BABES-BOLYAI UNIVERSITY

Faculty of Chemistry and Chemical Engineering

Contributions to the Chemistry of Organoselenium Compounds

PhD Thesis Abstract

Pöllnitz Alpár Zoltán

Scientific advisor:
Prof. Dr. CRISTIAN SILVESTRU

Cluj-Napoca
2011

Jury

President: Prof. Dr. Luminita Silaghi-Dumitrescu   Babes-Bolyai University

Reviewer: Prof. Dr. Marius Andruh   University of Bucharest

Reviewer: Prof. Dr. Jean-Francois Carpentier   Babes-Bolyai University

Reviewer: Prof. Dr. Ion Grosu   Rennes 1 University

Date of defence: 22th of June, 2011

Contents

3. Original contributions

3.1. Overview

This chapter presents the contributions brought to the chemistry of hypervalent organoselenium compounds and metal selenolates within the research performed in order to elaborate the present thesis. The results obtained can be divided in three main subchapters according to the approached class of compounds:

➢ Diorgano diselenium(I) compounds

Compounds from this class have attracted considerable interest in the last decade mainly due to their biological activity or to their use in organic synthesis. Our interest in new diorgano diselenium(I) compounds is due to their utility as starting materials in the chemistry of organolselenium(II) halides and metal selenolates.

➢ Organoselenium(II) halides

Compounds from this class are useful reagents in organic synthesis. More recently organoselenium(II) chlorides have been used to prepare selenolates of the type ZnCl(SeR)[125] thus offering new perspectives regarding the preparation of air-stable organometallic zinc compounds with potential catalytic activity.

➢ Metal selenolates

Selenolates of Ti and Zr are a very poorly described class of compounds in literature. Such compounds can be considered as third class Ziegler-Natta catalysts. Selenolates of the type $(RSe)_2MCl_2$ (M = Ti, Zr) are expected to have catalytical activity in the polymerization of 1-alkenes.

Zinc- and cadmium selenides deposited as thin films have semiconducting properties. Such thin films can be obtained by MOCVD which can use as Single Source Precursors Group 12 metal selenolates.

3.2. Diorgano diselenium(I) compounds

3.2.1. Preparation

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**2**) has been prepared according to a procedure described in the literature.[20] The new diselenide [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**5**) has been prepared similarly by *ortho*-lithiation of the organic ligand followed by reaction with elemental selenium of the resulting lithium derivative [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li. Hydrolysis of the lithium selenolate to selenol followed by aerial oxidation of the latter yielded the desired diselenide **5**.

R = Me(**1**), Et(**4**)   R = Me(**2**), Et(**5**), ^{i}Pr(**7**)
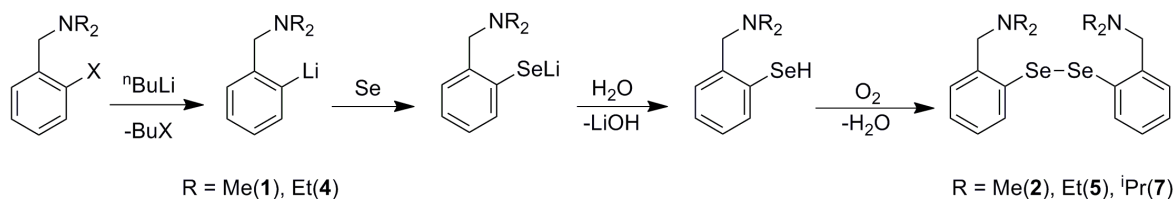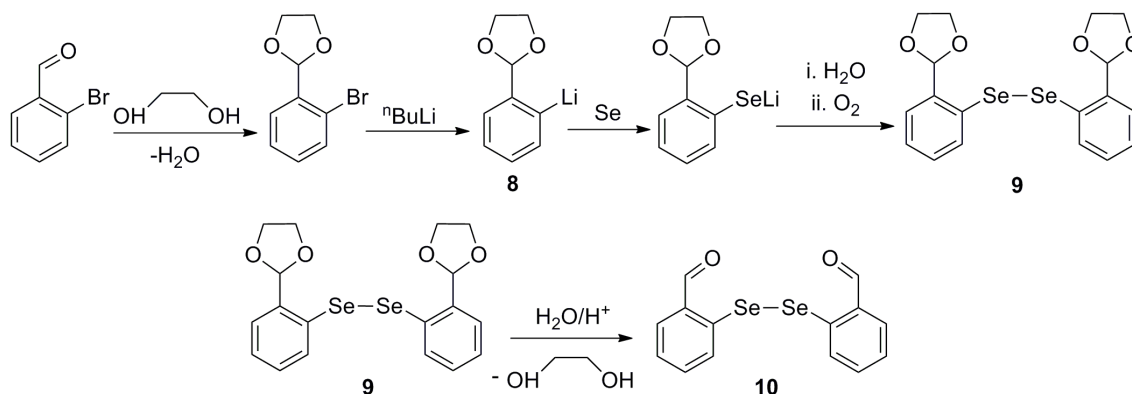
Scheme 24.

Scheme 26.

2-bromobenzaldehyde was transformed into the corresponding acetal by refluxing in toluene with ethylene glycol using a Dien-Stark trap.

Compounds **11-14** were prepared by simple condensation between **10** and the corresponding amines. It was found that nor reaction in dichloromethane in presence of an anhydrous salt like Na$_2$SO$_4$ or refluxing in toluene with a Dean-Stark trap with or without acid catalyst, did not yield any condensation product. The unreacted starting materials could be quantitatively recovered in all cases. The desired condensation reactions were found to take place in acetotonitrile without using TosOH or anhydrous Na$_2$SO$_4$.
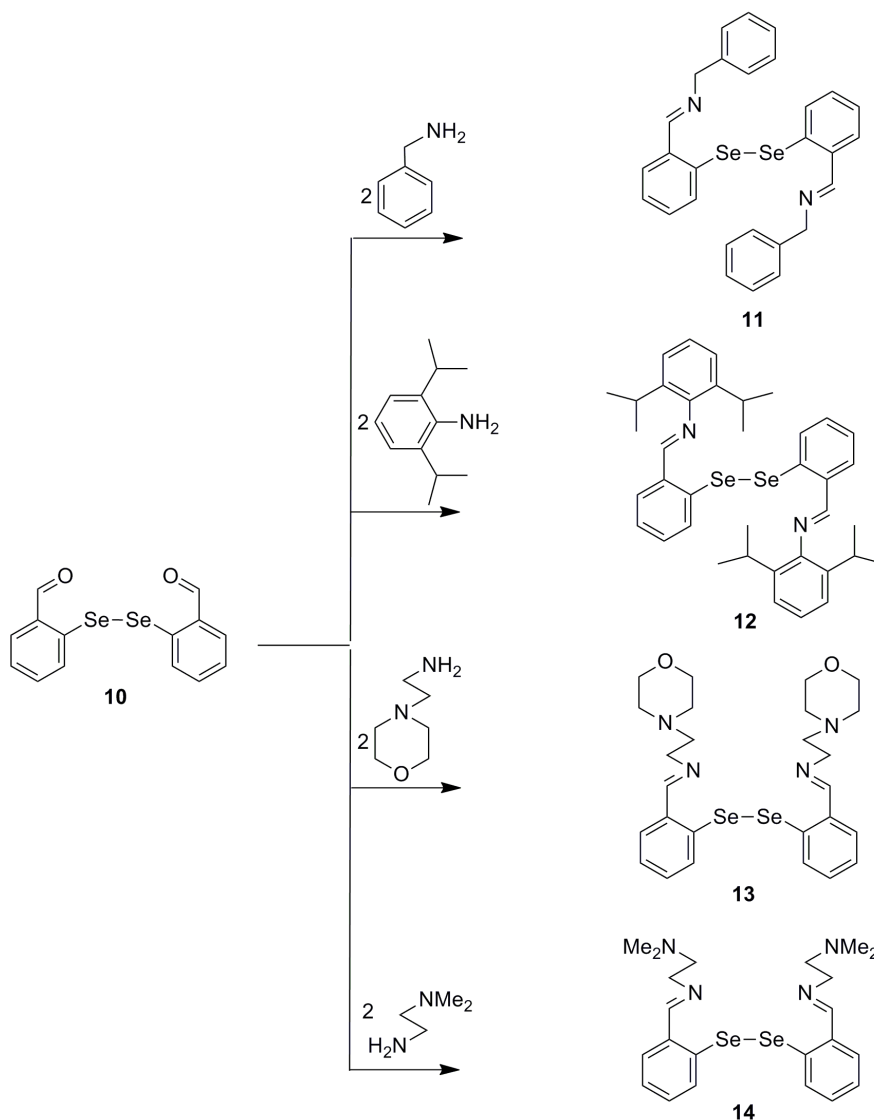
Scheme 27.

3.2.2. NMR spectroscopy

^{1}H NMR spectroscopy was used to identify compounds **2**[20], **3**[126], **6**[127], **9**[25] and **10**[39] which have already been reported in the literature. In the case of the new compounds **5**, **7** and **11-14** the assignment of resonances in the ^{1}H and ^{13}C NMR spectra was made with the aid of 2D NMR (HSQC, HMBC and COSY) correlation spectra. The aliphatic region of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**5**) displays as expected a triplet resonance for the methyl protons of the ethyl group (δ 1.05 ppm), a quartet for the methylene protons of the ethyl grup (δ 2.61 ppm) and a singlet for the methylene protons of the pendant arm (δ 3.72 ppm). The aromatic region consists of a very deshielded resonance corresponding to the protons in the *ortho* position to selenium (δ 7.79

ppm) and another broad multiplet resonance(δ 7.13 ppm) corresponding to the remaining three non-equivalent protons of the phenyl ring.
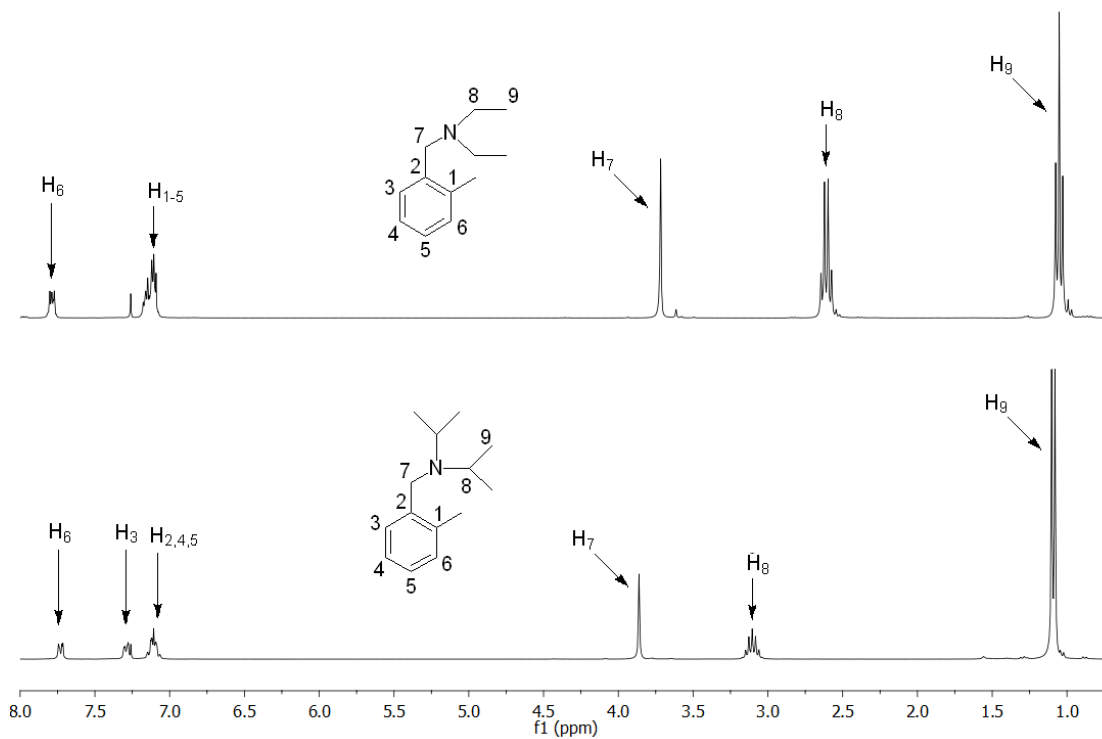
Figure 16. ^{1}H NMR spectra of compounds **5** (up) and **7** (down)

