Babes-Bolyai University
Faculty of Chemistry and Chemical Engineering
Chemistry Department

PhD Thesis

Ligands containing group 15 and/or 16 donor atoms and their *d* metal complexes

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Objectives of the present study

The studies developed during the present PhD Thesis were focused on:

- The synthesis and structural chgaracterization of late *d* metal complexes (Cu, Co) with hypervalent triarylphosphanes of type $PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$ (x = 1-3)

- The synthesis and structural chgaracterization of new diorganochalcogen(II) ligands bearing dihydroxo or monohydroxo functionalities.

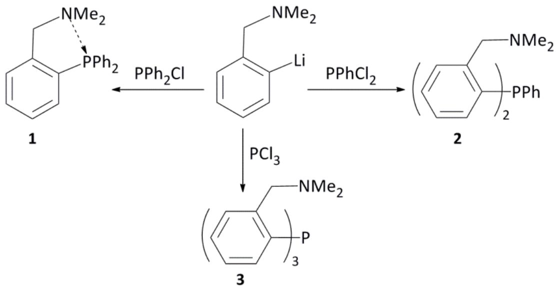
- The synthesis and structural chgaracterization of late *d* metal (Cd, Zn, Ag, Pd) complexes with diorganochalcogen(II) ligands bearing dihydroxo or monohydroxo functionalities.

II. Chelating P_xN_y triorganophosphanes and their transition metal complexes

II.2. Results and discussion

II.2.A. Hypervalent triarylphosphanes

Triorganophosphanes of type $PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$ (x = 1-3) were prepared according to literature procedures, by reacting the lithiated amine with PPh_xCl_{3-x} in the appropriate molar ratio, as depicted in Scheme II.2.1.[9,10]



Scheme II.2.1. Synthesis of the hypervalent triarylphosphanes

Several analytical data for these ligands are given in Table II.2.1.

Table II.2.1. Analitical data for phosphanes **1** – **3**

	Compound	**^{31}P, $CDCl_3$ (ppm)**	M.p. (^oC)
1	$PPh_2(C_6H_4CH_2NMe_2\text{-}2)$	-15,3 ($^1J_{PC}$ = 18.8 Hz)	54
2	$PPh(C_6H_4CH_2NMe_2\text{-}2)_2$	-25,1 ($^1J_{PC}$ = 20.3 Hz)	48
3	$P(C_6H_4CH_2NMe_2\text{-}2)_3$	-35.3s ($^1J_{PC}$ = 19.1 Hz)	87

The identity and purity of the triarylphosphanes **1** – **3** were proved by comparing their ^1H and ^{31}P NMR spectra with the values reported in literature. For these species there is no clear evidence for the N→P intramolecular coordination in solution. In all three cases the $N(CH_3)_2$ protons give singlet resonances, while the protons in the methylene groups attached to nitrogen (NCH_2) show doublet resonances in case of phosphanes **1** and **3**, due to ^1H – ^{31}P coupling ($^4J_{PH}$ = 1.6 Hz in **1** and 1.5 Hz in **3**, respectively), and an ABX spin system in case of phosphane **2**. The latter pattern is determined both by the diastereotopicity of the CH_2 protons and the ^1H – ^{31}P coupling (A: 3.57dd, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 2.1 Hz and B: 3.63dd, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 2.3 Hz) (see Figure II.2.1).

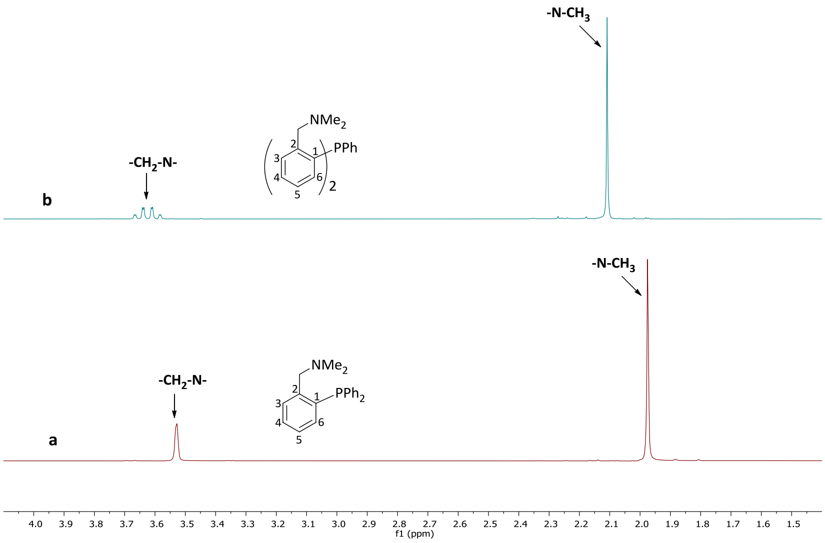


Figure II.2.1. Aliphatic region in the ^{1}H NMR spectra of phosphanes **1** (a) and **2** (b)

Crystal and molecular structure of PPh($C_6H_4CH_2NMe_2$-2)$_2$ (2)

Single crystals of PPh($C_6H_4CH_2NMe_2$-2)$_2$ (**2**) were obtained by slow diffusion of n-hexane in a solution of this compound in CH_2Cl_2 and the molecular structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the *P-1* space group. The crystal contains two independent molecules (**2’** and **2’’**) in the unit cell. The ORTEP-like diagram with the numbering scheme for this ligand is depicted in Figure II.2.2.

In both molecules **2'** and **2''** there is only one nitrogen atom coordinated to phosphorus: N(1)···P(1) 2.912(3) Å in molecule **2'** and N(3)···P(2) 2.971(3) Å in molecule **2''**.

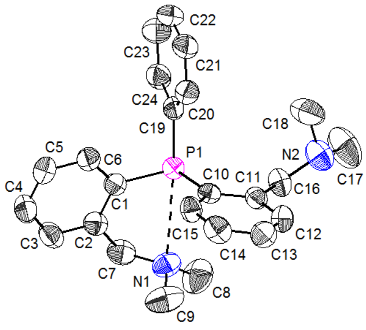


Figure II.2.2. ORTEP-like representation at 50% probability and atom numbering scheme of $S_{N1}C_{P1}$-**2’** isomer.

The other nitrogen atom is displayed far away from the coordination sphere of phosphorus, at a distance of 4.35 Å in molecule **2'** and respectively 4.30 Å in molecule **2''**. These distances are much larger than the sum of the van der Waals radii of the corresponding atoms [Σr_{vdW}(N,P) = 3.44 Å[27]].

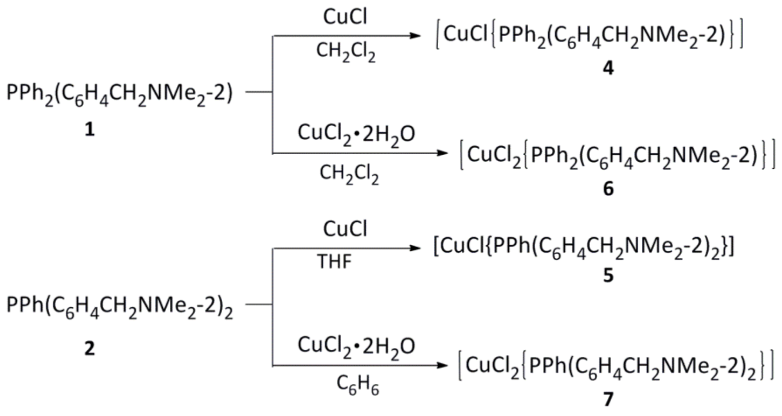
As a result of the N→P intramolecular coordination a five membered PC_3N ring is formed. The ring is not planar, but folded along the $P\cdots C_{methylene}$ axis, with the nitrogen atom lying out of the best plane defined by the residual PC_3 system. As a consequence, planar chirality is induced, with the aromatic ring as chiral plane and the nitrogen atom as pilot atom.[26] The phosphane ligand **2** crystallizes as a mixture of R_N and S_N isomers. The coordination geometry around the phosphorus atom might be described as distorted *pseudo*-trigonal bipyramidal, if the phosphorus lone pair of electrons is also considered. The atoms N(1), C(19) in molecule **2'** and N(3), C(43) in molecule **2''** lie in apices, with bond angles N(1)-P(1)-C(19) of 173.15(13)° and N(3)-P(2)-C(43) of 172.45(13)°, respectively. The other two carbon atoms attached to phosphorus and the lone pair are situated in the trigonal plane. In this way, a second type of chirality is induced to the phosphorus centre in the trigonal-bipyramidal environment. As a cosequence, the crystal of ligand **2** contains a mixture of $S_{N1}C_{P1}$, $R_{N1}A_{P1}$, $R_{N3}C_{P2}$ and $S_{N3}A_{P2}$ isomers.

