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PhD Thesis
Abstract

Organo Gold, Silver and Copper Complexes

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Keywords: nitrogen/selenium ligands, nitrogen/sulfur ligands, coordination compounds ,
aurophilicity, agostic interactions, structure elucidation

Part 1

Synthesis and reactivity of selenolated carborane complexes with gold, silver and copper derivatives

Part 2

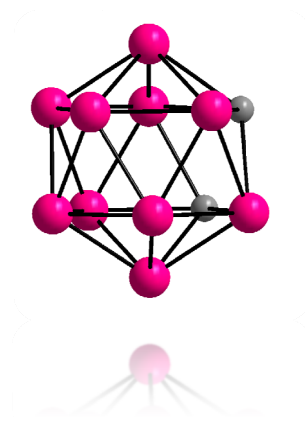
Synthesis and reactivity of NN'N or SeNSe pincer type ligands with gold, silver and copper derivatives

Part 3

Synthesis and reactivity of thio tetrazole ligands with gold and silver derivatives

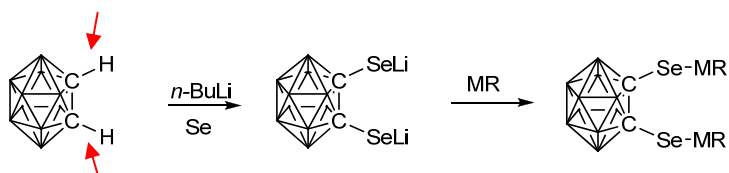
Part 1

Synthesis and reactivity of new selenolated carborane complexes with gold, silver and copper derivatives



1.2. OBJECTIVES

The target of this work was to functionalize the C-H bond through the C-H bond activation process selenium. The main purpose was the design, synthesis and characterization of selenium carboranes complexes with silver, gold and copper metals. Different functional groups were employed to synthesize the organometallic complexes. (Scheme 6).



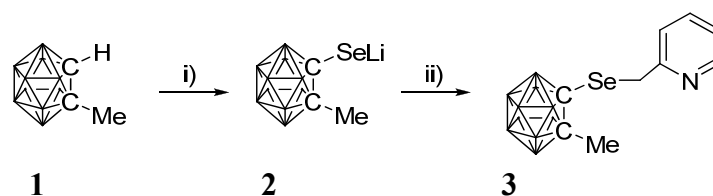
Scheme 6. Functionalization scheme for selenium carborane complexes, $\text{M}=\text{Ag}, \text{Au}, \text{Cu}$

1.3. RESULTS AND DISCUSSIONS

New ligands incorporating *closo* icosahedral carborane units in organic fragments NSe (pyridine-selenium) or NSe₂ (pyridine-diselenium) have been synthesized.

1.3.1. Synthesis and reactivity of 1-Se carborane containing N,Se coordination core with silver

The reaction of [C₂B₁₀H₁₁Me] (**1**) with *n*BuLi followed by the insertion of the selenium lead to the intermediate **2**, (**Scheme 7**). Further addition of the electrophile 2-(bromomethyl)pyridine yielded the ligand [(PyCH₂)(SeC₂B₁₀H₁₀Me)](**3**).



Scheme 7. Reagents and conditions: i) dry Et₂O, *n*BuLi (-78°C, 1h), Se (r.t., 2h); ii) [PyCH₂Br] (0°C, 2h), 55%

The crystal and molecular structure of **3** was determined by single-crystal X-ray diffraction studies, (**Figure 16**). In the crystal of **3** intermolecular contacts between selenium and hydrogen atoms in the carborane cages lead to a chain polymer association, see **Figure 17**.

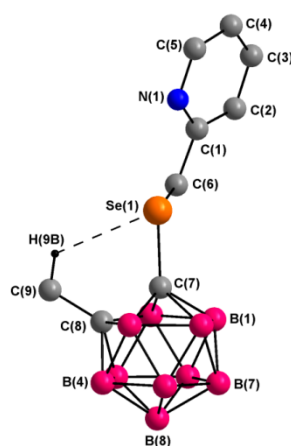


Figure 16. Molecular structure with atom numbering scheme of ligand **3**

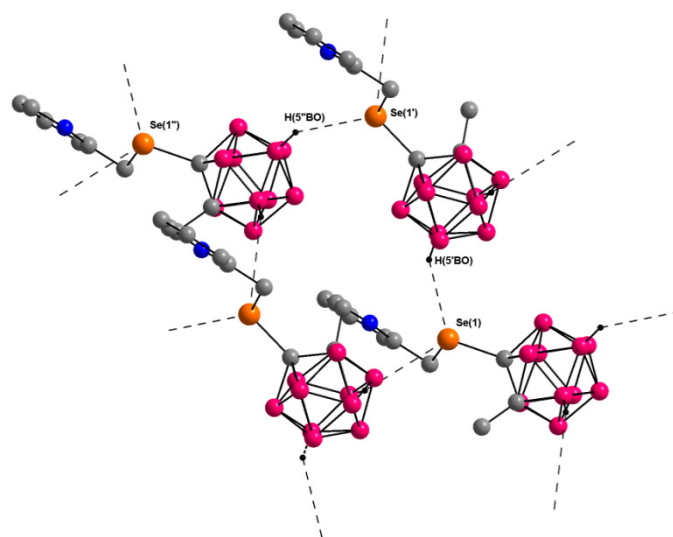
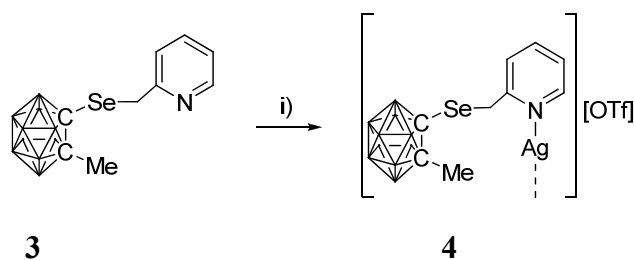


Figure 17. Chain polymer associations in the crystal of **3** based on B-H...Se contacts

In our ongoing interest in the coordination chemistry of the transition metals organoselenium derivative **3** was reacted with [AgOTf], and complex [Ag{(PyCH₂)(SeC₂B₁₀H₁₀Me)}](OTf) (**4**) was obtained, see **Scheme 8**. It is very likely that carborane derivative **3** is involved in the coordination process with nitrogen as source of donor atom. It is supported by ¹H, ¹³C, ¹⁹F NMR and IR spectroscopy. The dashed line represents a possible formation of a dimer or polymer.



Scheme 8. Reagents and conditions: i) [AgOTf], Et₂O, 1h, r.t., 78%

¹³C NMR spectroscopy was also used to characterize compound **4**, (**Figure 18**).

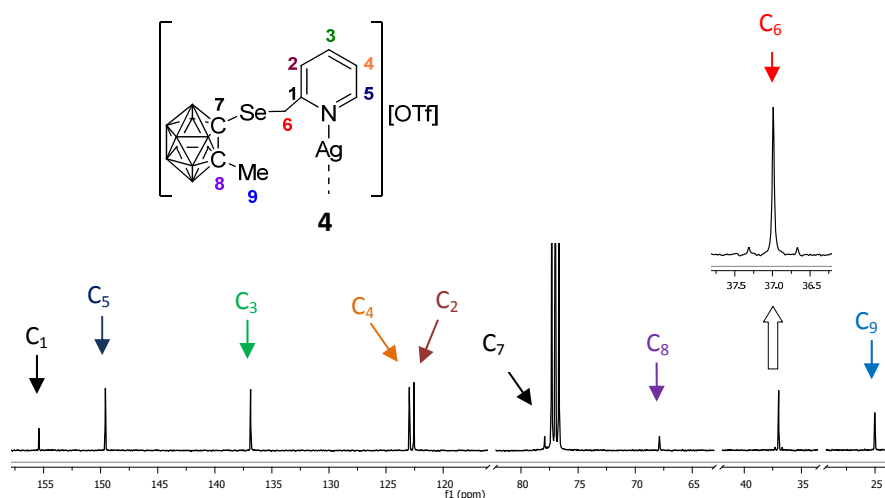
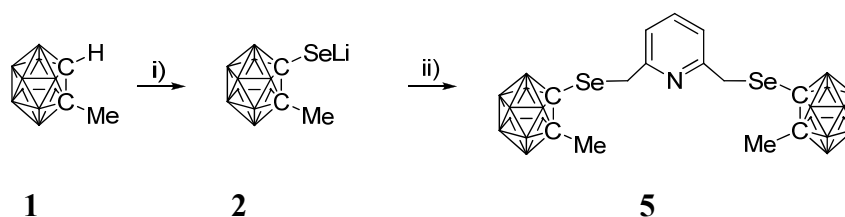


Figure 18. Detail from ^{13}C NMR spectrum (CDCl_3 , 101 MHz) of compound **4**

Inspection of the IR spectrum of **4** revealed that the triflate anion is ionic in nature,¹ but also the presence of Ag-N vibration was detected at 396 cm^{-1} .

1.3.2. Synthesis and reactivity of 1-Se carborane containing NSe₂ coordination core with silver and copper

The synthesis of $[(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_{10}\text{H}_{10}\text{Me}))_2]$ (**5**) has been carried out according to method described below. The reaction of $[\text{C}_2\text{B}_{10}\text{H}_{11}\text{Me}]$ (**1**) in Et_2O with $n\text{BuLi}$, followed by the addition of selenium and 2,6-bis(bromomethyl)pyridine affords, (**Scheme 9**).