In the case of compound **7** the aliphatic region shows the expected heptet (δ 2.61 ppm) and dublet (δ 1.09 ppm) resonances for the *iso*-propyl group. In the aromatic region the most deshielded resonance (δ 7.72 ppm) corresponds to the protons H$_6$, while the resonace at δ 7.30 ppm is due to the protons H$_3$ (Figure 16, down). The multiplet resonance at δ 7.11 ppm is due to the remaining two aromatic protons.
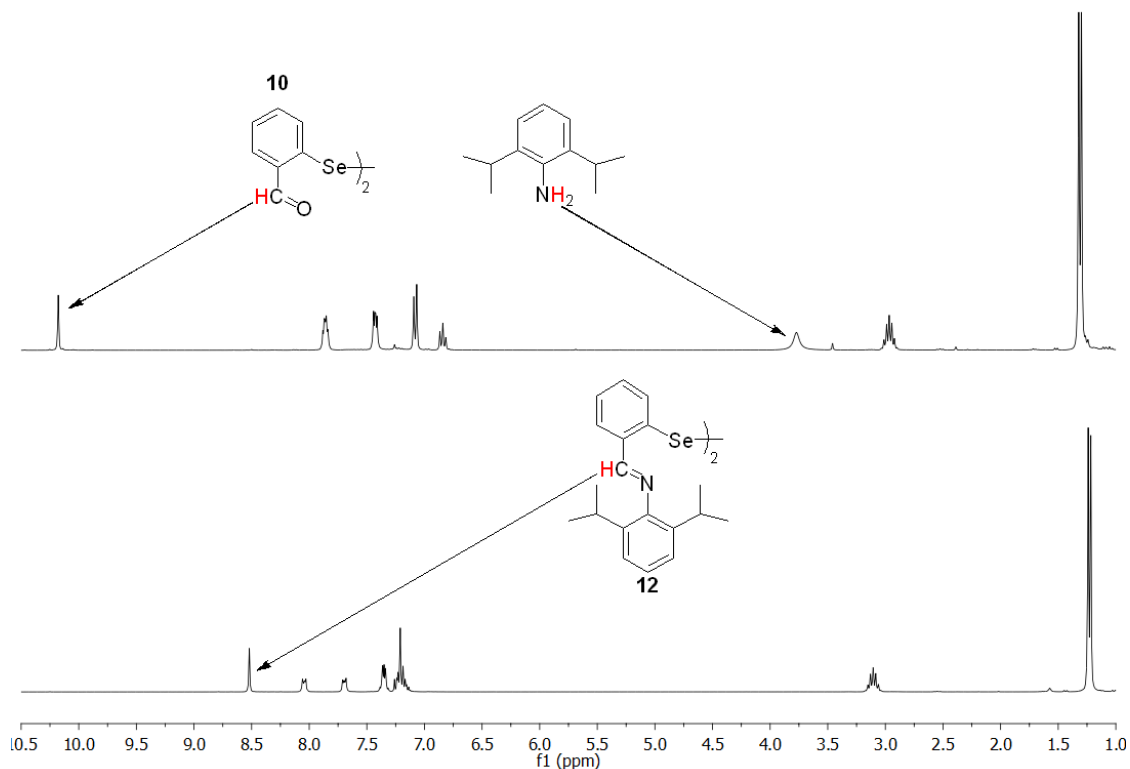
Figure 17. ^{1}H NMR spectra of the reaction products of **10** with 2,6-diisopropylaniline in toluene using a Dean-Stark trap in the presence of TosOH (up) and in acetonitrile, no catalyst (down)

^{1}H NMR was used to monitor the reaction between aldehyde **10** and 2,6-diisopropylaniline until condensation was achieved. Figure 17 shows the ^{1}H NMR spectra of the products of this reaction after 24h of refluxing in toluene using a Dean-Stark trap (up) and after two hours of refluxing in acetonitrile (down). In the first case the presence of the characteristic resonance for the -CHO proton of the aldehyde (δ 10.16 ppm) and the resonace at δ 3.77 ppm corresponding to the $-$NH_2 protons of the 2,6-diisopropylamine show that no reaction took place. When the reaction was carried out in acetonitrile the absence of the signals corresponding to the protons of the $-$CHO and the $-$NH_2 groups, respectively, indicates full conversion of the starting materials to the desired imine **12** with a characteristic $-$CH=N- resonance at δ 8.67 ppm. Similarly, in the case of diselenides **11, 13** and **14** the ^{1}H NMR spectra clearly show the formation of the carbon-nitrogen double bond due to the upfield shift observed for the CH proton from 10.16 ppm (aldehyde) to δ 8.67 (**11**), 8.53 (**13**), 8.57 (**14**) ppm (imine).

3.2.4. Single-crystal X-ray diffraction studies

Suitable crystals for single-crystal X-ray diffraction have been obtained for diselenides **5, 7** and **11.**

Intramolecular selenium–nitrogen interactions of significant strength are established in the diselenide **5** [N1···Se1 2.713(5) and N2···Se2 3.068(6) Å] [Σr_{vdW} (Se,N) 3.54 Å].[43]
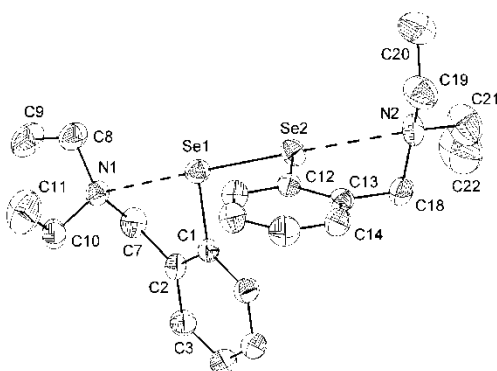
Figure 18. ORTEP-like representation at 30% probability and atom numbering scheme for isomer [R_{N1},S_{N2}]-**5** (hydrogen atoms are omitted for clarity)
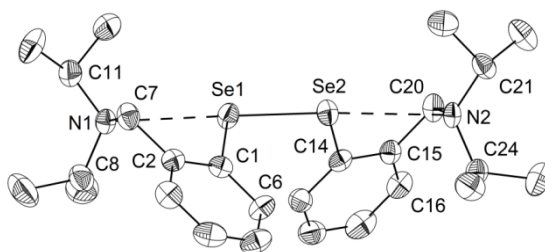
Figure 19. ORTEP-like representation at 30% probability and atom numbering scheme for isomer [S_{N1},S_{N2}]-**7** (hydrogen atoms are omitted for clarity)

The intramolecular N→Se coordination results in five-membered SeC$_3$N rings, folded along the imaginary Se···C$_{methylene}$ axis, with nitrogens displaced out of the best SeC$_3$ planes. This induces planar chirality, with nitrogen as pilot atom and the aromatic ring as chiral plane, similarly to the situation described for other related diselenides. As a consequence the compound crystallizes as a racemate consisting of 1:1 mixtures of (R_{N1},S_{N2}) and (S_{N1},R_{N2}) isomers, with respect to the two chelate rings in a molecular unit.

As a result of the strong intramolecular N→Se coordination in **7** [N1···Se1 2.955(6) and N2···Se2 2.958(5) Å] the geometry around each selenium atom is distorted T-shaped. Compound **7** crystallizes as a racemate consisting of a 1:1 mixture of (S_{N1},S_{N2}) and (R_{N1},R_{N2}) isomers, with respect to the two chelate rings in a molecular unit.
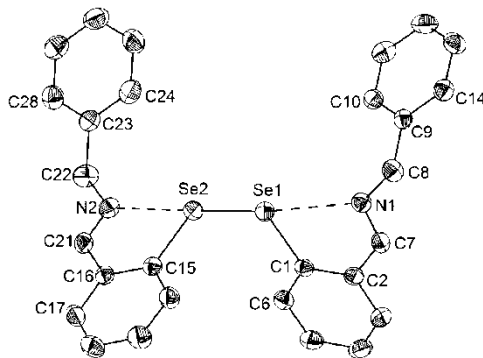
Figure 20. ORTEP-like representation at 30% probability and atom numbering scheme for **11** (hydrogen atoms are omitted for clarity)

The strong intramolecular selenium–nitrogen interactions for the compound **11** [N1···Se1 2.795(2) and N2···Se2 2.650(2)Å] are similar to those found for new compounds **5** and **7**.

Compound **11** crystallizes as diastereoisomer *E* regarding both -C=N- double bonds. The sum of the angles around each nitrogen atom [360.0(2)° for N1 and 359.6(2)° for N2] is consistent with a trigonal planar geometry and sp^2 hybridization of the nitrogen atom. Also the five-membered chelate ring formed by intramolecular coordination is planar. Hence the planar chirality existing in the *amino* derivatives **5** and **7** is absent in the *imino* derivative **11.**

3.3. Organoselenium(II) halides

3.3.4. Preparation

[2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeCl (**15**) was prepared by oxidative cleavage of the Se-Se bond with stoichiometric amounts of sulphuryl chloride according to the reaction in Scheme 28.
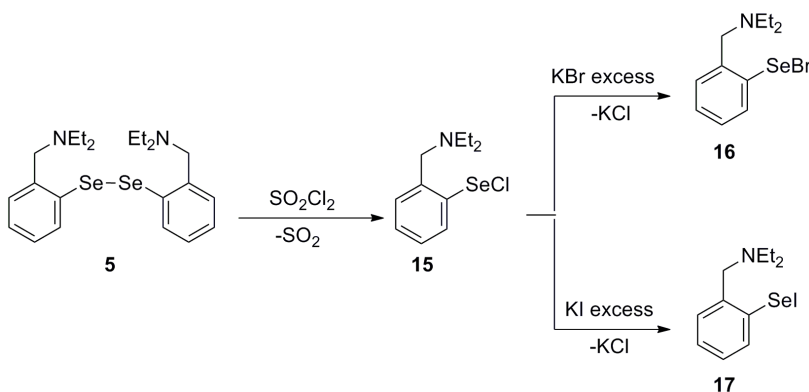
Scheme 28.

3.3.5. NMR spectroscopy

Solution behavior of the organoselenium halides was investigated using multinuclear NMR spectroscopy. ^{1}H NMR spectra of the products confirms the proposed structures. In all three cases resonances are shifted when comparing to the starting diselenide **5.** ^{1}H NMR spectra of the chloride **15,** bromide **16** and iodide **17** are shown in Figure 24.
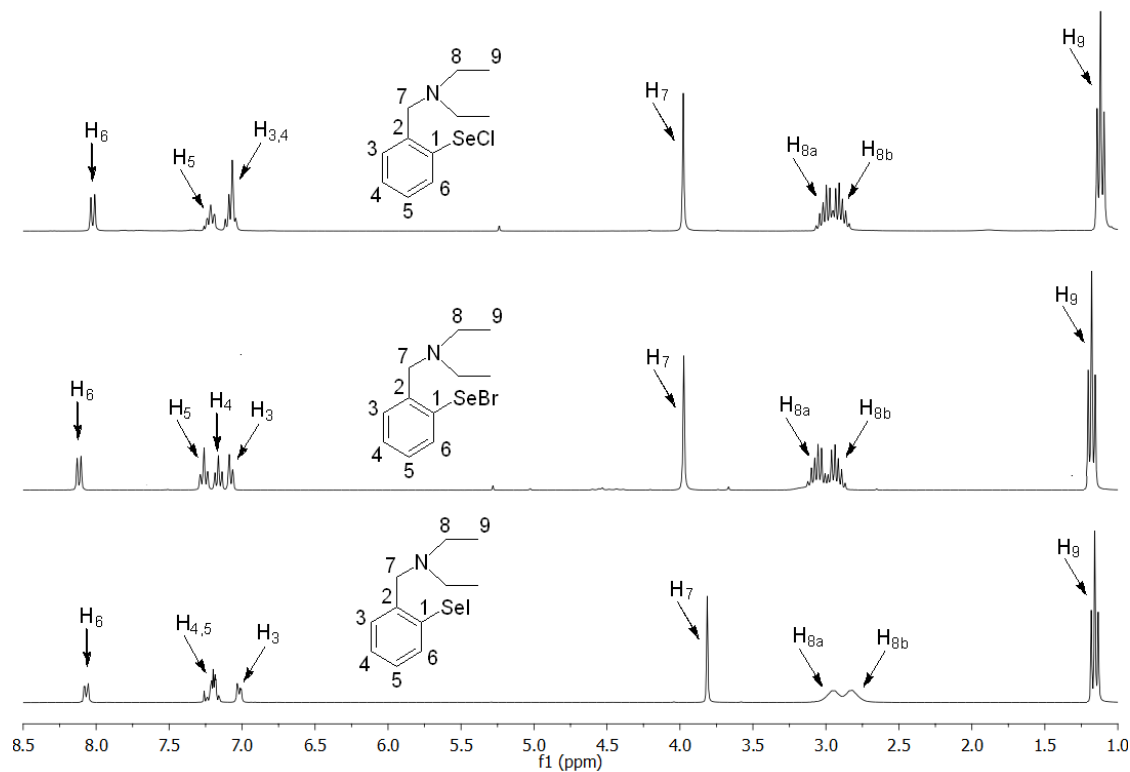
Figure 24. ^{1}H NMR spectra of **15** (up)**, 16** (middle)**, 17** (down)

The aromatic region of the ^{1}H NMR spectra of the three halides exhibit a very deshielded doublet resonance for the protons in *ortho* position to selenium. Protons H_3, H_4, and H_5 are grouped differently in all three cases but it is worth noting that in the case of bromide **16** all non equivalent aromatic protons have well resolved corresponding resonances.

An interesting feature in the aliphatic region of the ^{1}H NMR spectra of all three compounds is that the two protons of the methylene group of the ethyl groups attached to nitrogen are non equivalent. As a result a complex ABX type pattern is observed for these diastereotopic protons. For a better understanding of this pattern a theoretical interpretation was proposed and simulations were carried out for the protons in position 8 of compounds **15** and **16.**

3.3.6. Single-crystal X-ray diffraction studies

Single-crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of n-hexane into a CH_2Cl_2 solution of **15** or **16**. Both chloride **15** and bromide **16** crystallize with two independent, very similar, molecules (**15a / b** and **16a / b**, respectively) in the unit cell and therefore we will refer only to molecules **15a** and **16a** in the subsequent discussion. The molecular structures are shown in Figures 25 and 26. Selected interatomic distances and angles are listed in Table 15.

The molecules of both **15** and **16** exhibit strong internal coordination of the nitrogen atom from the pendant arm to the selenium centre, *trans* to the selenium–halogen bond [N(1)–Se(1)–Cl(1) 175.45(9)° in **15a**; N(1)–Se(1)–Br(1) 175.53(9)° in **16a**].

