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Review

The chemistry of selenosilanes: a topic overview

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Abstract: Selenium-containing molecules represent a valuable class of compounds with a variety of applications in chemical and biological fields. Selenated reagents are used as intermediates to introduce functional groups (*e.g.* double bonds) onto different substrates or in the synthesis of various selenated derivatives. Among the variety of selenium-contaning reagents, silyl selenides are frequently used to transfer a selenated moiety due to the smooth functionalization of the Se-Si bond, which allows the generation of selenium nucleophilic species under mild conditions. While the use of the analogous sulfur nucleophiles, namely silyl sulfides, has been widely explored, a relative limited number of reports on selenosilanes have been provided. This contribution will focus on the application of selenosilanes as nucleophiles in a variety of organic transformations, as well as under radical and redox conditions. The use of silyl selenides to prepare metal complexes and as selenium precursors of materials for atomic layer deposition will also be discussed.

Keywords: silyl selenides; heterocycles; nucleophilic substitutions; ring opening reactions; selenides; diselenides; selenols; metal complexes.

1. Introduction

Selenated compounds represent an interesting class of molecules, which find an increasing interest for their application in different fields of chemistry [1,2]. They are employed in organic synthesis, in biochemistry - for example as antioxidants, anticancer, antimicrobials -, in inorganic chemistry and in material science. Different methods are described to introduce a selenated moiety into different substrates and among them methodologies based on the reactivity of silyl derivatives represent an efficient alternative approach [3-5]. Silyl selenides in fact can be regarded as the synthetic equivalents of the corresponding hydrogenated compounds (*i.e.* $RSeSiMe_3$ = RSeH; $(Me_3Si)_2Se$ = H_2Se), but more stable and safe, hence easier to prepare, to store, to handle and to measure. In addition, trimethylsilyl selenides, together with trimethylsilyl sulfides, can also be used as soft silylating agents, as well as in the protection of carbonyl groups.

2. Synthesis of selenosilanes

Some silyl selenides are commercially available - for example $PhSeSiMe_3$ - or can be prepared by different methods, mainly depending on the group on the selenium atom. A typical approach for the synthesis of (phenylseleno)trimethylsilane, $PhSeSiMe_3$ **2a** or (methylseleno)trimethylsilane, $MeSeSiMe_3$ **2b** is the reduction of the parent diselenides **1a**,**b** under suitable reducing conditions (Scheme 1) [6-14].

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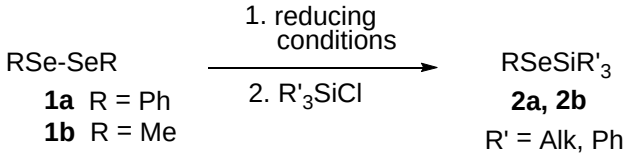
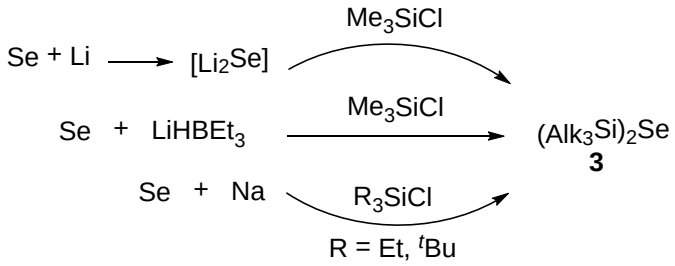


Reducing conditions (*selected examples, references in parentheses*):
- Na/THF or dioxane[6-10]
- Li/ liq. NH_3[11]
- $LiAlH_4$ / dry ether[8, 12]
- $Ru_3(CO)_{12}/PhCH_3/120°C$[13]
- cathodic reduction[14]

Scheme 1. Synthesis of $RSeSiR'_3$ **2a, 2b**

The preparation of butylseleno silanes and oligosilanes was reported by Herzog through the reaction of BuSeLi (obtained from BuLi and Se^0) with differently substituted chlorosilanes $Me_xPh_ySiCl_{(4-x-y)}$ [10].

Bis(trimethylsilyl)selenide $(Me_3Si)_2Se$ (hexamethyldisilaselenane, HMDSS) **3a** is synthesized by treating Se(0) with Li(0) [15,16], or with lithium triethylborohydride [17] followed by addition of the chlorosilane. Silyl selenides with larger groups (Et_3Si, $^tBuMe_2Si$) than Me_3Si were prepared from Na/Se(0) and the suitable chloroalkylsilane (Scheme 2) [18].



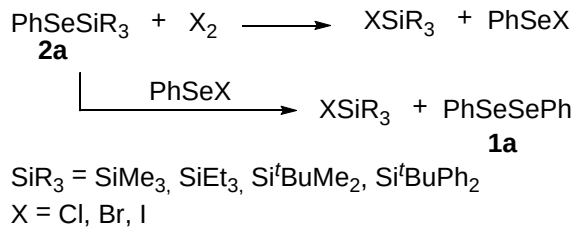
Scheme 2. Preparation of bis(trialkylsilyl)selenides **3**

3. Selenosilanes in chemical synthesis

3.1 Silyl selenides in the nucleophilic substitutions on organic substrates

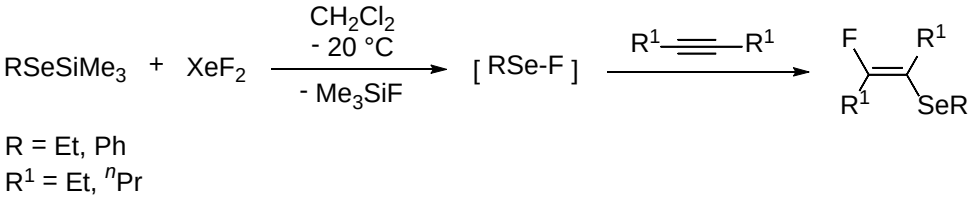
3.1.1 Reaction with halogens or halogenated compounds

The functionalization of the Si-Se bond under mild conditions enabled the nucleophilic transfer of the seleno moiety onto a variety of organic substrates. In this context, (phenylseleno)trimethylsilane **2a** has been widely used in different organic reactions. Detty and Seidler [19] reported the reaction with halogens to afford silyl halides. The reaction with Cl_2 was performed in a solvent (CCl_4 or 1,2-dichlorobenzene), while Br_2 and I_2 were used under neat conditions (Scheme 3).



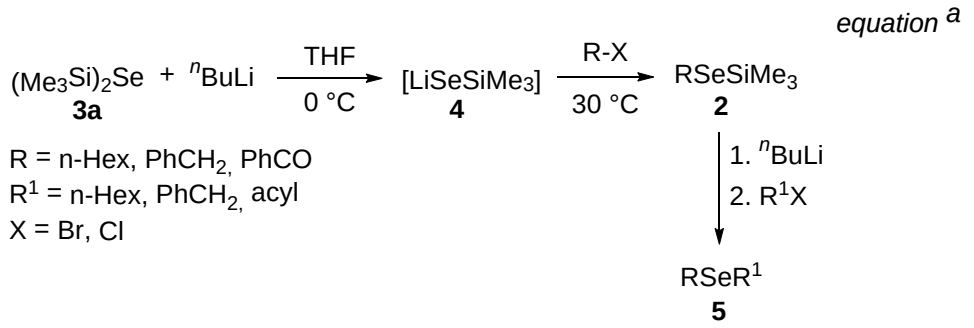
Scheme 3. Reaction of **2a** with halogens

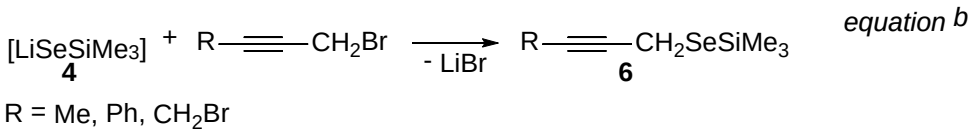
Diphenyldiselenide **1a** was formed as by-product, which can be reused to prepare the (phenylseleno)silane. Trialkylsilyl halides were also obtained by reaction of xenon difluoride with selenosilanes providing RSe-F intermediates, which were then treated with acetylenes to give selenated fluoro-olefines (Scheme 4) [11].



Scheme 4. Reaction of xenon difluoride with silylselenides

The treatment of bis(trimethylsilyl)selenide **3a** with *n*-BuLi, and alkylation with alkyl halides to provide silyl selenides **2** was reported by Segi and co-workers (Scheme 5, *equation a*) [20]. Further reaction of silyl selenides **2** with *n*-BuLi and alkyl or acyl halides gave unsymmetrical selenides **5** (Scheme 5, *equation a*).

