Nucleophilic Chalcogen-containing Reagents

XX Nucleophilic chalcogen containing reagents

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ABSTRACT/WEB SUMMARY

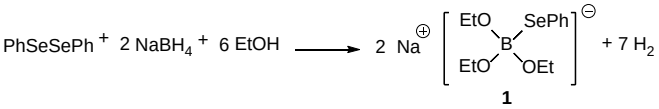
Nucleophilic sulfur- and selenium-containing reagents include versatile classes of compounds with broad application in organic and inorganic synthesis. In this chapter, synthetic applications of ‘unconventional’ chalcogen nucleophilic reagents, containing chalcogen-boron, chalcogen-aluminium, chalcogen-silicon, and chalcogen-tin bonds, are reviewed. Focusing on more recent developments, reactions of these species with a variety of electrophilic partners is presented. Particular emphasis is devoted to advances in the field achieved over the last two decades.

X.1 Introduction

The use of sulfur and selenium nucleophiles in organic and inorganic synthesis has been widely investigated. A broad range of functional group transformations can be accomplished by using nucleophilic chalcogen reagents. Additionally, biologically and synthetically valuable sulfur- and selenium-containing compounds have been prepared by using such nucleophilic species. The synthesis and the reactivity of nucleophilic sulfur and selenium reagents have already been reviewed in books and books chapters.[1,2] Metal thiolates and selenolates – which represent the commonly employed chalcogen nucleophilic reagents – have been comprehensively discussed therein. This chapter will focus on 'unconventional' nucleophilic sulfur and selenium reagents containing chalcogen-boron, chalcogen-aluminium, chalcogen-silicon, and chalcogen-tin bonds. Features of synthesis and reactivity of such species will be presented with particular emphasis on recent advances in the field, surveying the literature between 2000 and 2021.

X.2 Nucleophilic species containing the chalcogen-boron bond

Sulfur and selenium boron species have emerged as versatile reagents for the formation of C-S and C-Se bonds. The reduction of diphenyl diselenide with sodium borohydride – which is one of the easiest and most widely used procedures for the generation of nucleophilic selenium species – affords the sodium selanylborate reagent **1** (Scheme X.1) as an exquisite nucleophile in a wide array of transformations, such as the conversion of epoxy ketones and esters into the corresponding β-hydroxy ketones and esters.[3] This Se-mediated functional group interconversion has also been exploited for the construction of the WXYZ ring of maitotoxin and the HIJK ring of brevisulcenal-F.[4]



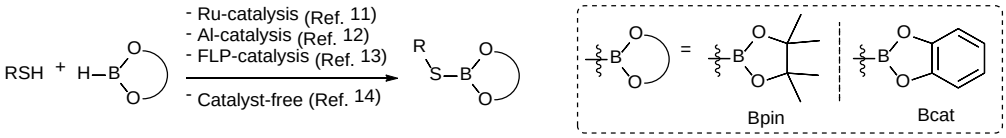
Scheme X.1. Formation of sodium selanylborate **1**.

Sulfanylboranes and selanylboranes are used in a variety of organic reactions including additions, substitutions, and nucleophilic ring opening reactions. For example, the Pd-catalysed thioboration of terminal alkynes with 9-(organylsulfanyl)-9-borabicyclo[3.3.1]nonane derivatives provide the corresponding addition products with high regio- and stereo-selectivity.[5] Tris(phenylseleno)borane and tris(methylseleno)borane [$(PhSe)_3B$ and $(MeSe)_3B$, respectively] react with alkynes through a radical mechanism affording the corresponding (*Z*)-vinyl selenides with high stereoselectivity. The reaction is initiated by oxygen and can be employed for the synthesis of functionalised heterocycles and carbocycles *via* radical cyclisation of enynes.[6] The use of selanylboranes in nucleophilic ring opening reactions (NROR) of epoxides[7] and in the conversion of carbonyl compounds into the corresponding selenoacetals[8] have also been described.

Sulfanylboranes are commonly prepared from thiols or metal thiolates and haloboranes. Disulfides and aryldiiodoboranes can be employed for the synthesis of sulfanylboranes. Similarly, the preparation of selanylboranes generally relies on the reactivity of selenols, selenolates, and diselenides with haloboranes. The synthesis and the reactivity of sulfanylboranes and selanylboranes have been reviewed in 2005 by Habben and Kaufmann.[9] Therefore, this chapter will not focus on topics covered therein.

Besides sulfanylboranes and selanylboranes, owing to their peculiar reactivity and significant synthetic potential, thioborates [$R^1S{-}B(OR^2)_2$] and selenoborates [$R^1Se{-}B(OR^2)_2$] are attracting considerable interest among organic chemists. Thioborates are used as precursors of a wide array of sulfur-containing biologically active compounds.[10] Thioborates are commonly prepared through the dehydrocoupling of thiols with boranes. Both metal-catalysed and metal-free approaches have been reported for the formation of S–B bonds (Scheme X.2). For example, the Nolan's ruthenium-catalysed methodology enables the synthesis of a broad range of thioborates in excellent yield.[11] A number of thioborates can also be prepared by using an aluminium dihydride catalyst.[12] An alternative approach towards thioborates relies on the use of the frustrated Lewis pair (FLP) $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ as catalyst for the dehydrogenative coupling of thiols with pinacolborane (HBpin).[13] A mild

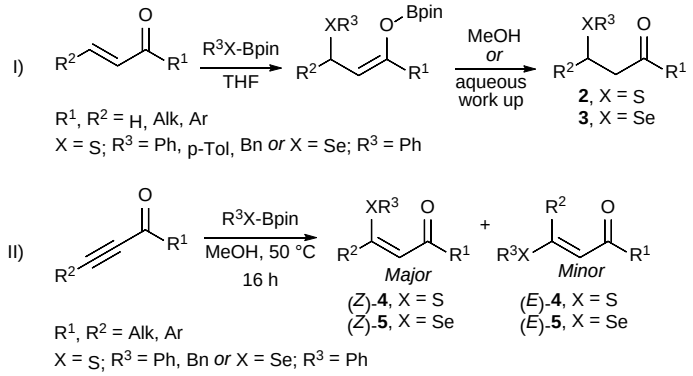
catalyst-free procedure for the formation of S─B bonds, proceeding *via* Lewis acid-base adducts featuring a hydridic B─H group and an acidic S─H moiety in close proximity, has also been reported.[14]



Scheme X.2. Synthesis of thioborates.

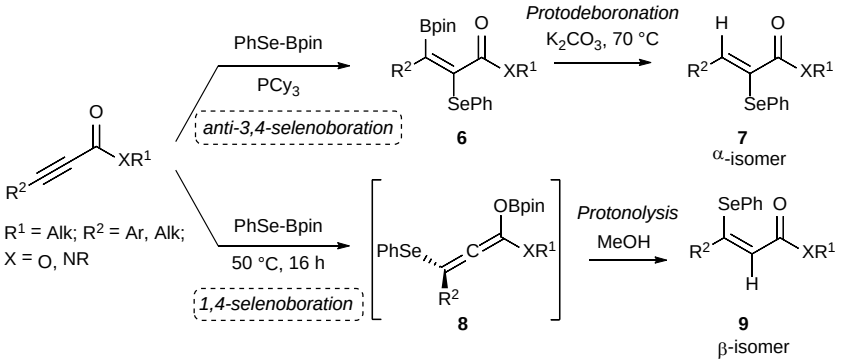
Thioborates are employed in the thioboration of α,β-unsaturated aldehydes and ketones. Owing to its Lewis acid properties, the boryl moiety of RS─Bpin interacts with the carbonyl oxygen of the substrate promoting the nucleophilic attack of the RS unit onto the α,β-unsaturated compound, which leads to 1,4- or 1,2-addition product depending on the nature of the substrate. Both 1,4- and 1,2-thioboration products are converted into β-sulfido carbonyl derivatives **2,3** upon treatment with methanol; the 1,2-thioborane intermediate plausibly undergoes rearrangement during the in situ protic work up.[15] PhSeBpin, prepared by Rh-catalysed dehydrogenative borylation of benzeneselenol (PhSeH) with pinacolborane, reacts efficiently with α,β-unsaturated carbonyl derivatives under catalyst-free conditions to afford the corresponding conjugate addition products (Scheme X.3, equation I). Interestingly, additions of PhSeBpin to alkenes do not require the use of co-solvents, such as MeOH.[16]

The “pull-push” effect of the boryl moiety of chalcogenoborates R^3X─Bpin (X = S, Se) also enables the delivery of chalcogen-containing groups onto electron-poor alkynes. Ynones react with thioborates and selenoborates under catalyst-free conditions providing good yield of the corresponding vinyl sulfides and selenides. The conjugate addition occurs with good stereoselectivity leading preferentially to (*Z*)-alkenyl chalcogenides **4** and **5** (Scheme X.3, equation II). Reactions using selenoboranes generally exhibit a higher *Z*/*E* ratio compared to the related additions with thioboranes.[17]



Scheme X.3. Addition of chalcogenoboranes to α,β-unsaturated carbonyl compounds.

