



Babeş-Bolyai University
Faculty of Chemistry and Chemical Engineering



STUDIES ON SYNTHESIS, STRUCTURE AND CHEMICAL REACTIVITY OF SOME NEW ORGANO-CHALCOGEN COMPOUNDS

Abstract PhD Thesis

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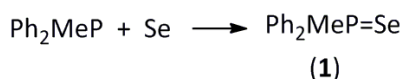
Keywords: selenium; synthesis; chalcogenides; macrocycle; NMR spectroscopy.

III. Original contributions

III.A. Triarylphosphane chalcogenides and new group 11 complexes

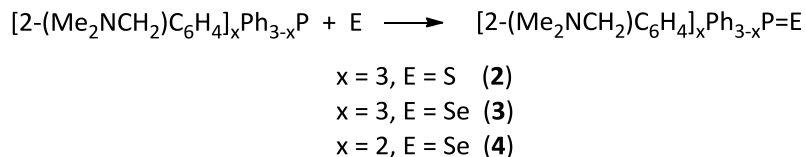
III.A.1. Results and discussion

This work deals with the synthesis and characterization in solution and in solid state of some new triarylphosphane chalcogenides. The complexes of **1** with group 11 transition metals have been prepared and structurally characterized.⁹⁴



Scheme 1. Reagents and conditions: toluene, Se, reflux.

Triarylphosphane chalcogenides of type $\text{R}_x\text{Ph}_{3-x}\text{P}=\text{E}$ [$\text{R} = 2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$, $\text{E} = \text{S}$, $x = 3$ (**2**), $\text{E} = \text{Se}$, $x = 3$ (**3**) and $\text{E} = \text{Se}$, $x = 2$ (**4**)] were prepared by reacting the appropriate triarylphosphane with elemental selenium or sulfur in a 1:1 molar ratio (**Scheme 2**). The solution behaviour of compounds **2** – **4** was investigated by multinuclear NMR spectroscopy (^1H , ^{13}C and ^{31}P). The molecular structures of derivatives **2** and **3** were determined by single-crystal X-ray diffraction.



Scheme 2. Reagents and conditions: dry THF, chalcogene, reflux.

The ^1H and ^{13}C NMR spectra are consistent with the organic groups attached to phosphorus. The assignments of the ^1H and ^{13}C resonances were made using 2D (HMBC and HSQC) NMR experiments. The multiplicity of the resonances is determined by the proton–proton, phosphorus–proton and phosphorus–carbon couplings, respectively. In the ^1H NMR spectra of the compounds **2** – **4** at room temperature (**Figure 1**) the NMe_2 groups display singlet resonance around δ 2.0 ppm. The methylene protons give a singlet resonance for compounds **2** and **3**, while for compound **4** an AB spin system is observed, due to the prochiral phosphorus atom in the last case. This behavior suggests no intramolecular $\text{N} \rightarrow \text{P}$ interaction in solution.

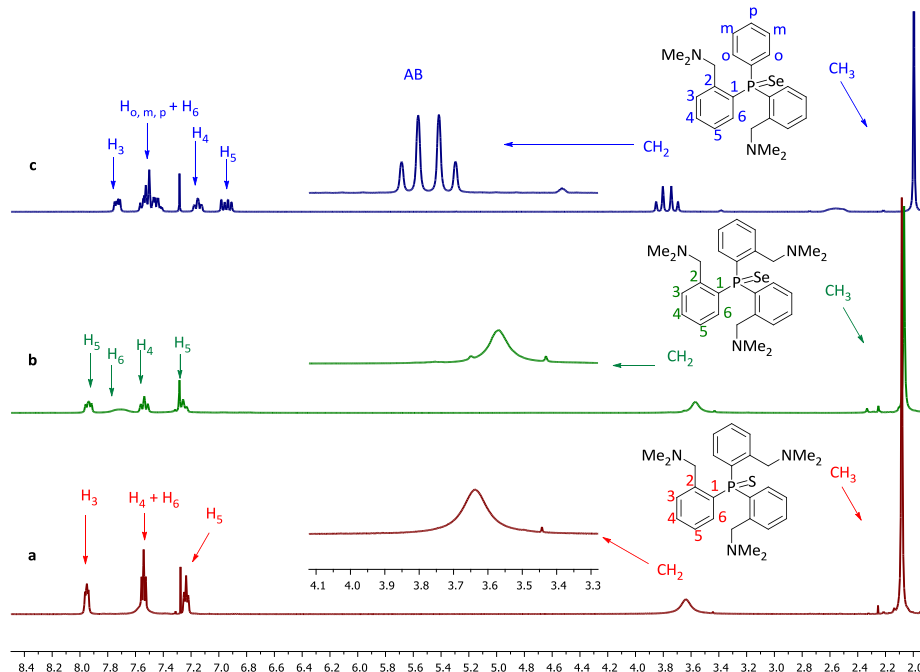


Figure 1. Stacked ^1H NMR spectra (CDCl_3 , 300 MHz) of (a) compound **2**, (b) compound **3** and (c) compound **4**.

The molecular structures of compounds **2** (Figure 3) and **3** (Figure 4) were established by single-crystal X-ray diffraction studies. No nitrogen–phosphorus intramolecular interactions were observed in these compounds. A distorted tetrahedral environment is observed around the phosphorus centers and a *pseudo*-tetrahedral one around nitrogen. In compound **2** the N2 atom is brought much closer to phosphorus than the other two nitrogen atoms, [P1–N2 3.346(35), P1–N1 4.598(52), P1–N3 4.620(42) Å, vs. Σr_{vdW} (NP) 3.44 Å], but no intramolecular interaction can be considered, the sp^3 free electron pair of nitrogen being not directed towards the phosphorus atom. The phosphorus–chalcogen interatomic distances are consistent with double P=E, *i.e.* P=S 1.962(2) in **2** and P=Se 2.118(1) Å in **3**, respectively.

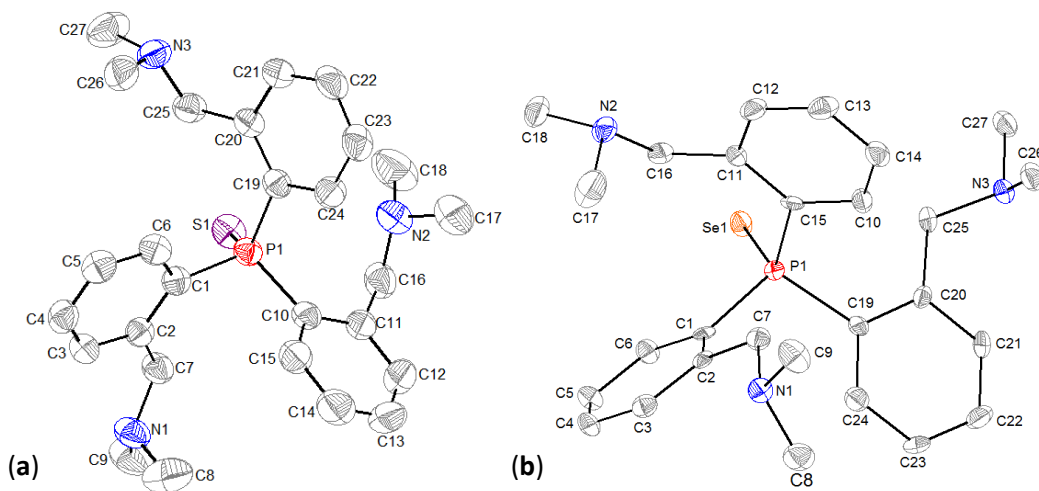
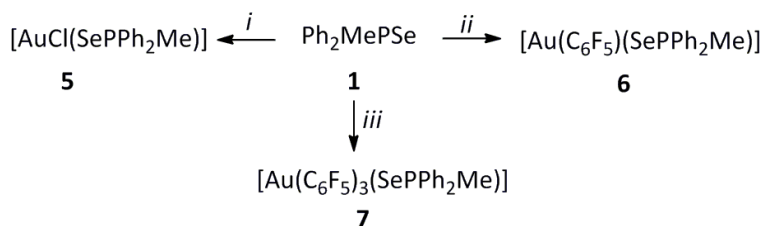


Figure 3. Molecular structure with atom numbering scheme of (a) compound **2** and (b) compound **3**. The hydrogen atoms were removed for clarity. The atoms are drawn with 30% probability ellipsoids.

The triorganophosphane selenide ligand Ph₂MeP=Se (**1**) was reacted in a 1:1 molar ratio with the appropriate gold starting material, as depicted in **Scheme 3**.



Scheme 3. Reagents and conditions: *i*) DCM, AuCl(tht), r.t.; *ii*) (C₆F₅)Au(tht), DCM, r.t.; *iii*) (C₆F₅)₃Au(tht), DCM, r.t.

Compounds **5** – **7** were characterized by spectroscopic methods in solution and also in solid state by single-crystal X-ray diffraction. The ¹H, ³¹P, ⁷⁷Se and ¹⁹F NMR spectroscopy, as well as the X-ray diffraction studies are in accordance with the expected structure. The NMR spectra were recorded in CDCl₃, at room temperature. The ¹H NMR spectra of the compounds display the expected pattern comparing with the ligand **1** (**Figure 5**). The aliphatic signal appears as a doublet, due to the phosphorus–proton coupling. In the aromatic region, the phenyl groups present multiplet resonances characteristic for the *ortho*-, *meta*- and *para*- protons, respectively. The resonances characteristic for the *ortho*-protons appear as a doublet of doublets of doublets, due both to the phosphorus–proton and proton–proton couplings.

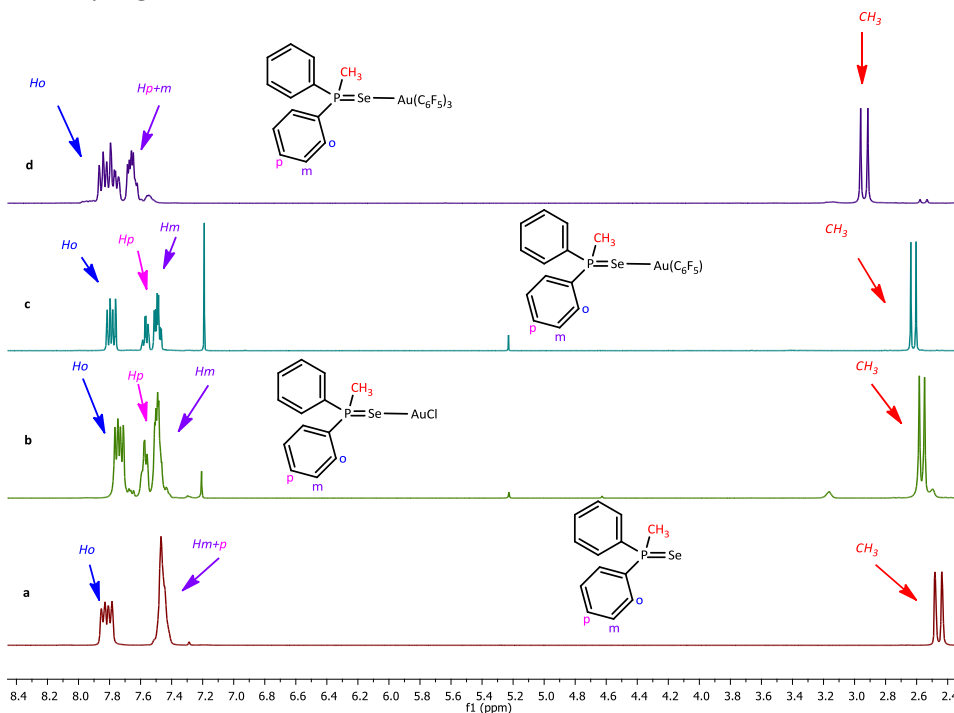


Figure 5. Detail from stacked ¹H NMR spectra (CDCl₃, 300 MHz) of (a) ligand **1**, (b) compound **5**, (c) compound **6**, and (d) compound **7**.

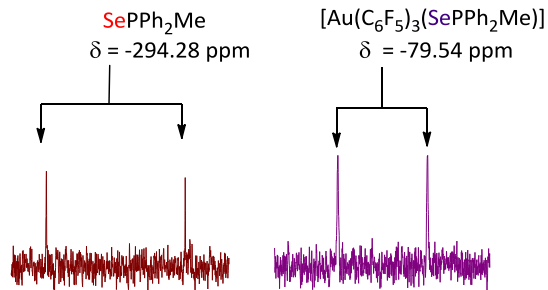


Figure 7. Detail from ^{77}Se NMR spectra (CDCl_3 , 58 MHz) of ligand **1** and compound **7**.

The ^{77}Se NMR spectra show a doublet signal as expected, due to the selenium–phosphorous coupling (**Figure 7**). The chemical shifts are reported relative to dimethylselenide (δ 0 ppm) by assuming that the resonance of Ph_2Se_2 , used as standard, is at δ 461 ppm. In the gold complex **7** the value of the ^{77}Se resonance is δ -79.54 ppm, low field shifted comparing to ligand **1** (δ -294.28 ppm), due to the interaction between the selenium and the gold atoms.

The ^{19}F NMR spectra of **6** and **7** contain three resonances with the expected patterns for the C_6F_5 groups (**Figure 8**). In case of the square-planar compound **7** the three C_6F_5 groups attached to gold give two different ^{19}F sets of resonances in a 1:2 molar ratio for the non equivalent C_6F_5 groups (one of them *trans* to selenium and the other two *trans* each-other, respectively).

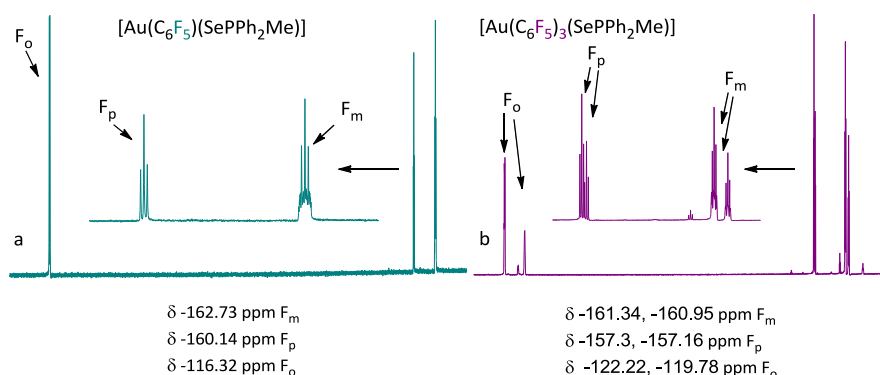


Figure 8. Details from ^{19}F NMR spectra (CDCl_3 , 282 MHz) of: (a) compound **6** and (b) compound **7**.