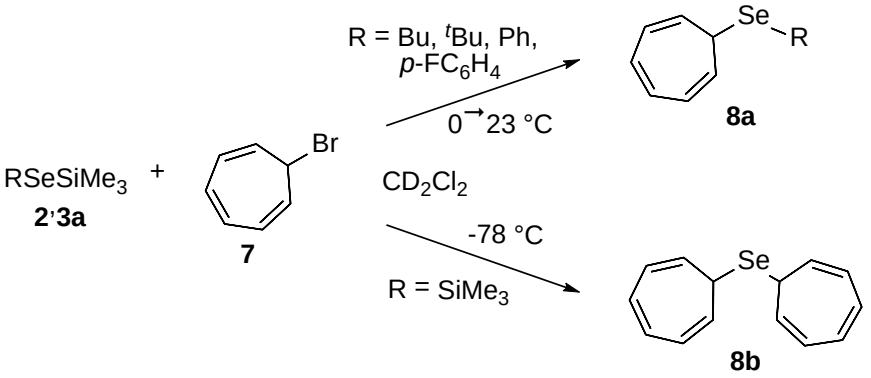




Scheme 5. Synthesis of alkyl silyl selenides **5** (*eq. a*) and propargyl selenoethers **6** (*eq. b*).

Based on a slightly modified procedure, Corrigan described the reaction of [LiSeSiMe3] **4** with propargyl bromides to obtain propargyl selenoethers **6** by nucleophilic substitution (Scheme 5, *equation b*) [21]. Characterization by NMR spectroscopy and mass spectrometry were also provided. Reaction of different selenosilanes **2,3a** with tropylium

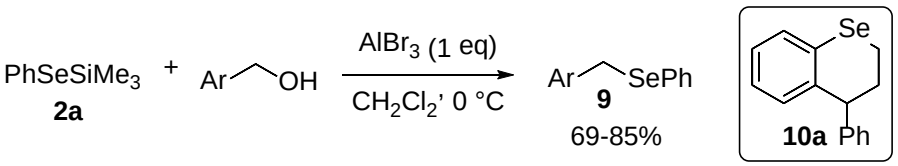
bromide **7** led to 1-cyclohepta-2,4,6-trienyl-selanes **8a,b**, which were characterized by ^{1}H, ^{13}C and ^{77}Se NMR data, including $^{1}J(^{77}Se\text{-}^{13}C)$ measurement. DFT calculations were also reported (Scheme 6) [22].



Scheme 6. Synthesis of 1-cyclohepta-2,4,6-trienyl-selanes **8**

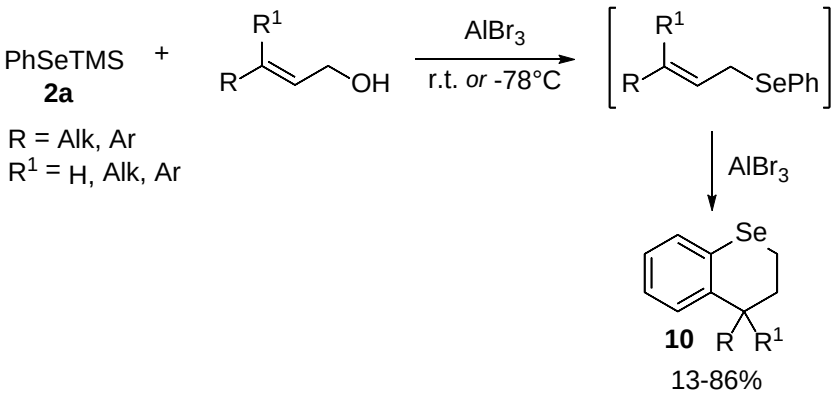
3.1.2 Reaction with benzyl and allylic alcohols

As reported by Abe, Harayama and co-workers, (phenylseleno)trimethylsilane **2a** in combination with a Lewis acid was used as efficient nucleophile in the direct conversion of benzyl alcohols into benzyl selenides **9** (Scheme 7) [8]. Compared to other Lewis acids (*e.g.* ZnI_2, $TiCl_4$, $AlCl_3$, $BF_3{\cdot}Et_2O$), better results were obtained with $AlBr_3$, and higher yields were observed when the $PhSeSiMe_3$:$AlBr_3$ system was used at a 1:1 ratio.



Scheme 7. Synthesis of benzyl selenides **9**

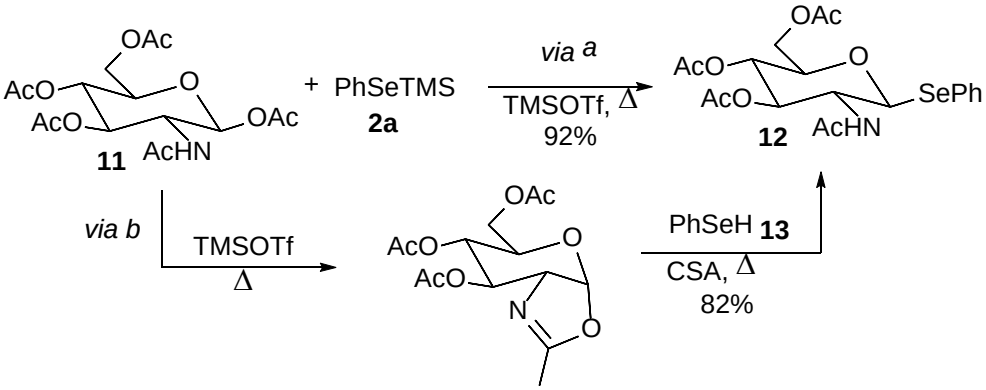
When a non-benzylic hydroxy group was reacted, such as 2-phenyl ethanol, no formation of the expected phenyl(2-phenyl)ethyl selenide was observed, while cinnamyl alcohol afforded the benzoselenane derivative **10a**, formed through a [3,3]-sigma tropic rearrangement of the initially formed selenide $PhSeCH_2CH{=}CHPh$. (Methylseleno)trimethylsilane **2b** behaved as less efficient nucleophile under the same conditions, leading to the corresponding methyl selenides in rather low yields. The behaviour of allylic alcohols was general, as reported by Abe *et al.* upong reacting differently substituted allylic alcohols with $PhSeSiMe_3$/$AlBr_3$ to give selenochroman derivatives **10** through a one-pot reaction (Scheme 8) [23].



Scheme 8. Synthesis of selenochroman derivatives **10**

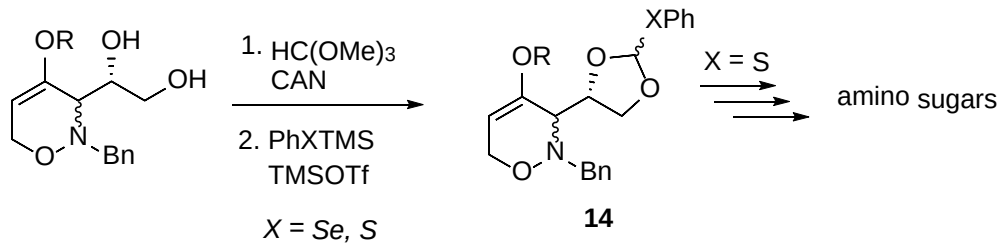
3.1.3 Reaction with acetates and ethers

Selenoglycosides represent important intermediates for the synthesis of carbohydrate derivatives. Gallagher and co-workers reported the direct selenoglycosidation of peracetylated amino sugars **11** (galactosamine, mannosamine and glucosamine derivatives) by treatment with (phenylseleno)trimethylsilane **2a** and silyl triflate, providing the corresponding anomeric selenides **12,** as precursors of α-*C*-glycosides, after substitution of an acetoxy group (Scheme 9, *via a*) [24]. Interestingly, when benzeneselenol **13** was used instead of the selenosilane, the formation of the selenoglycosides **12** required a two-step procedure (*via* oxazoline) (Scheme 9, *via b*).



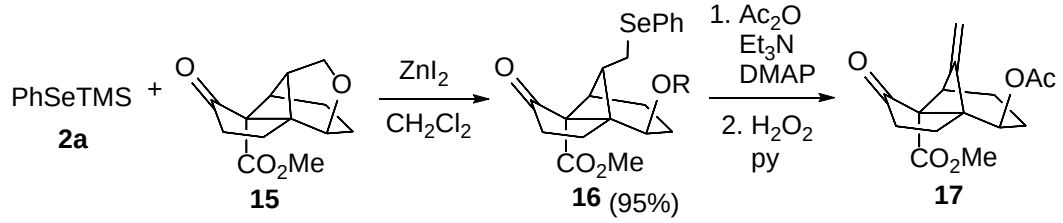
Scheme 9. Direct selenoglycosidation of 2-*N*-acetamido-sugars **11** with $PhSeSiMe_3$ **2a** (*via a*) or PhSeH **13** (*via b*)

In the study for the preparation of amino sugars from 1,2-oxazines, Pfrengle and Reissig reported the reaction of PhSeTMS **2a** (as well as of PhSTMS) to synthesize *syn*- and *anti*-isomers of a 2-phenylseleno (or 2-phenylthio) substituted 1,3-dioxolanes **14** (Scheme 10) [25]. The phenylthio derivative was demonstrated as a precursor of amino sugar derivatives, obtained by a stereodivergent synthesis.