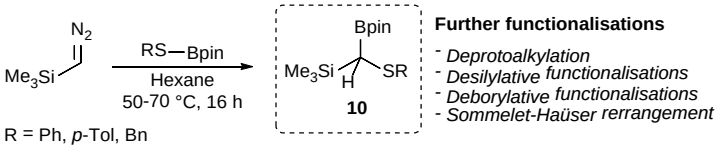
PhSe-Bpin also reacts with α,β-acetylenic esters and amides to afford the corresponding α- and β-vinyl selenides as a function of the reaction conditions (Scheme X.4). Products **6**, arising from the *anti*-3,4-selenoboration path, are formed upon treatment of α,β-acetylenic esters and amides with PhSe-Bpin in the presence of PCy_3. Such products can be easily converted into the corresponding α-hydroselenated derivatives *via* protodeboronation using K_2CO_3. On the other hand, when PhSe–Bpin is reacted with α,β-acetylenic derivatives at 50 °C under catalyst-free conditions the reaction proceeds through 1,4-selenoboration to afford intermediates **8**, which undergo protonolysis providing β-seleno- α,β-unsaturated derivatives **9** (Scheme X.4).[18]



Scheme X.4. *anti*-Selenoboration of alkynes.

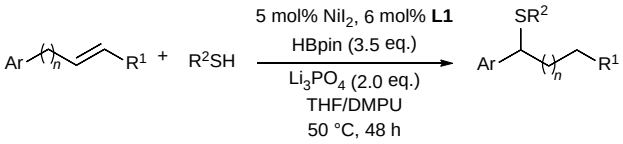
Thioborates have also been used in reactions with trimethylsilyldiazomethane (Me_3SiCHN_2) to afford polyfunctionalised derivatives **10**. The insertion of the diazo compound into the B–S σ bond of thioborates provides access to compounds bearing a polysubstituted sp^3 carbon

[H–C(SR)(Bpin)($SiMe_3$)] which can be further subjected to a range of base-assisted transformations, including deborylative and desilylative C–C bond forming strategies (Scheme X.5).[19]



Scheme X.5. Synthesis of polysubstituted functionalisable one-carbon fragments **10**.

Thioborates can be used as thiolation reagents in the Ni-catalysed hydrothiolation of alkenes and alkynes. The reaction enables the remote C–H thiolation of different alkenes bearing a variety of remote aryl rings *via* a NiH-catalysed migratory hydrothiolation mechanism. Such a reaction can be efficiently performed using thiols as thiolation regents in the presence of pinacolborane (HBpin), as reported in the Scheme X.6. The mechanism is demonstrated to proceed *via* RS–Bpin species, generated *in situ* from the thiol and pinacolborane through a Ni-catalysed oxidative addition-reductive elimination sequence.[20]



Scheme X.6. Ni-catalysed selective hydrothiolation of alkenes with thiols. Key R^2S–Bpin species are formed *in situ*. **L1**, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

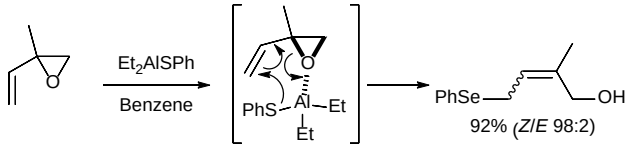
TolSBpin and PhSeBpin were also efficiently employed in reactions with acyl chlorides affording the corresponding thiol- and selenol-esters along with ClBpin.[21]

X.3 Nucleophilic species containing the chalcogen-aluminium bond

Aluminium thiolates and selenolates are used as versatile reagents for the selective formation of new C–S and C–Se bonds. Aluminium thiolates are generally prepared upon reaction of alkylaluminium compounds with thiols or by treatment of aluminium hydrides with thiols or disulfides.[22] Analogously, aluminium selenolates are commonly prepared from

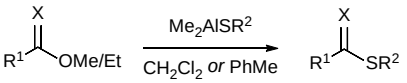
alkylaluminium compounds and elemental selenium or from aluminium hydride and selenols or diselenides.[23]

Aluminium thiolates react with a broad range of functional groups enabling the delivery of sulfurated moieties. For example, the reaction of Et_2AlSPh with vinyl epoxides affords the corresponding 1,4-addition products with high stereoselectivity (Scheme X.7).[24]



Scheme X.7. 1,4-addition of Et_2AlSPh to vinyl epoxides.

Aluminium thiolates also react with esters providing simple access to thiolesters. This route enables the straightforward conversion of methyl and ethyl esters into the corresponding synthetically valuable thiolesters (Scheme X.8).[25] The reaction of aluminium thiolates with α,β-unsaturated esters generally yields the conjugate addition products. A related procedure, relying on the reaction of selenoic acid *O*-methyl esters with aluminum thiolates can be employed for the synthesis of *S*-alkyl arenecarboselenothioates.[26] Aluminium thiolates and selenolates also react with aldehydes to afford the corresponding chalcogenoesters via a Tishchenko-type hydride transfer process.[27,28]



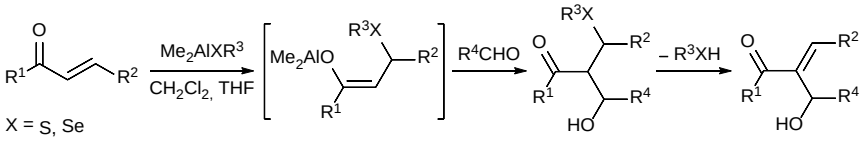
X = O; R^1, R^2 = Alk, Ar; X = Se, R^1 = Ar, R^2 = Alk

Scheme X.8.

Alkyl fluorides can be efficiently reacted with dialkylaluminium thiolates and selenolates to afford the corresponding chalcogenides. Primary alkyl fluorides smoothly react with $^{i}Bu_2AlXPh$ (X = S, Se, Te) through a S_N2 mechanism providing the corresponding alkyl-phenyl chalcogenides in good yields.[29]

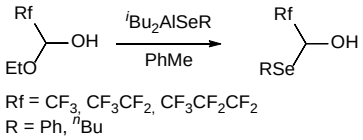
The reaction of aluminium thiolates and selenolates with α,β-unsaturated ketones provides the corresponding conjugate addition products. The resulting aluminium enolate

intermediates can be efficiently reacted with aldehydes to give the aldol products which, after formal thiol or selenol elimination, lead to α-substituted-α,β-unsaturated ketones (Scheme X.9).[30] α,β-Unsaturated nitriles also undergo conjugate addition upon treatment with aluminium thiolates.[31]



Scheme X.9. Functionalisation of α,β-unsaturated ketones through aluminium thiolates and selenolates.