The resulted coordination geometry around the selenium centre is a distorted T-shaped (*C,N*)SeX core (X = Cl, Br) and thus compounds **15** and **16** can be described as neutral, hypervalent 10-Se-3 species.[130, 131]
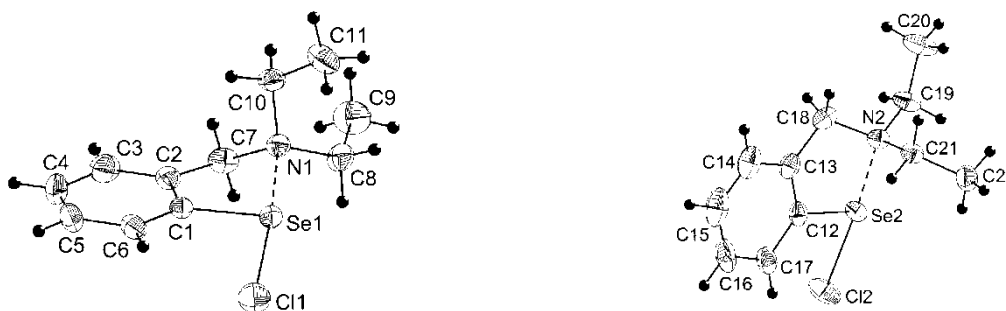
Figure 25. ORTEP-like representation at 30% probability and atom numbering scheme for isomers R_{N1}-**15a** (left) and R_{N2}-**15b** (right)
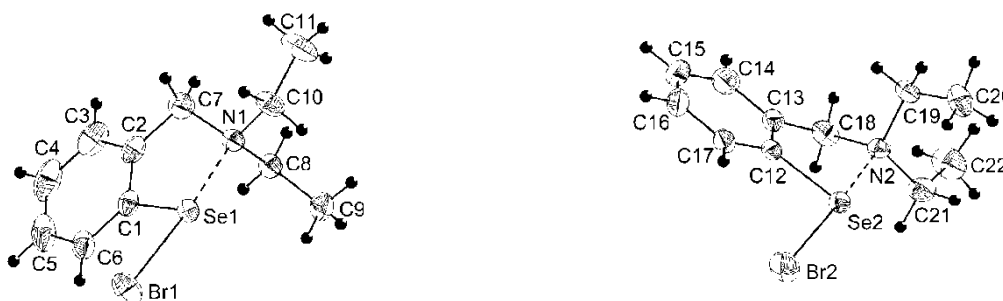
Figure 26. ORTEP-like representation at 30% probability and atom numbering scheme for isomers S_{N1}-**16a** (left) and R_{N2}-**16b** (right)

The deviation from the ideal N–Se–X angle of 180° is due to the constraints imposed by the coordinated amine arm. The strength of the internal N→Se interaction [Se(1)–N(1) 2.182(3) Å in

15a; 2.179(3) Å in **16a**] [Σr_{vdW}(Se,N) 3.54 Å][43]**Error! Bookmark not defined.**   seems to be insignificantly affected by the different electronegativity of the halogen attached to selenium. These interactions are somewhat weaker than in the related [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeX derivatives (Se–N 2.137(2) Å [48], 2.135(4) Å [47] for X = Cl; 2.143(6) Å for X = Br [20]). The length of the selenium-halogen bonds in **15** [Se(1)–Cl(1) 2.4338(15) Å] and **16** [Se(1)–Br(1) 2.5674(7) Å] is similar to those observed in the related [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeX derivatives (Se–Cl 2.471(2) Å [48], **Error! Bookmark not defined.** 2.4757(7) Å [47]; Se–Br 2.634(1) Å [20]). As expected for a *3c–4e* system, the linear arrangement of the N→Se–X unit results in an elongation of the selenium-halogen bonds compared to those observed, for example, in the organoselenium(II) halides [2,4,6-Me$_3$C$_6$H$_2$]SeX [Se–Cl 2.186(1) Å, Se–Br 2.335(1) Å].[132]

The crystals of **15** and **16** contain a 1:1 mixture of (R_{N1})-**15a** / (S_{N1})-**15a** and (R_{N2})-**15b** / (S_{N2})-**15b** isomers and (R_{N1})-**16a** / (S_{N1})-**16a** and (R_{N2})-**16b** / (S_{N2})-**16b** isomers, respectively.

Intra- and intermolecular halogen-hydrogen contacts were observed in the crystals of **15** and **16**. The strong intramolecular halogen-hydrogen interaction is obviously the result of the internal N→Se interaction which brings the aromatic hydrogen *ortho* to the selenium atom in the close proximity of the halogen in the molecular unit [Cl(1)···H(6) 2.61 Å in **15a**; Br(1)···H(6) 2.77 Å in **16a**].

In the case of the adduct **15·HCl** the nitrogen atom of the pendant arm is protonated [the H1 atom was localized from the electron density map] and therefore it is not interacting with selenium. The chlorine atoms are attached to selenium *trans* to each other [Cl1–Se1–Cl2 176.71(4)˚]. The Cl1–Se1–Cl2 system is asymmetric, the presence of a second halogen atom bonded to the chalcogen centre at a significantly long distance [Se1–Cl2 2.6078(13) Å] resulting in a considerable shortening of the Se1–Cl1 bond [2.3021(13) Å] in comparison to the value found for **15** [Se1–Cl1 2.4338(15 Å]. The adduct **15·HCl** can thus be described as a *zwitterionic* compound of the type [2-{Et$_2$N$^+$(H)CH$_2$}C$_6$H$_4$]SeCl$_2^-$, with a distorted T-shaped CSeCl$_2$ core (ionic, hypervalent 10-Se-3 species **Error! Bookmark not defined.˙Error! Bookmark not defined.**). A Cl2···H1 hydrogen bond [2.30(2) Å] is established intramolecularly and presumably it is responsible for the long Se1–Cl2 distance, compared to the Se1–Cl1 bond length, and for the asymmetry of the Cl–Se–Cl system.

3.4.   Metal selenolates

3.4.1. Organoselenium precursors

3.4.1.1.   Preparation

Sodium selenolates **18** and **20** were prepared by reductive cleavage of the selenium-selenium bond in compounds **2** and **5**, respectively, with sodium. For this purpose, a THF

solution of the corresponding diorgano diselenium(I) compound was added to a sodium mirror (large excess) under inert atmosphere. The resulting selenolates **18** and **20** were isolated in very good yields as colorless solids.
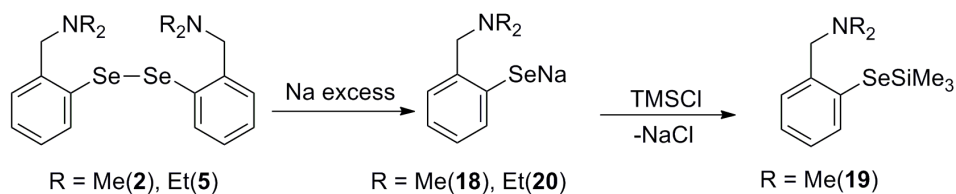
Scheme 29.

The trimethylsilyl derivative **19** was prepared by the metathesis reaction between sodium selenolate **18** and trimethylsilyl-chloride in a 1 : 1.1 ratio. After separation of the resulted NaCl the product was isolated in very good yield as a pasty off-white solid.

Potassium selenolate **21** was prepared by reductive cleavage of the selenium-selenium bond of the corresponding diselenide **11** using 2 molar equivalents of potassium tri-sec-butyl hydroborate (K-Selectride) (Scheme 30).
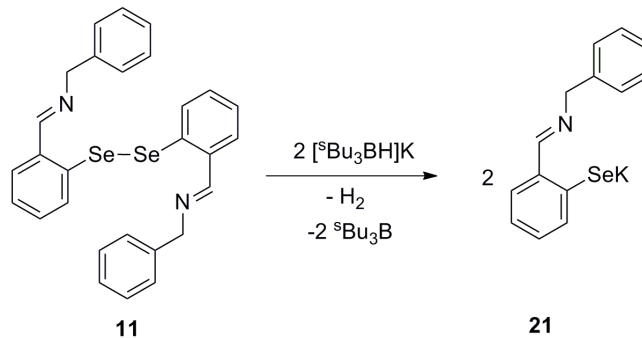
Scheme 30.
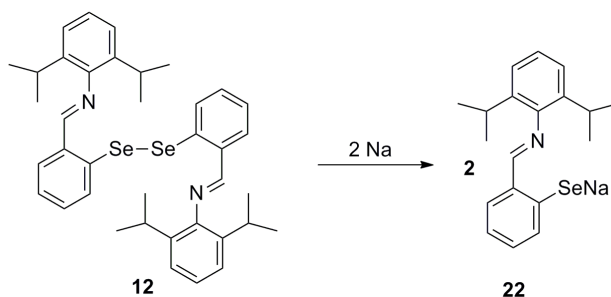
Scheme 31.

A reduction using a sodium mirror was also attempted for compounds **11** and **12** but results were unexpected and they will be discussed in Chapter 3.5 of the present thesis. Successful reduction of diselenide **12** was achieved using stoichiometric amounts of sodium sand to yield sodium selenolate **22** (Scheme 31).

3.4.1.2. NMR spectroscopy

^{1}H NMR spectra were recorded in THF-d8 for the selenolates **18**, **20**, **21** and **22** and in C_6D_6 for compound **19**. ^{13}C NMR was recorded for compounds **18**-**20**.
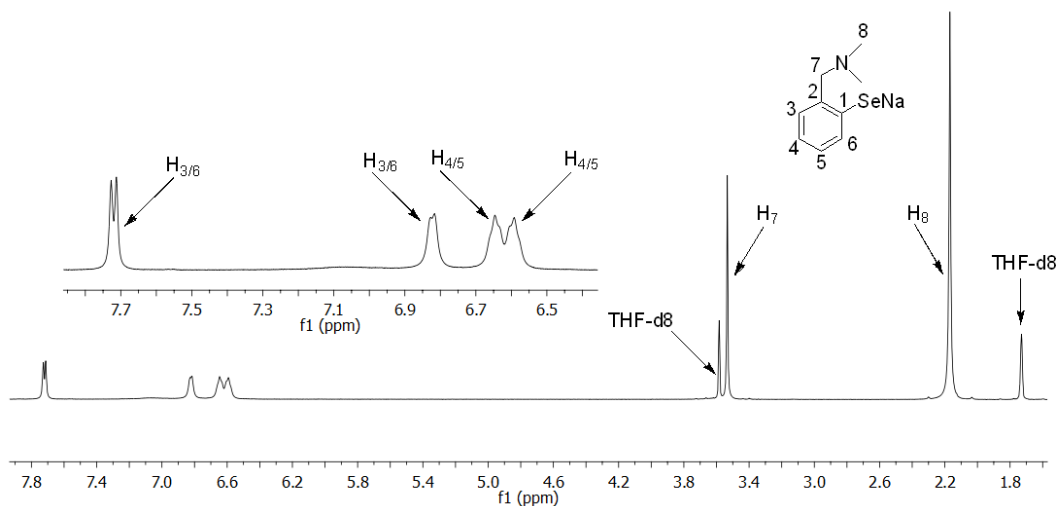
Figure 35. ^{1}H NMR spectrum of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeNa (**18**)

Figure 35 shows the ^{1}H NMR spectrum of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeNa (**18**). As expected the aliphatic region displays two singlet resonances corresponding to the protons of the methyl (δ 2.17 ppm) and the methylene (δ 3.53 ppm) groups respectively. The aliphatic region of the ^{1}H NMR spectrum of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeSiMe$_3$ (**19**) (Figure 36) displays a similar pattern to that of compound **18** having in addition a very shielded resonance corresponding to the protons of the trimethylsilyl moiety.

The potassium selenolate **21** has been characterized by ^{1}H NMR in THF-d8 (Figure 39).