The gold complexes **6** and **7** are essentially monomeric species, although in complex **6** the gold–gold distance between two neighboring molecules is just at the limit below the sum of the van der Waals radii for gold [$3.3387(7)$ Å vs. $\Sigma r_{\text{vdw}}(\text{Au}, \text{Au})$ 3.40 Å].⁹⁸ The organophosphorus(V) ligand behaves as a monometallic monoconnective moiety in both gold complexes, being attached to the metal centre through selenium. In complex **6** the coordination geometry about the gold(I) atom is linear, slightly distorted [C1–Au1–Se1 $176.72(2)^\circ$]. Taking into account the weak $\text{Au}\cdots\text{Au}$ contact, a T-shaped coordination geometry can be assigned [$\text{Au2}\cdots\text{Au1–Se1}$ $75.22(2)^\circ$ and $\text{Au2}\cdots\text{Au1–C1}$ $108.06(2)^\circ$]. In complex **7** the gold atom has a square planar geometry. The C_6F_5 group *trans* to selenium is twisted to

almost 90° with respect to the other two pentafluorophenyl rings. The phosphorus atoms have tetrahedral coordination geometries in both complexes, while the selenium atoms have distorted *pseudo* tetrahedral coordination geometries [Au1–Se1–P1 94.06(5)° in **7** and 102.98(4)° in **6**, respectively].

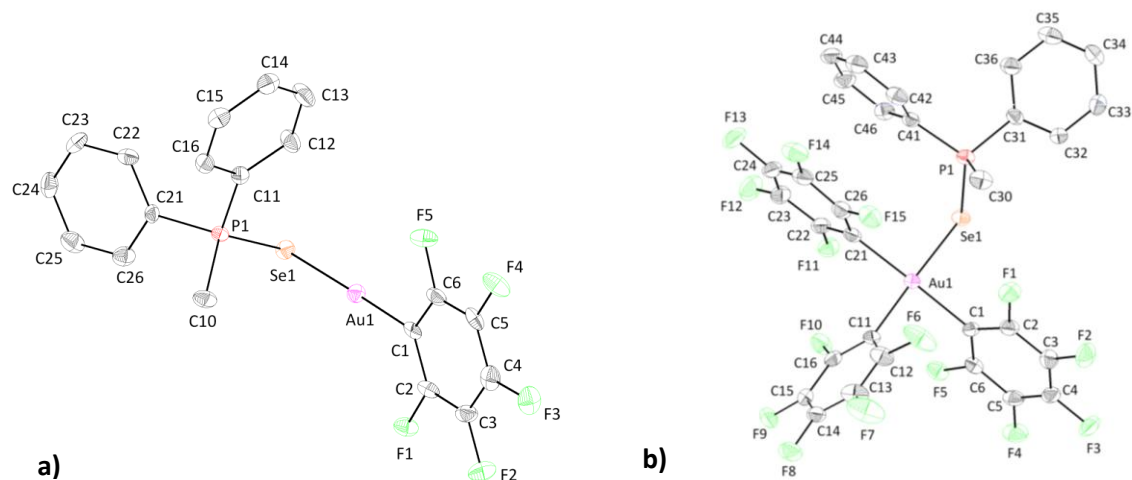


Figure 10. Molecular structure with atom numbering scheme of: (a) compound **6** and (b) compound **7**; the hydrogen atoms were removed for clarity. The atoms are drawn with 50% probability ellipsoids.

The diffuse reflectance ultraviolet visible spectra (DRUV) were recorded for the gold complexes **6** and **7**. The spectrum of complex **6** consists of a band with two maxima at 231 and 260 nm and that of **7** a band with a maximum at 276 nm. Both complexes are weakly emissive in the solid state, complex **6** only at 77 K and complex **7** at room temperature and at 77 K. Complex **6** displays one emission as shown in **Table 3** at 500 nm (**Figure 11**) and complex **7** shows two emissions, one at 360 and a not well resolved structured band at about 446 nm.

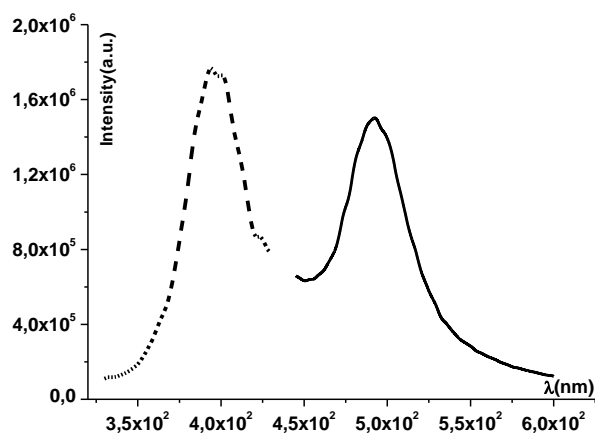
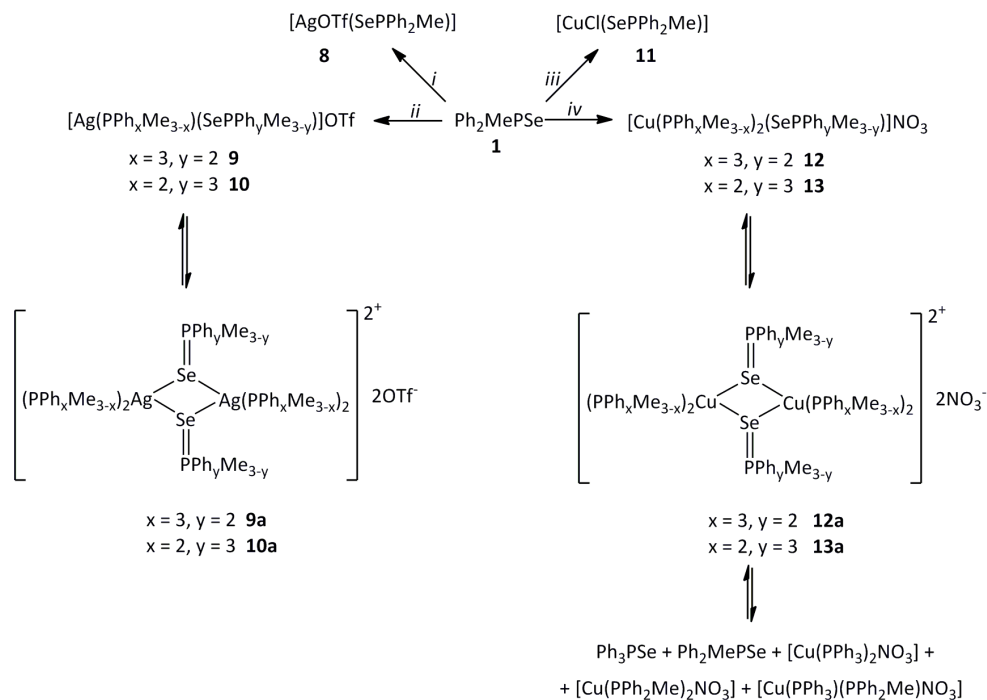


Figure 11. Excitation (dashed line) and emission (straight line) spectrum of complex **6** at 77K.

Crystalline solids were obtained by the reaction of the ligand **1** with silver and copper complexes in 1:1 molar ratio (see **Scheme 4**). Silver complexes were synthesized in acetone at room temperature stirring the reaction mixture from 30 minutes to 1 h. Copper complexes were obtained from DCM, at room temperature, with stirring 24 h.

^1H and ^{31}P NMR data for the complexes containing only one type of organophosphorus ligand (triorganophosphane selenide, compounds **8** and **11**) suggest the existence of only one species in solution, while for the complexes containing more than one type of organophosphorus ligands the NMR spectra suggest a dynamic behavior. However, for the phenyl and the methyl groups attached to phosphorus the ^1H NMR spectra (**Figure 12**) exhibit resonances with the expected pattern due to the proton–proton and phosphorus–proton couplings, respectively.

The ^{31}P NMR spectra of the complexes **8** and **11** (**Figure 13**) exhibit singlet resonances corresponding to the SePPh_2Me moiety (δ 27.8 ppm for **8** in acetone- d_6 and 21.17 ppm for **11** in CDCl_3 solution), with characteristic ^{77}Se and ^{13}C satellites.



Scheme 4. Reagents and conditions: *i*) AgOTf, Acetone, 2h, r.t.; *ii*) Ag(PPh₃)OTf, Acetone, 2h, r.t.; *iii*) CuCl, CH₂Cl₂, 24h, r.t.; *iv*) Cu(PPh₃)₂NO₃, CH₂Cl₂, 24h, r.t.

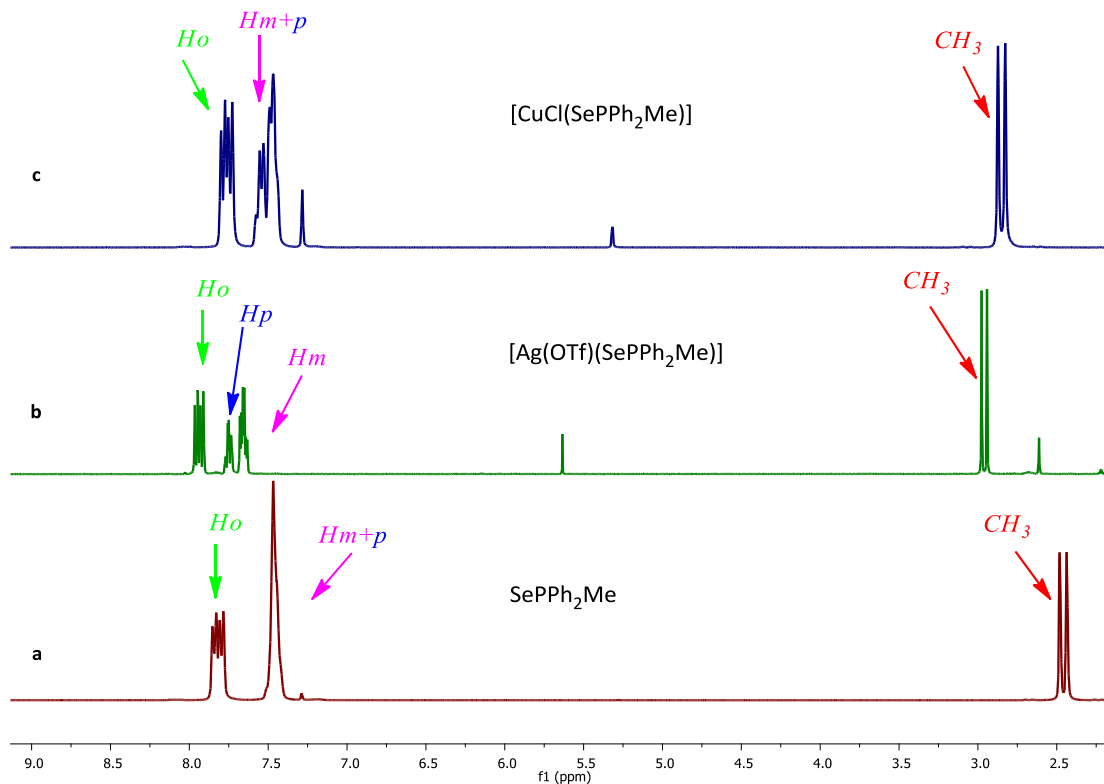


Figure 12. Detail from stacked ^1H NMR spectra (CDCl₃, 300 MHz) of: (a) ligand **1**, (b) compound **8** and (c) compound **11**.

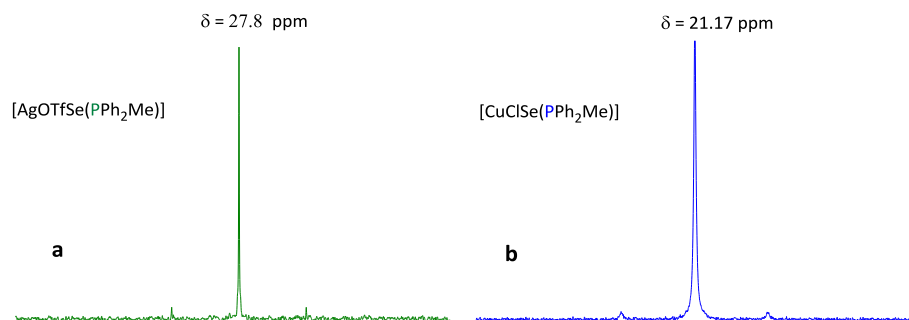


Figure 13. Detail from ^{31}P NMR spectra: (a) compound **8** (acetone-*d*₆, 300 MHz); (b) compound **11** (CDCl₃, 121 MHz).

The IR spectrum of the silver-containing species **8** (Figure 14) show bands at 1280(vs), 1218(vs), 1155(s) and 1021(vs) cm⁻¹. The triflate moiety is ionic bonded to silver. This observation comes with the proof that the asymmetric vibration of sulfuryl ion, that occurs near 1280 cm⁻¹, is not split in two bands.

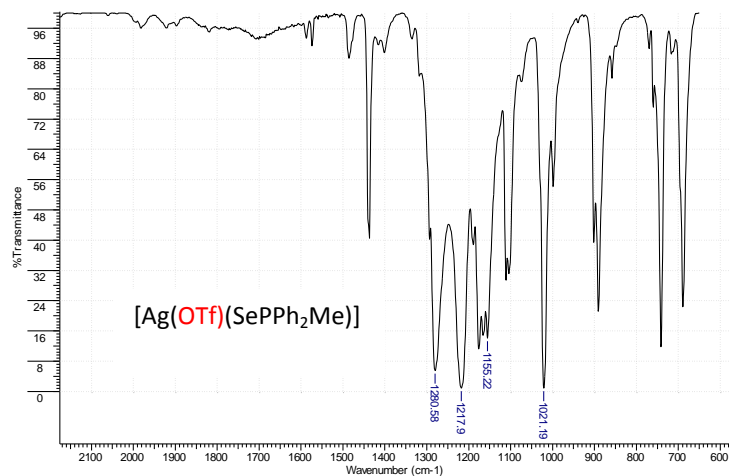


Figure 14. The IR spectrum of complex **8**.