II.2.B. Copper complexes with triarylphosphanes

The phosphane ligands **1** and **2** were used in the synthesis of complexes that contain copper(I) and copper(II) atoms, respectively. The copper complexes were obtained by reacting the respective triarylphosphanes with CuCl or $CuCl_2$ in dichloromethane, benzene or THF (Scheme II.2.2), and some analytical data for them are given in Table II.2.3.

Table II.2.3. Analytical data for the copper complexes **4** – **7**

No.	Compound	^{31}P NMR δ(ppm)	μ [BM]	ESR spectra
4	$[CuCl\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$	-11.3,br.; -10.3, br	-	-
5	$[CuCl\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$	-23.9, br.	-	-
6	$[CuCl_2\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$	-	1.94	$g_{\parallel}$ 1.98 $g_{\perp}$ 2.27
7	$[CuCl_2\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$	-24.4,br., 38.5	2.18	$g_{\parallel}$ 2.04 $g_{\perp}$ 1.92



Scheme II.2.2. Synthesis of copper(I) and copper(II) complexes

The NMR spectra bring evidences for the solution behaviour of the discussed compounds. In the aliphatic region the ^{1}H NMR spectrum of compound **4** presents singlet resonances both for the methyl and the methylene protons, while in case of compound **5** the resonance corresponding to the CH_2 protons appears as an AB spin system centred at δ 3.45 ppm, with δ_A 3.40 and δ_B 3.51 ppm (Figure II.2.4).

In case of complex **7** the ^{1}H NMR spectrum suggests a mixture of two species, in a molar ratio of approx. 1 : 0.75. The broad aspect of the resonances might be the result of the presence of the paramagnetic Cu(II) in solution.

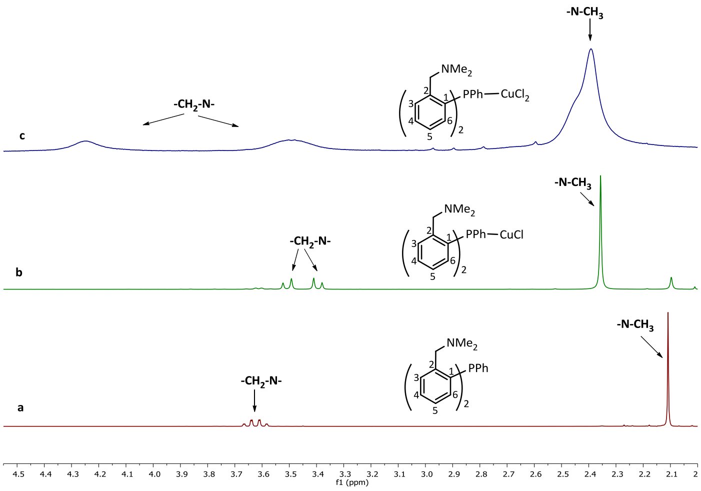


Figure II.2.4. Aliphatic region in ^{1}H NMR spectra of compounds **2**, **5** and **7** ($CDCl_3$, RT)

The ^{31}P NMR spectra consist in all cases of broad resonances, slightly shifted in comparison with the free phosphane.

Crystal and molecular structure of [CuCl{$PPh_2(C_6H_4CH_2NMe_2$-2)}] (4)

The compound crystallizes in the monoclinic P2(1)/n space group. The Ortep-like diagram with the atom numbering scheme is given in Figure II.2.9. The nitrogen atom in the pendant arm is intramolecularly coordinated to copper [N(1)···Cu(1) 2.172(4) Å]. In this way a six-membered metallacycle is formed.

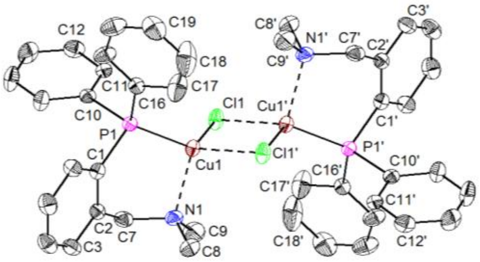


Figure II.2.9. Dimeric association of R_{N1} and $S_{N1'}$isomers in compound **4**

The ring has a boat conformation, with P(1) and C(7) in apices [dihedral angles Cu(1)P(1)C(1)/Cu(1)C(1)C(2)N(1) 22.63^{o} and N(1)C(2)C(7)/Cu(1)C(1)C(2)N(1) 63.77^{o}]. The intramolecular N→Cu coordination induces planar chirality. As a consequence the compound crystallizes as a mixture of *R* and *S* isomers which are associated in dimeric units by bridging chlorine atoms [Cl(1)···Cu(1') 2.3406(13) Å *vs.* Σr_{vdW}(Cu,Cl) 3.20 Å[27,58]]. As a consequence a tricyclic system is formed, with a planar Cu_2Cl_2 core. The ligands are oriented *trans* each other, with respect to the relative positions of the nitrogen and phosphorus atoms to the planar Cu_2Cl_2 core. The coordination geometry about copper is distorted tetrahedral.

Crystal and molecular structure of [CuCl{$PPh(C_6H_4CH_2NMe_2$-2)$_2$}]·C_6H_6 (5·C_6H_6)

Single-crystals of [CuCl{$PPh(C_6H_4CH_2NMe_2$-2)$_2$}] were grown from a benzene/ n-hexane mixture of solvents and the compound crystallized as **5**·C_6H_6, in the monoclinic P2(1)/c space group. The Ortep-like diagram of **5**·C_6H_6 is depicted in Figure II.2.10.

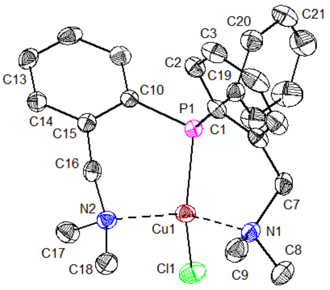


Figure II.2.10. Ortep-like diagram of R_{N1},R_{N2}-**5**·C_6H_6 with 50% probability ellipsoids. Hydrogen atoms and benzene were removed for clarity.

The ligand acts as a *N,P,N*-tridentate moiety towards copper, thus determining a distorted tetrahedral coordination geometry. The high distortion [P(1)-Cu(1)-Cl(1) 134.73^{o}] is probably determined by the constraints imposed by the six-membered rings. Due to the strong intramolecular N→Cu interactions [N(1)···Cu(1) 2.319(1) Å, N(2)···Cu(1) 2.191(1) Å, *vs*. Σr_{vdw}(Cu,N) = 3.10 Å[27]], two six membered chelate rings are formed. These interactions are of similar strength with those found in the related copper complexes with ligand **3**.[34,37] Both rings have boat conformations, with C(7) and P(1) and C(16) and P(1) respectively, in apices. The coordination geometry at the phosphorus atom is distorted tetrahedral.

The intramolecular N→Cu coordination induces planar chirality, thus resulting in a mixture of isomers, namely R_{N1},R_{N2} and S_{N1},S_{N2}.

The R_{N1},R_{N2} and S_{N1},S_{N2} isomers are associated in a polymeric chain by hydrogen bonding between chlorine and a hydrogen atom belonging to a phenyl ring [Cl(1)···H(13') 2.765(4) Å vs. Σr_{vdW}(Cl,H) 3.01 Å] (Figure II.2.11).

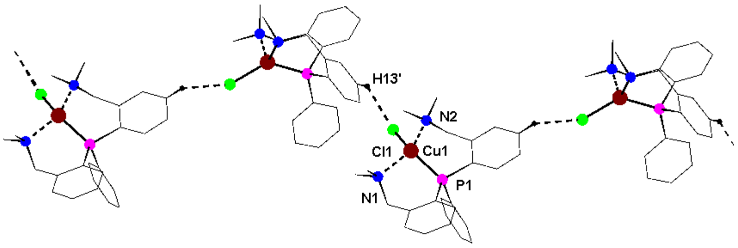
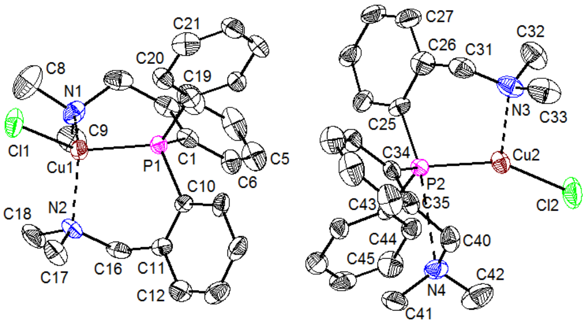


Figure II.2.11. Polymeric chain in **5**·C_6H_6. Solvent molecules were omitted.