To avoid *over-reduction*, the selenium-selenium bond in [{(2,6-[i]Pr$_2$C$_6$H$_4$)NCH}C$_6$H$_4$]$_2$Se$_2$ (**12**) was reduced/cleaved with stoichiometric amount of Na sand. The reaction was monitored for 15 days in an NMR tube in THF-d8. Figure 40 shows the ^{1}H NMR spectra of the strating diselenide **12** (up) and of the resulting sodium selenolate **22** (down).
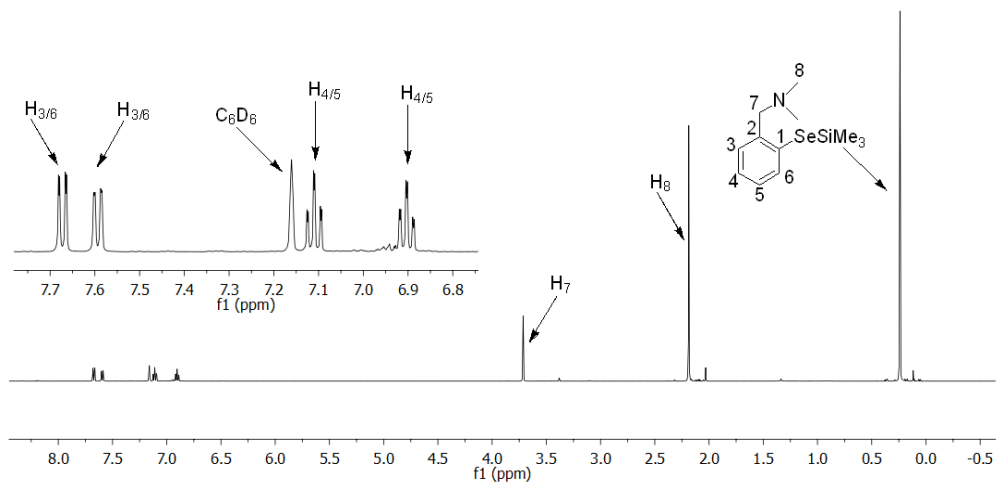
Figure 36. ^{1}H NMR spectrum [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeSiMe$_3$ (**19**)
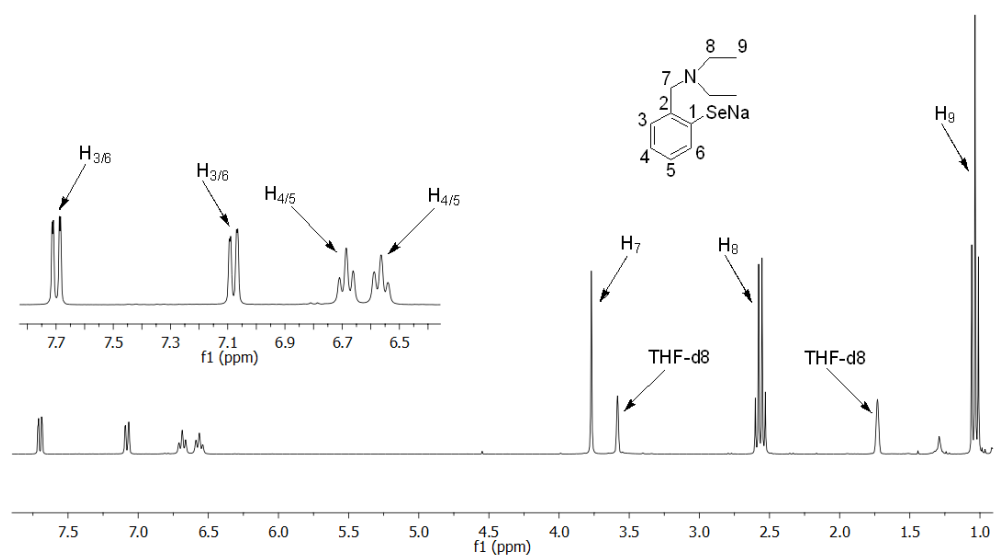
Figure 37. ^{1}H NMR spectrum of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeNa (**20**)
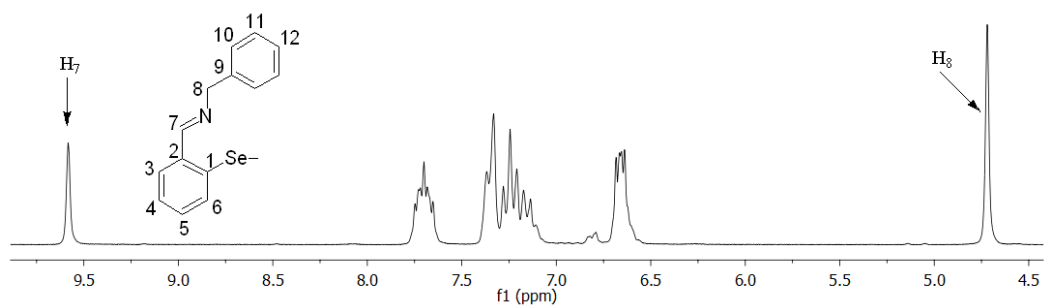
Figure 39. ^{1}H NMR spectrum of **21** in THF-d8
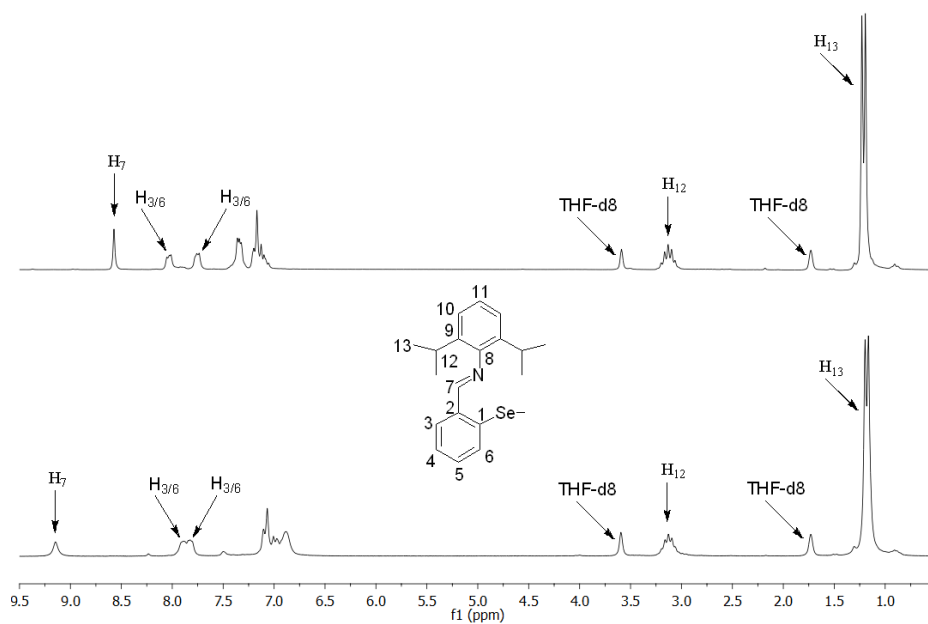
Figure 40. ^{1}H NMR spectra of diselenide **12** (up) and sodium selenolate **22** (down)

3.4.2. Zirconium selenolates

3.4.2.1. Preparation
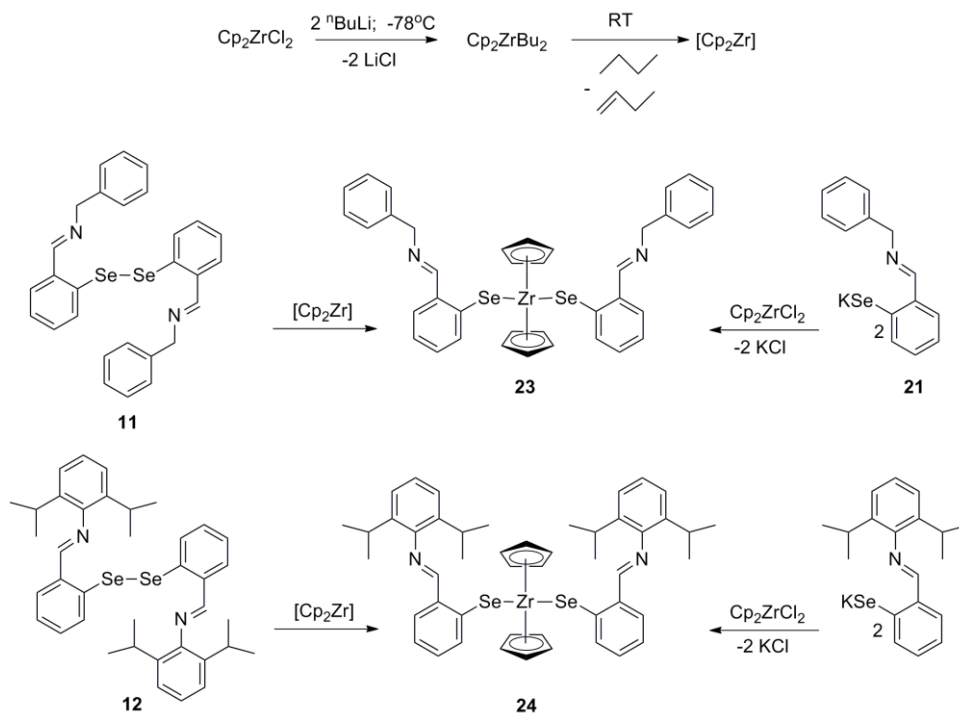
Scheme 32.

For the preparation of zirconocene selenolates two synthetic approaches were considered. The first approach consists of reductive cleavage of the selenium-selenium bond of a diorgano diselenium(I) compound with the *in situ* generated Zr(II) species [Cp$_2$Zr] while the second approach consists of the metathesis reactions between Cp$_2$ZrCl$_2$ and the corresponding potassium selenolates.

Zirconocene was prepared by reacting Cp$_2$ZrCl$_2$ with two equivalents of butyllithium at low temperature, followed by reductive elimination of two butyl groups (as butane and butene) at consequent warming to room temperature (Scheme 32).

The resulting dark brown solids **23** and **24** are extremely air-sensitive. Any attempts of purification and recrystallization lead to their decomposition.

3.4.2.2.   NMR spectroscopy

The zirconocene selenolates **23** and **24** were characterized by ^{1}H NMR spectroscopy in C$_6$D$_6$. Figure 41 shows the ^{1}H NMR spectra of compound **23** obtained by *direct synthesis* (up) and by a metatethic pathway (down). At first glance it is clear that the direct method using [Cp$_2$Zr] yields a compound with greater purity. The most upfield resonance at δ 4.63 ppm corresponds to the protons of the methylene group of the benzyl moiety. The singlet resonance at δ 5.55 ppm is due to the ten equivalent protons of the two ciclopentadienyl rings. In the aromatic region two multiplet signals correspond to the H$_{3/6}$ protons of the C$_6$H$_4$ rings, while the most downfield shift was observed for the resonance corresponding to the iminic proton H$_7$.
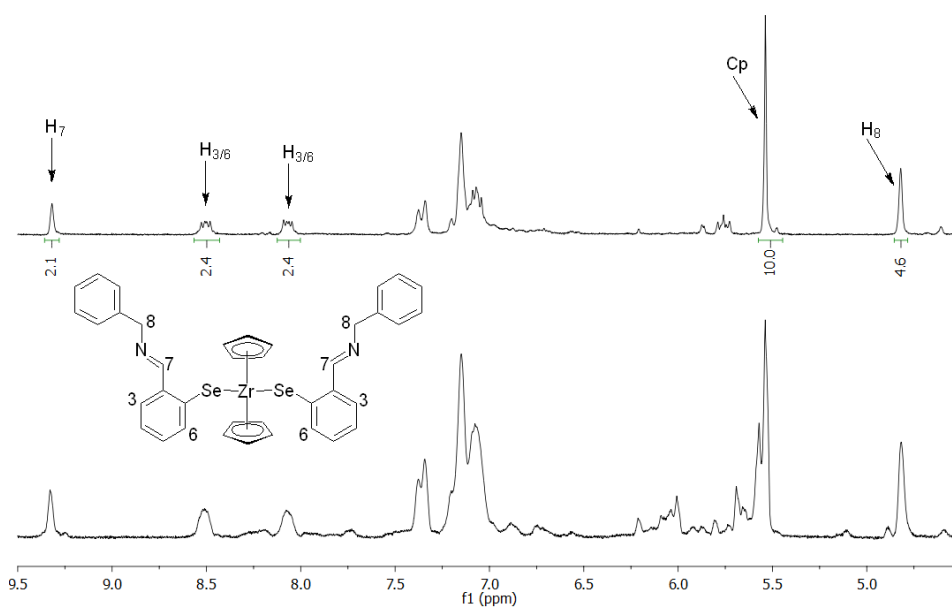
Figure 41. ^{1}H NMR spectra of compound **23** obtained by *direct synthesis* (up) and by metatethic pathway (down).

From the NMR spectra shown in Figure 41 we can undoubtedly conclude that the product of the two reactions is identical. Also it seems that the *direct* synthesis yields a product with higher purity probably due to better control over the stoichiometry of the reaction.

3.4.3. Group 12 metal selenolates

3.4.3.1. Preparation

Zinc(II)- and cadmium(II) selenolates **25-30** have been prepared by metathesis reactions between anhydrous MCl_2 and two equivalents of the corresponding alkali metal selenolates (Scheme 33).
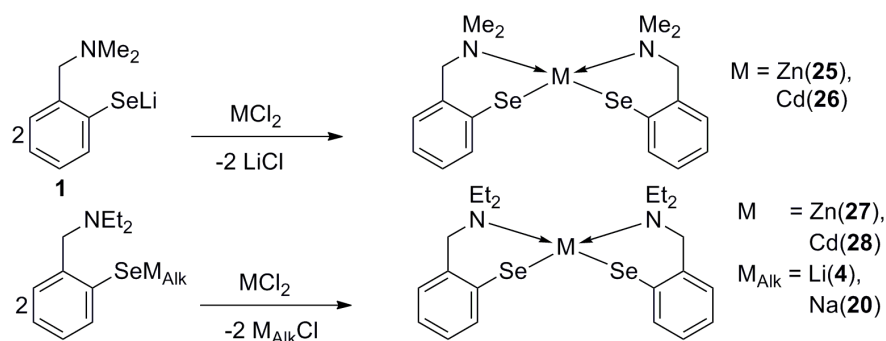
Scheme 33.

Lithium selenolates have been used to prepare compounds **25**, **26** and **28** while sodium selenolate **20** was used to prepare zinc complex **27**.
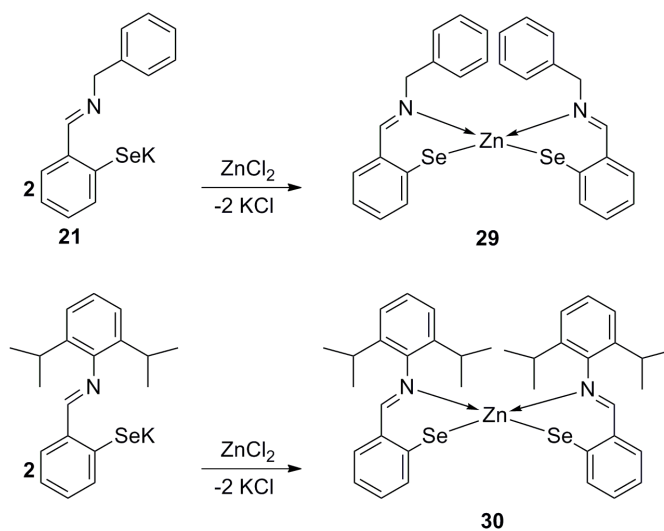
Scheme 34.

The zinc selenolates **29** and **30** have been prepared starting from the corresponding potassium selenolates which have been synthesized according to the procedure described in chapter 3.4.1.1. The resulting greenish-yellow solids are moderately air-sensitive and they decompose to the corresponding diselenides in few hours.

