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Heterocyclic compounds with a silicon atom and another non-adjacent different heteroatom

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1. Introduction

Interest in organosilicon compounds has increased considerably in the last decade. This is due to the fact that incorporation of a silicon atom in a carbon framework of molecules modifies their properties, e.g., modification of the electric properties of conducting polymers or other physical properties have been reported.[1] Similarly, modifications of physiological and biological activities are known.[2]

Numerous heterocyclic compounds possessing one or more silicon atoms have been reported.[3] The preparation of compounds in which the silicon atom and the other different heteroatom are in the 1,2-positions appears very common. Examples of compounds in which these heteroatoms are separated by one (or more) carbon atom are, however, less well known. The aim of this review is to examine such compounds. Heterocycles incorporating a metal atom in the cycle will not be discussed. We will examine, successively, the different ring sizes.

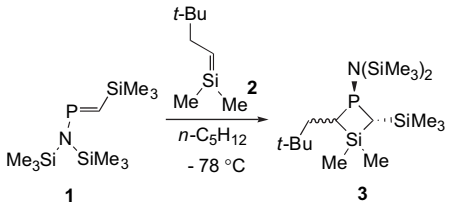
2. Preparation of four-membered heterocyclic compounds

For this ring size, examination of the literature shows that compounds with silicon and phosphorus, nitrogen, sulfur or oxygen atoms in the 1,3-positions are known. In Scheme 1, the IUPAC names and structures of these uncommon heterocycles have been summarized.

Two main approaches, cycloadditions and ring closures, to this ring size have been developed. In fact, very few preparations have been reported.

2.1. Formation by cycloaddition

The main approaches to these compounds imply [2+2] or two [2+1] cycloadditions. [2+2] Cycloadditions were reported for the formation of phosphasiletanes. Neilson and co-workers studied the reactivity of silene **2** and found that this compound can react with methylenephosphine **1** to give an 8:1 mixture of the two isomers **3**.[4] The stereochemistry of the main isomer was postulated to be the one in which the Me_3Si and neopentyl substituents on the ring are both trans to the $(Me_3Si)_2N$ group. These compounds were stable enough to be distilled (Scheme 2).

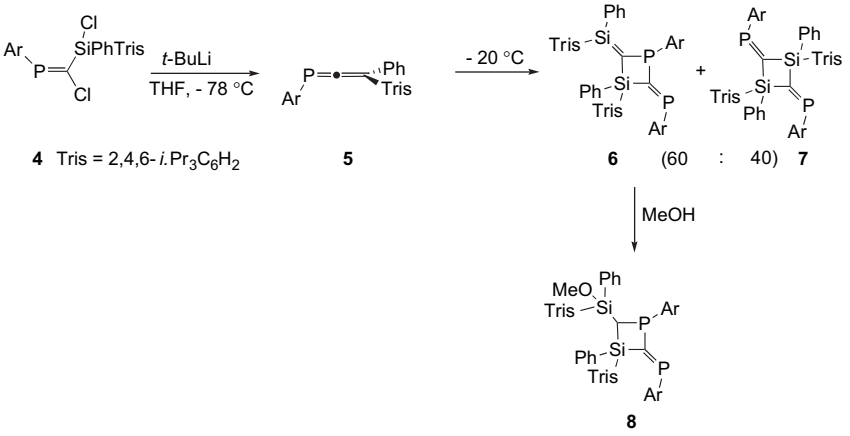


Scheme 2.

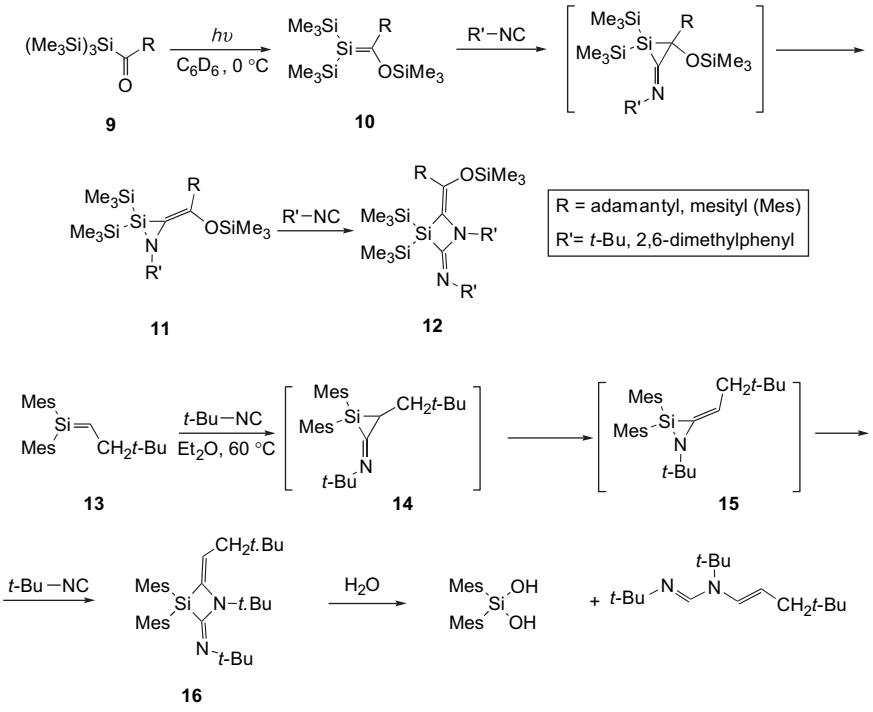
Dimerization at −30 °C of the very reactive 3-phospha-1-silaallene **5** (Ar=2,4,6-tri-*tert*-butylphenyl) formed at −78 °C by dedichlorination of (chlorosilyl)chlorophosphalkene **4**, led to a 60:40 mixture of two products **6** and **7**.[5] The major compound **6**, however, appeared to have a low stability, and its characterization was performed after transformation into compound **8** by the addition of methanol (Scheme 3). A large steric hindrance of the groups fixed at the phosphorus and silicon atoms seems to be essential for the formation of stable silaallenes **5**.[6]

Addition of isocyanides to stable silenes **10**, formed by photochemically induced isomerization from acylsilanes **9**, led to the formation of 1,3-azasiletidines by two successive [2+1] cycloadditions[7] (Scheme 4). The postulated siliaaziridines **11** were detected when the R substituent was an adamantyl group. The presence of bulky substituents seems, here also, to be crucial for the formation of silenes **10** and for the isolation of azasiletidines **12**. Similar results were reported with silene **13**.[8] Reaction of this stable compound with *tert*-butyl isocyanide in ether at 60 °C led to 1,3-azasiletidine **16**. This product was formed by the addition of

Scheme 1.



Scheme 3.



Scheme 4.

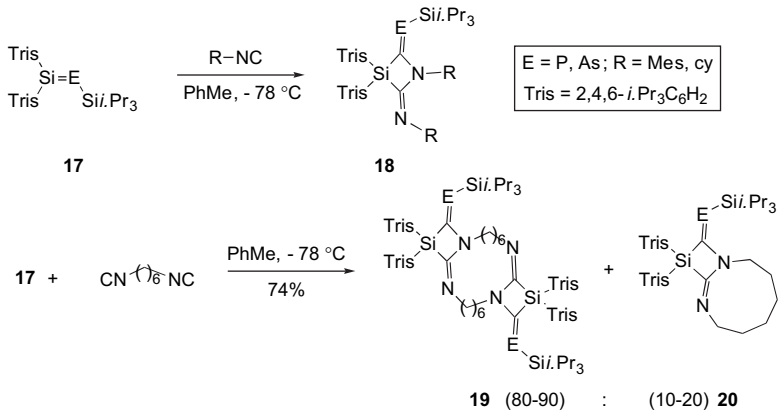
the isocyanide to silene **13**, to give silirane **14**. This latter compound rearranged into the more stable azasiliridine **15**, and addition of a second molecule of isocyanide led quantitatively to the azasiletidine **16**. This compound appeared to be water sensitive and gave rise to cleavage products.

Driess and co-workers studied the reactivity of silylidenephosphanes and arsanes **17**, and found that these compounds reacted with 2 equiv of isocyanide to lead to azasiletidines **18**,[9] as in the previous examples, by two successive [2+1] cycloadditions (Scheme 5). When the reaction was carried out with a diisocyanide, the tricyclic compounds **19** were the major products[9b] and the bicyclic derivatives **20** were the minor components.

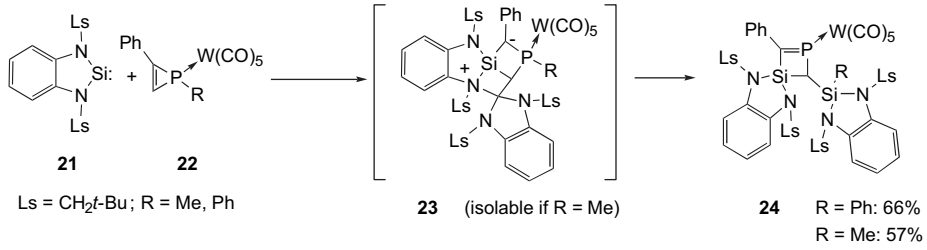
A recent report showed that stabilized phosphasiletanes can be obtained by the reaction of silylene **21** with 1-*H*-phosphirenes **22**.[10] When the substituent on the phosphorus atom was a phenyl group, the phosphasiletane was unstable and phosphasiletene **24** was isolated (Scheme 6). If, however, the phenyl moiety was replaced by a methyl group, to decrease the migration rate of the substituent from the phosphorus to the silicon atom, a phosphasiletane intermediate **23** (R=Me) was isolated, isomerization occurring upon heating at 75 °C.

2.2. Formation by cyclization

Voronkov's group showed that bis(chloromethyl)dimethylsilane **25** reacted with potassium hydrosulfide to give thiasiletane **26** in 55% yield (Scheme 7).[11] This cyclization was not observed with the more basic sodium salt. Ab initio and density functional theory calculations indicated that the cyclobutane ring of compound **26** is not planar.[12] These

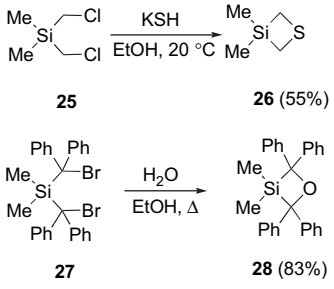


Scheme 5.



Scheme 6.

calculations showed that no electronic interactions exist between the silicon and sulfur atoms. These conclusions are in agreement with those deduced from IR or electron diffraction spectra and X-ray structure.[13]

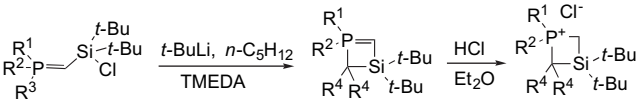


Scheme 7.

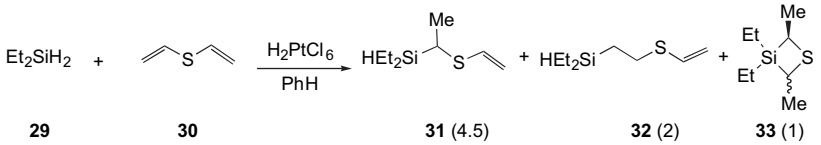
The first oxasiletane obtained using this methodology was formed by the reaction of bis(bromodiphenylmethyl)dimethylsilane **27** with water in ethanol at reflux (Scheme 7).[14] The structure of compound **28** was subsequently confirmed by X-ray diffraction. Dibromosilapropane **27** reacted similarly with H_2S, to lead to the corresponding thiasiletane (16% yield).[15]

The preparation of thiasiletanes is also possible by intramolecular hydrosilylation of unsaturated sulfides. Voronkov and co-workers showed that the reaction of diethylsilane **29** with divinyl sulfide **30** in the presence of H_2PtCl_6 at 100 °C for 12 h led to thiasiletane **33** in low yield (1:1 mixture of the two diastereomers). The major reaction products **31** and **32** resulted from a monohydrosilylation (Scheme 8).[16] Heating of the unsaturated hydrogenosilane **31** in the presence of the catalyst, under the same reaction conditions, gave rise to the exclusive formation of thiasiletane **33**. Improved results for the cyclization of silane **31** were reported using the Wilkinson catalyst (73% yield).[17]

An original preparation of phosphasiletenes **35a**,**b** (Scheme 9) was reported involving the reaction of silylmethylenephosphoranes **34a**,**b** with *tert*-butyllithium. This lithium reagent abstracted one of the acidic hydrogens of the isopropyl or methyl substituents fixed on the phosphorus atom, and intramolecular substitution of the chlorine atom on the silicon took place. The structure of the cyclic product **35a** was secured by X-ray diffraction. These phosphasiletenes easily



Scheme 9.

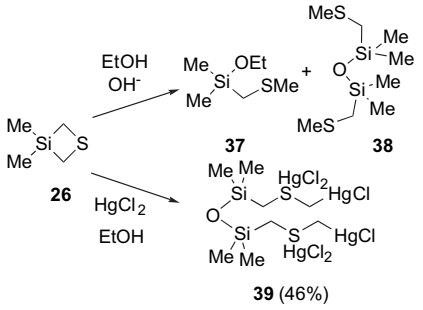


Scheme 8.

added HCl to give the corresponding 1,3-phosphasiletan-1-iums **36a**,**b**.[18]

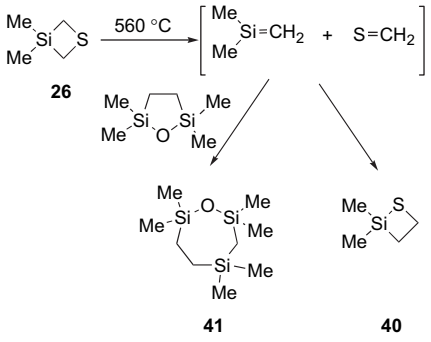
2.3. Reactivity and applications

The reactivity of thiasiletanes has been briefly examined and it was found that the cyclobutanic C–Si bonds in thiasiletane **26** were easily cleaved (exothermic reactions) by reaction with potassium hydroxide or mercuric chloride in ethanol, to give **37** and **38**, or **39**, respectively (Scheme 10).[11]



Scheme 10.

Gusel'nikov and co-workers have studied the thermal stability of this family of compounds. At temperatures between 500 and 700 °C, the compounds underwent [2+2] cycloreversions. Pyrolysis of thiasiletane **26** led to the intermediate formation of dimethylsilene, which reacted with the in situ-formed thioformaldehyde to yield 1,2-thiasiletane **40**. Co-pyrolysis in the presence of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane gave the insertion product **41** (Scheme 11).[19]



Scheme 11.

3. Preparation of five-membered heterocyclic compounds

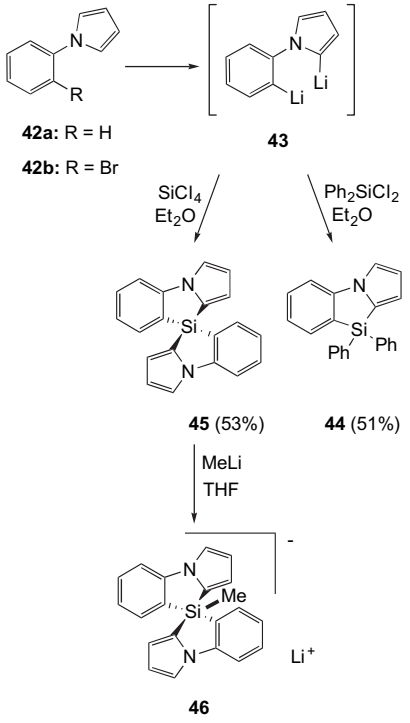
Compounds with silicon and oxygen, sulfur, nitrogen, phosphorus, selenium or boron atoms in the 1,3 positions have been reported. In Scheme 12, the IUPAC names and structures of these heterocycles have been summarized.

The different methods of preparing these heterocycles are listed by the nature of the bond formed in the cyclization step. The more studied methods imply the reaction of 1,3-dianions with dihalosilanes and these are included in the ring closures by silicon–carbon bond formation. Ring closures by the formation of heteroatom–carbon and carbon–carbon bonds have also been examined.

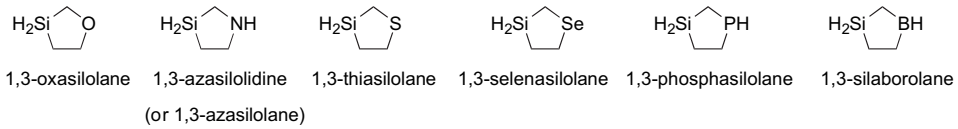
3.1. Preparation by formation of silicon–carbon bonds

Two strategies have been explored to obtain these five-membered heterocyclic compounds in such conditions. The first method implies the reaction of 1,1-dichlorosilanes with 1,4-dimetallic species and the second uses the intramolecular cyclization of difunctionalized linear compounds.

3.1.1. Preparation by reaction of dihalosilanes with dianionic species. Cheeseman and Greenberg showed that the reaction of 2,2′-dilithio-1-phenylpyrrole **43** with diphenyldichlorosilane led to the corresponding heterocyclic compound **44** in good yield (Scheme 13).[20] The dilithiated compound **43** was generated from 1-phenylpyrrole **42a** (2 equiv BuLi, TMEDA) or from 1-(2-bromophenyl)-1-*H*-pyrrole **42b** (2 equiv BuLi). By reaction with $SiCl_4$, the lithiated compound **43** led to the spiranic product **45**. After



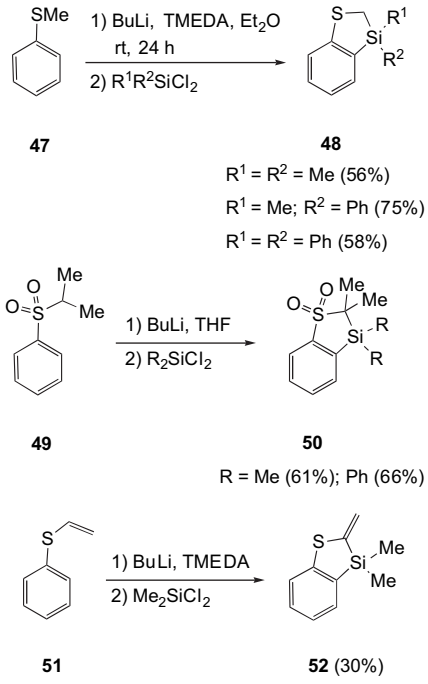
Scheme 13.



Scheme 12.

reaction with methyllithium, this latter product led to the formation of the pentacoordinate silicate **46**. Exchange of lithium by a tetrabutylammonium cation yielded a more stable compound, which was fully characterized. Dynamic equilibria of the pseudorotamers of such a silicate have been observed.[21]

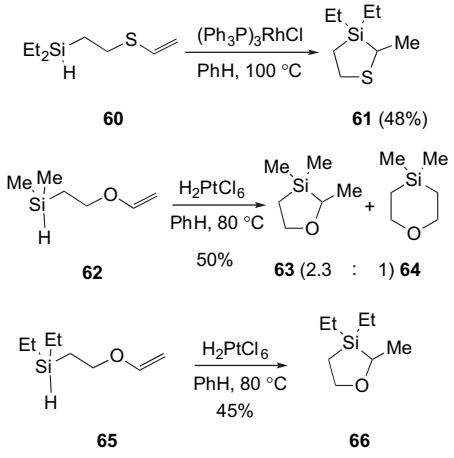
Reaction of methylphenylsulfane **47** with 2 equiv of *n*-BuLi in ether led to a 1,4-dianion. The reaction of this latter dianion with dichlorosilanes gave the corresponding thiasilolanes **48** in good yields (Scheme 14),[22] and reaction with tetrachlorosilane led to a spiro compound. A similar dianion formation was found starting from sulfone **49**, and BuLi in THF,[23] and dioxothiasilolanes **50** were obtained in good yields. The same group showed that thiasilolane **52** could be formed from vinylthiobenzene **51** using a similar strategy.[24]



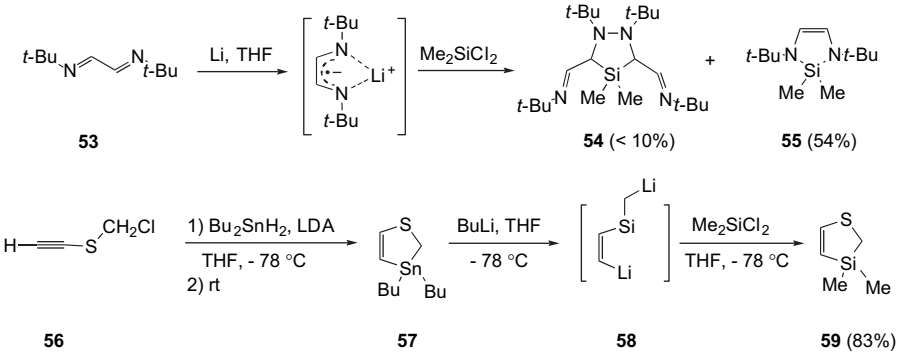
Scheme 14.