X-ray diffraction studies upon single-crystals grown from the solid isolated in the reaction between $CuCl_2$ and ligand **2** (from a CH_2Cl_2/n-hexane, 1/4 v/v, mixture of solvents) evidenced also the formation of the Cu(I) compound [CuCl{PPh($C_6H_4CH_2NMe_2$-2)$_2$}], crystallized in the monoclinic P2(1) space group. Such reduction processes were observed also before in case of other reaction mixtures containing phosphanes, which are known as reducing reagents.[34] By contrast with the above described species, in this case the crystal contains two independent molecules, **5a** and **5b**, in the unit cell, one of them (**5a**) with a similar structure as that one described above, namely with both nitrogens coordinated to phosphorus [N(1)···Cu(1) 2.464(8) and N(2)···Cu(1) 2.169(8) Å]. In the other one (**5b**) only one nitrogen atom is coordinated to copper [N(3)···Cu(2) 2.175(8) Å, while the other nitrogen is coordinated to phosphorus [N(4)···P(2) 3.032(9) Å, vs. Σr_{vdw}(P,N) = 3.40 Å[27]]. The Ortep-like diagram for this species is depicted in Figure II.2.12.



5a **5b**

Figure II.2.12. Ortep-like diagrams of molecules **5a** and **5b** with atom numbering scheme. The atoms are drawn with 30% probability ellipsoids. The hydrogen atoms were removed for clarity.

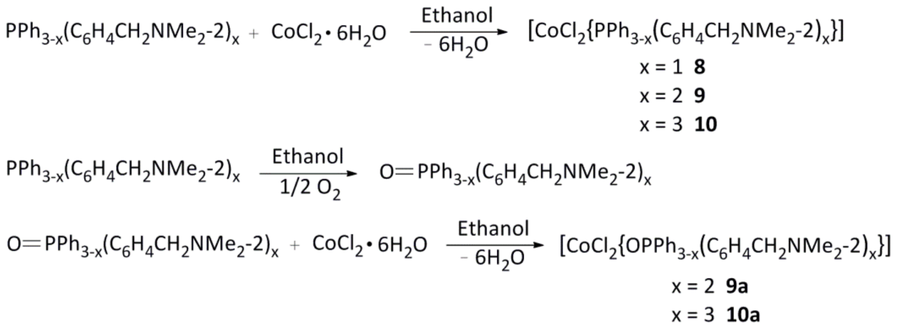
The intramolecular N→Cu and N→P intramolecular coordination induces planar chirality and therefore the compound crystalizes as a mixture of isomers, R_{N1},R_{N2} and S_{N1},S_{N2} for molecule **5a** and S_{N3},R_{N4} and R_{N3},S_{N4}, for molecule **5b**, respectively. Moreover, due to the N→P intramolecular coordination the P(2) atom becomes also chiral, and therefore the chirality to this atom determines the formation of C_{P2} and A_{P2} isomers. Finally, the isomers corresponding to the molecule **5b** can be described as S_{N3},R_{N4},C_{P2} and R_{N3},S_{N4},A_{P2}. The coordination geometry about copper and phosphorus in molecule **5a** can be described as distorted tetrahedral, while in case of molecule **5b**, the coordination geometry about copper is distorted T-shaped and about P(2) it is a trigonal bipyramid, with C(25) and N(4) in apices and the trigonal plane formed by Cu(2), C(34) and C(44). P(2) is displayed at 0.44 Å above the trigonal plane. The six-membered metallacycles have boat conformations in both molecules.

For the Cu(II) compounds **6** and **7**, the magnetic moments suggest a tetrahedral environment about Cu(II) (1.94 and 2.18 B.M. *vs*. the theoretical value of 1.73 B.M.). The ESR spectra confirmed also the presence of the paramagnetic Cu(II) species.

II.2.C. Cobalt(II) complexes with triarylphosphanes

The synthesis of these complexes was achieved by reacting the corresponding triarylphosphanes with $CoCl_2 \cdot 6H_2O$ in ethanol, in a 1:1 molar ratio (Scheme II.2.4.).

When phosphane **1** was used, only complex **8**, soluble in ethanol, was formed. In case of phosphanes **2** and **3**, besides the desired complexes **9** and **10**, the oxidation products **9a** and **10a** were also isolated, probably due to initial oxidation of the starting organophosphorus ligands in solution.



$$PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x + CoCl_2\cdot 6H_2O \xrightarrow[-\,6H_2O]{\text{Ethanol}} [CoCl_2\{PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$$

x = 1 **8**
x = 2 **9**
x = 3 **10**

$$PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x \xrightarrow[1/2\,O_2]{\text{Ethanol}} O{=}PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$$

$$O{=}PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x + CoCl_2\cdot 6H_2O \xrightarrow[-\,6H_2O]{\text{Ethanol}} [CoCl_2\{OPPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$$

x = 2 **9a**
x = 3 **10a**

Scheme II.2.4. Synthesis of the Co(II) complexes with triarylphosphanes **1** - **3**

All species were obtained as blue solids, soluble only in alcohols (methanol or ethanol, species **8**, **9a** and **10a**) and both in alcohols, acetonitrile and chlorinated solvents (**9** and **10**).

NMR and mass spectrometry measurements in methanol indicated the oxidation of the phosphane ligands to the phosphane oxides $OPPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$. A mixture of compounds $[CoCl_2\{PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$ and $[CoCl_2\{OPPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$ (x = 2, 3) was finally formed.

Complexes **9** and **10** could be separated from the oxidized species **9a** and **10a**, based on their different solubilities. The phosphane oxide complexes are insoluble in chlorinated solvents, while complexes **9** and **10** are soluble in methylene chloride.

The resonances observed in the NMR spectra are broad, due to the paramagnetic nature of the Co(II) complexes.

The ^{31}P NMR spectra for the complexes **8** – **10** contain resonances which prove the presence of P(III) species in solution and have the δ values slightly shifted compared to the resonances of the free ligands. The ^{31}P NMR spectra for the oxidized compounds present chemical shifts characteristic for P(V) species (Table II.2.6).

Table II.2.6. Analytical data for the Co(II) complexes

No.	Compound	^{31}P NMR δ (ppm)(solvent)	μ [B.M.]	Electronic spectra (vis.) λ_{max} [nm]
8	$[CoCl_2\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$	-16.4 (CD_3OD)	4.49	624; 671[a]
9	$[CoCl_2\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$	-22.8 ($CDCl_3$)	4.02	628; 644[a]
10	$[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_3\}]$	-34.9 (CD_3OD)	3.74	654; 693[a]
9a	$[CoCl_2\{OPPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$	42.5 (CD_3OD)	3.92	651[a] 589,688[b]
10a	$[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_3\}]$	47.2 (CD_3OD)	3.84	662

[a] in ethanol, [b] in CH_3CN

All compounds form blue solutions in ethanol or acetonitrile and the electronic spectra show absorption bands in the range 589 - 693 nm, characteristic for tetrahedral Co(II) complexes.[95]

II.3. Conclusions

- Hypervalent triarylphosphanes of type $PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$ (x = 1 – 3) were used as ligands towards Cu(I), Cu(II) and Co(II) ions.
- The molecular structure of the triarylphosphane $PPh(C_6H_4CH_2NMe_2\text{-}2)_2$ (**2**) was determined by single-crystal X-ray diffraction. There are two similar independent molecules in the unit cell, and in each of them only one N→P intramolecular coordination was observed.
- Two new copper(I) complexes, $[CuCl\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$ (**4**) and $[CuCl\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$ (**5**) were obtained and structuraly characterized by ^1H and ^{31}P NMR, mass spectrometry and single-crystal X-ray diffraction.
- The molecular structure of compound **4** revealed the intramolecular N→Cu interaction. The molecules are further associated in dimeric units by bridging chlorine atoms.
- The single-crystals of **5** grown from a benzene solution consist of $[CuCl\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]\cdot C_6H_6$ molecules, in which both nitrogen atoms of the pendant arms are coordinated to copper. The monomeric units are further associated in polymeric chains by hydrogen bonding.
- The attempts to grow single-crystals of the product isolated from the reaction between $PPh(C_6H_4CH_2NMe_2\text{-}2)_2$ and $CuCl_2$ from a CH_2Cl_2 solution lead to the copper(I) complex **5** instead of the adduct $[CuCl_2\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$ (**7**). The isolated single-crystals contain two independent molecules in the unit cell with different behaviour of the triorganophosphane.
- Three new cobalt(II) complexes of type $[CoCl_2\{PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$ (x = 1-3) were prepared and characterized by ^1H and ^{31}P NMR, mass spectrometry, electronic spectroscopy and magnetic susceptibility.
- When the synthesis of the complexes $[CoCl_2\{PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$ (x = 2, 3) was performed in air, the corresponding oxidised species $[CoCl_2\{OPPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x\}]$ (x = 2, 3) were also obtained. Mass spectra and IR spectra suggested also the formation of the oxidized species.