3.4.3.2. NMR spectroscopy

Figure 43 shows the ^{1}H and ^{13}C NMR spectra recorded at room temperature for zinc selenolate **25**. As a result of the strong N→Zn intramolecular coordination in solution the two protons of the methylene group become non equivalent giving rise to an AB spin system consisting of two doublet resonances at δ 3.14 and 4.07 ppm.
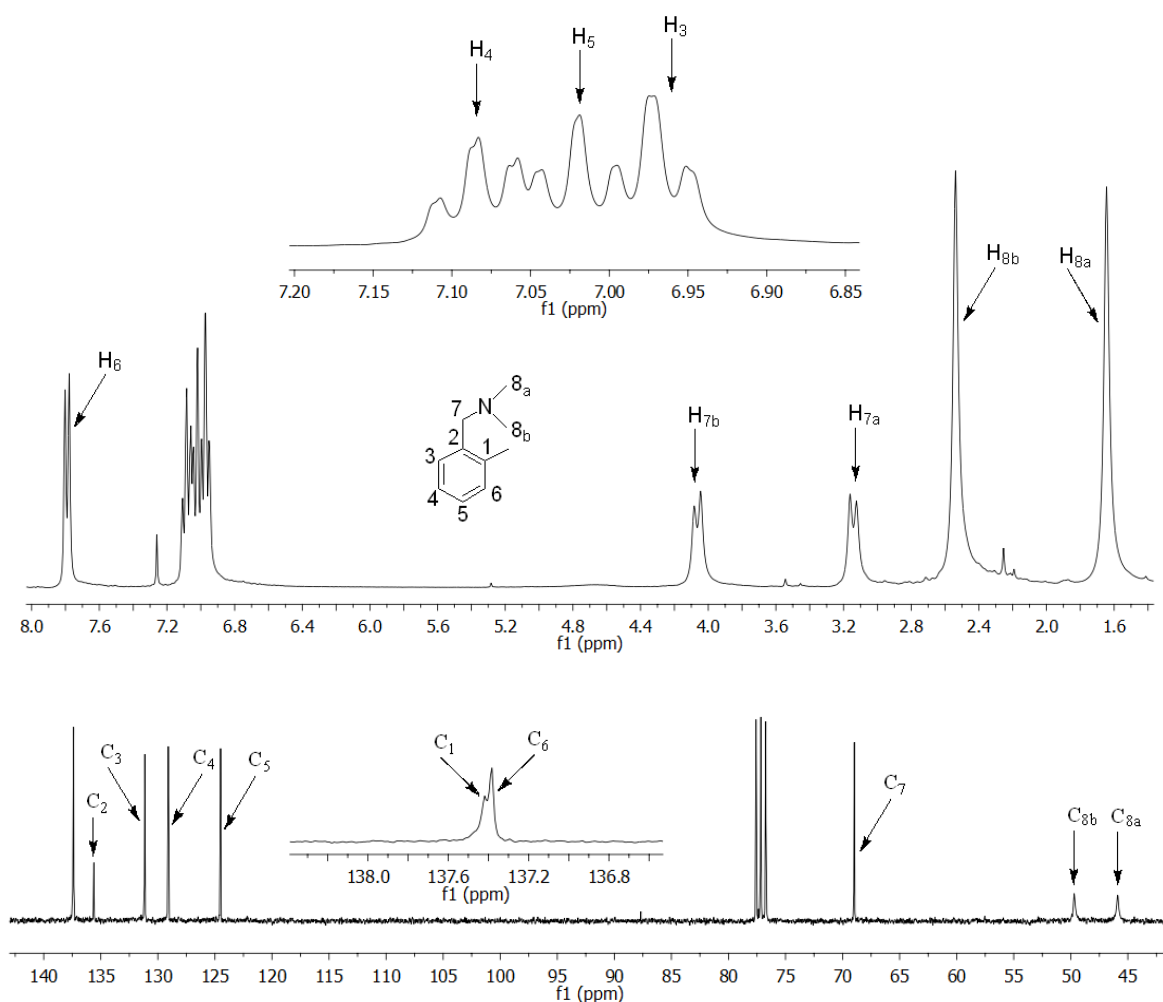
Figure 43. ^{1}H and ^{13}C NMR spectra of compound **25**

Also the two methyl groups bonded to nitrogen give rise to two singlet resonances at δ 1.65 and 2.54 ppm. The non equivalence of the methyl groups could also be observed in the ^{13}C

NMR spectrum, where carbon resonances corresponding to C_{8a} and C_{8b} were observed at δ 45.91 and 49.54 ppm. Assignments of resonances in the ^{1}H and ^{13}C NMR spectra of compound **25** were made with the aid of COSY, HSQC, HMBC correlation experiments.

^{1}H NMR spectrum recorded at room temperature [Figure 44 (up)] for cadmium selenolate **26** displays a set of broad resonances for the protons of the methylene and methyl groups at δ 3.57 and 1.99 ppm respectively. Variable temperature NMR experiments were carried out for this compound to estimate the coalescence temperature and to calculate the free enthalpy $\Delta G^{\ddagger}_c$ for the corresponding dynamic processes. The coalescence for both type of protons was achieved at -5 ˚C and $\Delta G^{\ddagger}_c = 54.5$ kJ mol^{-1} was calculated with the Eyring equation.
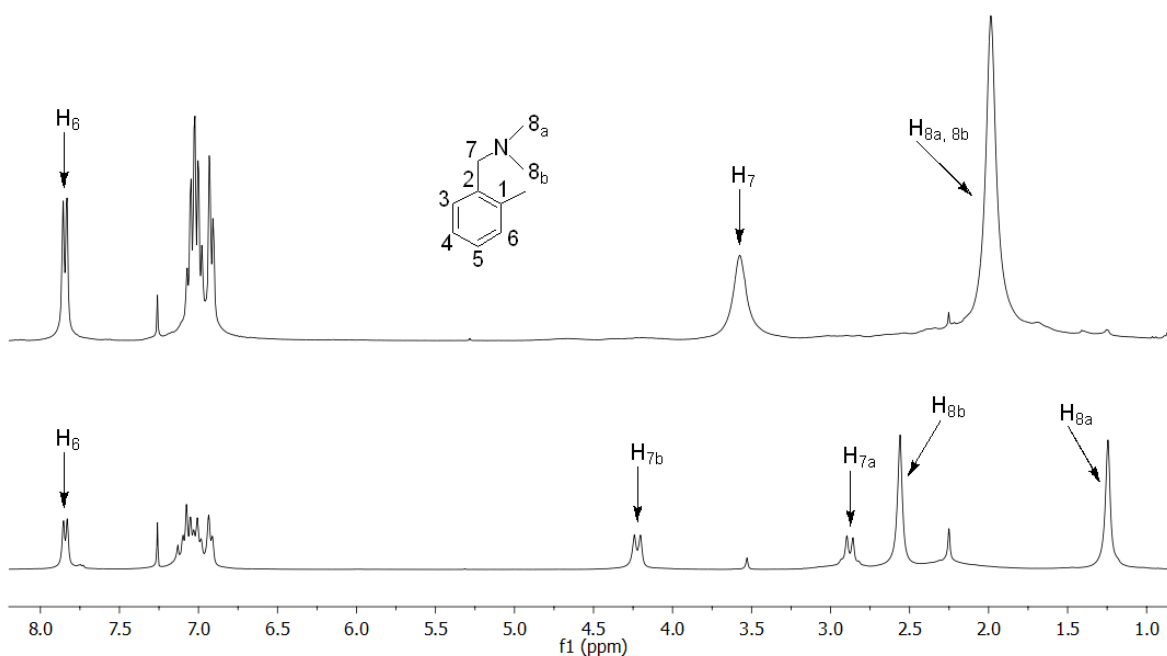
Figure 44. ^{1}H NMR spectra of compound **26** at RT (up) and -60 ˚C (down)

The low temperature ^{1}H NMR spectrum of compound **26** has a very similar pattern to the one observed for the zinc analogue **25** at room temperature. The singlet resonances at δ 3.60 and 2.30 ppm are due to the resulting diselenide **2** from the hydrolysis of selenolate **26** while carrying out the VT NMR experiments.

In the ^{1}H NMR spectra recorded at room temperature for compounds **27** and **28** broad resonances can be observed in both cases for all aliphatic protons, thus suggesting weak intramolecular N→M [M = Zn(**27**), Cd(**28**)] interactions in solution.

For cadmium compound **26** the ^{113}Cd NMR was recorded and displayed, as expected, only one singlet resonance as expected at δ -196.2 ppm.

The room-temperature ^{1}H NMR spectrum of compound **29** (Figure 45) displays an AB spin system in the aliphatic region for the methylenic proton of the benzyl moiety attached to nitrogen. In the aromatic region the highest upfield shift was observed for the *ortho* protons (H$_{10}$) of the same benzyl group while the H$_6$ protons were found to be the most deshielded aromatic protons.
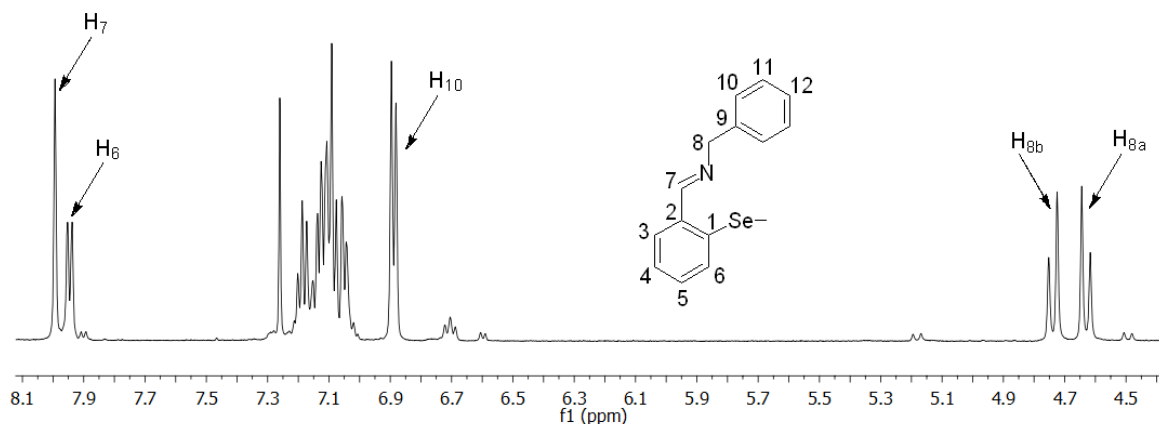
Figure 45. ^{1}H NMR spectrum of compound **29**

The characteristic iminic proton gives rise to a singlet resonance at δ 7.99 ppm shifted significantly upfield when compared to the related diselenide **11** (δ 8.67 ppm). Variable temperature NMR experiments were carried out in order to find the coalescence temperature for the methylenic protons but raising the temperature up to 50 ˚C was not enough to reach coalescence as protons H$_{8a}$ and H$_{8b}$ were still non equivalent at this temperature.

The ^{1}H NMR spectrum recorded at room temperature for compound **30** was showing evidence of a dynamic process taking place in solution, thus making difficult the interpretation of the spectrum. Variable temperature NMR experiments were carried out for this compound. ^{1}H NMR spectra were recorded from -40 ˚C to +50 ˚C with 5˚ increments to find the coalescence temperature. Also ^{13}C, ^{77}Se, COSY, HSQC and HMBC spectra were recorded at -40˚ C, RT and +50˚ C. The ^{1}H and ^{13}C NMR spectra recorded at -40 ˚C for compound **30** are given in Figure 46. Assignments of chemical shifts in all cases were made with the aid of correlation spectra.
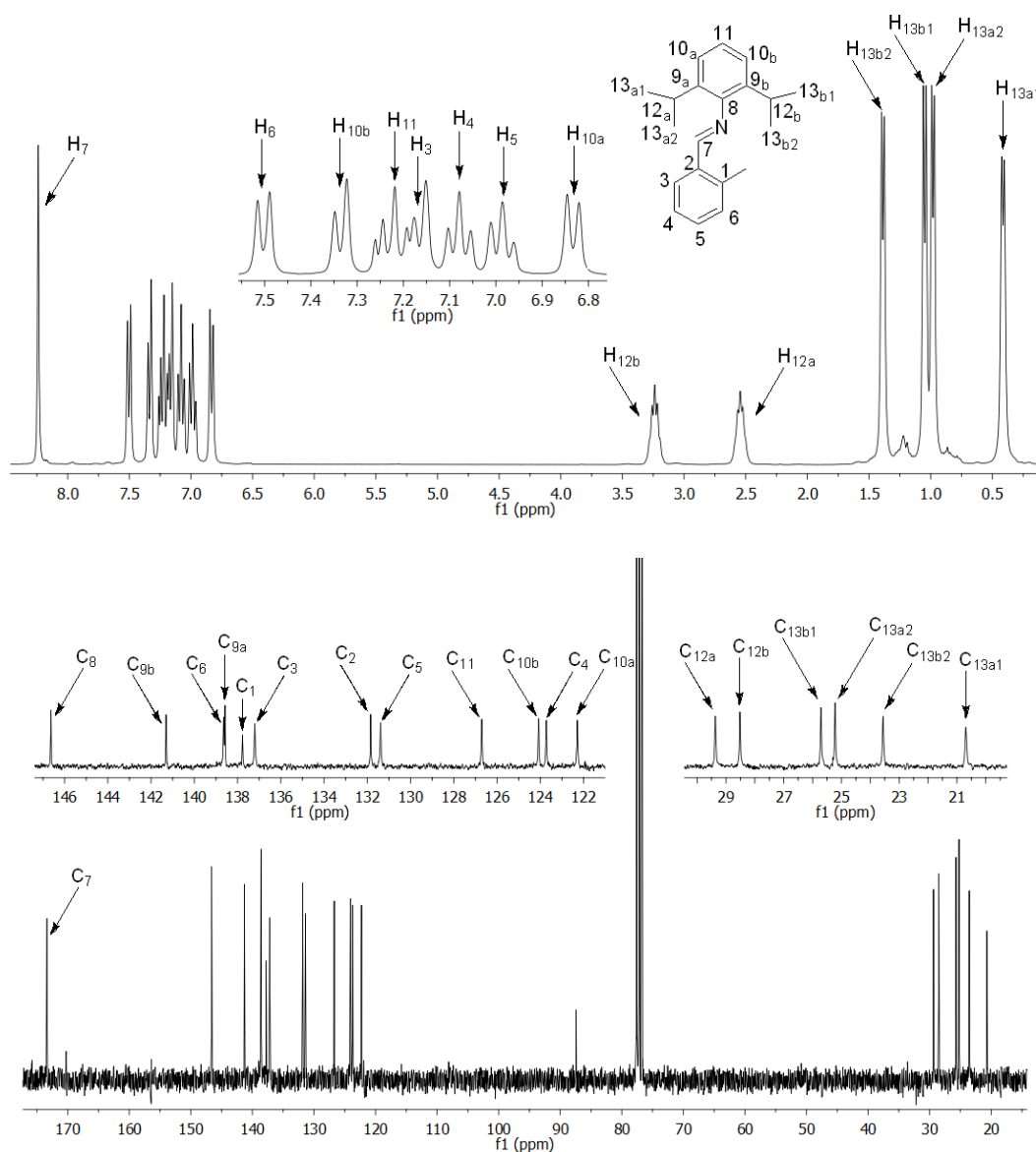
Figure 46. ^{1}H (up) and ^{13}C (down) NMR spectra of compound **30** at -40 ˚C

