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Rezumat

Complecsi Organo Aur, Argint si Cupru

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Cuvinte cheie: liganzi azot/seleniu, liganzi azot/sulf, compusi coordinativi, aurofilicitate, interactiuni agostice, elucidarea structurii

Partea 1

Sinteza si reactivitatea compusilor carboran selenolati cu derivati de aur, argint si cupru

Partea 2

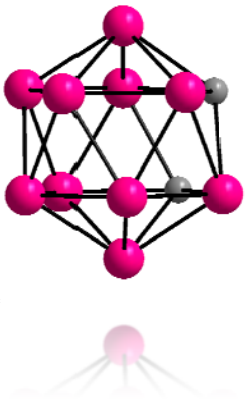
Sinteza si reactivitatea liganzilor de tip pincer NN'N si SeNSe cu derivati de aur, argint si cupru

Partea 3

Sinteza si reactivitatea liganzilor de tip tio tetrazole cu derivati de aur si argint

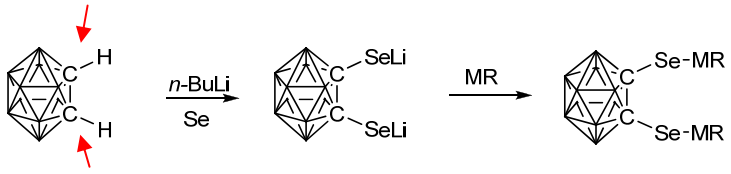
Partea 1

Sinteza si reactivitatea compusilor carboran selenolati cu derivati de aur, argint si cupru



1.2. OBIECTIVE

Principalul obiectivul a fost functionalizarea legaturii C-H din gruparea carboran folosind seleniu. Designul, sinteza si caracterizarea complecsilor carboran selenolati cu aur, argint si cupru au reprezentat obiectivele specifice. Pentru a realiza acest lucru au fost folosite diferite grupari functionale, (**Scheme 6**).



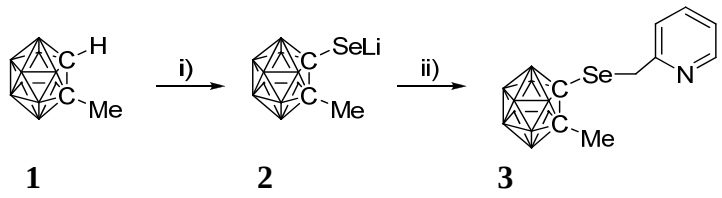
Scheme 6. Schema de functionalizare pentru compusii carboran selenolati, M=Ag, Au, Cu

1.3. REZULTATE SI DISCUTII

Au fost sintetizati noi liganzi care incorporeaza fragment NSe (piridina-seleniu) sau NSe_2 (piridina-diseleniu) in unitatea *closo* carboran.

1.3.1. Sinteza ligandului 1-Se carboran ce contine NSe si reactivitatea acestuia inspre argint

Reactia dintre [$C_2B_{10}H_{11}Me$)] (**1**) si *n*BuLi urmata de insertia seleniului conduce la intermediarul **2**, (**Schema 7**). In continuare aditia electrofilului 2-(bromometil)piridina permite formarea ligandului [($PyCH_2$)($SeC_2B_{10}H_{10}Me$)](**3**).



1 **2** **3**

Schema 7. Reactivi si conditii: i) dry Et_2O, *n*Buli (-78°C, 1h), Se (r.t., 2h); ii) [$PyCH_2Br$] (0°C, 2h), 55%

Prin difractie de raze X a fost determinata structura ligandului **3**, (**Figura 16**). In structura acestuia s-a observat prezenta unor interactiuni intermoleculare selenium hidrogen ce a condus la formarea unui lant polimeric, (**Figura 17)**.

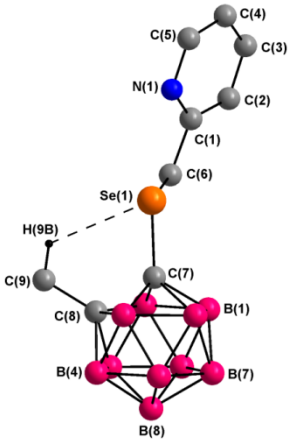


Figura 16. Structura moleculara a ligandului **3**

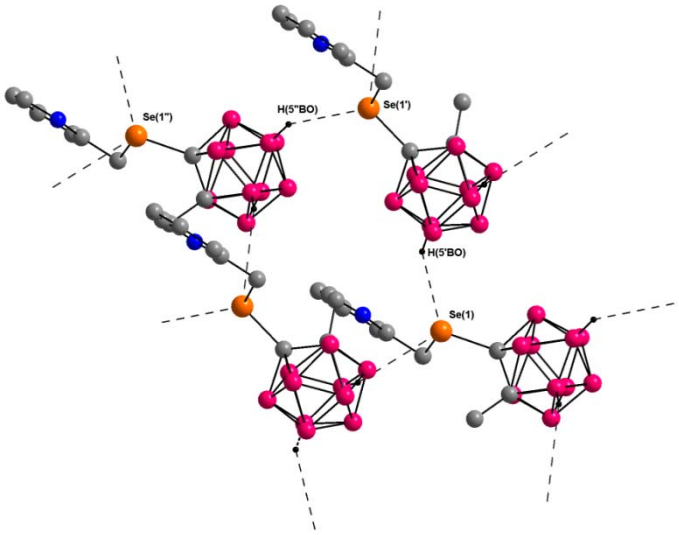
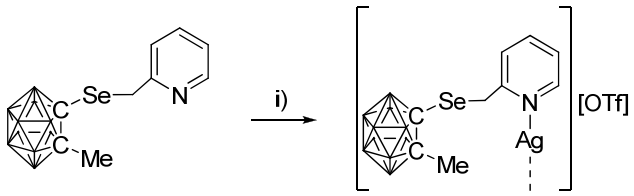


Figura 17. Lant polimeric in structura compusului **3** bazat pe interactiuni B-H···Se

In vederea realizarii obiectivelor propuse in domeniul chimiei coordinative a metalelor tranzitionale, ligandul **3** a fost reactionat cu [AgOTf], in urma sintezei compusul [Ag{($PyCH_2$)($SeC_2B_{10}H_{10}Me$)}](OTf) (**4**) a fost preparat, (**Schema 8**). Compusul **3** este implicat in procesul de coordinare prin intermediul azotului ca si atom donor. Structura compusului **4** este confirmata prin analize spectroscopice ^{1}H, ^{13}C, ^{19}F RMN si IR. In **Schema 8** linia punctata reprezinta o posibila formare de dimeri si polimeri.



3 **4**

Schema 8. Reactivi si conditii: i) [AgOTf], Et_2O, 1h, r.t., 78%

In **Figura 18** este prezentat spectrul ^{13}C RMN al compusului **4**.

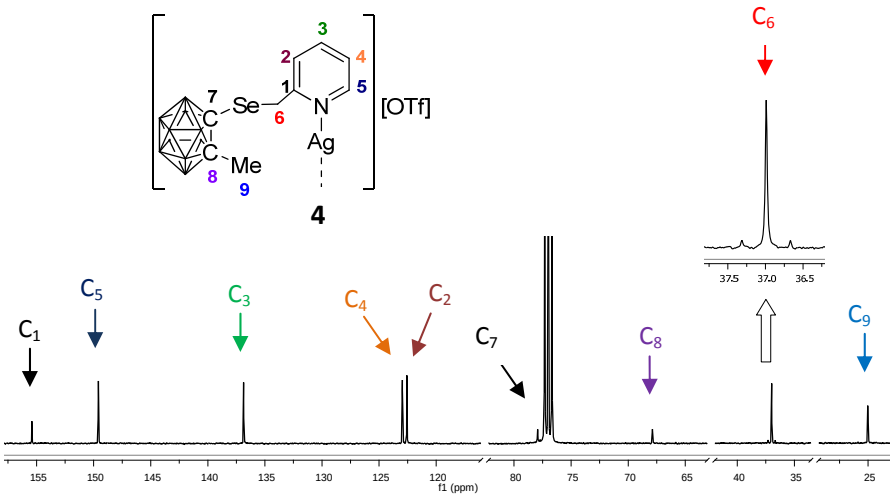
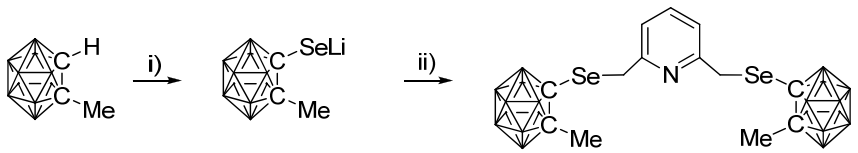


Figura 18. Detaliu din spectrul ^{13}C RMN ($CDCl_3$, 101 MHz) al compusului **4**

O inspectie detaliata a spectrului IR al compusului **4** a sugerat faptul ca gruparea triflat este de natura ionica. A doua observatie este in legatura cu banda de vibratie Ag-N ce a fost detectata la 396 cm^{-1}.

1.3.2. Sinteza ligandului 1-Se carboran ce contine NSe_2 si reactivitatea acestuia inspre argint si cupru

Sinteza ligandului [$(Py(CH_2)_2(SeC_2B_{10}H_{10}Me)_2$] (**5**) a fost realizata conform metodei descrise mai jos. Prin reactia dintre [$C_2B_{10}H_{11}Me$)] (**1**) in Et_2O cu *n*BuLi, urmata de aditia seleniului si apoi a 2,6-bis(bromometil)piridina s-a sintetizat compusul **5**, (**Schema 9**).



1 **2** **5**

Schema 9. Reactivi si conditii: i) dry Et_2O, *n*Buli (-78°C, 1h), Se (r.t., 2h); ii) [$Py(CH_2Br)_2$] (0°C, 2h), 45%

Structura compusului **5** a fost confirmata prin difractie de raze X, (**Figure 24**).