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III. Diorganochalcogen(II) ligands with alkoxo or aryloxo functionalities and their behavior towards late *d* metals

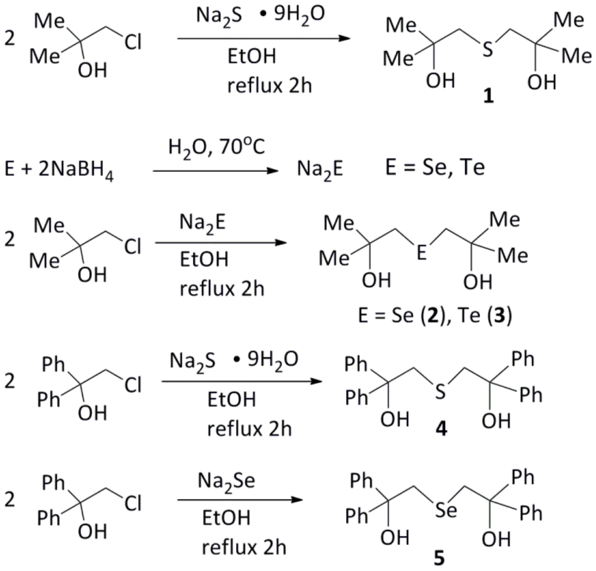
III.2. Results and disscusion

III.2.A. Diorganochalcogen(II) dihydroxide ligands

The sulfur bridged dialkoxo ligand bis(2-hydroxy-2-methylpropyl)sulfide $[Me_2C(OH)CH_2]_2S$ was obtained according to the published method involving the reaction between $Na_2S \cdot 9H_2O$ with 1-chloro-2-methyl-2-propanol.[26] The similar diols bridged by the heavier chalcogens Se and Te, $[Me_2C(OH)CH_2]_2E$ (E = Se, Te), as well as the phenyl substituted compounds $[Ph_2C(OH)CH_2]_2E$ (E = S, Se) were obtained by a slightly modified method (Scheme III.2.1).

Table III.2.1. Chalcogen bridged diols and their trimethylsilyl derivatives

	Compound	**M.p.**	**δ ^{77}Se / ^{125}Te**
1	$[Me_2C(OH)CH_2]_2S$	46	-
2	$[Me_2C(OH)CH_2]_2Se$	50	37.22
3	$[Me_2C(OH)CH_2]_2Te$	45	-0.93
4	$[Ph_2C(OH)CH_2]_2S$	114	-
5	$[Ph_2C(OH)CH_2]_2Se$	123	51.66
6	$[Me_2C(OSiMe_3)CH_2]_2S$	liquid	-
7	$[Me_2C(OSiMe_3)CH_2]_2Se$	liquid	95.66
8	$[Ph_2C(OSiMe_3)CH_2]_2S$	77-8	-



Scheme III.2.1. Synthesis of the chalcogen bridged diols

The reduction of elemental chalcogens (selenium and tellurium) with natrium borohydride in aqueous NaOH 10% afforded natrium chalcogenides which were subsequently treated with 2-chloro-1,1-diphenyl-ethanol in a 1 : 2 molar ratio. The desired diols were isolated as colorless solids. The obtained diols and their $SiMe_3$ substituted derivatives along with some analytical data are given in Table III.2.1.

The NMR spectra revealed the expected resonances. In the case of the methyl substituted diols, the ^1H NMR spectra present one singlet resonance for the equivalent methyl protons and another singlet resonance for the equivalent methylene protons. The resonance corresponding to the Se-CH_2 (δ 2.81 ppm in **2**) and Te-CH_2 protons (δ 2.96 ppm in **3**) are accompanied by satelites due to the corresponding proton – chalcogen couplings (Figure III.2.1). In case of the phenyl substituted compounds, the expected multiplet resonances in the aromatic region were observed. The O*H* protons give broad, singlet resonances in all cases.

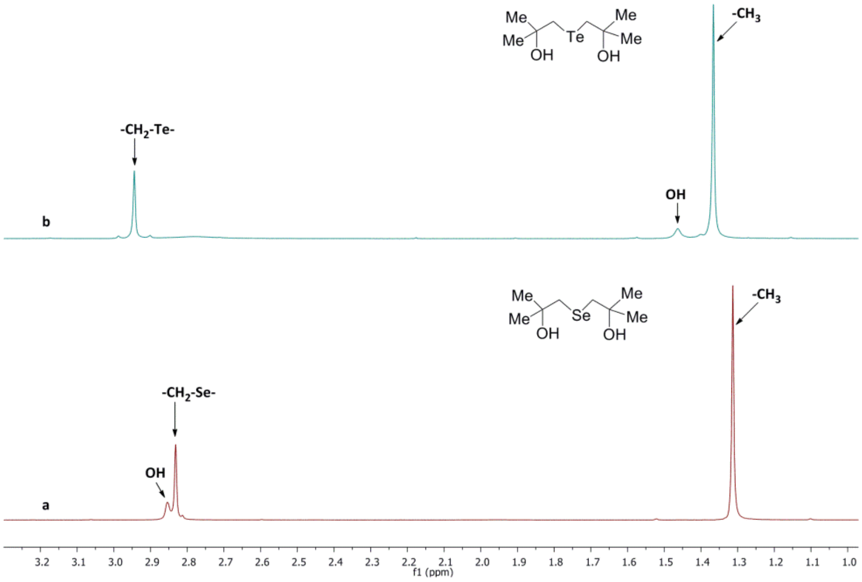


Figure III.2.1. ^1H NMR spectra ($CDCl_3$, 300 MHz) of compounds **2** (a) and **3** (b)

Crystal and molecular structure of $[Ph_2C(OH)CH_2]_2Se$ (5) and $[Ph_2C(OSiMe_3)CH_2]_2S$ (8)

Single-crystals of compounds **5** and **8** were grown by slow diffusion of n-hexane in a CH_2Cl_2 solution and their solid state structures were determined by single-crystal X-ray diffraction. The two compounds crystallize in the monoclinic P2(1)/c (**5**) and the triclinic P-1 (**7**) space groups, respectively. The Ortep-like diagram with the atom numbering scheme of compound **5** is depicted in Figure III.2.6. The selenium atom is sp^3 hybridized, with the C(1)-Se(1)-C(15) angle of 98.61°. The molecules are further associated in dimeric units by hydrogen bonding [O(2)···H(10') 2.15 Å *vs*. $\Sigma r_{vdW}(O,H)$ = 2.72 Å[47]] (Figure III.2.7). The other hydrogen atom is involved in an intramolecular interaction with the selenium atom H(20)···Se(1) 2.73 Å *vs*. Σr_{vdW}(Se,H) = 3.10 Å[47]]. The interatomic distances O(1)···Se(1) and O(2)···Se(1) are of 2.945(2) Å and 3.227(2) Å, respectively. Both these values are lower than the sum of the van der Waals radii of the oxygen and selenium atoms [Σr_{vdW}(O,Se) = 3.42 Å], thus suggesting weak O→Se intramolecular interactions.

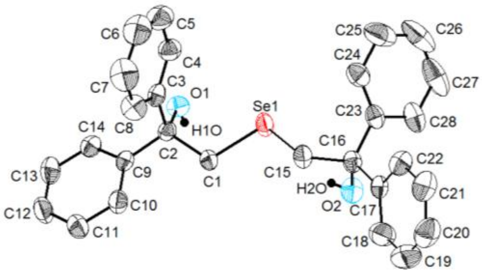


Figure III.2.6. Molecular structure of [$Ph_2C(OH)CH_2]_2Se$; other hydrogen atoms than OH were removed for clarity. The atoms are drawn with 50% probability ellipsoids

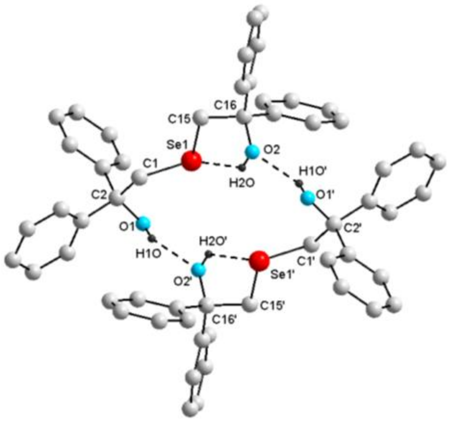


Figure III.2.7. Dimeric association in [$Ph_2C(OH)CH_2]_2Se$ (**5**)

The ortep-like diagram for compound **8** is given in Figure III.2.8. The sulfur atom is sp^3 hybridized, with the angle C(2)-S(1)-C(2a) of 106°. The C(2) and C(2a) atoms have distorted tetrahedral environments [C(1)-C(2)-S(1) 116.7°], with a slightly higher distortion than in compound **5** [C(2)-C(1)-Se(1) 109.41(14)° and C(16)-C(15)-Se(1) 111.68(15)°]. The silicon atoms are also tetrahedral.