Although the two selenolato ligands bonded to zinc are equivalent the lack of symmetry induced by the presence of intramolecular coordination leads to the non equivalence of the two halves of the 2,6-^{i}Pr$_2$C$_6$H$_3$ moiety. At 50 ˚C a fast dynamic process takes place in solution can be observed in both ^{1}H and ^{13}C NMR spectra as all *iso*-propyl groups become equivalent (Figure 47).
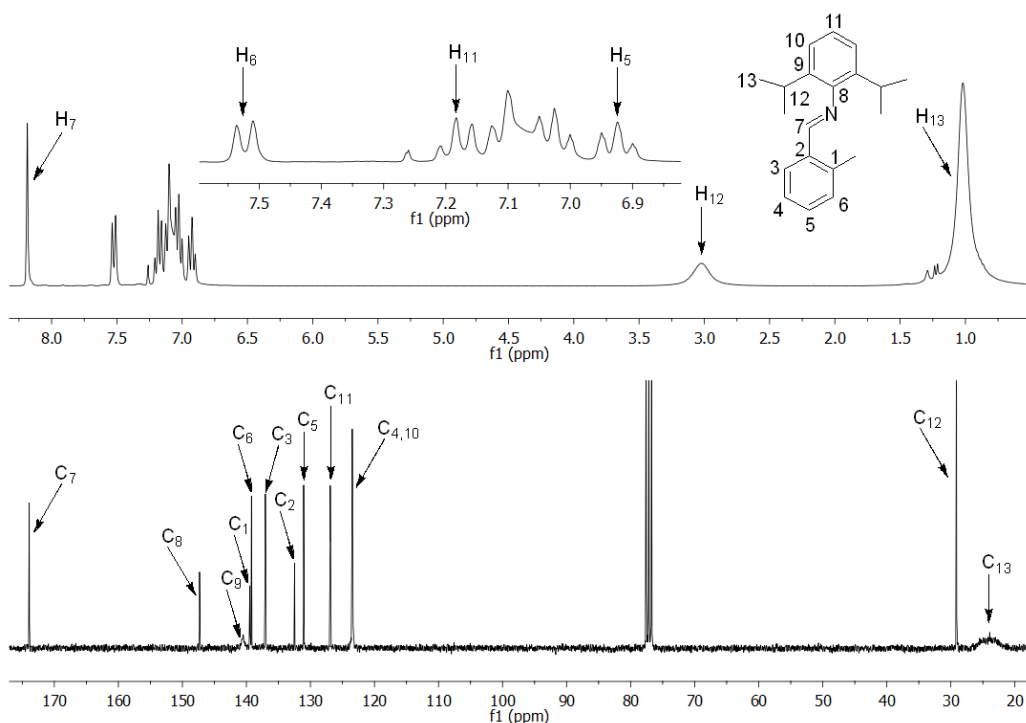
Figure 47. ^{1}H (up) and ^{13}C (down) NMR spectra of compound **30** at 50 ˚C

3.4.3.5. Single-crystal X-ray diffraction studies

Single crystals of the complexes **25** and **26** suitable for X-ray diffraction studies were obtained from a CH_2Cl_2/n-hexane mixture (1/5, v/v). Relevant interatomic distances and angles are listed in Table 18, while the ORTEP-like diagrams are depicted in Figures 50 and 51, respectively. For the cadmium derivative **26** two independent molecules are present in the unit cell.
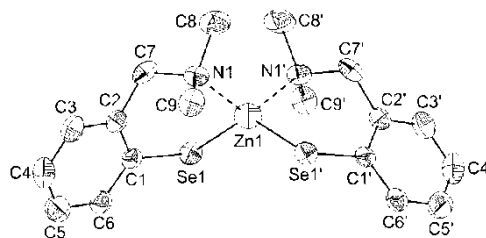
Figure 50. ORTEP-like representation at 30% probability and atom numbering scheme for **25** (hydrogen atoms are omitted for clarity) [symmetry equivalent atoms are given by ''prime'']

In both compound **25** and **26** the organoselenolato groups behave as monometallic biconnective moieties, being attached to the metal centre covalently by selenium [Zn1–Se1

2.390(2) in **25**; Cd1-Se1 2.534(1) / Cd1-Se2 2.546(1) Å in **26a** and Cd2-Se3 2.519(1) / Cd2-Se4 2.517(1) Å in **26b**] and secondary by the nitrogen atoms of the pendant arms.
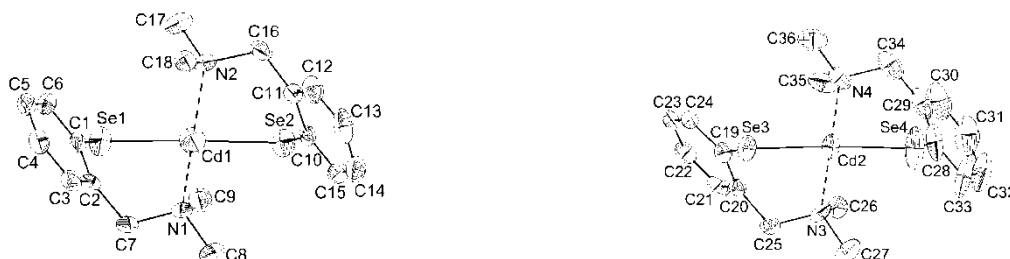
Figure 51. ORTEP-like representation at 30% probability and atom numbering scheme for **26a** (left) and **26b** (right) (hydrogen atoms are omitted for clarity)

The intramolecular N→Zn coordination induces planar chirality. Compound **25** crystallizes in the chiral space group *P*2(1)2(1)2(1) (orthorhombic) and therefore the investigated crystal contains only the ($R_{Zn1(Se1)}$,$R_{Zn1(Se1')}$) isomer. In **25** around the metal center two bidentate *N,Se* donor ligands have the right-handed (Δ or *P*) helicity along the *C2*-axis passing through the centre of the Se1···Se1' edge, Zn and the centre of the N1···N1' edge.

Figure 52. Right-handed (Δ or *P*) configuration of **25** viewed along the molecular *C2* axis (left). For comparison a similar zinc complex with two *N,O* bidentate Schiff-base ligands with left-handed (Λ or *M*) configuration is shown (right).[138] Only the six-membered chelate rings are shown for clarity.

The molecules of this cadmium complex are similar to those of the Zn analogue **25** with respect to the tetrahedral environment of the metal centre. Due to the planar chirality induced by the intramolecular N→Cd coordination the compound crystallizes as a 1:1 mixture of ($R_{Cd1(Se1)}$,$R_{Cd1(Se2)}$) / ($S_{Cd1(Se1)}$,$S_{Cd1(Se2)}$)-**26a** and ($R_{Cd2(Se3)}$,$R_{Cd2(Se4)}$) / ($S_{Cd2(Se3)}$,$S_{Cd2(Se4)}$)-**26b** isomers.

The main difference in the molecular structure of the two derivatives consists in the orientation of the aromatic rings in the molecular unit with respect to the best plane described by the nitrogen and the methylene carbon atoms. In the zinc(II) complex **25** the two C_6H_4 rings are placed on the same side of the N_2C_2 plane as are the selenium and the metal atoms, so that any intramolecular C-H$_{methyl}$···π (Ph$_{centroid}$) contact is prevented [Figure 53 (left)]. By contrast, in the cadmium(II) complex **26** the aromatic rings are placed on the opposite side of the N_2C_2 plane

with respect to the selenium and the metal atoms [Figure 53 (right)]. This brings the aromatic rings closer to the methyl groups attached to nitrogen and weak C-H$_{methyl}$···π (Ph$_{centroid}$) are established [C9-H9B···Ph$_{centroid}$(C10-C15) 2.85 Å and C18-H18C···Ph$_{centroid}$(C1-C6) 3.03 Å for **26a**; C26-H26A···Ph$_{centroid}$(C28-C33) 2.87 Å and C35-H35B···Ph$_{centroid}$(C19-C24) 3.01 Å for **26b**].
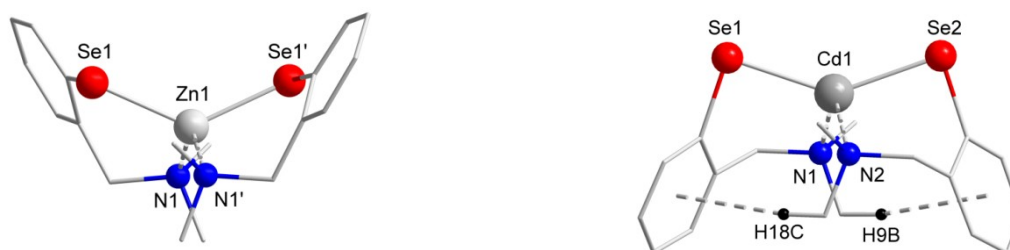
Figure 53. Molecular structures of **25**(left) and **26**(right)

Single crystals of the complexes **29** and **30** suitable for X-ray diffraction studies were obtained from a CH$_2$Cl$_2$/*n*-hexane mixture (1/5, v/v) in inert atmosphere. Relevant interatomic distances and angles are listed in Table 19, while the ORTEP-like diagrams are depicted in Figures 56 and 57, respectively.
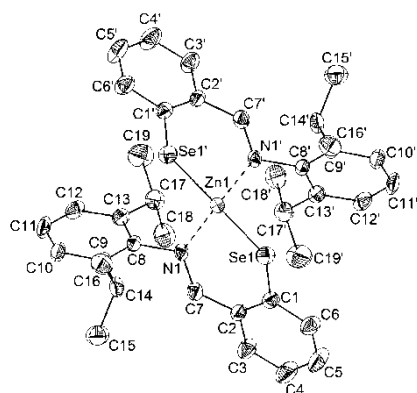
Figure 56. ORTEP-like representation at 30% probability and atom numbering scheme for **29** (hydrogen atoms are omitted for clarity) [symmetry equivalent atoms are given by ''prime'']
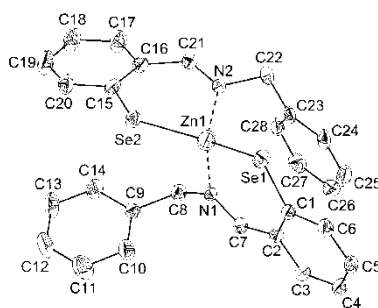
Figure 57. ORTEP-like representation at 30% probability and atom numbering scheme for **30** (hydrogen atoms are omitted for clarity)

In both compound **29** and **30** the organoselenolato groups behave as monometallic biconnective moieties, being attached to the metal centre covalently by selenium [Zn1–Se1 2.3563(7) in **29**; Zn1-Se1 2.352(1) / Zn1-Se2 2.366(1) Å in **30**] and secondary by the nitrogen of the pendant arms.

Due to the planar chirality induced by the intramolecular N→Zn coordination compound **29** crystallizes as a 1:1 mixture of ($R_{Zn1(Se1)}$,$R_{Zn1(Se1')}$) / ($S_{Zn1(Se1)}$,$S_{Zn1(Se1')}$) isomers.

In the molecule of **30** the nitrogen atom N1 is coplanar with C1, C2, C7 and Se1 of the best C$_3$Se plane in the Zn1Se1C$_3$N1 chelate ring as a result of the delocalization of the carbon-nitrogen double bond over the N1-C7-C2-C1 fragment, consistent with the steching vibration observed in the IR spectrum of **30** for the double bond of the imino group.

3.5.   Serendipitous coupling products

3.5.3.   Preparation

In our attempts to obtain the zinc selenolates **29** and **30** by reacting the corresponding sodium selenolates (obtained *in situ* by reducing the diorgano diselenides **11** and **12** with a sodium mirror) with ZnCl$_2$, we serendipitously obtained the coupling products **31** and **32** (Scheme 35).
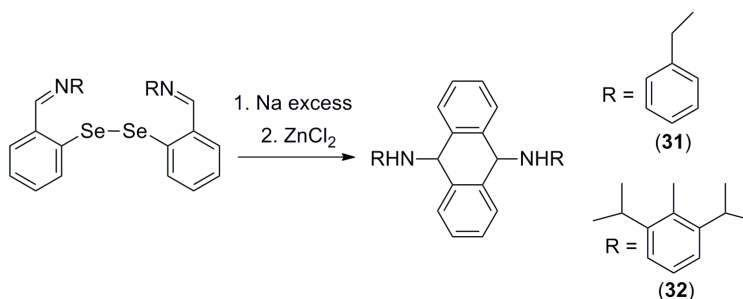
Scheme 35.

Trying to explain the formation of the unexpected products we found that several research groups have reported that reduction of transition metal complexes supported by Schiff-base ligands with elemental sodium yielded products with new formed C-C bonds formed.[139-145] Recently a mechanism was reported for a samarium complex with a Schiff-base ligand.[146]

In our case experimental observations lead us to believe that impurities in the THF such as peroxides might play a role in the mechanism of the reaction.

