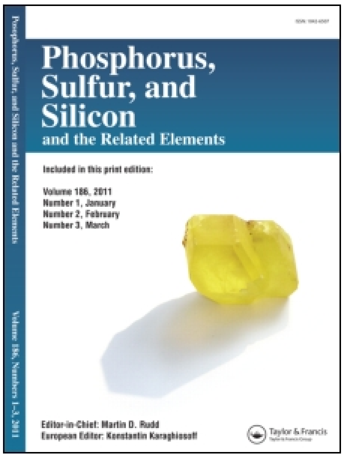

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Intramolecularly Coordinated Organoselenium Darivatives: Syntheses, Structure and Reactivity

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Intramolecularly Coordinated Organoselenium Darivatives: Syntheses, Structure and Reactivity

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Although intramolecularly coordinated organotellurium derivatives have been extensively studied in recent years, the analogous derivatives of selenium have received little attention. We have recently started work on syntheses, structures and reactivity of intramolecularly coordinated organoselenium compounds. The synthesis of these compounds makes extensive use of the *ortho*-lithiation reaction followed by insertion of selenium into Li-C bond.

Keywords: intramolecular nonbonded interactions; ligands; organic synthesis; MOCVD; organochalcogens; selenium macrocycle

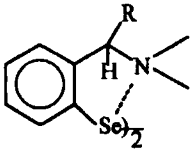
1. INTRODUCTION

Organoselenium derivatives stabilised by intramolecular nonbonded Se···Y (Y=H, N, O, S, Se, F) interactions are extremely versatile and have attracted considerable current interest. In organic compounds selenium is usually found in a divalent state with two covalently bonded substituents and two lone pairs of valence electrons. By bonding in this way selenium is able to complete its octet of electrons thus giving it a noble gas configuration. It has been found, however, that in the solid state and in solution selenium frequently further interacts with a nearby heteroatom or heteroatoms (O, N, S, etc.) producing a pseudo-high-valent selenium species.[1] This phenomenon can be explained by assuming a nonbonded interaction between divalent selenium and a heteroatom derived from the hypervalent nature of selenium. The intramolecularly coordinated organoselenium compounds find many applications. These include; a) use as ligands in chiral and achiral catalysis, b) use as ligands for the isolation of monomeric precursors for metal organic chemical vapour deposition (MOCVD) of semiconductors, c) in the synthesis of selenium-aza macrocycles, d) use as electrophilic and nucleophilic reagents in asymmetric synthesis. This article describes a brief account of work on synthesis structures and reactivity of intramolecularly coordinated organoselenium compounds which have potential as ligands and reagents in organic synthesis.

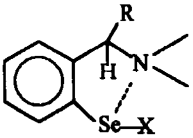
2. RESULTS AND DISCUSSION

2.1 Intramolecularly Coordinated Organoselenium Compounds as Ligands

There is a considerable interest in the area of organoselenium ligands especially intramolecularly stabilized organoselenium ligands from the structural as well as coordination chemistry point of view. Uemura *et al*[2a-c] have extensively used optically active ferrocenyl diselenides with in-built donor sp^3 nitrogen for very high chiral induction, whereas Tomoda *et al*[2d-f] have demonstrated in a series of papers that organoselenium derivatives with a coordinating amino group can be used not only for the catalytic conversion of olefins to allylic ethers but also for asymmetric inter- and intra-oxyselenenylation reactions. Our group has reported the synthesis and structural characterization of bis(2-dimethylaminomethyl)phenyl diselenide (**1**) and its use in the catalytic conversion of alkenes to allylic acetates.[3] Kaur *et al* showed the existence of Se···N interactions in the corresponding tribromide, $RSeBr_3$, **4** in solution.[3] The compound was found to equilibrate between coordinated and non-coordinated forms. For the halides **3** and **4** a large deshielding was observed in chemical shift with respect to the diselenide and for the monoselenides, the trend noted was RSeBr (δ987) > RSeI (δ818). Crystal structures obtained for compounds **1** and **3** were found to be iso-structural with a typical 10-Se-3 selane T-shaped geometry seen around selenium with strong non-valent Se···N interaction.