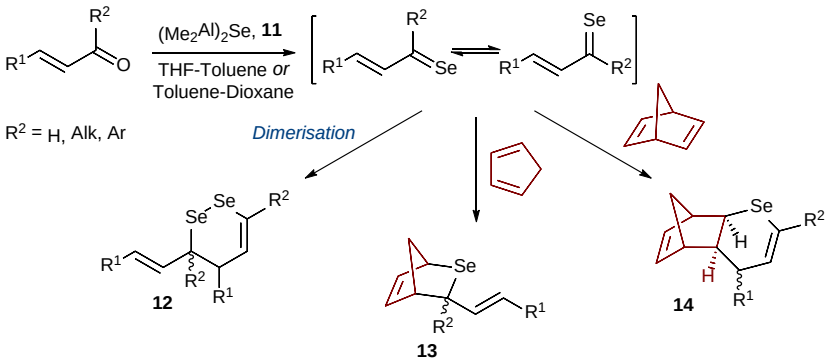
The reactivity of acetals and hemiacetals with aluminium thiolates and selenolates has also been investigated. Acetals can be converted into monothioacetals and monoselenoacetals upon treatment with Et_2AlSPh or $^{i}Bu_2AlSePh$.[32,33] An excess of aluminium reagent can be used to promote the conversion of acetals into diselenium acetals. Soft selenium-centered nucleophiles such as $^{i}Bu_2AlSePh$ and $^{i}Bu_2AlSe^{n}Bu$ react with perfluoro hemiacetals leading to the corresponding 1-(organoselanyl)perfluoroalkanols in quantitative yield (Scheme X.10).[34]



Scheme X.10. Reaction of perfluoro hemiacetals with aluminium selenolates.

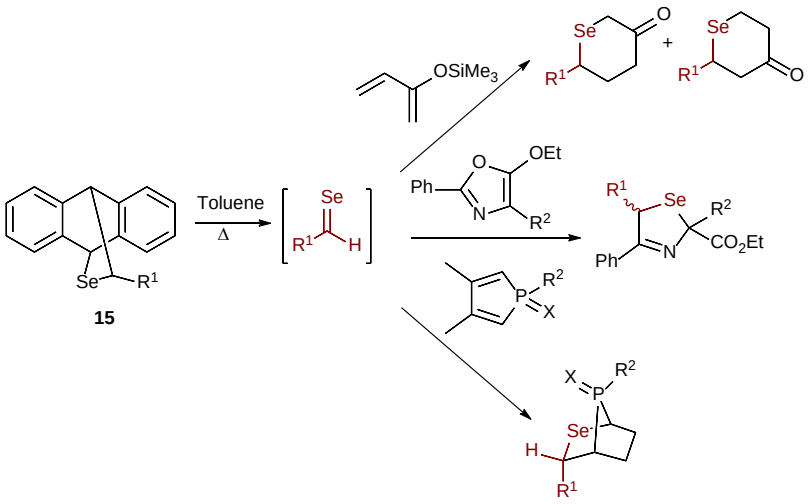
The conversion of an *O*,*O*-acetal into the corresponding *O*,*Se*-acetal with $^{i}Bu_2AlSePh$ has also been exploited to access a key intermediate used in one of the available routes for the synthesis of the left wing of the ciguatoxin CTX1B.[35] The intramolecular radical cyclisation of *O*,*S*- and *O*,*Se*-acetals, prepared *via* the reactivity of aluminium chalcogenolates, also enabled the construction of the oxepane ring G of ciguatoxin CTX3C.[36,37]

Bis(dimethylaluminium)selenide **11**, which can be prepared either by reaction of dimethylaluminium chloride with bis(trimethylsilyl)selenide or upon treatment of trimethylaluminium with bis(tributylstannyl)selenide in toluene,[23,38] is an effective selenylating reagent towards carbonyl compounds. Ketones and aldehydes are easily converted into the corresponding selenocarbonyl derivatives, which can be trapped with dienes to afford the Diels-Alder adducts. Selenocarbonyl compounds are unstable and generally not isolable; however, sterically hindered derivatives such as selenofenchone can be isolated.[38] The reaction of **11** with α,β-unsaturated selenoaldehydes and selenoketones also provides the corresponding α,β-unsaturated selenoaldehydes and selenoketones. Although the monomeric form of these derivatives is too unstable to be isolated, they undergo "head-to-head" [4+2] dimerization to afford diselenin derivatives **12**. α,β-Unsaturated selenocarbonyl compounds also serve as 2*π* dienophiles in reactions with cyclopentadiene and as 4*π* heterodienes in Diels-Alder cycloadditions with norbornadiene, enabling the rapid synthesis of selena-heterocycles **13** and **14** (Scheme X.11).[39]



Scheme X.11. Synthesis and reactivity of α,β-unsaturated selenocarbonyl derivatives.

The [4+2] cycloadducts **15**, obtained upon treatment of aromatic or aliphatic aldehydes with **11** in the presence of anthracene, are stable at room temperature but easily undergo thermal retro Diels-Alder reactions to provide the corresponding selenoaldehydes (or selenals), which serve as versatile precursors of a number of selenium-containing derivatives (Scheme X.12).[40,41]



Scheme X.12.Generation and functionalization of selenoaldehydes.

Acetals can also be employed as the starting material to generate selenoaldehydes, whose *in situ* trapping with dienes provides the corresponding Diels-Alder adducts. Cyclic acetals with one exocyclic acetal oxygen atom afford systems bearing a hydroxy group at the terminal position. Dihydropyranyl methyl ethers give functionalised derivatives having a terminal formyl group.[38]

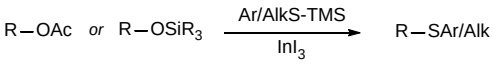
X.4 Nucleophilic species containing the chalcogen-silicon bond

The sulfide moiety is present in many important structures, as pharmaceutical and agrichemical compounds, natural products and finds application as building block in organic chemistry and organocatalysis.[42-45] In this context, organothiosilanes and organoselenosilanes[46] are used as more efficient nucleophiles to transfer a sulfurated moiety with respect to the corresponding thiols for the milder functionalization with electrophilic species[47].

X.4.1. Reaction with acetates and ethers

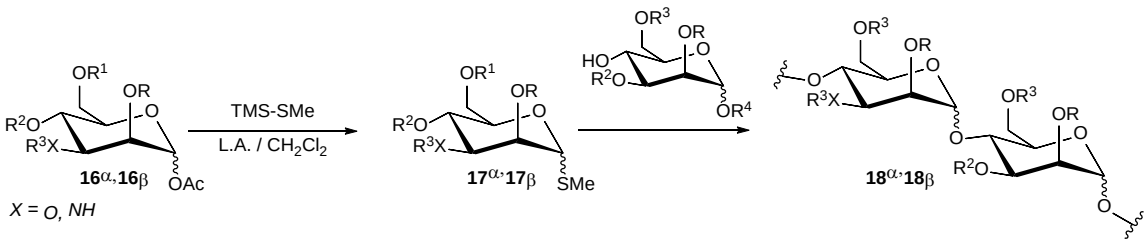
Aryl- and alkylthiosilanes were suitable reagents in the nucleophilic substitution on substrates containing different functional groups, as acetyloxy, ethers and silyl ethers, halides, to provide a variety of unsymmetrical sulfides under suitable catalytic conditions.

InI_3 promoted substitution of acetoxy and siloxy groups by aryl- and alkylthiosilanes in alkyl acetates, including carbohydrate substrates, enabled the synthesis of a variety of thioethers, avoiding the use of metal thiolates (RSMet) which often led to several byproducts (Scheme X.13).[48,49]



Scheme X.13. In_3-promoted thiolation of acetoxy and siloxy groups.

The substitution of an acetoxy group by a sulfurated moiety was extensively used in carbohydrate chemistry as thioglycosides represent versatile and widely used intermediates able to activate the anomeric position to further elaborations to obtain a plethora of more complex oligosaccharides. The synthesis of thioglycosides by treatment of glycosyl acetates with thiols is frequently employed, but often leads to undesired side reactions. The lower nucleophilicity of the silyl sulfide allowed a higher stereoselective attack on the anomeric carbon with respect to the related thiols. A huge number of examples are reported on the stereocontrolled replacement of the anomeric acetoxy group in reagents **16** by treatment with TMSSMe**,** usually promoted by Lewis acids, as the general example depicted in Scheme X.14. The obtained methylthio derivatives **17** are widely used as intermediates to access oligosaccharides **18**.