In the case of the solid product isolated from reaction (ii), *i.e.* [Ag(PPh_xMe_{3-x})(SePPh_yMe_{3-y})]OTf, the ¹H NMR spectrum shows in the aliphatic region two resonances, in an 1:4 molar ratio (δ 1.85 ppm, ²J_{P^H} 5.9 Hz and δ 2.60 ppm, ²J_{P^H} 13.6 Hz). The observed coupling constants are in accordance with the presence of both a P(III) and a P(V) species containing P^{*Me*} protons.

A 2D H,P-HMQC spectrum was recorded at room temperature for the reaction (ii) in order to confirm the formations of the two derivatives **9** and **10** (Figure 19).

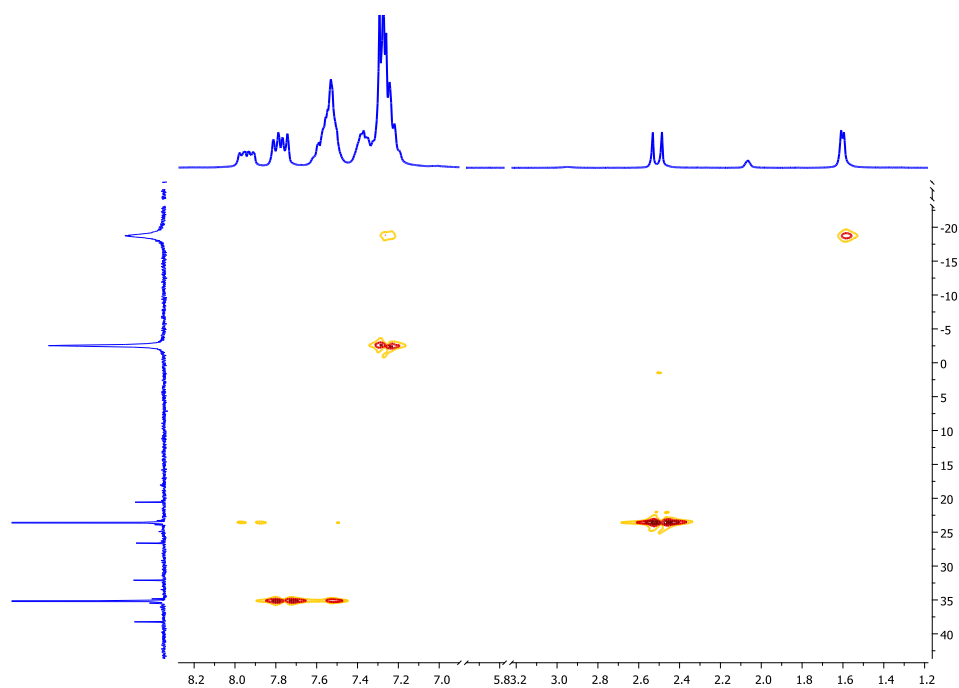


Figure 19. The 2D H,P-HMQC spectrum (CDCl₃, 300 MHz) of the solid isolated from reaction (ii).

The APCI+ mass spectra of the solid resulted from reaction (ii) presents the molecular ion $[\text{AgOTf}(\text{PPh}_3)(\text{SePPh}_2\text{Me})^+]$ (m/z 800.9, 80%) as well as the ion $[\text{Ag}(\text{PPh}_3)(\text{SePPh}_2\text{Me})^+ + \text{Se}]$ (m/z 729.6, 100%).

In addition, the IR spectrum (**Figure 21**) of the solid isolated from reaction (ii) corresponding to the silver-containing species show bands at 1262 (vs), 1222(s), 1151(s) and 1027(s) cm^{-1} , suggesting a ionic behavior of the triflate group.^{106,107}

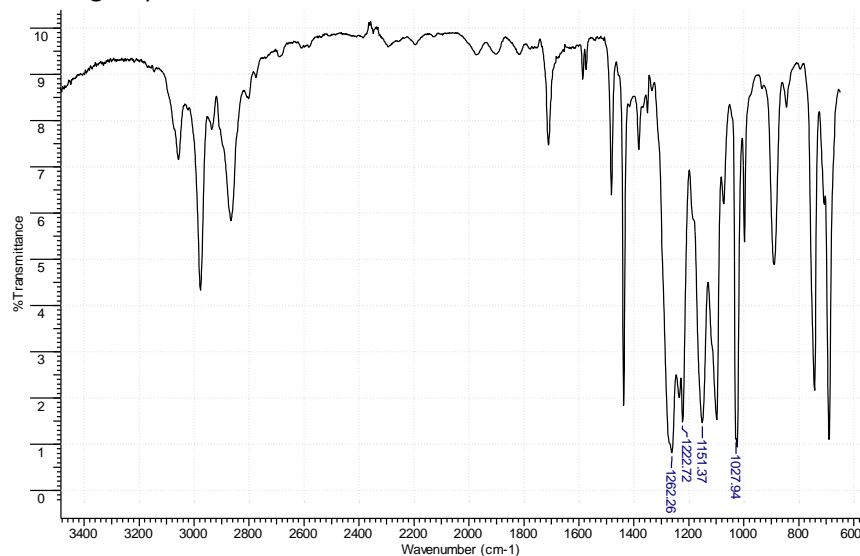


Figure 21. The IR spectrum of solid isolated from reaction (ii).

The solid isolated from reaction (iv) proved a similar behavior in solution as it was described above for the silver species $\{[\text{Ag}(\text{PPh}_x\text{Me}_{3-x})(\text{SePPh}_y\text{Me}_{3-y})\text{OTf}]_n\}$ ($n = 1, 2$). The ^{31}P NMR spectra recorded at room temperature either in CDCl_3 or acetone- d_6 solution, presents four resonances, two of them at high field, sharp, accompanied by ^{77}Se satellites, and the other two broad, at low field. These four signals might be considered as forming two sets of resonances, similarly with the situation described before for the silver(I) species **9** and **10**. However in the case of the copper(I) species the monomer and the dimer are in a 1:2 molar ratio. Moreover, the ^{31}P NMR chemical shifts are similar with those observed for the species SePPh_2Me , SePPh_3 and $[\text{CuNO}_3(\text{PPh}_3)_2]$, respectively (**Table 4**). The fourth resonance at $\delta -17.4$ ppm was tentatively assigned to $[\text{CuNO}_3(\text{PPh}_2\text{Me})_2]$. Taking into account this similarity, we presume that even if in reaction (iv) an equilibrium process involving both transfer of selenium from SePPh_2Me to PPh_3 and association in dimeric units takes place in a first instance, according to **Scheme 4**, due to the high lability of the resulted copper(I) species and the overcrowded metal center, an advanced process of dissociation occurred, resulting in SePPh_2Me , SePPh_3 , $\text{CuNO}_3(\text{PPh}_2\text{Me})_2$, $\text{CuNO}_3(\text{PPh}_3)_2$ and $\text{CuNO}_3(\text{PPh}_2\text{Me})(\text{PPh}_3)$ species. An evidence in this sense is also the fact that attempts to grow single-crystals of the solid isolated from this reaction resulted in SePPh_3 or $\text{CuNO}_3(\text{PPh}_3)_2$. Low temperature ^{31}P NMR spectra of the copper species brought no clear evidence for an equilibrium between a mixture of monomeric (**12** and **13**) and dimeric (**12a** and **13a**) species, as was described above for the silver(I) complex species **9** and **10**, respectively, but such a process cannot be excluded. At -75 °C, the two ^{31}P

resonances corresponding to the phosphines, PPh_3 and PPh_2Me , respectively, attached to copper have an aspect of multiplets (**Figure 22**). This aspect suggests the existence of a third bis(triorganophosphane)copper(I) species in solution, *i.e.* $[\text{CuNO}_3(\text{PPh}_3)(\text{PPh}_2\text{Me})]$, and it might be determined by very close chemical shift values of the PPh_3 and PPh_2Me ligands in the three types of bis(triorganophosphane)copper(I) complexes and by the fact that at such low temperature even the two phosphorus atoms in species containing the same triorganophosphanes attached to the metal center are no more equivalent.

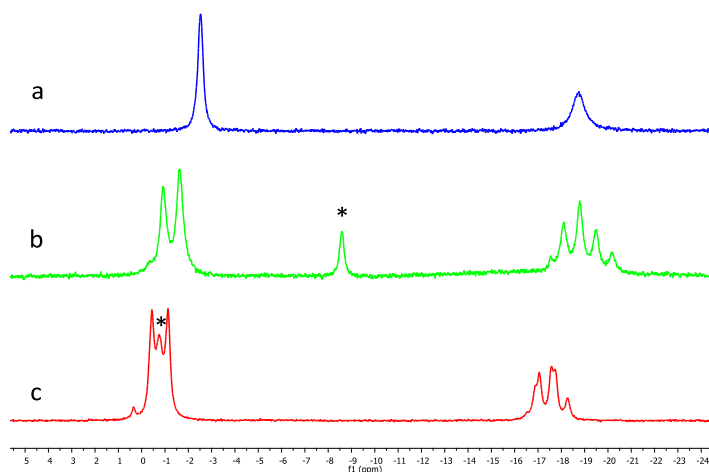


Figure 22. Room temperature (a) and low temperature [213K (b), and 198K (c)] ^{31}P NMR spectra of the solid isolated from reaction (iv). (-25 - +5 ppm region).

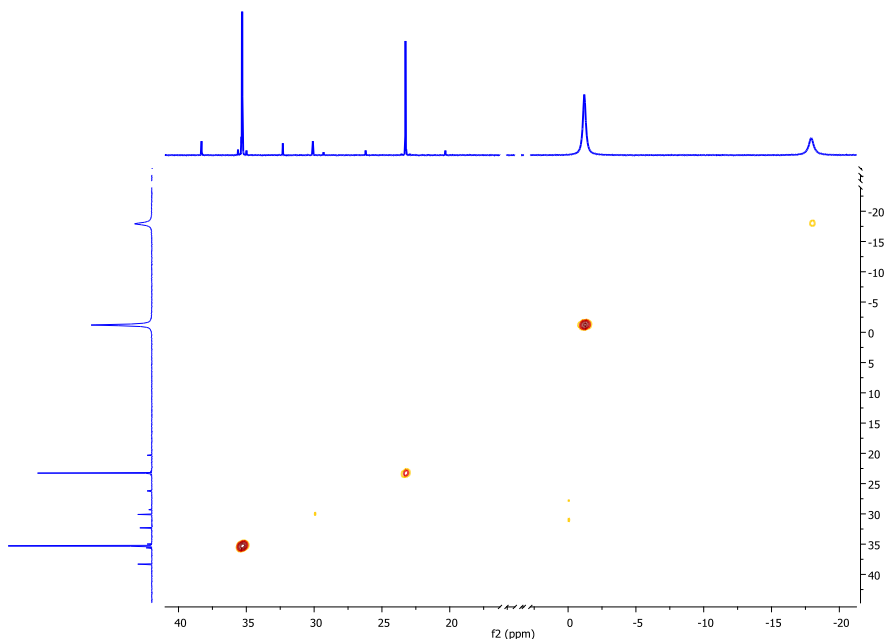


Figure 24. Detail from 2D P,P-COSY spectrum (CDCl_3 , 121 MHz) of the solid isolated from reaction (iv).

2D ^{31}P - ^{31}P COSY (**Figure 24**) and ^{31}P - ^1H HMQC (**Figure 25**) correlation experiments were used to assign the resonances for the copper(I) species present in solution as result of the dynamic processes described for reaction (iv).

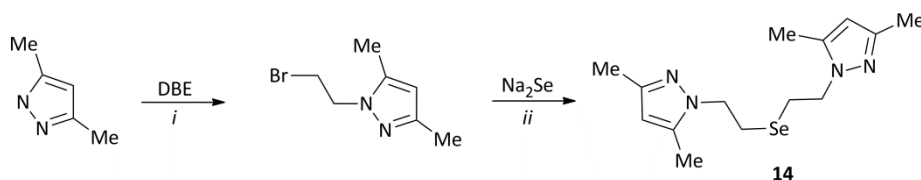
III.A.2. Conclusions

- Three new triarylphosphane chalcogenides were synthesized and structurally characterized in solution by multinuclear NMR spectroscopy and compounds **2** and **3** in solid state by single-crystal X-ray diffraction.
- Several group 11 metal complexes $[\text{AuCl}(\text{SePPh}_2\text{Me})]$ (**5**), $[\text{Au}(\text{C}_6\text{F}_5)(\text{SePPh}_2\text{Me})]$ (**6**), $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{SePPh}_2\text{Me})]$ (**7**), $[\text{AgOTf}(\text{SePPh}_2\text{Me})]$ (**8**) and $[\text{CuCl}(\text{SePPh}_2\text{Me})]$ (**11**) were isolated and structurally characterized in solution by multinuclear NMR spectroscopy.
- For the gold complexes **6** and **7** monomeric structures were determined by single-crystal X-ray diffraction and they were further optimized by DFT calculations.⁹⁴ In case of compound **6** weak aurophilic gold(I)⋯gold(I) contacts were also observed in the crystal. The DRUV spectra have shown that complexes **6** and **7**, as well as the ligand SePPh_2Me , are emissive in the solid state, complex **6** only at 77 K and complex **7** and the free ligand both at room temperature and at 77 K. TD-DFT calculations were performed in order to investigate the electronic properties which determine the luminescence of complexes **6** and **7**, as well as of the ligand $\text{Ph}_2\text{MeP}=\text{Se}$ in the solid state.⁹⁴
- The products isolated from the reactions between SePPh_2Me and $[\text{AgOTf}(\text{PPh}_3)]$ or $[\text{CuNO}_3(\text{PPh}_3)_2]$ proved to have a dynamic solution behavior involving the transfer of selenium from the P(V) species SePPh_2Me to the P(III) phosphane PPh_3 . In case of the silver(I) species the NMR experiments brought further evidence for dimerization processes resulting in $[\text{Ag}(\text{PPh}_3)(\mu\text{-SePPh}_2\text{Me})_2](\text{OTf})_2$ (**9a**) and $[\text{Ag}(\text{PPh}_2\text{Me})(\mu\text{-SePPh}_3)_2](\text{OTf})_2$ (**10a**), while in case of the Cu(I) species the NMR experiments suggest the decomposition of initially formed products, resulting in the copper(I) complexes $[\text{CuNO}_3(\text{PPh}_3)_2]$, $[\text{CuNO}_3(\text{PPh}_2\text{Me})_2]$ and $[\text{CuNO}_3(\text{PPh}_3)(\text{PPh}_2\text{Me})]$ and the triorganophosphane selenides SePPh_2Me and SePPh_3 in equilibrium, even if in the first stage of the reaction the formation of monomeric $[\text{CuNO}_3(\text{PPh}_3)_2(\text{SePPh}_2\text{Me})]$ (**12**) and $[\text{CuNO}_3(\text{PPh}_2\text{Me})(\text{SePPh}_3)]$ (**10**), and dimeric $[\text{Cu}(\text{PPh}_3)(\mu\text{-SePPh}_2\text{Me})_2](\text{NO}_3)_2$ (**12a**) and $[\text{Cu}(\text{PPh}_2\text{Me})(\mu\text{-SePPh}_3)_2](\text{NO}_3)_2$ (**13a**) might be also envisaged. DFT calculations are in accordance with a head-to-tail conformation for **9a**, thus supporting the hypothesis that both Ag centers in a dimeric unit could be alternatively involved in the $\text{Ag}\cdots\text{Se}$ contact so that a fast equilibrium on NMR time scale between the dimer featuring the $\text{Ag}^{\text{A}}\cdots\text{Se}^{\text{B}}$ interaction and the dimer featuring the $\text{Ag}^{\text{B}}\cdots\text{Se}^{\text{A}}$ contact takes place, in accordance with the ³¹P NMR spectrum at room temperature. The attempt to optimize a hypothetical dimer **13a** showing structural features similar to those calculated for **10a** suggest the elimination of PPh_2Me , with formation of an unstable dinuclear species $[\text{Cu}_2(\text{PPh}_3)_2(\text{SePPh}_2\text{Me})(\text{Se})]^{2+}$, which might prelude the further decomposition, in accordance with the NMR spectra.⁹⁴