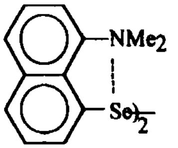


(1) R = H
(2) R = Me



(3) R = H, X = Br
(4) R = H, X = Br_3
(5) R = Me, X = Br
(6) R = Me, X = Br_3

Analogous chiral ligands were also synthesized from (S)-(-)-N,N-dimethyl-1-phenethylamine (**2**, **5**, **6**) by methods similar to that used for the achiral ligands described previously.[4] The diselenide **7**, in which there are strong nonbonded Se...N interactions, was isolated and structurally characterized.[5] A comparison of structure and reactivity among intramolecularly coordinated low-valent organochalcogen complexes derived from N,N-dimethylnaphthylamine and N,N-dimethylbenzylamine has been made by Singh and coworkers.[6] It is found that the stability and reactivity of the compounds mainly depends upon the strength of E...N (E = Se, Te) interaction and the steric bulkiness of the ligand. The more rigid naphthylamine based ligand shows different reactivity and bonding properties compared with the more flexible N,N-dimethylbenzylamine based ligand. These include: (i) the chalcogenides, R_2E could not be isolated in the case of N,N-dimethylnaphthylamine whereas N,N-dimethylbenzylamine afforded the chalcogenides in excellent yield. (ii) The reactions of the lithiated compound derived from N,N-dimethylnaphthylamine with $Te(dtc)_2$ or TeI_2, however, afforded RTe(dtc) or RTeI. (iii) The strength of Se...N or Te...N nonbonded interactions in N,N-dimethylnaphthylamine based compounds are much stronger than those derived from N,N-dimethylbenzylamine. (iv) The diselenide and ditelluride[6d] derived from N,N-dimethylnaphthylamine are chiral whereas the diselenide[3d] and ditelluride[6c] derived from N,N-dimethylbenzylamine are achiral. The E...N (E = Se, Te) intramolecular interactions in both the cases alter the bond lengths of E-X (E = Se, Te; X = Se, I, S) due to its *trans* influence.



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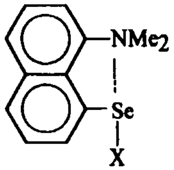
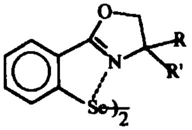
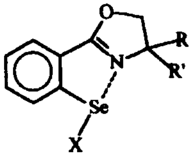


(8) X = Cl
(9) X = Br
(10) X = I

The synthesis of diselenides **11** and **12** was approached by the organolithium route. The lithium areneselenolates, were easily prepared by the direct metalation of 4,4'-dimethyl-2-phenyloxazoline and R(-)-4-ethyl-2-phenyloxazoline with n-BuLi in hexane followed by the addition of selenium powder in ether. Oxidation of the lithium selenolates then afforded the desired diselenides. The synthetically useful selenenyl halides (**13-17**) were prepared by the reactions of diselenides with halogens.[7] The stable chloro compound **13** was obtained as a crystalline solid in good yield by reacting the diselenide **11** with a stoichiometric amount of sulfuryl chloride. The bromo compounds **14** and **15** were synthesized by a similar method, with a stoichiometric amount of bromine. When the reactions of **11** and **12** were carried out with stoichiometric amounts of iodine the novel monoiodides **16** and **17** were obtained.