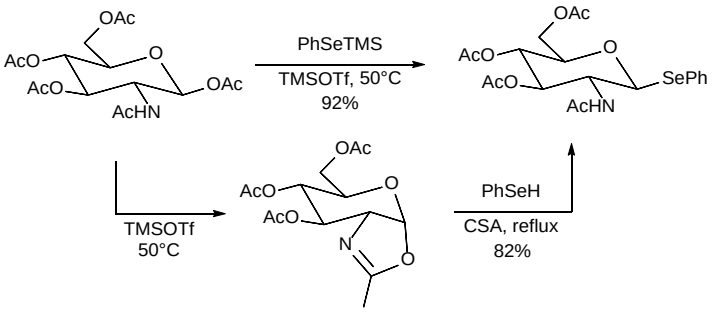


Scheme X.14. Synthesis of thioglycosides as oligosaccharides precursors.

Example of solid-phase synthesis of oligosaccharides using thioglycosides was also reported.[50] Numerous reactions of thiosilanes with carbohydrates were catalysed by trimethylsilyl trofluoro-methanesulfonate (TMSOTf). Some examples are the preparation of

N-acetylneuraminic acid thiomethylesters,[51-53] of galactosides,[54,55] of methylthio-L-glycero-α-D-manno-heptopyranoside derivatives.[56] Likewise, fluorine containing thioglycosides,[57] methylthio-substituted rhamnose derivatives[58,59] and *S*-glucofuranosyl compounds were prepared with TMSSMe under TMSOTf catalysis.[60] Introduction of the trichloroacetimidate group on the anomeric position of a D-xylopyranosyl-derivative was favoured exploiting the synthetic flexibility of thioglicoside intermediates, obtained from TMSSMe/TMSOTf.[61] Catalysis also of boron trifluoride etherate ($BF_3 \cdot Et_2O$) was efficient to transfer a -SMe group on β-D-xylopyranoside derivatives.[62]

In this context selenoglycosides as well represent important intermediates to provide carbohydrate derivatives. Selenoglycosidation was directly achieved by treatment of an amino sugar (galacto-, gluco- and manno-derivatives) with phenylseleno(trimethylsilane) (PhSeTMS) and TMSOTf, leading to the corresponding selenides as precursors of α-*C*-glycosides (Scheme X.15). When benzenselenol was reacted instead of the selenosilane, a two-step procedure was required (*via* oxazoline).[63]

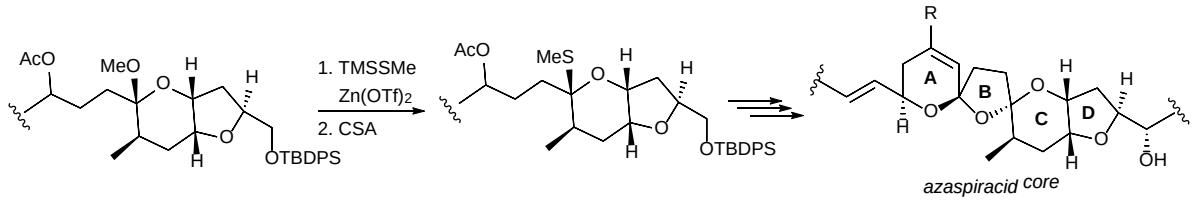


Scheme X.15. Synthesis of phenylselenoglycosides.

Not only acetoxy, but also other groups were suitably substituted by thiosilanes. Methylthio-substituted thioglycosides from sialic acid were accomplished by selective nucleophilic substitution of a silyl-containing alkyl ether [$O(CH_2)_2TMS$, OSE] by TMSSMe/TfOTMS.[64,65] Similarly, the replacement of the anomeric -OSE group by reaction with TMSSMe was applied to prepare the thioglycoside of a 3-*O*-levulinoylated derivative.[66] The replacement of a O-allyl moiety by treatment with methylthiosilane allowed the introduction of a smaller

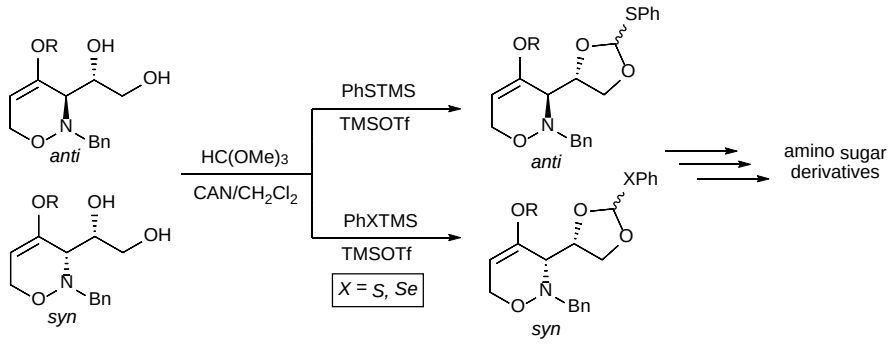
methylthio group on α-L-rhamnopyranosyl derivatives, to examine their potential as acceptors for *Np*AS (*Neisseria polysaccharea*).[67]

In the search for the construction of the ABCD ring system of the more complex azaspiracid (a novel shellfish poison), a central step was the use of the thioacetal intermediate (Scheme X.16), obtained through reaction of the methyl acetal with TMSSMe in the presence of $Zn(OTf)_2$, followed by acidic treatment.[68]



Scheme X.16. Methylthioacetal as intermediate in the synthesis of azaspiracid ring system.

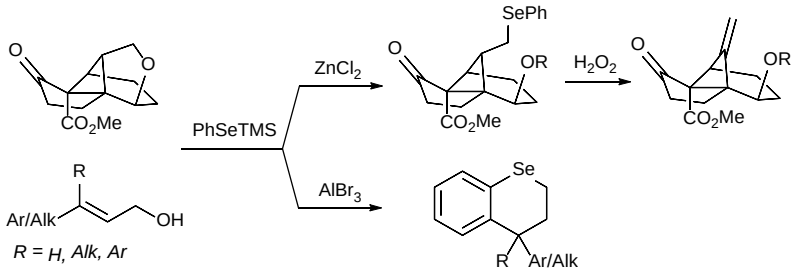
Moreover, for the preparation of amino sugars starting from enantiopure 1,2-oxazines, PhSTMS was used to introduce a phenylthio group on a dioxolane ring to afford *syn*- and *anti*-isomers (Scheme X.17). Likewise, the corresponding phenylseleno(trimethylsilane) led to the 2-phenylseleno substituted dioxolane. Further elaboration of the substituted dioxolanes provided a stereodivergent synthesis of amino sugar derivatives, exploiting the suitable electronic properties of the chalcogenated groups (Scheme X.17).[69]



Scheme X.17. Synthesis of 2-phenylthio- and phenyl-seleno substituted dioxolanes.

High stereoselective ring opening was applied to a α(1,4)-galactoside dioxolane by PhSTMS, under ZnI_2 catalysis, to provide a β-thioglycoside as intermediate of Terpioside B.[70]

Phenylseleno(trimethylsilane) in combination with zinc chloride and cyclic ethers,[71] or aluminium tribromide and allylic alcohols,[72] was employed for the synthesis of exocyclic alkenes and selenochroman derivatives, respectively. (Scheme X.18).



Scheme X.18. PhSeTMS/L.A. combination for the synthesis of bridged bicyclic alkenes and selenochromans.

