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.\(^9\)

\[
\text{Ph}_2\text{MeP} + \text{Se} \rightarrow \text{Ph}_2\text{MeP}=\text{Se}
\]  

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

Triarylphosphane chalcogenides of type \(\text{R}_x\text{Ph}_3\text{P}=\text{E} \) \([\text{R} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4, \text{E} = \text{S}, x = 3 \text{ (2)}; \text{E} = \text{Se}, x = 3 \text{ (3)}; \text{E} = \text{Se}, x = 2 \text{ (4)}\) 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 \((^1\text{H}, ^{13}\text{C} \text{ and } ^{31}\text{P})\). The molecular structures of derivatives 2 and 3 were determined by single-crystal X-ray diffraction.

\[
\begin{align*}
\text{[2-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_3\text{P} + \text{E} & \rightarrow \text{[2-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_3\text{P}=\text{E} \\
x = 3, \text{E} = \text{S} & \text{ (2)} \\
x = 3, \text{E} = \text{Se} & \text{ (3)} \\
x = 2, \text{E} = \text{Se} & \text{ (4)}
\end{align*}
\]

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

The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra are consistent with the organic groups attached to phosphorus. The assignments of the \(^1\text{H}\) and \(^{13}\text{C}\) 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 \(^1\text{H}\) NMR spectra of the compounds 2 – 4 at room temperature (Figure 1) the NMe\(_2\) groups display singlet resonance around \(\delta 2.0 \text{ ppm}\). 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.
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. Σ\text{vdW}(NP) 3.44 Å], but no intramolecular interaction can be considered, the \text{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, \text{i.e.} P=S 1.962(2) Å 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.

\[
\begin{align*}
5 & \quad \text{[AuCl(SePh₂Me)]} & 1 & \quad \text{Ph₂MePSe} & \quad \text{[Au(C₆F₅)(SePh₂Me)]} \\
& \quad \text{\textit{i}} & \quad \text{\textit{ii}} & \quad \text{\textit{iii}} & \quad 6 & \quad 7
\end{align*}
\]

Scheme 3. Reagents and conditions: \textit{i}) DCM, AuCl(tht), r.t.; \textit{ii}) (C₆F₅)Au(tht), DCM, r.t.; \textit{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 \(^1\)H, \(^{31}\)P, \(^{77}\)Se and \(^{19}\)F 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 \(^1\)H 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 \textit{ortho}-, \textit{meta}- and \textit{para}- protons, respectively. The resonances characteristic for the \textit{ortho}-protons appear as a doublet of doublets of doublets, due both to the phosphorus–proton and proton–proton couplings.

![Figure 5](link_to_image)

Figure 5. Detail from stacked \(^1\)H 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 ($\delta$ 0 ppm) by assuming that the resonance of Ph$_2$Se$_2$, used as standard, is at $\delta$ 461 ppm. In the gold complex 7 the value of the $^{77}$Se resonance is $\delta$ -79.54 ppm, low field shifted comparing to ligand 1 ($\delta$ -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$_6$F$_5$ groups (Figure 8). In case of the square-planar compound 7 the three C$_6$F$_5$ groups attached to gold give two different $^{19}$F sets of resonances in a 1:2 molar ratio for the non equivalent C$_6$F$_5$ 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. $\Sigma r_{vdW}(Au,Au)$ 3.40 Å]. 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 Au···Au contact, a T-shaped coordination geometry can be assigned [Au2···Au1–Se1 75.22(2)$^\circ$ and Au2···Au1–C1 108.06(2)$^\circ$]. In complex 7 the gold atom has a square planar geometry. The C$_6$F$_5$ group trans to selenium is twisted to
almost $90^\circ$ 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)$^\circ$ in 7 and 102.98(4)$^\circ$ in 6, respectively].

![Molecular structure with atom numbering scheme of compounds 6 and 7](image)

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 structurated band at about 446 nm.