III.B. New RR'Se and R₂Se₂ derivatives and their group 11 complexes

III.B.1. Results and discussion

In order to fulfill the proposed objectives, new diorganoselenium(II) compounds incorporating pyrazole units and diorganodiselenium(I) compounds with two pendant arms have been synthesized. Following literature methods, 1-(2-bromoethyl)-3,5-dimethyl-1H-pyrazole was synthesized by refluxing 3,5-dimethyl-1H-pyrazole with excess of 1,2-dibromoethane.¹³¹ The compound obtained from reaction *i*) was purified by flash chromatography using ethyl acetate as eluent. The second step was the synthesis of Na₂Se by a reaction of NaBH₄ with elemental selenium in water.¹³² R₂Se derivative was further obtained by reacting Na₂Se with the corresponding organic bromide as depicted in **Scheme 6**.



Scheme 6. Reagents and conditions: *i*) NaOH, TBAB; *ii*) NaBH₄, H₂O, NaOH, EtOH.

¹H, ¹³C, ⁷⁷Se NMR and 2D NMR spectra have been performed in order to provide useful information about the nature of the formed molecular species. In the aliphatic area of the ¹H NMR spectrum of ligand **14**, the existence of the methyl groups attached to the pyrazole ring is confirmed by two singlet signals at δ 2.17 ppm and 2.23 ppm, respectively. Furthermore, two triplet signals at δ 2.83 ppm and 4.12 ppm, respectively, confirm the presence of the -CH₂CH₂- moiety. In the aromatic region, the proton attached to carbon C₂ of the pyrazole ring appears as a singlet at δ 5.75 ppm (**Figure 28**).

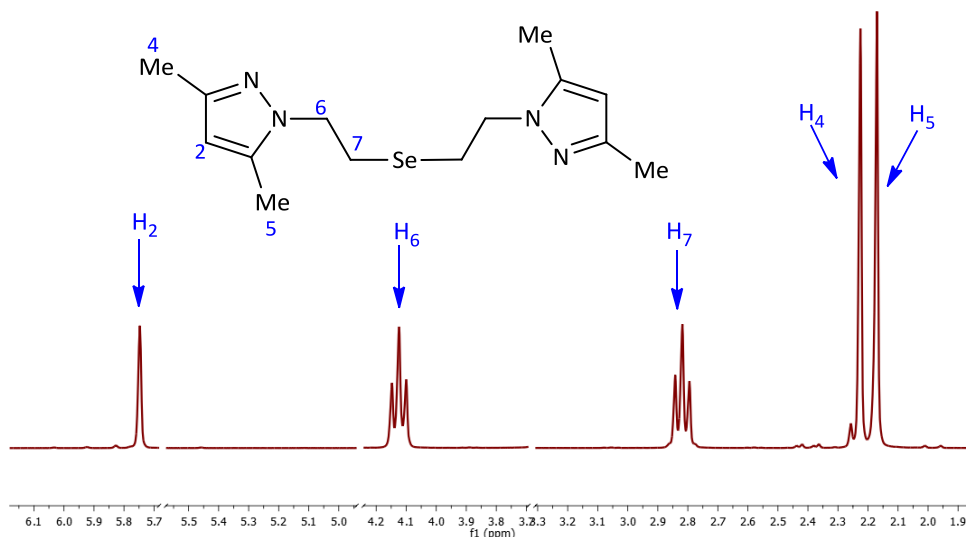
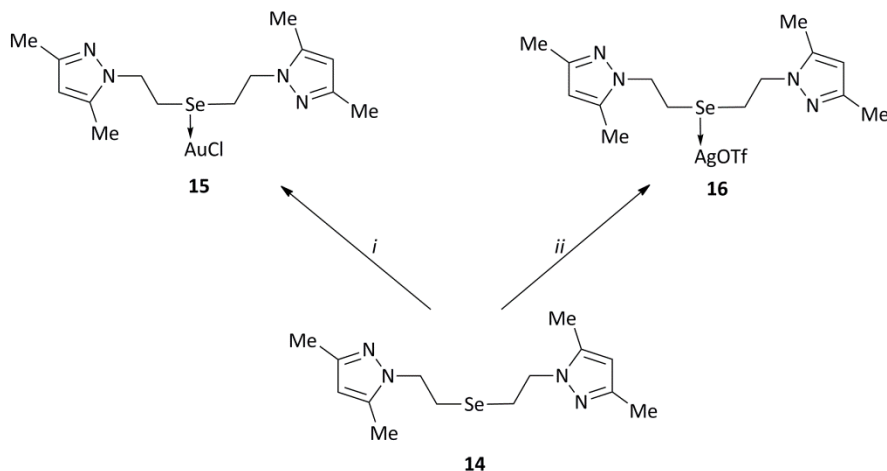


Figure 28. Detail from the ¹H NMR spectrum (CDCl₃, 300 MHz) of **14**.

The ligand **14** was characterized also by mass spectrometry (ESI MS). The ligand **14** exhibits in the ESI+ mass spectrum the *pseudo*-molecular ion at m/z 349.7 (10%) $[M^+Na]$ and the base ion at m/z 464.2 (100%) $[(RSeEt)_2^+]$, while the ESI- mass spectrum shows a peak at m/z 385.2 (100%) $[(RSeEt)_2-Se^-]$.

The reaction between $[AuCl(tht)]$ or $AgOTf$, respectively, and the ligand **14** in a 1:1 molar ratio yielded the complexes **15** and **16** (Scheme 7). These synthetic procedures required the use of DCM as solvent, a short reaction time and no light in the case of silver compounds.



Scheme 7. Reagents and conditions: *i*) $AuCl(tht)$, DCM r.t.; *ii*) $AgOTf$, DCM, r.t.

NMR analyses, including one- and two-dimensional techniques for 1H and ^{13}C have been applied in order to study the structure of compounds **15** and **16** in solution. In the 1H NMR spectrum three singlet and two triplet resonances were assigned to the protons of the organic group, as can be observed from the spectra depicted in **Figure 32**. The signals are slightly upfield shifted in complexes compared to the starting ligand. Chemical shifts were assigned based on the COSY spectrum, according to the numbering scheme described below (see **Figure 34** for compound **16**).

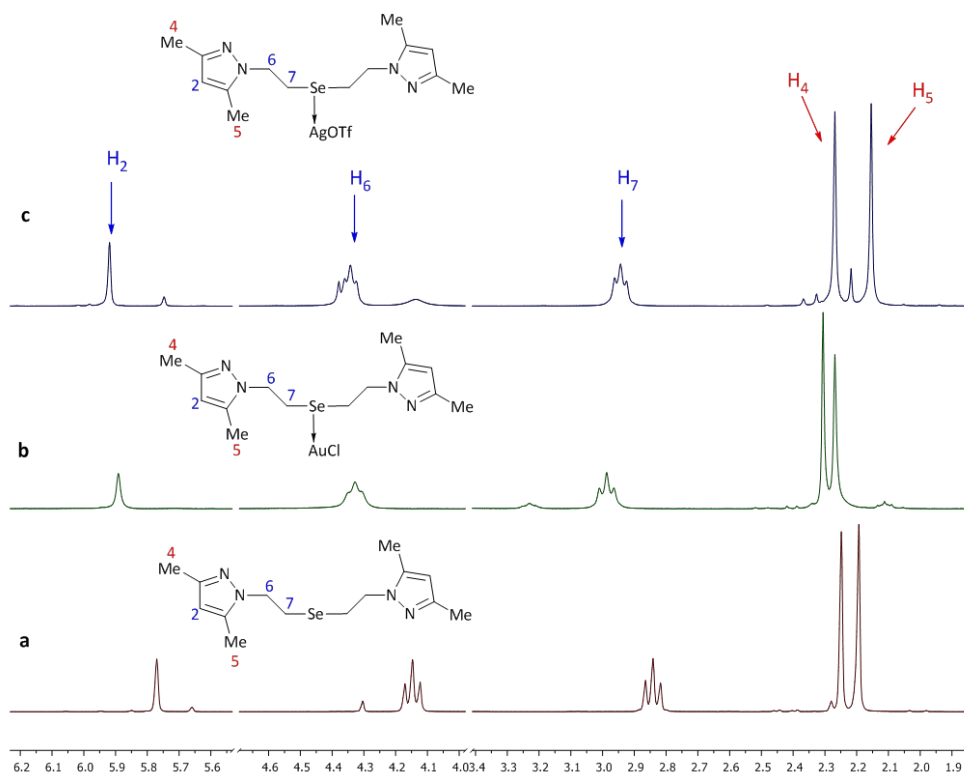


Figure 32. Detail from stacked ^1H NMR spectra (CDCl_3 , 300 MHz) for: (a) ligand **14**; (b) compound **15**, and (c) compound **16**.

Trifluoromethanesulfonate (OTf^-) is an excellent leaving group with clean cleavage at the metal-oxygen bond and is a strongly electron-withdrawing ligand because of the combined inductive effects of the CF_3 and SO_2 moieties.¹³⁴ Many investigations showed that silver(I) has the tendency to form coordination dimers or polymers. In the ^{19}F NMR spectra of **16** a single resonance at $\delta -78.28$ ppm was assigned to the three equivalent fluorine atoms in the CF_3SO_3 fragment (**Figure 36**).

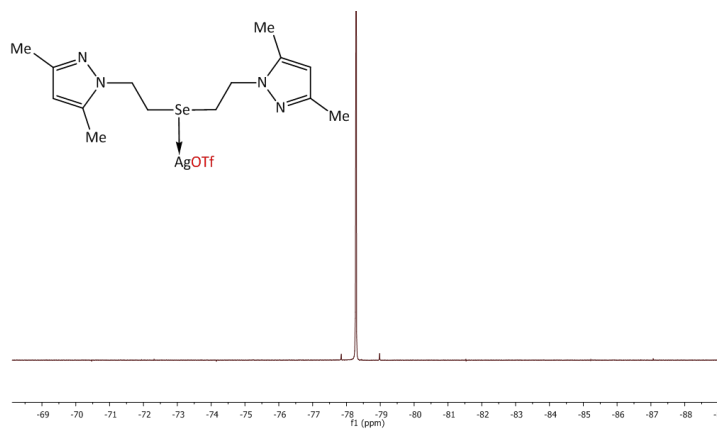


Figure 36. The ^{19}F NMR spectrum (CDCl_3 , 121.4 MHz) of the silver complex **16**.

The ^{77}Se NMR spectroscopy has been employed to obtain a full characterization of the compounds. The ^{77}Se NMR spectra display a broad resonance at δ 144.6 ppm for the complex **15** and a single sharp resonance at δ 129.39 ppm for the silver complex **16**. The resonances are shifted downfield and upfield, respectively, compared to the free ligand (δ 139.54 ppm) (**Figure 37**).

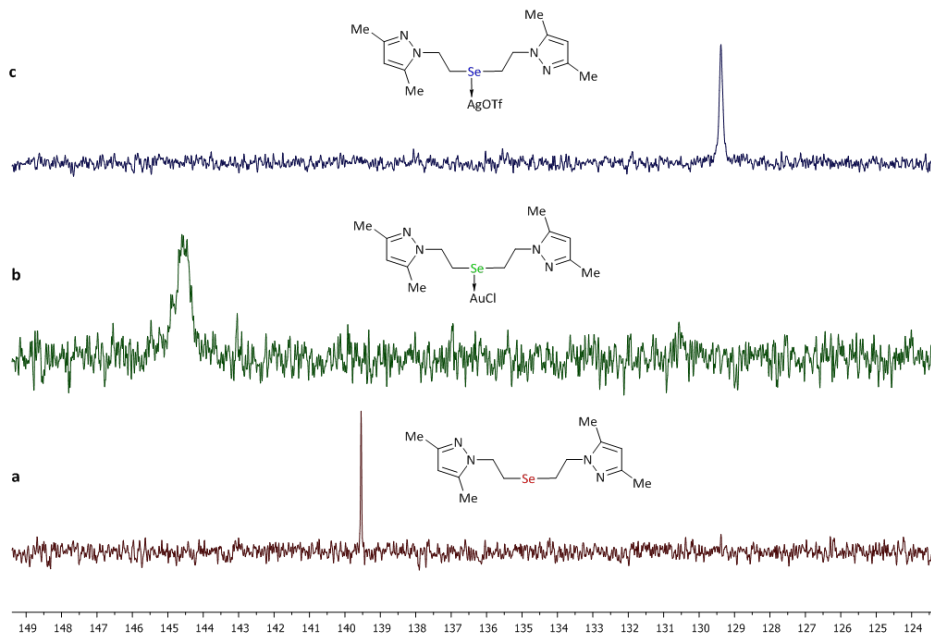


Figure 37. Stacked ^{77}Se NMR spectra (CDCl_3 , 58 MHz) of: (a) ligand **14**; (b) compound **15**, and (c) compound **16**.