Scheme 9. Reagents and conditions: i) dry Et_2O , $n\text{BuLi}$ (-78°C , 1h), Se (r.t., 2h); ii) $[\text{Py}(\text{CH}_2\text{Br})_2]$ (0°C , 2h), 45%

The proposed structure of **5** was confirmed by X-ray crystallography, (**Figure 24**).

¹ S. J. Angus-Dunne, *Transit. Metal Chem.*, 2006, **31**, 268.

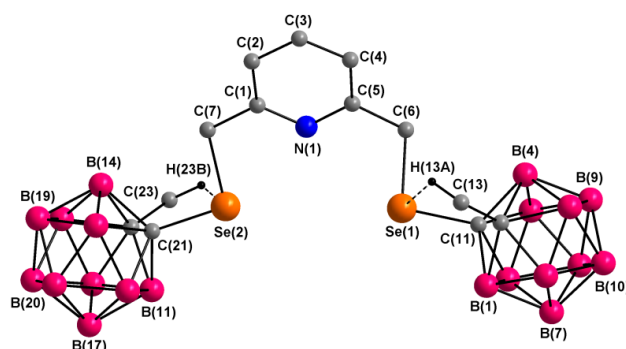


Figure 24. Molecular structure of selenolated ligand **5** with atom numbering scheme

In the crystal of **5** a linear polymer is formed through weak intermolecular interactions between selenium and hydrogen atoms in the pyridine ring, [*cf.* $\Sigma r_{\text{vdw}}(\text{Se},\text{H})$ 3.45 Å], see **Figure 25**.

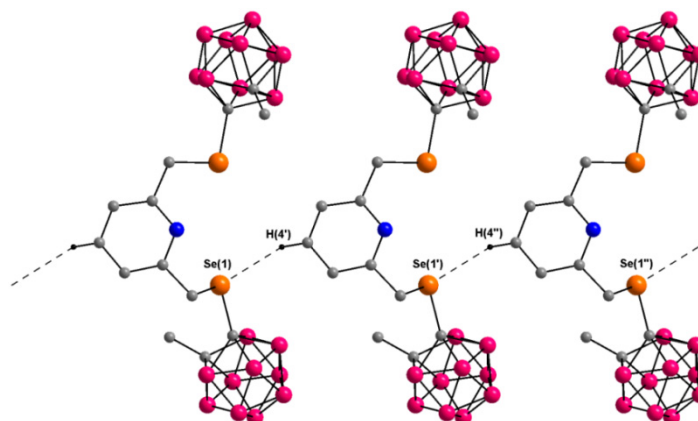
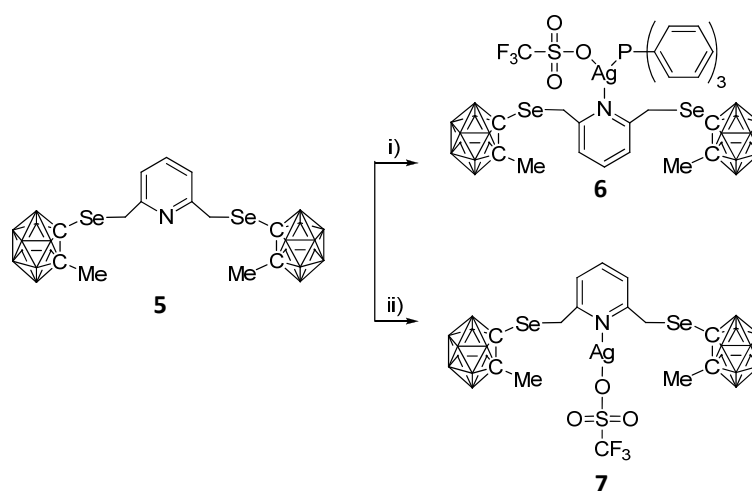


Figure 25. View along *b* axis of a linear network in the crystal of **5** based on intermolecular C-H...Se bonding

We have extended the study of tflates complexes and in this way subsequent transformations of ligand **5** were performed. Subsequently, **5** was reacted with $[(\text{PPh}_3)\text{Ag}(\text{OTf})]$ and $[\text{AgOTf}]$, leading to $[(\text{PPh}_3)(\text{OTf})\text{Ag}\{(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_{10}\text{H}_{10}\text{Me})_2)\}]$ (**6**) respectively $[(\text{OTf})\text{Ag}\{(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_{10}\text{H}_{10}\text{Me})_2)\}]$ (**7**), (**Scheme 10**).



Scheme 10. Reagents and conditions: i) $[\text{Ag}(\text{PPh}_3)(\text{OTf})]$, CH_2Cl_2 , 1h, r.t., 89%; ii) $[\text{AgOTf}]$, CH_2Cl_2 , 2h, r.t., 54%

Comparing their ^1H NMR spectra it was observed that with respect to **5**, in complexes **6** and **7** the resonances are shifted to left upon coordination, (**Figure 26**).

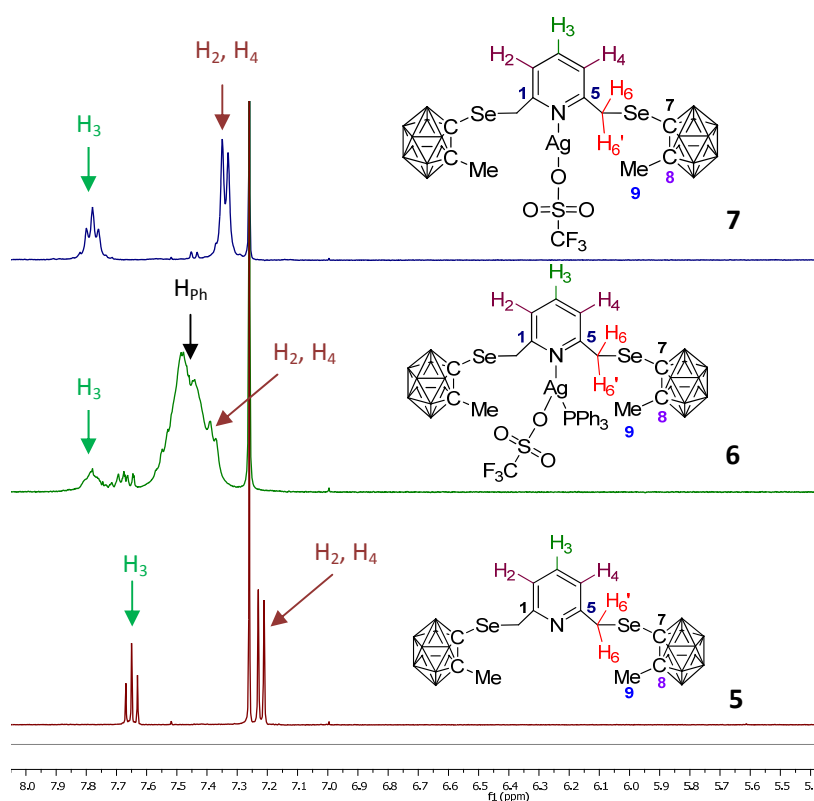
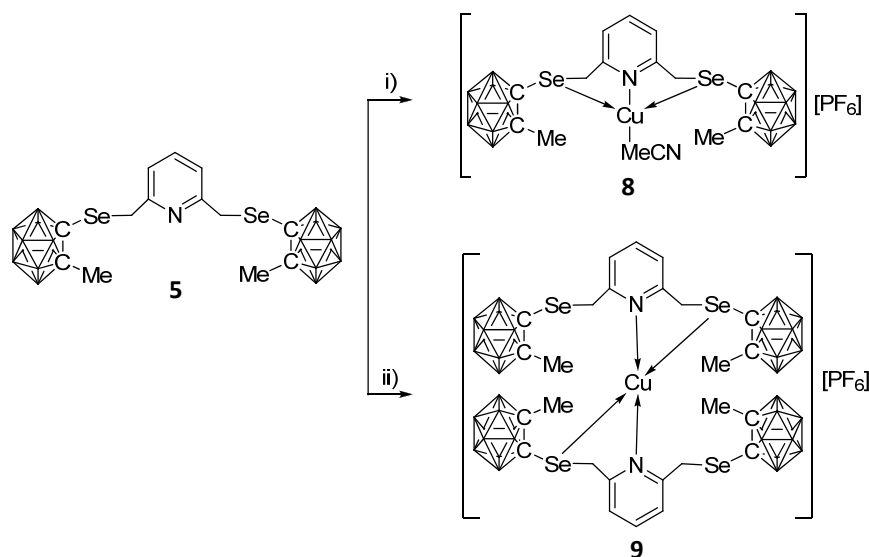


Figure 26. Stacked ^1H NMR spectra (CDCl₃, 400 MHz) for complexes **5**, **6** and **7**; Detail from the aromatic region

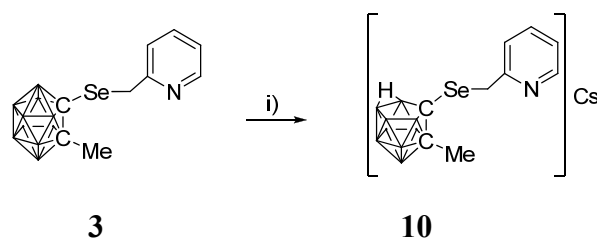
Through IR spectroscopy it was revealed that in **6** and **7** the triflate moiety remained covalently bonded to silver. A comparative study of the IR spectra of silver complexes **6** and **7** resulted in the observation that the N-Ag vibration arise as a broad band at 422 cm^{-1} for **6** respectively 392 cm^{-1} in case of **7**.