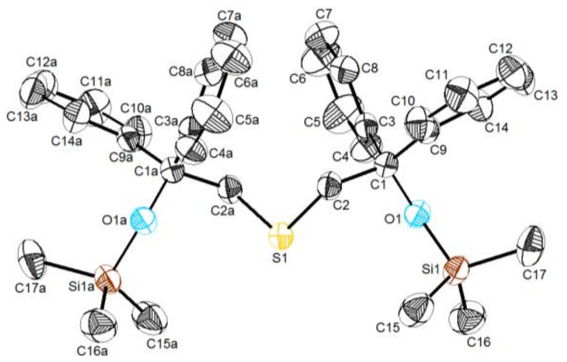
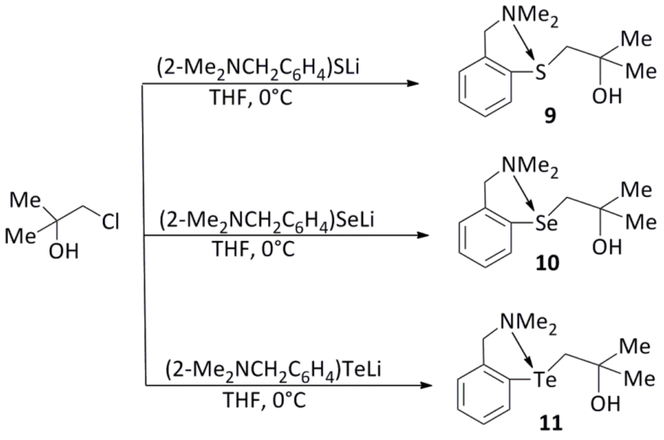


Figure III.2.8. Molecular structure of $[Ph_2C(OSiMe_3)CH_2]_2S$ (**8**); hydrogen atoms were removed for clarity. The atoms are drawn with 50% probability ellipsoids.

III.2.B. Diorganochalcogen(II) monohydroxide ligands

Compounds of type $[Me_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)E$ (E = S, Se, Te) were obtained by reacting 1-chloro-2-methyl-2-propanol with $(2\text{-}Me_2NCH_2C_6H_4)ELi$ in a 1:1 molar ratio. The lithiated reagents were freshly prepared by treating N,N-dimethylbenzylamine with n-buthyllithium, followed by insertion of chalcogen. The chemical reactions are indicated in Scheme III.2.3.



Scheme III.2.3. Preparation of diorganochalcogen(II) monohydroxide ligands

The monohydroxide ligands were isolated as colorless (**9**) or yellow (**10**) oils, after purification by vacuum distillation of the crude products, or as an orange solid (**11**).

The ^{1}H and ^{13}C NMR spectra of the monohydroxide ligands **9** - **11** exhibit the expected resonances. In the aliphatic region, the ^{1}H NMR spectra contain four sharp, singlet resonances, corresponding to the two types of methyl (*i.e.* at δ 1.26 and 2.24 ppm for the

N*Me*$_2$ and C*Me*$_2$, respectively, in **10**) and the two types of methylene (*i.e.* at δ 3.05 and 3.53 ppm for the SeC*H*$_2$ and NC*H*$_2$, respectively, in **10**) protons.

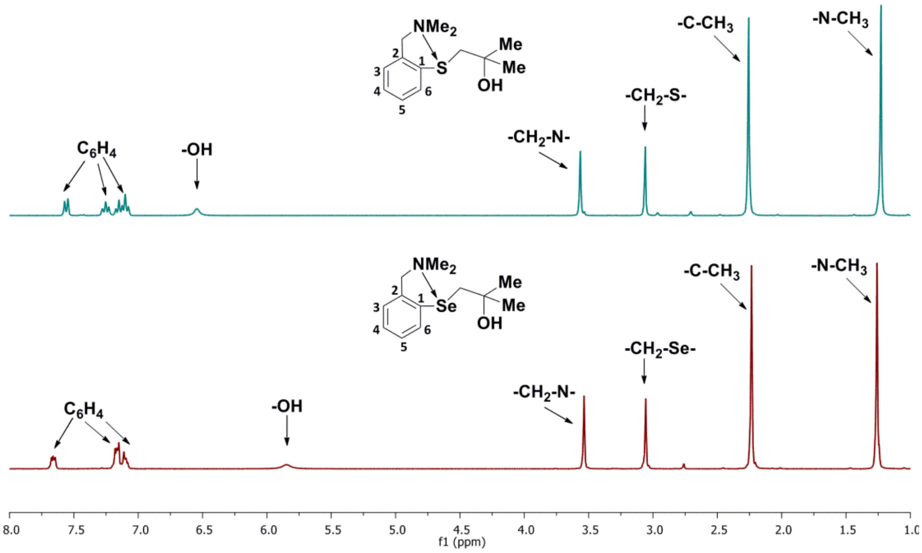


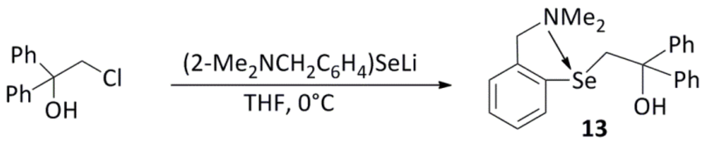
Figure III.2.9. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) of compounds **9** and **10**

No evidence for any intramolecular interaction in solution could be outlined from the ^{1}H NMR spectra. In the aromatic region, the expected multiplet resonances for the four non-equivalent protons in the phenyl ring are present. The ^{1}H NMR spectra of compounds **9** and **10** are depicted in Figure III.2.9.

The ^{77}Se NMR spectrum of compound **10** presents a singlet resonance at 192.47 ppm.

In the case of [Me$_2$C(OH)CH$_2$](2-Me$_2$NCH$_2$C$_6$H$_4$)Te (**11**) the ^{1}H and ^{125}Te NMR spectra revealed a mixture of two compounds. Further separation was required and vacuum distillation was used. The NMR investigations proved that the final residue which remained after distillation is the desired compound. The ^{125}Te (proton coupled) NMR indicated a triplet resonance at 277.87 ppm.

The ligands [Ph$_2$C(OH)CH$_2$](2-Me$_2$NCH$_2$C$_6$H$_4$)E [E = S (**12**), Se (**13**)] were similarly prepared, by reacting 1-chloro-2,2-diphenylethanol with (2-Me$_2$NCH$_2$C$_6$H$_4$)ELi in a 1:1 molar ratio (Scheme III.2.4).



Scheme III.2.4. Synthesis of [Ph$_2$C(OH)CH$_2$](2-Me$_2$NCH$_2$C$_6$H$_4$)Se

Crystal and molecular structure of $[Ph_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se$ (13)

The molecular structure of compound **13** was determined by single-crystal X-ray diffraction. The Ortep-like diagram with the atom numbering scheme is given in Figure III.2.12.

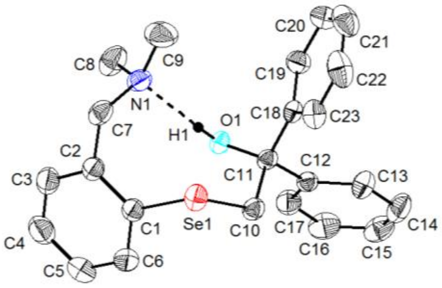


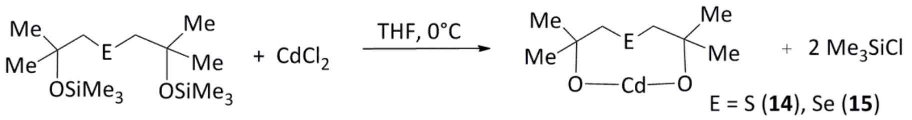
Figure III.2.12. Ortep-like diagram of $[Ph_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se$ (**13**) with 30% probability ellipsoids; hydrogen atoms, excepting O*H*, were removed for clarity.