For a better characterization, variable temperature ^{77}Se NMR studies in solution were employed for these complexes. Such studies are facilitated by the great sensitivity of ^{77}Se chemical shifts and offer data for a structural analysis of selenium-containing compounds. A dynamic behavior is observed in the ^{77}Se spectra of compound **15** (**Figure 38**). The broad signal (δ 144.60 ppm) at 293 K, on lowering the temperature, is upfield shifted (δ 131.67 ppm) at 218 K. The broad signal can be explained by a dimerisation of the gold compound which is very frequent in the case of gold complexes.

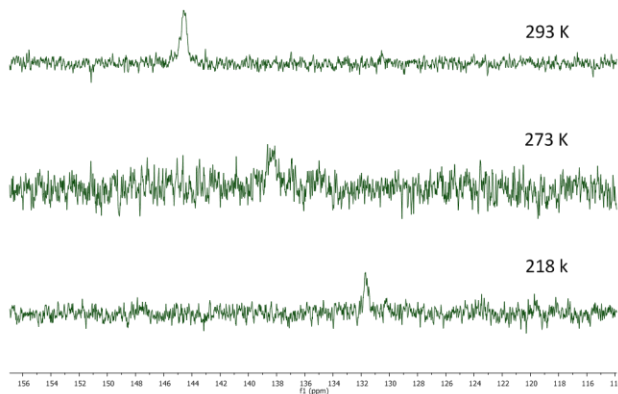


Figure 38. Variable-temperature ^{77}Se NMR spectra of complex **15** (CDCl_3 , 58 MHz).

The two metal complexes were investigated also by ESI mass spectrometry. The distinct pattern in the mass spectra of inorganic, organic and organometallic compounds is mainly due to the larger number of isotopes for the metals. In organometallic compounds, usually the metal retains the positive charge and the ligand departs as a radical. This fact takes place fundamentally because metal-containing species are more electropositive and usually have lower ionization potentials than the ligands. This fact is noticeable in the case of the investigated metal complexes; in the presence of polyisotopic elements, the isotopic pattern of the heavy element appears in all the fragments containing that element of the spectrum.¹³⁵ The ESI+ mass spectrum of compound **15** (**Figure 39**) revealed four peaks at m/z 327.1 (100%) corresponding to $[R_2Se^+ + H]$, m/z 524.1 (37%) for $[R_2SeAu^+ + H]$, m/z 635.1 (1%) for $[M^+ + Se]$ and m/z 725.1 (24 %) for $[R_2SeAu^+ + Au]$, while the ESI- mass spectrum presents one peak at m/z 521 (100%) corresponding to $[R_2SeAu^-]$.

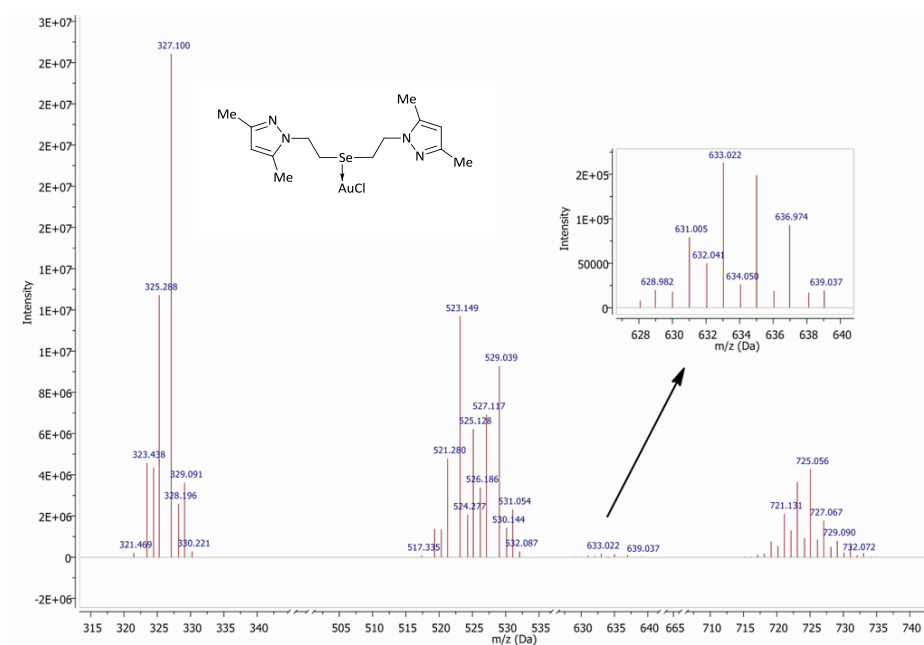
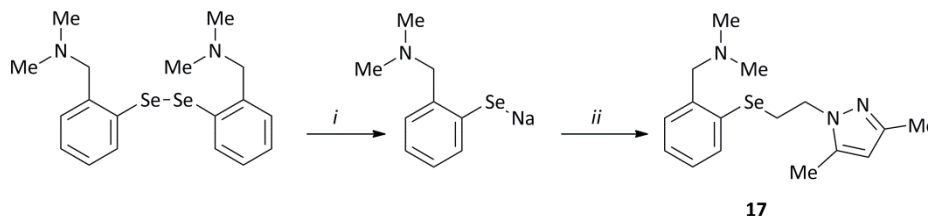
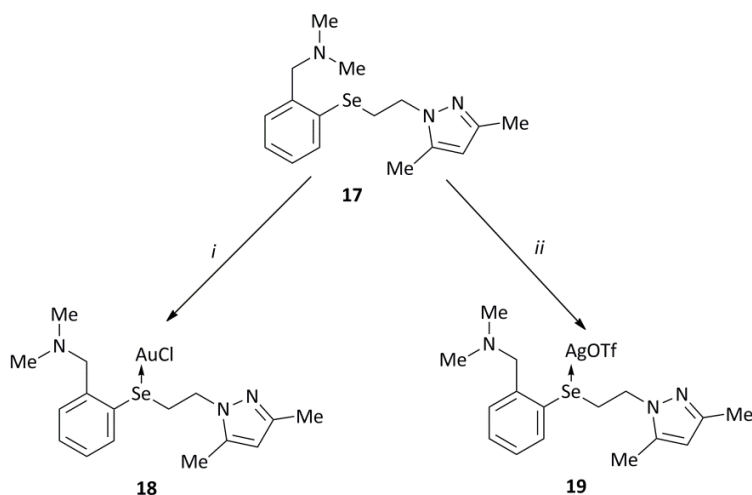


Figure 39. Detail from ESI+ mass spectrum of compound **15**.

The $RR'Se$ species has been successfully prepared by reducing 1,1'-[diselanediy]bis(2,1-phenylene)]bis(N,N-dimethylmethanamine) with sodium followed by metathesis reaction with the corresponding organic bromide (**Scheme 8**).



Scheme 8. Reagents and conditions: *i*) Na, THF, r.t.; *ii*) 1-(2-bromoethyl)-3,5-dimethyl-1H-pyrazole, THF, r.t.



Scheme 9. Reagents and conditions: *i)* AuCl(tht), DCM, r.t.; *ii)* AgOTf, DCM, r.t.

In order to prepare metal complexes with neutral ligand **17**, [AuCl(tht)] and AgOTf, respectively, were used as starting materials (**Scheme 9**). Similar techniques as in the case of compounds **15** and **16** were employed. Special attention was paid to the silver complex as its synthesis must be carried out avoiding the light. The reaction time and the work-up method were chosen for the optimal situation in order to avoid decomposition.

Complexes **18** and **19** were characterized in solution by multinuclear NMR (^1H , ^{13}C , ^{19}F , ^{77}Se) spectroscopy; VT and 2D NMR experiments were also used. The pattern of the ^1H NMR spectra for complexes **18** and **19** with respect to the ligand **17** is consistent with the coordination of the gold and silver derivative in solution. In the aliphatic area of both spectra the existence of the four methyl groups is confirmed by three peaks at δ 2.20, 2.23, 2.26 ppm in **18** and 1.99, 2.28, 2.59 ppm in **19**. The methylene protons of the dimethylaminobenzyl group appear also as a singlet at δ 3.52 ppm (**18**) and 3.70 ppm (**19**), respectively, while the protons of the ethylene moiety appear as two triplets (δ 3.35, 3.52 ppm in **18** and 3.42, 3.70 ppm in **19**, respectively (**Figure 40**). In the aromatic region of both spectra, a singlet resonance signal, corresponding to the proton H_{12} in pyrazole was observed. The phenyl proton $\text{H}_{6'}$ appear as a doublet, while the $\text{H}_{3'-5'}$ protons in **18** and protons $\text{H}_{3'-6'}$ in **19**, respectively, appear as a multiplet. It is worthwhile to mention that in complex **19** the resonance corresponding to the protons H_5 are shifted to right (higher field), while the protons $\text{H}_{6'}$ are shifted to left (lower field).

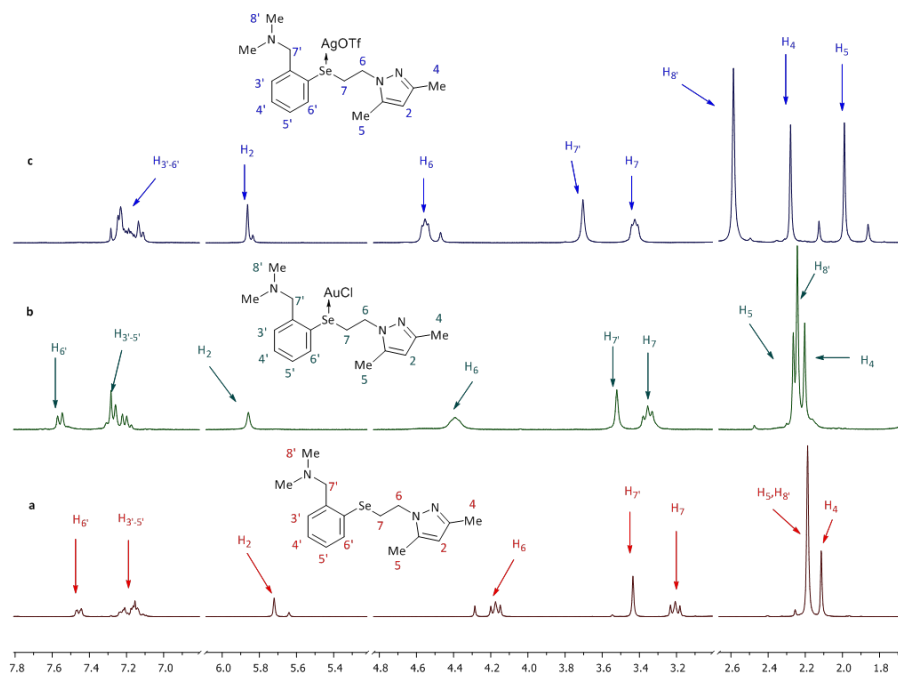


Figure 40. Detail from stacked ^1H NMR spectra (CDCl_3 , 300 MHz) for |: (a) ligand **17**, (b) complex **18**, and (c) complex **19**.

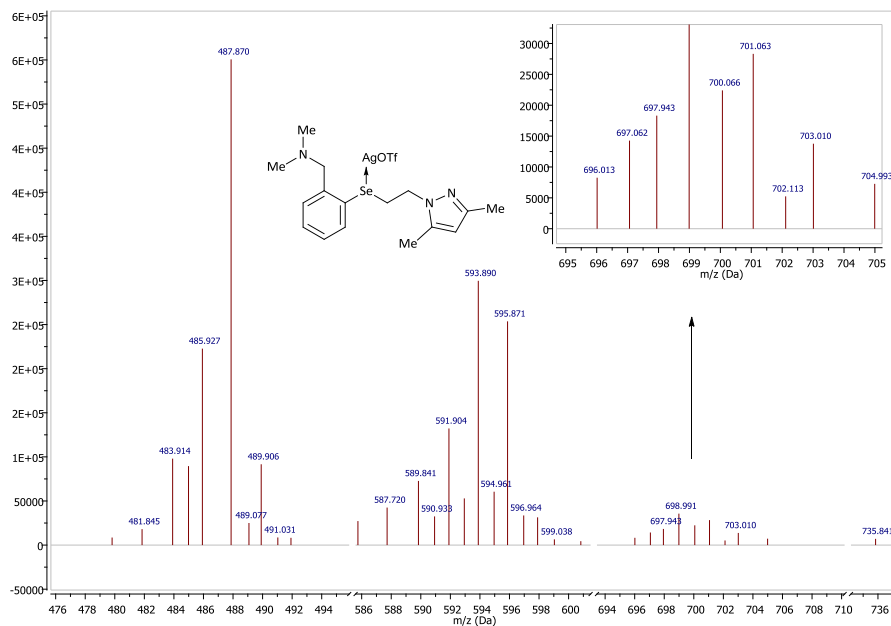


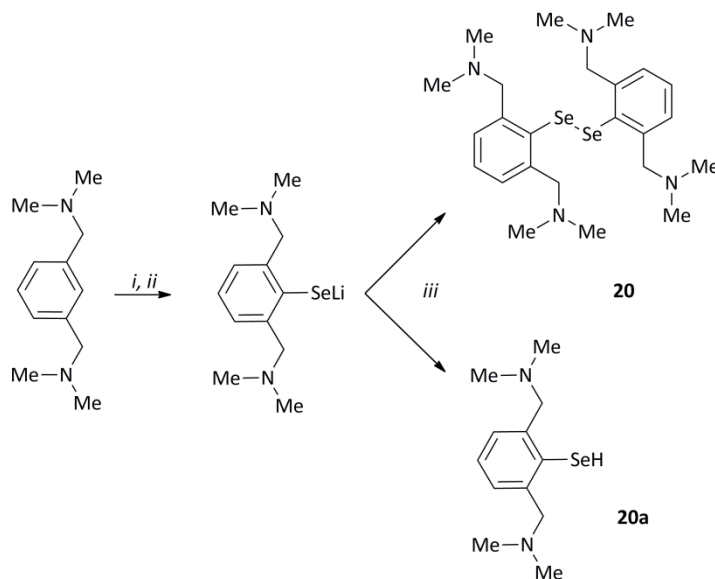
Figure 47. Detail from the ESI+ mass spectrum of compound **19**.