Within the general framework, further reactions implied the use of copper derivatives and in this way **5** was reacted with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in 1:1 respectively 2:1 molar ratio, leading to complexes $[(\text{MeCN})\text{Cu}\{(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_{10}\text{H}_{10}\text{Me})_2)\}_2](\text{PF}_6)$ (**8**) respectively $[\text{Cu}\{(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_{10}\text{H}_{10}\text{Me})_2)\}_2](\text{PF}_6)$ (**9**), see **Scheme 12**.



Scheme 12. Reagents and conditions: i) $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$, CH_2Cl_2 , 2h, r.t., 85%; ii) $\frac{1}{2}$ $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$, CH_2Cl_2 , 2h, r.t., 77%

With respect to **5**, the ^1H NMR spectrum of **8** and **9** display the same pattern in the aromatic region, the resonances are shifted to left after the coordination of copper derivative. Moreover, the resonance assigned to the MeCN protons is seen at δ 2.21 ppm in **8** (**Figure 32**), while in **9** the protons from the MeCN group do not appear.



Scheme 13. Reagents and conditions: i) CsF, EtOH, 25h reflux, 97%

In **Figure 38** is illustrated the ^1H NMR spectrum of **10**.

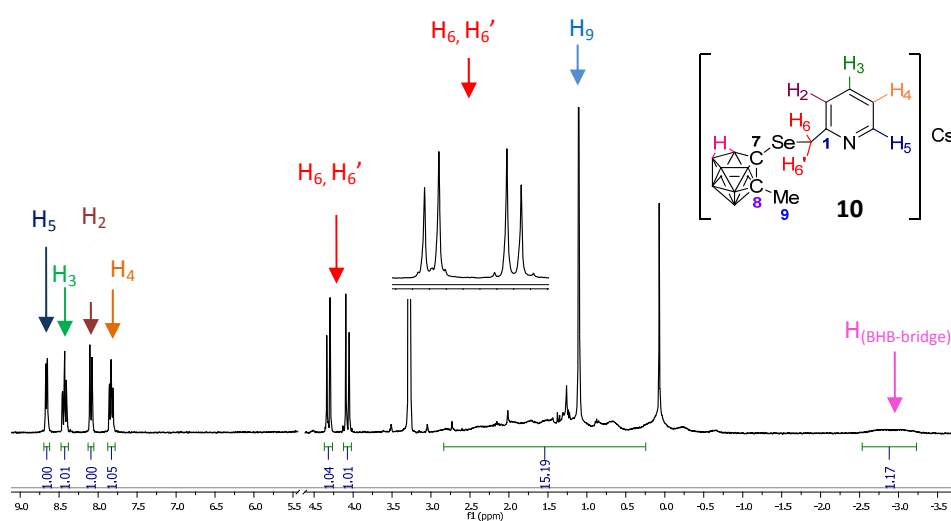


Figure 38. ^1H NMR spectrum (CDCl_3 , 300 MHz) of complex **10**

In the ES(-) MS spectrum of **10** peaks corresponding to $[\text{M}-\text{Cs}]^-$ were detected at m/z 318, (**Figure 40**).

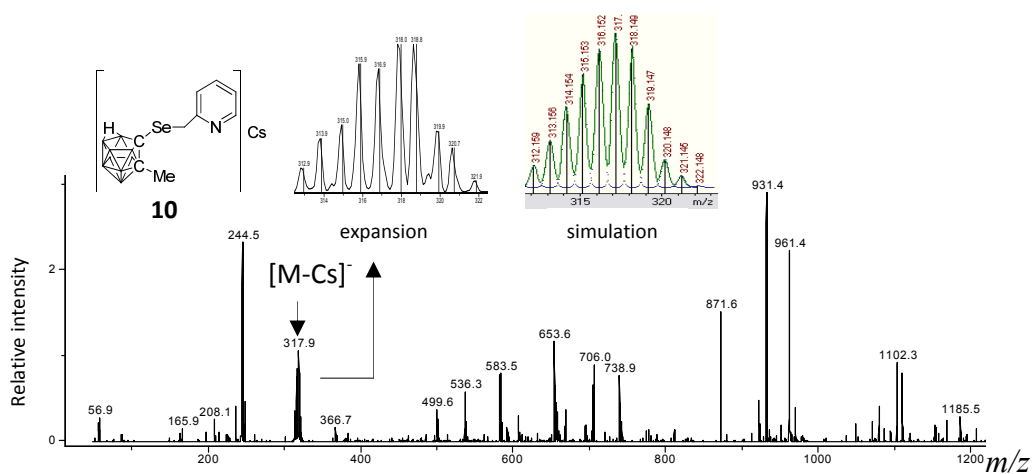
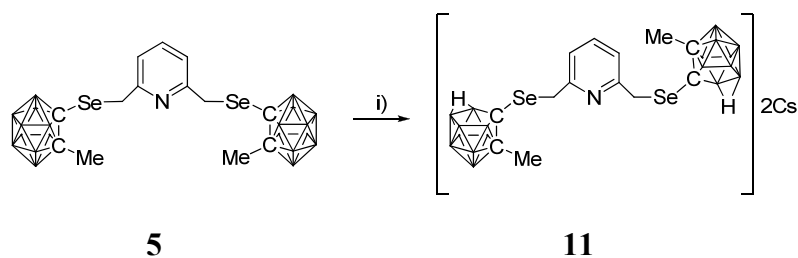


Figure 40. ES(-) MS spectrum of **10**, including a simulation (right insert) of the isotopic pattern

The partial degradation of ligand **5** was achieved, by dissolving the *closo* compound **5** in a solution of CsF in ethanol under refluxing conditions. In this case two B-H groups were removed leading to compound $[(\text{Py}(\text{CH}_2)_2(\text{SeC}_2\text{B}_9\text{H}_9\text{Me})_2)]^-\text{Cs}^+$ (**11**), see **Scheme 14**.



Scheme 14. Reagents and conditions: i) CsF, EtOH, 25h reflux, 95%

The NMR spectra confirmed the partial degradation process. The appearance of the B-H-B resonance is in agreement with the existence of the *nido* specie and was detected at δ - 2.52 ppm as a very broad signal, (**Figure 41**).

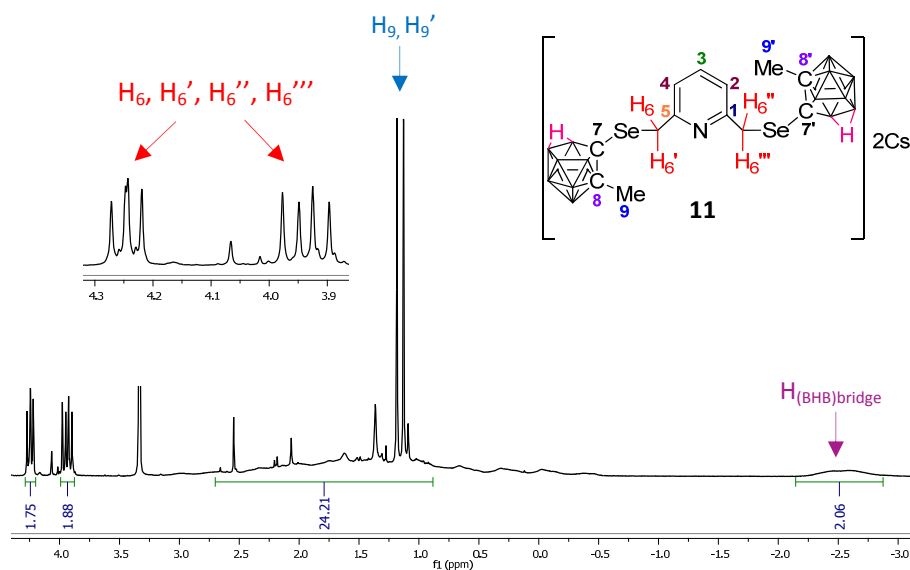


Figure 41. Detail from the aliphatic region of the ^1H NMR spectrum (methanol- D_4 , 400 MHz) of **11**

Furthermore, the ES(-) MS spectrum of **11** indicates the presence of the expected compound. The anionic fragment $[\text{M}-2\text{Cs}+\text{H}]^-$ was formed by losing the two cesium atoms and was detected at m/z 556, **Figure 43**.