![Excitation (dashed line) and emission (straight line) spectrum of complex 6 at 77K](image)

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.

$^1$H 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 $^1$H 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$_3$Me moiety (6 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(PPh$_3$)$_2$OTf, Acetone, 2h, r.t.; iii) CuCl, CH$_2$Cl$_2$, 24h, r.t.; iv) Cu(PPh$_3$)$_2$NO$_3$, CH$_2$Cl$_2$, 24h, r.t.
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 \( (ii) \), \( i.e. \) \( [\text{Ag(PPh}_3\text{Me)}_x\text{(SePPh}_3\text{Me}_{3-x})]\text{OTf} \)
the \(^1\text{H NMR spectrum shows in the aliphatic region two resonances, in an} 1:4 \text{ molar ratio (} \delta 1.85 \text{ ppm,} \ 2J_{\text{PH}} \ 5.9 \text{ Hz and} \delta 2.60 \text{ ppm,} \ 2J_{\text{PH}} \ 13.6 \text{ Hz). The observed coupling constants are in accordance with the presence of both a P(III) and a P(V) species containing PMe protons.}

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

Figure 19. The 2D \( \text{H,P-HMQC spectrum (CDCl}_3, \ 300 \text{ MHz) of the solid isolated from reaction} \ (ii).
The APCI+ mass spectra of the solid resulted from reaction (ii) presents the molecular ion [AgOTf(PPh₃)(SePPh₂₃Me)²⁺] (m/z 800.9, 80%) as well as the ion [Ag(PPh₃)(SePPh₂₃Me)]⁺ + 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).](image)

The solid isolated from reaction (iv) proved a similar behavior in solution as it was described above for the silver species {[Ag(PPh₃)(SePPh₂₃Me)ₙ][OTf]₀} (n = 1, 2). The $^{31}$P NMR spectra recorded at room temperature either in CDCl₃ or acetone-$d₆$ 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 SePPh₂₃Me, SePPh₃ and [CuNO₃(PPh₃)₂], respectively (Table 4). The fourth resonance at δ −17.4 ppm was tentatively assigned to [CuNO₃(PPh₃Me)₂]. Taking into account this similarity, we presume that even if in reaction (iv) an equilibrium process involving both transfer of selenium from SePPh₂₃Me to PPh₃ 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 SePPh₂₃Me, SePPh₃, CuNO₃(PPh₂₃Me), CuNO₃(PPh₃), and CuNO₃(PPh₃Me)(PPh₃) 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 SePPh₃ or CuNO₃(PPh₃)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$_2$Me, 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. [CuNO$_3$(PPh$_3$)(PPh$_2$Me)], and it might be determined by very close chemical shift values of the PPh$_3$ and PPh$_2$Me 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](image)