The ESI+ mass spectrometry brought evidences for the complexation of gold and silver, respectively, with the ligand **17**. For the compound **18** the ESI+ mass spectrum presents two peaks at m/z 338.0 (100%) [$\text{RR}'\text{Se}^+ + \text{H}$] and m/z 532.0 (10%) [$\text{RR}'\text{SeAu}^+$]. The ESI- mass spectrum of **18** (**Figure 46**) revealed

peaks at m/z 532 (10%) for $[RR'SeAu^-]$ and m/z 802.9 (20%) for $[M^-+AuCl]$. The ESI+ mass spectrum of compound **19** (**Figure 47**) revealed three peaks at m/z 487.9 (100%) for $[M^-+Ag+H]$, m/z 593.9 (75%) for $[M^++H]$ and 701 (2%) for $[M^++Ag+H]$, while the ESI- mass spectrum revealed three peaks at m/z 339.7 (75%) for $[RR'Se^-]$, m/z 447.0 (48%) for $[RR'SeAg^-]$ and m/z 657.2 (100%) for $[M^-+SO_2]$.

The bis[2,6-bis(dimethylaminomethyl)phenyl]diselenium(I),¹³⁷ was prepared using the *ortho* lithiation route, *i.e.* the reaction of 1,3-bis(dimethylaminomethyl)benzene with $nBuLi$, followed by insertion of elemental selenium into the new formed carbon-lithium bond (**Scheme 10**). The organolithium reagent was isolated as orange oil, sensitive to moisture and soluble in hexane. The organolithium reagent was treated with selenium powder in anhydrous THF, under argon atmosphere. After all elemental selenium was consumed, the reaction mixture containing the lithium selenolate was poured into water and left overnight in an efficient fume hood to complete the oxidation process to bis[2,6-bis(dimethylaminomethyl)phenyl]diselenide (**20**) (see **Scheme 10**). Recrystallization of **20** from DCM and hexane yield orange crystals of **20a**. The formation of the selenol can be explained by the reaction of the lithium organoselenolate with water which can lead to **20a** and lithium hydroxid.

The ^{77}Se NMR spectrum of the compound **20a** is consistent with the formation of the selenol species. A singlet ^{77}Se resonance is observed around 1200 ppm (**Figure 48**), the signal being split due to the proton-selenium coupling. In the 1H NMR spectrum of **20a** a singlet resonance is observed at 2.1 ppm and was assigned to the proton attached to the selenium.



Scheme 10. Reagents and conditions: *i*) $nBuLi$, hexane, r.t.; *ii*) Se, THF r.t.; *iii*) H_2O , O_2 .

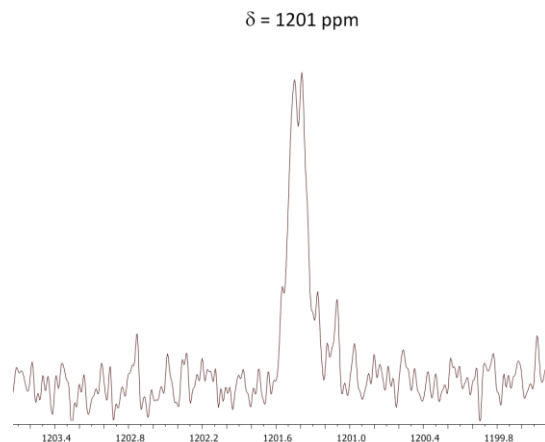


Figure 48. The ^{77}Se NMR spectrum (CDCl_3 , 58 MHz) of compound **20a**.

The selenol $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{SeH}$ (**20a**) crystallizes with three molecule of water. Strong intramolecular $\text{N}\cdots\text{Se}$ interactions [2.177(3) and 2.174(3) Å] are established by both N atoms of the pendant arms in the molecule of **20a**, in *trans* positions to each other [$\text{N}-\text{Se}-\text{N}$ 162.01(15)°]. This results in a T-shaped (C,N,N')Se core. Similar values for $\text{N}\cdots\text{Se}$ interactions [2.185(3) and 2.181(3) Å] were found in the molecular structure of C,N,N' -[2,6-bis(dimethylaminomethyl)phenyl]selenium(II) bromide.¹³⁹

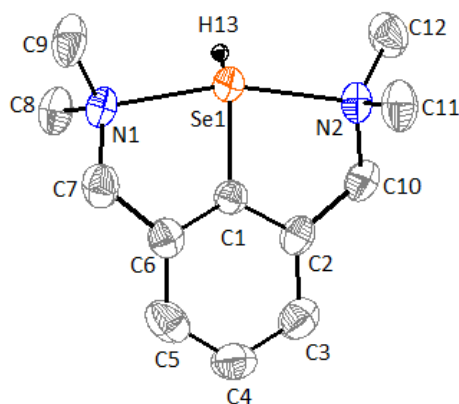
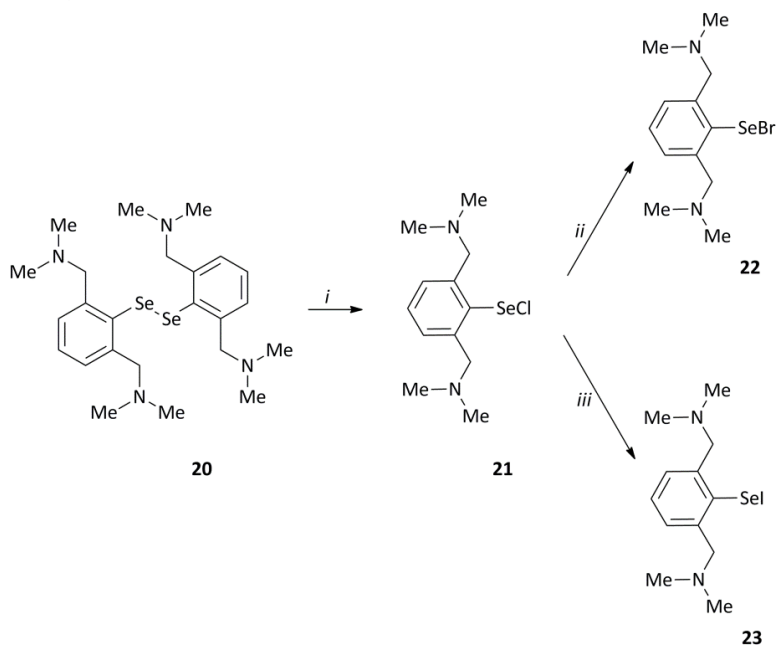


Figure 49. Molecular structure with atom numbering scheme of compound **20a** (only the hydrogen atom attached to selenium is shown). The atoms are drawn with 50% probability ellipsoids.

The room temperature ^1H , ^{13}C and ^{77}Se NMR spectra of compound **20** are consistent with the formation of the desired diorganodiselenium(I) derivative, $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]_2\text{Se}_2$. The ^1H NMR spectrum (**Figure 50**) exhibits singlet resonances for the protons of the pendant arms: δ 2.99 for the equivalent methyl groups (H_8) and δ 4.20 ppm for the methylene protons (H_7), respectively. The

aromatic protons appear as an unresolved multiplet at δ 7.28 ppm. The ^{77}Se NMR spectrum of **20** (Figure 52) provides evidences towards the formation of targeted diorganodiselenium(II) derivatives. One sharp signal at δ 395.6 ppm was observed.

The *C,N,N'*-[2,6-bis(dimethylaminomethyl)phenyl]selenium(II) chloride (**21**) was obtained by the cleavage of the Se–Se bond in bis[2,6-bis(dimethylaminomethyl)phenyl]diselenide (**20**) with SO_2Cl_2 , at room temperature, in carbon tetrachloride. Washing the isolated product **21** in DCM solution with a saturated KOH solution yielded the pure organoselenium chloride in good yield as a yellow solid. The organoselenium(I) bromide (**22**) and iodide (**23**), containing the same organic ligand, were obtained by reacting the chloride **21** with excess amounts of KBr and KI, respectively, in acetone at room temperature (Scheme 11).



Scheme 11. Reagents and conditions: *i*) SO_2Cl_2 , CCl_4 , r.t.; *ii*) KBr, Acetone; *iii*) KI, Acetone.

The solution behavior of the organoselenium(II) halides was investigated by ^1H , ^{13}C and ^{77}Se NMR spectroscopy. The ^1H NMR spectra of the products are consistent with the proposed structures. In all three cases resonances are shifted when comparing to the starting diselenide **20**. The ^1H NMR spectra of **21** – **23** display in the aromatic region one broad resonance around 7.30 ppm corresponding to the protons from the aromatic ring (see Figure 52). The spectra also exhibits two singlet resonance signals for the methylene and methyl protons of the pendant arms. The ^{13}C NMR spectroscopy was also used to characterize compounds **21** – **23** and the results are in agreement with the proposed structure.

The ^{77}Se NMR spectra confirm the formation of the desired compounds. One singlet signal is observed at δ 1202.2 ppm for the compound **21**, which is strongly low field shifted comparing to the starting diorganodiselenide **20** (δ 395.6 ppm). These values are in agreement with the values for analogue compounds described in the literature.^{140,141} (Figure 54).

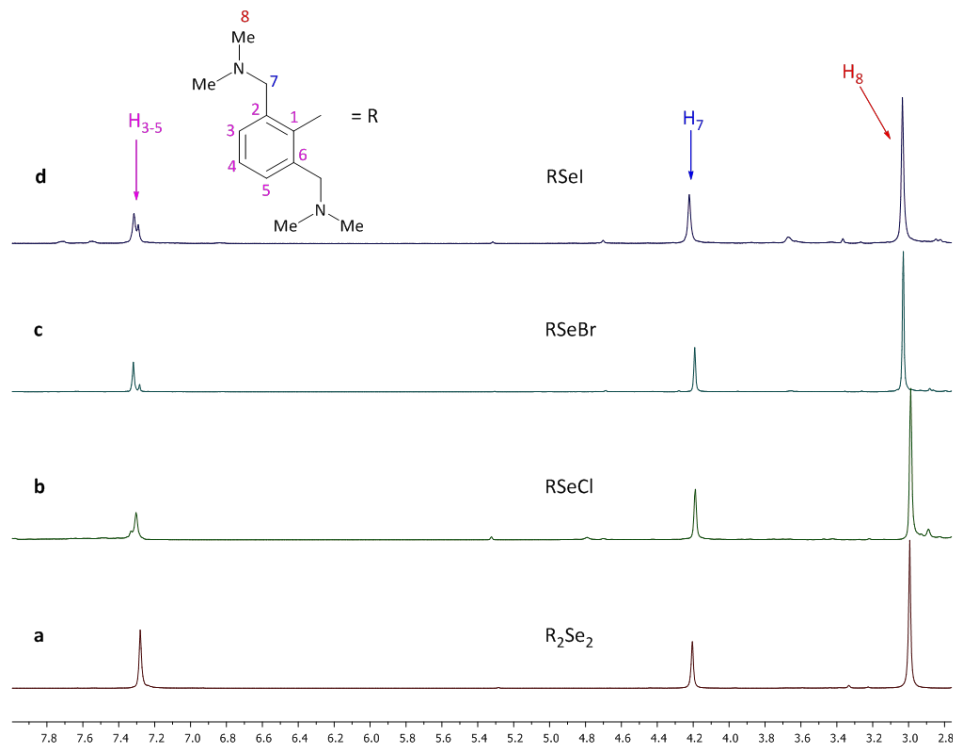


Figure 52. Stacked ^1H NMR spectra (CDCl₃, 300 MHz) for: (a) ligand **20**, (b) compound **21**, (c) compound **22**, and (d) compound **23**.

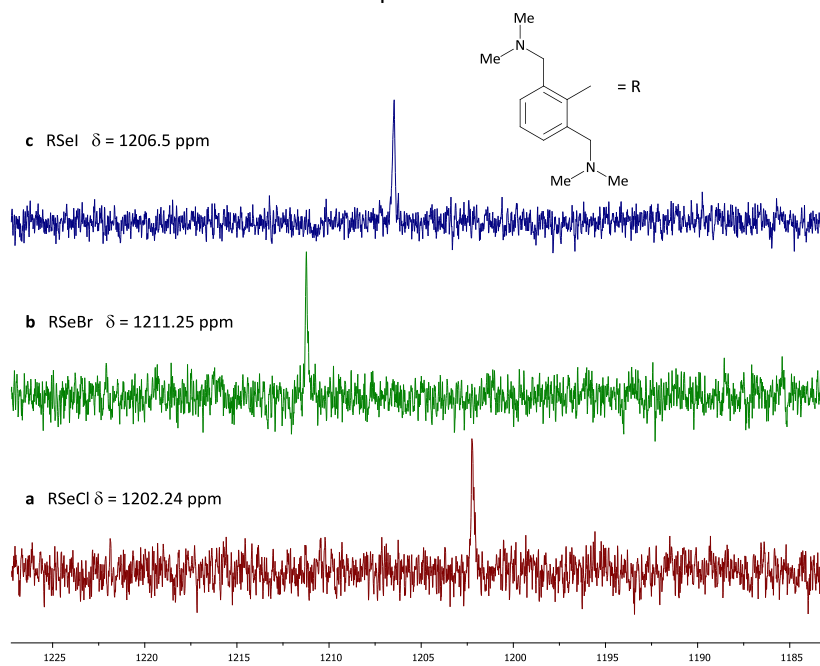


Figure 54. Stacked ^{13}C NMR spectra (CDCl₃, 58 MHz) for: (a) compound **21**, (b) compound **22**, and (c) compound **23**.