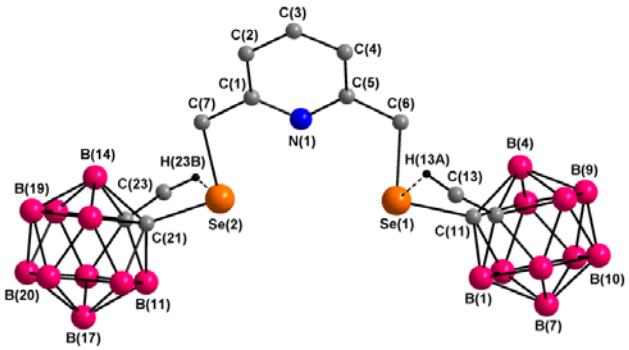


Figure 24. Structura moleculara a ligandului **5**

In cristalul compusului **5** prezenta interactiunilor intermoleculare seleniu hidrogen conduce la formarea unui lant polimeric, [*cf*. Σr_{vdw}(Se,H) 3.45 Å], (**Figura 25**).

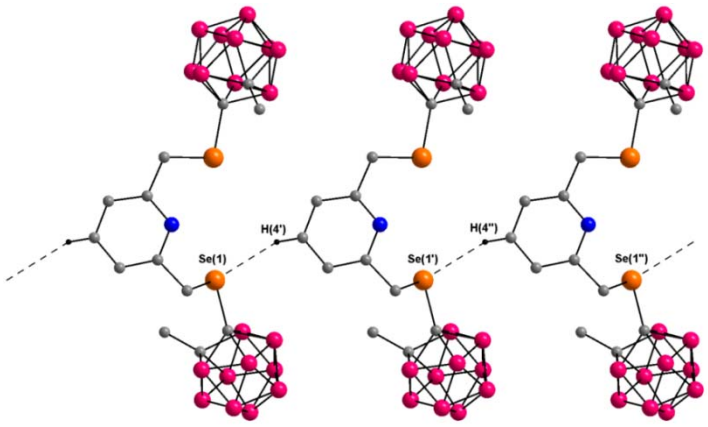
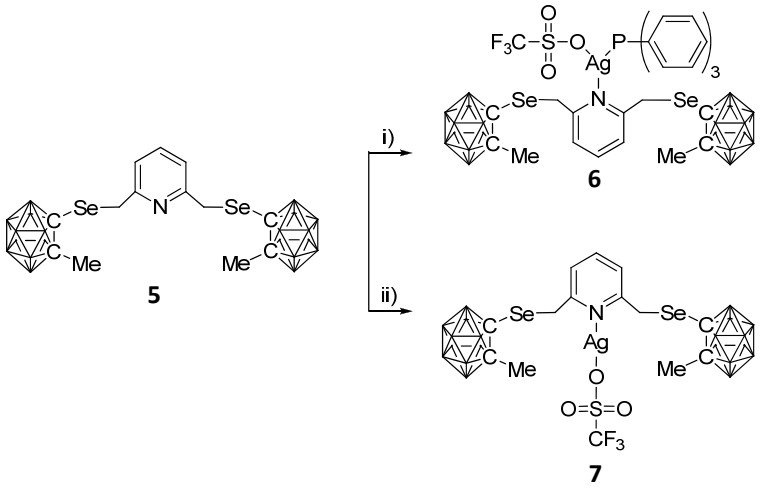


Figura 25. Vedere de-a lungul axei *b* a lantului polimeric format in cristalul compusului **5**

Studiul complecsilor ce contin gruparea triflat a fost extins si in acest scop ligandul **5** a fost reactionat cu [(PPh_3)Ag(OTf)] si [AgOTf], rezultand compusii [(PPh_3)(OTf)Ag{($Py(CH_2)_2(SeC_2B_{10}H_{10}Me)_2$}] (**6**), [(OTf)Ag{($Py(CH_2)_2(SeC_2B_{10}H_{10}Me)_2$}] (**7**), (**Schema 10**).



Schema 10. Reactivi si conditii: i) [Ag(PPh$_3$)(OTf)], CH_2Cl_2, 1h, r.t., 89%; ii) [AgOTf], CH_2Cl_2, 2h, r.t., 54%

Comparand spectrele ^{1}H RMN ale complecsilor **6** si **7** cu cel al ligandului **5** s-a observat ca in urma coordinarii in **6** si **7** rezonantele sunt deplasate spre stanga, (**Figura 26**).

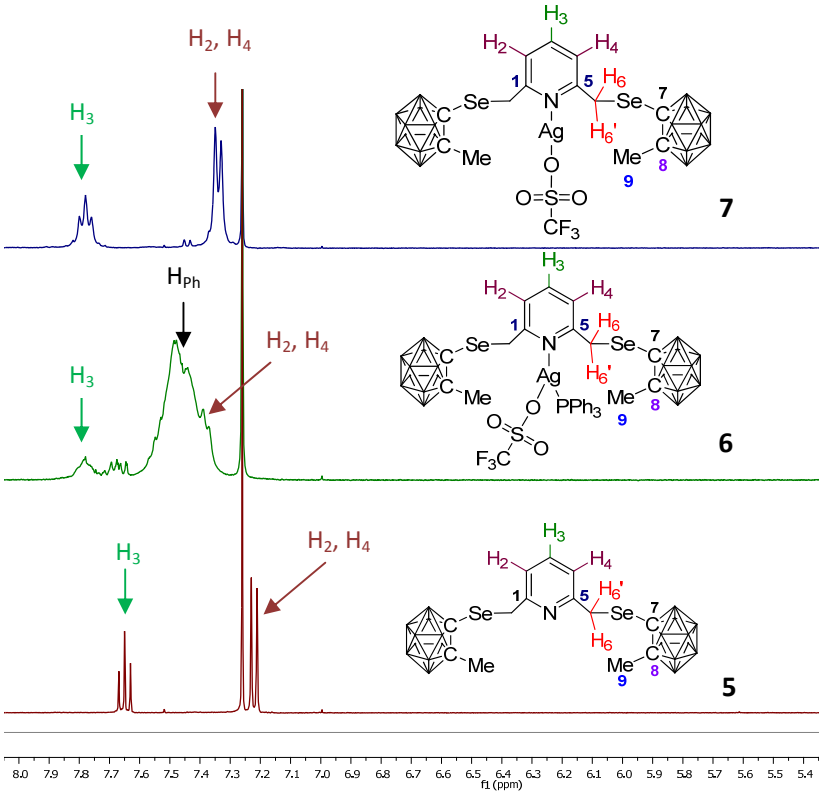
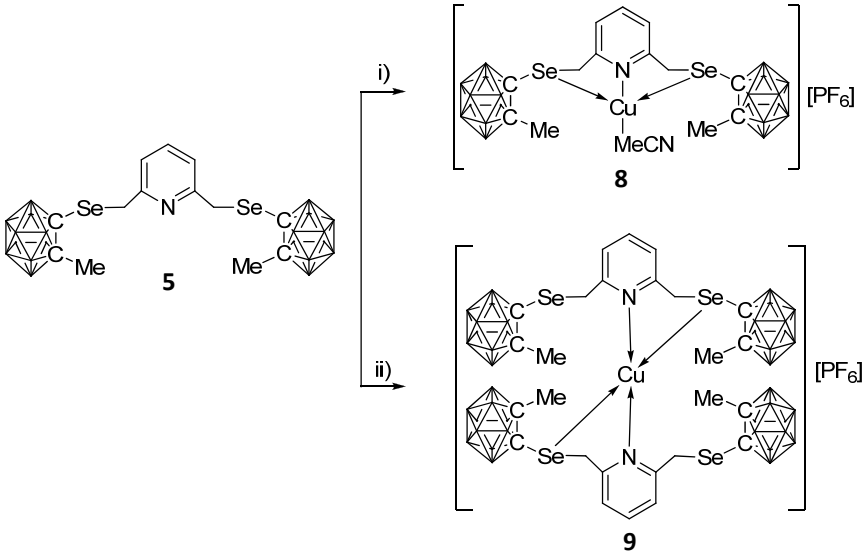


Figura 26. Spectre ^{1}H RMN suprapuse ($CDCl_3$, 400 MHz) pentru compusii **5**, **6** si **7**; Detaliu din zona aromatica

Utilizand analize spectroscopice IR a fost stabilit faptul ca in urma coordinarii gruparea triflat a ramas legata covalent de argint. Un studiu comparativ al spectrelor IR al compusilor **6** si **7** rezulta in observarea benzii de vibratie N-Ag la 422 cm^{-1} in **6** respectiv 392 cm^{-1} in **7.**

In continuare urmatoarele reactii au implicat folosirea de materii prime ce contin cupru, in acest scop reactia dintre **5** si $[Cu(MeCN)_4]PF_6$ in raport molar de 1:1 respectiv 2:1 conduce la compusii $[(MeCN)Cu\{(Py(CH_2)_2(SeC_2B_{10}H_{10}Me)_2\}](PF_6)$ (**8**) si $[Cu\{(Py(CH_2)_2(SeC_2B_{10}H_{10}Me)_2\}_2](PF_6)$ (**9**), (**Schema 12)**.



Schema 12. Reactivi si conditii: i) $[Cu(MeCN)_4]PF_6$, CH_2Cl_2, 2h, r.t., 85%; ii) ½ $[Cu(MeCN)_4]PF_6$, CH_2Cl_2, 2h, r.t., 77%

Spectrele ^1H RMN ale compusilor **8** si **9** prezinta in zona aromatic acelasi patern RMN ca si ligandul **5**, cu observatia ca rezonantele sunt deplasate spre stanga in **8** si **9** datorita procesului de coordinare. Cu toate acestea zona alifatica prezinta interes, semnalul corespunzator protonilor din gruparea MeCN apare la δ 2.21 ppm in **8** (**Figura 32**), iar in **9** acest semnal nu apare.