Scheme 10. Synthesis of phenylseleno- and phenylthio-substituted 1,2-oxazine derivatives **14**

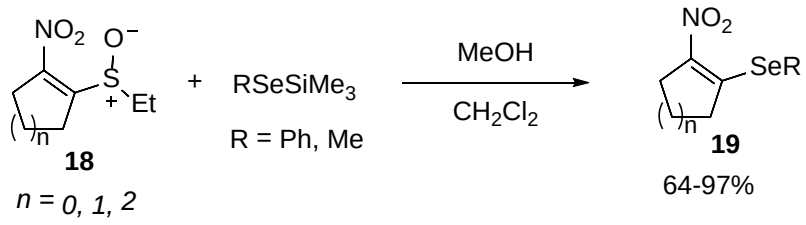
The reaction of a cyclic ether **15** with phenylseleno(trimethylsilane)/$ZnCl_2$, which was converted into the bridged alkene **17** after oxidation and selenoxide elimination, providing the corresponding selenide **16**, was described by Crimmins and Hauser (Scheme 11) [26].



Scheme 11. Phenylseleno derivatives as precursor of exocyclic alkenes

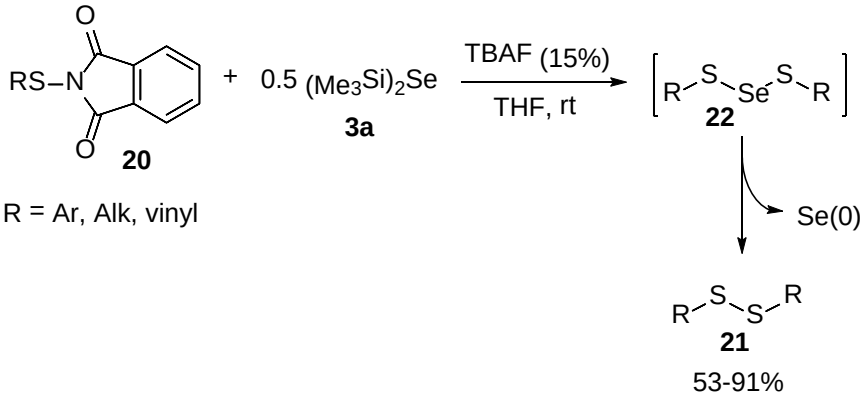
3.1.4 Reaction of selenosilanes with sulfurated organic substrates

β-Heterosubstituted nitroalkenes represent useful synthons in organic chemistry [27]. Taking into account that the sulfinyl group is a good living group, Abe, Harayama and co-workers reported the reaction of β-sulfinyl nitroalkenes **18** with Se-nucleophiles to prepare β-seleno-α,β-unsaturated nitroalkenes **19** [27]. It was found that phenyl selenolate PhSeNa was not able to provide the expected vinyl selenides, while benzeneselenol PhSeH, generated *in situ* from the corresponding (phenylseleno)trimethylsilane **2a** in methanol, was efficient as a nucleophile. Therefore the reaction of unsaturated sulfoxides with $PhSeSiMe_3$ **2a** and MeOH led to the desired phenyl selenides **19** through a clean addition-elimination reaction (Scheme 12). (Methylseleno)trimethylsilane was also efficient to prepare related methyl selenides in good yields.



Scheme 12. Synthesis of β-selenated nitroalkenes **19**

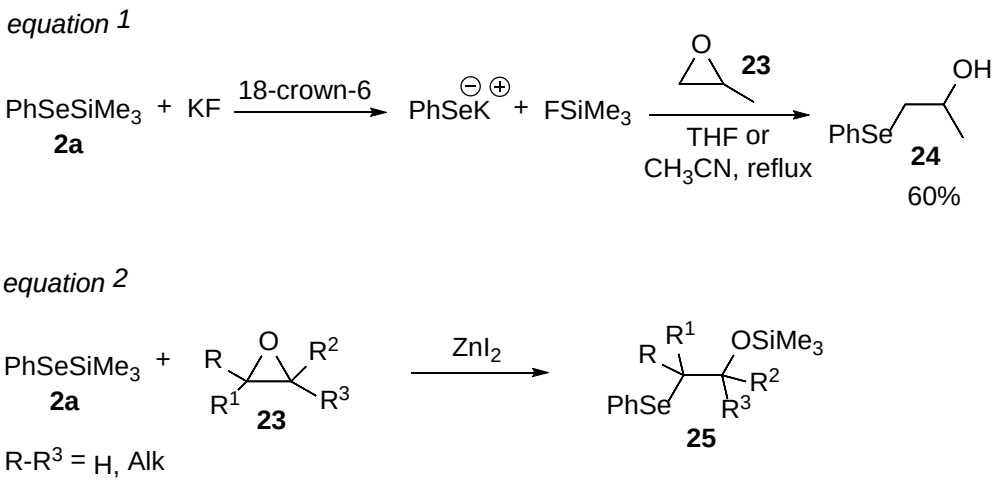
N-Thiophthalimides **20** were used as electrophilic sulfur-transfer reagents with bis(trimethylsilyl)selenide **3a** under TBAF catalysis to give variously functionalized disulfides **21** (Scheme 13) [28]. The formation of a selenotrisulfide **22** could be proposed as a possible intermediate, which then provides the substituted disulfides after elimination of elemental selenium.



Scheme 13. Selenosilane promoted synthesis of disulfides from *N*-thiophthalimides

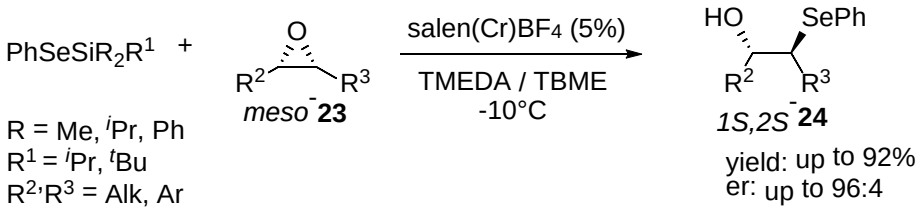
3.1.5 Ring opening of heterocyclic rings (O, S, N) by selenosilanes

Besides the reaction reported by Murai, Sonoda *et al.* [29] on the ring opening of tetrahydrofurans by PhSeTMS, most of the examples with oxygenated heterocycles concern the opening of epoxides by selenosilanes. Epoxides **23**, as well as thiiranes and aziridines, are rather reactive species towardss nucleophiles for the high strain of the three-membered ring. In this context β-hydroxy selenides **24** are interesting compounds which find application as versatile intermediates for a variety of synthetic transformations [30] and for their different chemical and biological properties [31]. The nucleophilic substitution of silyl selenides onto epoxides therefore represents a convenient method to access this class of bifunctionalized molecules. Ring opening of epoxides **23** by (phenylseleno)trimethylsilane **2a**, as a potassium phenylselenide source, in the presence of KF/18-crown-6, was described by Detty to obtain β-hydroxy selenides **24** (Scheme 14, *equation 1*) [32]. The reaction was efficient also with other organic substrates, as α,β-unsaturated carbonyls, lactones, esters and halides. Sonoda and Murai reported the reaction under ZnI_2 catalysis, to provide β-siloxyalkyl phenyl selenides **25** (Scheme 14, *equation 2*) [33].



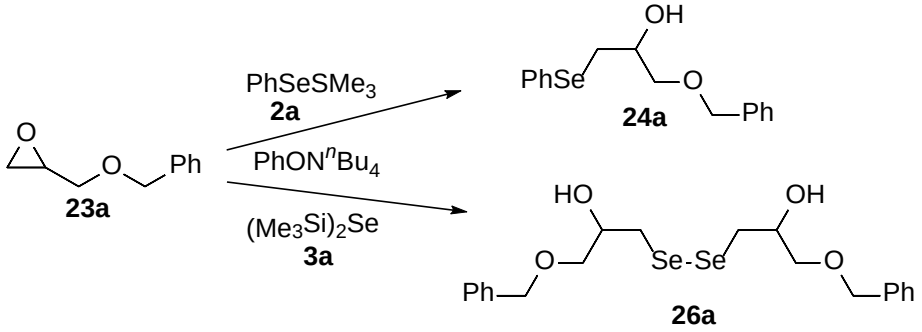
Scheme 14. Reaction of $PhSeSiMe_3$ with epoxides

Enantioselective desymmetrization represents a powerful method to achieve chiral compounds. Organocatalyzed reactions for desymmetrization of epoxides and aziridines with a variety of heteronucleophiles have been quite recently reviewed by Wang [34]. Tiecco and co-workers reported the asymmetric ring opening of *meso*-epoxides (*meso*-**23**) by (phenylseleno)silanes, under salen(Cr)complexes catalysis, to afford various optically active acyclic and cyclic β-hydroxy selenides (*S,S*)-**24** (Scheme 15) [35]. The enantioselectivity of the process depends on the structure of the starting oxirane.



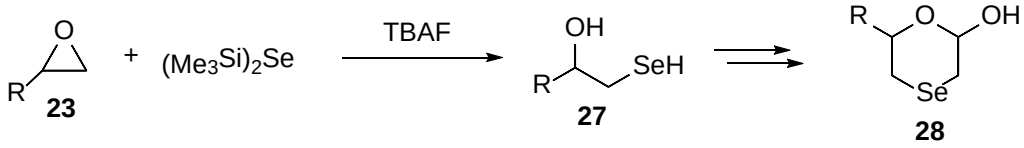
Scheme 15. Enantioselective ring opening of *meso*-epoxides by (phenylseleno)silanes

We reported that (phenylseleno)trimethylsilane **2a** efficiently reacted with benzylglycidol **23a** under $PhON^nBu_4$ catalysis leading to β-phenylselenoalcohol **24a** (Scheme 16), while when bis(trimethylsilyl)selenide **3a** was used, the formation of the corresponding β-hydroxydiselenide **26a** was observed (Scheme 16) [36].