Reaction of *N*,*N*′-1,2-ethanediylidene-di(*tert*-butylamine) **53** with lithium followed by the addition of dichlorodimethylsilane was reported to yield products **54** and **55** via a radical cation intermediate (Scheme 15).[25] Diazasilolidine **54** (C-silylation compound) formed after dimerization of the radical cation was isolated in low yield. The major product **55** resulted from the N-silylation. This main process was exclusively observed when dichloromethylsilane[25] or trichloromethylsilane[26] was used as quenching agent or when *N*,*N*′-1,2-ethanediylidene-di(2,6-dimethylbenzeneamine) was used as substrate.[26] Thiasilolene **59** has been prepared by the reaction of dilithiated compound **58** with dichlorodimethylsilane. This intermediate **58** was obtained by cleavage of the carbon–tin bonds of the cyclic compound **57**, by reaction with butyllithium at low temperature. The stannylated compound **57** was prepared in two steps from chloromethyl ethynyl sulfide **56** by reaction with $LiHSnBu_2$ followed by intramolecular hydrostannylation (Scheme 15).[27]

3.1.2. Preparation by formation of a carbon–silicon bond. One of the best methods to form a carbon–silicon bond is probably the hydrosilylation reaction. The Voronkov group studied the intramolecular version of this reaction, in particular for the preparation of thiasilolane **61** from vinyl sulfide **60** (Scheme 16). The most effective catalyst to carry out these cyclizations appeared to be the Wilkinson catalyst.[16b,17] Competitive formation of six-membered compounds was not observed. When the reaction was catalyzed by chloroplatinic acid, lower yields were obtained.[16a] This hydrosilylation was also found to be possible starting from 2-vinyloxyethylsilanes **62** and **65**. In the presence of chloroplatinic acid as catalyst, intramolecular cyclizations were observed, and regioselectivity seemed to depend upon the silicon atom substituents. With diethylsilane **65**,



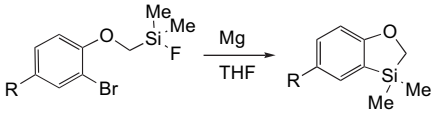
Scheme 16.



Scheme 15.

only the five-membered ring compound was obtained, while, with dimethylsilane **62**, a mixture of compounds **63** and **64** was formed, resulting from the competitive *endo* and *exo* cyclizations.[28]

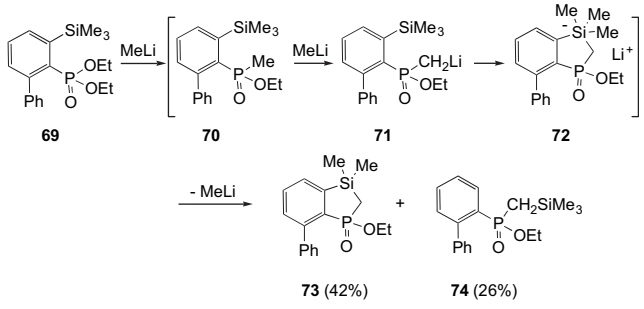
Nietzschmann and co-workers reported that benzoxasilolanes **68a**,**b** could be obtained by reaction of dihalo derivatives **67a**,**b** with magnesium (Scheme 17).[29] The scope of this very simple method, when an aryl organometallic intermediate should lead to a nucleophilic attack on the silicon atom, has never been examined.



67a: R = H **68a** (61%)
67b: R = Me **68b** (65%)

Scheme 17.

An original preparation of benzophosphasilolenes such as **73** was reported by Vedejs and co-workers by the reaction of 2-trimethylsilylarylphosphonate **69** with methyllithium (Scheme 18).[30] This transformation implies the substitution of one of the ethoxy groups fixed at the phosphorus atom by a methyl (intermediate **70**), followed by abstraction of one of its acidic hydrogens by methyllithium to give **71**. Subsequent nucleophilic attack of the silicon atom led to siliconate **72**. Elimination of methyllithium gave rise mainly to the heterocyclic compound **73**. In the absence of an aryl substituent in the α-position of the aromatic ring of compound **69**, this cyclization was not observed.

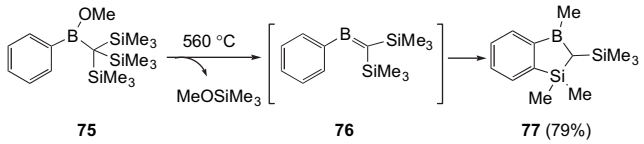


69 **70** **71** **72**

73 (42%) **74** (26%)

Scheme 18.

Flash vacuum pyrolysis (560 °C) of phenylborinate **75** led to the intermediate formation of a methylene borane **76**. This compound, later, after a 1,3-shift of one of the methyl groups fixed at the silicon atom, led to the formation of silaborolane **77** (Scheme 19).[31] When the substituent fixed on the boron



75 **76** **77** (79%)

Scheme 19.

atom is a benzyl instead of a phenyl group, benzosilaborinanes were obtained (see Scheme 85).

The preparation of silaheterocycles by the formation of Si–C bonds was also reported to be possible in the case of the formation of reactive intermediates such as silenes or silylenes. The formation of an azasilole was reported by Tilley et al. during their study concerning the reactivity of a tris(trimethylsilyl)silylscandium(III) derivative **78**.[32] Its reaction with 2-isocyano-1,3-dimethylbenzene led to the formation of azasilole **80**, in which the scandium metal was complexed by two nitrogen atoms (Scheme 20).[32] The formation of the azasilole was tentatively explained by the insertion of one molecule of isocyanate into the Sc–Si bond to give, first, the isolable intermediate **79**, which, after the addition of a second equivalent of isocyanate, led to the product **80**, the structure of which secured by X-ray crystallographic analysis.

Hindered disilenes were found to be in equilibrium with silylenes by moderate heating. Reaction of disilene **81** with mesityl isocyanate resulted in the formation of the intermediate **82**. By a nucleophilic attack of the silicon atom of this intermediate at the *o*-position of the mesityl group and migration of the mesityl and methyl groups, the product **84** was formed, via the postulated intermediate **83**. The structure of **84** was confirmed by X-ray crystallographic analysis (Scheme 21).[33]

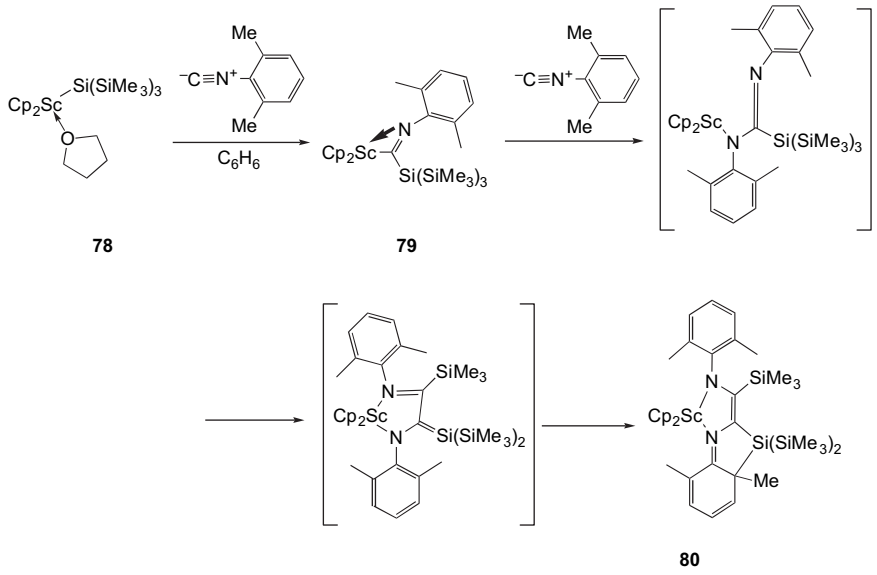
3.2. Preparation by formation of carbon–heteroatom bonds

Intramolecular cyclization of alcohol **85** in the presence of NaH led to oxasilolane **86** (Scheme 22).[34] The electronic diffraction spectra of this compound were determined out and compared to the ab initio calculations.

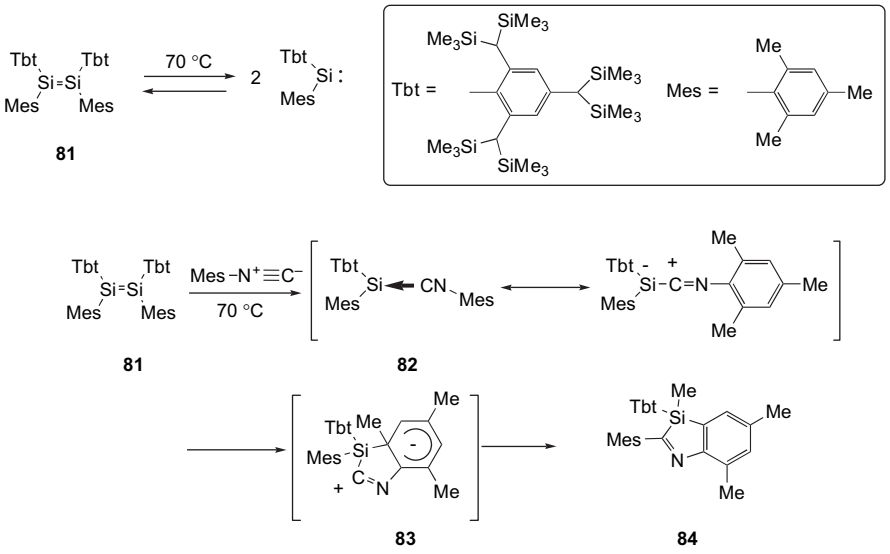
Reich and co-workers have studied the reactivity of 2,3-bis-(trimethylstannyl)-1,3-butadiene **87**.[35] By reaction with 1 equiv of MeLi, followed by silylation with a chlorosilane, they isolated compound **88**. This compound, later, after reaction with 1 equiv of methyllithium and addition of selenium, led to the bis(methylidene)selenosilolane **89**. This unstable compound was used to prepare the Diels–Alder adduct **90** (Scheme 23).

Two different groups have reported interesting syntheses of 4-silaproline derivatives. Tacke and co-workers found that the racemic silaproline ester **93** could be obtained in two steps from 2,5-dihydropyrazine **91** by metallation with butyllithium followed by alkylation using bis(chloromethyl)dimethylsilene and hydrolysis with HCl (Scheme 24).[36] Heating of alkylated compound **92** at 120 °C led to azasilolidine **94**. (*R*)-Silaproline ester **93** was also prepared by this method starting from (*R*)-2,5-dihydro-2-isopropyl-3,6-dimethoxypyrazine (Schöllkopf pyrazine **95** in Scheme 25) (overall yield: 20%).[36b]

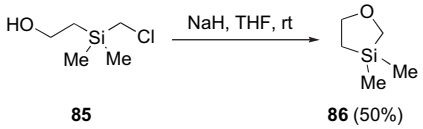
A second approach to (*R*)-silaproline esters has been reported.[37] Alkylation of Schöllkopf pyrazine **95** with bis-(iodomethyl)dimethylsilane give a mixture of the two diastereomers **96** and **97**. The major isomer was isolated and transformed into (*R*)-*N*-protected silaproline **98**



Scheme 20.



Scheme 21.

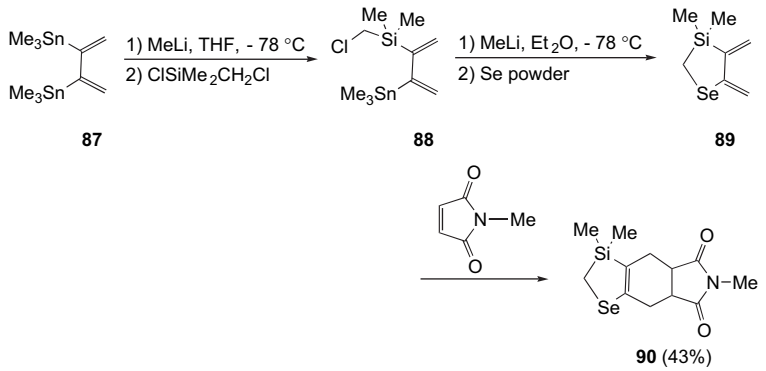


Scheme 22.

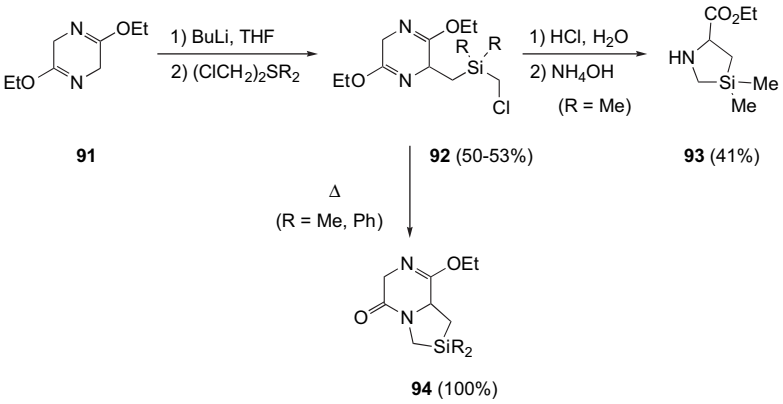
(Scheme 25). Reaction with the (*S*)-pyrazine gave similarly the silaproline with the (*S*) configuration. These silaprolines appear to be 14-fold more lipophilic than proline. Replacement of a proline unit in the C-terminal segment NT(8–13) of neurotensin by silaproline improved the resistance to biodegradation without a great modification of their biological activities.[38] Similar results were observed by incorporation of silaproline in substance P.[39]

The Voronkov group showed that the method used for the preparation of 1,3-thiasiletanes by the reaction of α,ω-dihalosilaalkanes with KSH (Scheme 7) could not be applied to the formation of 1,3-thiasilolanes. Another approach was reported to be possible in the case of sulfur compounds. Thiasilolane **101** was obtained by reaction of allyl(chloromethyl)silane **99** with alcoholic KSH solution. The intermediate thiolate anion **100** was not detected (Scheme 26).[40] The six-membered ring compound (*endo* cyclization) was not formed. This method was, however, applied to the formation of the six-membered compound by *exo* mode cyclization (see Scheme 72).

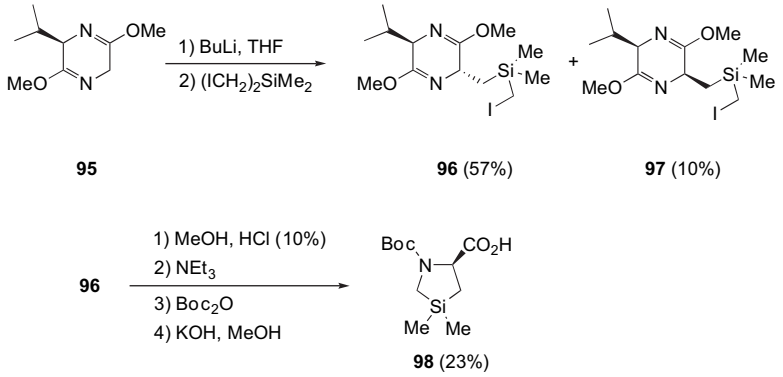
The same group has also studied the formation of thiasilolanes by radical cyclization. This method appears interesting, due to the easy formation of a thiyl radical and its propensity to add to carbon–carbon double bonds. Reaction of divinylsilane **102** with H_2S under irradiation in the presence of YCl_3 as photocatalyst led mainly to a mixture of thiasilolane **101** and thiasililane **103** (Scheme 27).[41] In the



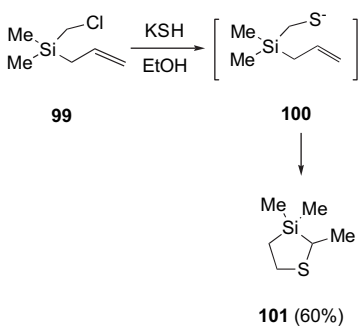
Scheme 23.



Scheme 24.



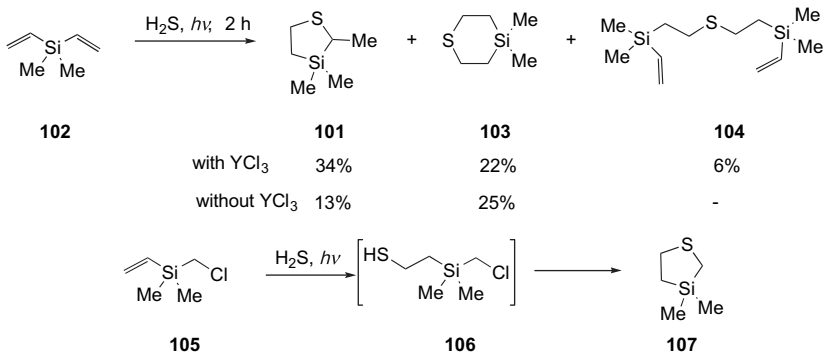
Scheme 25.



Scheme 26.

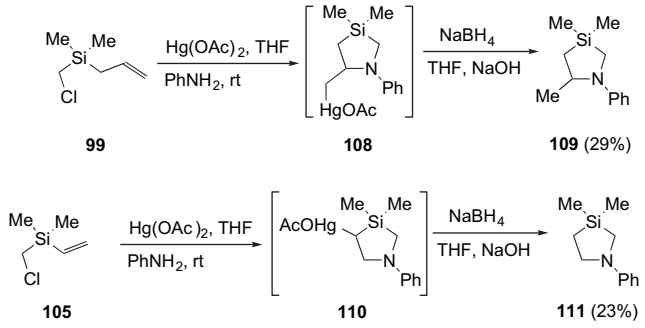
absence of YCl_3, the side product **104** resulting from an intermolecular reaction of the intermediate thiol was not formed, but product **101** was obtained in lower yield.[40] Irradiation of 2-[dimethyl(vinyl)silyl]ethanethiol led to the same mixture of regioisomers **101** and **103**. Another route to the thiasilolanes, e.g., **107**, briefly explored, uses the intramolecular cyclization of 2-(chloromethyldimethylsilyl)-ethanethiol **106**, postulated as an intermediate in the addition of H_2S onto the carbon–carbon double bond of vinylsilane **105**.[40]

Electrophilic cyclizations have also been reported to be useful for the preparation of azasilolidines and oxasilinanes.



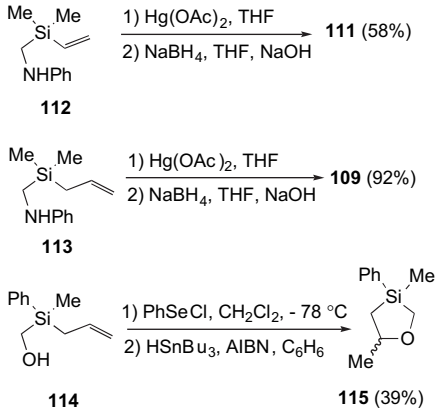
Scheme 27.

The Russian group showed that alkenyl(chloromethyl)-silanes **99** and **105** reacted with aniline in the presence of mercury(II) acetate to afford in low yields, after reductive elimination, the corresponding azasilolidines **109** and **111** (Scheme 28).[42] These reactions occurred by the intermediate formation of the aminoalkyl(chloromethyl)dimethylsilanes, which cyclized to the mercury derivatives **108** and **110**.