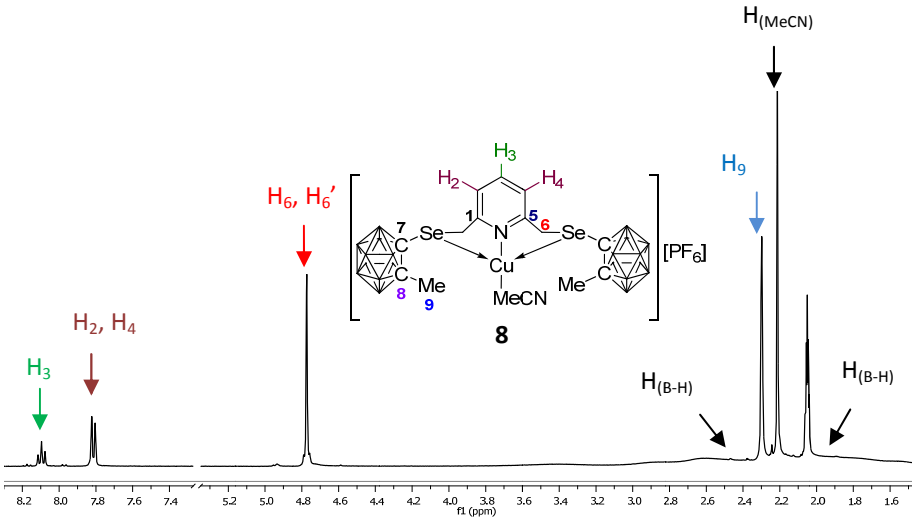


Figura 32. Spectrul ^{1}H RMN (acetona-d_6, 400 MHz) al compusului **8**

Pentru o caracterizare completa a compusilor **8,** (**Figura 35)** si **9** analize prin spectrometrie MALDI(+) MS au fost realizate, rezultatele obtinute confirmand formarea complecsilor.

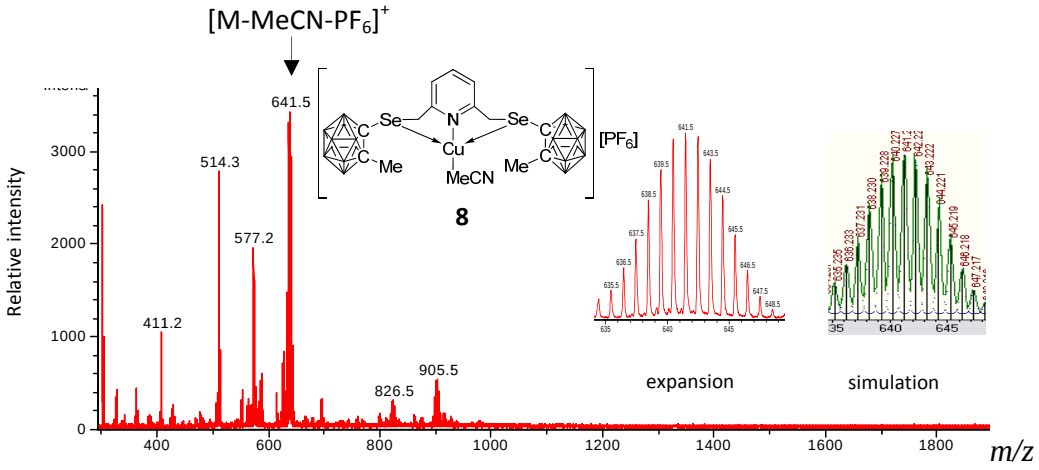
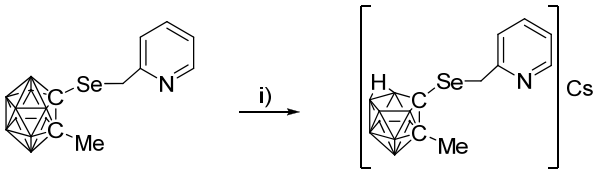


Figura 35. Spectrul MALDI(+) MS al complexului **8**, incluzand o simularea (figura din dreapta) a paternului de fragmentare izotopic

1.3.3. Sinteza compusilor *nido* carborani

Avand aceste rezultate, am incercat in continuare sa eliminam o grupare B-H din fragmentul carboran din liganzii **3** si **5**. Pentru a realiza acest lucru **3** si **5** au fost supusi unei reactii de deboronare prin aditia CsF in etanol, in care au fost eliminate una sau doua grupari B-H din speciile *closo*, fapt ce a condus la formarea speciilor *nido* $[(Py(CH_2)(SeC_2B_9H_9Me)]^-Cs^+$ (**10**), (**Schema 13**) si $[(Py(CH_2)_2(SeC_2B_9H_9Me)_2]^-Cs^+$ (**11**), (**Schema 14**).



3 **10**

Schema 13. Reactivi si conditii: i) CsF, EtOH, 25h reflux, 97%

In **Figura 38** este ilustrat spectrul ^{1}H RMN al compusului **10**.

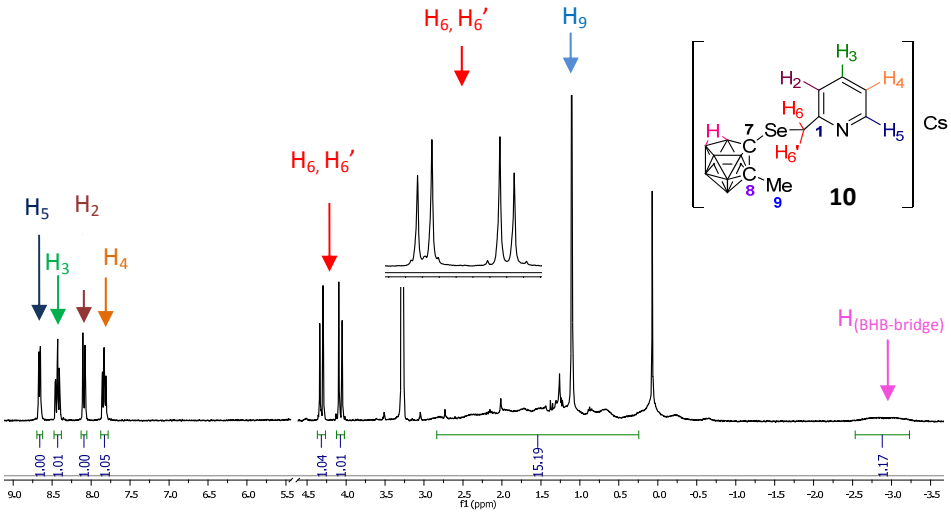


Figura 38. Spectrul ^{1}H NMR ($CDCl_3$, 300 MHz) al compusului **10**

In spectrul de ES(-) MS al compusului **10** peak-ul corespunzator fragmentului [M-Cs]$^-$ a fost detectat la *m/z* 318, (**Figura 40**).

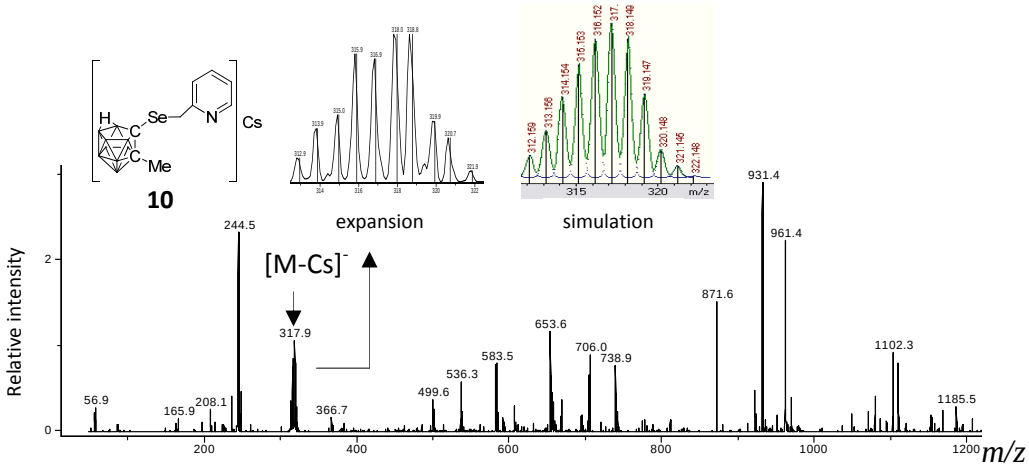
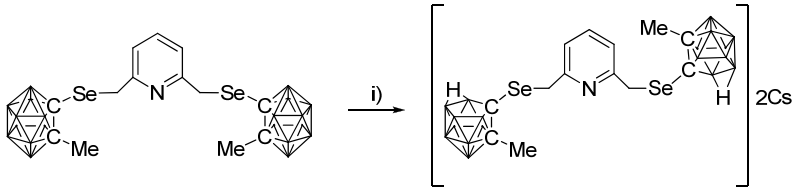


Figura 40. ES(-) MS spectrum of **10**, incluzand o simulare (figura din dreapta) a paternului isotopic de fragmentare

Degradarea partiala a ligandului **5** a fost facuta dizolvand compusul *closo* carboran **5** intr-o solutie de CsF in etanol, in acest caz au fost eliminate doua grupari B-H formandu-se *nido* derivatul $[(Py(CH_2)_2(SeC_2B_9H_9Me)_2]^-Cs^+$ (**11**), vezi **Schema 14**.



5 **11**

Schema 14. Reactivi si conditii: i) CsF, EtOH, 25h reflux, 95%

Spectrul ^{1}H RMN a confirmat faptul ca procesul de degradarea partiala a condus la specia *nido* **11** prin aparitia semnalului corespunzator protonului din gruparea B-H-B ce a fost observat la valoarea δ -2.52 ppm ca si un semnal larg, (**Figura 41**).