(11) R = R' = Me
(12) R(-), R = Et, R' = H



(13) R = R' = Me; X = Cl
(14) R = R' = Me; X = Br
(15) R = Et, R' = H; X = Br
(16) R = R' = Me; X = I
(17) R = Et, R' = H; X = I

In general arylbenzyl and aryl allyl selenides are unstable and decompose readily to give coupled hydrocarbon products and free selenium. However, the unsymmetrical selenides are useful synthetic reagents in heterocyclic chemistry. Singh *et al* synthesized a series of this type of compounds **19-22** (scheme 1a) along with novel benzylic compounds **24-26** (scheme 1b).[7a] These compounds were found to be slightly unstable but were stable enough for satisfactory analysis and NMR spectroscopy. Selenides **19-22** were analyzed by ^{1}H NMR spectroscopy. They were found to have only a weak Se···N interaction. The signals due to -CH_2- protons were shifted downfield which suggested that the introduction of benzyllic groups had reduced the interaction. The same trend was observed for compounds **24-26**. The ^{77}Se chemical shifts for these benzylic compounds were shifted relatively upfield due to the presence of benzylic groups which were covalently bonded to the Se atom and could not accept further electron density from selenium.

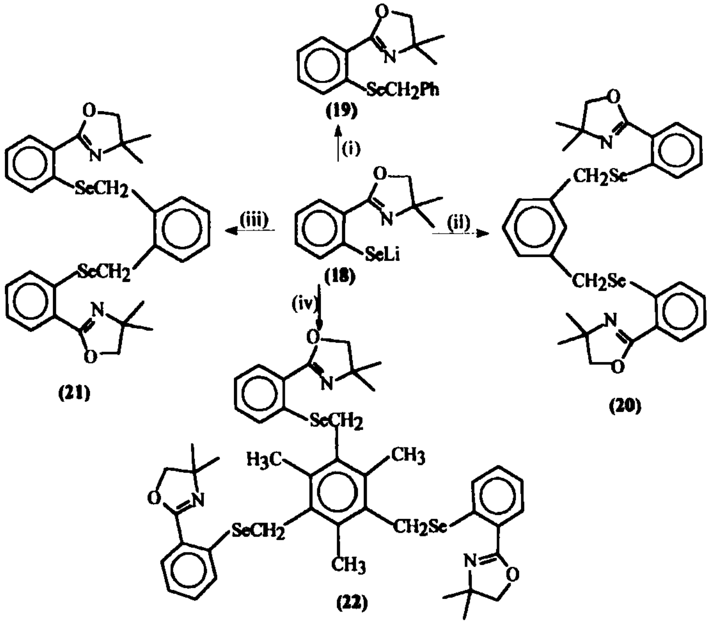
Recently Singh *et al* have reported the synthesis and characterisation of two new diaryl chalcogenides based on 4,4-

dimethyl-2-phenyloxazoline substrate.[7c] These chalcogenides can act as tridentate ligands and are potentially capable of forming six-membered rings upon chelation.

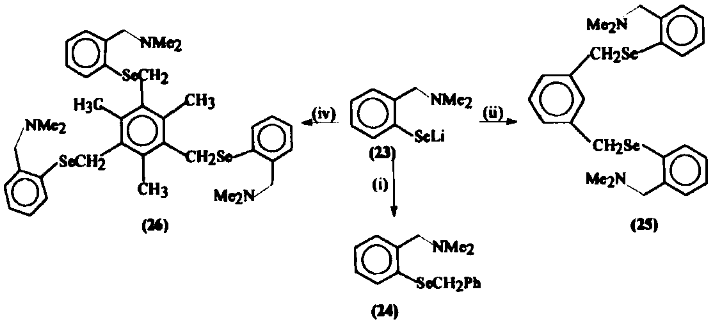
2.2 MOCVD

Metal organic chemical vapour deposition (MOCVD) is a relatively recently developed technique used for the manufacture of electronic devices. The importance of chalcogenide semiconductors has led to much current interest in the synthesis of novel organochalcogenide precursors for MOCVD. The bis-diethyl dithicarbamates are effective precursors for materials such as CdS and good quality films can be deposited. However, attempts to use the analogous selenium compounds led to films, which were heavily contaminated with elemental selenium.