III.B.2. Conclusions

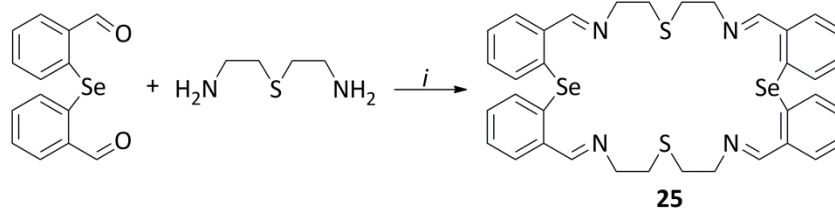
- New diorganoselenium(II), [(3,5-Me₂C₃HN₂)CH₂CH₂]₂Se (**14**) and [(3,5-Me₂C₃HN₂)CH₂CH₂][2-(Me₂NCH₂)C₆H₄]Se (**17**), and diorganodiselenium(I), [2,6-(Me₂NCH₂)₂C₆H₃]₂Se₂ (**20**), were prepared and fully characterized by NMR spectroscopy in solution and by mass spectrometry.
- [(3,5-Me₂C₃HN₂)CH₂CH₂]₂Se (**14**) and [(3,5-Me₂C₃HN₂)CH₂CH₂][2-(Me₂NCH₂)C₆H₄]Se (**17**) were obtained by reacting (3,5-Me₂C₃HN₂)CH₂CH₂Br with Na₂Se and the sodium selenolate [2-(Me₂NCH₂)C₆H₄]SeNa, respectively. Both compounds were isolated and their purity and composition were confirmed by elemental analysis. The new diorganoselenium(II) derivatives were structurally characterized by NMR spectroscopy in solution and mass spectrometry.
- The behavior of **14** and **17** as ligands was investigated in the coordination chemistry of gold and silver. The NMR spectroscopy and mass spectrometry was used to confirm the proposed structures of the coinage metal complexes.
- The diorganodiselenium(I) derivative [2,6-(Me₂NCH₂)₂C₆H₃]₂Se₂ (**20**) was prepared using the *ortho*-lithiation route. From the hydrolysis reaction the selenol [2,6-(Me₂NCH₂)₂C₆H₃]SeH (**20a**) was also isolated. Its molecular structure was established by single-crystal X-ray diffraction pointing out that both nitrogen atoms are strongly coordinated to selenium, in *trans* to each other.
- Organoselenium(I) chloride [2,6-(Me₂NCH₂)₂C₆H₃]SeCl (**21**), containing a ligand with two pendant arms, was obtained in good yield by the Se-Se bond cleavage in **20**. Halogen exchange reactions afforded the isolation of the new organoselenium(I) bromide (**22**) and iodide (**23**), respectively. All halides were characterized by NMR spectroscopy and mass spectrometry.

III.C. Macrocyclic ligands containing N/chalcogen donor atoms and pendant arm cyclic amino-thioethers

III.C.1. Results and discussion

Incorporating Se into macrocyclic ligands in addition to other donor atoms (S, O and N) would lead to an increased size of the cavity and an interesting coordination behavior can be expected. Starting from this presumption, the new selenium-containing macrocycle **25** was prepared and fully characterized in solution and in solid state.

The novel selenium-containing 28-membered macrocycle **25** was obtained by the condensation of bis(*o*-formylphenyl)selenide and bis(2-aminoethyl)sulfide (**24**), in acetonitrile (**Scheme 13**).



Scheme 13. Reagents and conditions: *i*) MeCN; 24 h; r.t.

Compound **25** was characterized in solution by ^1H , ^{13}C , ^{77}Se and 2D NMR studies. Further details regarding interpretation and assignments of the NMR spectra are presented below. The aliphatic region of the ^1H NMR spectrum of **25** (**Figure 55**) exhibits two multiplet resonances, corresponding to the protons of the ethylene bridges. In the aromatic region three different resonances are observed, *i.e.* one multiplet signal corresponding to the protons H_{3-5} , one doublet for H_6 and a multiplet signal for the proton attached to the carbon double bonded to the nitrogen atom.

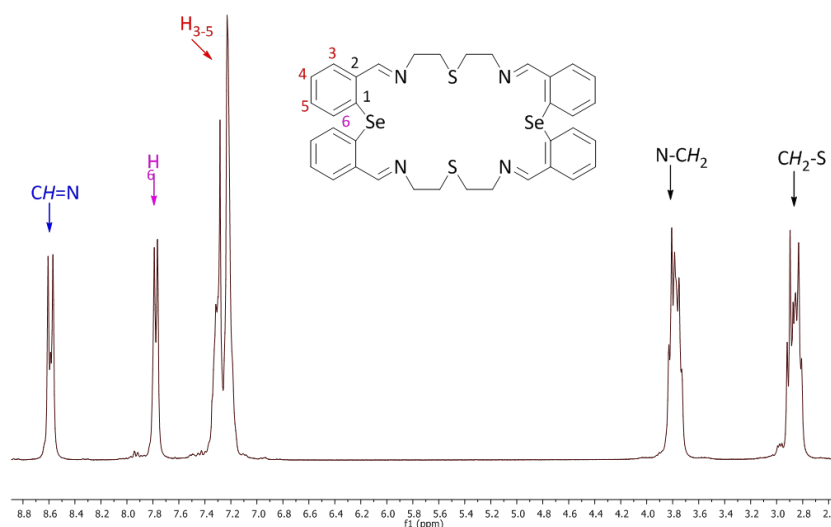


Figure 55. The ^1H NMR spectrum (CDCl_3 , 300 MHz) of the macrocycle **25**.

The crystal and molecular structure of **25** was determined by single-crystal X-ray diffraction. Relevant bond distances and angles are given in **Table 7** and the molecular structure with the atom numbering scheme is shown in **Figure 59**. The structure confirms that the macrocycle **25** has a 28-membered cavity. Intramolecular selenium-nitrogen interactions are established; the bond length $\text{Se}(1)\cdots\text{N}(1)$ of 2.7619(8) Å is longer than the single covalent bonds and remarkably shorter than the sum of the van der Waals radii for the corresponding atoms, [*cf.* $\Sigma r_{\text{cov}}(\text{Se},\text{N})$ 1.87 Å, $\Sigma r_{\text{vdW}}(\text{Se},\text{N})$ 3.54 Å].¹⁵⁶ The transannular $\text{Se}(1)\cdots\text{Se}(1')$ distance of 8.893(3) Å is much longer than the sum of the van der Waals radii (ca. 4 Å). The coordination geometry around selenium atom is T-shaped, due to the $\text{Se}\cdots\text{N}$ intramolecular interaction. Only one nitrogen atom is intramolecularly coordinated to the selenium atom

resulting in a 10-Se-3 hypervalent structure. The distance Se(1)-C(1) and Se(1)-C(10) is 1.938(8) Å and is a little longer than the sum of the Pauling single bond covalent radii for selenium (1.17 Å) and sp² hybridized carbon (0.74 Å). This bond distance can be comparable to the Se-C bond length of 1.933(8) Å in 1-(methylselanyl)-8-(phenylselanyl)naphthalene,¹⁵⁷ and 1.931(3) Å in bis(diphenylselenide)-1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane Schiff base.¹⁵⁸ The C(10)-Se(1)-C(1) angle for macrocycle **25** is 98.9(3)°, also comparable with the C-Se-C angle [97.54(13)°], for the macrocyclic ligand described in literature, containing nitrogen instead of sulfur in the branched part of the cavity.

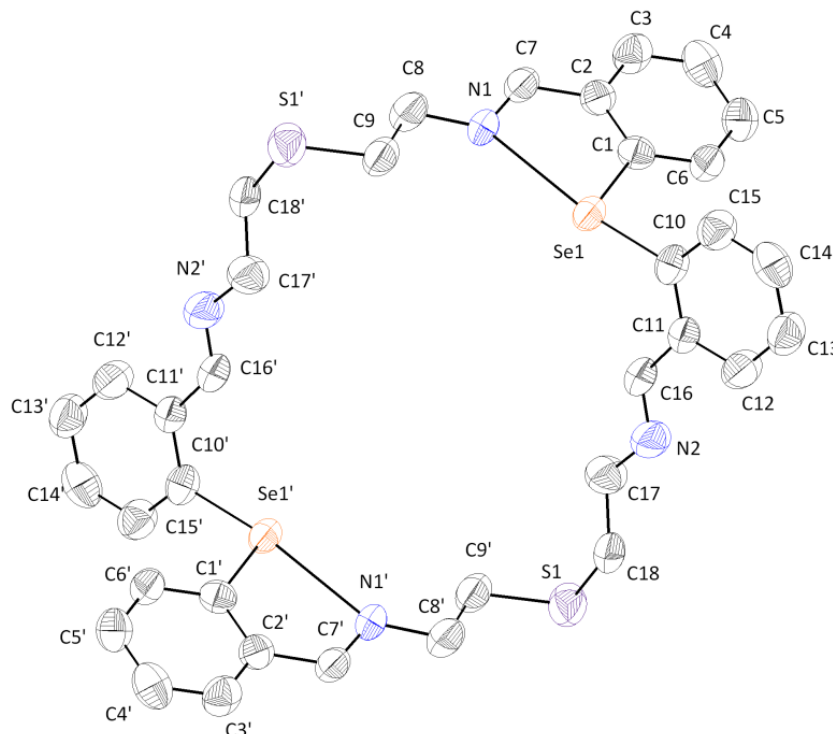
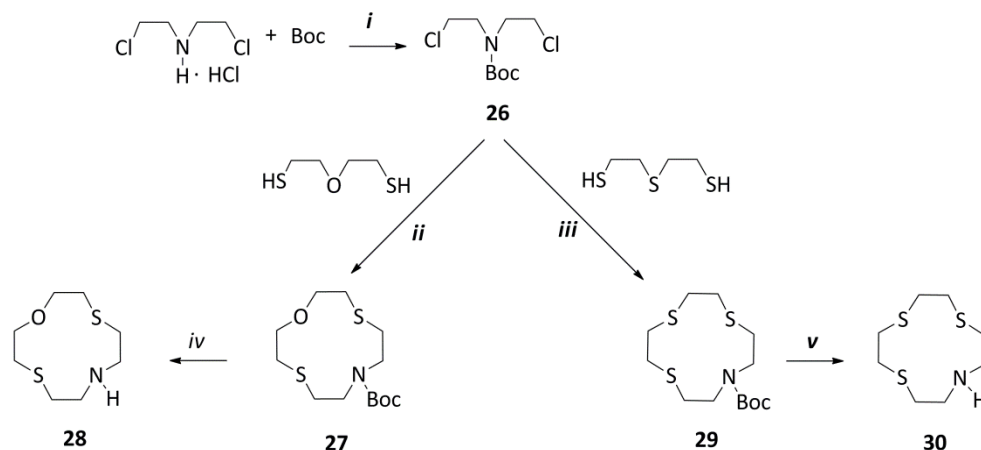


Figure 59. The molecular structure of compound **25**, with atom numbering scheme (the hydrogen atoms were removed for clarity). The atoms are drawn with 50% probability ellipsoids.

The 12-membered macrocycles containing nitrogen and sulfur were prepared according to literature methods. In order to prepare the 1-aza-4,10-dithia-7-oxacyclododecane (**28**) and 1,4,7-trithia-10-azacyclododecane (**30**) (**Scheme 14**), the *N-tert*-butoxycarbonyl-bis(2-chloroethyl)amine (**26**) was obtained by adding slowly di-*tert*-butyl dicarbonate to a solution of bis(2-chloroethyl)amine hydrochloride and NaOH. The *Boc*-protected chloroethylamine (**26**) was used further in a cyclization reaction with bis(2-mercaptoethyl)ether and bis(2-mercaptoethyl)sulfide, in DMF, under high dilution conditions. The *Boc*-protected macrocycles **27** and **29** were deprotected with a solution of trifluoroacetic acid and DCM at room temperature.¹⁵⁹ The *Boc*-protected macrocycle **27** was purified by flash chromatography using a mixture of DCM/MeOH (97.5:2.5 v/v) as eluent, while **29** was dissolved in 50 mL hot toluene and after one night at -20 °C a white solid was obtained. The 12-membered macrocycles **28** and **30** have been purified by recrystallization from DCM/Et₂O.



Scheme 14. Reagents and conditions: *i*) NaOH, H₂O, r.t.; *ii*); *iii*) Cs₂CO₃, DMF, 55 °C; *iv*); *v*) CF₃COOH, DCM, 2h, r.t.

The molecular structure of the macrocycle **28** was established by single-crystal X-ray diffraction. The geometry of the molecule may be described as a distorted quadrangular crown. The sulfur atoms are oriented with their lone pairs out of the ring (exodentate). Carbon-sulfur bond lengths range are in range 1.797(2)° - 1.813(2)°, consistent with those found in other crown ethers.¹⁶⁰ The C-S linkage preference is to adopt *gauche* conformations, while the C-C bonds adopt the *anti* conformations. The C-C bond distances are in range of 1.487(3) - 1.497(3) Å and are shorter than the value for C(sp³)-C(sp³) linkages 1.54 Å.⁹⁸ The sulfur atoms don't have the tendency to occupy the corners of a quadrangle as found in [12]aneNS₃ and many other structures.¹⁶¹

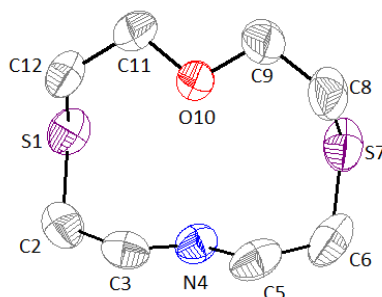
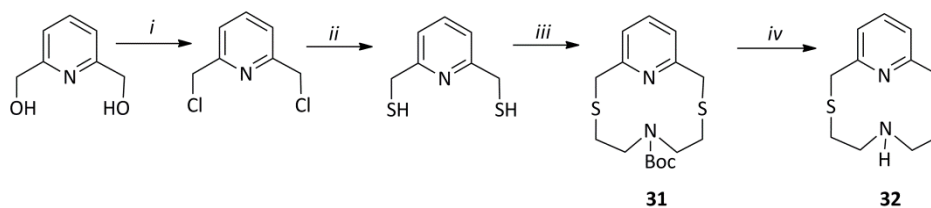


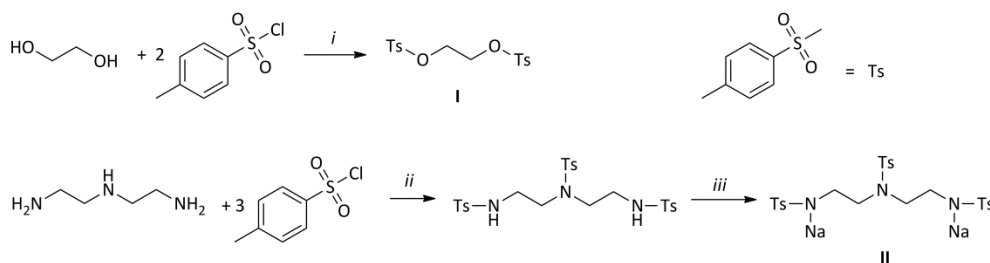
Figure 60. Molecular structure with atom numbering scheme of compound **28** (the hydrogen atoms were removed for clarity). The atoms are drawn with 50% probability ellipsoids.