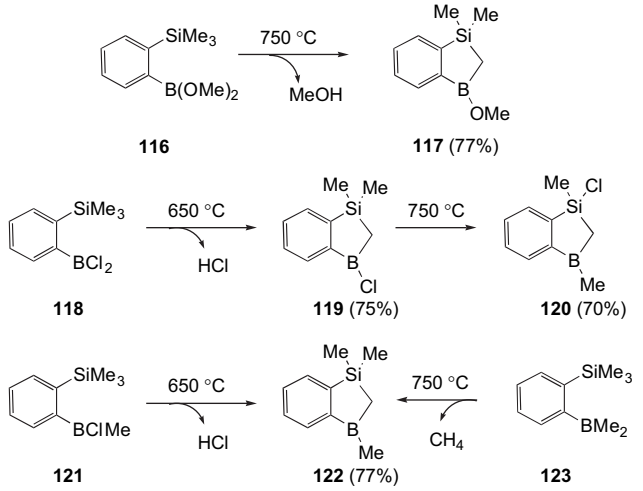
Scheme 28.

In a subsequent study, it was shown that these heterocyclic compounds could be obtained more efficiently by intramolecular aminomercuration of alkenyl(aminomethyl)silanes, e.g., aminosilanes **112** and **113** led to azosilolidines **111** and **109** in good yields (Scheme 29).[43] Higher-ring-size compounds were obtained in lower yields. The absence of the formation of azasilinanes during the cyclization of compound **113** was explained by the well-known ability of silyl groups to stabilize a neighboring β-carbocation.[44] Seleno etherification of alcohol **114** followed by reductive elimination led to oxasilolane **115** as a 1:1 mixture of two diastereomers in moderate yield. At the present time, the potential of this reaction has not been fully explored (Scheme 29).[45]



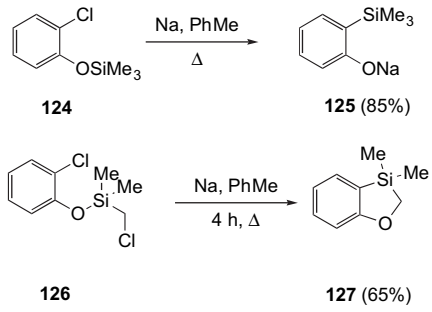
Scheme 29.

Schacht and Kaufmann have studied the flash vacuum pyrolysis of (2-trimethylsilylphenyl)boranes, e.g., thermolysis of borane **116** led to silaborolane **117** and methanol in good yield (Scheme 30).[46] The mechanism of these reactions seems to take place by a radical pathway. Flash vacuum pyrolyses of chloroboranes **118** and **121** occurred at lower temperature than methoxyboranes to give **119** and **122**, respectively. This result is a consequence of the easier extrusion of hydrogen chloride compared to that of methanol. At higher temperature, chloroborane **119** was rearranged into chlorosilane **120**. The transformation of methylborane **123** into silaborolane **122**, by extrusion of methane, was also reported to occur at high temperature.



Scheme 30.

Nietzschmann and co-workers studied the reaction of 2-halophenoxysilanes such as **124** in the presence of sodium or *n*-butyllithium. A [1,3]-carbanionic rearrangement was observed, leading to the formation of 2-silylphenate **125** (Scheme 31).[47] When one of the substituents fixed at the silicon atom was a chloromethyl group, e.g., **126**, this rearrangement led to the formation of the benzooxasilolane **127**.[29,48]

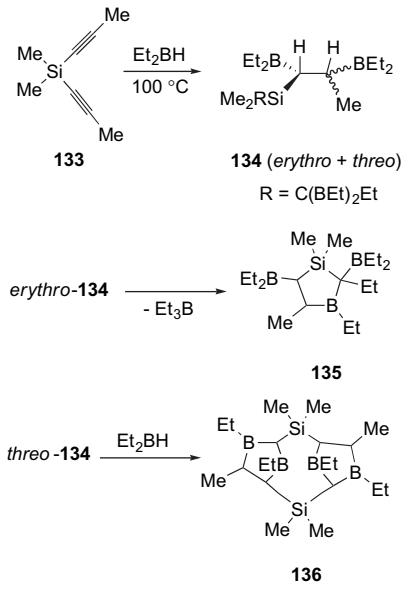


Scheme 31.

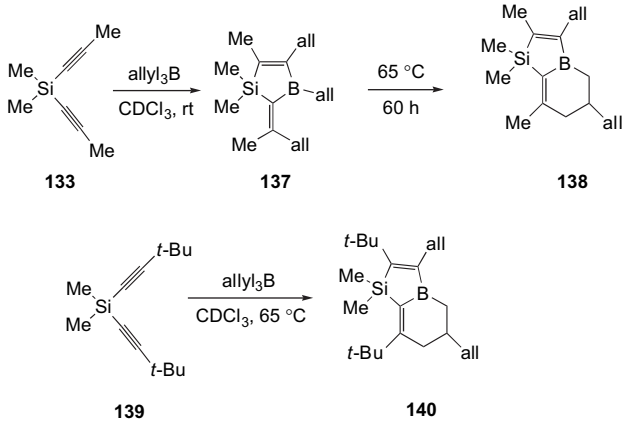
Sato and co-workers showed that azasilolines **129** were obtained in low yields, among various products, by an intermolecular reaction of trialkylsilylethylamines **128** with benzyne (Scheme 32).[49] These results prompted this group to study an intramolecular version of this reaction, to avoid the formation of numerous side reaction products. The reaction of (aminomethyl)(3-chlorophenyl)silanes **130a–c** with phenyllithium in ether led to the intermediate formation of benzyne derivatives **131a–c**, which were trapped by the nitrogen atom to give compounds **132a–c** in acceptable yields (Scheme 32).[50]

Köester and co-workers showed that siladiyne **133** reacted with an excess of diethylborane to give a mixture of *threo*- and *erythro*-3,3,5,6-tetrakis(diethylboryl)-4,4-dimethyl-4-silaheptanes **134**. The *threo* isomer reacted further with diethylborane to lead to product **136**, while elimination of triethylborane occurred leading to the formation of silaborolane **135** with the *erythro* isomer (Scheme 33).[51] The mechanism of these transformations was not clarified.

Subsequently, the same group examined the addition of diynylsilanes with triallylborane. Starting from diynylsilane **133**, methylenesilaborole **137** was obtained, which, by heating at 65 °C, was rearranged into the bicyclic silaborole **138**.[52] With the less reactive diynylsilane **139**, the methylenesilaborole was not detected, and silaborole **140** was isolated as a unique product (Scheme 34). This cycloaddition was not observed in the case of dimethylbis(2-phenylethynyl)silane. Reaction of diynylsilane **139** with 1-boraadamantane was found to lead also to the formation of a silaborolane.[53]

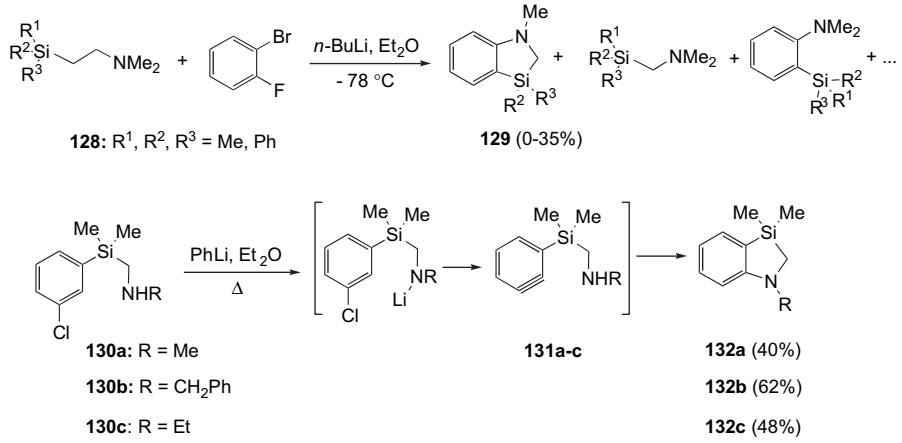


Scheme 33.



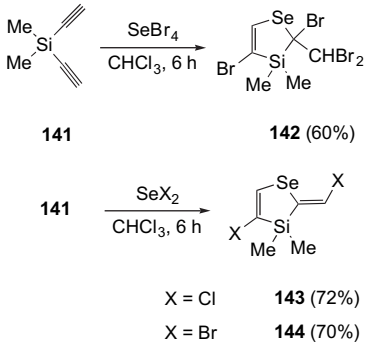
Scheme 34.

Electrophilic addition of $SeBr_4$, $SeCl_2$ and $SeBr_2$ and to diethynylsilane **141** was reported to lead by successive



Scheme 32.

electrophilic reactions to the formation of selenosilolenes **142–144** (Scheme 35).[54,55]



Scheme 35.

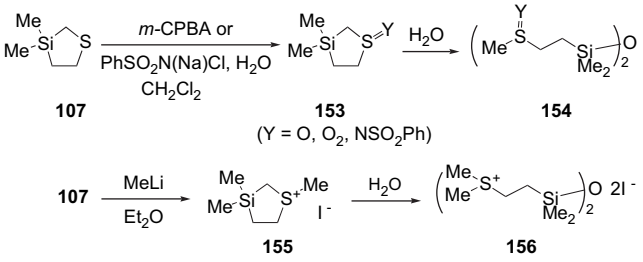
3.3. Preparation by formation of carbon–carbon bonds

The preparation of thiasilolene **148** was reported by intramolecular cyclization of ethynylsilane **145** initiated by tributyltin hydride in benzene. The initial radical **146** evolved by cyclization, cleavage, and further cyclization into the radical **147**. Finally, this latter radical gave rise to the formation of compound **148** (Scheme 36).[56]

Recently, Tanaka and co-workers have also reported an example of cyclization by the formation of a carbon–carbon bond. They studied the radical cyclization of nucleoside 2-sila-5-hexenyl radicals. When a methyl group was present on carbon 2′ (Scheme 37, compound **149**), they observed a competition between the 5-*exo* and 6-*endo* cyclizations. In the reaction mixture, compound **150** was the major component, compound **151** the minor component, and the glycosidic bond-rearranged product **152** was also isolated. This latter product is probably formed by rearrangement of the 5-*exo* cyclization product **150** after radical C–N bond cleavage. In the absence of this methyl group, only the product corresponding to 6-*endo* cyclization was observed (see Scheme 91).[57]

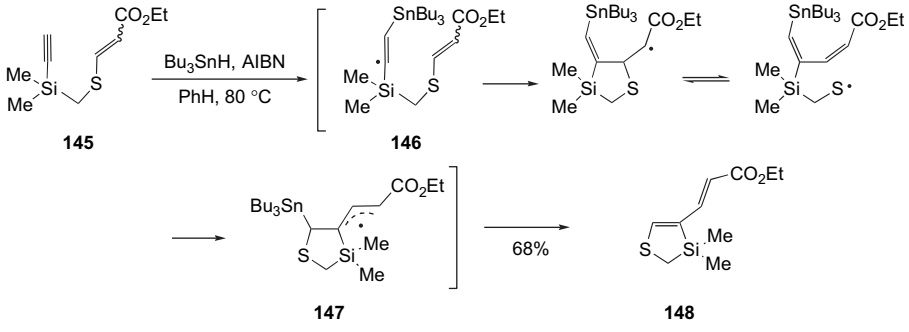
3.4. Reactivity and applications

Thiasilolanes reacted with *m*-chloroperbenzoic acid to give the corresponding sulfoxides and sulfones (Scheme 38, compounds **153**: Y=O and O_2). These sensitive compounds were cleaved to give **154** (Y=O and O_2) in the presence of hydrolytic solvents such as water. Similar ring openings of sulfimide **153** to **154** (Y=NSO_2Ph) and sulfonium salt **155** to **156** were reported.[58] The corresponding six-membered ring compounds appear to be more stable.

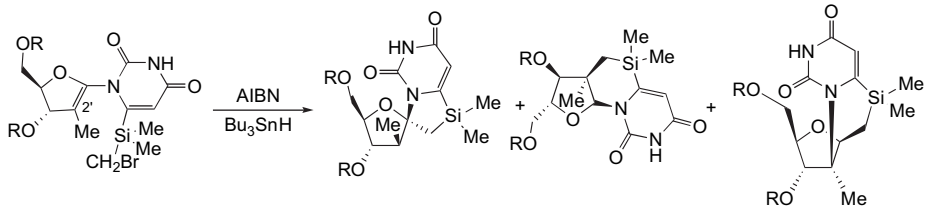


Scheme 38.

The reaction of benzoazasilolidines **132a**,**b** with benzyne was examined.[50] Stevens' rearrangement products **157a**,**b** were obtained when the substituents fixed at the nitrogen

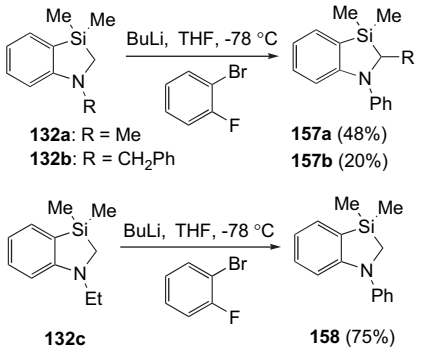


Scheme 36.



Scheme 37.

atom were benzyl or methyl groups. When the substituent was an ethyl group (compound **132c**), however, product **158** was obtained, formed by a Hoffmann elimination reaction (Scheme 39).



Scheme 39.

In conclusion, many approaches have been examined for the preparation of five-membered heterocyclic compounds containing a silicon atom and another heteroatom. In general, however, these methods have not been explored in detail and work seems necessary to improve the preparations and examine their scope. Contrary to the corresponding four-membered-ring heterocyclic compounds, these compounds appear to be stable enough to allow subsequent reactions and their use for the synthesis of more complex frameworks.

4. Preparation of six-membered heterocyclic compounds

Heterocyclic compounds with silicon and oxygen, sulfur, nitrogen, phosphorus, selenium, tellurium or boron atoms in the 1,3- or 1,4-positions are known. In Scheme 40, IUPAC representative names and structures of these heterocycles have been summarized.

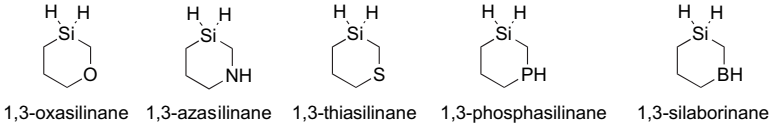
As for the synthesis of five-membered heterocycles (vide infra), different strategies have been developed to obtain this ring size, and they are subdivided by the nature of the bond formed in the cyclization step.

4.1. Preparation by formation of carbon–silicon bonds

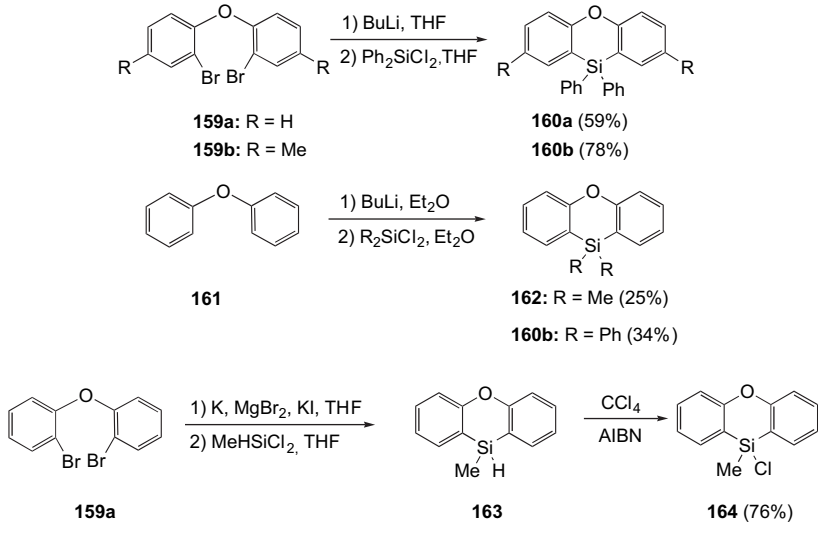
4.1.1. Preparation by reaction of dihalosilanes with dianionic species. This method implies the reaction of silane derivatives (mainly *gem*-dichlorosilanes) with 1,5-dianions.

4.1.1.1. Preparation of oxasilinanes. Different groups have simultaneously developed this method. The first oxasilinanes appear to have been synthesized by Hitchcock and co-workers.[59] Compounds **160a**,**b** were obtained by reaction of 2,2′dibromodiphenyl ethers **159a**,**b** with butyllithium followed by the addition of 1,1-dichlorosilanes (Scheme 41).

At the same time, Gilman and Oita found that lithiation of diphenyl ether **161** could give rise to the formation of products **160a** and **162** (R=Me). These reactions, carried out in ether, led to lower yields (25–40%) than those obtained by the Hitchcock approach.[60] Gilman and Miles prepared several compounds with different substituents on the silicon atom (**162**: R=benzyl, *n*-dodecyl) with the aim of obtaining synthetic lubricants of low melting point and high volatilization point.[61] These results were confirmed in two subsequent reports.[62,63] Corey and Chang have examined in detail these two approaches to oxasilinanes, and found that the halogen–metal exchange led to dilithio intermediates in better yields than the direct metallation.[64] Utilization of sodium as the



Scheme 40.

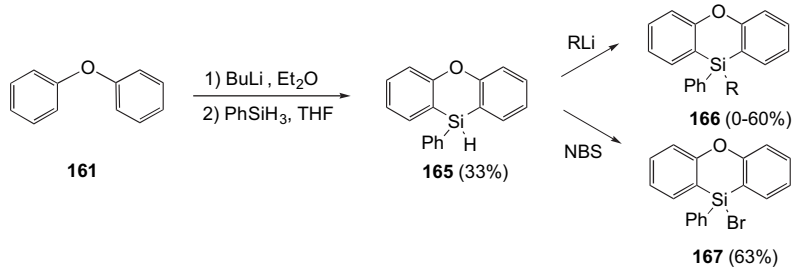


Scheme 41.

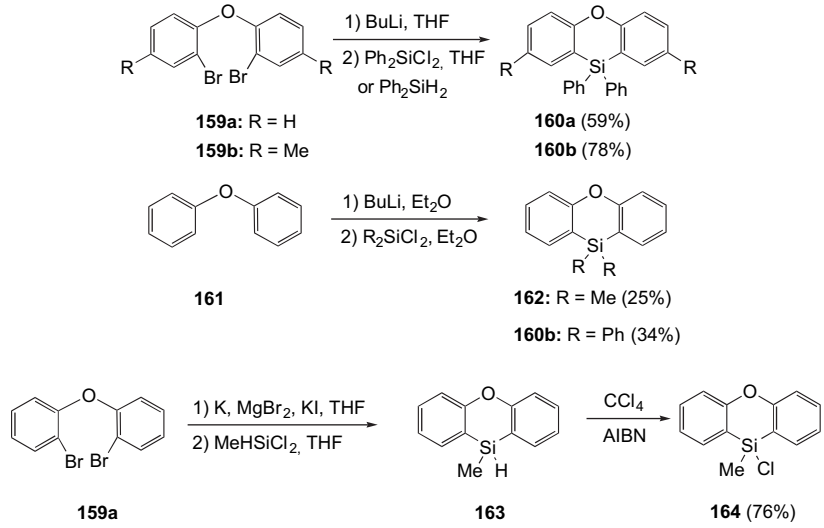
metal has been reported to be less efficient.[65] More recently, it was reported that the reaction of 2,2′-dibromophenyl ether **159a** with Riecke magnesium led, after reaction with methyldichlorosilane, to oxasilinane **163** in good yield. This latter compound reacted with CCl_4 in the presence of AIBN to give chlorosilane **164** (Scheme 41).[66] This method was also applied to the preparation of 10-methyl-10*H*-phenothiasiline (vide supra). Formation of oxasilinanes by this method is not limited to the reaction of dichlorosilanes, hydrogenosilanes also being used with success as quenching agents (Scheme 42).[64,67] Reaction of phenylsilane with the dilithium derivative formed from diphenyl ether **161**, led to hydrogenosilane **165**. This compound was subsequently transformed into silanes **166**, by reaction with organolithium reagents, or to bromosilane **167**, by reaction with *N*-bromosuccinimide.