Kaur and coworkers reported the synthesis of monomeric, hydrocarbon-soluble mercury (II) selenolates, $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ **27**, $Hg[(S)\text{-}SeC_6H_4CHMeNMe_2\text{-}2]_2$ **28**, $Hg[(R,S)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ **29** and $Hg[(S,R)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ **30**, stabilized by internal chelation forming a six-membered ring with Hg.[8] Crystal structures for compounds **27** and **30** were obtained, in both cases the Hg atom was four-coordinate.

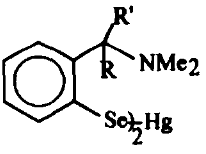


SCHEME 1a

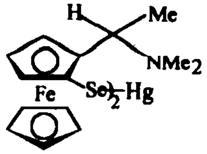


SCHEME 1b

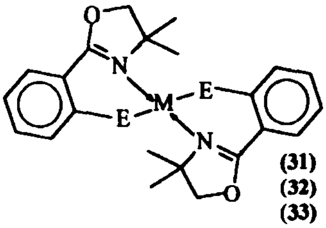
SCHEME 1. Synthetic routes to the aromatic selenenyl derivatives a) **19-22** and b) **24-26**. Reagents and conditions: i) $PhCH_2Cl$, 0^0C, 2h; ii) α,α'-dibromo-m-xylene, 0^0C, 2h; iii) α,α'-dibromo-o-xylene, 0^0C, 2h; iv) 1,3,5-bromomethyl mesitylene, 0^0C, 2h.



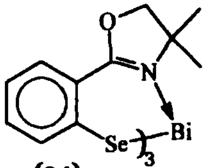
(27) R = R' = H
(28) R = H, R' = Me



(29) [R,S;R,S] (+)
(30) [S,R;S,R] (-)



(31) E = Se; M = Zn
(32) E = Se; M = Cd
(33) E = Se; M = Hg



(34)

Singh *et al* recently succeeded in preparing examples of zinc, **31**, cadmium, **32** and mercury, **33**, selenolato complexes which were isolable and have been well characterized.[9] Compound **31** was found to be the first example of a helically chiral zinc complex derived from a bidentate selenolate ligand. All three complexes were monomeric and the degree of association was controlled by the internal chelation of the oxazoline ligand. The first example of a structurally characterized monomeric bismuth selenolate **34** has also been recently reported by Singh *et al.*[10] The crystal structure of **34** showed that there were no close intermolecular contacts and that the lone pair of electrons located on the bismuth was stereochemically active.

2.3 Selenium Containing Azamacrocycles:

The design of highly selective receptors for metal ions is of great importance in the area of ion transport and chemosensing applications. The design and synthesis of such molecules have continued to develop since the pioneering work of Pedersen,[11a-b] Lehn[11c] and Cram[11d]. Interest in the chemistry of macrocyclic ligands containing heavier chalcogen (Se, Te) started from the fact that the lower electronegativity combined with their greater σ electron-donating properties of Se/Te should yield complexes with interesting structures and redox behaviour.[12] Moreover, the incorporation of the NMR active nuclei (^{77}Se/^{125}Te) would give valuable structural information about the macrocyclic ligands and their complexes. There are few reports on the polyselenoether macrocycles. Recently, we have reported an easy, high yield synthesis, structure and preliminary coordination of a novel tellurium azamacrocycle with Pd(II) and Pt(II).[13]

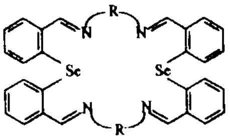
The 22-, 24- and 28-membered selenium containing macrocyclic ligands (**35-37**) were prepared from the precursor bis(*o*-formylphenyl) selenide in high yield as white solids. Here the intramolecular Se...N interaction plays an important role in the formation of macrocycles by reducing the unfavourable lone pair-lone pair repulsion between the nitrogen atoms. All could be recrystallised from $CHCl_3/CH_3CN$ (1:1) solution as colorless needles. Reduction of the azomethine groups in all the three macrocyclic ligands was accomplished by the treatment of macrocycles with excess of $NaBH_4$ in ethanol. The resulting tetraamino derivatives (**38-40**) were converted to the protonated tetrabromide derivatives (**41-43**) by the treatment with 48% hydrobromic acid. The macrocyclic cryptand (**44**) was also synthesized from the [2+3] condensation of tris(2-aminoethyl)amine with bis(*o*-formylphenyl) selenide.