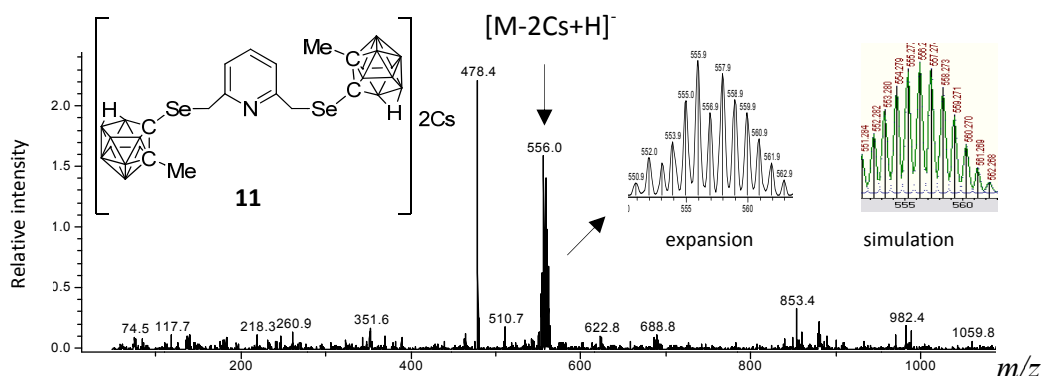
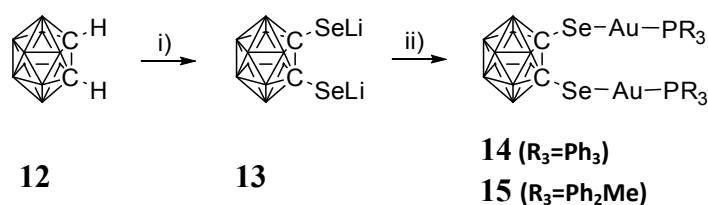


Figure 43. ES(-) MS spectrum of **11**, including a simulation (right insert) of the isotopic pattern

1.3.4. Synthesis and reactivity of 1,2-Se carborane with gold

Starting from the [1,2-*closo*-C₂B₁₀H₁₂] (**12**) we activated the C-H groups using *n*BuLi and further addition of elemental selenium afforded the lithiated intermediary **13**. Subsequent transformations implied the use *in situ* of gold derivatives [(PR₃)AuCl] leading to selenolated gold carborane complexes [(PR₃)₂Au₂(Se₂C₂B₁₀H₁₀)], [PR₃= PPh₃ (**14**), PR₃= PPh₂Me (**15**)], see **Scheme 15**.



Scheme 15. Reagents and conditions: i) *n*BuLi, Et₂O (0°C, 1h), Se(r.t., 3h); ii) [(PR₃)AuCl], Et₂O, 3h, 10°C, 55% (**14**), 50% (**15**)

To confirm the structure, suitable crystals for X-ray diffraction studies were obtained from a solution of **15** in methanol by slow evaporation, (**Figure 48**). In complex **15** intramolecular gold-gold interactions of significant strength were established, Au(1)⋯Au(2) 2.940(4) Å, [cf. $\sum r_{cov}$ (Au,Au) 2.68 Å, $\sum r_{vdW}$ (Au,Au) 3.4 Å]. The coordination around gold atom Au(1) is linear with an angle Se(1)-Au(1)-P(1) of 170.74(7)° while for Au(2) a distorted planar geometry with the angle Se(2)-Au(2)-P(2) 154.57(8)° is observed.

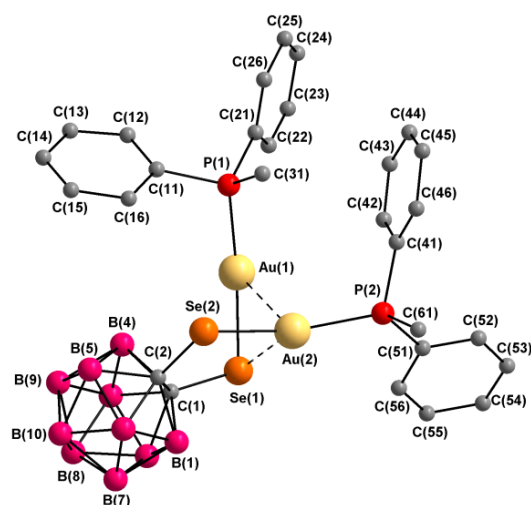


Figure 48. Molecular structure of gold complex **15**, the hydrogen atoms have been removed for clarity

This may, however, be explained by the interaction between Se(1) and Au(2) of 3.0266(13) Å, [$\sum r_{cov}(\text{Se,Au})$ 2.51 Å, $\sum r_{vdW}(\text{Se,Au})$ 3.7 Å]. In the solid state, two [(PPh₂Me)₂Au₂(Se₂C₂B₁₀H₁₀)] units form a dinuclear complex (**Figure 49**).

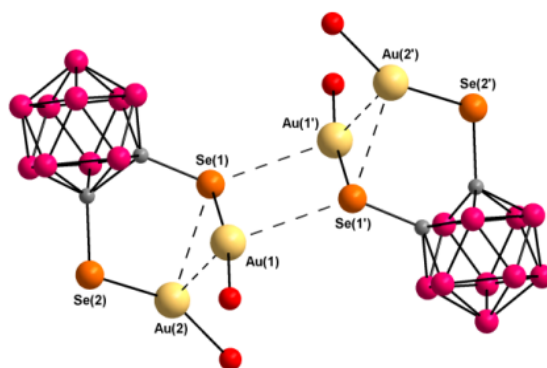


Figure 49. Dinuclear unit in crystal of complex **15**, the phenyl and methyl groups attached to phosphorus, but also the hydrogen atoms were omitted for clarity

1.4. CONCLUSIONS

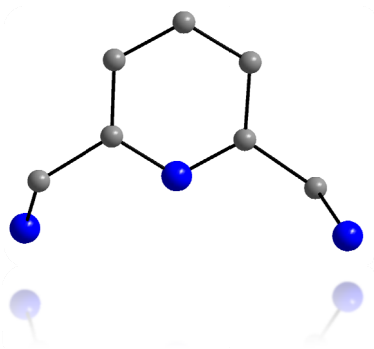
1. Organoselenolated carborane ligands [(PyCH₂)(SeC₂B₁₀H₁₀Me)] (**3**) and [(Py(CH₂)₂(SeC₂B₁₀H₁₀Me)₂] (**5**) were prepared by C-H activation of *closo* [C₂B₁₀H₁₁Me] (**1**) with *n*BuLi (1:1 ratio) in diethyl ether followed by the addition of finely ground selenium powder. Further addition in situ of 2-(bromomethyl)pyridine respectively 2,6-bis(bromomethyl)pyridine yields **3** and **5**. Crystal X-ray diffraction studies, IR and NMR spectroscopy and mass spectrometry analyses confirmed the proposed structures for the both ligands. The coordination behavior of these ligands towards silver and copper derivatives was investigated. Also in these cases the analytical data confirm the proposed structures. The synthesized metal complexes are anionic or neutral. When **3** was reacted with silver triflate in 1:1 molar ratio the resulting complex [Ag{(PyCH₂)(SeC₂B₁₀H₁₀Me)}](OTf) (**4**) is ionic in nature. By contrast, in case of **5**, the coordination reactions with silver triflate triphenylphosphine respectively silver triflate gives the neutral complexes [(PPh₃)(OTf)Ag{(Py(CH₂)₂(SeC₂B₁₀H₁₀Me)₂}] (**6**), [(OTf)Ag{(Py(CH₂)₂(SeC₂B₁₀H₁₀Me)₂}] (**7**).

2. The carboranyl NSe respectively NSe₂, *closo* compounds described above have an easy pathway to become anionic ligands maintaining the original NSe and NSe₂ coordinating moiety. The partial degradation reaction of the *closo* species **3** and **5**, involving the removal of one or two boron atoms, lead to *nido* compounds [(Py(CH₂)(SeC₂B₉H₉Me)]⁻Cs⁺ (**10**) respectively [(Py(CH₂)₂(SeC₂B₉H₉Me)₂)]⁻Cs⁺ (**11**).

3. Gold complexes [(PPh₃)₂Au₂(Se₂C₂B₁₀H₁₀)] (**14**) and [(PPh₂Me)₂Au₂(Se₂C₂B₁₀H₁₀)] (**15**) were prepared by C-H activation of [1,2-*closo*-C₂B₁₀H₁₂] (**12**) involving reaction with *n*BuLi (1:1 ratio) in diethyl ether followed by selenium insertion. Further addition in situ of [(PPh₃)AuCl] or [(PPh₂Me)AuCl] afforded **14** and **15**. The molecular structure of **15** was determined by X-ray diffraction studies and the presence of aurophilic interactions was observed. The work covered in this part demonstrates the many benefits of using carboranes and metallocarboranes as components in the organometallic chemistry.

Part 2

Synthesis and reactivity of NN'N or SeNSe pincer type ligands with gold, silver and copper derivatives



2.2. OBJECTIVES

Being known the importance of pincer derivatives in organometallic chemistry, our main target was to prepare different neutral NN'N and SeNSe pincer derivatives and to study their interaction with metals.

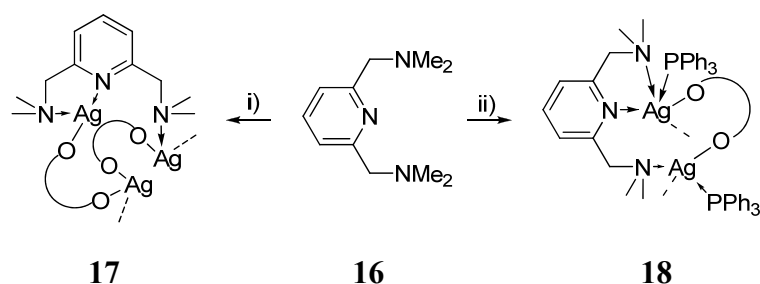
The NN'N and SeNSe pincers can be subject of interaction with gold, silver and copper ligands (e.g. [HAuCl₄], [(PPh₃)Ag(OTf)] and [Cu(MeCN)₄]PF₆) in different molar ratios.

Also the reactivity and coordination chemistry of NN'N and SeNSe pincers is an objective we want to follow. Detailed investigations and understanding of similarities can bring interesting information on this type of pincers.