4.1.1.2. Preparation of azasilinanes. Simultaneously with the preparation of oxasilinanes, Gilman and co-workers studied the preparation of azasilinanes using this methodology. Compounds **169** and **170a**,**b** were obtained by the reaction of the *N*-alkyl-2,2′-dilithiodiphenylamine prepared from **168** with dichlorosilanes[68] and dihydrogenosilanes[68d] (Scheme 43). Compound **169** was also obtained by the reaction of the dilithio intermediate with triphenylchlorosilane, one of the phenyl groups being expelled (42% yield).[69] Azasilinanes **170a**,**b** bearing hydrogen on the silicon atom were used for further functionalization by reaction with organolithium compounds to form **171a**,**b** (Scheme 43).

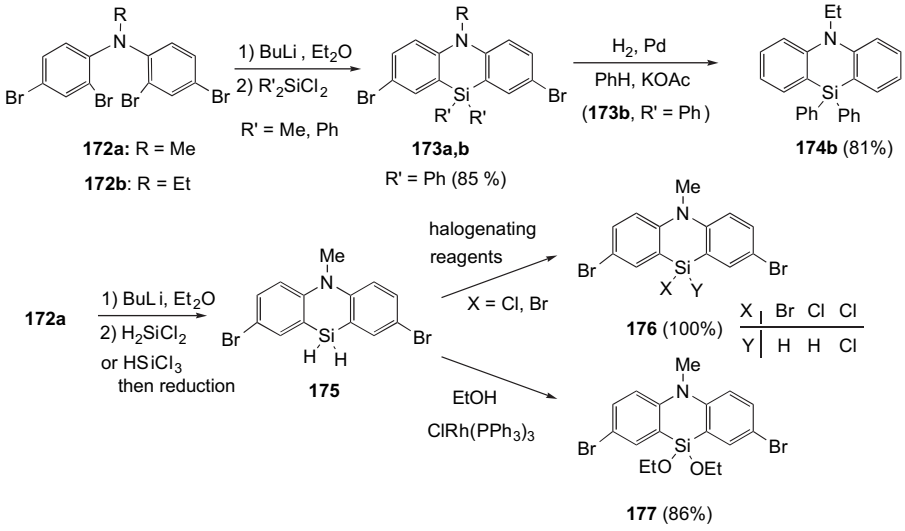
The main drawback of the work developed by Gilman et al. was the difficult preparation of the dibrominated compound **168**. Wasserman and co-workers showed that dibenzoazasilinanes could be obtained from the tetrabromodiphenylamines **172a**,**b** (Scheme 44), formed by polybromination of diphenylamine and alkylation. Reaction of amines **172a**,**b** with BuLi led to a regioselective Br–Li exchange and the resulting dilithio intermediates react with dichlorosilanes to give the cyclic compounds **173a**,**b**. Subsequent hydrogenolysis of the C–Br bonds gave rise to the azasilanes, e.g., **174b** (R′=Ph) in good overall yields.[70] The same products were obtained by the reaction of **173a**,**b** with BuLi, followed by hydrolysis. Contrary to the claim of Wasserman, substitution of the two bromine atoms was found to be difficult using BuLi.[71] The preparation of phenazasilenes was reported to be more convenient using monoalkylsilanes, instead of chlorosilanes.[72] Two different pathways were used to obtain phenazasilene **175** from tetrabromo compound **172a**. After formation of the dilithio intermediate, the quenching was carried out using H_2SiCl_2 (23% yield) or, better, $HSiCl_3$ followed by in situ reduction of the monochlorosilane (58% yield) (Scheme 44).[73] Reactions of compound **175** with CCl_4 in the presence of $ClRh(PPh_3)_3$ or NBS led to compounds **176** (X=H; Y=Br, Cl) resulting from monohalogenation, and reaction with $SOCl_2$ led easily to the dichlorosilane (**176**; X, Y=Cl). Dialkoxysilanes such as compound **177** were formed by the reaction of dihydrosilane **175** with primary alcohols in the presence of Wilkinson's catalyst.



Scheme 42.



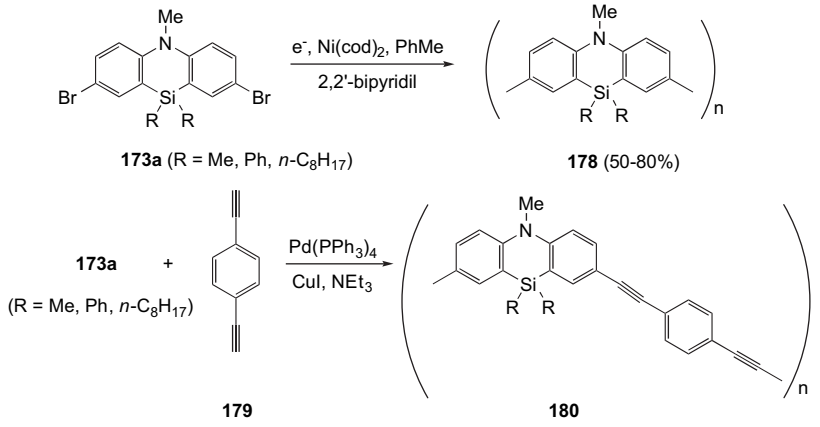
Scheme 43.



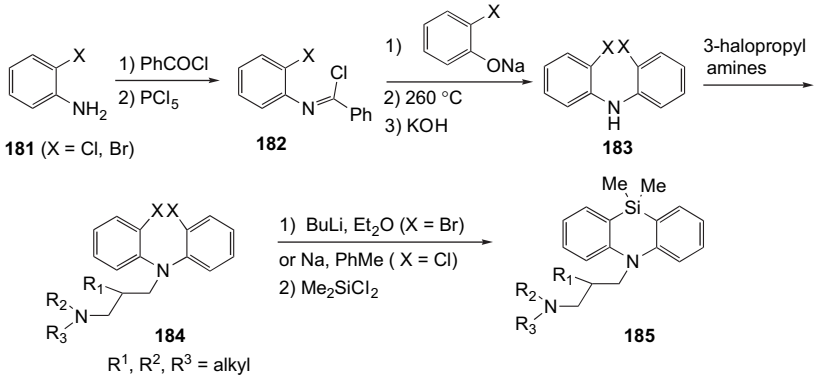
Scheme 44.

Electrochemical polymerization reactions of bromophenazathiasilins have been examinated.[74] Phenazasilines **173** led in the presence of nickel salts to the formation of polymers **178**. Polymerization in the presence of 1,4-diethylnylbenzene **179** was reported to give copolymers **180**. Similar polymerization was observed starting from 1,3-diethynylbenzene. These polymers show reversible electrochromic properties upon electrochemical treatment (Scheme 45).[75]

Using Gilman's method, the Wannagat group prepared azasilinanes *N*-substituted by a 3-(dialkylamino)propyl group from dibromoamines obtained by the sequence reported in Scheme 46 (75–80% yields).[76] Chloroimines **182**, synthetized from 2-haloanilines **181**, reacted with 2-halophenates to give diphenylamines **183**. Subsequent addition of 3-halopropylamines led to 1,3-diamino compounds **184**, which were transformed by Gilman's method to the desired



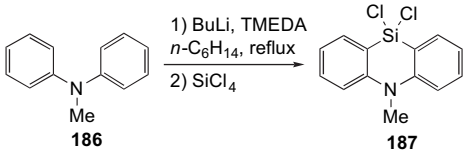
Scheme 45.



Scheme 46.

azasilinanes **185**. The authors showed that the dichloro derivatives could also be used if sodium was used as metal, but lower yields were obtained (32%). These silaacridanes have thymoleptic properties, comparable to those of their carbon analogues.[77]

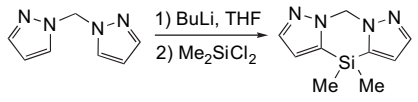
The preparation of phenazasiline **187** was also reported to be possible directly from diphenylamine **186**. To the dilithiated intermediate obtained by the reaction of amine **186** with butyllithium in the presence of TMEDA in hexane at reflux was added tetrachlorosilane in default quantity (Scheme 47).[78]



186 **187**

Scheme 47.

Different 1,3,5-diazasilinanes have also been synthesized by this methodology. The reaction of butyllithium with bis(pyrazol-1-yl)methane **188**, followed by the addition of dichlorodimethylsilane, led to the tricyclic compound **189** (Scheme 48).[79] When dichlorodiphenylsilane was used as the electrophile, the yield of the silaheterocyclic product was only 10%.

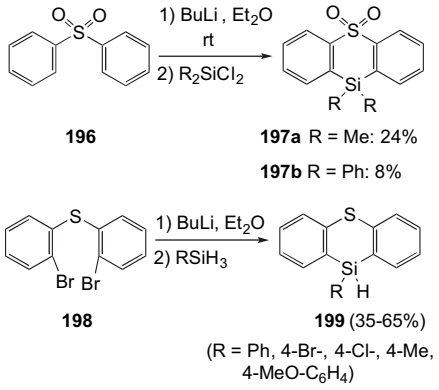


188 **189** (63%)

Scheme 48.

Linear aminals led to the same reaction. Karsch and coworkers showed that treatment of bis(amino)methanes **190** with *tert*-butyllithium in pentane led to the isolable dianions **191**. These latter dianions reacted with dichlorosilanes to give the corresponding diazasilinanes **192** (Scheme 49).[80] Sieburth and Mutahi have recently reported the preparation of silanediols, which inhibit protease enzymes, in particular, HIV protease. Among these compounds, the silaheterocyclic derivative **195** was obtained in two steps from the urea derivative **193** and then **194** using the same approach (Scheme 49).[81]

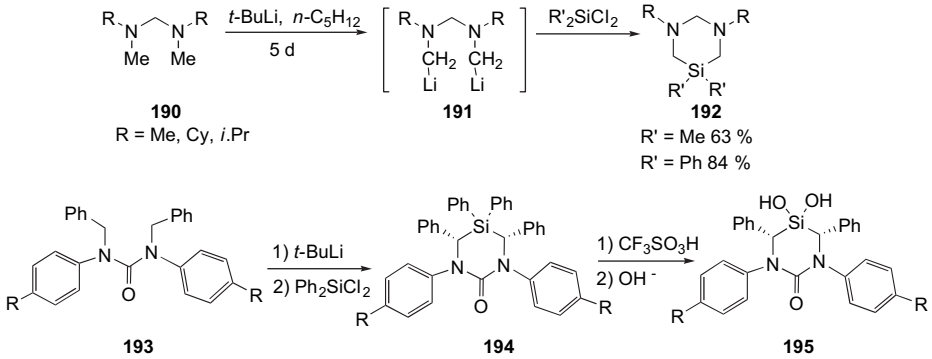
4.1.1.3. Preparation of thia- and phosphasilinanes. Simultaneously with the preparation of oxa- and azasilinanes, Gilman and Oita examined the formation of thiasilinanes. Reaction of diphenylsulfone **196** with butyllithium in ether led to the corresponding 2,2′-dilithiodiphenyl sulfone, which reacted with dichlorosilanes to lead to the formation of phenothiasilenes **197a**,**b** in modest yields (Scheme 50).[82] Subsequently, it was shown that utilization of lithium 2,2,6,6-tetramethylpiperidide as base in THF allowed an increase in the yield to 69% in the case of compound **197a**.[83] Reduction by $LiAlH_4$ of the sulfones to the sulfides was reported.[84] The direct formation of thiasilinanes **199** was shown to be possible starting from bis(2-bromophenyl)sulfide **198** (Scheme 50). Reaction of the dilithiated intermediate was reported with monoalkyl- or monoarylsilanes[85] and dichlorosilanes.[85,86] The main drawback of this method seems to be the difficult formation of the starting dibromide **198**.



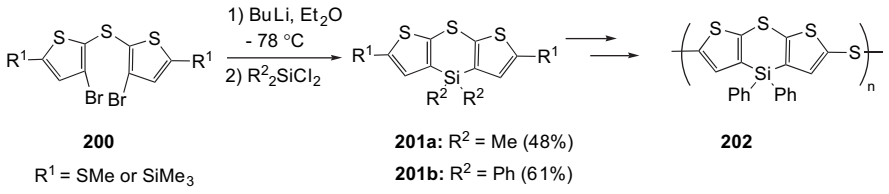
Scheme 50.

This method was also reported to be useful for the preparation of thiasilines **201a**,**b**. These compounds were prepared from sulfides **200** by Br–Li exchange with butyllithium followed by reaction with dichlorosilanes (Scheme 51).[87] Oxidation of compounds **201** with 1 or 2 equiv of *m*-chloroperbenzoic acid led to the corresponding mono and dioxides. Compound **201b** (R^1=Br) was transformed into polymer **202**, which, after doping with $FeCl_3$, showed interesting conducting properties.

The formation of 1,4-phosphasilinanes was reported by the reaction of bis(2-chlorophenyl)phosphines **203** with lithium

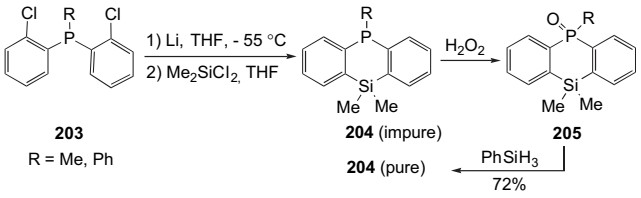


Scheme 49.



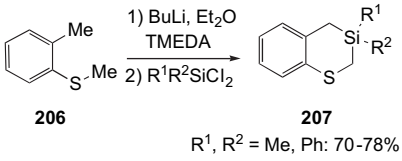
Scheme 51.

in THF, followed by the addition of dichlorodimethylsilane. Impure phosphasilinanes were obtained. After oxidation into the phosphine oxides **205**, subsequent reduction using phenylsilane led to pure 1,4-phosphasilinanes (Scheme 52).[88] The structures of compounds **204** were secured by X-ray crystallography.[89]



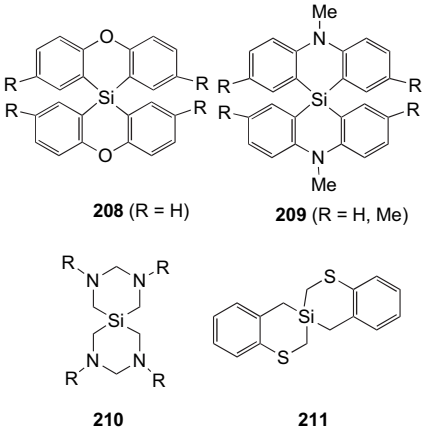
Scheme 52.

This methodology was not limited to the formation of 1-sila-4-heteroatomic compounds. Cabiddu and co-workers reported the first preparation of 1-sila-3-thiacyclohexane derivatives using the same approach. They showed that aromatic thio ethers such as compound **206** underwent direct dimetallation by reaction with 2 equiv of *n*-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine (TMEDA). The reaction of these dianions with electrophiles was examined. 1,3-Thiasilinanes **207** were obtained when dichlorosilanes were used (Scheme 53).[90] No reaction was observed when a second methyl group was present in the *meta* or *para* position of the sulfur atom on the aromatic ring.



Scheme 53.

4.1.1.4. Reactions with $SiCl_4$. In parallel to the utilization of dichlorosilanes, different reports have indicated the utilization of $SiCl_4$ as quenching agent. Spiro compounds were, in general, obtained.[22,59,60,64,67,69,71,72,80,90,91] The first example involving this reaction was reported by Hitchcock.[59] The spiro ethers **208** substituted in the *meta* position of the silicon atom were not, however, obtained (compound **208**; R=Me), probably due to steric hindrance. This harmful aspect due to the presence of a substituent in *meta* position was not observed for the formation of azasilinanes **209**.[71] Similar formations of spiro compounds **210** and **211** (Scheme 54) have been reported using the respective dilithiated derivatives of the compounds **192**[80] and **206**.[90] An attempt to prepare 10,10′-spirodibenzothiasilin-5,5,5′,5′-tetroxide using tetrachlorosilane as a quenching agent was not successful.[82]

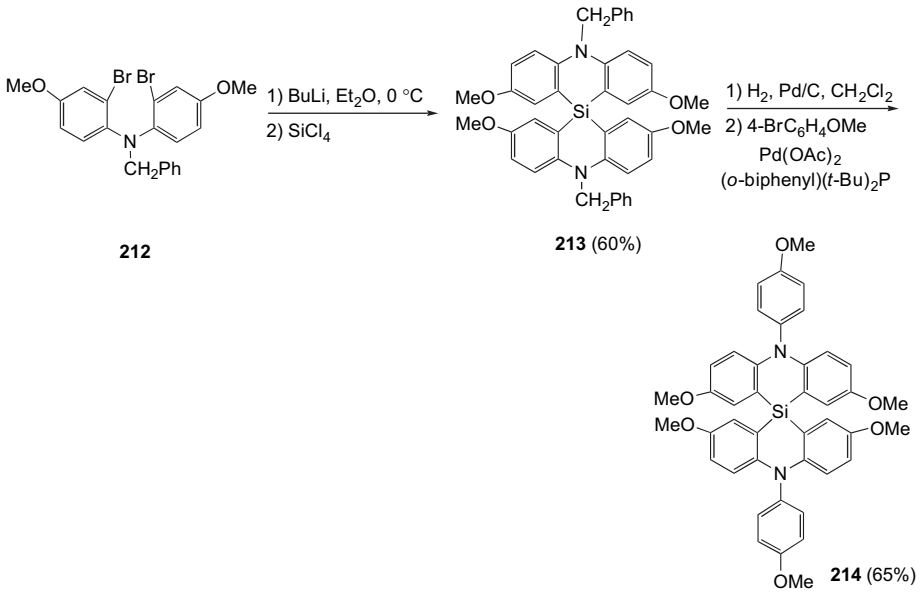


Scheme 54.

Access to the spiro compound **214** was recently reported. This compound was prepared via the *N*,*N*′-bis(benzyl) spiro compound **213**, which was obtained by the Gilman method by the reaction of dibromoamine **212** with butyllithium followed by the addition of tetrachlorosilane. Compound **214** reacted with $SbCl_5$ in methylene chloride to give the first stable bis-radical cation (Scheme 55).[91]

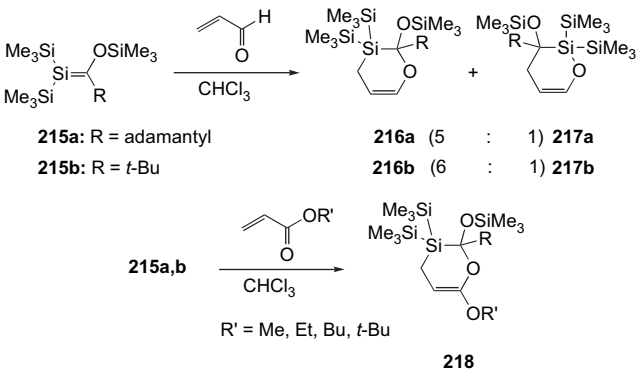
4.1.2. Preparation by formation of a carbon–silicon bond. Few results have been reported concerning the possibility of obtaining oxa- or thiasilinanes by intramolecular hydrosilylation. In a study reported[28] 10 years ago, Voronkov et al. claimed that thiasilanes could not be obtained by intramolecular hydrosilylation. The preparation of oxasilinanes using such a method has been reported in the case of vinyl enol ethers, but oxasilonanes were the major products of these reactions (Scheme 16).[28]

4.1.2.1. Preparation of oxasilinanes. Brook and coworkers have studied the cycloaddition of stable silenes **215** with α,β-ethylenic carbonyl compounds. In the case of propenal, formation of the two regioisomers **216** and **217** was observed, but, the major product was the 3-oxa-1-silacyclohexene **216**. Similar results were observed in the reaction of methyl vinyl ketone (Scheme 56).[92] In these two examples, when substituents were present on the carbon–carbon double bond of the unsaturated carbonyl compound, 1,3-oxasilinenes were never obtained. Quantitative formation of 1,3-oxasilinenes **218** was observed during the reaction of acrylates with **215**, but these cycloadditions were not observed with crotonates.[93] The results were explained by an interaction of the LUMO of the carbonyl compounds



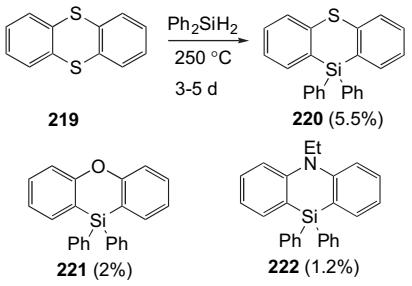
Scheme 55.

with the HOMO of the dienophile. The presence of β-substituents on the carbon–carbon double bond introduced steric interactions, which modified the regio- and chimioselectivity of the reaction.