The coordination chemistry of the selenaaza macrocycles with transition metal ions like Pd(II), Ni(II) and Co(II) was studied. The reaction of ligand **35** with Pd(II) led to the hydrolytic cleavage of macrocycle (**45**) where the Pd(II) ion is coordinated by two nitrogen and two selenium atoms. However, ligand **36** afforded the expected complex (**46**) with four nitrogen coordinated to the metal ion in a square planar arrangement. Reactions of Co(II) and Ni(II) with **35** afforded the octahedral complexes **47** and **48** respectively.[14]

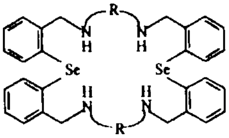
2.4 Organic Synthesis:

In recent times organoselenium compounds have gained an increasing popularity in organic chemistry because of their mild and selective reactions under mild conditions. Organoselenium moieties can act as either nucleophiles or electrophiles under mild conditions and can easily be incorporated into a wide variety of substrates. Because of these attractive features the use of organoselenium compounds in organic synthesis is a subject which has been reviewed extensively.[15] The intramolecular coordination of selenium with a heteroatom such as oxygen or nitrogen in this type of compound leads to the formation of a heterocycle in a fixed conformation thus increasing the stereoselectivity.

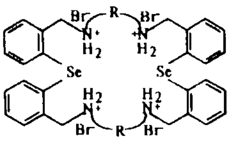
The [2,3]sigmatropic rearrangement of selenium oxides to an allylic carbon is one of the most common reactions used for indirect functionalisation by the transfer of a group from selenium to carbon electrophile.



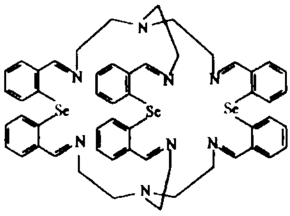
(35) R = CH_2CH_2
(36) R = $CH_2CH_2CH_2$
(37) R = $CH_2CH_2NHCH_2CH_2$



(38) R = CH_2CH_2
(39) R = $CH_2CH_2CH_2$
(40) R = $CH_2CH_2NHCH_2CH_2$



(41) R = CH_2CH_2
(42) R = $CH_2CH_2CH_2$
(43) R = $CH_2CH_2NHCH_2CH_2$



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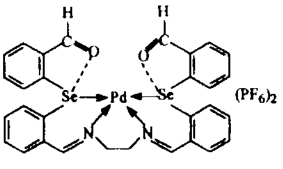
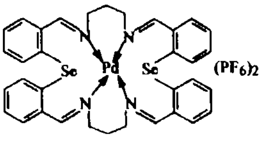


(45)



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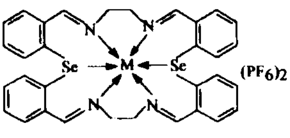
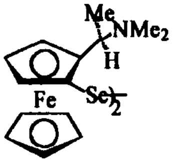


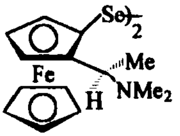
(47) M = Co; **(48)** M = Ni

Uemura and co-workers have succeeded in the asymmetric [2,3]sigmatropic rearrangement of chiral selenimides giving the chiral sulfonamide with up to 87% enantiomeric excess.[16a] Kurose *et al* have recently reported nucleophilic reaction of the allylic chloroselenutanes with N-protected amines followed by the [2,3]sigmatropic rearrangement of the resulting chiral allylic selenimides.[16b] Kshirsagar *et al* described the use of [2,3]sigmatropic rearrangement in the stereospecific synthesis of pseudocodeine.[16c] This method was found to be more efficient than the existing method, which led to a mixture of isomers. Uemura *et al* applied two optically active diferrocenyl diselenides (**49a** and **49b**) to induce highly enantioselective asymmetric selenoxide elimination leading to chiral allenecarboxylic derivatives.[16d]