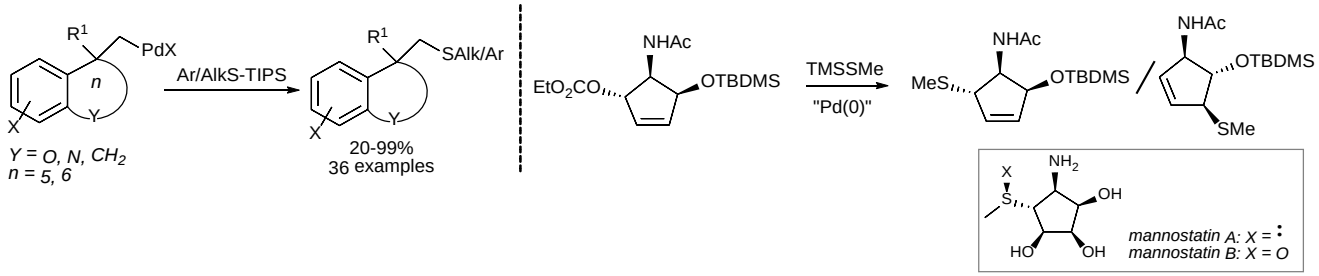
X.4.2. Reaction with acyl chlorides

Selenosilanes were able to transfer the organo-selenyl moiety onto aryl- and alkyl- acyl chlorides. Depending on the type of silyl selenide, PhSeTMS or bis(trimethylsilyl)selenide [$(TMS)_2Se$, HMDSS] and on the stoichiometric ratio, selenolesters, selenoanhydrides and diacyl diselenides were synthesized.[73] Acyl chlorides were also reacted at room temperature both with PhSeTMS and with different organoselenosilanes containing two -SeTMS groups, such as 1,4-TMSSe-C_6H_4-SeTMS, 4,4'-TMSSe-$(C_6H_4)_2$-SeTMS and 1,1'-Fe(η^5-C_5H_4SeTMS)$_2$ to provide aromatic mono- and diselenoesters, showing that silylselenides behave as a convenient and reactive source of $ArSe^-$. With more hindered acyl chlorides higher temperature was necessary.[74]

X.4.3. Palladium-promoted carbothiolations

Phenylthio- and alkylthio triisopropylsilanes (TIPS-SR) were successfully employed in the synthesis of alkyl-aryl and dialkyl sulfides *via* a palladium-catalyzed carbothiolation on a σ-alkyl Pd-intermediate.(Scheme X.19, *left*).[75] A palladium-promoted methylthiolation with TMSSMe was obtained on the allylic carbonate in Scheme X.19 (*right*) to prepare the corresponding thioethers, precursors of mannostatin A analogues.[76] The reaction with

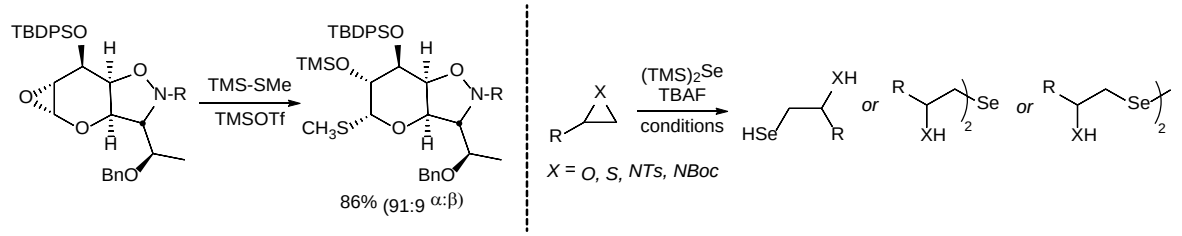
thiophenol failed, probably for the high affinity of sulfur compounds with Pd, with subsequent poisoning of the catalyst. The use of a thioderivative bearing a bulky protecting group (PhS-TIPS), unable to coordinate the Pd, was capable to overcome this drawback.



Scheme X.19. Palladium-promoted methylthiolation.

X.4.4. Ring opening of heterocycles by chalcogenosilanes

Thiosilanes were usefully employed in the ring-opening of strained heterocycles, as epoxides and aziridines, to access a variety of versatile building blocks to prepare more complex molecules. In the study for the synthesis of the amino sugar fragment of the lincosamide antibiotics, the epoxide of a glycal was reacted with TMSSMe/TMSOTf to afford the corresponding β-OTMS methyl sulfide with high regio- and stereocontrol (Scheme X.20, *left*).[77]

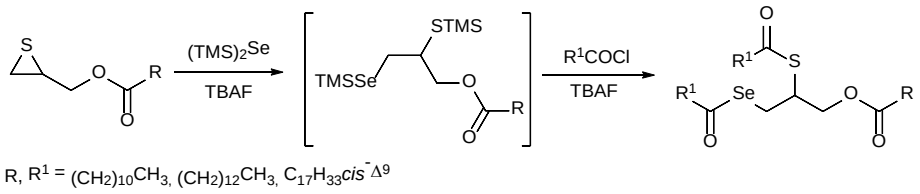


Scheme X.20. Ring opening of three-membered heterocycles.

Phenylthio(trimethyl)silane was reacted with epoxides also under tetrabutylammonium phenoxide (PhON^{n}Bu$_4$) catalysis to afford β-hydroxyalkyl phenyl sulfides in good yields.[78] A bifunctionalized silyl sulfide, namely bis(trimethylsilyl)sulfide (TMS-S-TMS, HMDST), found a broad application in the TBAF or PhON^{n}Bu$_4$ catalyzed opening of differently substituted epoxides, allowing a direct access to a wide range of β-mercaptoalcohols in a highly regio- and stereoselective way.[78,79] Thiiranes as well enabled to access 1,2-dithiols after treatment

with $(TMS)_2S$ and TBAF.[80,81] Bis(trimethylsilyl)sulfide and (phenylthio)trimethysilane were also reacted with aziridines to achieve chiral enantioenriched 1,2-mercaptoamines and β-amino phenylsulfides through a regio- and stereoselective nucleophilic substitution. The procedure was applied to *N*-Ts and *N*-Boc protected aziridines, as well as to unsubstituted derivatives.[82]

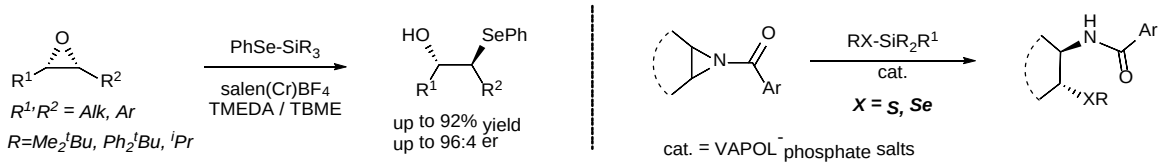
The nucleophilic substitution onto three membered heterocycles was also performed using selenosilanes.[83] Regio- and enantioselective ring opening of epoxides, thiiranes and aziridines with bis(trimethylsilyl)selenide - $(TMS)_2Se$, HMDSS - afforded an entry to β-hydroxy, β-mercapto and β-amino diselenides and selenides, through a tuning of the reaction conditions (Scheme X.20, *right*).[84] The reaction carried out under strictly controlled conditions (eq. of TBAF, time, T) allowed a direct access to β-substituted alkyl selenols.[85] Ring opening of suitable substituted thiiranes of glycidol by HMDSS led to sulfur- and selenium isosters of triacyl glycerols, exploiting the activation of the Si-chalcogen bonds of the chalcogenosilane intermediates for the following *in situ* reaction with fatty acid acyl chlorides (Scheme X.21).[86]



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

Scheme X.21. Synthesis of sulfur- and selenium isosters of triacyl glycerols.