The crystal of compound **13** consists of discrete molecules separated by normal van der Waals radii. Se(1) has a *sp*^{3} hybridization, with the angle C(1)-Se(1)-C(10) of 98.72°. The nitrogen atom in the pendant arm does not interact with selenium [Se(1)-N(1) 3.52 Å *vs*. Σr_{vdW}(Se,N) 3.44 Å[47]], but it is involved in intramolecular hydrogen bonding with H(1) [H(1)···N(1) 2.03 Å *vs*. Σr_{vdW}(H,N) 2.74 Å]. In this way the oxygen atom arrives close to selenium, at a distance lower than the sum of the respective van der Waals radii [O(1)···Se(1) 3.261(2) Å vs. Σr_{vdW}(O,Se) 3.42 Å[47]].

III.2.C. Coordination behavior of diorganochalcogen(II) ligands with alkoxo functionalities towards *d* metals

III.2.C.1. Group 12 metal complexes

The cadmium(II) complexes **14** and **15** were prepared by reacting the trimethylsilyl derivatives **6** and **7**, respectively, with cadmium(II) chloride in a 1:1 molar ratio. (Scheme III.2.5). The two complexes were isolated as slightly orange (**14**) and colorless (**15**) solids, respectively. The isolated species could not be dissolved in $CDCl_3$, so that the NMR spectra were recorded in methanol-*d*$_4$.

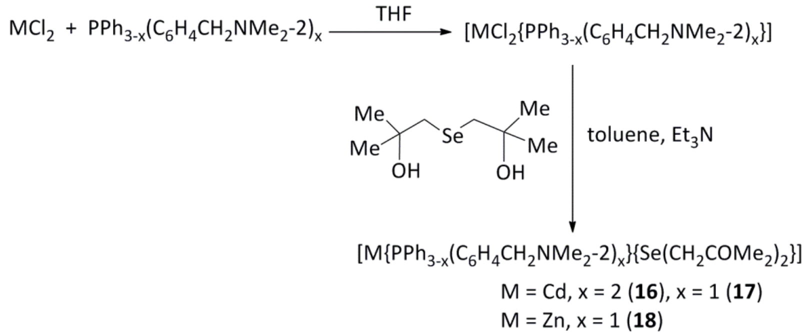


Scheme III.2.5. Synthesis of Cd((II) complexes with dialkoxo ligands

The ^{1}H NMR spectrum of [$CdS\{CH_2C(O)Me_2\}_2$] (**14**) revealed the existence of two species in solution: one of them (species I) give rise to two singlet resonances for the methyl protons (δ 1.39 and 1.43 ppm) and an AB spin system centred at 3.06 ppm (δ_A 2.96 and δ_B 3.17 ppm) for the CH_2 protons. This behavior might be consistent with the intramolecular S→Cd coordination, which rigidised the molecule in such a configuration, that the methyl groups and the methylene protons, respectively, are no more equivalent. The other species (II) is characterized by two singlet resonances for the equivalent CH_3 and CH_2 protons, respectively. In [$CdSe\{CH_2C(O)Me_2\}_2$] (**15**) only the species characterized by equivalent CH_3 and CH_2 protons was observed (δ 1.28 ppm for CH_3 and 2.73 ppm for CH_2, practically identical with the values found in the ^{1}H NMR spectrum of **14**).

When the monohydroxo ligand **10** was reacted with $CdCl_2$ in a 2:1 molar ratio a mixture of products was obtained, and the attempts to separate it in individual components failed.

Having these results, we tried to change the synthesis strategy in order to obtain more soluble species, presumably with monomeric structure in solution. In this respect we increased the coordination number to the metal by using bulky hypervalent phosphanes of type $PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$ (x = 1, 2) (Scheme III.2.6). [$CdCl_2PPh_x(C_6H_4CH_2NMe_2\text{-}2)_{3-x}$] (x = 1, 2) were obtained *in situ* by reacting $CdCl_2$ with the corresponding triarylphosphane[129] and then it was reacted with a 1:2 stoichiometric mixture of ligand **2** and triethylamine.



Scheme III.2.6. Synthesis of the group 12 metal complexes **16** – **18**

Similarly was obtained the zinc(II) complex **18**.

Complexes **16** and **17** were investigated by ^{1}H, ^{13}C and ^{77}Se NMR. The ^{1}H and ^{13}C NMR resonances were assigned by 2D NMR spectroscopy (HMBC and HSQC). Figure III.2.14. presents the ^{1}H NMR spectra of the two complexes in comparison with the free ligand. In the aliphatic region, the resonances assigned to the CMe_2, NMe_2, CH_2Se and CH_2N protons, respectively, appear in the expected ratio, 1:1 in case of compound **16** and 2:1 in case of compound **17**, respectively. The CH_3 resonances appear as singlets. The CH_2Se resonances appear as singlets as well in both compounds (2.83 ppm in **16** and 2.81 ppm in **17**), while the CH_2N resonances appear as a singlet in compound **17** (3.82 ppm) and as an AB spin system in compound **16** (δ 3.66 ppm, with δ_A 3.52 and δ_B 3.80 ppm, $^{2}J_{HH}$ 12.95 Hz).

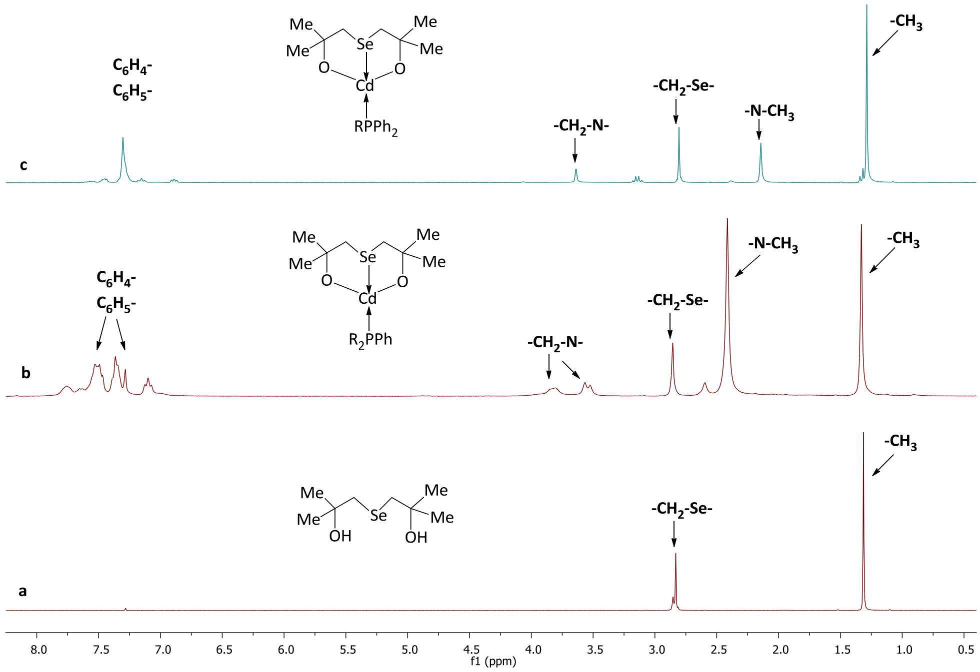


Figure III.2.14. ^{1}H NMR spectra ($CDCl_3$, 300 MHz, r.t.) of $[Me_2C(OH)CH_2]_2Se$ (a), $[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$ (**16**) (b) and $[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$ (**17**) (c)

The aromatic protons in both compounds show multiplet resonances, as expected.

The ^{31}P and ^{77}Se NMR data for the cadmium complexes are summarized in Table III.2.4, along with the data for the corresponding free ligands or their deprotonated forms.

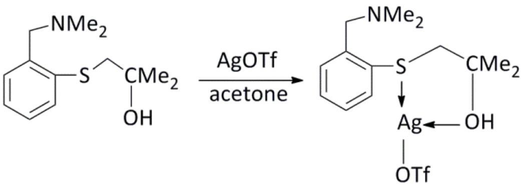
Table III.2.4. ^{31}P and ^{77}Se NMR data for the Cd(II) complexes and the starting ligands

Cpd. No.	**Compound formula**	**δ ^{31}P NMR (ppm)**	**δ ^{77}Se NMR (ppm)**
	$PPh(C_6H_4CH_2NMe_2\text{-}2)_2$	-25.1	-
	$PPh_2(C_6H_4CH_2NMe_2\text{-}2)$	-15.3	-
2	$[Me_2C(OH)CH_2]_2Se$	-	37.37
7	$[Me_2C(OSiMe_3)CH_2]_2Se$	-	95.66
15	$[Cd\{Se(CH_2C(O)Me_2)_2\}]$		Not observed
16	$[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$	-22.93	35.22
17	$[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$	-14.97	43.23
18	$[Zn\{Se(CH_2C(O)Me_2)_2\}\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$	- 23.60	Not observed

In the absence of stabilizing triarylphosphanes, the attempts to obtain similar complexes with zinc, using the same procedures as in case of the described cadmium complexes, failed. The resulting products were either complex mixtures or only starting materials. Only compound **18** could be isolated and spectroscopicaly characterized.