Scheme 16. Ring opening of epoxide **23a** by silyl selenides under tetrabutylammonium phenoxide catalysis

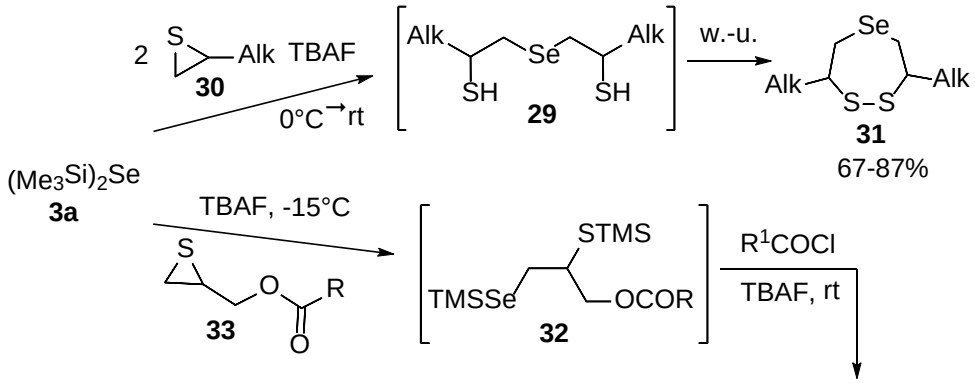
Furthermore, the β-hydroxyselenol **27**, prepared by reaction of epoxides with HMDSS [37] and treated with a suitable bromo ester, behaved as the precursor of six-membered chalcogen-containing heterocycles, such as 6-substituted 2-hydroxy 1,4-oxaselenolanes **28**, obtained as mixture of stereoisomers (Scheme 17) [38].



Scheme 17. Synthesis of six-membered seleno-heterocycles **28**

The reaction of bis(trimethylsilyl)selenide **3a** (HMDSS) was also performed with thiiranes under TBAF catalysis. Depending on the reaction conditions, from thiiranes **30** were regioselectively obtained 3,7-disubstituted-1,2,5-dithiaselenepanes **31** (Scheme 18, *equation 1*) [39], reasonably formed by intramolecular oxidative ring closure of the β-mercapto selenide intermediate **29**. When suitable fatty acid ester substituted thiiranes **33** of glycidol were reacted with HMDSS/TBAF, to afford the bis-silyl intermediate **32**, which were *in situ* treated with fatty acid acyl chlorides, a regioselective one-pot synthesis of mixed sulfur- and selenium isosters of triacyl glycerols **34** was achieved (Scheme 18, *equation 2*) [40]. The physico-chemical properties of these novel fatty acid chalcogeno esters were determined and compared to those of the fully oxygenated triglycerides.

equation 1

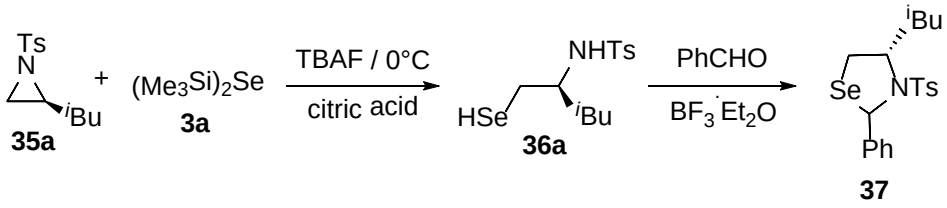


R, R^1 = $(CH_2)_{10}CH_3$, $(CH_2)_{12}CH_3$, $C_{17}H_{33}$*cis*-Δ^9

equation 2

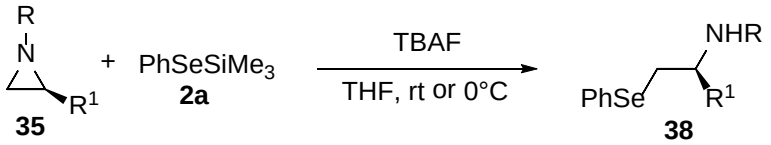
Scheme 18. Synthesis of mixed chalcogeno compounds by ring opening of thiiranes **30, 33** with HMDSS

Our group found that also a *N*-protected aziridine **35a** reacted with HMDSS **3a** to provide a regio- and enantioselective synthesis of the 1,2-amino selenol **36a** (together with the corresponding diselenide) as precursor of the 2,4-disubstituted 1,3-selenazolidine **37** upon treatment with aldehydes (Scheme 19) [41].



Scheme 19. Reaction of bis(trimethylsilyl)selenide with aziridine **35a**

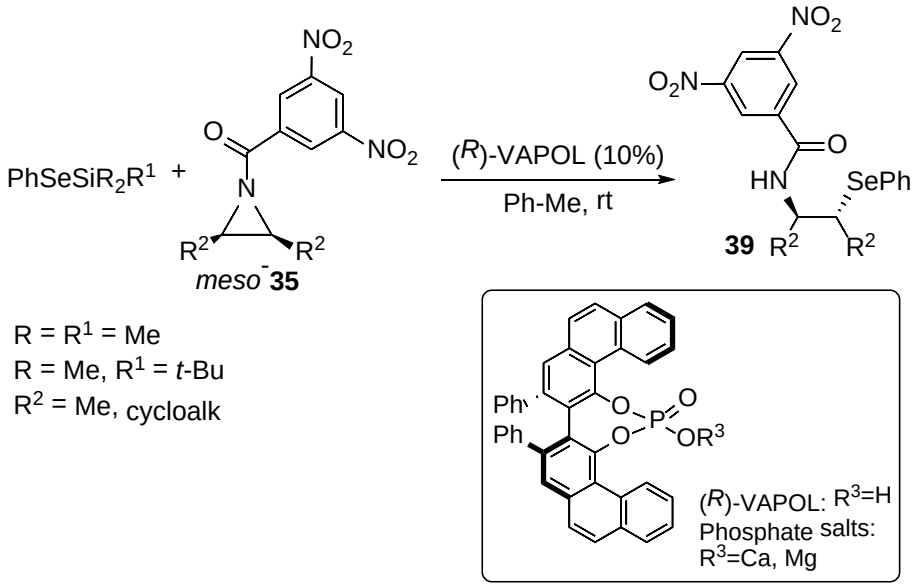
Regio- and enatioselective ring opening of activated (R = Ts, Boc) and unactivated (R = H) aziridines **35** was also described with (phenylseleno)trimethylsilane **2a** under metal-free conditions, enabling the synthesis of chiral enantioenriched *N*-protected and unprotected β-arylseleno amines **38** (Scheme 20) [42].



R = H, Ts, Boc
R^1 = CH_3, *i*Pr, CH_2Ph,

Scheme 20. Ring opening of protected and unprotected aziridines by $PhSeSiMe_3$

In 2011 Della Sala and co-workers reported the first example of organocatalyzed desymmetrization of *meso*-*N*-acylaziridines (*meso*-**35**) with selenosilanes promoted by the chiral phosphoric acid (*R*)-VAPOL leading to β-*N*-acyl-substituted phenyl selenides **39** (Scheme 21) [43].

