2020**, *511*, 119841.
https://doi.org/10.1016/j.ica.2020.119841, Impact Factor 2020: 2.545

3. *New hypercoordinated triaryltelluronium derivatives of organophosphorus ligands. Synthesis and structural characterization*, **E. Denes**, M. Vlassa, C. Silvestru, A. Silvestru, *Rev. Roum. Chim*, **2021**, *66*, 33-40.
DOI: 10.33224/rrch.2021.66.1.03, Impact Factor 2020-2021: 0.278

4. *New hypercoordinate diorganotin(IV) compounds with ionic behaviour*, **E. Denes**, L. Marongiu, M. Arca, V. Lippolis, A. Silvestru, *Inorg. Chim. Acta*, *in preparation*.

5. *New di- and triorganolead(IV) compounds with dichalcogenoimidodiphosphinato ligands. Solution behaviour and solid state structure*, **E. Denes**, C. Silvestru, A. Silvestru, *J. Organomet. Chem.*, *in preparation*.