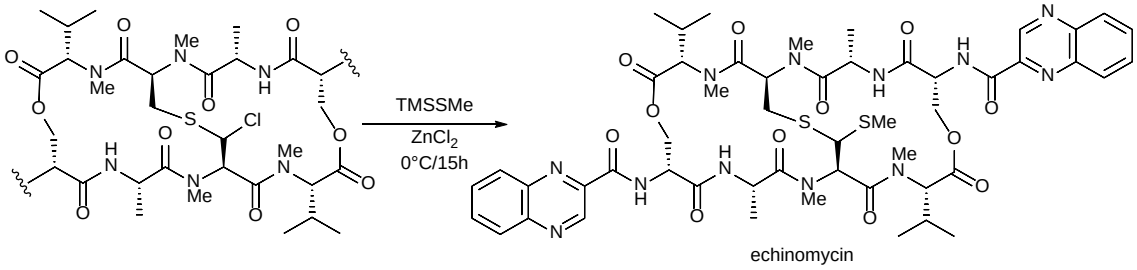
Asymmetric ring opening of *meso*-epoxides by phenyl(selenosilanes) under salen(Cr)complexes led to acyclic and cyclic β-hydroxy selenides (Scheme X.22).[87] Likewise, desymmetrization of *meso*-azyridines was achieved with substituted silyl sulfides RSTMS (R = Me, Bn, CN) or silyl selenides ($PhSeSiR_2R^1$) under VAPOL-phosphate salts catalysis, leading to chiral β-amino chalcogenides (Scheme X.22).[88,89]



Scheme X.22. Asymmetric ring opening of *meso*-epoxides and –aziridines.

X.4.5. Nucleophilic substitution on halogenated compounds

Halogenated substrates as well conveniently reacted with chalcogenosilanes. Echinomycin is a bicyclic octadecadepsipeptide bridged with a methylthioacetal moiety, with relevant biological properties (Scheme X.23). A total synthesis was recently reported, and in the last step the S_N2 reaction of the chlorine to introduce the methylthio group was unsuccessful with NaSMe, while using TMSSMe, and $ZnCl_2$ as a promoter, allowed isolation of echinomycin.[90]



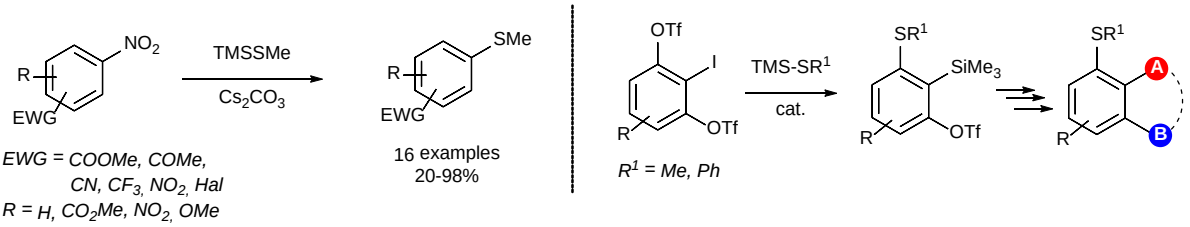
Scheme X.23. Methylthiolation with TMSSMe in the total synthesis of Echinomycin.

Thiosilanes behaved as efficient nucleophiles also to access thio-derivatives of tribenzotriquinacenes, useful rigid building blocks in molecular architecture with C_3 symmetry. The substitution of the bromine was achieved reacting alkyl(silyl) sulfides instead of the corresponding thiols.[91] Selenosilanes [RSeTMS, $(TMS)_2Se$] as well were used to synthesize cyclohepta-2,4,6-trienyl selenides by nucleophilic substitution from the corresponding tropylium bromide.[92]

X.4.6. Aromatic nucleophilic substitution with organothiosilanes

TMSSMe and TMSSPh were involved in aromatic nucleophilic substitutions on properly activated aromatic substrates, as arenediazonium tetrafluoroborates to prepare aryl methyl- and aryl phenyl sulfides.[93] A combination of methylthio(trimethylsilane) and cesium

carbonate was found to be a more efficient methylthiolation system in the reaction with nitroarenes than mehanethiol or sodium methoxide (NaSMe) (Scheme X.24, *left*).[94]

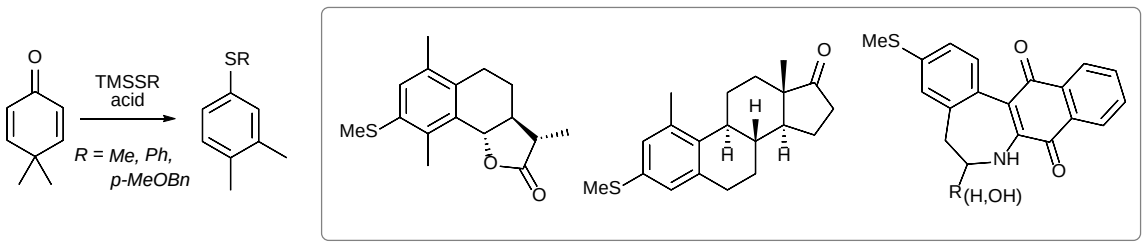


Scheme X.24. Aromatic nucleophilic substitution with silyl sulfides.

Silylthiolation of iodoaryl triflates with thiosilanes led to a variety of polyfunctionalized aromatic compounds (Scheme X.24, *right*).[95,96] Likewise, activated aryl- and heteroaryl halides were reacted with thiosilanes through functionalization of S-Si bonds under Cl/Br ions catalysis.[97] Nucleophilic substitution also of an amino group was achieved with TMSSMe/isoamyl nitrite on 2-amino thiazoles.[98]

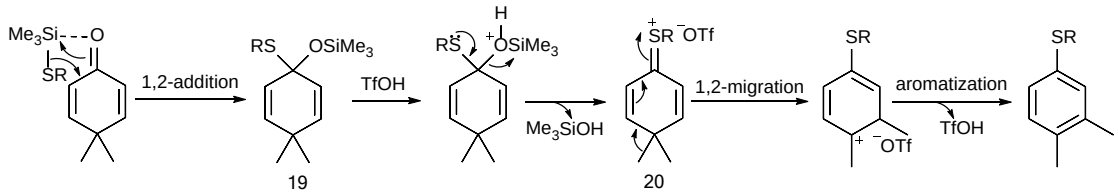
X.4.7. Reaction with carbonyl containing compounds

Addition reactions toward carbonyl substrates of alkyl- and arylthiosilanes is a well-known procedure for selective carbonyl protection under appropriate acid catalysis.[99]. In this context, thiosilanes were involved in the dienone-phenol type rearrangement to synthesise aryl thioethers under acidic conditions (Scheme X.25).[100] Conversely, the treatment of cyclohexadienone with thiols and Lewis acids gave the unsymmentrical sulfides in very poor yields, showing the advantages of using silyl sulfides.



Scheme X.25. Dienone-phenol type rearrangement *via* thiosilanes.

A proposed reaction mechanism is illustrated in Scheme X.26. The intermediate **19** would be formed by an unusual 1,2 addition of the thiosilane onto the C=O group. After elimination of silanol, the thionium ion intermediate **20** undergoes 1,2-migration of the alkyl group and aromatization to aryl thioether.

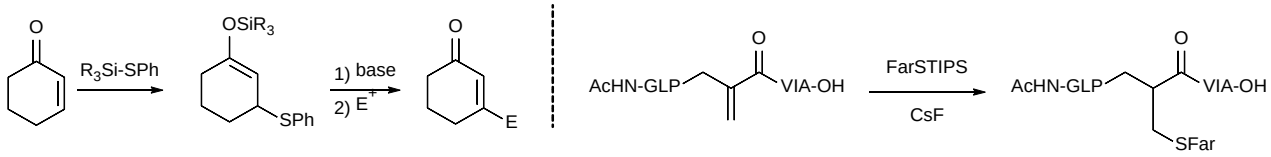


Scheme X.26. Proposed reaction mechanism.