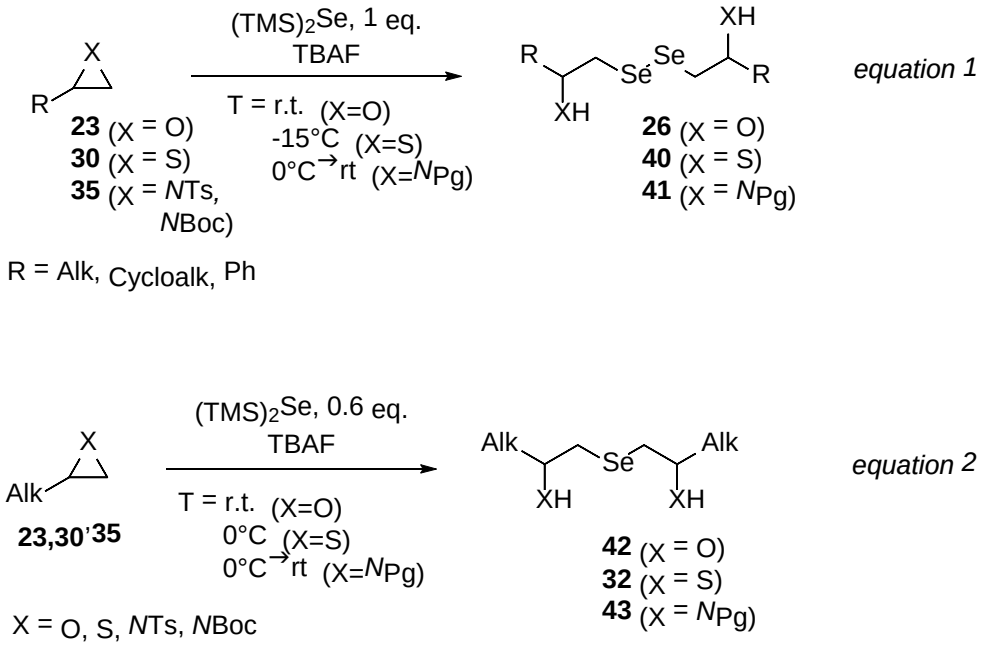


Scheme 21. Organocatalyzed desymmetrization of *meso*-aziridines

The silyl selenide with the more sterically hindered silyl group (SiMe2*t*-Bu) showed a poor reactivity and required longer reaction time (4-12 days) with respect to the (phenylseleno)trimethylsilane. Better results were obtained when a mixture PhSeSiMe3/PhSeH was used, leading to the enantioenriched amine derivatives in shorter time, high yields and high enantioselectivity. However, it was demonstrated that the silyl-nucleophile was necessary, as the reaction of the same aziridine with (*R*)-VAPOL and the selenol alone gave the product with 45% ee (97% ee with PhSeSiMe3/PhSeH). In 2013 the desymmetrization of *meso*-aziridines was re-investigated by Della Sala [44]. It was found that when VAPOL was treated with HCl to have the metal-free chiral phosphoric acid as organocatalyst, the ring opening products were formed as racemates in low yields. On the other hand, using a mixture 1:1 of calcium and magnesium phosphate salts of VAPOL, the amine derivatives were obtained in high yields and high ee. Therefore, the metal-free phosphoric acid is not the effective catalyst to promote the desymmetrization of *meso*-aziridines with silyl nucleophiles. The earlier reported results could be then attributed to the action of Ca and Mg phosphate salts, present as unexpected impurities in VAPOL, which could act through a dual Lewis acid-base activation.

As a further step in the study of the behaviour of silyl selenides, our group reported the regio- and enantioselective ring opening of epoxides **23**, thiiranes **30** and aziridines **35** by bis(trimethylselenide) **3a**, and TBAF as catalyst, providing a convenient and general access to a variety of β-substituted diselenides **26**, **40**-**41** (Scheme 22, *equation 1*) and selenides **42, 32, 43** (Scheme 22, *equation 2*) through a fine tuning of the reaction conditions (ratio of reagents, temperature) [45]. Antioxidant catalytic activity of these compounds was also evaluated, some of them showing a significant glutathione peroxidase (GPx)-like activity [46]. Furthermore, some derivatives proved to be

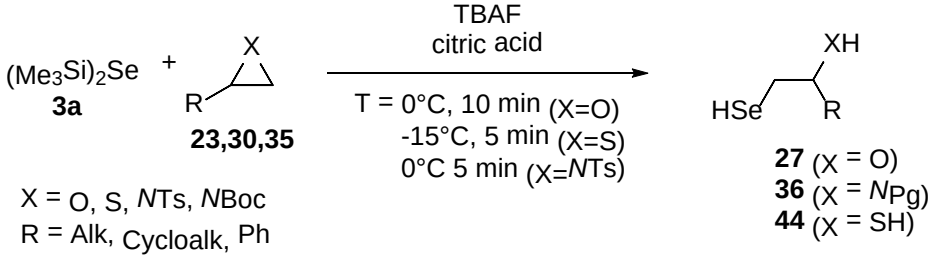
non-toxic, showing no effect on cell viability. The cytotoxicity of selected β-hydroxy selenides was likewise investigated on normal human dermal fibroblasts [47].



Scheme 22. Selenosilanes induced selective synthesis of diselenides and selenides

In addition, the ring opening of three membered heterocycles by (phenylselenotrimethyl)silane was efficiently performed in a variety of ionic liquids, able to act as reaction media and, in some cases, also as catalysts, leading to β-functionalized selenides [48].

Extending the scope of this methodology, when strained heterocycles were reacted with bis(trimethylsilyl)sulfide/TBAF under strictly controlled conditions (equivalents of TBAF, time, T) a direct access to β-hydroxy, β-mercapto and β-amino alkyl selenols **27,36,44** was obtained, arising from a regioselective nucleophilic attack on the less hindered side of the heterocycle (Scheme 23) [37]. Interestingly, the ring-opening reaction of enantioenriched substrates provided the synthesis of chiral non-racemic selenols. Taking into account their propensity to be oxidized to diselenides, the β-substituted selenols displayed an unexpected stability, which can be attributed to hydrogen bond interaction between the selenol and the hydroxy moieties, as indicated by *ab-initio* DF calculations on selected model systems.

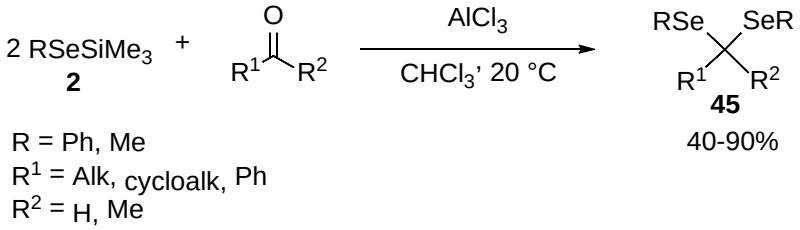


Scheme 23. Sinthesis of β-substituted selenols

3.2 Reaction with C=O containing compounds

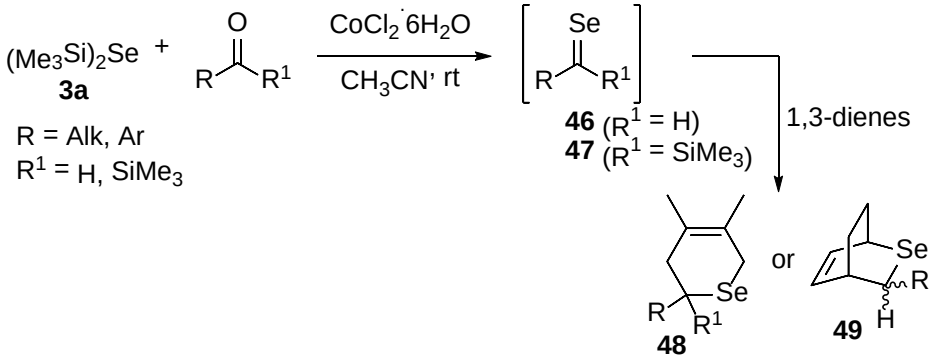
3.2.1. Reaction with aldehydes and ketones

Selenosilanes were efficiently reacted with carbonyl compounds to provide selenoacetals **45**, which are used as valuable reagents in organic reactions. Krief *et al.* reported the selenoacetalization of aldehydes and ketones with selenosilanes under acidic conditions (Scheme 24) [49]. Based on the oxygenophilic character of silicon, silylselenides were expected to react without any catalysts. Differently from what observed with the sulfurated analogues - $RSSiMe_3$ (and also with selenoboranes), it was found that the cleavage of the Se-Si bond required an acid catalyst to give the selenoacetalization. Better results were obtained by *in situ* formation of $RSeSiMe_3$ (prepared by diselenide/$LiAlH_4$/$ClSiMe_3$) followed by addition of the carbonyl compound under Lewis acid catalysis.



Scheme 24. Synthesis of selenoacetals and selenoketals

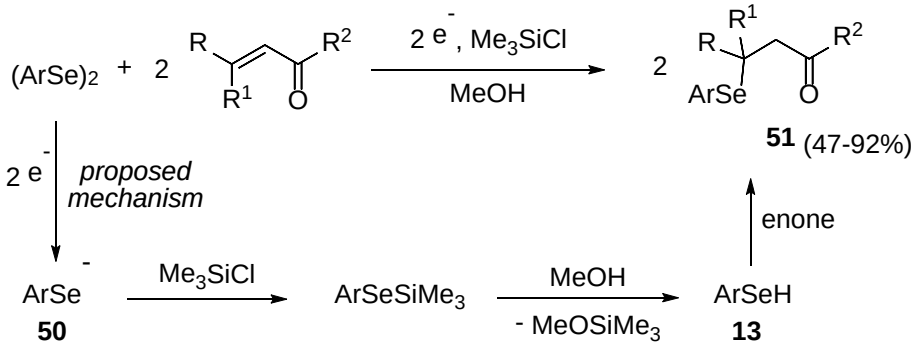
The use of silylselenides avoids employing selenols, which are known to be rather unstable. This is important in particular for the methylselenol, also because its high volatility and bad smell. Our group reported the reaction of bis(trimethylsilyl)selenide **3a** with aldehydes and acylsilanes, which in the presence of $CoCl_2 \cdot 6H_2O$ afforded selenoaldehydes **46** and selenoacylsilanes **47**, isolated as Diels-Alder cycloadducts **48,49** (Scheme 25) [50].



Scheme 25. Synthesis of selenoaldehydes and selenoacylsilanes

Selenenylation of α,β-unsaturated carbonyls by electrolysis with diaryl diselenides and chlorotrimethylsilane was reported by Torii and co-workers [51]. Aryl selenide

anions **50** are electrochemically generated using Pt electrode in a methanolic solution and treated with the enone, the diselenide and Me_3SiCl (Scheme 26). The reaction affords the β-seleno substituted carbonyl compounds **51** through the mechanism proposed in the Scheme 26. Aryl selenols **13** are *in situ* formed, precursors of the selenated adducts **51**. Furthermore, the addition of the chlorosilane was crucial, since without this reagent, or using less than 1 equivalent, only starting material was recovered.