Scheme 56.

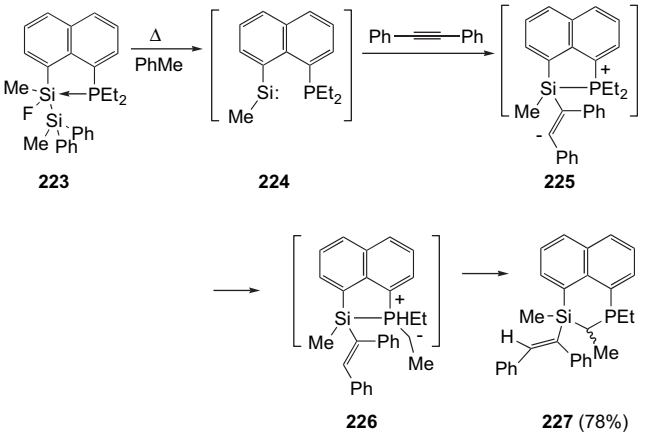
4.1.2.2. Preparation of thiasilinanes. Gilman and co-workers found that heating of thiaanthracene **219** with diphenylsilane for several days at 250–260 °C led to the formation of phenoxythiasiline **220** in 5.5% yield (Scheme 57).[94] Other sulfur heterocyclic compounds led also, under the same conditions, to sila-substituted products. By this method, compounds **221** and **222** have been obtained. The



Scheme 57.

yields were, however, always very low and this reaction has not been further developed to date.

4.1.2.3. Preparation of phosphasilinanes. Tamao and co-workers have reported an interesting preparation of silylene **224** by thermal decomposition of phosphosilane **223** (Scheme 58).[95] When the reaction was carried out in the presence of diphenylacetylene, phosphosilinane **227** was isolated in good yield as a mixture of two diastereomers (2:1). Addition of silylene to diphenylacetylene should give zwitterionic intermediate **225**, which rearranged into the six-membered compound **227** after a ring expansion of zwitterionic intermediate **226** formed by proton migration. The course of the reaction was different if two phenyl substituents were present on the phosphorus atom instead of the ethyl groups and formation of a seven-membered heterocycle was observed (see Scheme 121).



Scheme 58.

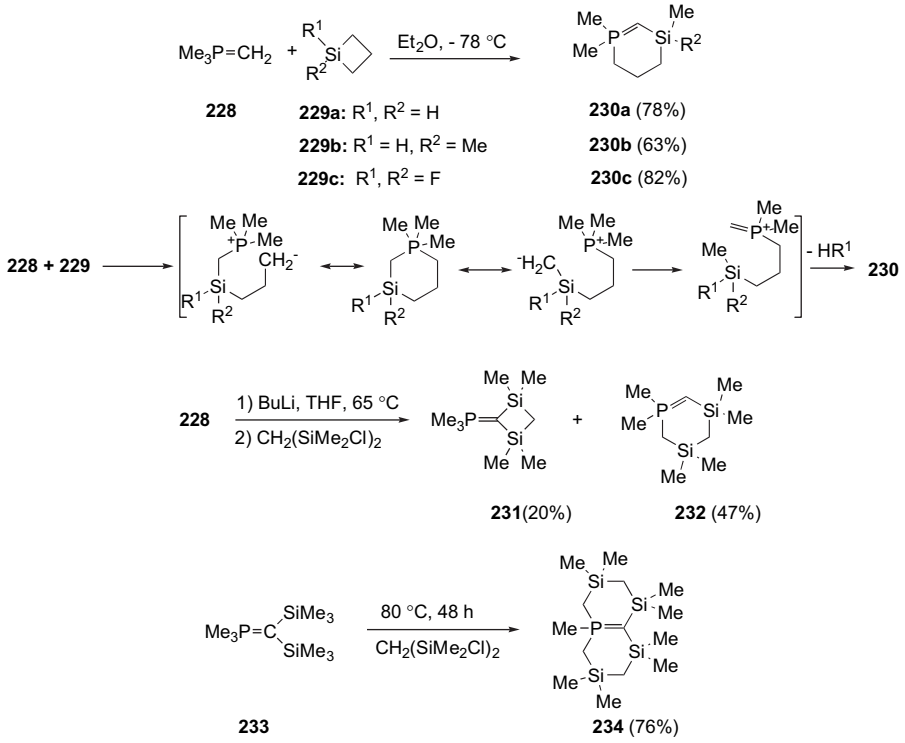
Schmidbauer et al., during their study of methylenephosphoranes, have examined[96,97] their reactivity with silyl compounds. Ylide **228** reacted with silacyclobutanes **229** to give compounds **230**. These reactions should occur through ring

opening (C–Si bond cleavage) and subsequent recyclization with elimination of dihydrogen or hydrogen fluoride (Scheme 59).[96] The formation of compounds **230** was not observed with triisopropylmethylenephosphorane. Reaction of methylenetrimethylphosphorane **228** with 2 equiv of butyllithium led, after addition of bis(chlorodimethylsilyl)-methane, to a mixture of compounds **231** and **232**. When the reaction was carried out, e.g., in THF at 65 °C, compound **232** was obtained in 47% yield.[97] Compound **232** was isolated after formation of the phosphonium salt by the addition of HCl. The same group described the formation of the bicyclic compound **234** by heating bis(chlorodimethylsilyl)methane with bis(trimethylsilyl)methylenetrimethylphosphorane **233**.

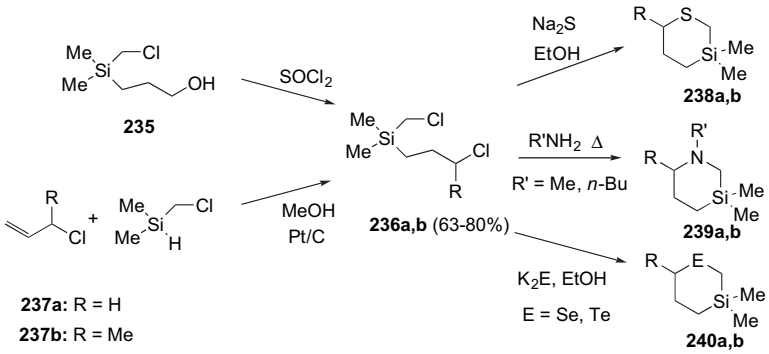
4.2. Preparation by formation of carbon–heteroatom bonds

4.2.1. Preparation by reaction of functionalized silanes with heteroatom-containing reagents. The simplest methodology implies the reaction of di(haloalkyl)silanes with heteroatomic reagents such as amines or sulfur derivatives. Fessenden and Coon first used this approach.[98] Reaction of alcohol **235** with $SOCl_2$ led to chloromethyl-(3-chloropropyl)silane **236a**, which reacted with sodium sulfide and primary amines to lead to the formation of the corresponding heterocyclic compounds **238a** and **239a**, respectively, in good yields (Scheme 60). Dedeyne and Anteunis have developed this work.[99] The preparation of dihalosilaalkanes **236a**,**b** was achieved by the hydrosilylation of allyl chloride derivatives **237a**,**b** with Pt/C as catalyst. Unstable 1,3-seleno and 1,3-tellurosilanes **240a**,**b** were also obtained using this approach.

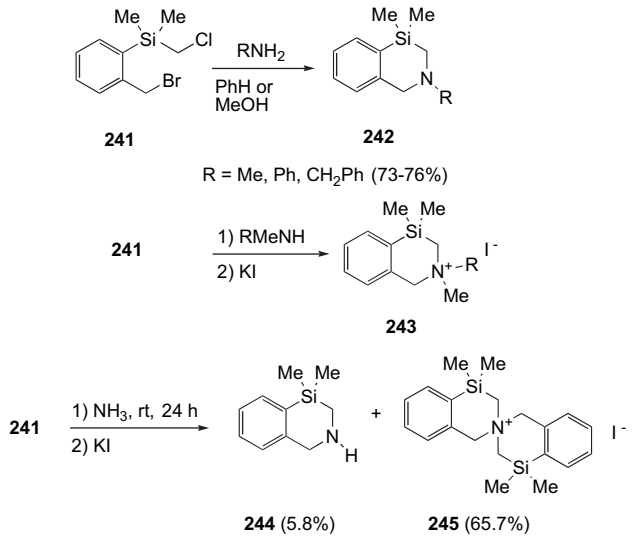
Sato and co-workers have applied the same methodology to the syntheses of compounds **242** and **243** by reaction of chloromethylsilane **241** bearing a bromomethylphenyl group with amines (Scheme 61). In the case of ammonia, a spiranic ammonium derivative **245** was mainly obtained, together with a small amount of secondary amine **244**.[100]



Scheme 59.

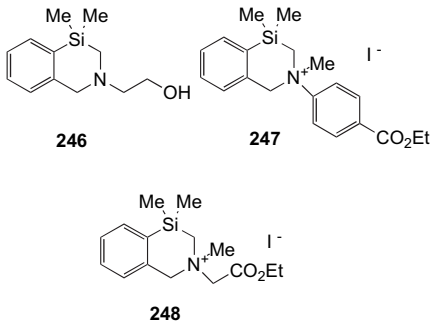


Scheme 60.



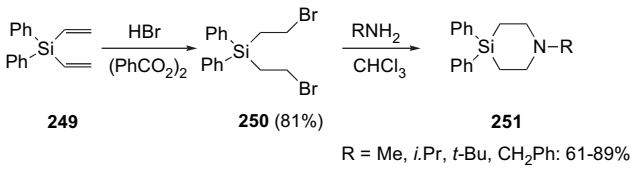
Scheme 61.

Lukevics and co-workers used this method for the preparation of compounds having biological properties (Scheme 62). Compound **246** showed antiblastic activity, closed to that of the parent carbon compound.[101] In the case of compounds **247** and **248**, psychotropic activity and acute toxicity were reported.[102] The psychotropic activity of compound **248** was not observed for the parent carbon compound, which possesses sedative activity.[103]



Scheme 62.

This strategy was also found to be efficient for the preparation of 1,4-azasilinanes. The first report was due to Jutzi's group. The bis(bromoethyl)silane **250** was obtained by radical addition of HBr to divinylsilane **249**, and was treated with various primary amines (Scheme 63).[104] Another approach to these azasilinanes **251**, much less efficient (0–5%), implied the direct addition of lithium amides to divinylsilanes.[104] Compounds **251** showed an interesting binding



Scheme 63.

ability on the neurotransmitter receptor in the homogenate of rat brains and to different receptors. It was reported that UV irradiation was more efficient for the 1,2-addition of HBr to vinylsilanes than chemical initiators.[105]

Subsequently, Tacke's group undertook significant work in this field. Numerous silapiperidines with antipsychotic activity have been obtained.[106] In particular, a silapiperidine **254** non-substituted on the nitrogen atom has recently been prepared from **252**, via **253**. This compound could be viewed as a synthon allowing the preparation of more complex compounds (Scheme 64).[107] Cleavage of an aryl–silicon bond in **255**, using a strong acid, allowed access to new silaperidols such as compound **257** (via **256**).[108]

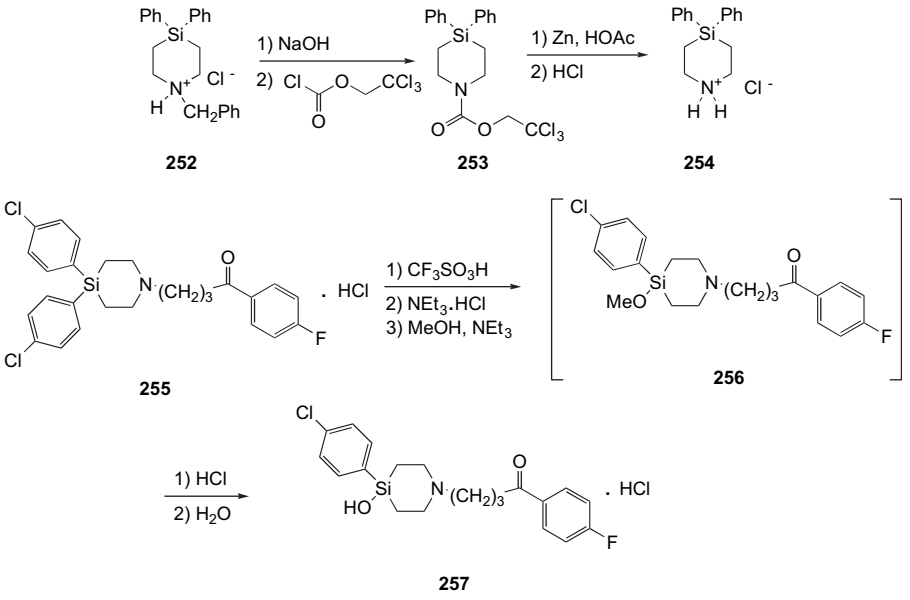
Kim and Cho have reported another interesting approach to 4-silapiperidines from divinylsilanes. Instead of the formation of dibromides, they prepared diol **258** by hydroboration of divinylsilane **249** using 9-BBN and subsequent oxidation (Scheme 65).[109] Diol **258** was transformed into ditosylate **259**, which reacted easily with various primary amines to give the desired 1,4-azasilinanes **260**. The high yields observed for the formation of compounds such as **260** led the authors to propose this procedure as a new method for the protection of primary amines. Regeneration of the free amines was carried out by reaction of the 4-silapiperidines with a combination of tetrabutylammonium fluoride and cesium fluoride (1:1) in DMF or THF.

The preparation of a 1,3-diphospha-5-silacyclohexane **263** has been reported by the reaction of 1,3-diiodosilapropane **261** with tetraethyl methylenediphosphonate **262**. The trans stereochemistry of compound **263** was confirmed by X-ray structure analysis (Scheme 66).[110]

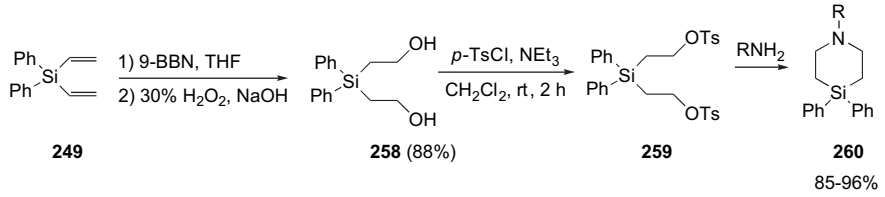
The methodology, which implies the electrophilic reaction of heteroatom-containing reagents with polymetallated silanes, was also examined. Nakayama's group used this method for the preparation of phosphasilatriptycene **265**. Its synthesis was realized as reported in Scheme 67, starting from tris(thienyl)silane **264**. Reaction of this latter silane with 3 equiv of butyllithium followed by the addition of triphenyl phosphite led to the triptycene **265** in low yield.[111] The reactions of this latter compound with *m*-chloroperbenzoic acid or 1,2-epithiocyclohexane gave easily the corresponding phosphine oxide and phosphine sulfide (79–97%).

More recently, Sawamura and co-workers also used this approach for the preparation of phosphasilinane **269**. Phenyltrivinylsilane **266** was converted into triol **267** through hydroboration followed by H_2O_2/NaOH oxidation. This triol was converted into the tri-iodide **268**. The reaction of the dilithium derivative with the complex $PhPH_2$–BH_3 led to phosphasilinane **269**. The transformation of this phosphine into bicyclic silaphosphine **271** was then accomplished via phosphonium salt **270**. Compound **271**, the structure of which was established by X-ray diffraction appeared to be stable to air at room temperature (Scheme 68).[112]

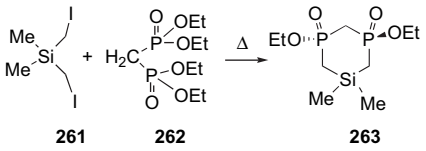
The strain of propellanes, by modification of the carbon atom hybridization, allows the formation of lithiated derivatives by reaction with butyllithium in the presence of TMEDA. This property was applied in the case of



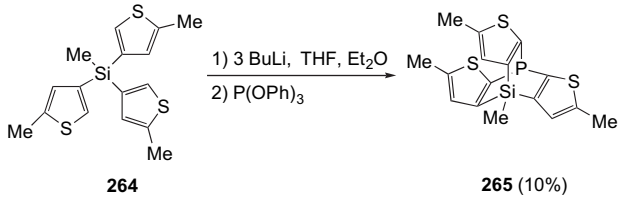
Scheme 64.



Scheme 65.



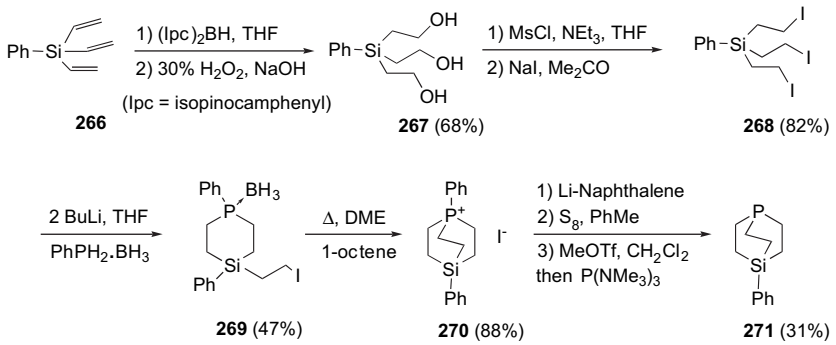
Scheme 66.



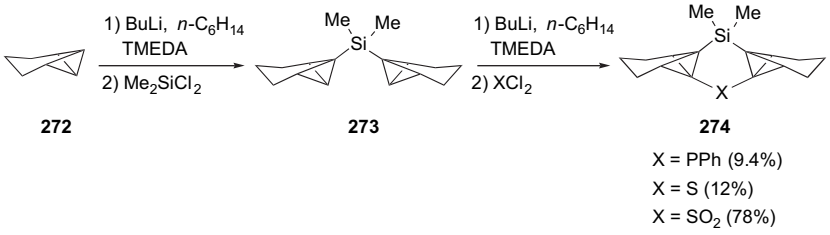
Scheme 67.

bis(tricyclo[4.1.0.0^{2,7}]heptanyl)silane **273**[113] to obtain the dilithiated derivative, which reacted with dichlorophosphorus or dichlorosulfur electrophiles to lead to the heterocyclic compounds **274** (Scheme 69).[114] Except in the case of SO_2Cl_2, the yields were low. Silane **273** was obtained by metallation of tricyclohexane **272** followed by the addition of dichlorodimethylsilane.

4.2.2. Preparation by intramolecular cyclization of functionalized silanes. Fessenden and Coon appear to be the first to have developed this method for the preparation of heterocyclic compounds with a silicon atom and another heteroatom. Hydrosilylation of allyl trimethylsilyl ethers **275a–c** with (chloromethyl)dimethylsilane using platinum over carbon as catalyst allowed the preparation of alcohols **276a–c** after hydrolysis of the trimethylsilyl ethers.[98] These

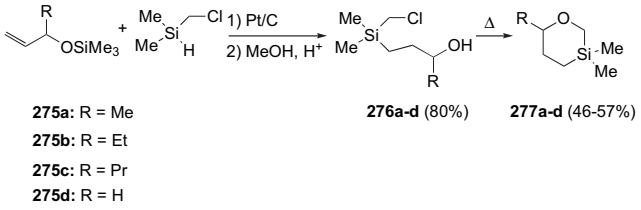


Scheme 68.