Addition of TMSSMe to a keto sugar was employed to prepare the corresponding thioketal in high yield, which was an intermediate for the total synthesis of shishijimicin A and its analogues.[101]

The treatment of different carbonyl compounds, as aldehydes, ketones and acylsilanes with bis(trimethylsilyl)sulfide (HMDST) under $CoCl_2 \cdot 6H_2O$ or TMSOTf catalysis, allowed a direct access to the corresponding thiocarbonyls, which can be trapped as Diels-Alder cycloadducts.[102] An alternative access to thioacylsilanes was obtained through the benzotriazole-mediated methodology.[102] Thionation of bis(acylsilanes) with HMDST provided sulfurated heterocycles with different ring size, depending on the spacers length between the C(=O)*Si* moieties.[102] The corresponding bis(trimethylsilyl)selenide enabled the synthesis of alkyl and aryl selenoaldehydes, trapped as Diels-Alder adducts.[73]

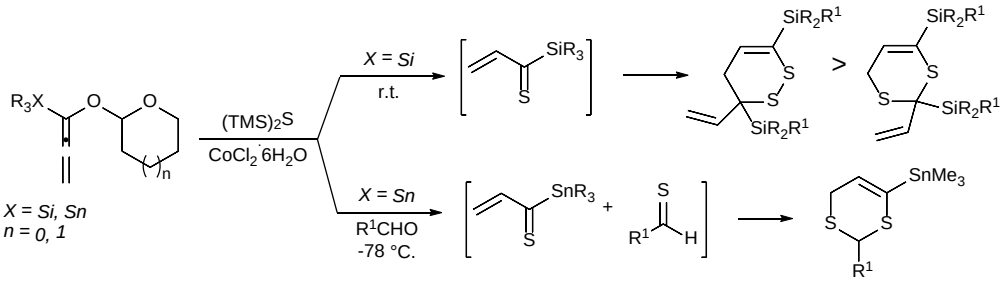
Reaction of α,β-unsaturated carbonyl compounds with thiosilanes enabled to synthesize β-phenylthio silyl ethers as intermediates to access 3-substituted cyclohexenones using an umpolung strategy (Scheme X.27, *left*).[103] Thia-Michael addition of the farnesylthio triisopropylsilane (FarSTIPS) onto an α,β-unsaturated carbonyl derivative of a peptide was employed in a convergent synthesis of peptide conjugates (Scheme X.27, *right*).[104]



Scheme X.27. Thia-Michael addition.

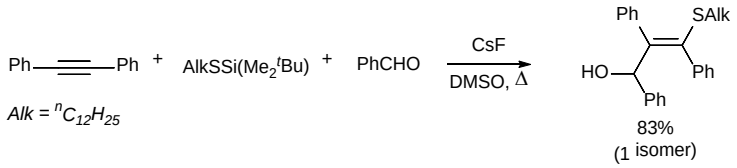
X.3.8. Reaction with allenes and alkynes

The reaction of bis(trimethylsilyl)sulfide with differently silylated and stannylated allenes promoted by $CoCl_2 \cdot 6H_2O$ provided, respectively, α,β-unsaturated thioacylsilanes and α,β-unsaturated thioacylstannanes as heterodienes/heterodienophiles. (Scheme X.28).[102]



Scheme X.28. Reaction of chalcogenosilanes with allenes

Hydrothiolation of alkynes with alkyl thiosilanes led to a stereoselective access to alkenyl sulfides. The use of thiosilanes instead of thiols allowed a further functionalization upon reaction with aldehydes to form new carbon-carbon bonds (Scheme X.29).[105]



Scheme X.29. Hydrothiolation of alkynes with silyl sulfides.

X.5 Species containing the chalcogen-tin bond

Trialkyl- and triarylstannylsulfides and selenides (R_3SnSR', R_3SnSeR') are useful chalcogen nucleophiles that have found applications in organic synthesis, medicinal chemistry, and material science. These species can be directly prepared reacting thiols and selenols with stannyl halides. However, the reactions of stannyl hydrides or bis-stannyl derivatives with

disulfides and diselenides are valuable alternatives.[106-109] These latter opportunities represent a crucial advantage offered by R_3SnSR', R_3SnSeR' reagents since, often, thiols and, above all, selenols are difficult to prepare and to handle.

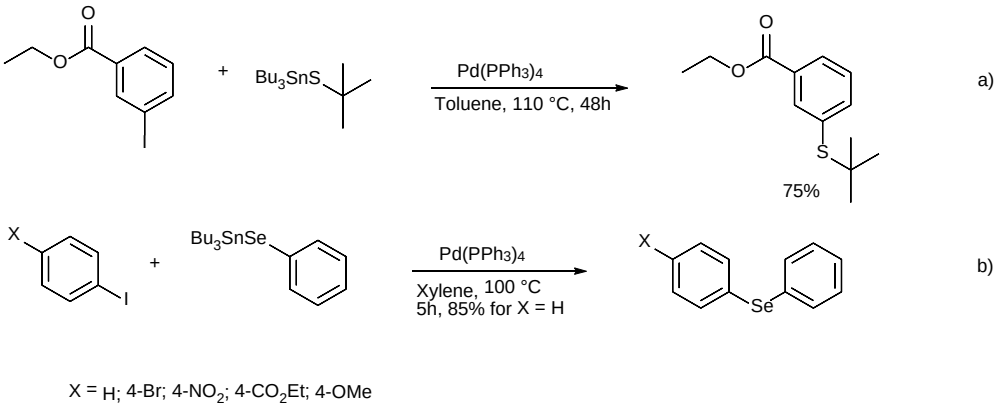
In this chapter we describe the principal applications based on the nucleophilic behaviour of triorganylstannyl sulfides and selenides.

X.5.1. Stannyl sulfides and selenides in Stille-like and related metal catalysed cross-coupling reactions

Trialkyl and tryarylstannyl sulfides and selenides have found several applications as chalcogen nucleophiles in Stille-like reactions with aryl and vinyl halides. After the very first report by Terada and others,[110] several modifications and upgrades have appeared. The insertion of a sulfur residue on an aromatic ring has been reported to be operative from aryl and heteroaryl iodides and bromides in the presence of a Pd(0) catalyst, like $Pd(PPh_3)_4$, in boiling toluene or xylenes.[111-123] The procedure revealed to be successful also for the insertion of selenium aryl residues operating under pretty similar conditions.[107,120,124,125] As an example, in Scheme X.30 *path a*, is described the reaction of 3-iodo ethylbenzoate with tributyl(tert-butylthio)stannane to give a sulfide used for the preparation of chemiluminescent probes useful for the detection of cholinesterase activity.[112] Under very similar condition aryl iodides and tributyl(phenylseleno)stannane react to allow the preparation of unsymmetrical diaryl selenides [Scheme X.30, *path b*)].[124]

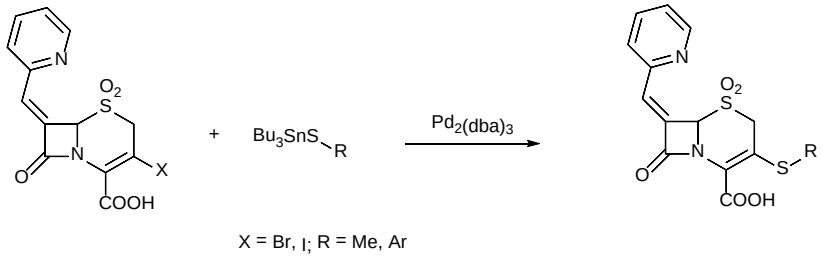
The methodology tolerates a variety of substituents on the aromatic ring and, at least in the sulfur series for the first decade of this century, has been used for the introduction of S-alkyl and S-aryl moieties on derivatives with applications in medicinal chemistry.[111-115] More recently, probably due to the common concerns about toxicity of stannyl derivatives, this reaction has found much more applications for the construction of sulfides and selenides exploited in material science.[116-125] As a matter of fact, many different variations and upgrades have been settled since to facilitate and increase the range of this chalcogen version of the Stille reaction. Thus, it has been reported that thiofunctionalyzation can be

promoted working under microwave irradiation,[126] while insertion of arylselenyl residues has been carried out using copper (CuI) and nickel ($NiBr_2$) catalysts in the presence of suitable ligands, either under classical heating[127] or microwave irradiation.[128]



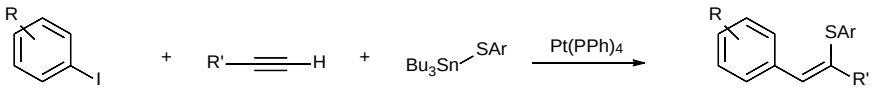
Scheme X.30. Stille-like reactions of stannylsulfides and selenides on aryl electrophiles.