**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).

2D $^{31}$P–$^{31}$P COSY (Figure 24) and $^{31}$P–$^1$H 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 \([\text{AuCl(SePPh}_2\text{Me)}]\) (5), \([\text{Au(C}_6\text{F}_5)(\text{SePPh}_2\text{Me})]\) (6), \([\text{Au(C}_6\text{F}_5)_2(\text{SePPh}_2\text{Me})]\) (7), \([\text{AgOTf(SePPh}_2\text{Me)}]\) (8) and \([\text{CuCl(SePPh}_2\text{Me)}]\) (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. 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 SePPh2Me, 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 Ph2MeP=Se in the solid state.94
- The products isolated from the reactions between SePPh2Me and [AgOTf(PPh3)] or [CuNO3(PPh3)2] proved to have a dynamic solution behavior involving the transfer of selenium from the P(V) species SePPh2Me to the P(III) phosphane PPh3. In case of the silver(I) species the NMR experiments brought further evidence for dimerization processes resulting in \([\text{Ag(PPh}_3](\mu-\text{SePPh}_2\text{Me}))_2(\text{OTf})_2\) (9a) and \([\text{Ag(PPh}_3\text{Me})(\mu-\text{SePPh}_3)]_2(\text{OTf})_2\) (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 SePPh2Me and SePPh3 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 \([\text{CuNO}_3(\text{PPh}_3)(\text{SePPh}_3)]\) (10), and dimeric \([\text{Cu(PPh}_3](\mu-\text{SePPh}_2\text{Me}))_2(\text{NO}_3)_2\) (12a) and \([\text{Cu(PPh}_3\text{Me})(\mu-\text{SePPh}_3)]_2(\text{NO}_3)_2\) (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 Ag···Se contact so that a fast equilibrium on NMR time scale between the dimer featuring the AgA···SeB interaction and the dimer featuring the AgB···SeA 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 PPh3Me, with formation of an unstable dinuclear species \([\text{Cu}_2(\text{PPh}_3)_2(\text{SePPh}_2\text{Me})_2\text{Se}^2]^{-}\), 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. The compound obtained from reaction \textit{i}) was purified by flash chromatography using ethyl acetate as eluent. The second step was the synthesis of \textit{Na₂Se} by a reaction of \textit{NaBH₄} with elemental selenium in water. \textit{R₂Se} derivative was further obtained by reacting \textit{Na₂Se} with the corresponding organic bromide as depicted in Scheme 6.

Scheme 6. Reagents and conditions: \textit{i)} NaOH, TBAB; \textit{ii)} NaBH₄, H₂O, NaOH, EtOH.

\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{77}Se 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 \textsuperscript{1}H 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 \textit{-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 \textsuperscript{1}H 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 \(^1\text{H}\) and \(^{13}\text{C}\) have been applied in order to study the structure of compounds 15 and 16 in solution. In the \(^1\text{H}\) 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).
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 CF₃ and SO₂ moieties. 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 CF₃SO₃ fragment (Figure 36).
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 $\delta$ 144.6 ppm for the complex 15 and a single sharp resonance at $\delta$ 129.39 ppm for the silver complex 16. The resonances are shifted downfield and upfield, respectively, compared to the free ligand ($\delta$ 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 ($\delta$ 144.60 ppm) at 293 K, on lowering the temperature, is upfield shifted ($\delta$ 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. The ESI+ mass spectrum of compound 15 (Figure 39) revealed four peaks at m/z 327.1 (100%) corresponding to \([\text{R}_2\text{Se}^+\text{H}]\), m/z 524.1 (37%) for\([\text{R}_2\text{SeAu}^+\text{H}]\), m/z 635.1 (1%) for \([\text{M}^+\text{Se}]\) and m/z 725.1 (24 %) for \([\text{R}_2\text{SeAu}^+\text{Au}]\), while the ESI- mass spectrum presents one peak at m/z 521 (100%) corresponding to \([\text{R}_2\text{SeAu}^-]\).

![Figure 39](image-url). Detail from ESI+ mass spectrum of compound 15.

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

![Scheme 8](image-url). Reagents and conditions: \(i\) Na, THF, r.t.; \(ii\) 1-(2-bromoethyl)-3,5-dimethyl-1H-pyrazole, THF, 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 (\(^{1}\text{H},^{13}\text{C},^{19}\text{F},^{77}\text{Se}\)) spectroscopy; VT and 2D NMR experiments were also used. The pattern of the \(^{1}\text{H}\) 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 H\(_{6'}\) appear as a doublet, while the H\(_{3'-5'}\) protons in 18 and protons 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 H\(_{8}\) are shifted to left (lower field).
Figure 40. Detail from stacked $^1$H 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%) [RR'Se$^+$+H] and $m/z$ 532.0 (10%) [RR'SeAu$^+$]. The ESI- mass spectrum of 18 (Figure 46) revealed
peaks at \( m/z \) 532 (10\%) for \([\text{RR'}\text{SeAu}^-]\) and \( m/z \) 802.9 (20\%) for \([\text{M}^+\text{AuCl}]\). The ESI+ mass spectrum of compound 19 (Figure 47) revealed three peaks at \( m/z \) 487.9 (100\%) for \([\text{M}^-\text{Ag}+\text{H}]\), \( m/z \) 593.9 (75\%) for \([\text{M}^+\text{H}]\) and 701 (2\%) for \([\text{M}^-\text{Ag}+\text{H}]\), while the ESI- mass spectrum revealed three peaks at \( m/z \) 339.7 (75\%) for \([\text{RR'}\text{Se}^-]\), \( m/z \) 447.0 (48\%) for \([\text{RR'}\text{SeAg}^-]\) and \( m/z \) 657.2 (100\%) for \([\text{M}^-\text{SO}_2]\).