3.5.4. NMR spectroscopy

^{1}H (Figure 60) and ^{13}C NMR spectra were recorded for compound **32**. The presence of a doublet resonance in the aliphatic region uncorrelated to a carbon atom in the HSQC spectrum was evidence of the reduction of the *imino* group to *amino* group and consequent presence of resonance corresponding to a −N*H*- proton in the ^{1}H NMR spectrum of this compound at δ 4.14 ppm. The neighboring -CH- group gives rise to a doublet resonance δ 4.99 ppm. Since no resonance was observed in the ^{77}Se NMR spectrum it was supposed that compound **32** did not contain selenium.
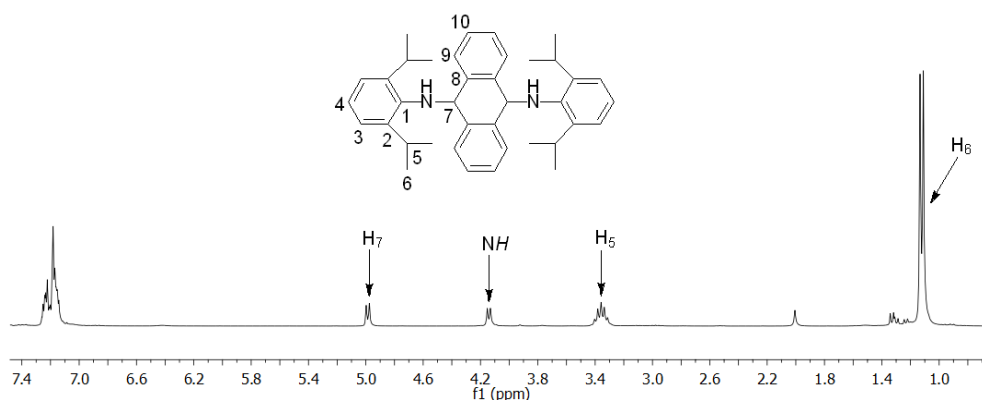
Figure 60. ^{1}H NMR spectrum of compound **32**

3.5.4. Single-crystal X-ray diffraction studies

Single crystals of compound **32** suitable for X-Ray diffraction were obtained by slow evaporation of an acetonitrile solution. The ORTEP-like diagram is depicted in Figure 63.
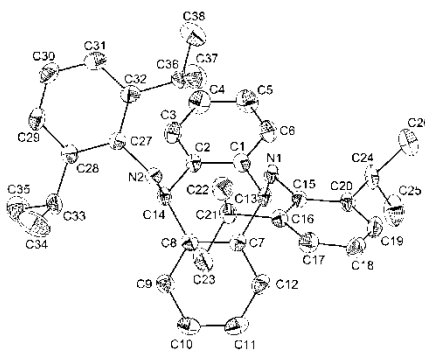
Figure 63. ORTEP-like representation at 30% probability and atom numbering scheme for **32** (hydrogen atoms are omitted for clarity)

5. Conclusions

Our objectives were to obtain new hypervalent diorgano diselenium(I) compounds and organoselenium halides and to use these as starting materials for the preparation of new Group 4 and Group 12 metal selenolates.

Six new diorgano diselenium(I) compounds were obtained and investigated by IR, multinuclear and 2D NMR spectroscopy, and for 3 of them the crystal and molecular structure was determined by single-crystal X-ray diffraction. A general, efficient synthetic route was elaborated to obtain diselenides supported by Schiff base ligands. Room-temperature ^{1}H NMR experiments reveal no intramolecular N→Se coordination in solution. The equivalence of the diastereotopic protons on the NMR timescale can also be the result of fast nitrogen inversion or fast conformational exchange of the five-membered chelate rings that would be formed by intramolecular coordination. Single-crystal X-ray diffraction studies revealed a T-shaped (*C,N*)SeSe core due to a strong intramolecular N→Se interaction *trans* to the second Se atom and therefore the compounds can be described as *hypervalent* 10-*Se*-3 species. In the case of the *amino* derivatives the intramolecular N→Se interactions induce planar chirality [with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively]. The crystals of diselenides **5** and **7** contain 1:1 mixtures of *R* and *S* isomers.

A series of organoselenium halides was obtained and investigated by multinuclear and 2D NMR spectroscopy, and for 2 of them as well as for one adduct with HCl the crystal and molecular structure was determined by single-crystal X-ray diffraction. ^{1}H NMR experiments reveal a complex pattern for the methylene protons of the ethyl groups for all members of the series. In the case of the chloride and of the bromide simulations were performed and a theoretical interpretation was proposed for the complex multiplets observed. Single crystal X-ray diffraction studies revealed a T-shaped (*C,N*)SeX core due to a strong intramolecular N→Se interaction *trans* to the halogen atom and therefore the compounds can be described as *hypervalent* 10-*Se*-3 species. Secondary intermolecular halogen-selenium interactions were not established. In the case of the adduct **15·HCl** although the intramolecular coordination was absent, the T-shaped geometry was achieved by an additional Se-Cl bond. For a better understanding of the electronic structure of the organoselenium(II) halides and on the role played by the nature of the halogen species on the formation of the three-body system N→Se–X (X = halogen), density functional theory (DFT) calculations were performed and the data obtained were compared with the structural data obtained by X-ray diffraction.

Three new sodium selenolates, one potassium selenolate and one trimethylsilyl derivative were obtained and characterized by ^{1}H and ^{13}C NMR spectroscopy. These are very useful reagents for metathesis reactions with different metal chlorides to obtain corresponding metal selenolates. Also it was demonstrated that reduction of a diselenide with potassium tri-sec-

butyl hydroborate (K-Selectride) yields the corresponding potassium selenolates in contrast with the analogous reaction of a diselenide with sodium borohydride which yields a complex anion incorporating the boron of the sodium borohydride.

Two new zirconocene selenolates were obtained using two different synthetic pathways in each case. The compounds were investigated by ^{1}H NMR. Further investigations were prevented by the extremely high sensitivity of the compounds.

Four new zinc(II) selenolates and two new cadmium(II) selenolates were obtained and investigated by IR, multinuclear and 2D NMR spectroscopy at different temperatures, mass spectrometry and for 4 of them the crystal and molecular structure was determined by single-crystal X-ray diffraction. Zinc selenolates **29** and **30** are the first examples of Schiff-base complexes of zinc with selenium in the position of ligating atom. VT NMR experiments were carried out for cadmium selenolate **26** and zinc selenolate **30** to estimate the coalescence temperature and to calculate the free enthalpy $\Delta G^{\ddagger}_c$ for the corresponding dynamic processes. X-Ray diffraction studies reveal that crystals of compound **25** contain only one of the enantiomers of the helically chiral compound. This is the second example of a helically chiral tetrahedral zinc complex with bidentate selenolato ligands. In the case of compound **30** the delocalization of the carbon-nitrogen double bond over the N1-C7-C2-C1 fragment is obviously due to its planarity, consistent with the steching vibration observed in the IR spectrum of **30** for the double bond of the imino group.

Two new organic coupling products were obtained in attempts to prepare zinc selenolates and were investigated by multinuclear and 2D NMR spectroscopy, mass spectrometry and for one of them the crystal and molecular structure was determined by single-crystal X-ray diffraction. Although similar carbon-carbon bond formation was observed in several cases when reducing metal complexes with metallic sodium, the mechanisms of the reactions are not yet well established.

In most cases supramolecular architectures were found in the solid state based on intermolecular C-H⋯π (Ph$_{centroid}$) or hydrogen-halogen interactions resulting in mono-, bi-, and tridimensional polymers in the crystal.

References:

1. J. J. Berzelius, *Fys. Kemi Mineralogi*, **1818**, *6*, 42.
2. C. J. Löwig, *Pogg. Ann.*, **1836**, *37*, 552.
3. J. T. Rotuck, A. L. Pope, H. E. Hanther, A. B. Swanson, D. G. Hafeman, W. G. Hoekstra, *Science,* **1973**, *197,* 588.
4. Cherif F. Matta (ed.), *Quantum biochemistry,* Wiley-VCH, New York, **2010**, *Ch. 20,* 585, and references cited therein
5. V. N. Gladyshev, G. V. Kryukov, *Biofactors*, **2001**, *14,* 87.
6. M. Uchiyama, S. Satoh, A. Ohta, *Tetrahedron Lett.,* **2001**, *42,* 1559.
7. M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoni, A. Temperini, *Chem. Eur. J.,* **2002**, *8(5),* 1118.
8. S. Fukuzawa, K. Takahashi, H. Kato, H. Yamazaki, *J. Org. Chem.,* **1997**, *62,* 7711.
9. H. Takada, Y. Nishibayashi, S. Uemura, *J. Chem. Soc. Perkin Trans. 1,* **1999**, 1511.
10. Y. Nishibayashi, S. K. Srivastava, H. Takada, S. Fukuzawa, S. Uemura, *J. Chem. Soc. Chem. Commun.,* **1995**, 2321.
11. T. Wirth, *Tetrahedron Lett.,* **1995**, *36(43),* 7849
12. T. Wirth, K. J. Kulicke, G. Fragale, *Helv. Chim. Acta,* **1996**, *79,* 1957.
13. Kin-ya Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.
14. C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria, J. C. Koci, *J. Am. Chem. Soc.*, **1980**, *102*, 7753.
15. H. Schiff, *Ann. Suppl.,* **1864**, *3*, 343.
16. Z. Liu, W. Gao, J. Zhang, D. Cui, Q. Wu, Y. Mu, *Organometallics,* **2010**, *29,* 5783.
17. A. Coulson, *Nature,* **1969**, *221,* 1106.
18. K. A. R. Mitchell, *Chem. Rev.,* **1969**, *69,* 157.
19. H. Bock, B. G. Ramsey, *Angew. Chem.,* **1973**, *85,* 112.
20. R. Kaur, H. B. Singh, R. P. Patel, *J. Chem. Soc., Dalton Trans.*, **1996**, 2719.
21. M. Iwaoka, S. Tomoda, *Phosphorus Sulfur Silicon,* **1992**, *67*, 125.
22. M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.*, **1996**, *118*, 8077.
23. M. Kulcsar, A. Beleaga, C. Silvestru, A. Nicolescu, C. Deleanu, C. Todasca, A. Silvestru, *Dalton Trans.*, **2007**, 2187.
24. G. Mugesh, A. Panda, S. Kumar, S. D. Apte, H. B. Singh, R. J. Butcher, *Organometallics*, **2002**, *21*, 884; **2001**, *123*, 839.
25. G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, R. J. Butcher, *J. Am. Chem. Soc.*, **2001**, *123(5)*, 839.
26. A. Panda, G. Mugesh, H. B. Singh, R. T. Butcher, *Organometallics*, **1999**, *18*, 1986.
27. M. Iwaoka, S. Tomoda, *J. Org. Chem.*, **1995**, *60*, 5299.
28. H. Ehara, M. Noguchi, S. Sayama, T. Onami, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1429
29. P. G. Jones, M. C. Ramirez de Arellano, *J. Chem. Soc., Dalton Trans.*, **1996**, 2713.
30. A. Panda, S. S. Zade, H. B. Singh, G. Wolmershauser, *J. Organomet. Chem.,* **2005,** *690,* 3142.
31. S. Kumar, K. Kandasamy, H. B. Singh and R. J. Butcher, *New . J . Chem .,* 2004, 28, 640.
32. G. Mugesh, A. Panda, H. B. Singh, R. J. Butcher, *Chem. Eur. J.*, **1999**, *5*, 1411.

33. G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, R. J. Butcher, *J. Chem. Soc., Chem. Commun.*, **1998**, 2227.
34. T. Wirth, F. Gianfranco, *Chem. Eur. J.*, **1997**, *3*, 1894.
35. L. A. Braga, S. J. N. Silva, D. S. Luedtke, R. L. Drekener, C. C. Silveira, J. B. T. Rocha, L. A. Wessjohann, *Tetrahedron Letters,* **2002**, *43(41),* 7329.
36. Y. Miyake, Y. Nishibayashi, S. Uemura, *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 2233.
37. K. Kandasamy, S. Kumar, H. B. Singh, R. J. Butcher, K. T. Holman, *Eur. J. Inorg. Chem.*, **2004**, 1014.
38. S. Kumar, S. Panda, H. B. Singh, G. Wolmershauser, R. J. Butcher, *Struct. Chem.,* **2007**, *18,* 127.
39. M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.*, **2004** , *126(16),* 5309.
40. M. Buehl, W. Thiel, U. Fleischer, W. Kutzelnigg, *J. Phys. Chem.,* **1995**, *99 (12),* 4000
41. T. Chivers, D. D. Doxsee, R. W. Hilts, *Inorg. Chem.*, **1993**, *32 (15),* 3244
42. H. Duddeck, S. Malik, T. Gati, G. Toth, M. I. Choudhary, *Magn. Reson. Chem.,* **2002,** *40(2),* 153
43. J. Emsley, *Die Elemente*, Walter de Gruyter, Berlin, **1994**.
44. *IUPAC Nomenclature of Organic chemistry*, Pergamon Press, Oxford, **1979**
45. G. Mugesh, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.*, **1999**, *577*, 243.
46. K. Kandasamy, S. Kumar, H. B. Singh, G. Wolmershauser, *Organometallics*, **2003,** *22,* 5069.
47. M. T. Klapoetke, B. Krumm, K. Polborn, , *J. Am. Chem. Soc.*, **2004** , *126(3),* 710.
48. M. Kulcsar, A. Silvestru, C. Silvestru, J. E. Drake, C. L. B. MacDonald, M. E. Hursthouse, M. E. Light, *J. Organomet. Chem.,* **2005**, *690(13),* 3217.
49. G. Mugesh, H. B. Singh, R. J. Butcher, *Tetrahedron Asymmetry*, **1999**, *10*, 237.
50. P. G. Jones, M. C. Ramirez de Arellano, *Chem. Ber.*, **1995**, *128*, 741.
51. G. Llabres, M. Baiwir, J.-L. Piette, L. Christiaens, *Org. Magn. Reson.,* **1981** , *15(2),* 152.
52. S. M. Goldfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarwar, *J. Chem. Soc., Dalton Trans.*, **1997**, 1031.
53. M. Iwaoka, H. Komatsu, S. Tomoda, *J. Organomet. Chem.*, **2000**, *611*, 164.
54. G. Mugesh, H. B. Singh, R. P. Patel, R. J. Butcher, *Inorg. Chem.*, **1998**, *37*, 2669.