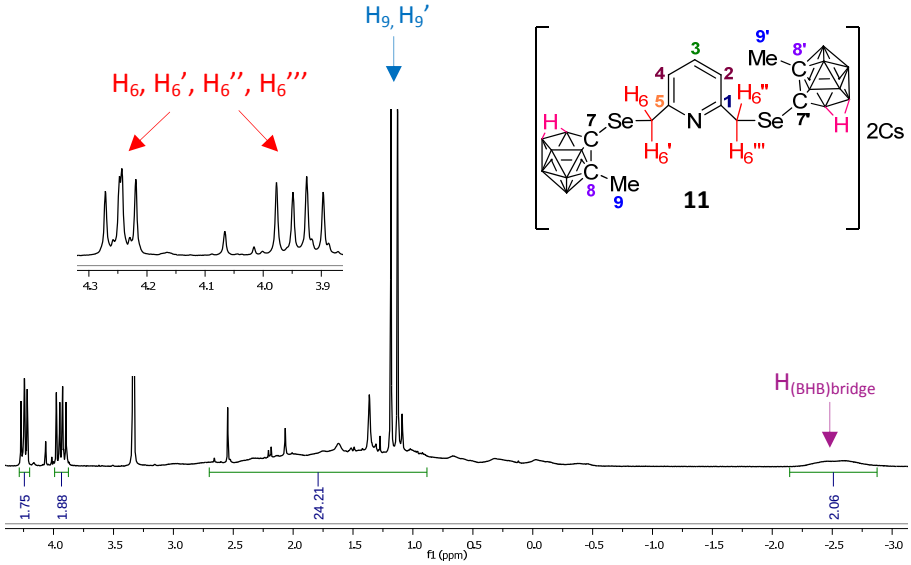


Figure 41. Detaliu din zona alifatica a spectrului ^{1}H RMN (metanol-D_4, 400 MHz) al compusului **11**

In continuare spectrul ES(-) MS al speciei *nido* **11** indica prezenta fragmentului anionic $[M-2Cs+H]^-$ ce s-a format prin pierderea celor doi atomi de cesiu si a fost detectat la valoare *m/z* 556, **Figura 43**.

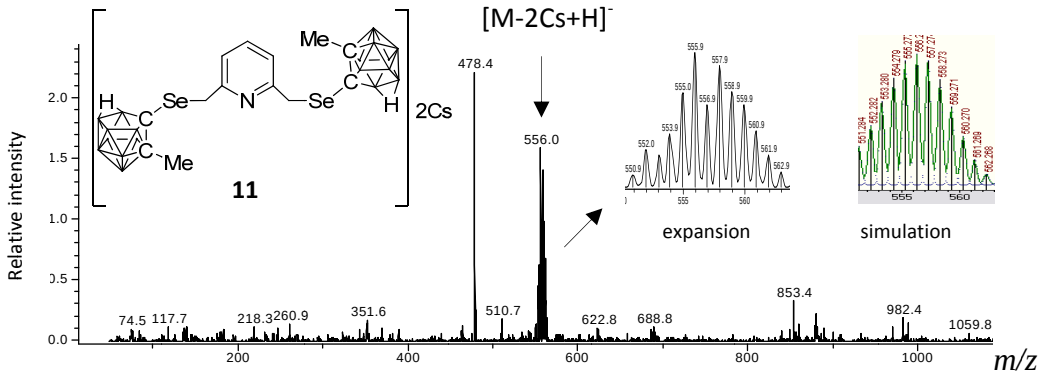
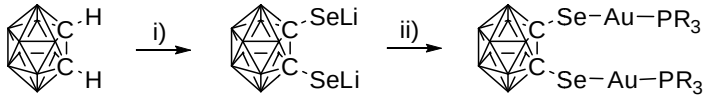


Figura 43. Spectrul ES(-) MS al compusului **11,** incluzand si o simulare (figura din dreapta) a paternului de fragmentare izotopic

1.3.4. Sinteza si reactivitatea 1,2-Se carboran cu gold

Pornind de la [1,2-*closo*-$C_2B_{10}H_{12}$] (**12**) am activat gruparea C-H folosind *n*BuLi si prin aditia seleniului s-a format intermediarul litiat **13**. Urmatoarea transformarea implica folosirea in *situ* a derivatilor de aur [$(PR_3)AuCl$] ce conduce la complecsii aur selenolati [$(PR_3)_2Au_2(Se_2C_2B_{10}H_{10})$], [$PR_3$= PPh_3 (**14**), PR_3= PPh_2Me (**15**)], vezi **Schema 15**.



12 **13** **14 (R_3=Ph_3)** **15 (R_3=Ph_2Me)**

Schema 15. Reactivi si conditii: i) *n*BuLi, Et_2O (0°C, 1h), Se(r.t., 3h); ii) [$(PR_3)AuCl$], Et_2O, 3h, 10°C, 55% (**14**), 50% (**15**)

Pentru a confirma structura, cristale potrivite pentru analize de difractie de raze X au fost obtinute prin evaporarea unei solutii de **15** in metanol, (**Figura 48**). In cristalul complexul **15** interactiuni intramoleculare aur-aur au fost stabilite, 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]. Geometria de coordinare in jurul atomului Au(1) este liniara cu unghiul Se(1)-Au(1)-P(1) of 170.74(7)^o si in jurul atomului Au(2) planar distorsionata cu unghiul Se(2)-Au(2)-P(2) 154.57(8)^o.

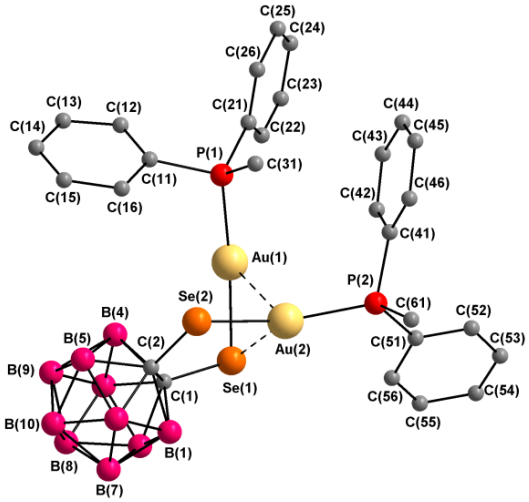


Figura 48. Structura moleculara a complexului de aur **15**, atomii de hidrogen au fost omisi pentru claritate

Geometria de coordinare din jurul atomului Au(2) poate fii explicata prin interactiunea dintre Se(1) si Au(2) de 3.0266(13) Å, [$\sum r_{cov}$ (Se,Au) 2.51 Å, $\sum r_{vdW}$ (Se,Au) 3.7 Å] ce permite ca doua unitati de [$(PPh_2Me)_2Au_2(Se_2C_2B_{10}H_{10})$] sa fomeze un dimer, (**Figura 49**).

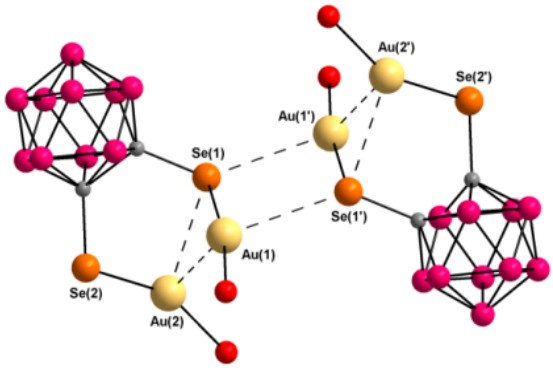


Figura 49. Unitate dimerica in cristalul complexului **15**, gruparile fenil si metil, dar si atomii de hidrogen au fost omisi pentru claritate

1.4. CONCLUZII

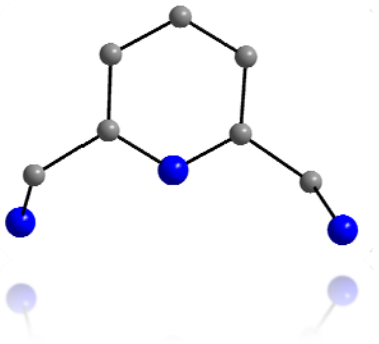
1. Liganzii carboran organoselenolati [($PyCH_2$)($SeC_2B_{10}H_{10}Me$)] (**3**) si [($Py(CH_2)_2$($SeC_2B_{10}H_{10}Me)_2$] (**5**) au fost preparati prin procedeul de activare a legaturii C-H a compusului *closo* [$C_2B_{10}H_{11}Me$)] (**1**) folosind *n*BuLi (1:1 raport molar) in dietil eter urmat de aditia seleniului sau a 2-(bromometil)piridina respectiv 2,6-bis(bromometil)piridina. Structura liganzilor a fost confirmata prin analize de difractie de raze X, spectroscopie IR si RMN dar si spectrometrie de masa. A fost deasemenea investigata si capacitatea de coordinare a acestor liganzi cu derivati de argint si aur. Si in acest caz datele analitice confirma structura complecsilor sintetizati, ce pot fii ionici sau neutri. Cand ligandul **3** este reactionat cu triflat de argint in raport molar de 1:1 complexul preparat [Ag{($PyCH_2$)($SeC_2B_{10}H_{10}Me$)}](OTf) (**4**) este de natura ionica. In cazul ligandului **5**, reactiile de coordinare cu triflat de argint si triflat de argint trifenilfosfina dau [(PPh_3)(OTf)Ag{($Py(CH_2)_2$($SeC_2B_{10}H_{10}Me)_2$}] (**6**) si [(OTf)Ag{($Py(CH_2)_2$($SeC_2B_{10}H_{10}Me)_2$}] (**7**), complecsi fiind neutrii.

2. Compusii *closo* carboranil NSe respectiv NSe_2, descrisi mai sus au capacitatea sa devina liganzi anionici pastrand fragmentul initial de coordinare NSe sau NSe_2. Prin reactia de degradare partiala a speciilor *closo* **3** si **5,** se prepara speciile *nido* [($Py(CH_2)$($SeC_2B_9H_9Me$)]$^-Cs^+$ (**10**) respectiv [($Py(CH_2)_2$($SeC_2B_9H_9Me)_2$]$^-Cs^+$ (**11**).