The bis[2,6-bis(dimethylaminomethyl)phenyl]diselenium(I), 137 was prepared using the ortho lithiation route, \textit{i.e.} the reaction of 1,3-bis(dimethylaminomethyl)benzene with \( ^7\text{BuLi} \), 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 \( ^77\text{Se} \) NMR spectrum of the compound 20a is consistent with the formation of the selenol species. A singlet \( ^77\text{Se} \) resonance is observed around 1200 ppm (Figure 48), the signal being split due to the proton-selenium coupling. In the \( ^1\text{H} \) NMR spectrum of 20a a singlet resonance is observed at 2.1 ppm and was assigned to the proton attached to the selenium.

\[\text{Scheme 10. Reagents and conditions: } i) \ ^7\text{BuLi}, \text{hexane, r.t.; } ii) \text{Se, THF r.t.; } iii) \text{H}_2\text{O, O}_2.\]
Figure 48. The $^{77}$Se NMR spectrum (CDCl$_3$, 58 MHz) of compound 20a.

The selenol [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]SeH (20a) crystallizes with three molecule of water. Strong intramolecular N···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 [N—Se—N 162.01(15)$^\circ$]. This results in a T-shaped (C,N,N')Se core. Similar values for N···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 $^1$H, $^{13}$C and $^{77}$Se NMR spectra of compound 20 are consistent with the formation of the desired diorganodiselenium(I) derivative, [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$Se$_2$. The $^1$H NMR spectrum (Figure 50) exhibits singlet resonances for the protons of the pendant arms: $\delta$ 2.99 for the equivalent methyl groups (H$_8$) and $\delta$ 4.20 ppm for the methylene protons (H$_7$), respectively. The
aromatic protons appear as an unresolved multiplet at δ 7.28 ppm. The 77Se NMR spectrum of 20 (Figure 52) provides evidences towards the formation of targeted diorganodiselenium(I) 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 SO2Cl2, 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) SO2Cl2, CCl4, r.t.; ii) KBr, Acetone; iii) KI, Acetone.

The solution behavior of the organoselenium(II) halides was investigated by 1H, 13C and 77Se 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 13C NMR spectroscopy was also used to characterize compounds 21 – 23 and the results are in agreement with the proposed structure.

The 77Se 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 $^1$H NMR spectra (CDCl$_3$, 300 MHz) for: (a) ligand 20, (b) compound 21, (c) compound 22, and (d) compound 23.

Figure 54. Stacked $^{13}$C NMR spectra (CDCl$_3$, 58 MHz) for: (a) compound 21, (b) compound 22, and (c) compound 23.
III.B.2. Conclusions

- New diorganoselenium(II), \([(3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{CH}_2\text{CH}_2]_2\text{Se} \ (14)\) and \([(3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{CH}_2\text{CH}_2]_2\text{Se}(2-\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4] \ (17)\), and diorganodiselenium(1), \([2,6\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3]_2\text{Se}_2 \ (20)\), were prepared and fully characterized by NMR spectroscopy in solution and by mass spectrometry.