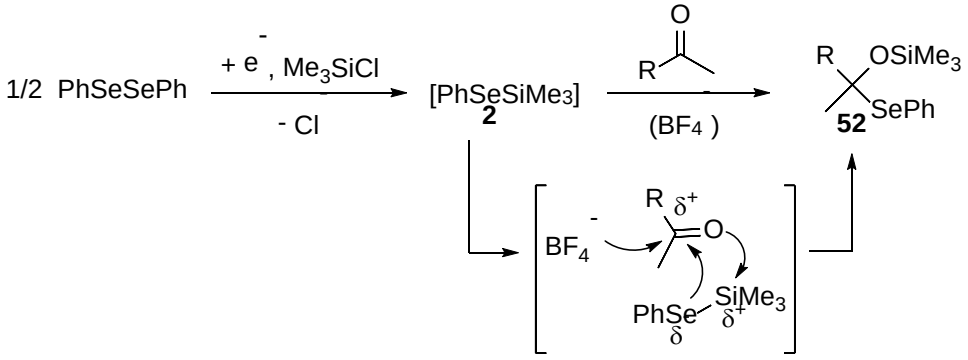


Ar = Ph, *p*-$MeOC_6H_4$

Enone = Mesityl oxide, 3-methyl-2-cyclopentenone, 2-methyl-2-cyclopentenone, carvone, pulegone, 1-methoxycarbonyl-1-cyclohexene

Scheme 26. Aryl selenenylation of enones with diselenides/Me_3SiCl by electroreductive procedure

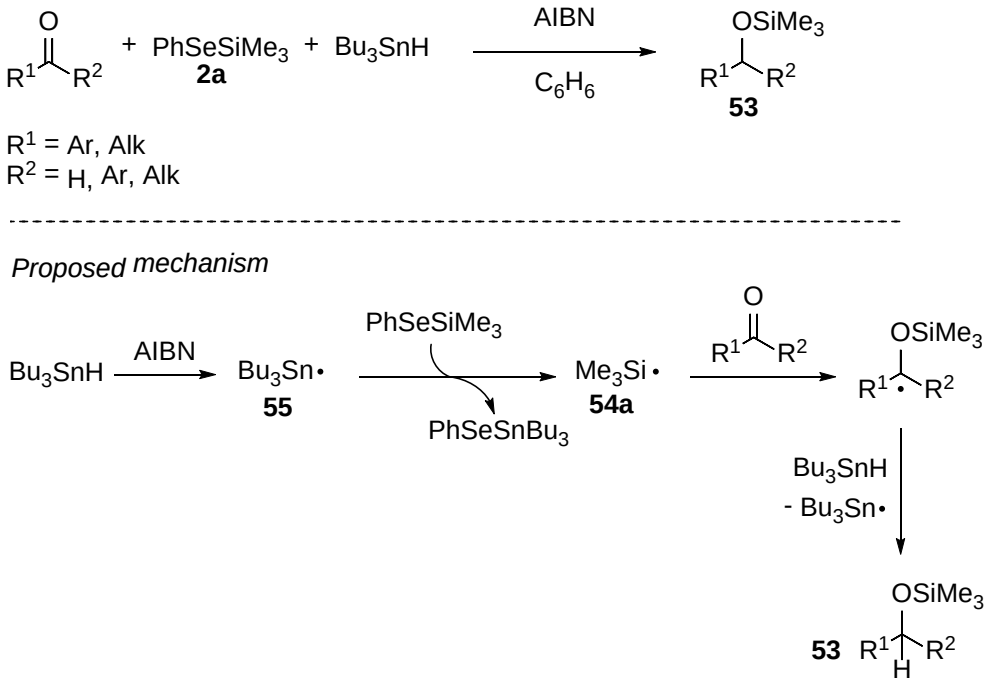
A similar reaction was reported by Jouikov *et al.* dealing with the cathodic reduction of diselenides (and disulfides) to form $PhSe^-$ (or PhS^-) anions, which in the presence of trimethylchlorosilane gave the corresponding (trimethylsilyl)selenides **2** (and sulfides) in good yields (Scheme 27) [14]. The treatment with carbonyl compounds resulted in the formation of silyl ethers **52** of hemiseleno- (or hemithio-) ketals and acetals. It was also found that the functionalization of carbonyls was preferably performed using silylselenides in a one pot procedure, without their isolation.



Scheme 27. Electrochemical reduction of diphenyldiselenide in the presence of Me_3SiCl and carbonyls

When a mixed dichalcogenide PhSSePh was reduced under electrolytic conditions, the rate of the S_N2 reaction of the $PhSe^-$ anion on the Si-Cl bond was faster than the attack of the PhS^- anion. This is in agreement with the stronger nucleophilic character of the selenolate anion compared to the thiolate, due to the larger size of Se, and therefore the greater localization of the negative charge on Se in the $PhSe^-$ species.

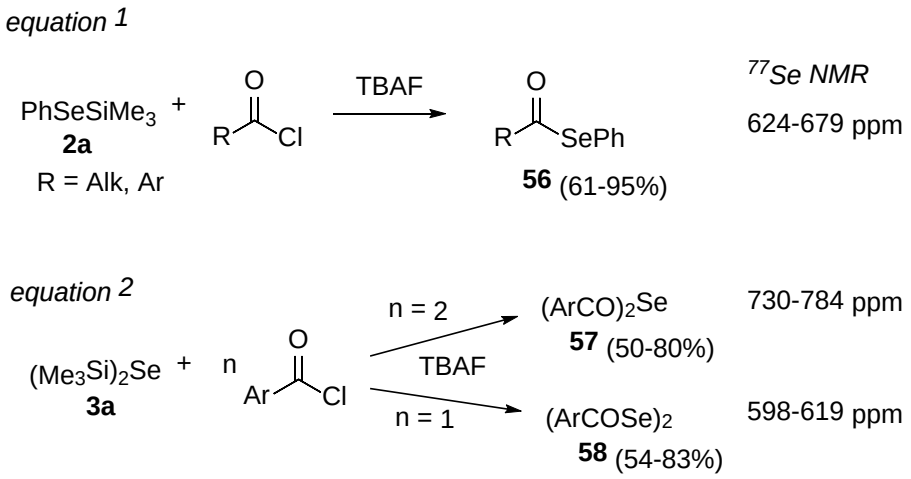
Sonoda and co-workers reported the hydrosilylation of carbonyl compounds under radical conditions to obtain silyl ethers **53**, formed through the treatment of carbonyls with (phenylseleno)trimethylsilane **2a**, tributylstannyl hydride and AIBN (Scheme 28) [52]. On the basis of the proposed mechanism, a silyl radical **54a** is *in situ* formed by the activation of Se-Si bonds with the stannyl radical **55**.



Scheme 28. Hydrosilylation of carbonyls with the $PhSeSiMe_3/Bu_3SnH/AIBN$ system

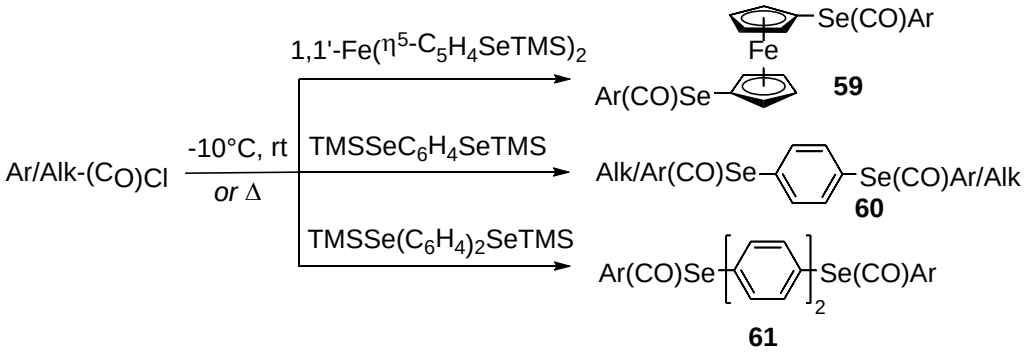
3.2.2. Reaction with acyl chlorides

Silyl selenides were also reacted with acyl chlorides leading to a selective synthesis of selenolesters, selenoanhydrides and diacylselenides depending on the type of the selenosilane used and on the stoichiometric ratio of the reagents. Treatment of acyl chlorides, under TBAF catalysis, with (phenylseleno)trimethylsilane **2a**, led to selenolesters **56** (Scheme 29, *equation 1*), while when bis(trimethylsilyl)selenide **3a** was reacted in 2:1 or 1:1 ratio a selective access to selenoanhydrides **57** or diacyl diselenides **58**, respectively, was achieved (Scheme 29, *equation 2*) [53]. ^{77}Se NMR chemical shifts were also reported, showing typical values for these classes of selenated compounds.