III.2.C.2. Silver(I) complexes

The coordination behavior of the monoalkoxide ligands towards silver was tested in the reaction of $[Me_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)S$ with AgOTf (Scheme III.2.8). Because silver compounds are light sensitive, the reaction was performed in the absence of light. The direct reaction between the ligand and AgOTf was performed both in acetone and in dichloromethane at room temperature.



Scheme III.2.8. Synthesis of the Ag complex **19**.

The ^1H NMR spectrum of this compound revealed the resonances corresponding to the different methyl and methylene groups, respectively, in the molecule, in the expected molar ratio, shifted in comparison with the starting ligand (Figure III.2.19).

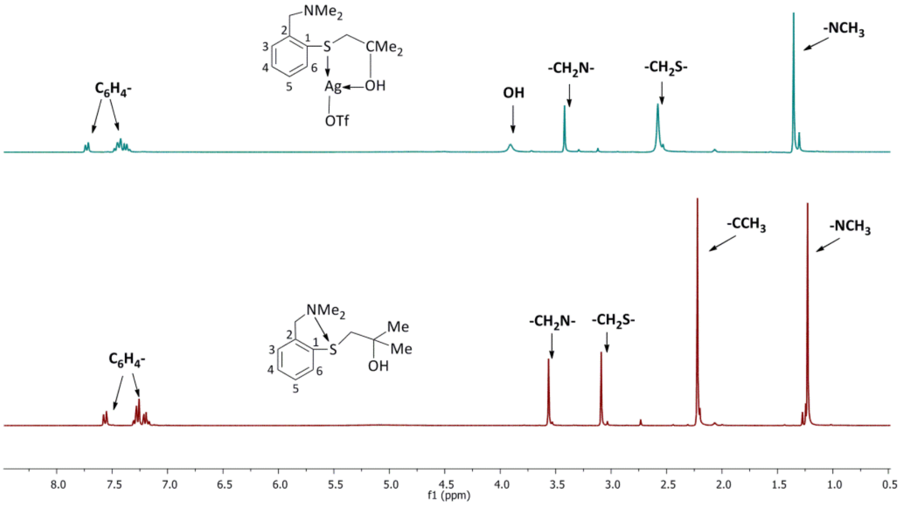


Figure III.2.19. Stacked ^1H NMR spectra of $[Me_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)S$ (down) and compound **19** (up).

The infrared spectrum shows several very strong bands at 1258, 1168, 1048/1032, and 639/654 cm^{-1}, which were assigned to the $\nu(SO_3)$ (1258 and 1048/1032 cm^{-1}) and $\nu(CF_3)$ (1258, 1168 and 639/654 cm^{-1}) stretching vibrations, respectively. The splitted pattern of the bands at 1048/1032 and 639/654 cm^{-1} suggests a covalent behavior of the OTf ligand.[130]

Crystal and molecular structure of $[AgOTf\{S[CH_2C(OH)Me_2](C_6H_4CH_2NMe_2\text{-}2)\}]$ (19)

Single-crystals suitable for X-ray diffraction studies were grown from an acetone/n-hexane mixture of solvents (1/5, v/v). The Ortep like diagram is depicted in Figure III.2.22.

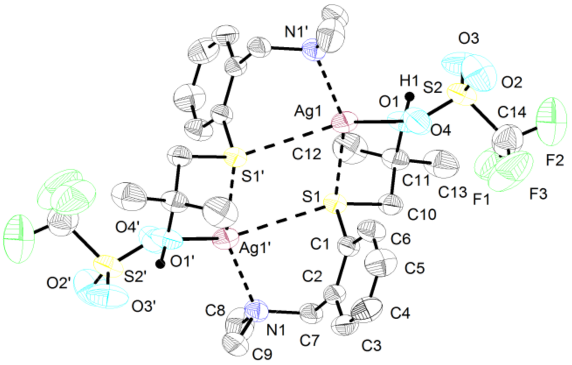


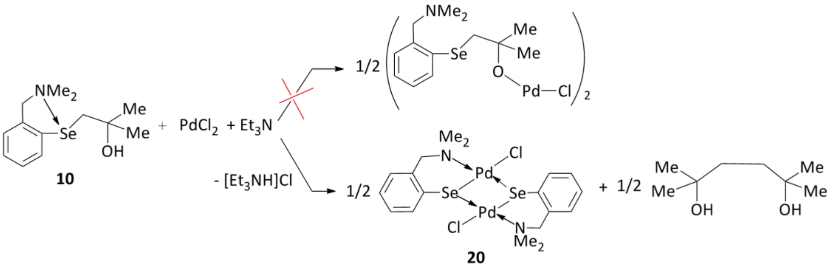
Figure III.2.22. Dimeric association of $R_{N'}$ and S_N isomers in $[AgOTf\{S[CH_2C(OH)Me_2](C_6H_4CH_2NMe_2\text{-}2)\}]$ **(19)**. Ellipsoids are drawn with 50% probability. Hydrogen atoms, excepting O*H*, were omitted for clarity

The compound crystallizes in the monoclinic P2(1)/n space group. The molecules are associated in dimeric units by bridging ligands. The ligand units act as *S,O,N* tridentate, bimetallic tetraconective moieties. Each silver atom is chelated by sulfur and oxygen, while the nitrogen atom is involved in an intermolecular interaction with the other molecule [S(1)···Ag(1) 2.5092(8), O(1)···Ag(1) 2.503(3) and N(1)···Ag(1)’ 2.251(3) Å, *vs*. Σr_{vdW}(S,Ag) 3.55, Σr_{vdW}(O,Ag) 3.10, Σr_{vdW}(N,Ag) 3.24 Å[47]]. Moreover, each sulfur atom of a ligand unit interacts with the silver atom of the neighboring molecule [S(1)···Ag(1)’ 3.16 Å]. The triflate is covalently bonded to silver by oxygen. A consequence of this coordination behavior is the formation of two condensed tricyclic systems, sharing a central, planar Ag_2S_2 core. In this way results a distorted trigonal bipyramidal environment around the silver atom, with S(1) and N(1’) in apices [S(1)···Ag(1)···N(1’) 151.13(7)^{o}].

The intermolecular N→Ag coordination determine planar chirality, with nitrogen as pilot atom and the phenyl ring as chiral plane. In this way each dimmer in the crystal is formed by *R* and *S* isomers.

III.2.C.3. Palladium(II) complexes

From the reaction between $[Me_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se$ and $PdCl_2$ in a 1:1 molar ratio, in presence of triethylamine, instead of the expected complex $[PdCl\{Se(CH_2C(O)Me_2)(C_6H_4CH_2NMe_2\text{-}2)\}]$, was isolated the dinuclear species $[PdCl(SeC_6H_4CH_2NMe_2\text{-}2)]_2$ (Scheme III.2.9).



Scheme III.2.9. The reaction between $PdCl_2$ and ligand **10**.

The same palladium containing product could be isolated, as an orange powder, even if the deprotonation of the ligand was achieved by lithiation, or if a 1:1 or a 2:1 molar ratio between **10** and $PdCl_2$ was used.

The presence of an intramolecular N→Se coordination in the free ligand in solution might facilitate the cleavage of the C–Se bond. The isolated Pd(II) complex has a very low solubility both in chlorinated solvents and in DMSO. These observations are in agreement with the data reported previously about diorganoselenium(II) species of type RR'Se, for which a similar cleavage of the C–Se bond in the presence of either Pd(II) or Pt(II) salts was observed.[131-133]

The ^1H NMR spectrum of the orange crystalline product has the expected resonances for compound **20** (Figure III.2.24). As a consequence of the intramolecular coordination of nitrogen in solution, either to selenium or to palladium, in the aliphatic region the NMe_2 groups, as well as the CH_2 protons **in** the pendant arm are no more equivalent and give rise to two different resonances for the nonequivalent CH_3 (δ 2.37 and 2.95 ppm) groups and an AB spin system (δ 3.64 ppm, with δ_A 3.42 and δ_B 3.83 ppm, $^2J_{HH}$ = 12.2 Hz) for the CH_2 protons. In the aromatic region were observed the expected multiplet resonances.