In order to obtain the 12-membered macrocycle **32**, pyridine-2,6-diylidimethanol was reacted with SOCl₂ to obtain the 2,6-bis(chloromethyl)pyridine which was further reacted with thiourea. The *Boc*-protected macrocycle **31** was obtained by a high dilution cyclization reaction and was deprotected with CF₃COOH and DCM (**Scheme 15**). The white solid, 12-membered macrocycle **32** was purified by flash chromatography (silica) using DCM/MeOH.¹⁶⁵



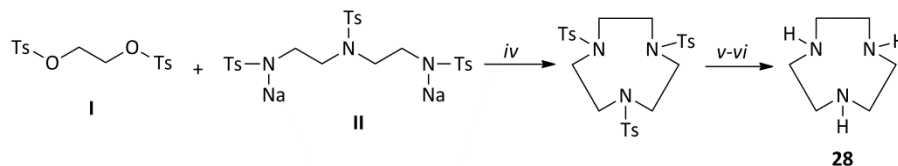
Scheme 15. Reagents and conditions: *i*) SOCl_2 , DCM, 2 h, 0 °C; *ii*) thiourea, EtOH, 2 h, reflux; *iii*) **26**, Cs_2CO_3 , DMF, 55 °C; *iv*) CF_3COOH , DCM, 2h, r.t.

The 9-membered macrocycle **33** was prepared according to literature methods.¹⁶⁶ The synthesis of this type of macrocycle required six steps, as described in **Schemes 16** and **17**.



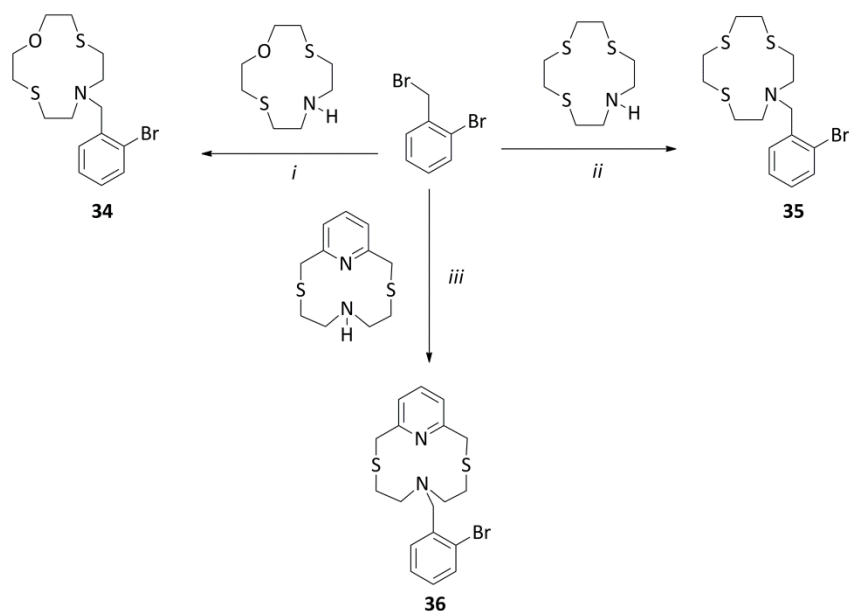
Scheme 16. Reagents and conditions: *i*) H_2O , NaOH, 0 °C; *ii*) H_2O , NaOH, 0 °C; *iii*) EtOH, Na.

In the first three steps, the starting materials diethylenetriamine- N,N,N'' -tritosylate (**I**) and disodium diethylenetriamino- N,N,N'' -tritosylate (**II**) were prepared in good yields (see **Scheme 16**). The cyclization reaction (*iv*) of **I** and **II** in DMF using high dilution techniques allows the formation of N,N,N'' -tritosylate-1,4,7-triazacyclononane. The macrocycle **33** was obtained by further deprotection and protonation of the N,N,N'' -tritosylate-1,4,7-triazacyclononane (see **Scheme 17**).



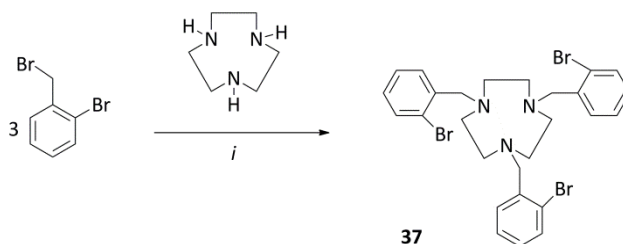
Scheme 17. Reagents and conditions: *iv*) DMF, 72 h, 105 °C; *v*) H_2SO_4 , 72 h, 105 °C; *vi*) toluene, H_2O , NaOH, 20 h, reflux.

Pendant arm amino-thioethers **34**, **35** and **36** were synthesized by reacting directly the macrocycles **28**, **30** and **32** with stoichiometric amounts of 2-bromobenzyl bromide in MeCN in the presence of K_2CO_3 (**Scheme 17**).



Scheme 18. Reagents and conditions: *i*); *ii*); *iii*); MeCN, 72 - 96 h, K₂CO₃, reflux.

The macrocycle **37** was prepared by the reaction between the macrocycle **34** and bromobenzyl bromide in a 1:3 molar ratio in toluene in the presence of KOH (**Scheme 19**).



Scheme 19. Reagents and conditions: *i*) toluene, 72 h, KOH, reflux.

Structural characterization was performed by ¹H, ¹³C and 2D NMR spectroscopy as well as mass spectrometry studies and the data obtained supported the structure of compounds **34** – **37**. The molecular structure of compound **35** was established by single-crystal X-ray diffraction. As a general remark for the compounds **34**, **35** and **36**, the ¹H and ¹³C NMR spectra are consistent with the equivalence of the protons in the macrocyclic ring, due to the symmetry of the molecule.

The molecular structure of the macrocyclic compound **35** was established by single-crystal X-ray diffraction.

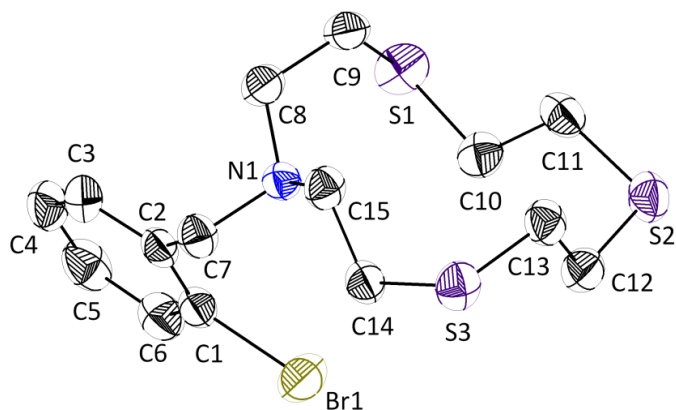


Figure 65. Molecular structure with atom numbering scheme of compound **35** (the hydrogen atoms were removed for clarity). The atoms are drawn with 50% probability ellipsoids.

A closer look to the molecule of **35** revealed intramolecular Br(1)···H(6) interactions [2.8673(3) Å], the interatomic distance being between the sum of the respective covalent and van der Waals radii [$\Sigma r_{cov}(H,Br)$ 2.18 Å and $\Sigma r_{vdW}(H,Br) = 3.15$ Å].⁹⁸ The geometry of the macrocycle in **35** can be described as a distorted quadrangular crown. The sulfur atoms are oriented with their lone pairs out of the ring (exodentate) and the tendency of sulfur atoms in the macrocyclic ring is to occupy the corners of the quadrangular type structure. Exodentate orientation of sulfur atoms arises from the preference of C–S linkages to adopt *gauche* conformation, while the C–C bonds take on the *anti* conformation.

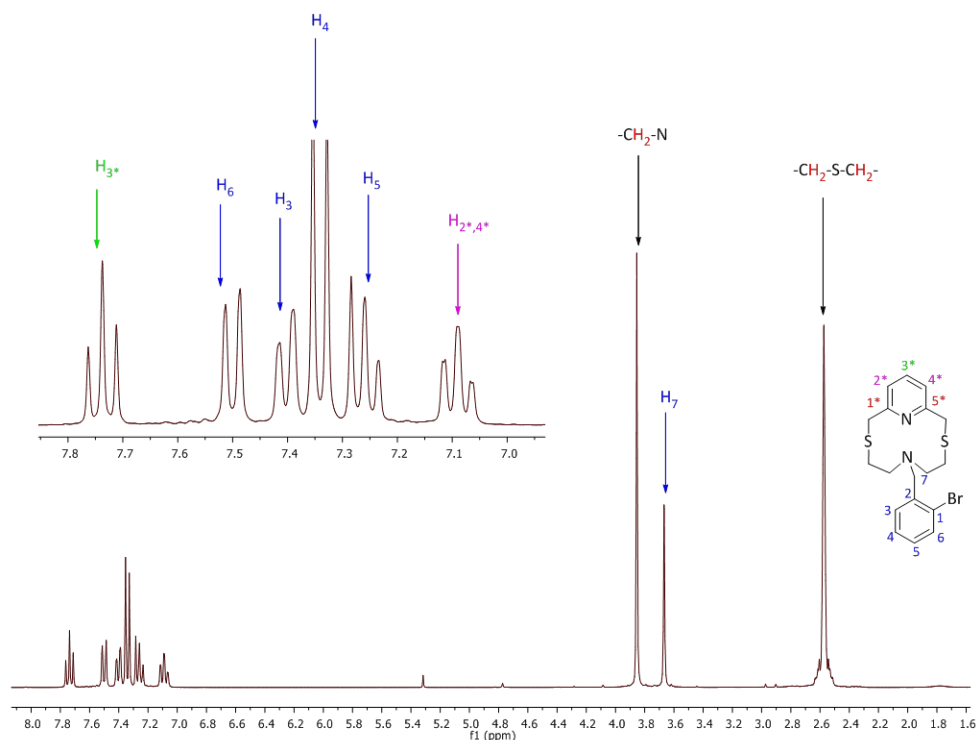


Figure 66. The ¹H NMR spectrum (CDCl₃, 300 MHz) of compound **36**.

The pattern of the ^1H NMR spectrum of **36** presents two resonances in the aliphatic region, corresponding to the protons of the macrocyclic ring at δ 2.57 and 3.86 ppm, respectively, and one singlet resonance for the methylene protons in the pendant arm. Furthermore, in the aromatic region three triplet and three doublet resonances appear (**Figure 66**). The assignment of the multiplet resonances for the compound **36** was based on their integral ratio and multiplicity and was confirmed by 2D-COSY NMR experiments.

Compound **37** exhibits in the aliphatic region of the ^1H NMR spectrum an AB spin system for the protons from the 9-membered ring and one singlet resonance for the methylene protons from the pendant arm, while in the aromatic region the corresponding resonances for the aromatic protons were observed (**Figure 69**).

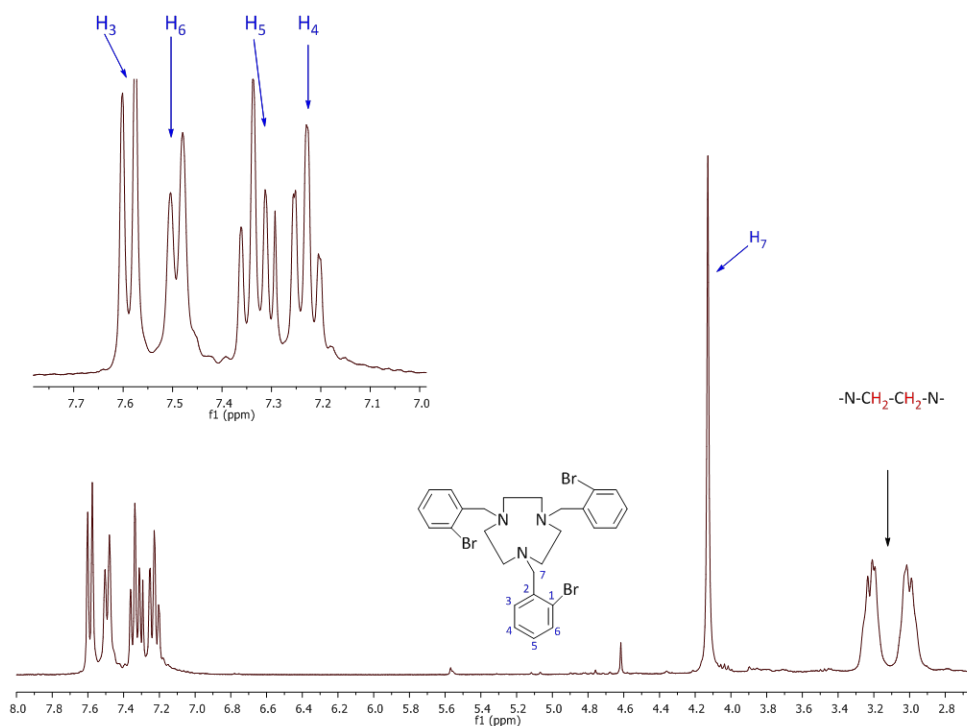


Figure 69. ^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **37**.

III.C.2. Conclusions

- The new selenium-containing 28-membered macrocycle **25** was obtained by the condensation of bis(*o*-formylphenyl)selenide and bis(2-aminoethyl)sulfide in acetonitrile. Compound **25** was characterized in solution by NMR spectroscopy. The molecular structure of the macrocycle **25** was established using single-crystal X-ray diffraction studies.
- The 12-membered macrocycles **28**, **30** and **32**, containing nitrogen and sulfur atoms, were prepared by cyclization reactions in DMF under high dilution conditions. The purity of the starting

material **26** and the macrocycles **27 – 32** was proved by spectroscopic methods in solution (^1H and ^{13}C NMR spectroscopy) and in solid state by single-crystal X-ray diffraction studies for macrocycle **28**.

- The 9-membered macrocycle **33** was prepared. The synthesis of this type of macrocycles is time-consuming, requiring six steps.
- New pendant arm-containing amino-thioethers **34**, **35** and **36** were synthesized by reacting directly the macrocycles **28**, **30** and **32** with stoichiometric amounts of 2-bromobenzyl bromide (1:1 molar ratio), in MeCN, in the presence of K_2CO_3 . Compound **37** was prepared by the reaction between macrocycle **33** and 2-bromobenzyl bromide in 1:3 molar ratios, in toluene, in the presence of KOH. All new pendant arm-containing amino-thioethers were purified by flash chromatography on silica gel using different solvent mixtures as eluents. Structural characterization of the compounds **34 – 37** was performed by ^1H , ^{13}C and 2D NMR spectroscopy, mass spectrometry, single-crystal X-ray diffraction studies and elemental analysis.

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