3. Complecsii de aur [($PPh_3)_2Au_2(Se_2C_2B_{10}H_{10}$)] (**14**) si [($PPh_2Me)_2Au_2(Se_2C_2B_{10}H_{10}$)] (**15**) au fost preparati prin activarea legaturii C-H din [1,2-*closo*-$C_2B_{10}H_{12}$] (**12**), procedeu ce implica reactia cu *n*BuLi (1:1 raport molar) in dietil eter urmat de insertia seleniului. Aditia in situ a [(PPh_3)AuCl] sau [(PPh_2Me)AuCl] a permis sintetizarea complecsilor **14** si **15**. Structura moleculara a compusului **15** a fost determinata prin difractie de raze X si in cristalul acestuia prezenta interactiunilor aurofilice a fost observata. Studiul realizat in partea 1 demonstreaza numeroasele utilizari ale compusilor carborani si metalcarborani ca si componenti in chimia organometalica.

Partea 2

Sinteza si reactivitatea liganzilor de tip pincer NN'N si SeNSe cu derivati de aur, argint si cupru



2.2. OBIECTIVE

Fiind cunoscuta importanta derivatilor de tip pincer in chimia organometalica obiectivul nostru a fost sinteza unor liganzi pincer NN'N and SeNSe si de a studia reactivitatea acestora inspre diferite metale.

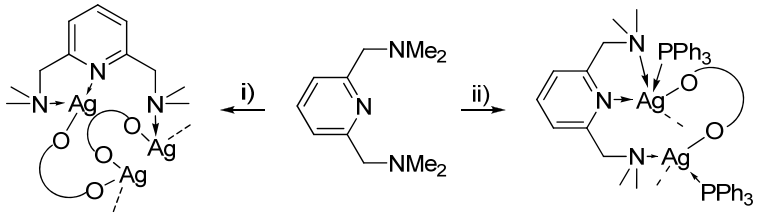
Pincerii NN'N si SeNSe pot fii reactionati cu derivati de aur, argit si cupru (ex. $[HAuCl_4]$, $[(PPh_3)Ag(OTf)]$ si $[Cu(MeCN)_4]PF_6$) in diferite rapoarte molare.

Reactivitatea si chimia coordinativa a pincerilor NN'N and SeNSe, a fost principalul obiectiv propus. Investigarea in detaliu cat si intelegerea asemanarilor intre complecsii cu liganzi pincer a fost al doilea obiectiv propus.

2.3. REZULTATE SI DISCUTII

2.3.1. Sinteza si reactivitatea ligandului de tip pincer NN'N cu derivati de argint

Prin reactia dintre ligandul NN'N (**16**) cu [CF_3COOAg] si [$(PPh_3)(AgOTf)$] in raport molar de 1:1 respectiv 1:2 au fost sintetizati complecsii {$(CF_3COOAg)_n[(Me_2NCH_2)_2Py]_n$} (**17**) si [$(PPh_3)(OTf)Ag_2(Me_2NCH_2)_2Py$] (**18**), (**Schema 16**).



17 **16** **18**

Schema 16. Reactivi si conditii: i) [CF_3COOAg], CH_2Cl_2, 1h, r.t., ii) 2[$(PPh_3)Ag(OTf)$], CH_2Cl_2, 1h, r.t., 92%

Comparand spectrele ^{1}H RMN ale complecsilor **17** si **18** cu cel al ligandului NN'N **16** se observa faptul ca procesul de coordinare a avut loc, vezi **Figura 57**.

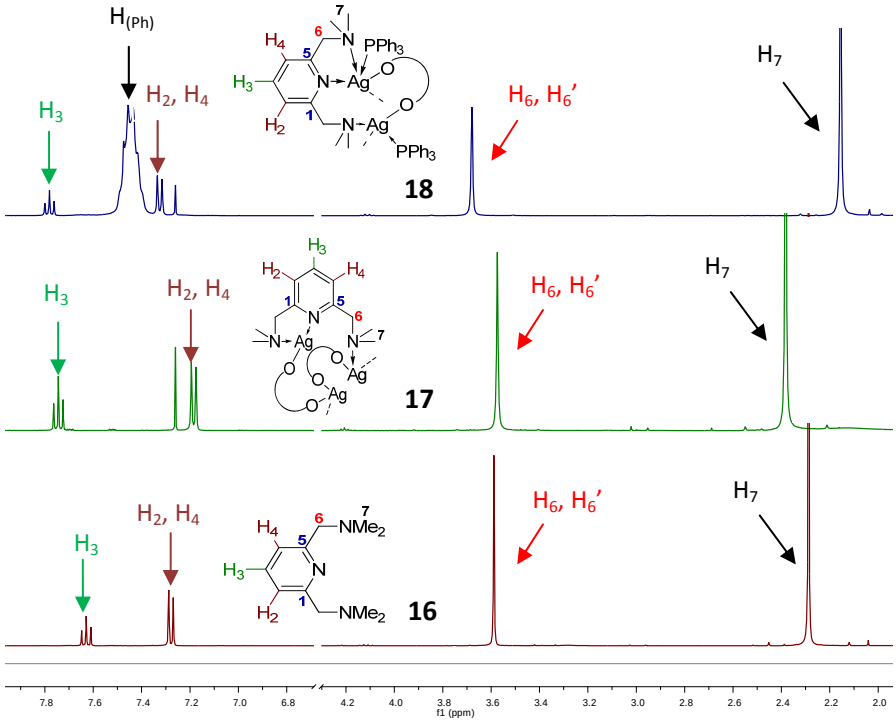


Figura 57. Detaliu din spectrele suprapuse ^{1}H RMN ($CDCl_3$, 400 MHz) ale **16**, **17** si **18**

Prin studii de difractie de raze X s-a observant faptul ca **17** cristalizeaza ca si polimer, (**Figura 67** si **Figura 68**), prezenta interactiunilor argentofilice fiind deasemenea observata, Ag(1)···Ag(2) 3.075(5) Å si Ag(3)···Ag(2) 3.008(4) Å, [*cf*. Σr_{vdw}(Ag,Ag) 3.4 Å].

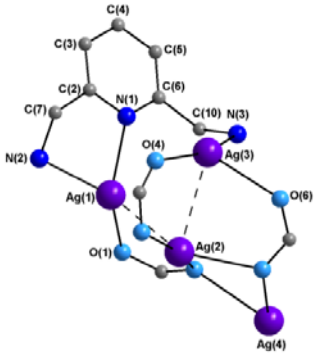


Figura 67. Unitate monomerica in cristalul compusului **17**

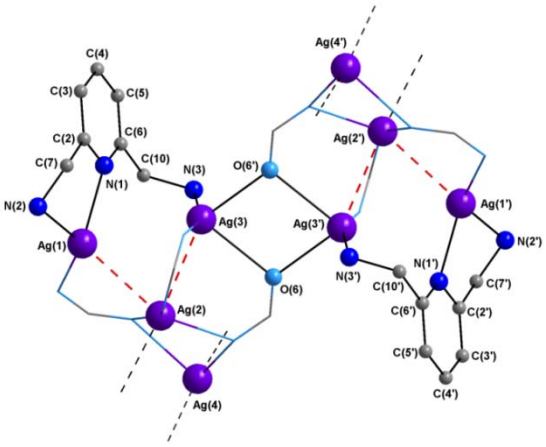
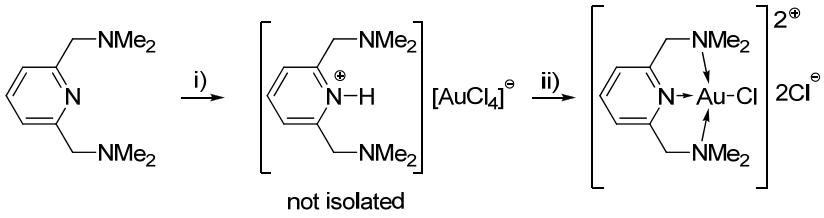


Figura 68. Parte a lantului polimeric prezent in cristalul compusului **17**

2.3.2. Sinteza complexului pincer NN'N aur

Complexul de aur(III) [ClAu(NN'N)]Cl_2 (**20**) a fost preparat prin reactia directa dintre H[$AuCl_4$]·3H_2O si NN'N (**16**). In conditii de reactie blande se formeaza ca si intermediar o sare a ligandului protonat [(NN'HN)][$AuCl_4$] (**19**), vezi **Schema 23**.

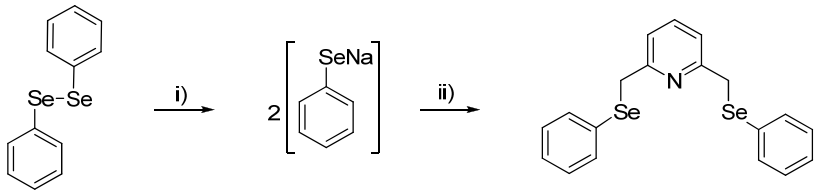


16 **19** **20**

Schema 23. Reactivi si conditii: i) $H[AuCl_4]\cdot 3H_2O$, Et_2O, 30', r.t.; ii) $NaHCO_3$, THF, 24h, r.t., 87%

2.3.3. Sinteza ligandului SeNSe si reactivitatea acestui inspre derivati de aur

Prin reactia de reducere a Ph_2Se_2 **21** cu $NaBH_4$ se formeaza intermediarul **22**, aditia in continuare a 2,6-bis(bromometil)piridina conduce la compusului $[Py(CH_2)_2(SePh)_2]$ (**23**), vezi **Schema 24**.



21 **22** **23**

Schema 24. Reactivi si conditii: i) $NaBH_4$, EtOH, 20', r.t.; ii) $[Py(CH_2Br)_2]$, r.t., 1h, 95%

Structura moleculara a compusului **23** a fost determinata prin difractie de raze X, vezi **Figura 76**.