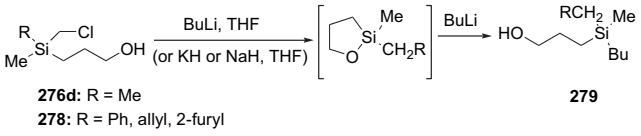
Scheme 69.

compounds led to the formation of oxacyclic compounds **277a–c** by simple heating (Scheme 70). Dedeyne and Anteunis have completed this work.[99] The cyclization of alcohols **276a**,**d** to **277a**,**d** was also found to be possible by reaction with Na_2CO_3.



Scheme 70.

Hudrlik and co-workers confirmed these results for the preparation of compound **277d** (R=H) (Scheme 70). They also showed that, when the alcohols **276d** and **278** were treated with BuLi or alkaline hydrides instead of sodium carbonate, a completely different reaction pathway occurred, leading mainly to alcohols **279** by transfer of a silicon atom substituent to the carbon atom bearing the halogen (Scheme 71).[115]

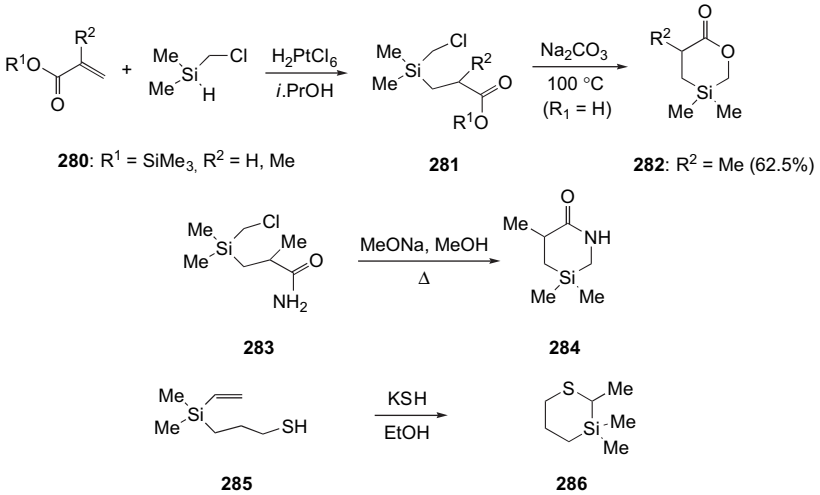


Scheme 71.

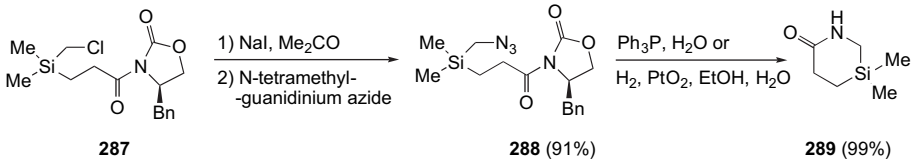
Subsequently, Mironov and co-workers applied this methodology to the preparation of 6-, 9-, and 14-membered silalactones. Substrates **281** necessary for the cyclization steps were prepared by hydrosilylation of α,β-ethylenic esters **280** by (chloromethyl)dimethylsilane using H_2PtCl_6 as catalyst (Scheme 72). Lactones **282** were obtained in good yields by reaction with anhydrous sodium carbonate. When the hydrosilylation was carried out with the unsubstituted acrylate **280** (R^2=H), the lactone **282** was obtained without isolation of the intermediate ester.[116] This lactone appeared unstable and gave a dimer upon standing at room temperature. It was reported, later, that these lactones could be obtained using a one-pot procedure if 20% aqueous sodium carbonate was added to the crude reaction mixture resulting from the hydrosilylation step.[117] Cross-linked silalactone polymers were prepared and tested for permeability to gases. One application could be the reduction of the CO_2 content of CO_2–O_2 mixtures.[118] Lactam **284** was obtained by reaction of amide **283** with sodium methylate.[116,119] The same group also reported the formation of thiasilinane **286** in medium yield by reaction of thiol **285** with KSH (Scheme 72).[40a] Formation of the seven-membered ring compounds was not observed using this method.

Recently, the preparation of lactam **289** was reported by reduction of azide **288**, obtained from **287**, with triphenylphosphine in the presence of water or by catalytic hydrogenation. The intermediate amine, which makes the intramolecular substitution, was not detected (Scheme 73).[120]

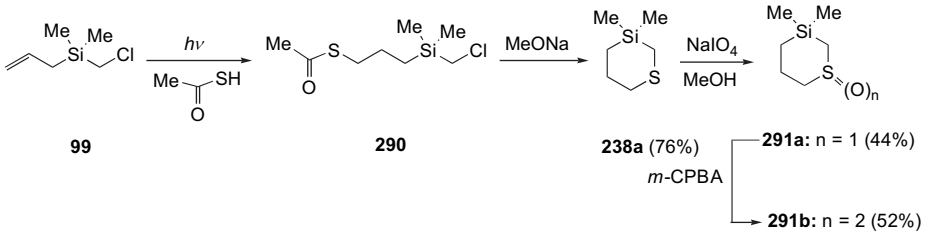
Kirpichenko and co-workers have reported an efficient preparation of 1,3-thiasilinane **238a** after saponification of



Scheme 72.



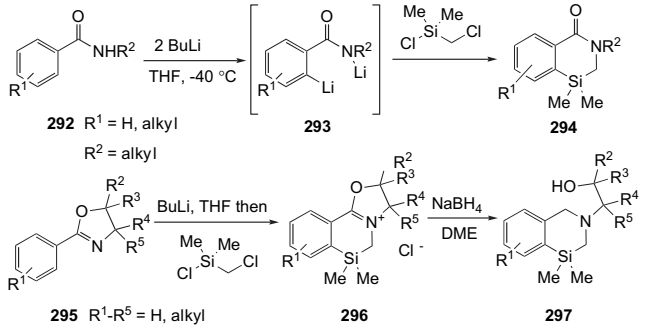
Scheme 73.



Scheme 74.

thioacetate **290**, obtained by radical 1,2-addition of thioacetic acid to allylsilane **99** (Scheme 74).[121] Selective oxidations of the sulfur atom allowed for the first time the preparation of sulfone **291a** and sulfoxide **291b**.

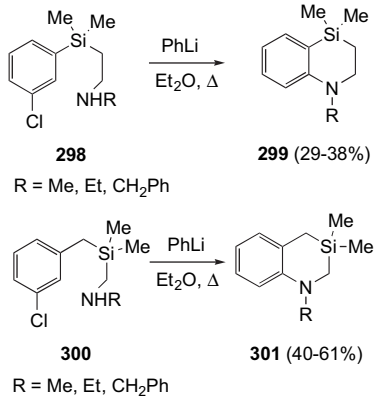
Barcza has reported interesting preparations of 1,3-benzoazasilinane derivatives using 1,4-dilithiated species. Reaction of *N*-alkylbenzamides **292** with 2 equiv of butyllithium led to the dilithiated intermediates **293**, which reacted with chloro(chloromethyl)dimethylsilane to give benzoazasilinanes **294** via chloromethylphenylsilane intermediates.[122] Using a similar methodology, tricyclic oxazolidinium compounds **296** were obtained after monolithiations of oxazolines **295** and their reduction led to 1,3-benzoazasilinanes **297** (Scheme 75).[123] These compounds possess sleep-inducing activities. Derivatives having neurotransmitter antagonist properties have subsequently been reported.[124]



Scheme 75.

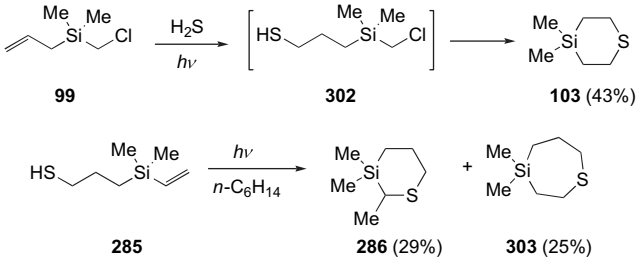
Sato and co-workers prepared 1,4- and 1,3-benzoazasilines **299** and **301** from **298** and **300** using the intramolecular reaction of benzyne moiety with lithium amide (Scheme 76).[125] This method was also studied for the preparation of azasilolines (Scheme 32).

Voronkov and co-workers have shown that 4-thiasilinane **103** could be obtained by a radical addition of H_2S to allylsilane **99** via **302** (Scheme 77; see also Scheme 27).[40,41] Six-membered ring compounds could not be obtained during the



Scheme 76.

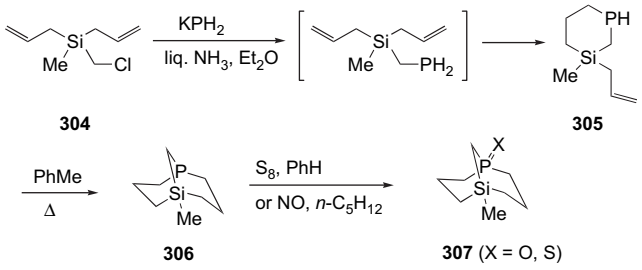
irradiation of 2-[allyl(dimethyl)silyl]ethanethiol. The *endo* cyclization leading to the seven-membered compound was observed (see Scheme 112). Starting from the 3-sila regioisomer **285**, the two heterocyclic compounds **286** and **302** were formed by, respectively, 6-*exo* and 7-*endo* cyclizations.[126]



Scheme 77.

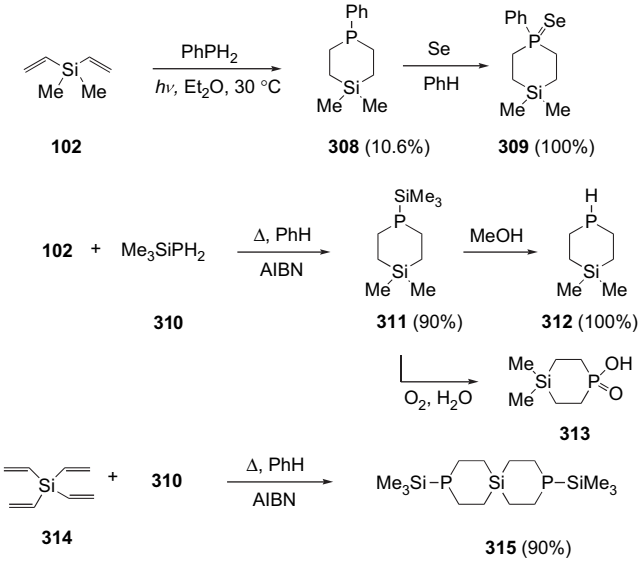
Radical additions of compounds containing P–H bonds are well-known reactions.[127] The first application of this reaction to unsaturated silanes, with the target to prepare cyclic compounds, was reported 20 years ago by Kuehne and coworkers, who examined the reaction of potassium dihydrogen phosphide with diallyl(chloromethyl)silane **304**.[128a] At

low temperature in liquid ammonia, only the monocyclic compound **305** was obtained. Heating of this latter compound in toluene at reflux gave rise to the formation of the bicyclic compound **306**. This compound reacted easily with sulfur, NO (Scheme 78), chlorodiethylphosphine, and methyl iodide to give $P^{(V)}$ derivatives **307**.[128]



Scheme 78.

Intermolecular addition of phenylphosphine to divinylsilane **102** led in low yield (11%) to phosphasilinane **308**. This compound was stabilized as selenophosphine **309**.[129] Norman's group obtained much better yields using trimethylsilylphosphine **310**.[130] In all these reactions, only small amounts (<10%) of the five-membered heterocycles were isolated. Release of the trimethylsilyl group from compound **311** was achieved in methanol to give the parent phosphasilinane **312**. Oxidation with oxygen of compound **311** led to the phosphinic acid derivative **313**. Spiro compound **315** was obtained in the same way starting from tetravinylsilane **314** (Scheme 79). Attempts to obtain higher-ring-size heterocycles using this method were not successful.[130]



Scheme 79.

Electrophilic cyclizations have been explored for the preparation of azasilinanes and silaborinanes. The first study using this method was reported by Barluenga and co-workers for the preparation of silapiperidines.[131] During this study, concerning the aminomercuration of unsaturated compounds, the reactivity of allylsilanes was examined. The reaction of arylamines with allyltrimethylsilane **316** led to the formation of the 2-aminoalkylsilanes **317** after reductive demercuration (Scheme 80). In the case of diallylsilane **318**, monomercuration products were formed, which, after reduction, allowed the preparation of the unsaturated amines **319**. A second aminomercuration followed by a reduction led to azasilinanes **320** in modest yields. Kirpichenko and co-workers confirmed this difficult formation of six-membered heterocyclic compounds, compared to the five-membered products (Scheme 29).[43] Vinylsilane **321** gave mainly, as expected, 1,3-azasilepane **323** and 1,3-azasilinane **322** in lower yield (Scheme 80). A very low yield (3%) for the ring closure of dimethyl(2-phenylaminoethyl)vinylsilane to 4-silapiperidine was reported. Allylsilane **324** gave 1,4-azasilinane **325** in moderate yield. [43]

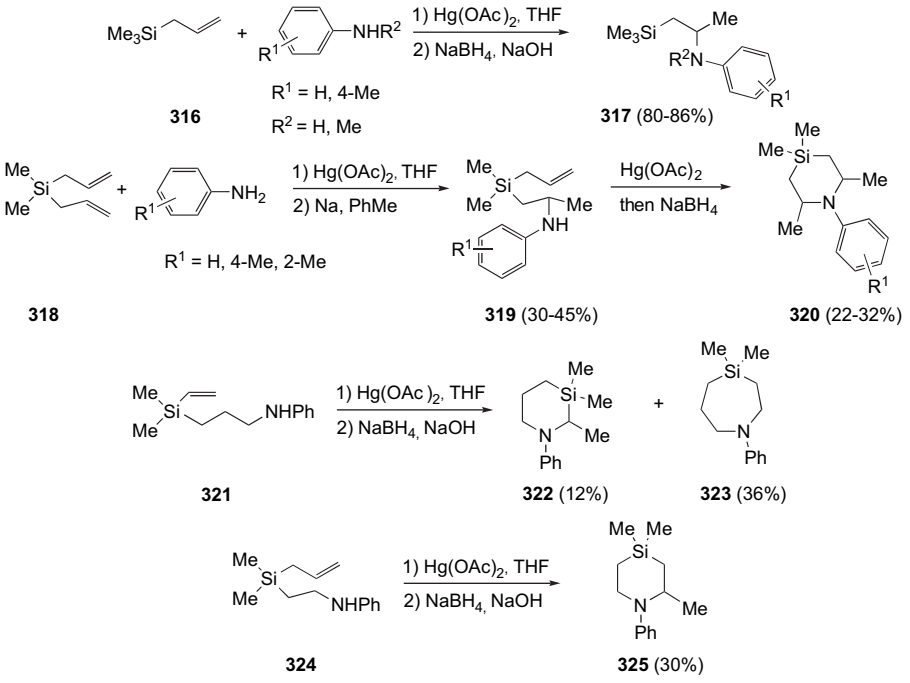
Hawthorne has studied the reaction of *tert*-butylborane with 1,3- and 1,4-dienes. The preparation of 1,4-silaborinanes by the reaction of divinylsilane **102** with boranes has been reported. Boronheterocyclic compound **326** was obtained in good yield using an amine–borane complex (Scheme 81).[132] Soderquist and co-workers showed that the formation of 1,4-silaborinanes such as compound **327** was very efficient if the reaction was carried out in two steps. The first reaction implied the addition of 9-borabicyclo[3.3.1]nonane (9-BBN) to divinylsilane **102**, and the second step an exchange using the borane–dimethyl sulfide complex. These steps could be carried out in a one-pot reaction. Transformation of silaborinane **327** into silacyclohexanone **328** was also reported, and this constitutes a convenient preparation of this compound.[133]

Bioreduction of silyl ketone **329** using the yeast *Trigonopsis variabilis* led to the formation of a 1:1 mixture of the diastereomers **330** in high enantiomeric excesses. After separation, each diastereomer **335** was transformed into the acetonide **331** by hydrogenolysis of the benzyl group followed by reaction with acetone dimethyl acetal (Scheme 82).[134] This enantioselective bioreduction of chiral silaketones constitutes a good method to prepare optically active compounds with a silicon stereogenic center.

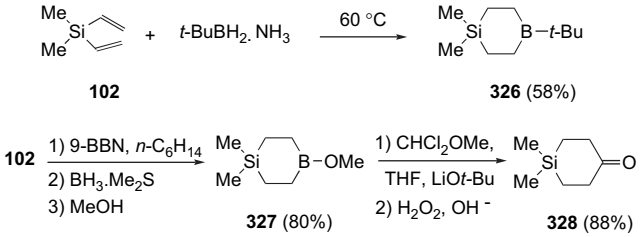
Sieburth and Kim reported the formation of 1,3-azasilinane **333** during the oxidation of alcohol **332** with a benzyloxycarbonylaminomethylsilyl group. When the nitrogen atom was protected as phthalimide, such a cyclization was prevented (Scheme 83).[135]

Linderman and Chen have studied the intermolecular allylation reaction of mixed 1-(allylsilyl)alkyl acetals, e.g., allylsilanes **334** reacted in the presence of Lewis acids to lead, after basic treatment, to silanols **335.** If two methyl groups were fixed on the terminal carbon of the double bond (compound **336**), this reaction was not observed and the oxasilinone **337** resulting from a diastereoselective cyclization was isolated in good yield (Scheme 84).[136]

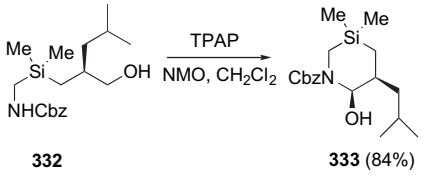
It has been mentioned earlier in this report that the pyrolysis of phenyl tris(trimethylsilyl)methyl borinates led to the formation of silaborolanes (Scheme 19). Flash vacuum pyrolysis of an analogous benzyl borinate **338** led to the formation of 1,3-silaborinane **340**, via the methylene borane intermediate **339** (Scheme 85).[31]



Scheme 80.



Scheme 81.

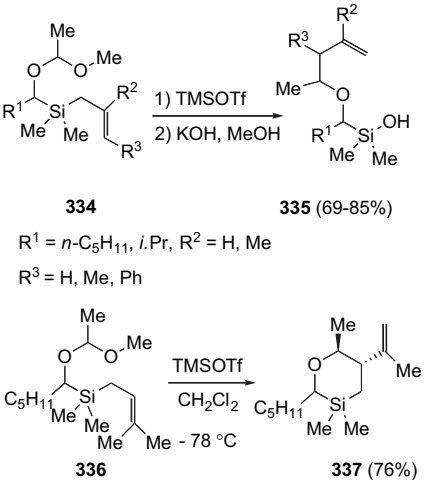


Scheme 83.

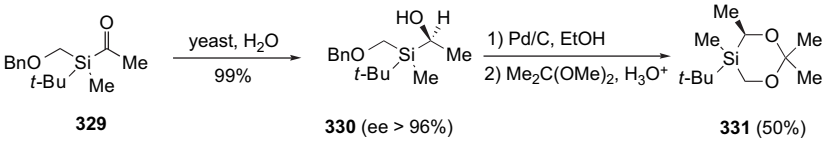
Intramolecular trapping of 2-(dimethylaminomethyl)-phenylsilene **342** formed by flash vacuum pyrolysis of (1-trimethylsilylalkyl)methoxysilane **341** was reported to give 1,3-azasilinane **343** (Scheme 86).[137] Thermolysis in a sealed tube at 350 °C led to the formation of the desilylated product **344**.

4.3. Preparation by formation of carbon–carbon bonds

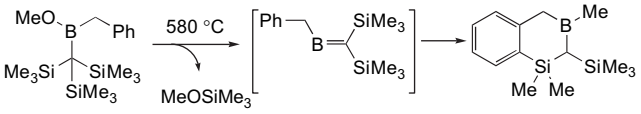
Coelho and Blanco have studied the intramolecular Diels–Alder reaction of various chiral silatrienic compounds. Heating at 110–140 °C of amides **345** gave the bicyclic compounds **347** as a mixture of diastereoisomers (Scheme 87).[138,139] The oxabicyclo[2.2.2]octenone intermediate **346** (R=Cy) could be isolated if the Diels–Alder reaction was carried out at 80 °C.[139] This cycloaddition was not observed starting from the corresponding ester. Diels–Alder cycloadditions also occurred when the diene was fixed on the



Scheme 84.