- \([(3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{CH}_2\text{CH}_2]_2\text{Se} \ (14)\) and \([(3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{CH}_2\text{CH}_2]_2\text{Se}(2-\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4] \ (17)\) were obtained by reacting \((3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{CH}_2\text{CH}_2\text{Br}\) with \(\text{Na}_2\text{Se}\) and the sodium selenolate \([2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SeNa}\), 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 \([2,6\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3]_2\text{Se}_2 \ (20)\) was prepared using the ortholithiation route. From the hydrolysis reaction the selenol \([2,6\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3]_2\text{SeH} \ (20a)\) 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 \([2,6\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3]_2\text{SeCl} \ (21)\), 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. Macro cyclic ligands containing N/calcogen 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 $^1$H, $^{13}$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 $^1$H 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 $^1$H 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 Se(1)···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. $\Sigma_{co}$(Se,N) 1.87 Å, $\Sigma_{vdW}$(Se,N) 3.54 Å]. The transannular Se(1)···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 Se···N intramolecular interaction. Only one nitrogen atom is intramolecularly coordinated to the selenium atom.
resulting in a $10\text{-Se-3}$ 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 sp$^2$ 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-dioxacyclotetrascene Schiff base.$^{158}$ The C(10)-Se(1)-C(1) angle for macrocycle 25 is 98.9(3)$^\circ$, also comparable with the C–Se–C angle [97.54(13)$^\circ$], 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-mercaptopoethyl)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/Et$_2$O.
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) Å, consistent with those found in other crown ethers. 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(sp^3)-C(sp^3) linkages 1.54 Å. The sulfur atoms don’t have the tendency to occupy the corners of a quadrangle as found in [12]aneNS_3 and many other structures.

In order to obtain the 12-membered macrocycle 32, pyridine-2,6-diyl dimethanol was reacted with SOCl_2 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 CF_3COOH and DCM (Scheme 15). The white solid, 12-membered macrocycle 32 was purified by flash chromatography (silica) using DCM/MeOH.
Scheme 15. Reagents and conditions: \(i\) \(\text{SOCl}_2\), DCM, 2 h, 0 °C; \(ii\) thiourea, EtOH, 2 h, reflux; \(iii\) 26, \(\text{Cs}_2\text{CO}_3\), DMF, 55 °C; \(iv\) \(\text{CF}_3\text{COOH}\), DCM, 2 h, 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: \(i\) \(\text{H}_2\text{O}\), NaOH, 0 °C; \(ii\) \(\text{H}_2\text{O}\), NaOH, 0 °C; \(iii\) EtOH, Na.

In the first three steps, the starting materials diethylenetriamine-\(\text{N,N',N''-tritosylate}\) (I) and disodium diethylenetriamino-\(\text{N,N',N''-tritosylate}\) (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 \(\text{N,N',N''-trytosilate-1,4,7-triazacyclononane}\). The macrocycle 33 was obtained by further deprotection and protonation of the \(\text{N,N',N''-trytosilate-1,4,7-triazacyclononane}\) (see Scheme 17).

Scheme 17. Reagents and conditions: \(iv\) DMF, 72 h, 105 °C; \(v\) \(\text{H}_2\text{SO}_4\), 72 h, 105 °C; \(vi\) toluene, \(\text{H}_2\text{O}\), 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 \(\text{K}_2\text{CO}_3\) (Scheme 17).
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).

Structural characterization was performed by $^1$H, $^{13}$C 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 $^1$H and $^{13}$C 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.
A closer look to the molecule of 35 reveled 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 [Σr_{cov}(H,Br) 2.18 Å and Σr_{vdW}(H,Br) = 3.15 Å]. 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 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of compound 36.
The pattern of the $^1$H 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 $^1$H 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. $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of compound 37.](image)

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 13C 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 K2CO3. 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, 13C and 2D NMR spectroscopy, mass spectrometry, single-crystal X-ray diffraction studies and elemental analysis.
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