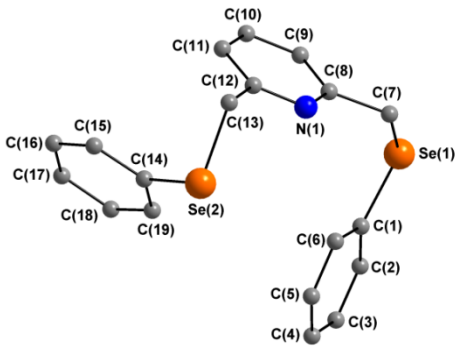


Figura 76. Structura moleculara a compusului **23**

In cristalul compusului **23** au fost stabilite interactiuni C-H···Se intra- si intermoleculare, **Figura 77**, intre atomii de hidrogen din gruparea metal si centrii de selenium, care conduc la formarea unui lant polimeric, [*cf*. Σr_{vdw}(Se,H) 3.45 Å].

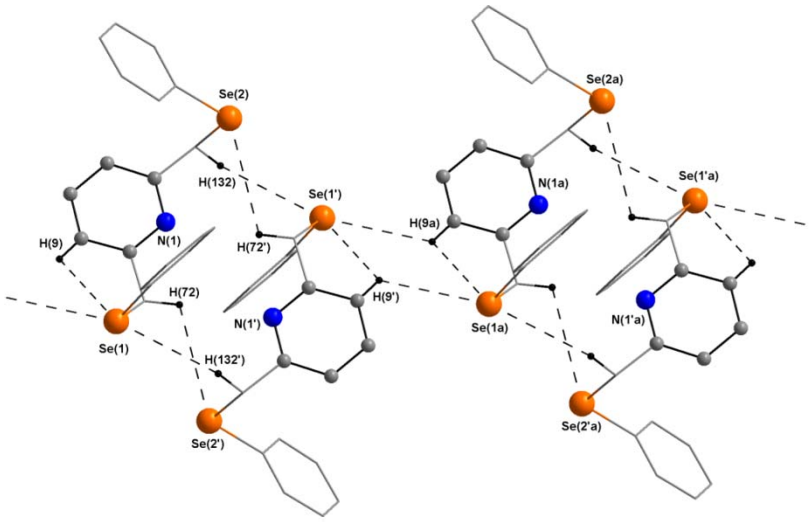
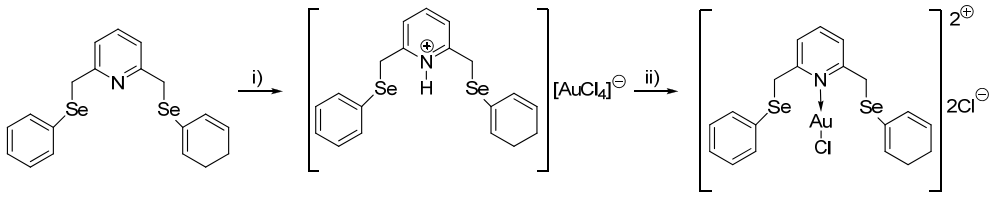


Figura 77. Lant plimeric format in cristalul compusului **23** bazat pe interactiuni C-H···Se intra- si intermoleculare

Complexul de aur **25** a fost sintetizat in condiitii de reactie similare ca si pentru compusul **20**, vezi **Schema 25**.

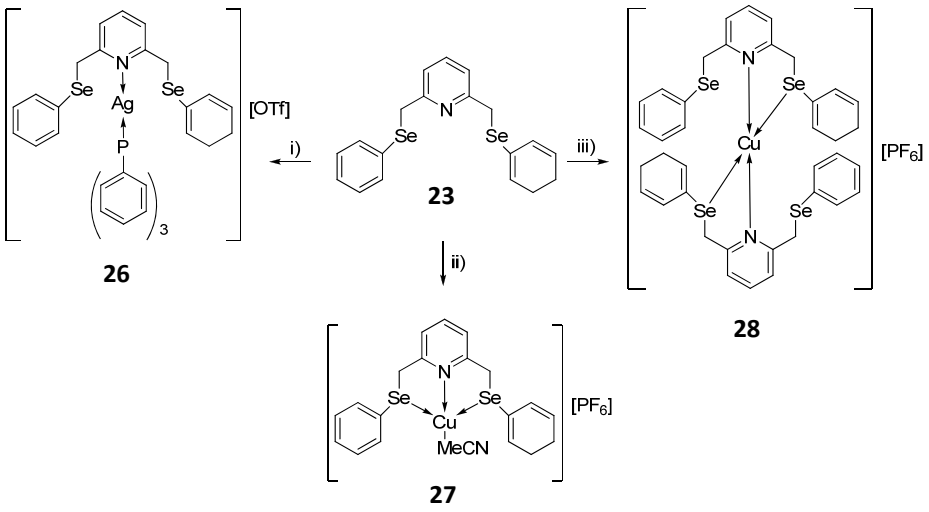


23 **24** **25**

Schema 25. Reactivi si conditii: i) $H[AuCl_4]\cdot 3H_2O$, Et_2O, 30', r.t.; ii) $NaHCO_3$, THF, 24h, r.t.

2.3.4. Sinteza complecsilor de argint si cupru ai ligandului pincer SeNSe

Complecsii $[(PPh_3)Ag\{Py(CH_2)_2(SePh)_2\}](OTf)$ (**26**), $[(MeCN)Cu\{Py(CH_2)_2(SePh)_2\}](PF_6)$ (**27**) si $[Cu\{Py(CH_2)_2(SePh)_2\}_2](PF_6)$ (**28**) au fost sintetizati prin reactia dintre **23** si $[(PPh_3)Ag(OTf)]$ sau $[Cu(MeCN)_4]PF_6$ in raport molar de 1:1 pentru **26** sau in 1:1 si 2:1 in cazul complecsilor **27** si **28** (**Schema 26**). O comparatie a spectrelor ^{1}H RMN ale compusilor **26**, **27** si **28** este prezentata in **Figura 79**.



Schema 26. Reactivi si conditii: i) $[Ag(OTf)(PPh_3)]$, dry CH_2Cl_2, 1h, r.t., 82%; ii) $[Cu(MeCN)_4]PF_6$, dry CH_2Cl_2, 3h, r.t., 87%; iii) ½ $[Cu(MeCN)_4]PF_6$, dry CH_2Cl_2, 3h, r.t., 92%

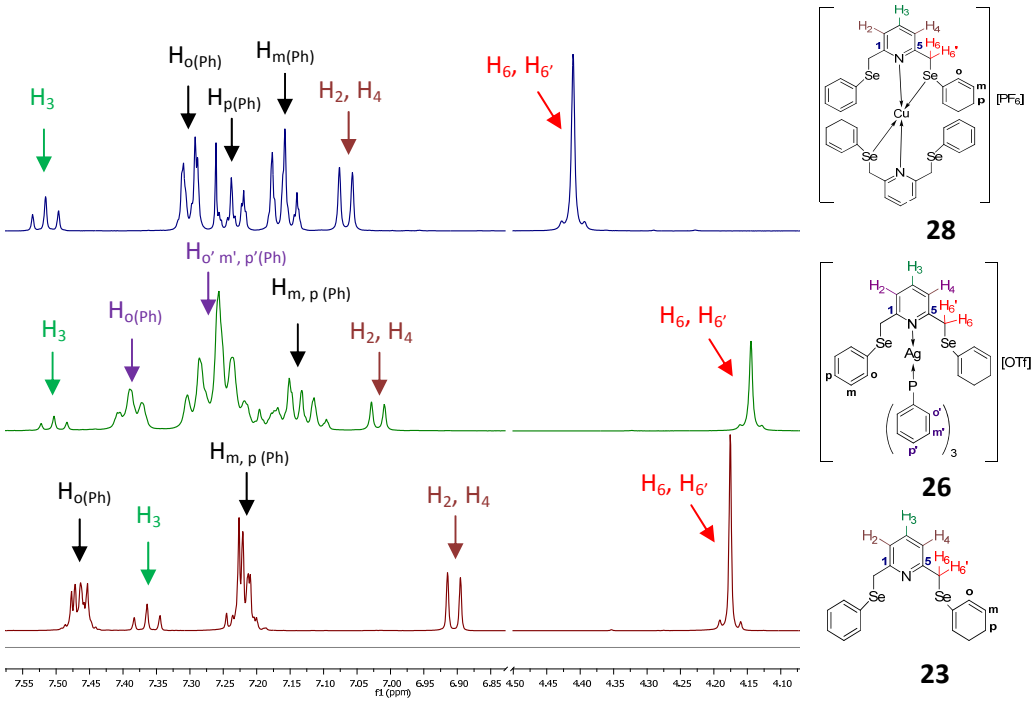


Figura 79. Detaliu din spectrele ^1H RMN suprapuse ($CDCl_3$, 400 MHz) ale compusilor **23, 26** si **28**

Spectrometria de masa a fost folosita pentru a analiza complecsii **26**, **27** si **28**, spectrul de masa ES(+) MS al complexului **26** fiind caracterizat prin aparitia peak-ului molecular la valoarea *m/z* 787.7, (**Figura 86**).