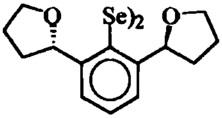
Functionalisation of alkenes by the use of selenium compounds offers attractive possibilities for synthetic organic chemistry. One of the most important reactions of this type is methoxyselenylation. The first methoxyselenylation reaction of various alkenes was reported by Tomoda *et al* in 1988.[17] It was found that a decrease in nucleophilicity of the counter anion (i.e. an increase in electrophilicity of the selenium reagent) could enhance the de of the reaction. Fukuzawa *et al* reported asymmetric methoxyselenylation using a ferrocenyl-based chiral selenium reagent (**49**).[18] Deziel and workers synthesized one of the most effective chiral organoselenium reagents (**50**) which was found to exert improved overall facial selectivity up to 98% de.[19] Diselenides with chiral pyrrolidine moieties have been characterized by Tomoda *et al*[20] and chiral diselenides derived from camphor have been employed by Back *et al*[21] in asymmetric electrophilic selenenylation. All these diselenides possess a heteroatom close to selenium. The strong Se...X interaction may allow the chiral sources on the heteroatom to come close to the reaction center in the transition state of the reaction. Due to this distinct asymmetric induction is expected. However, most of them have been prepared by multistep syntheses with low overall yield. Wirth presented some new chiral diselenides (**51**) which were also readily accessible in a few steps.[22] In the addition to alkenes distereoselektivities of up to 88% were achieved.



(49a) (R,S) $(Fc^*Se)_2$



(49b) (S,R) $(Fc^*Se)_2$



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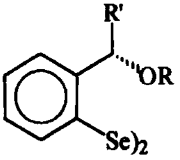
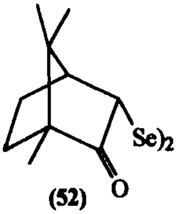
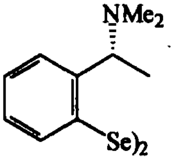


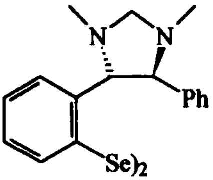
(51a) R = H, R' = Me
(51b) R = H, R' = Et
(51c) R = H, R' = *i*-Pr
(51d) R = H, R' = *t*-Bu
(51e) R = R' = Me
(51f) R = Me, R' = Et
(51g) R = Me, R' = *t*-Bu
(51h) R = Me, R' = CH_2Ph
(51i) R = Et, R' = Me
(51j) R = *t*-Bu, R' = Me
(51k) R = $(CH_2)_2OMe$, R' = Et



(52)



(53a) R = H
(53b) R = $SiMe_3$



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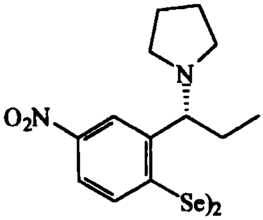

(55)

The selenium compounds synthesized in this way were suitable for use in further reactions as potential free radical precursors or for further functionalisation. Santi *et al* have reported that camphorselenenyl sulfate could be conveniently employed in the asymmetric selenomethoxylation of alkenes.[23a,b] Recently they have also reported camphor diselenide (52) and ammonium persulfate-induced oxyselenenylation-deselenenylation reactions of alkenes as a convenient one pot synthesis for enantiomerically enriched allylic alcohols and ethers.[23c]

The mechanistic course of the asymmetric methoxyselenylation was investigated in detail by Wirth *et al.*[24] In this type of reaction seleniranium ions formed by addition of chiral Se electrophiles to alkenes are the intermediates. The stability of the seleniranium ion is strongly dependent on the Se...heteroatom interaction. Kim *et al* reported the oxyselenenylation of cyclohexane with (S,S)-hydrobenzoin.[25] More recently a series of novel 3-camphor based diselenides were reported.[26]