2.3. RESULTS AND DISCUSSIONS

2.3.1. Synthesis and reactivity of NN'N pincer ligand with silver derivatives

The reaction of ligand NN'N (**16**) and $[\text{CF}_3\text{COOAg}]$ and $[(\text{PPh}_3)(\text{AgOTf})]$ in 1:1 molar ratio yielded complexes $\{(\text{CF}_3\text{COOAg})_n[(\text{Me}_2\text{NCH}_2)_2\text{Py}]_n\}$ (**17**) and $[(\text{PPh}_3)(\text{OTf})\text{Ag}_2(\text{Me}_2\text{NCH}_2)_2\text{Py}]$ (**18**), (**Scheme 16**).



Scheme 16. Reagents and conditions: i) $[\text{CF}_3\text{COOAg}]$, CH_2Cl_2 , 1h, r.t., ii) $2[(\text{PPh}_3)\text{Ag}(\text{OTf})]$, CH_2Cl_2 , 1h, r.t., 92%

The pattern of the ^1H NMR spectra for complexes **17** and **18** with respect to the NN'N moiety **16** is consistent with the coordination of the silver derivative in solution, see **Figure 57**.

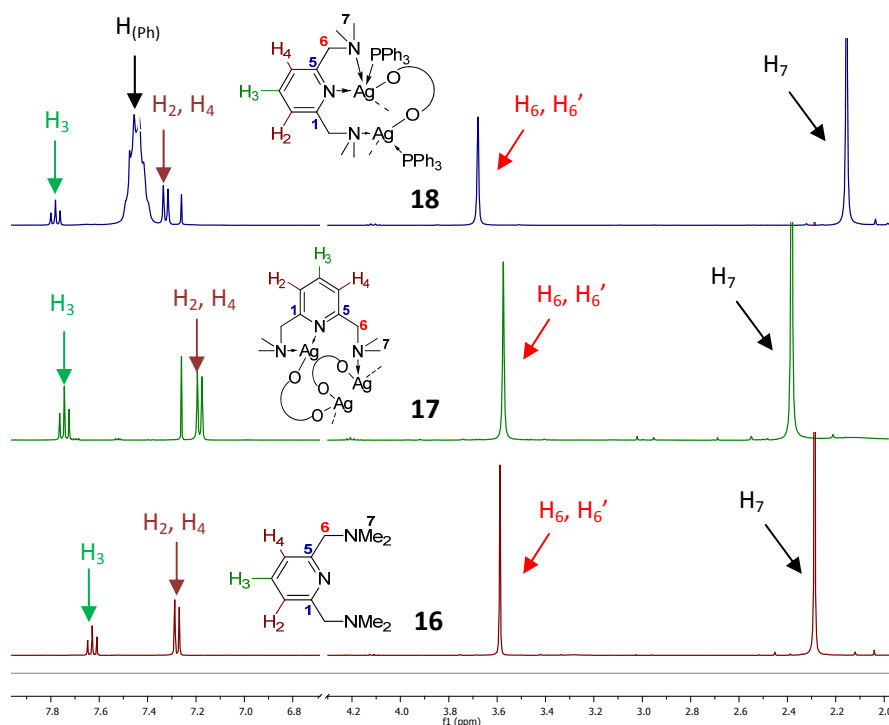


Figure 57. Detail from stacked ^1H NMR spectra (CDCl_3 , 400 MHz) of **16**, **17** and **18**

X-ray diffraction studies revealed that **17** crystallize as a polymer. The molecular structure with the atom numbering scheme is shown in **Figure 67** and **Figure 68**. The presence of Ag(1)⋯Ag(2) contacts of 3.075(5) Å and Ag(3)⋯Ag(2) of 3.008(4) Å was noticed, [*cf.* $\Sigma r_{\text{vdw}}(\text{Ag}, \text{Ag})$ 3.4 Å].

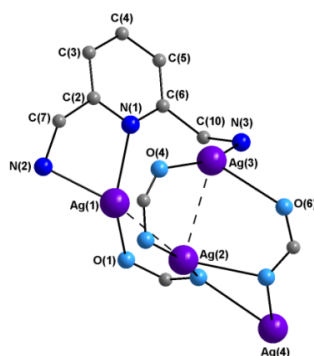


Figure 67. Perspective view of the monomeric form of complex **17**

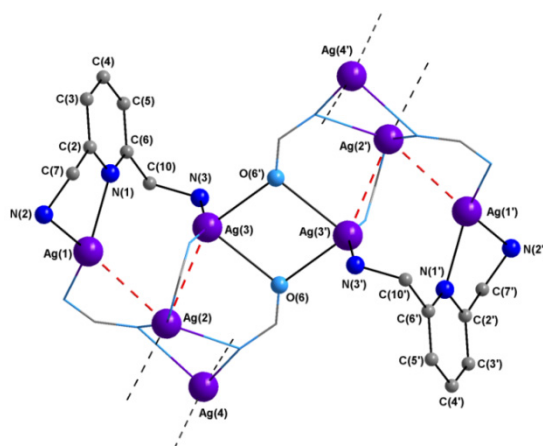
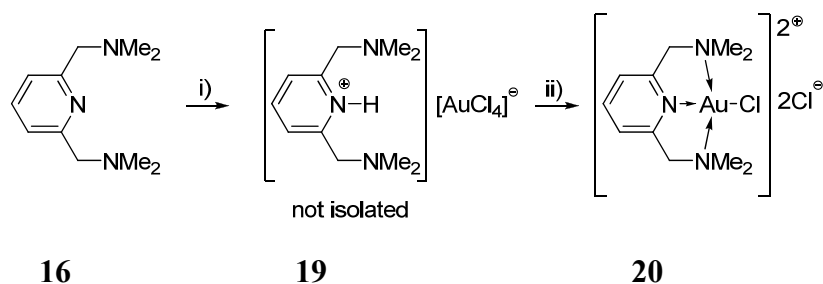


Figure 68. Perspective view of the polymeric form of complex **17**

2.3.2. Synthesis of NN'N pincer complex with gold derivatives

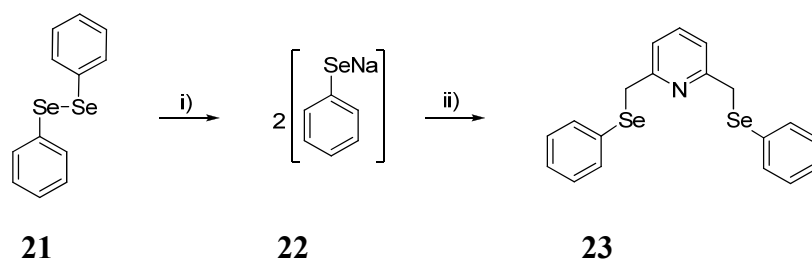
Gold(III) complex $[\text{ClAu}(\text{NN}'\text{N})\text{Cl}_2]$ (**20**) was prepared from direct reaction of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ with NN'N (**16**), in mild conditions affords in a first stage the a salt of the protonated ligand $[(\text{NN}'\text{HN})][\text{AuCl}_4]$ (**19**), see **Scheme 23**.



Scheme 23. Reagents and conditions: i) $\text{H}[\text{AuCl}_4]\cdot 3\text{H}_2\text{O}$, Et_2O , 30', r.t.; ii) NaHCO_3 , THF, 24h, r.t., 87%

2.3.3. Synthesis and reactivity of SeNSe complexes of gold

The reduction of Ph_2Se_2 **21** with NaBH_4 afforded the intermediate **22** and further addition of 2,6-bis(bromomethyl)pyridine leads to the title compound $[\text{Py}(\text{CH}_2)_2(\text{SePh})_2]$ (**23**), see **Scheme 24**.



Scheme 24. Reagents and conditions: i) NaBH_4 , EtOH , 20', r.t.; ii) $[\text{Py}(\text{CH}_2\text{Br})_2]$, r.t., 1h, 95%

The molecular structure of **23** was obtained through X-ray diffraction studies, see **Figure 76**.

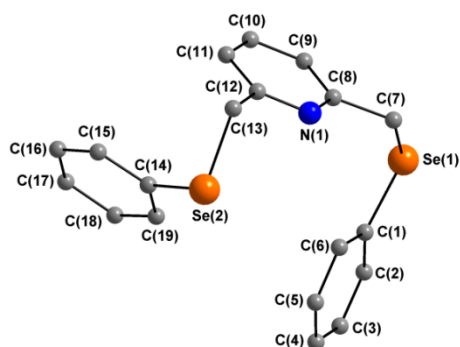


Figure 76. Molecular structure of **23**

Intra- and intermolecular hydrogen bonding C-H \cdots Se are established in the crystal of **23**, **Figure 77**, the formation of the hydrogen bonding involving the methylene groups leads to a polymeric chain, [*cf.* $\Sigma r_{\text{vdw}}(\text{Se},\text{H})$ 3.45 Å].