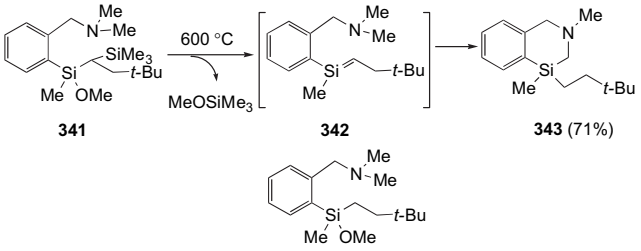


Scheme 82.



338 **339** **340** (92%)

Scheme 85.



341 **342** **343** (71%) **344**

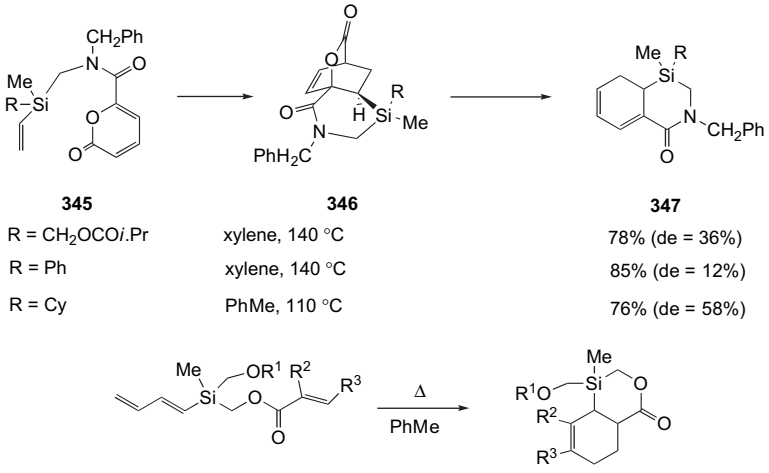
Scheme 86.

silicon atom. Heating of dienes **348** at 140–220 °C led to the desired products **349** in low to medium yields (Scheme 87).[140] In the case of acyloxymethylsilanes **348**, (R_1=acyl), these cycloadditions could be carried out in the presence of $EtAlCl_2$ in dichloromethane at room temperature. Mixtures of four diastereomers were generally obtained. When the two substituents fixed on silicon were methyl and 2-methoxyphenyl groups, a high diastereoselectivity was obtained in the acid-catalyzed reaction (90% of one diastereomer).[141] A comparable strategy was applied to the formation of seven-membered heterocycles (Scheme 116).

1,3-Oxasilinane **351** has been prepared from compound **350** by an intramolecular Diels–Alder reaction of benzyne with furan (Scheme 88).[142] This compound **351** was then transformed into the C-glycoside **352**, to test its antibiotic activity. This methodology was applied with the same efficiency for obtaining a 1,4-oxasilepane derivative (Scheme 117).

Taddei's group have reported a preparation of carbacephams in which one carbon atom of the six-membered ring was replaced by silicon.[143] [2+2] Cycloaddition of allylsilane **99** with an isocyanate led to the β-lactam **353**, which was *N*-alkylated to compound **354**. Cyclization of the corresponding iodide via an ester enolate led to the desired silacepham **355** (Scheme 89). The corresponding acid did not show any particular biological activity.

Fuchs and van Dort have studied a new method for the desulfonylation of alkyl sulfones **356**, bearing a bromomethylsilylphenyl group, induced by radical reactions to form **357** and **358** (Scheme 90).[144] When a vinyl substituent was present on the silicon atom of the sulfone (compound **359**), the radical



345 **346** **347**

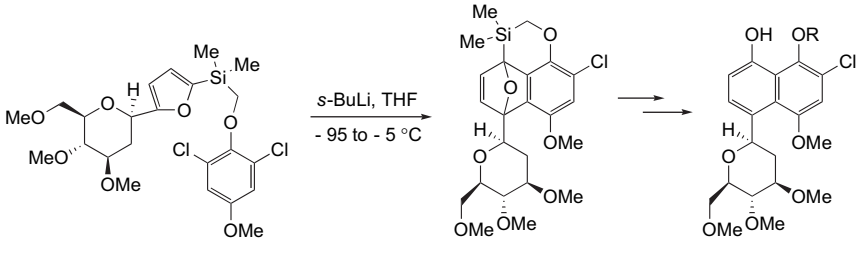
R = CH_2OCOi.Pr	xylene, 140 °C	78% (de = 36%)
R = Ph	xylene, 140 °C	85% (de = 12%)
R = Cy	PhMe, 110 °C	76% (de = 58%)

348 **349** (27-56%)

R^1 = H, COR (R = Me, CH_2Ph, *i*.Pr), Si*i*.Pr_3, CPh_3

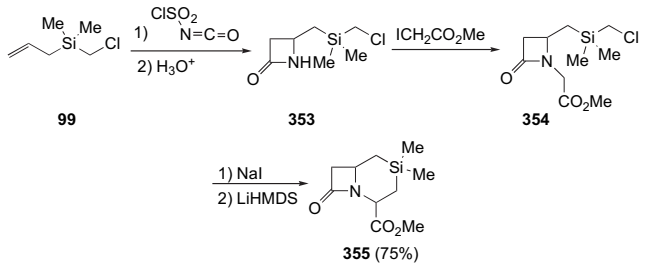
R^2 = R^3 = H; R^2 = Me, R^3 = H; R^2 = H; R^3 = COOMe

Scheme 87.



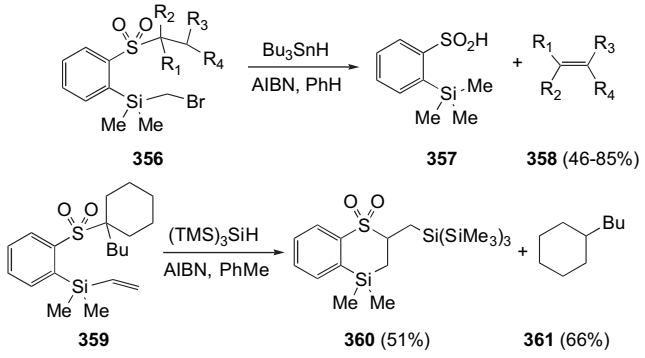
350 **351** (68%) **352**

Scheme 88.

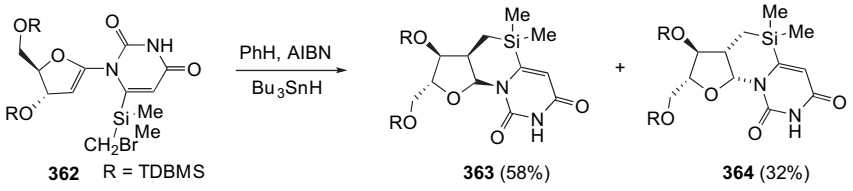


Scheme 89.

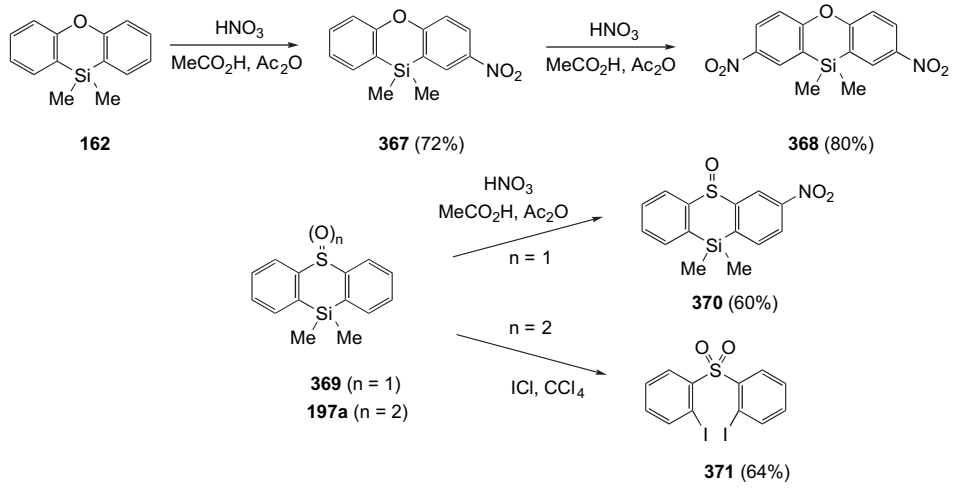
formed attacked the sulfur atom and induced the formation of benzothiasilinane **360** and butylcyclohexane **361**. It has recently been reported that this family of compounds and the corresponding benzooxasilinanes could be ligands of retinoid receptors and thus useful in numerous therapies.[145]



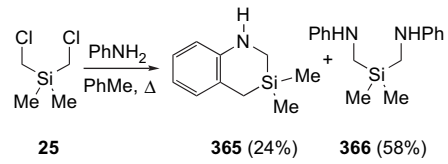
Scheme 90.



Scheme 91.



Scheme 93.



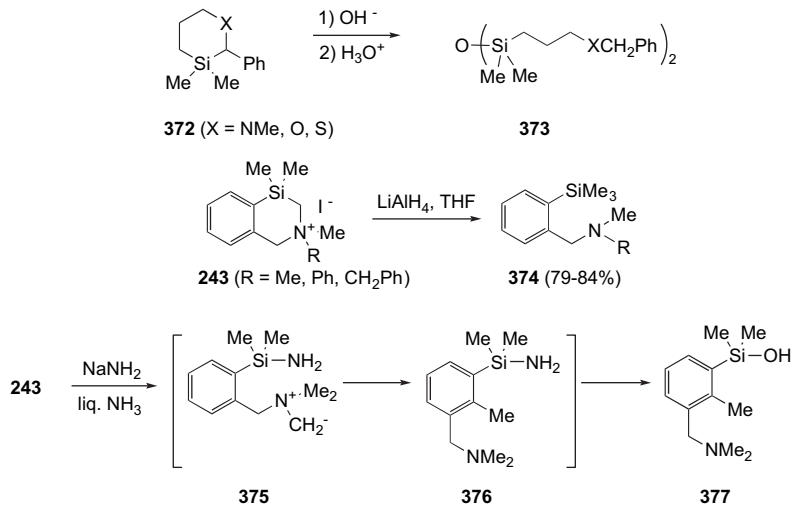
Scheme 92.

Tanaka and co-workers have studied the radical cyclization of nucleoside 2-sila-5-hexenyl radicals. They observed the formation of 1,3-azasilinanes **363** and **364**, formed by 6-*endo* cyclizations, by reaction of nucleoside **362** with tributyltin hydride in the presence of AIBN (Scheme 91; see also Scheme 37).[57]

Hwu and King have obtained a mixture of 1,3-azasilinane **365** and 1,1-dimethyl-*N*,*N*′-diphenylsilanediamine **366** after the heating of (dichloromethyl)dimethylsilane **25** with an excess of aniline (Scheme 92).[146]

4.4. Reactivity and applications

Six-membered silaheterocyclic compounds appear to be stable in numerous reaction conditions; e.g., dibenzooxasilinanes were reported to be stable in concentrated HNO_3 and hot acetic anhydride.[59] This stability allowed the mono- (**367**) and dinitration (**368**) of the aromatic rings of phenoxasilinine **162**. This nitration is also possible with thiasilinane **369** to **370** (Scheme 93).[147] Cleavage of the central thiasilinane core of **197a** by ICl has, however, been reported

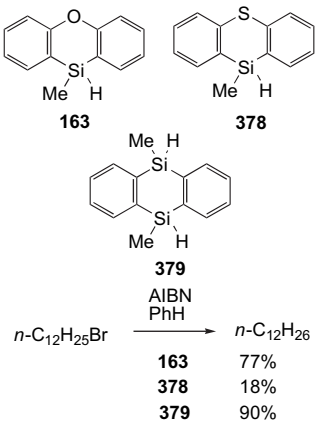


Scheme 94.

to occur with the formation of 1-(2-iodophenylsulfonyl)-2-iodobenzene **371**.[83] Cleavage was also observed in the reaction of 10,10-diphenyl-10*H*-phenoxasilin **160a** with lithium in dioxane, which gave, after hydrolysis, 2-hydroxyphenyltriphenylsilane.[82]

Alkaline hydrolytic cleavage of 1,3-heterosilinanes **372** to give **373** has been reported. These particular results seem to be due to stabilization by the phenyl group of the intermediate α-cabanion, formed after the Si–C bond cleavage (Scheme 94).[91] Reaction of azasilinium iodides **243** with $LiAlH_4$ led to benzylamines **374**, corresponding to cleavage of the $SiCH_2$–N^+ bonds.[100] In the presence of sodium amide in liquid ammonia, silanol **377** was obtained. This compound was obtained after a Sommelet–Hauser rearrangement of intermediate ylide **375**→**376**, formed by cleavage of the Si–CH_2N^+ bond.[148]

10-Methylphenoxasiline **163** and 10-methylphenothiasiline **378** were examined as reducing agents in the dehalogenation of organic halides (Scheme 95). These compounds appeared less efficient than 5,10-dimethylsilaanthrene **379**.[66]

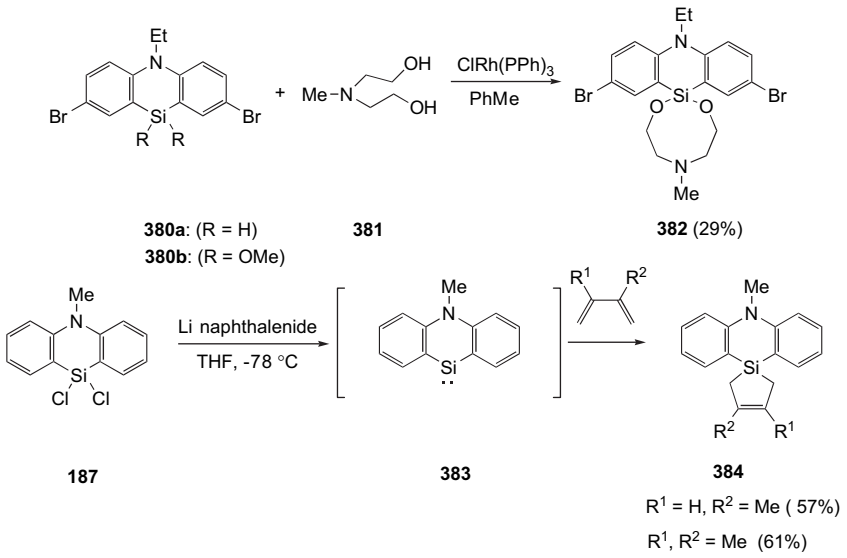


Scheme 95.

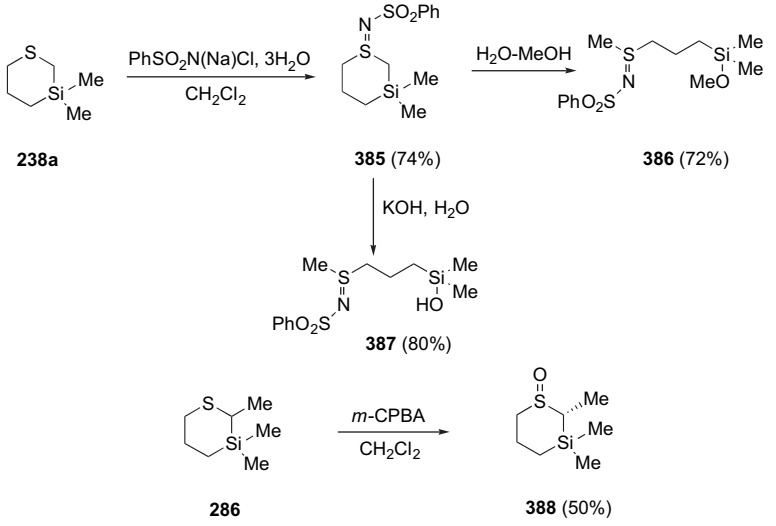
Spiro compound **382** was obtained by the reaction of dihydrophenazasiline **380a** with diol **381** in the presence of a Wilkinson catalyst (Scheme 96).[149] This compound was also prepared starting from the 10,10-dimethoxysilane **380b** (64%). Silylene **383** has been generated by the reaction of dichlorophenazasiline **187** with lithium naphthalenide at −78 °C. This unstable species was trapped by 1,3-butadiene derivatives and gave spiranic compounds **384** (Scheme 96).[78]

Shainyan and Kirpichenko have studied the reactivity of 1,3-thiasilinanes. Oxidation of 3,3-dimethyl-1,3-thiasilinane **238a** with *m*-chloroperbenzoic acid led to the formation of the sulfoxide or sulfone, depending upon the amount of reagent used (Scheme 74).[121] Similar results were obtained using $NaIO_4$ as oxidant.[58] Reaction with chloramine T under phase-transfer conditions gave the corresponding sulfimide **385**.[58,150] Ring opening by Si–C bond cleavage of this compound was observed in aqueous methanol to form **386** or in the presence of potassium hydroxide to give **387** (Scheme 97).[58] Addition of methyl iodide to compound **238a** led to a sulfonium salt, which was also opened in the presence of water.[58] When a substituent was located on the carbon atom between silicon and sulfur (compound **286**), oxidation using *m*-chloroperbenzoic acid led to a diastereoselective reaction to form **388** (Scheme 97).[151]

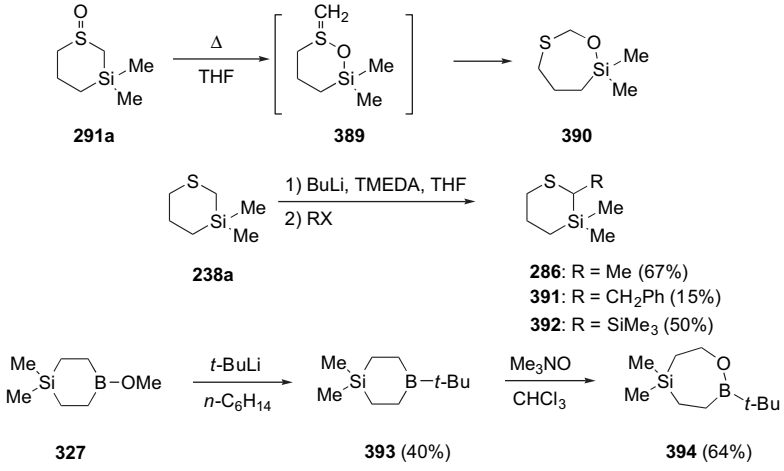
By heating in THF, sulfoxide **291a** undergoes a sila-Pummerer rearrangement, leading to the formation of the seven-membered compound **390** (Scheme 98).[152] This transformation was explained by the formation of intermediate **389**, which underwent a rearrangement with ring enlargement. This hypothesis was confirmed by a computational study.[153] Regioselective monoalkylations were observed by treatment of the carbanions of thiasilinane **238a** with alkyl and silyl halides to form compounds **286**, **391**, and **392** (Scheme 98).[154] 1,4-Silaborinane **393**, obtained by reaction of 1,4-silaborinane **327** with *tert*-butyllithium, reacted with 1 equiv of trimethylamine *N*-oxide at 0 °C to give the enlarged oxidation product **394** (Scheme 98).[155]



Scheme 96.



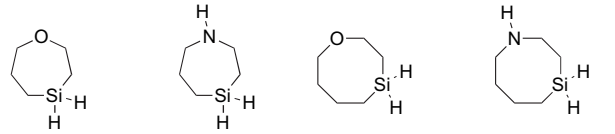
Scheme 97.



Scheme 98.

5. Preparation of seven-membered and higher heterocyclic compounds

Methods for the formation by ring closure of heterocyclic compounds with higher than six-membered rings are, in general, limited, compared to the methods known for the formation of five- and six-membered ring compounds.[156,157] This difference seems less obvious in the case of silaheterocyclic compounds. Methods used for the formation of normal cycles have often been used with success to form higher ring-sized compounds. This result seems to be due to the presence of a dialkylsilyl group instead of a methylene, which favors the cyclization process, probably by an influence of the *gem*-dialkyl effect. In Scheme 99, representative IUPAC names and structures for these ring-size compounds have been summarized.