55. D. V. Khasnis, M. Buretea, T. J. Emge, J. G. Brennan, *J. Chem. Soc. Dalton. Trans.,* **1995,** *16,* 45.
56. D. Liotta, W. Markiewicz, H. Santiesteban, *Tetrahedron Lett.,* **1977**, 4365.
57. D. Liotta, U. Sunay, H. Santiesteban, W. Markiewicz, J. *Org. Chem.,* **1981,** *46,* 2605.
58. M. Miyashita, M. Hoshino, A. Yoshikoshi, *Tetrahedron Lett.,* **1988**, *29,* 347.
59. L. Engman, J. S. E. Hellberg, *J. Organomet. Chem.* **1985**, *296*, 357.
60. A. I. Wallbank, M. J. Brown, C. Nitschke, J. F. Corrigan, *Organometallics,* **2004,** *23,* 5648.
61. W.-W.du Mont, S.Kubiniok, L.Lange, S.Pohl, W.Saak, I.Wagner, *Chem. Ber.,* **1991**, *124,* 1315.

62. K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.,* **1991,** *30,* 3683.
63. K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.,* **1993,** *32,* 4505.
64. M. Niemeyer, P. P. Power, *Inorg. Chim. Acta,* **1997,** *163,* 201.
65. D. Burbin, M. Niemeyer, *Eur. J. Inorg. Chem.* **2008,** *36,* 5609.
66. D. B. Collum, *Acc. Chem. Res.,* **1992,** *25,* 448.
67. K.B. Sharpless, R. F. Lauer, *J. Am. Chem. Soc.,* **1973,** *95,* 2697.
68. [1] M. Berardini, T. J. Emge and J. G. Brennan, *J. Chem. Soc., Chem. Commun.,* **1993,** 1537.
69. D. E. Gindelberger and J. Arnold, *J. Am. Chem. Soc.,* **1992,** *114,* 6242.
70. W.-F. Liaw, C.-H. Lai, C.-K. Lee, G.-H. Lee, S.-M. Peng*, J.Chem.Soc.,Dalton Trans.,* **1993,** 2421.
71. M.Berardini, T.J.Emge, J.G.Brennan, *Inorg. Chem.,* **1995,** *34,* 5327.
72. F.Theobald, H. Vivier, A. Laarif, *Organometallics* **1984,** *3,* 1495.
73. O. Jeannin, M. Nomura, M. Fourmigue, *J. Organomet. Chem.,* **2007,** *692,* 4113.
74. S. Ogawa, S.Yoshimura, N.Nagahora, Y. Kawai, Y. Mikata*c* , R. Sato, *Chem. Com.*, **2002,** 1918.
75. N.Nagahora, S. Ogawa, S.Yoshimura, Y. Kawai, R. Sato, *Bull. Chem. Soc. Jpn.,* **2003** , *76*, 1043.
76. M. Sato, t. Yoshida, *J. Organomet. Chem.,* **1974** , *67*, 395.
77. H. Koepf, *J. Organomet. Chem.,* **1968** , *14*, 353.
78. W. A. Howard, T. M. Trnka, G. Parkin, *Inorg. Chem.* **1995, 34,** 5900.
79. L-C. Song, C. Han, Q-M. Hu, Z.-P. Zhang, *Inorg. Chim. Acta,* **2004,** *357,* 2199.
80. W. A. Howard, G. Parkin, *J. Am. Chem. SOC.,* **1994,** *116,* 606.
81. M. Afzaal, M. A. Malik, P. O'Brien*, J. Mater. Chem.**,** 2010*, *20*, 4031.
82. J. Arnold, J. M. Walker, K. M. Yu, P. J. Bonasia, A, L. Seligson, E. D. Bourret, *J. Crystal Growth,* **1992**, *124***,** 647.
83. P. O'Brien, *Chemtronics,* **1991**, *5*, 61.
84. M. L. Steigerwald and C. R. Sprinkle, *J. Am. Chem. Soc.,* **1987,** *109,* 7200.
85. J. D. Brennan, T. Siegrist, P. J. Carroll, **S.** M. Struczynski, L. E. Brus and M. L. Steigerwald, *J. Am. Chem. Soc.,* **1989**, *1(11),* 4141.
86. B. Krebs, G. Henkel, *Angew. Chem., Int. Ed. Engl.,* **1991**, *30*, 769.
87. P. J. Blower, J. R. Dilworth, *Coord. Chem. Rev.,* **1987,** *76,* 121.
88. H. J. Gysling, in *The Chemistry* of *Organic Selenium and Tellurium Compounds,* eds.
89. S. Patai, Z. Rapport, *Wiley*, New York, **1986,** vol. 1, *ch. 18***,** 679-855.
90. I. G. Dance, *Polyhedron**, 1986*, *5*, 1037.
91. M.Bochmann, A.P.Coleman, A.K.Powell, *Polyhedron*, **1992**, *11*, 507.
92. M.Bochmann, K.J.Webb, M.B.Hursthouse, M.Mazid*, J.Chem.Soc.,Dalton Trans*., **1991**, 2317.
93. R.Subramanian, N.Govindaswamy, R.A.Santos, S.A.Koch, G.S.Harbison*, Inorg.Chem*., **1998**, *37,* 4929.
94. M.A.Malik, M.Motevalli, P.O'Brien, *Polyhedron*, **1999**, *18*, 1259.
95. M.Bochmann, G. C. Bwembya, R. Grinter, A. K. Powell, K. J. Webb, M. B. Hursthouse, K. M. A. Malik, M. A. Mazid, *Inorg. Chem*., **1994**, *33*, 2290.
96. M.Bochmann, K.J.Webb, M.B.Hursthouse, M.Mazid, *Chem.Commun*., **1991**, 1735.

97. K.Ruhlandt-Senge, P.P.Power, *Inorg. Chem*., **1993**, *32*, 4505.
98. D.Labahn, F.M.Bohnen, R.Herbst-Irmer, E.Pohl, D.Stalke, H.W.Roesky, *Z.Anorg.Allg.Chem*., **1994,** *620,* 41.
99. J.J.Ellison, K.Ruhlandt-Senge, H.H.Hope, P.P.Power, *Inorg. Chem*., **1995**, *34*, 49.
100. V.Wing-Wah Yam, Yung-Lin Pui, Kung-Kai Cheung, *J.Chem.Soc.,Dalton Trans.,* **2000,** 3658.
101. Vivian Wing-Wah Yam, Yung-Lin Pui, Kung-Kai Cheung, *New. J. Chem.,* **1999**, *23*, 1163.
102. M.Yosef, A.K.Schaper, M.Froba, S.Schlecht, *Inorg. Chem.,* **2005**, *44,* 5890.
103. M.A.Malik, M.Motevalli, P.O'Brien, *Polyhedron,* **1999**, *18,* 1259.
104. M.Bochmann, G.C.Bwembya, A.K.Powell, *Polyhedron,* **1993**, *12*, 2929.
105. Young-wook Jun, Ja-Eung Koo, Jinwoo Cheon, *Chem.Commun*., **2000**, 1243.
106. P.A.W.Dean, J.J.Vittal, *Main Group Met.Chem*., **2002,** *25*, 697.
107. E.S.Lang, M.M.Dias, S.S.dos Santos, E.M.Vazquez-Lopez, U.Abram, *Z.Anorg.Allg.Chem.,* **2004**, *630*, 462.
108. M.W.DeGroot, J.F.Corrigan, *Angew.Chem.,Int.Ed*., **2004**, *43*, 5355.
109. M.W.DeGroot, N.J.Taylor, J.F.Corrigan, *Inorg. Chem*., **2005**, *44*, 5447.
110. J.G.Brennan, T.Siegrist, P.J.Carroll, S.M.Stuczynski, L.E.Brus, M.L.Steigerwald, *J.Am.Chem.Soc*., **1989**, *111*, 4141.
111. Y. Cbeng, T. J. Emge, J. G. Brennan., *Inorg. Chem.,* **1994**, *33*, 3711.
112. K. Kandasamy, H. B. Singh, G. Wolmershauser, *Inorg. Chim. Acta.,* **2005,** *358,* 207.
113. G. Mugesh, H. B. Singh, *Inorg. Chem.* **1998,** *37,* 2663.
114. R. Kaur, H. B. Singh, R. P. Patel, S. K. Kulshreshtha, *J. Chem. SOC. Dalton Trans.,* **1996,** 461.
115. C. Santi, S. Santoro, L. Testaferri, M. Tiecco, *Synlett,* **2008,** 1471.
116. , J. P. Barrie, R. J. H. Clark, R. Withnall, D.-Y. Chung, K.- W. Kim, M. G. Kanatzidis, *Inorg. Chem*. **1994**, *33*, 1212.
117. M. A. Ansari, C. H. Mahler, G. S. Chorghade, Y.-J. Lu, J. A. Ibers, *Inorg. Chem*. **1990**, *29*, 3832.
118. K. Airola, S. Bartram, K. J. Rissanen, *Chem. Soc., Perkin Trans*., **1995**, *1,* 895.
119. D. Bradley, N. Kurchner, *J. Chem. Phys.* **1964,** *40,* 2258.
120. D. Bradley, N. Kurchner, *J . Chem. Phys.* **1964,** *40,* 2786.
121. S. Wang, J. P. Fackler, *Inorg. Chem.* **1989,** *28,* 2615.
122. M. Bochmann, K. J. Webb, M. Harman, M. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, **1990,** *29,* 638.
123. M. Bochmann, K. J. Webb, *J. Chem.* SOC. *Dalton Trans.,* **1991,** 2325.
124. A. **L.** Seligson, J. Arnold, *J. Am. Chem. SOC,.* **1993**, *115*, 8214.
125. C. Santi, S. Santoro, B. Battistelli, L. Testaferri, M. Tiecco, *Eur. J. Org. Chem.,* **2008**, 5387.
126. C. Branger, L. Garreau, Y. Frangin, S. Chalon, P. Dubois, *J. Labelled Compounds and Radiopharmaceuticals,* **1995,** *36(7),* 685.
127. Y. Makoto, A. Yoshitaka, N. Kyoto, *New J. Chem.,* **2010,** *34(8),* 1774.
128. A. L. Spek, **2005**, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
129. W. B. Jennings, B. M. Farrell, J. F. Malone, *Acc. Chem. Res.,* **2001,** *34,* 885.

130. K. Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999.**
131. [1] The N–X–L nomenclature system has been previously described: *N valence shell electrons about a central atom* X with L ligands. C.W. Perkins, J.C. Martin, A.J. Arduengo III, W. Lau, A. Alegria, K. Kochi*, J. Am. Chem. Soc.,* **1980,** *102,* 7753.
132. T.M. Klapötke, B. Krumm, P. Mayer, H. Piotrowski, M. Vogt, *Z. Anorg. Allg. Chem*., **2003,** *629,* 1117.
133. M. R. Detty, M. D. Seidler, *J. Org. Chem.* **1981**, *46*, 1283.
134. M. W. DeGroot, J. F. Corrigan, In *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*; M. Fujita, A. Powell, C. Creutz, Eds., Pergamon: Oxford, **2004**, *7*, 57.
135. Dehnen, S.; Eichho¨fer, A.; Fenske, D. *Eur. J. Inorg. Chem.* **2002**, *2*, 279.
136. O. Crespo, M. C. Gimeno, A. Laguna, M. Kulcsar, C. Silvestru, *Inorg. Chem.,* **2009,** *48(9),* 4134
137. O. Bumbu, C. Ceamanos, O. Crespo, M. C. Gimeno, A. Laguna, C. Silvestru, m. D. Villacampa, *Inorg. Chem.,* **2007,** *46(26),* 11457
138. C. Evans, D. Luneau, *J. Chem. Soc., Dalton Trans.,* **2002**, 83.
139. D. J. Darensbourg, W. Choi, P. Ganguly, C. P. Richers, *Macromolecules*, **2006,** *39,* 4374.
140. A. F. Mason, G. W. Coates, *J. Am. Chem. Soc.,* **2004**, *126,* 16326.
141. T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science, **2000,** *287,* 460.
142. B. D. Clercq, F. Verpoort, *J. Mol. Catal. A: Chem.,* **2002,** *180,* 67.
143. E. N. Jacobsen, *Acc. Chem. Res.,* **2000,** *33,* 421.
144. M. S. Taylor, D. N. Zalatan, A. M. Lerchner, E.N. Jacobsen, *J. Am. Chem. Soc.,* **2005,** *127,* 1313.
145. P. G. Cozzi, *Chem. Soc. Rev.*, **2004,** *33,* 410–421.
146. B-Y. Li, Y-M. Yao, Y-R. Wang, Y. Zhang, Q. Shen, *Inorg. Chem. Comm.,* **2008,** *11,* 349–352.
147. A. P. Pray, *Inorganic Syntheses*. XXVIII. New York: J. Wiley & Sons, **1990,** 321.
148. J. H. Reich, W. S. Goldenberg, B. O. Gudmundsson, A. W. Sanders, K. J. Kulicke, K. Simon, I. A. Guzei, *J. Am. Chem. SOC.,* **2001,** *123(33),* 8067.
149. A. Panda, S. C. Menon, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.,* **2001,** *623,* 87.
150. E. Negishi, F.E. Cederbaum, T. Takahashi, *Tetrahedron Lett.,* **1986,** *27*, 2829.
151. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.
152. DIAMOND – Visual Crystal Structure Information System, CRYSTAL IMPACT: Postfach 1251, D-53002 Bonn, Germany
153. G. M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction, University of Göttingen, Germany, **1996.**
154. H. Flack, *Acta Crystallogr., Sect. A,* **1983**, *39*, 876.