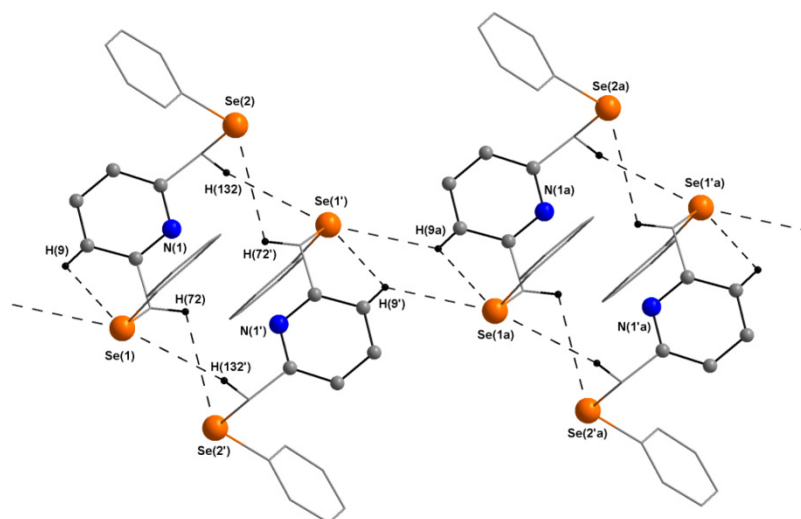
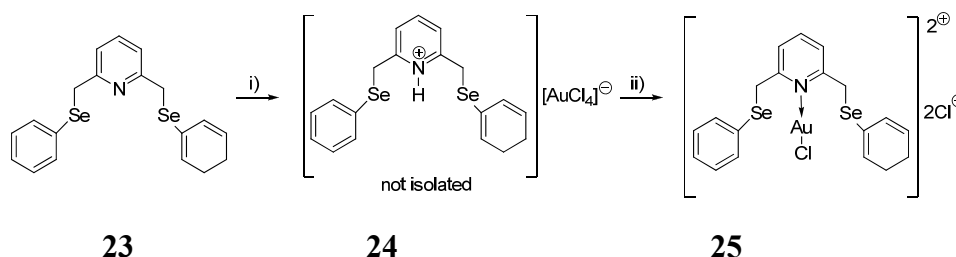


Figure 77. Chain polymer associations in the crystal of **23** based on C-H \cdots Se intra- and intermolecular contacts

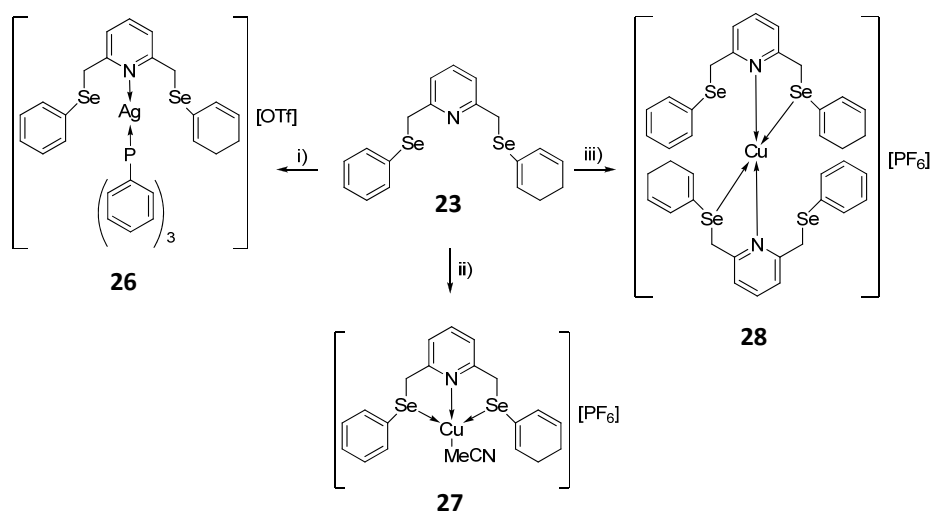
In a similar reaction conditions as for **20**, gold complex **25** was synthesized, see **Scheme 25**.



Scheme 25. Reagents and conditions: i) $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$, Et_2O , 30', r.t.; ii) NaHCO_3 , THF, 24h, r.t.

2.3.4. Synthesis of SeNSe pincer complexes of silver and copper

Complexes $[(\text{PPh}_3)\text{Ag}\{\text{Py}(\text{CH}_2)_2(\text{SePh})_2\}](\text{OTf})$ (**26**), $[(\text{MeCN})\text{Cu}\{\text{Py}(\text{CH}_2)_2(\text{SePh})_2\}](\text{PF}_6)$ (**27**) and $[\text{Cu}\{\text{Py}(\text{CH}_2)_2(\text{SePh})_2\}_2](\text{PF}_6)$ (**28**) are formed as a result of reaction between **23** with $[(\text{PPh}_3)\text{Ag}(\text{OTf})]$ or $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in 1:1 molar ratio for **26** or in 1:1 and 2:1 in cases of **27** and **28** (**Scheme 26**). A comparison of the ^1H NMR spectra of **26**, **27** and **28** is presented in **Figure 79**.



Scheme 26. Reagents and conditions: i) $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$, dry CH_2Cl_2 , 1h, r.t., 82%; ii) $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$, dry CH_2Cl_2 , 3h, r.t., 87%; iii) $\frac{1}{2} [\text{Cu}(\text{MeCN})_4]\text{PF}_6$, dry CH_2Cl_2 , 3h, r.t., 92%

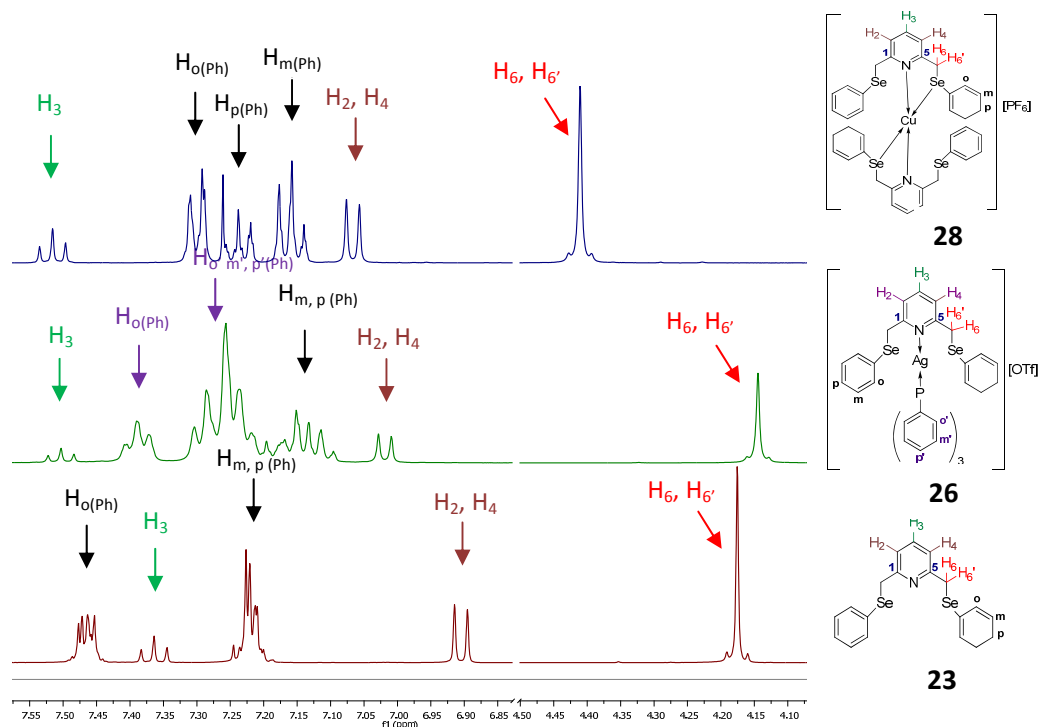


Figure 79. Detail from stacked ^1H NMR spectra (CDCl₃, 400 MHz) of compounds **23**, **26** and **28**

Mass spectrometry was undertaken for SeNSe complexes **26**, **27** and **28**, ES(+) MS spectrum of **26** being characterized by the appearance of molecular peak at m/z 787.7, **Figure 86**.

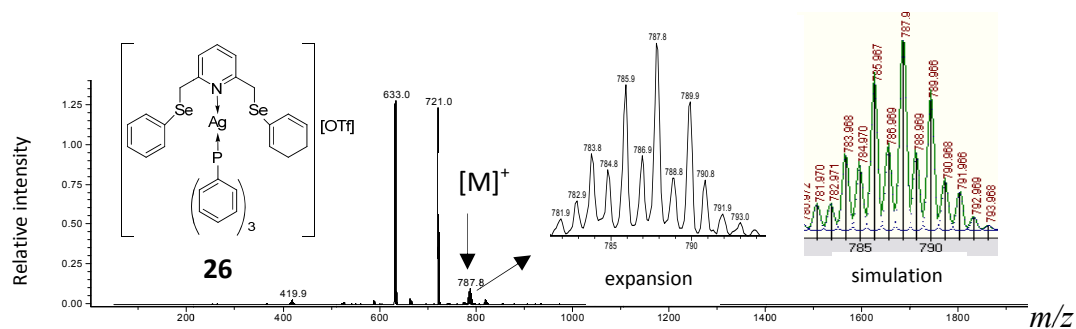


Figure 86. ES(+) MS mass spectrum of complex **26**, including a simulation (right insert) of the isotopic pattern

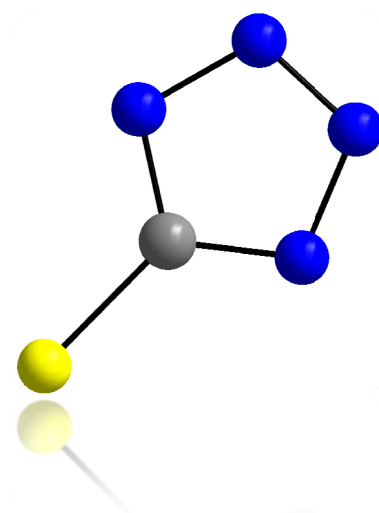
2.4. CONCLUSIONS

4. Pincer type ligands NN'N and SeNSe were prepared. A detail study of their coordination chemistry towards coinage metal group was performed. Complexation reactions between tridentate nitrogen donor NN'N [2,6-(Me₂NCH₂)₂Py] (**16**) and silver trifluoroacetate respectively silver triflate triphenylphosphine affords $\{(CF_3COOAg)_n[(Me_2NCH_2)_2Py]_n\}$ (**17**) and $[(PPh_3)(OTf)Ag_2(Me_2NCH_2)_2Py]$ (**18**). In case of **17**, the X-ray diffraction studies revealed a polymeric structure, while for **18**, the NMR, mass and IR studies indicated a neutral complex. When NN'N **16** is reacted with H[AuCl₄] the ionic complex $[ClAu(NN'N)]Cl_2$ (**20**) is obtained, where the gold atom is coordinated by the full set of donor atoms in the NN'N ligand.