Scheme 29. Selective access to selenolesters **56**, selenoanhydrides **57** and diacyl diselenides **58**

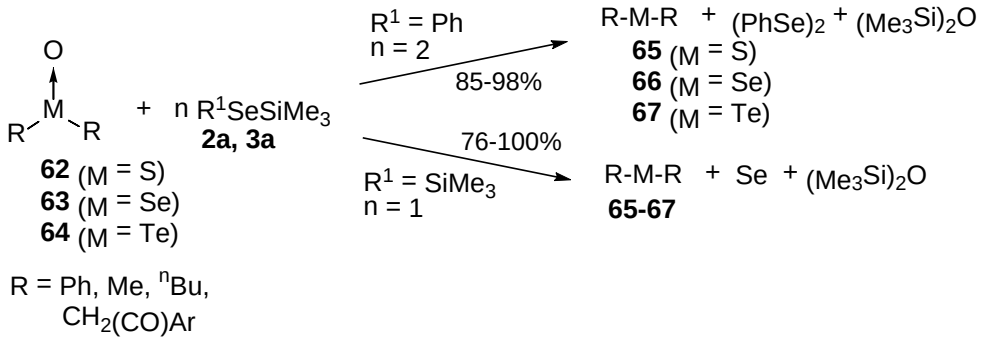
Besides (phenylseleno)trimethylsilane, Corrigan and Taher reported the reaction of a variety of acyl chlorides with organoselenosilanes containing two TMSSe- groups, as 1,1′-Fe(η^5-$C_5H_4SeTMS)_2$, 1,4-TMSSe-C_6H_4-SeTMS and 4,4′-TMSSe-$(C_6H_4)_2$-SeTMS to afford ferrocenyl- and alkyl/aryl-diselenoesters **59-61** (Scheme 30) [54].



Scheme 30. Synthesis of ferrocenyl- and alkyl/arylselenoesters **59-61**

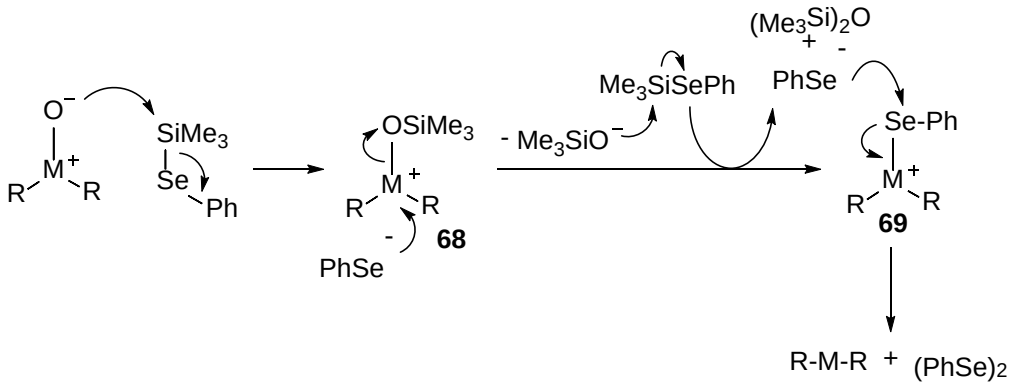
3.3 Reduction of oxides of the Group 16 elements (S, Se,Te)

Detty reported the use of (phenylseleno)trimethylsilane **2a** [55] and bis(trimethylsilyl)selenide **3a** [16] to reduce under mild conditions sulfoxides **62**, selenoxides **63** and telluroxides **64** to the corresponding sulfides, selenides and tellurides **65-67** in high yield (Scheme 31).



Scheme 31. Reduction of S-, Se- and Te-oxides by selenosilanes

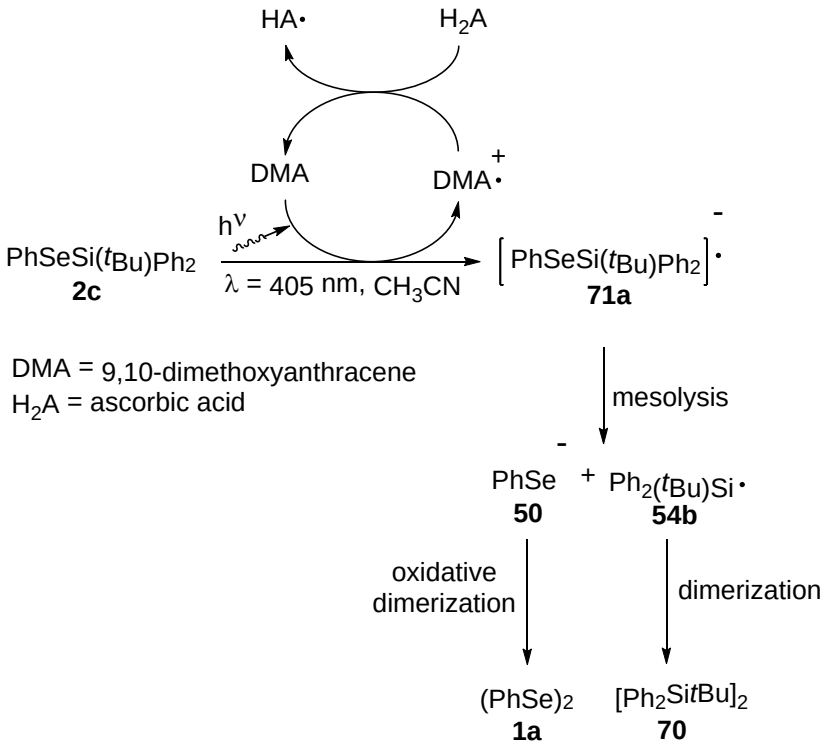
The method is compatible with different functional groups, as ketones, phenols, alcohols, olefins, sulfones and nitro derivatives. Based on the proposed mechanism, onium species $R_2M^+(OSiMe_3)$ **68** and $R_2M^+(SePh)$ **69** should be involved in this transformation, as depicted in the Scheme 32.



Scheme 32. Plausible mechanism for the reduction of chalcogen-oxides

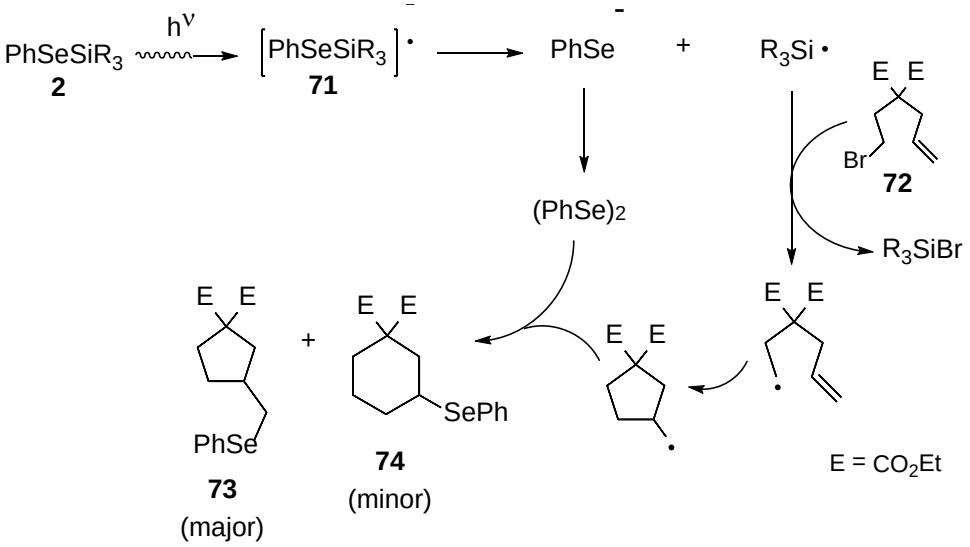
3.4 Reactivity of selenosilanes under radical conditions

Pandey, Mittal and co-workers investigated the PET (photosensitized electron transfer) promoted activation of selenosilanes to afford radical ions, as well as their fragmentation (mesolysis). *t*-Butyldiphenyl(phenylseleno)silane **2c** was selected for its appreciable stability to study the PET reductive activation of Se-Si bonds using a suitable photosystem, to generate the radical anion **71a** (Scheme 33) [56,57].



Scheme 33. PET activation of **2c** to radical anion **71a** and formation of dimers by mesolysis

The formation of the dimers **1a**,**70** could be rationalized through the mesolysis of the primary radical ion **71a** to form the phenylselenide anion **50** (490 nm) and the silyl radical **54b** (440 nm), which undergo to dimerization. It can be assumed that the fragmentation of **71a** is driven by the electronegativity difference between silicon and selenium. This efficient dissociation allowed to consider selenosilanes as silyl radical equivalents, whose chemical behaviour in bimolecular group transfer (BMGT) radical reactions was studied, as well as in intermolecular radical chain transfer addition reactions [56]. For example, for evaluating the use of selenosilanes for BMGT radical reactions, a mixture of compounds **2** and **72** was irradiated together with DMN - 1,5-dimethoxynaphthalene (as electron donor) and ascorbic acid (as co-oxidant), which provided the cyclization products **73** (major) and **74** (minor) (Scheme 34).