Crystal and molecular structure of $[PdCl(SeC_6H_4CH_2NMe_2\text{-}2)]_2\cdot 0.5CH_2Cl_2\cdot 0.5THF$ (20·$0.5CH_2Cl_2\cdot 0.5THF$)

Single crystals of the palladium complex were obtained by slow diffusion of n-hexane in a CH_2Cl_2/THF solution. As a result, the isolated crystals contain both CH_2Cl_2 and THF in the lattice. During our studies, the single-crystal X-ray structure of the related species **20**·$0.5CH_2Cl_2$ was reported by other authors.[134] The Ortep-like diagram with the numbering scheme is given in Figure III.2.25. The compound crystallizes in the chiral orthorhombic *P2(1)2(1)2* space group. The crystal contains two independent centrosymmetric dimers in the unit cell, $\mathbf{20}_{1/1'}$ and $\mathbf{20}_{2/2''}$ – subscript indices refer to the numbering of the palladium atoms in the dimeric moiety). The N→Pd coordination resulted in six-membered $SePdNC_3$ rings folded about the Se···CH_2 axis and induces planar chirality. The compound crystallize as a mixture of *S,S'*-$\mathbf{20}_{\mathbf{1/1'}}$ [Se(1)Pd(1)Se(1')Pd(1') core] and *R,R''*-$\mathbf{20}_{\mathbf{2/2''}}$ [Se(2)Pd(2)Se(2'')Pd(2'') core] isomers (with respect to the two $SePdNC_3$ rings of the dimeric unit). The selenium atoms are bridging the metal centres [Pd(1)–Se(1) / Pd(1)–Se(1') 2.3865(11) / 2.4017(10) Å, and Pd(2)–Se(2) / Pd(2)–Se(2'') 2.4028(10) / 2.3848(11) Å, respectively, *vs.* Σr_{cov}(Pd,Se 2.45 Å) and Σr_{vdW}(Pd,Se 3.60 Å)[47]]. Further selenium–palladium secondary interactions [Pd···Se 3.4315(12) and 3.4308(12) Å] generate [*S,S'*-$\mathbf{20}_{\mathbf{1/1'}}$]-[*R,R''*-$\mathbf{20}_{\mathbf{2/2''}}$] tetramers with a cubane-like structure.

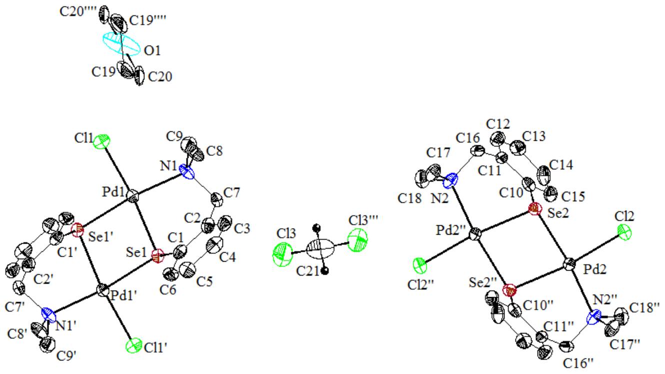


Figure III.2.25. Ortep-like digram of $[PdCl(SeC_6H_4CH_2NMe_2\text{-}2)]_2\cdot 0.5CH_2Cl_2\cdot 0.5THF$. (both *S,S'*-$\mathbf{20}_{\mathbf{1/1'}}$ [Se(1)Pd(1)Se(1')Pd(1') core] and *R,R''*-$\mathbf{20}_{\mathbf{2/2''}}$[Se(2)Pd(2)Se(2'')Pd(2'') core] are shown).

The coordination geometry around the palladium atoms is square planar, while each selenium atom is in a T-shaped environment. The CH_2Cl_2 molecules are involved in Cl···H hydrogen bonding with the *S,S'*-$\mathbf{20}_{\mathbf{1/1'}}$ dimer [$Cl(3)_{solvent}\cdots H(7A)_{methylene}$ 2.78 Å; *c.f.* $\sum r_{vdW}$(Cl,H) 3.01 Å [47]], thus resulting in a chain of cubanes. Additional weak intermolecular chlorine–hydrogen contacts between the parallel polymeric chains leads to a 3D network which accomodates THF molecules in the channels formed inside it.

III.3. Conclusions

- Diorganochalcogen(II) dihydroxide ligands of type $[R_2C(OH)CH_2]_2E$ [R = Me, E = S (**1**), Se (**2**), Te (**3**), R = Ph, E = S (**4**), Se (**5**)] were obtained and they were structurally characterized by multinuclear NMR (^1H, ^{13}C, ^{77}Se and ^{125}Te, as appropriate). Among them, compounds **2**, **3** and **5** were for the first time reported in this work.
The molecular structure of compound **5** was determined by single-crystal X-ray diffraction. The molecules are associated in dimeric units through hydrogen bonding.

- Compounds **1**, **2** and **4** were deprotonated with Me_3SiCl, leading to the trimethylsilyl derivatives of type $[R_2C(OSiMe_3)CH_2]_2E$ [R = Me, E = S (**6**), Se (**7**), R = Ph, E = S (**8**)]. The molecular structure of $[Ph_2C(OSiMe_3)CH_2]_2S$ was determined by single-crystal X-ray diffraction.

- Five new chalcogen monohydroxide ligands of type $[R_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)E$ [R = Me, E = S (**9**), Se (**10**), Te (**11**); R = Ph, E = S (**12**), Se (**13**)] were prepared and characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se and ^{125}Te, as appropriate). A monomeric structure was found by single-crystal X-ray diffraction in case of compound **13**. The O*H* proton is involved in intramolecular O*H*···N bonding.

- The cadmium(II) complexes of type $[Cd\{E[CH_2C(O)Me_2]_2\}]$ [E = S (**14**), Se (**15**)] were obtained as slight orange (**14**) or colorless (**15**) powders with low solubility in common organic solvents and their solution behavior was investigated in CD_3OD solutions by ^{1}H NMR. In case of compound **14** a mixture of two species was observed in solution. The low solubility of these species suggests a polymeric structure for these species.

- Two new cadmium complexes containing both the dialkoxo ligand $[Me_2C(O)CH_2]_2Se^{2-}$ and a stabilizing triarylphosphane of type $PPh_{3-x}(C_6H_4CH_2NMe_2\text{-}2)_x$ (x = 1 - 3), namely $[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh(C_6H_4CH_2NMe_2\text{-}2)_2\}]$ (**16**) and $[Cd\{Se(CH_2C(O)Me_2)_2\}\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$ (**17**) were obtained and structurally characterized by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se) and mass spectrometry.
The similar zinc complex $[Zn\{Se(CH_2C(O)Me_2)_2\}\{PPh_2(C_6H_4CH_2NMe_2\text{-}2)\}]$ (**18**) was also prepared and characterized by multinuclear NMR (^{1}H, ^{13}C, ^{31}P) and mass spectrometry.
Compounds **16** – **18** are soluble in $CDCl_3$, this fact suggesting a monomeric structure of the investigated species.

- The silver complex $[Ag(OTf)\{S[CH_2C(OH)Me_2\}(C_6H_4CH_2NMe_2\text{-}2)]$ (**19**) was obtained as a microcrystalline solid by reacting AgOTf with the ligand in protonated form. The NMR and MS spectra were in accordance with the desired compound. The single-crystal X-ray diffraction studies revealed a dimeric structure with *O,S,N*- tridentate biconective ligands.

- The palladium complex $[(PdCl(SeC_6H_4CH_2NMe_2\text{-}2)]_2$ (**20**) resulted in the reaction between $PdCl_2$ and ligand **10** in deprotonated form, as a consequence of splitting a Se–C bond in the ligand. The single-crystal X-ray diffraction studies revealed for **20**·$0.5CH_2Cl_2$·0.5THF a cubane-like structure formed by two pairs of dimers. The cubanes are associated in polymeric chains, which further form supramolecular assemblies by hydrogen bonding involving chlorine atoms of the CH_2Cl_2 molecules, while the THF molecules are included in the channels formed inside the 3D network.

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Publications resulted from the PhD Thesis

1. *New diorganoselenium*(II*) compounds and their behavior towards late transition metals*
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3. *Copper complexes with hypervalent triarylphosphanes.*
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4. *Diorganoselenium(II) ligands with hydroxo functionalities and their coordination behavior towards d metals.*
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Conferences

1. *New copper complexes with triarylphosphines*
R. Mitea, A. Covaci, I. Hosu, A. Silvestru
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2. *New dialcoxo ligands and their metal complexes*
R. Mitea and A. Silvestru
Academic Days of Timisoara, 12th Edition, Timisoara, Romania, May 2011.

3. *Diorganochalcogen (II*) *species bearing alkoxo functionalities and their coordination behavior*
R. Mitea and A. Silvestru
International Conference on Organometallic Chemistry, Lisbon, Portugal, September 2012.