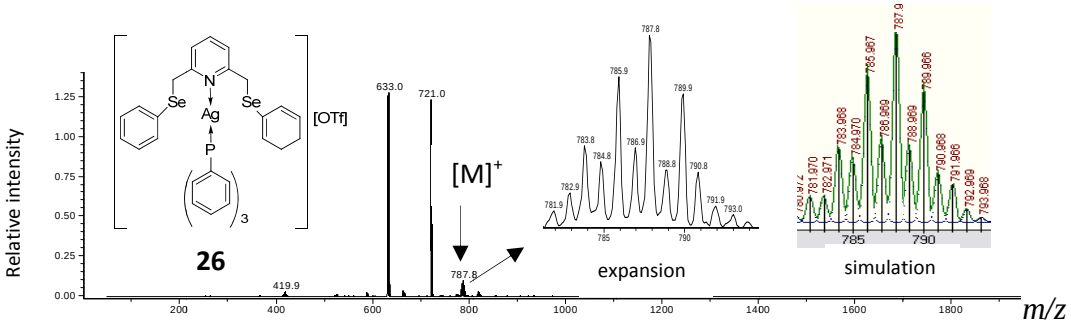


Figura 86. Spectrul de masa ES(+) MS al complexului **26**, incluzand o simulare (figura din dreapta) a paternului izotopic

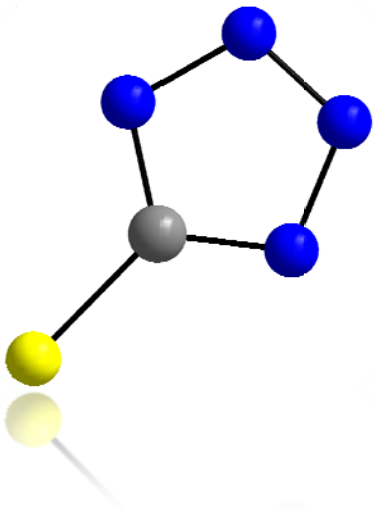
2.4. CONCLUZII

4. Liganzii de tip pincer NN'N si SeNSe au fost preparati. Un studiu detaliat in legatura cu posibilitatile de coordinare ale NN'N si SeNSe a fost realizat. Prin reactiile de complexare dintre ligandul tidentat NN'N [2,6-(Me_2NCH_2)Py] (**16**) si trifluoroacetat de argint respectiv triflat de argint trifenilfosfina au fost sintetizati compusii {$(CF_3COOAg)_n[(Me_2NCH_2)_2Py]_n$} (**17**) si [($PPh_3$)(OTf)$Ag_2(Me_2NCH_2)_2$Py] (**18**). In cazul compusului **17**, studiile de difractie de raze X au aratat o structura polimerica, iar pentru **18** analizele RMN, IR si spectrometria de masa indica un compus neutru. Cand NN'N **16** este reactionat cu H[$AuCl_4$] un complex ionic este format [ClAu(NN'N)]Cl_2 (**20**) in care atomul de aur este coordinat prin setul complet de atomi donori din ligandul NN'N.

5. Ligandul selenolat de tip pincer SeNSe [$Py(CH_2)_2(SePh)_2$] (**23**) a fost preparat prin ruperea legaturii seleniu seleniu din difenil diseleniura. Complecsii metalici [(PPh_3)Ag{$Py(CH_2)_2(SePh)_2$}](OTf) (**26**) respectiv [(MeCN)Cu{$Py(CH_2)_2(SePh)_2$}](PF_6) (**27**) si [Cu{$Py(CH_2)_2(SePh)_2$}$_2$](PF_6) (**28**) au fost sintetizati reactioand SeNSe **23** cu [(PPh_3)Ag(OTf)] si [Cu$(MeCN)_4$]PF_6. Analizele indica faptul ca, compusul de argint **26** este neutru, iar cei de cupru, **27** si **28** sunt de natura ionica.

Partea 3

Sinteza si reactivitatea liganzilor de tip tio tetrazol cu derivati de aur si argint



3.2. OBIECTIVE

Posibilitatea incorporari derivatilor metalelor pretioase intr-un fragment organic fie prin formarea unei legaturi covalente S-M sau fie printr-o legatura coordinativa S→M nu implica o strategie de sinteza bine pusa la punct, cu toate aceastea este o cale de sinteza foarte des utilizata. Reactivitatea liganzilor tio tetrazol este strans legata de efectele tautomerice, aceasta trasatura confera tetrazolilor denumirea de liganzi versatili in chimia coordinativa datorita modalitatilor diferite de coordinare ce pot aparea. Reactivitatea tio tetrazolilor fata de aur si argint nu a fost investigata in detaliu si din acest motiv in aceasta parte a tezei un studiu aprofundat in acest domeniu este prezentat. Pentru o mai buna intelegere a comportamentului in solutie cat si in stare solida a acestor tip de compusi a fost realizat si un studiu comparativ cu datele prezente in literatura pentru compusi tio tetrazol ce contin legatura Au-S ai Ag-S Pentru aceasta parte au fost stabilite doua obiective:

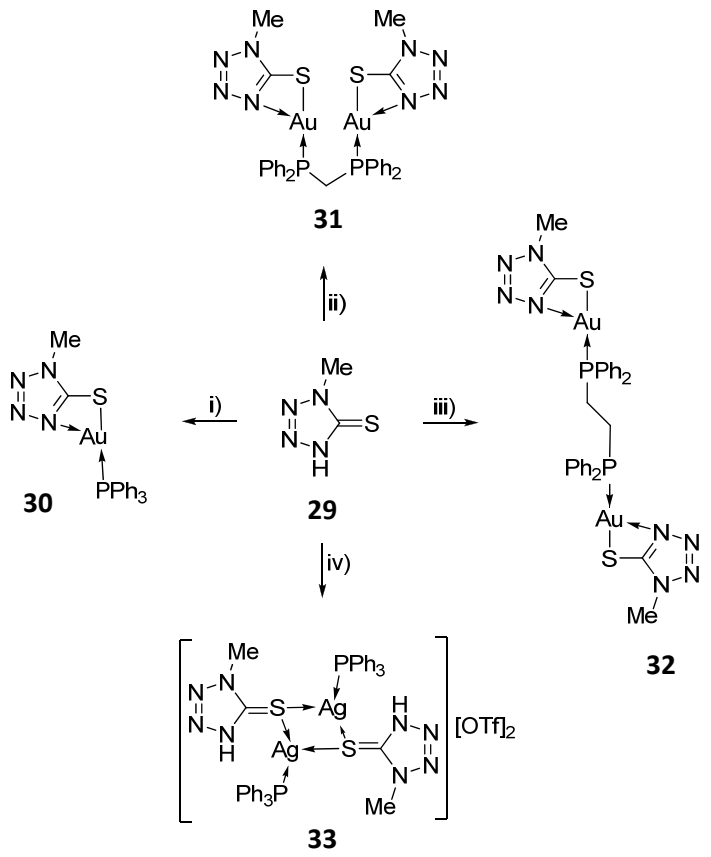
1. Designul de sisteme covalente sau coordinative in care interactiuni metalofilice (aurofilice sau argentofilice) pot aparea.

2. Studiul posibilitatilor de coordinare al tio tetrazolilor inspre derivati de aur si argint.

3.3. REZULTATE SI DISCUTII

3.3.1. Sinteza complecsilor de aur si argint cu ligandul 1-metil tetrazolin-5-tiona

Prin reactia dintre **29** si [(PPh_3)AuCl] in raport molar de 1:1 a fost sintetizat compusul [(PPh_3)Au(SCN_4Me)] (**30**), [(μ-dppm)Au_2Cl_2] (dppm=$Ph_2PCH_2PPh_2$) respectiv [(μ-dppe)Au_2Cl_2] (dppe=$Ph_2PCH_2CH_2PPh_2$) in raport molar de 2:1 au fost preparati [(μ-dppm)$Au_2(SCN_4Me)_2$] (**31**) si [(μ-dppe)$Au_2(SCN_4Me)_2$] (**32**). Complexul [(PPh_3)Ag($HSCN_4Me$)]$_2$($OTf)_2$ (**33**) a fost sintetizat in CH_2Cl_2 folosind conditii de reactie similare ca si pentru **30**, **31** si **32**, in acest caz derivatul [(PPh_3)Ag(OTf)] fiind folosit ca si agent de complexare, **Schema 30.**



Schema 30. Reactivi si conditii: i) [(PPh_3)AuCl], dry THF, NEt_3, 3h, r.t., 80%; ii) [(μ-dppm)Au_2Cl_2], dry THF, Et_3N, 3h, r.t., 91 %; iii) [(μ-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%

Structura complecsilor **31** si **32** a fost confirmata prin studii de difractie de raze X. Structura moleculara a compusului **31** contine doua molecule independente si din acet motiv in discutiile in legatura cu partea de cristalografie se vor face referiri la moleculele **31a** si **31b** (**Figura 103**). In ambele molecule atomii de aur sunt dicoordinati, prezentand o geometrie

aproape liniara, [P(1)-Au(1)-S(1) 173.05(5)° respectiv P(2)-Au(2)-S(2) 176.74(5)° in **31a** , iar P(3)-Au(3)-S(3) 169.13(5)° si P(4)-Au(4)-S(4) 173.03(5)° in **31b**]. Interactiuni aurofilice au fost observate in ambele cazuri, in molecula **31a** distanta Au(1)···Au(2) este de 3.2142(3) Å, iar in **31b** distanta este mai scurta Au(3)···Au(4) 3.1046(3) Å, [*cf*. $\sum r_{cov}$(Au,Au) 2.68 Å, $\sum r_{vdw}$(Au,Au) 3.4 Å].

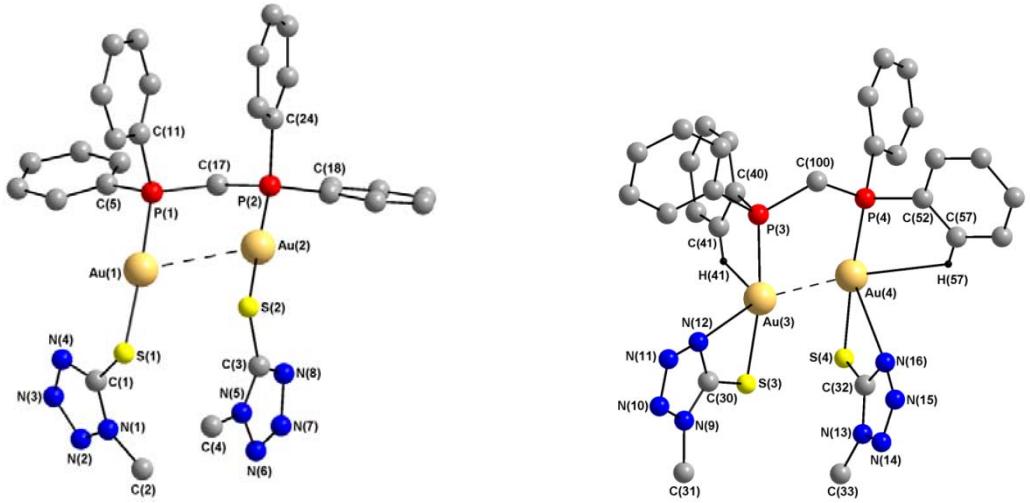


Figura 103. Structura moleculei **31a** (stanga) si **31b** (dreapta); Atomii de hidrogen neimplicati in interactiuni agostice au fost omisi pentru claritate

Structura moleculara a complexului **32** prezinta trei molecule independente, **32**(**a-c**), **Figura 105** and **Figura 107**.