Moreover, it has been demonstrated that the Pd catalysed insertion of selenyl residues can be carried using ionic liquids as solvents,[129] using polyfluoroarenes as substrates,[130] and aryl triflates as electrophiles.[131] Thus, the synthesis of aryl and heteroaryl sulfides and selenides using stannyl chalcogenides as nucleophiles is a valuable and flexible procedure that allows to avoid the use of thiols/thiolates and selenols/selenolates. Together with aryl halides and triflates, metal catalysed cross couplings allowed the insertion of alkyl- and arylthio residues on vinyl halides.[132-136] Thus, for example, the insertion of different S-alky and S-aryl groups on the six membered ring of a cefalosporin skeleton, showing activity as β-lactamase inhibitor, has been carried out with S-arylstannanes under $Pd_2(dba)_3$ catalysis as depicted in Scheme X.31.[134,135]



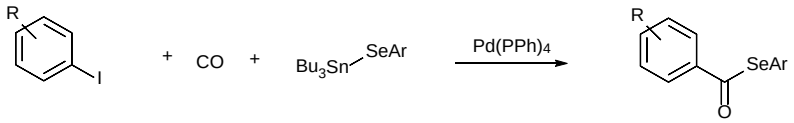
Scheme X.31. Stille-like reactions of stannylsulfides on vinyl electrophiles.

Trialkylthiostannanes have been used under Pt catalysis in a three components reaction for the ortho vinylation of aryl halides in the presence of terminal alkynes.[137,138] Different substituted aryl and heteroaryl iodides can be used as electrophiles to give the corresponding trisubstituted olefin as depicted in Scheme X.32.



Scheme X.32. Three component vinylation with stannylsulfides and terminal alkynes.

Due to the difficulty to prepare and store selenols and selenolates, the use of selenostannanes as suitable nucleophiles in metal catalysed cross couplings has been also applied for the preparation of selenoesters.[139-142] These derivatives can be obtained via a three components process reacting an aryl halide with a trialkylseleno stananne under a positive (5 atm) CO pressure in refluxing toluene using $Pd(PPh_3)_4$ as catalyst (Scheme X.33).[139] Selenoesters can be, even more directly, obtained reacting a selenostannane with an acyl chloride and $Pd(PPh_3)_4$ under condition similar to those reported in Scheme X.31. Actually, literature data available for this transformation are a bit controversial, since it has been reported that metal catalysis it is not necessary with acyl chlorides while is required using anhydrides as electrophiles.[141,142]



Scheme X.33. Three component acylation of stannylselenide with CO.

The conditions revealed to be suitable for the introduction of seleny residues onto electrophilic sp^2 carbons are also suitable for the seleno functionalyzation of electrophilic sp^3 carbons. The reactions of trialkylselenyl stannanes with α-bromo carbonyl compounds, as well as with propargylic, allylic and benzylic bromides occurs quite well affording the corresponding sulfides.[140,143] Using propargylic, allylic and benzylic bromides as

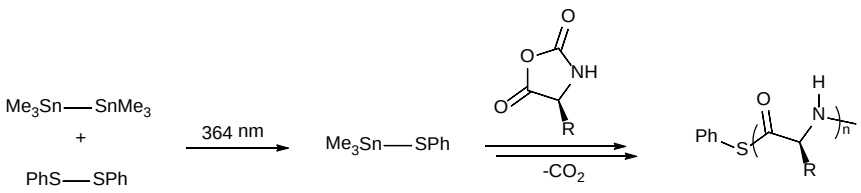
electrophiles, palladium pincer-complexes were often the catalyst of choice since to improve the final yield of the reactions.[144]

X.5.2. Other nucleophilic processes involving stannyl sulfides and selenides

When making thioglycosides, the high nucleophilicity of alkanethiolates in the presence of Lewis acids can lead to undesirable side reactions. Consequently, tributylstannyl (and trimethylsilyl, *vide* **X.4.1**) derivatives of thiols are employed to reduce the nucleophilicity of the thiol reagent. Indeed, the insertion of an S-alkyl or S-aryl group on a sugar anomeric carbon can be carried out with the corresponding tribultylstannylsulfide as glycosyl acceptor, an anomeric bromide or fluoride as glycosyl donor in the presence of tin(IV) chloride,[145] or BF_3OEt_2 as promoters.[146] The control of the stereochemistry at anomeric carbon depends upon the reaction conditions used that can allow the complete inversion during glycosylation as depicted in Scheme X.34.[146]

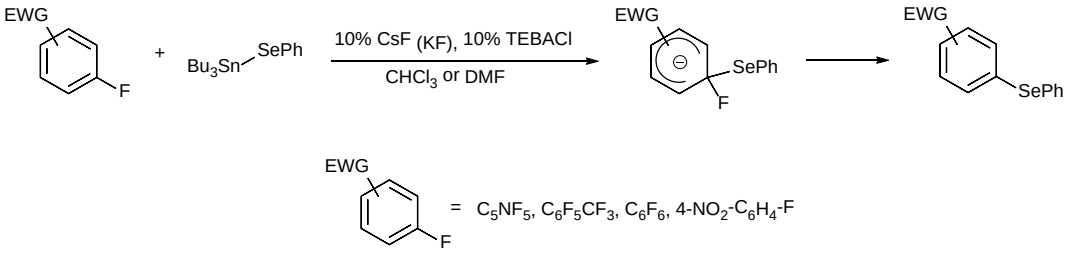
Scheme X.34. Thioglycosylation using stannyl sulfides.

A peculiar example of the peculiar nucleophilic character of stannyl sulfides is illustrated with the behaviour of the S-Sn Lewis pair in the ring-opening polymerization of α-amino acid *N*-carboxyanhydrides that allows a rapid and controlled formation of polypeptides with high molecular weight (Scheme X.35).[109] Remarkably, in this process, the promoter phenylthiotrimethyl stannane is photochemically generated in situ from diphenyl disulfide and hexadimethyldistannane under the polymerization condition.



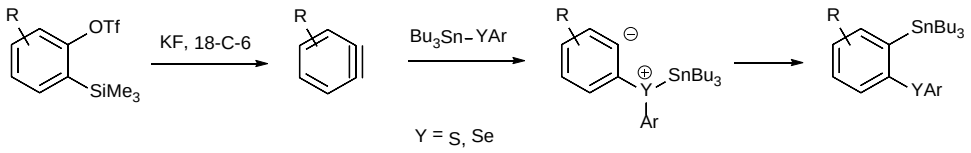
Scheme X.35. Trimethylstannyl sulfides as polymerization promoters.

Another remarkable opportunity of using arylselenylstannane as synthetic equivalents of the corresponding selenols and selenolates is the preparation of unsymmetrical diaryl selenides of very electron-poor arenes *via* an aromatic nucleophilic substitution process.[147] Depending upon the substitution pattern of the aryl fluoride used as electrophile, the reaction requires the use of sub-stoichiometry amounts of alkaline fluorides (KF or CsF) and(or) triethyl benzyl ammonium chloride (TEBACl) (Scheme X.36).[147]



Scheme X.36. S_NAr reactions using stannyl selenides as nucleophiles.

Eventually, either tributylstannyl sulfides[148] and selenides,[149] react with arynes, generated from *ortho*-trimethylsilyl triflates, KF and 18-crown-6, to give the corresponding o*rtho*-tributylstannyl aryl sulfides and selenides (Scheme X.37).. The proposed mechanism foresees the nucleophilic attack of the stannyl chalcogen to the aryne with formation of a zwitterionic sulfonium (or selenonium) ion that evolves to the final compound, reasonably, by an intramolecular attack of the aryl nucleophilic carbon to the tryalkyltin moiety.



Scheme X.37. Tributylstannyl sulfides and selenides reaction with arynes.

ACKNOWLEDGEMENTS

Acknowledgements need to be before the reference list.

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