5. Selenolated SeNSe $[Py(CH_2)_2(SePh)_2]$ (**23**) pincer ligand was prepared by cleavage of the selenium-selenium bond in the diphenyl selenide and reaction with 2,6 bis(bromomethyl)pyridine. Metal complexes $[(PPh_3)Ag\{Py(CH_2)_2(SePh)_2\}](OTf)$ (**26**) respectively $[(MeCN)Cu\{Py(CH_2)_2(SePh)_2\}](PF_6)$ (**27**) and $[Cu\{Py(CH_2)_2(SePh)_2\}_2](PF_6)$ (**28**) were prepared by reacting SeNSe **23** with $[(PPh_3)Ag(OTf)]$ and $[Cu(MeCN)_4]PF_6$. The analyses indicated that silver complex **26** is neutral, while the copper ones **27** and **28** are ionic.

Part 3

Synthesis and reactivity of thio tetrazole ligands with gold and silver derivatives



3.2. OBJECTIVES

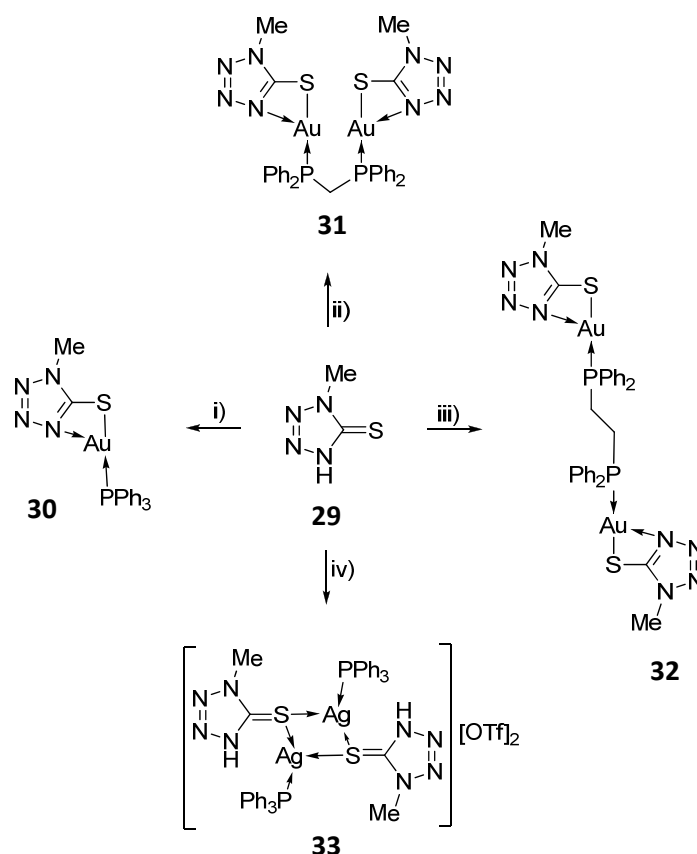
The possibility of direct introduction of new coinage metal derivatives via S-M covalent or coordinative bond formation is not a straightforward strategy, although is a very highly attractive synthetic procedure. The most fundamental reactivity pattern involves the tautomeric forms present in thio tetrazoles. This feature makes thio tetrazoles versatile ligands in coordination chemistry, as different coordination modes may appear. The reactivity of thio tetrazoles towards gold and silver has not been deeply investigated so far and for this reason the present work deals with a complete characterization of new gold and silver thio tetrazoles complexes. For a better understanding of the solution and solid state behavior of thio tetrazoles complexes with coinage the early examples of tetrazole complexes with Au-S and Ag-S bonds have been used. Therefore, for this work, two main objectives have been established:

- 1. To design new covalent or coordinative systems where metallophilic (aurophilic or argentophilic) interactions occur.*
- 2. To observe the different coordination modes of thio tetrazoles towards gold and silver derivatives.*

3.3. Results and Discussions

3.3.1. Synthesis of 1-methyl tetrazoline-5-thione complexes of gold and silver

The reaction between **29** and $[(PPh_3)AuCl]$ in 1:1 molar ratio yielded $[(PPh_3)Au(SCN_4Me)]$ (**30**) and $[(\mu-dppm)Au_2Cl_2]$ ($dppm=Ph_2PCH_2PPh_2$) respectively $[(\mu-dppe)Au_2Cl_2]$ ($dppe=Ph_2PCH_2CH_2PPh_2$) in 2:1 molar ratio afforded $[(\mu-dppm)Au_2(SCN_4Me)_2]$ (**31**) and $[(\mu-dppe)Au_2(SCN_4Me)_2]$ (**32**). Complex $[(PPh_3)Ag(HSCN_4Me)]_2(OTf)_2$ (**33**) was prepared in CH_2Cl_2 using similar reaction procedures, $[(PPh_3)Ag(OTf)]$ being used as complexation agent, **Scheme 30**.



Scheme 30. Reagents and conditions: i) $[(PPh_3)AuCl]$, dry THF, NEt_3 , 3h, r.t., 80%; ii) $[(\mu-dppm)Au_2Cl_2]$, dry THF, Et_3N , 3h, r.t., 91 %; iii) $[(\mu-dppe)Au_2Cl_2]$, dry THF, Et_3N , 3h, r.t., 81 %; iv) $[(PPh_3)Ag(OTf)]$, dry CH_2Cl_2 , 2h, r.t., 81%

The structure of complexes **31** and **32** were confirmed also using X-ray diffraction studies. The crystal structure of **31** contains two independent molecules and therefore subsequent discussion at molecular level will refer to molecules **31a** and **31b** (**Figure 103**). In both molecules the gold atoms are dicoordinated with an almost linear S-Au-P geometry [P(1)-Au(1)-S(1) $173.05(5)^\circ$ respectively P(2)-Au(2)-S(2) $176.74(5)^\circ$ in **31a** while P(3)-

Au(3)-S(3) 169.13(5)° and P(4)-Au(4)-S(4) 173.03(5)° in **31b**]. Auophilic interactions were observed in both cases. In the molecule of **31a** the Au(1)⋯Au(2) distance is 3.2142(3) Å, while in **31b** the distance is shorter Au(3)⋯Au(4) 3.1046(3) Å, [*cf.* $\sum r_{\text{cov}}(\text{Au,Au})$ 2.68 Å, $\sum r_{\text{vdw}}(\text{Au,Au})$ 3.4 Å].

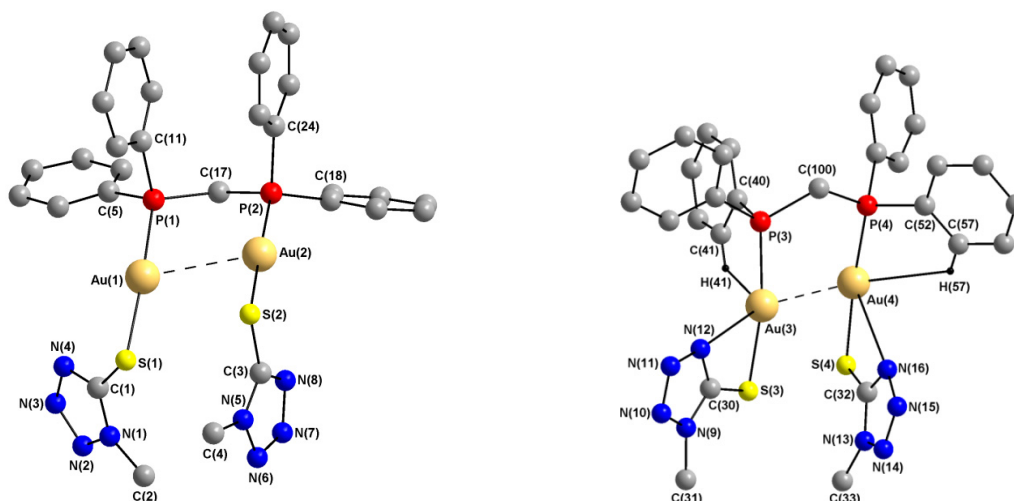


Figure 103. Structure of **31a** (left) and **31b** (right); Hydrogen atoms (except those involved in agostic interactions), are omitted for clarity

A clear highlight of this area of investigation is represented by the X-ray structure of complex **32** that revealed three independent complex molecules, **32(a-c)**, **Figure 105** and **Figure 107**.