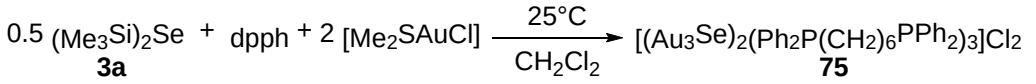


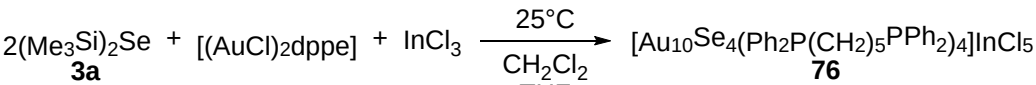
Scheme 34. Selenosilanes as BMGT reagents in cyclization reactions

The reaction was extended to the cyclization of bromoallyl ethers and bromopropargyl ethers as well providing substituted tetrahydrofuran derivatives.

3.5 Metal-selenium cluster compounds

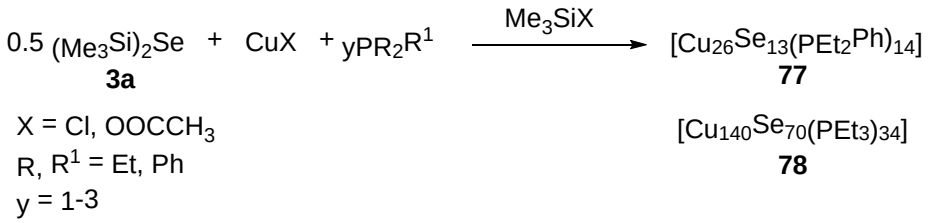
Fenske and co-workers reported the reaction of bis(trimethylsilyl)selenide **3a** with a phosphane ligand (*e.g.* dpph = $Ph_2P(CH_2)_6PPh_2$ or dppe = $Ph_2P(CH_2)_5PPh_2$) and [Me_2SAuCl] to prepare different gold complexes with chalcogenide bridges, as for example complexes **75** and **76** in Scheme 35 [58]. The structure of some gold-selenium compounds was determined by X-ray diffraction. For instance, complexes **75** and **76** crystallize in the monoclinic space group P21/c and C2/c, respectively, with four molecules per unit cell.





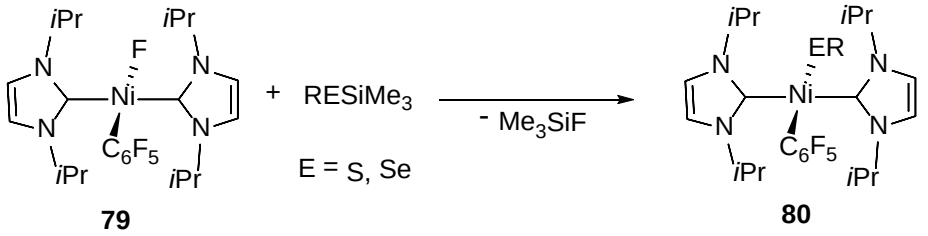
Scheme 35. Examples of preparation of some gold-selenium complexes with selenosilanes

Fenske investigated also the thermal properties (TGA, DSC) of two series of copper selenide clusters, as among others structures **77**, **78** depicted in the Scheme 36, obtained by reaction of $(Me_3Si)_2Se$ with CuX and PEt_2Ph or PEt_3 [59].



Scheme 36. Examples of synthesis of copper selenide cluster molecules

Within the study of the the C–F activation in Ni-complexes, Radius *et al*. investigated the selective replacement of the fluoride ligand by a variety of nucleophiles in the *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] complex **79**, which was selected as a model compound. The reaction with silyl chalcogenides (RESiMe$_3$, E = S, Se; R = Ph, ^{n}Pr, ^{i}Pr) provided the corresponding sulfurated and selenated complexes **80** with elimination of fluorotrimethylsilane, favoured by the formation of the strong Si-F bond (Scheme 37).

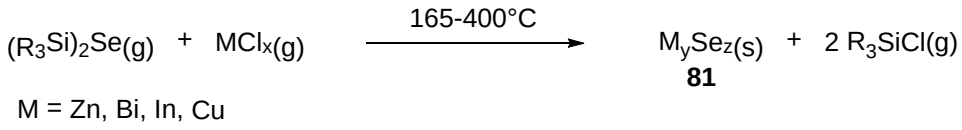


Scheme 37. Reaction of complex *trans*-**79** with silyl chalcogenides

The complexes with ^{n}Pr or ^{i}Pr groups adopt a square-planar geometry, as evidenced by single-crystal X-ray analysis. It was found that the Ni-S bond length is slightly shorter than the distance in the related complex [Ni(P^{n}Bu$_3$)$_2$(SC$_6$F$_5$)(C$_6$F$_5$)], as well as the Ni-Se distance resulted rather unusual.

3.7 Silyl selenides as Se-precursors for Atomic Layer Deposition (ALD)

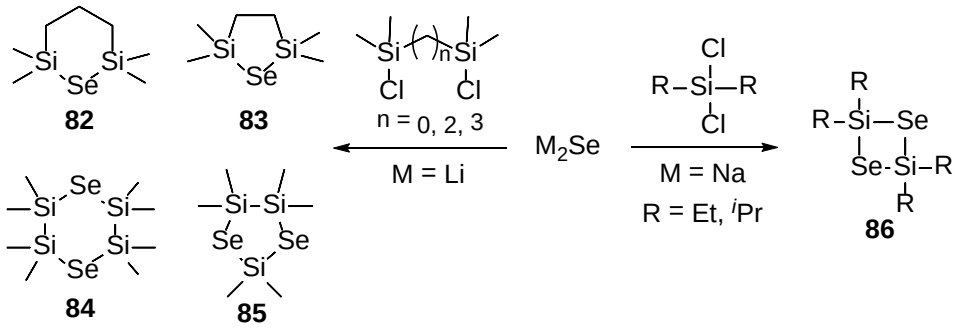
In 2009 Pore and co-workers reported the use of bis(trialkylsilyl)selenides (as well as of silyl tellurides) as precursors to obtain metal selenides **81** for atomic layer deposition (ALD) [60], a useful technique to deposit ultra-thin films of a few nanometres in a precise and controlled way for various applications, as for example semiconductor and other nanoscale devices [61]. Silyl selenides are volatile, thermally stable and very reactive towards metal compounds, thus suitable to produce selenated materials. Compared to alkyl selenides, selenosilanes react more efficiently for the elimination of ligands of the metal precursors. This behaviour can be ascribed to the formation of a bond between silicon (hard Lewis acid) with the harder base, upon exchange reaction with metal chlorides. High temperatures are necessary to have sufficient evaporation of the metal precursors (Scheme 38).



Scheme 38. Reaction of silyl selenides with metal chlorides

Different combinations of metal precursors and silyl compounds can be used. Besides metal chlorides, growth experiments using Cu(II) pivalate and $(Et_3Si)_2Se$ to obtain copper selenides showed that the stoichiometry between CuSe and Cu_2Se could be controlled, depending on the deposition temperature.

Bureš and co-workers investigated the behaviour of silyl selenides $(R_3Si)_2Se$ bearing different alkyl groups on the silicon (R = Me, Et, ^{i}Pr, ^{t}BuMe$_2$), evidencing a good volatility and stability. The trimethylsilyl substituted silylselenide, in combination with $MoCl_5$ as Mo precursor, was efficiently used for deposition of $MoSe_2$, while the *tert*-butyldimethylsilyl derivative evidenced no atomic layer deposition, because its significant stability [62]. The synthesis of various cyclic silylselenides **82-86,** obtained by *in situ* treatment of M_2Se (M = Li, Na) with suitable chlorosilanes, was also reported by Bureš *et al*. (Scheme 39) [63].



Scheme 39. Preparation of cyclic silylselenides

Their thermal behaviour was studied by TGA and DSC, showing by TGA a very good volatility with complete evaporation, while DSC measurements evidenced evaporation without decomposition. The thermal properties are mainly depending on the ring size and the number of Si/Se atoms in the ring. The cyclic selenosilanes were evaluated as Se precursors for atomic layer deposition, combined with $MoCl_5$, some of them evidencing a sufficient fast reaction with metal precursors to permit their application in ALD.

4. Conclusions

Selenated compounds represent an intersting class of molecules for their different applications in many fields, as organic chemistry, inorganic chemistry, materials science, medicinal chemistry, and biology. Therefore methods which allow a mild and general preparation of selenium containing compounds have received an incresing interest. In this regard, selenosilanes were demostrated as efficient reagents to introduce selenated

groups on a variety of substrates. The mild functionalization of the Si-Se bond allows silyl selenides to behave as synthetic equivalents of the analogous hydrogenated compounds, but more stable, less toxic and easier to handle. Thus, differently substituted selenosilanes found a growing number of applications in organic synthesis as versatile nucleophiles towards a variety of organic substrates, being able to undergo chemo-, regio- and stereoselective tranformations. Furthermore, selenosilanes are also used in reducing processes and radical reactions, as well as in the preparation of metal clusters and as Se-precursors of metal selenides for atomic layer deposition.

Author Contributions: Conceptualization, A.C. and D.T.; literature curation, A.C. and D.T.; writing-original draft preparation, A.C. and D.T.; revision of the manuscript: A.C. and D.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest

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