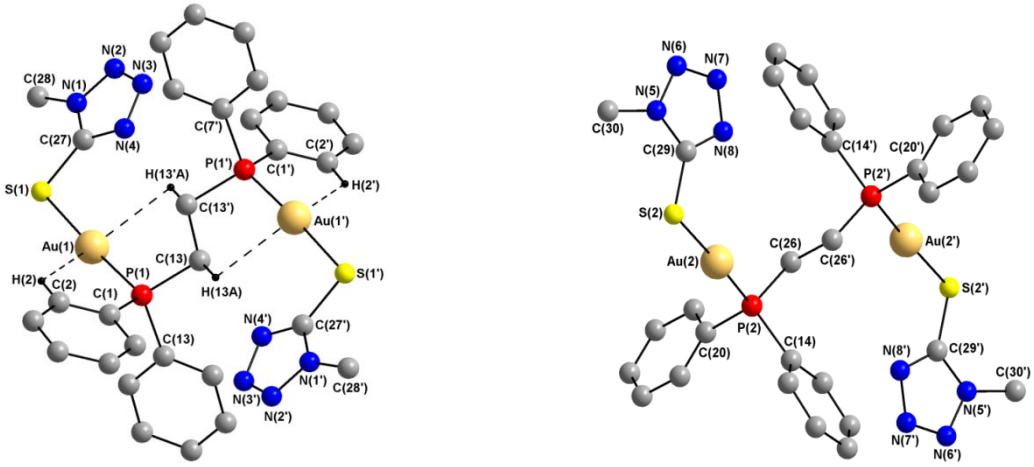


Figura 105. Structura moleculei **32a** (stanga) si **32b** (dreapta). Atomii de hidrogen neimplicati in interactiuni agostice au fost omisi pentru claritate

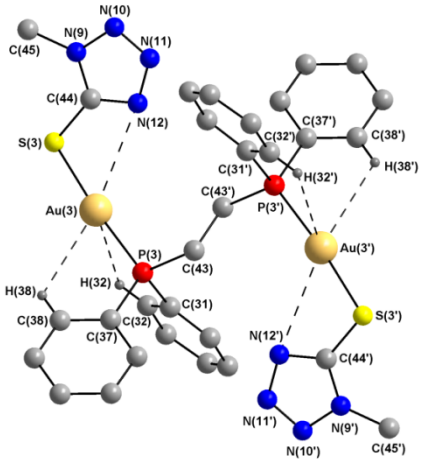


Figura 107. Structura moleculei **32c**. Atomii de hidrogen neimplicati in interactiuni agostice au fost omisi pentru claritate

Moleculele **32a** si **32b** formeaza un lant polimeric liniar prin interactiuni Au···Au intermoleculare, (**Figura 108**).

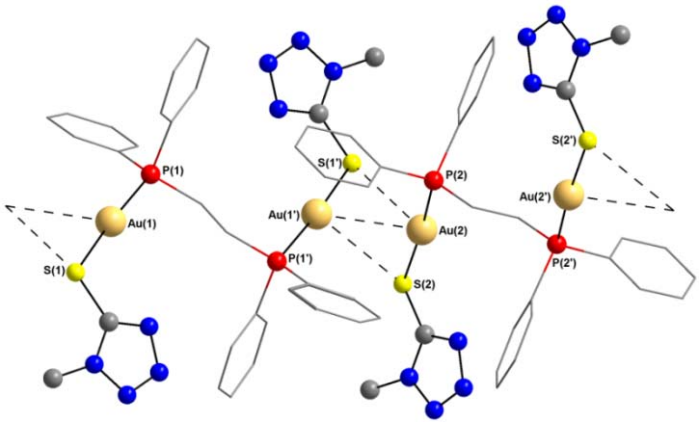


Figura 108. Lant polimeric in cristalul compusului **32** bazat pe inteactiuni intermoleculare Au···Au ai S···Au intre moleculele **32a** si **32b**

Prin difractie de raze X s-a observat faptul ca **33** cristalizeaza ca si dimer, (**Figura 109**), in cristal find observate interactiuni intramoleculare Ag(1)···Ag(2) de 3.0287(6) Å, [*cf.* $\sum r_{vdw}$(Ag,Ag) 3.4 Å], deasemenea si interactiuni intramoleculare de tip Ag···O [2.9978(48) si 3.0672(47) Å, *cf.* $\sum r_{vdw}$(Ag,O) 3.1 Å], vezi **Figura 109.**

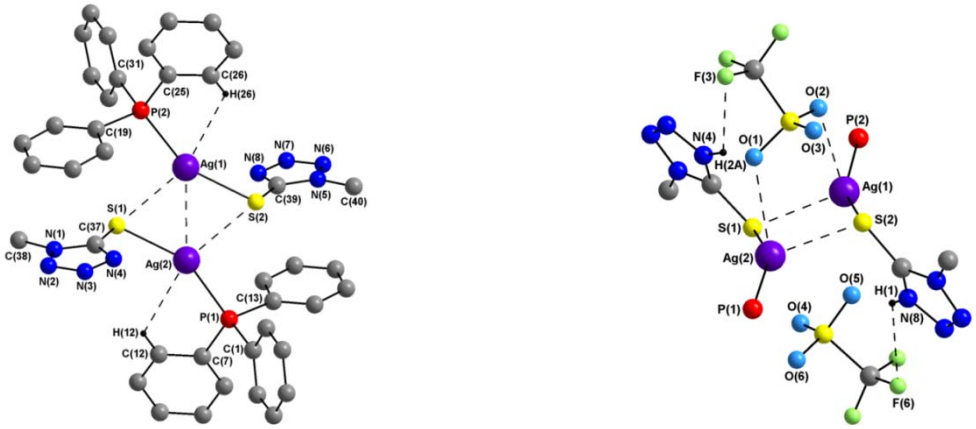


Figura 109. Structura moleculara a compusului **33**

Prin interactiuni N-H···F intre dimeri se formeaza un lant polimeric, H(40B)···F(2') 2.5787(36) Å, *cf*. $\sum r_{vdw}$(H,F) 3.05 Å], (**Figura 111**).

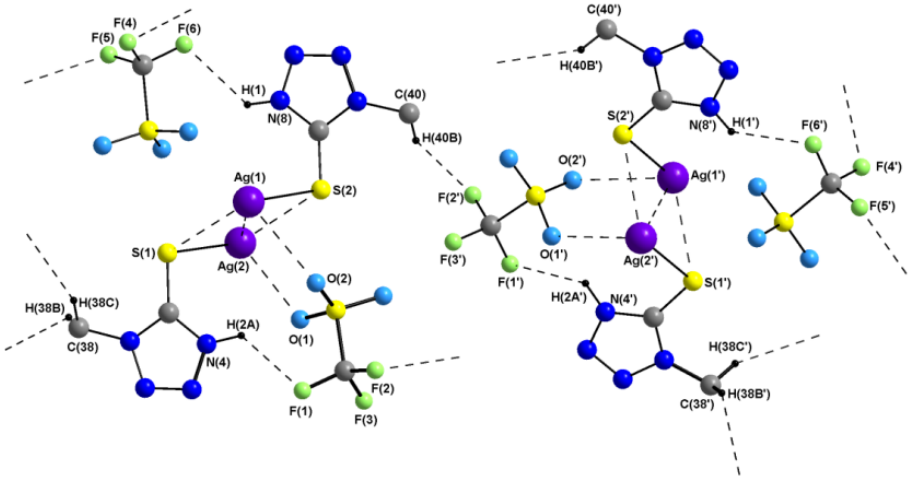


Figure 111. Lant polimeric prezent in cristalul compusului **33** bazat pe interactiuni de tip N-H···F si Ag···O

3.4. CONCLUZII

6. In concluzie am dezvoltat o metode eficienta de a sintetiza complecsi metalici ai ligandului tio tetrazol. Structurile lor moleculare determinate prin difractie de raze X au confirmat formularea initiala sugerata prin spectroscopie RMN/IR/RAMAN. Cu toate aceste un aranjament structural diferit a fost observat pentru compusul $[(PPh_3)Ag(HSCN_4Me)]_2(OTf)_2$ (**33**), care cristalizeaza ca si un dimer. Interactiuni intramoleculare Au···Au au fost detectate in $[(\mu\text{-dppm})Au_2(SCN_4Me)_2]$ (**31**), iar in $[(\mu\text{-dppe})Au_2(SCN_4Me)_2]$ (**32**) interactiunile aurofiilice intermoleculare conduc la formarea unui lant polimeric liniar. Asa cum a fost indicat prin analizele RAMAN si ulterior confirmat prin difractie de raze X in complecsii de aur (I) $[(PPh_3)Au(SCN_4Me)]$ (**30**), $[(\mu\text{-dppm})Au_2(SCN_4Me)_2]$ (**31**) si $[(\mu\text{-dppe})Au_2(SCN_4Me)_2]$ (**32**) coordinarea are loc si prin atomul de azot din grupare tetrazol. In compusul $[(PPh_3)Ag(HSCN_4Me)]_2(OTf)_2$ (**33**) ligandul coordineaza sub forma de tiona motiv pentru care atomul de azot din tetrazol isi pierde capacitatea de a coordina la argint. Interactiuni agostice slabe de tipul C-H···M au fost observate in structurile masurate si datele obtinute sunt in concordanta cu cele mentionate in literatura.

7. Rezultatele calculelor teoretice pe modelele complecsilor **30** si **32** sunt in concordanta cu geometriile observate prin difractie de raze X, iar in cazul complexului **33**, aceste analize nu au confirmat geometria observata in structura masurata.

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