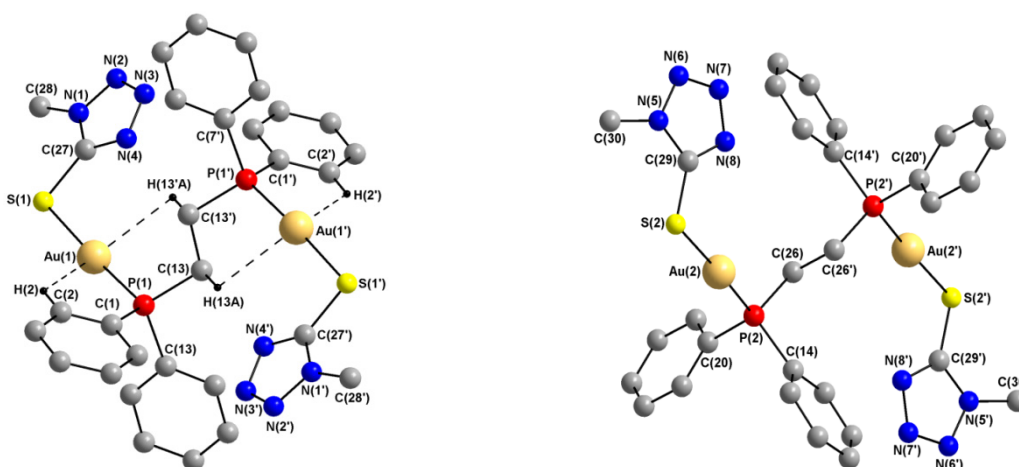


Figure 105. Structure of **32a** and **32b**; Hydrogen atoms (except those involved in agostic interactions), are omitted for clarity

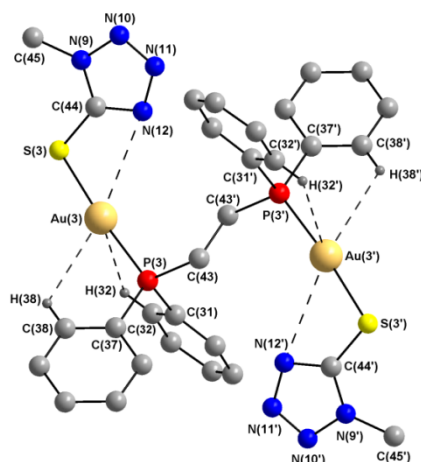


Figure 107. Structure of **32c** showing the atom numbering scheme; Hydrogen atoms (except those involved in agostic interactions), are omitted for clarity

Molecules **32a** and **32b** are associated through Au...Au intermolecular contacts leading to a polymeric chain, (**Figure 108**).

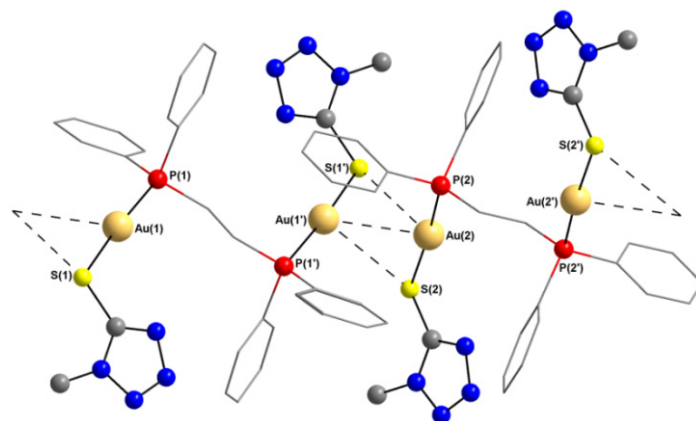


Figure 108. Chain polymer associations in the crystal of **32** based on Au...Au and S...Au interactions between molecules **32a** and **32b**

Single crystal X-ray diffraction analysis revealed that **33** crystallize as a dimer (**Figure 109**). The coordination geometry around Ag(I) atoms is best described as distorted T-shape. In the molecule Ag...Ag interactions Ag(1)...Ag(2) of 3.0287(6) Å, [*cf.* $\sum r_{\text{vdw}}(\text{Ag}, \text{Ag})$ 3.4 Å] are present. In the structure the triflate counterion forms a moderately weak Ag...O intramolecular bonding [2.9978(48) and 3.0672(47) Å, *cf.* $\sum r_{\text{vdw}}(\text{Ag}, \text{O})$ 3.1 Å], see **Figure 109**.

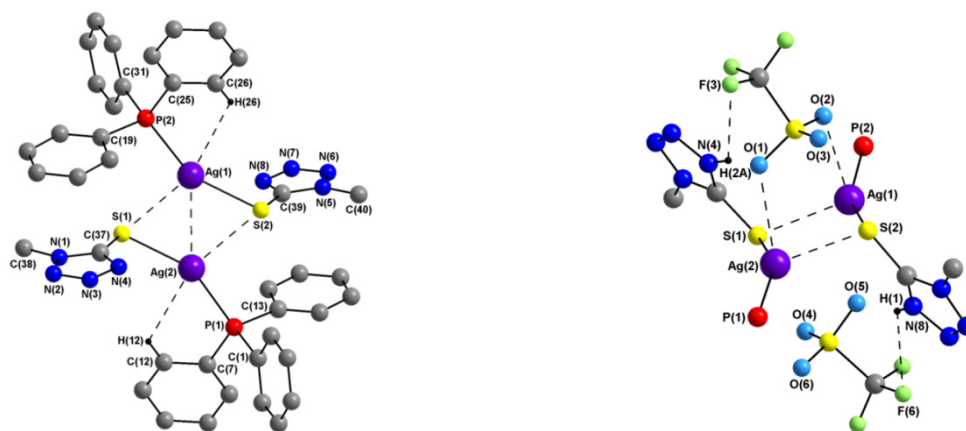


Figure 109. Structure of **33** showing the atom numbering scheme; Hydrogen atoms are omitted for clarity

A polymeric layer of dimmers is built through inter-dimer N-H \cdots F contacts H(40B) \cdots F(2') 2.5787(36) Å, *cf.* $\sum r_{vdw}(H,F)$ 3.05 Å], (**Figure 111**).

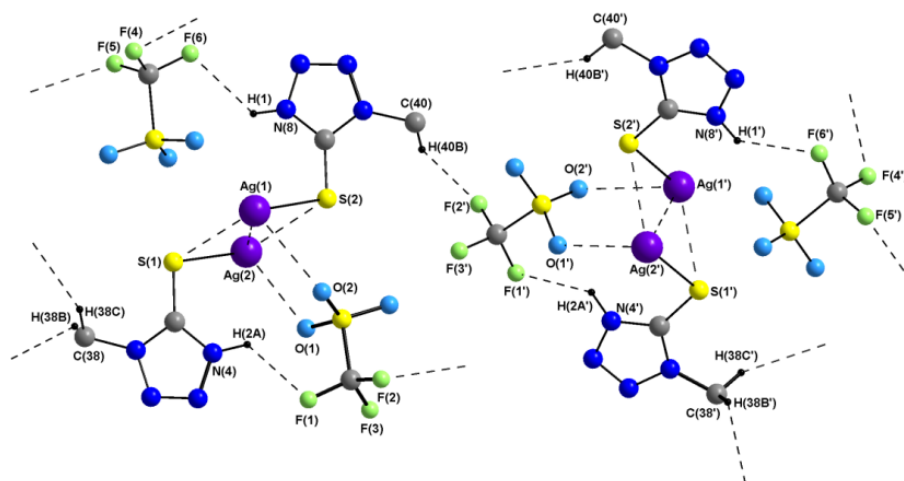


Figure 111. Chain polymer associations in the crystal of **33** based on N-H \cdots F and Ag \cdots O interactions.

3.4. CONCLUSIONS

6. In conclusion we have developed an efficient method of synthesizing metal sulfur tetrazole complexes. The crystal structures revealed their initial formulation suggested by IR, Raman and NMR analyses. However, a different structural framework was observed for $[(PPh_3)Ag(HSCN_4Me)]_2(OTf)_2$ (**33**), which crystallizes as a dimer. Intramolecular Au \cdots Au interactions were detected in $[(\mu-dppm)Au_2(SCN_4Me)_2]$ (**31**), while in $[(\mu-dppe)Au_2(SCN_4Me)_2]$ (**32**) intermolecular aurophilic bonding leads to the formation of a chain polymer. As indicated by Raman and confirmed by the crystallographic data, in gold (I) complexes $[(PPh_3)Au(SCN_4Me)]$ (**30**), $[(\mu-dppm)Au_2(SCN_4Me)_2]$ (**31**) and $[(\mu-dppe)Au_2(SCN_4Me)_2]$ (**32**) the coordination takes place also through the nitrogen atom. In $[(PPh_3)Ag(HSCN_4Me)]_2(OTf)_2$ (**33**) due to the presence of the thione form of the ligand, N in the tetrazole ring carries a proton and loses its ability to coordinate to Ag. The weak agostic interactions C-H \cdots M observed in the measured structures are in concordance with those mentioned in the literature. Nevertheless, they provide additional stability for the structures.

7. In summary the theoretical calculations on model of the complexes **30** and **32** are consistent to the geometries found by X-ray diffraction on single crystals, while in case of **33**, the theoretical calculations did not reproduce the geometry observed in the measured X-ray structure.

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