Iwaoka and Tomoda reported their preliminary results on the catalytic conversion of alkenes into allylic ethers or esters using diselenides as catalyst in 1992.[27] Diselenides having intramolecular Se...N interaction were used because it was thought that the interaction would stop disproportionation of the selenenic acid. Singh *et al* have also used diselenides in the catalytic conversion of alkenes into allylic acetates.[3] Wirth *et al* reported sequence of methoxyselenylation and oxidative β-hydride elimination of alkenes using only catalytic amounts of chiral reagents.[28]

Selenocyclisation have been widely used for the synthesis of various heterocyclic compounds. Using organoselenium compounds as reagents for ring formation is attractive particularly when combined with further manipulation of the seleno-group. In all the products selenium is positioned either three or four bond lengths away from the heteroatom thus leading to the possible formation of intramolecular interactions. Uemura and coworkers reported the results of highly diastereoselective asymmetric selenocyclisation of alkenes by the use of optically active chiral ferrocenyl selenyl bromide.[29a] Recently they have proposed a plausible reaction scheme for the cyclisation where the chiral selenylating agent approached the C=C double bond of the substrate from the least sterically congested direction giving a chiral episelenonium ion. This was followed by intramolecular back side attack of the nucleophile.[29b] Back *et al* have reported an effective cyclisation of unsaturated alcohols of unsaturated alcohols and carboxylic acids with camphor-based selenium electrophiles.[30] The application of chiral selenium electrophiles in cyclisation of alkenes bearing an internal nucleophile was described by Wirth *et al.*[31] Asymmetric arene-alkene cyclisation mediated by a chiral organoselenium reagent has been reported by Deziel and coworkers.[32]

Several selenium cations (RSe^+) have been reported which are not only of structural importance but have been found to posses potential oxidant properties. Furukawa *et al* reported the σ-selenane which is stabilised by a transannular Se...N bond.[33a] This selenane was shown to behave as an oxidising in the redox reaction of benzene thiol which gave diphenyl disulfide as the oxidation product. The same group also reported new cyclic σ-selenuranes which could be reduced readily upon treatment with PhSH, Ph_3P, phenothiazine or SmI_2.[33b] The use of the selenium functionality as a radical precursor has been used in the first synthesis of (+)-samin[34] and (+)-membrine[15a]. The use of chiral diselenides and their derivatives in the catalytic addition of organozinc reagents to aldehydes has been reported by Wirth.[35a] They recently reported the synthetic procedure for the preparation of nitrogen-containing chiral diselenides (**53-55**) which could be efficiently used as procatalysts for the asymmetric addition of diethylzinc to a variety of aldehydes affording secondary alcohols with high enantiomeric purity (up to 97% ee).[35b]

The transition metal catalysed asymmetric hydrosilylation reaction of ketones has been extensively studied. The complexes of organochalcogen ligands with transition metal salts were thought to be unsuitable for transition metal catalysed raction. Uemura *et al*, however, successfully used the chiral diferrocenyl dichalcogenides for the Rh(I) and Ir(I) catalyzed hydrosilylation reactions.[36]

3. SUMMARY

Recent studies on intramolecularly stabilized organoselenium compounds show that the Se···N intramolecular interactions play an important role not only as ligands for catalysis but also in their application as reagents in synthetic organic chemistry. The application of intramolecular coordination has been extended to the synthesis of novel organochalcogen ligands containing both "hard" and "soft" donor atoms. The intramolecularly coordinating ligands have also been used for the isolation of monomeric metal chalcogenolates, in particular, the group 12 metal (Zn, Cd, Hg) chalcogenolates which are useful precursors for the metal organic chemical vapour deposition (MOCVD) of semiconducting materials. These complexes are generally polymeric with bridging chalcogenolate ligands. More recently, considerable effort has been directed towards the design and 'template-free' synthesis of novel macrocycles containing selenium and tellurium and their coordination behaviour towards transition metal ions.

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