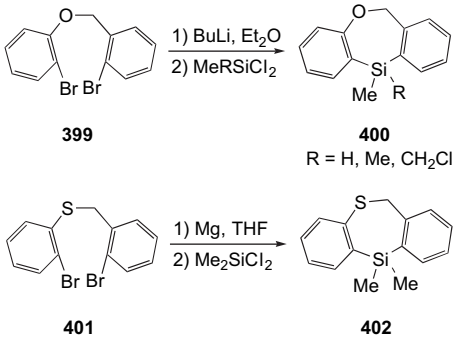
1,4-oxasilepane **1,4-azasilepane** **1,4-oxasilocane** **1,4-azasilocane**

Scheme 99.

5.1. Preparation by formation of carbon–silicon bonds

5.1.1. Formation by reaction of dihalosilanes with dianionic species. Different groups have reported the preparation of silaporphyrin analogues. Kauffmann and Kniese showed that the reaction of dithienylsilane **395** in THF at 0 °C with 2 equiv of butyllithium followed by the addition of dichlorodimethylsilane led to the formation of the cyclic compounds **396** and **397** in low yields (Scheme 100).[158] Utilization of LDA at −20 °C led to the same products, with, however, a noticeable increase in the yield of the larger compound **397**.[159] Similar results were reported starting from thiophene **398** (X=S) using a mixture butyllithium–potassium *tert*-butoxide–TMEDA at low temperature.[160] This last method was also shown to be efficient in the case of furan and *N*-methyl-pyrrole (Scheme 100).[160] Electrochemical reaction of 2,5-dibromo-1-methyl pyrrole in the presence of dichlorodimethylsilane gave rise to the formation of compound **396** (X=NMe) in a slightly better yield (22%).[161]

The Gilman–Hithcock method (Scheme 43) was investigated for the preparation of oxasilepines starting from the dibromo ether **399**. The chemoselectivity of the condensation reactions appeared to be low and the heterocyclic compounds **400** could not be fully characterized (Scheme 101).[61,162] The formation of thiasilepin **402** was successful from the dibromo precursor **401**, by reaction with magnesium and quenching of the organodimetallic intermediate with dichlorodimethylsilane. No product could be obtained when the reaction was carried out using butyllithium, but the thiasilepin was obtained in low yield from the dilithiated intermediate when chlorodimethylsilane was used as electrophile.[82] Surprisingly, the preparation of azasilepanes was reported to be unsuccessful using analogous dilithio or dimagnesio intermediates.[162]

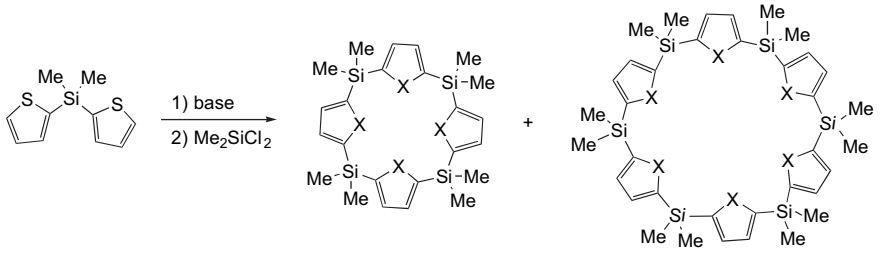


399 **400**

401 **402**

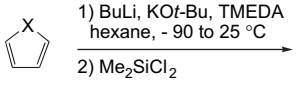
Scheme 101.

This method was also found to be convenient for the preparation of azasilocanes. Azasilocane **404a** was obtained in low yield by the reaction of the dibromo compound **403**



395 **396** (X = S) **397** (X = S)

BuLi	16%	2%
LDA	17%	15%

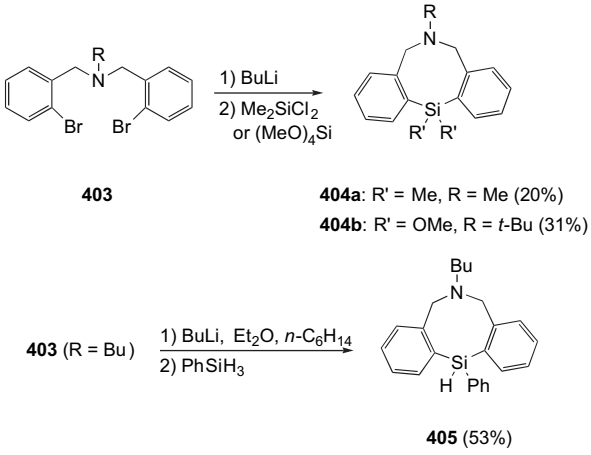


398 X = S, O, NMe **396** + **397**

X = S	18%	17%
X = O	16%	10%
X = NMe	12%	-

Scheme 100.

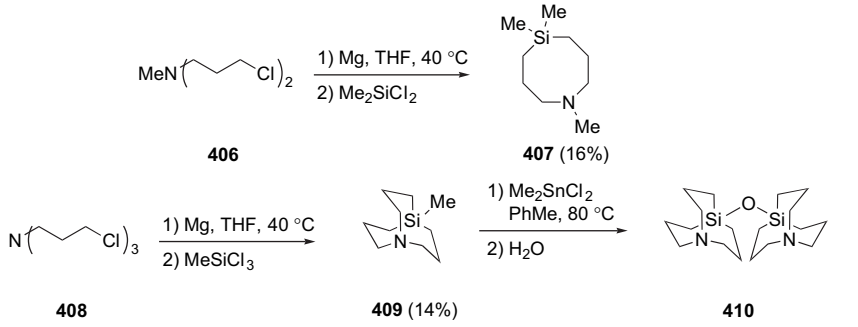
(R=Me) with butyllithium followed by the addition of dichlorodimethylsilane (Scheme 102).[163] The same approach was used for the preparation of compound **404b** using tetramethoxysilane as quenching agent of the dilithio intermediate.[164] More recently, the preparation of hydrosilane **405**, obtaining a mixture of two diastereomers, was reported using phenylsilane as quenching agent. The two isomers differed in that the Si–H bonds were apical or equatorial. The X-ray structure of the major apical isomer was published.[165]



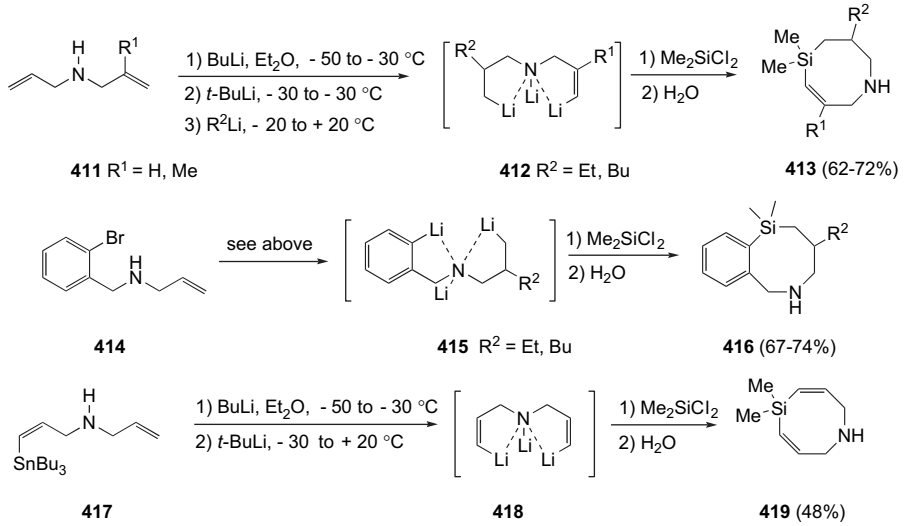
Scheme 102.

Tzschach and co-workers, with a view to examining the possible formation of a pentacoordinated silicon atom, have prepared 1,5-azasilocanes. Reaction of the bi- and trifunctionalized Grignard reagents, synthesized from the corresponding chlorides **406** and **408**, with, respectively, di- and trichlorosilanes led to 1,4-azasilocanes **407** and **409** in low yields. No shortening of the Si···N distance was observed according to the X-ray structure of compound **409** (Scheme 103).[166] Interestingly, treatment of the bicycloalkyl compound **409** with Me_2SnCl_2 allowed the selective cleavage of the Si–CH_3 bond to form **410**. Further studies undertaken by another group show that the pentacoordination of the silicon atom is possible when fluorine atoms are fixed on it.[164]

Barluenga and co-workers have studied the lithiation of allylamines and the formation of 1,4,7-trianionic intermediates was postulated. Reaction of these latter intermediates with dichlorosilane led to the formation of various azasilocanes, e.g., trilithiated intermediates **412** were obtained by the reaction of diallylamines **411** with butyllithium to substitute the proton of the amine, addition of *tert*-butyllithium to exchange one of the olefinic hydrogens and addition of alkyllithium to the second carbon–carbon double bond (Scheme 104).[167] When the trilithiated intermediates **412** were quenched by the addition of dichlorodimethylsilane, diazasilocanes **413** were obtained in good yields. This



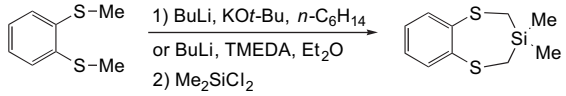
Scheme 103.



Scheme 104.

sequence was also carried in the case of amine **414** to give, via **415**, the benzoazasilocanes **416**. The preparation of the azasilocadiene **419** was reported starting from tin-substituted amine **417** via the trilithiated intermediate **418** (Scheme 104).[167]

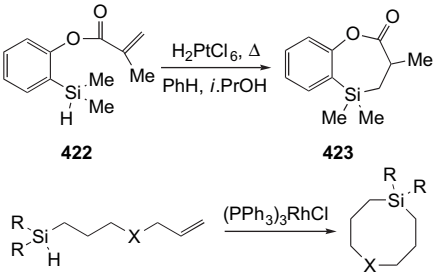
Cabiddu et al. during their study concerning the metallation of sulfur derivatives[22,23,90] examined the behavior of the bis(methylthio)benzene ether **420**. Benzodithiasilepin **421** was obtained in moderate yield after the addition of dichlorodimethylsilane to the corresponding dianion (Scheme 105).[168]



420 **421** (53%)

Scheme 105.

5.1.2. Preparation by formation of a carbon–silicon atom bond. In the preceding sections, the formation of four- and five-membered ring compounds by intramolecular hydrosilylation was reported to occur in satisfactory yields, while the formation of six-membered ring compounds seems difficult. The first report concerning the preparation of seven-membered ring compounds using this method was by Mironov and co-workers. With the α,β-ethylenic ester **422**, intramolecular addition of the Si–H bond catalyzed by H_2PtCl_6 gave the benzoxasilepane derivative **423**.[169] Voronkov's group used the Wilkinson catalyst to obtain eight-membered ring compounds **425** when sulfur,[16b] oxygen,[170] and nitrogen[171] atoms were present in the silaoctene chain **424** to cyclize (Scheme 106).



422 **423**

424a: R = Et, X = S **425a** (46%)

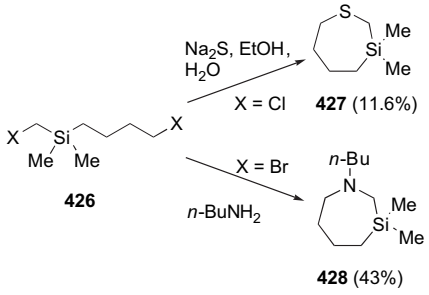
424b: R = Me, X = O **425b** (84%)

424c: R = Me, X = NMe **425c** (11%)

Scheme 106.

5.2. Preparation by formation of carbon–heteroatom bonds

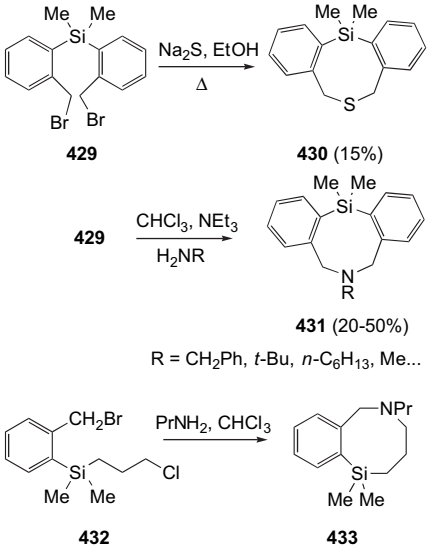
5.2.1. Preparation by reaction of functionalized silanes with heteroatom-containing reagents. Fessenden, after his report concerning the preparation of 3-sila-1-heterocyclohexanes from 1,5-dihalosilapentane derivatives, applied this method to the synthesis of 3-sila-1-heterocycloheptanes.[172] Reactions of 4-halobutyl(halomethyl)-dimethylsilanes **426** with Na_2S and butylamine led to the seven-membered heterocyclic compounds **427** and **428**, respectively (Scheme 107).



426

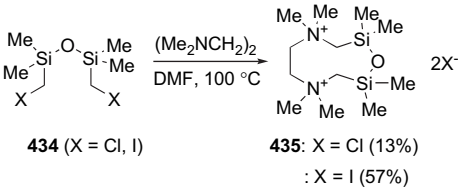
Scheme 107.

Heterosilocanes could also be prepared starting from mono or bis(*o*-bromomethylphenyl)silanes, e.g., dibenzothiasilocane **430** was obtained in low yield by reaction of the dibrominated silane **429** with sodium sulfide (Scheme 108).[84] Reaction of this silane **429** with primary amines led similarly to azasilocanes **431**.[162,173] This method was used by the Lukevic group to access benzocyclooctane **433** starting from 3-chloropropylsilane **432** bearing a 2-(bromomethyl)-phenyl substituent.[174]



Scheme 108.

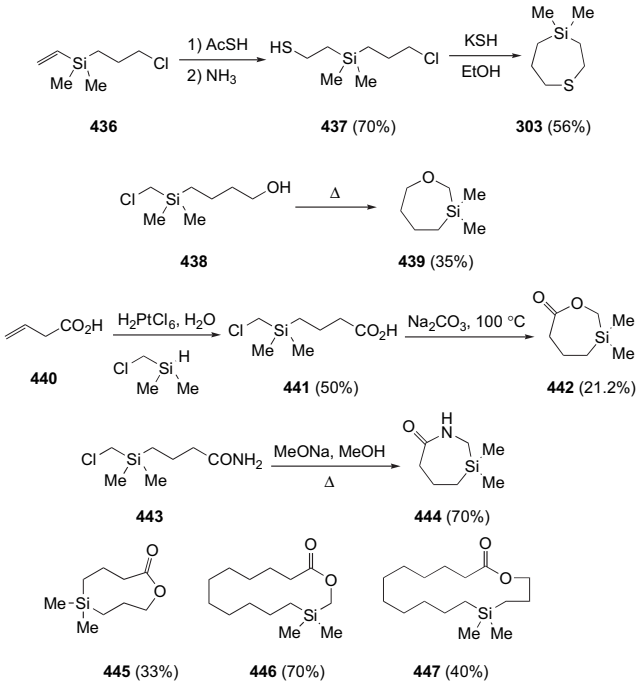
Formation of oxadiazadisilonanes **435** was reported by the reactions of a diamine with bis(halomethylsilyl) ethers **434**. The yield of this cyclization is remarkable for such a ring size, starting from the diiodinated substrate (Scheme 109).[175]



434 (X = Cl, I) **435**: X = Cl (13%)
: X = I (57%)

Scheme 109.

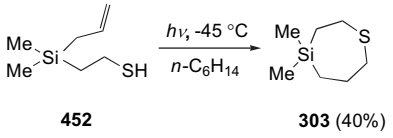
5.2.2. Preparation by intramolecular cyclization of functionalized silanes. The formation of 5- and 6-ring-sized 1,3-thiasilacycloalkanic compounds has been reported using intramolecular cyclizations of ω-halosilathiols.[40a] Voronkov and co-workers have subsequently reported that the procedure developed by Dedeyne[99] could be applied to the formation of seven-membered ring compounds (Scheme 110).[176] E.g., chlorothiol **437**, obtained by radical addition of thioacetic acid to vinylsilane **436** and subsequent treatment with ammonia, underwent an intramolecular cyclization to **303** when treated with KSH. These conditions could not, however, be applied to the formation of eight-membered ring compounds.[40a] 1-Oxa-3-silacycloheptane **439** was obtained, as in the case of six-membered compounds, by simple heating of alcohol **438**.[172] Mironov's group applied the Fessenden method to the preparation of different lactones and lactams (see Scheme 72). Similarly, the reaction of acid **441** and amide **443** with, respectively, sodium carbonate and sodium methylate led to the desired seven-membered compounds **442** and **444** (Scheme 110).[116,119] The medium-ring lactone **445** and large-ring lactones **446**, **447** were also obtained in satisfactory yields using this method.[177] The acids necessary for these cyclizations, such as acid **441**, were obtained by hydrosilylation of the carbon–carbon double bond of unsaturated acid **440** using (chloromethyl)dimethylsilane in the presence of chloroplatinic acid as catalyst. A one-pot procedure leads to improved results.[117]



Scheme 110.

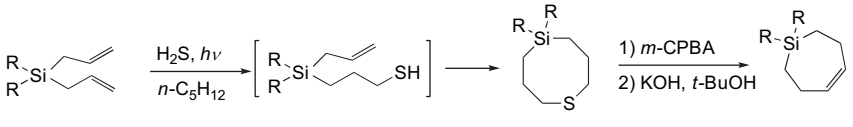
Weber et al. were the first to report that photochemically induced cyclization of unsaturated silathiols led to the formation of 1,5-thiasilocanes.[178] This reaction was subsequently developed mainly for the formation of five-membered ring silaheterocyclic compounds.[40,41,126] Irradiation of a mixture of diallylsilanes **448a**,**b** and H_2S in pentane at low temperature led to the formation of thiasilocanes **450a**,**b**, without any formation of the six- or seven-membered ring compounds. Similar results were reported with silanes **448c**,**d**, to form **450c**,**d**[179] or when the irradiation was carried out in the presence of the photocatalyst YCl_3.[180] The intermediate formation of the unsaturated thiols **449a–d** was confirmed by the fact that irradiation of compound **449a** led to thiasilocane **450a** with the same yield. Compounds **450a**,**b** were transformed into silacycloheptenes **451a**,**b** by a Ramberg–Backland reaction with the corresponding sulfones (Scheme 111).[178]

Kirpichenko et al., with the aim of studying the regioselectivity of these photocyclizations, compared the behavior of 4,4-dimethyl-4-silahex-5-ene-1-thiol **285** with that of 3,3-dimethyl-3-silahex-5-ene-1-thiol **452**. With vinylsilane **285**, a mixture of products, corresponding to the competition between the *endo* and *exo*-mode cyclizations, was observed (Scheme 77)[126] while, with the allylsilane **452**, only the seven-membered heterocyclic compound **303** was obtained (Scheme 112).[126,176]



Scheme 112.

The aminomercuration of 3-chloropropylsilanes bearing a vinyl or an allyl group in the presence of aniline was reported to lead mainly to the uncyclized 2-aminoalkylsilanes. From allylsilane **453**, an azasilepane **455** was isolated in very low yield together with **454** (Scheme 113).[42b] This work was resumed and the intramolecular aminomercuration of *N*-(4,4-dimethyl-4-silahex-5-en-yl)aniline **321** was reported



448a: R = Me
448b: R = Ph
448c: R = OMe
448d: R = F

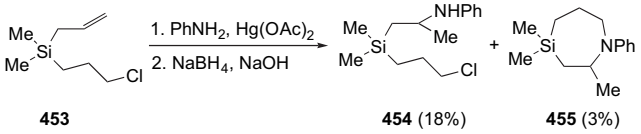
449a-d

450a (25%)[179], (35%)[40a]
450b (10%)[179]
450c (30%)[180]
450d (19%)[180]

451a (48%)
451b (40%)

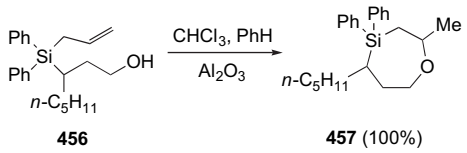
Scheme 111.

to lead mainly to the seven-membered ring compound **323** (Scheme 80).[43]



Scheme 113.

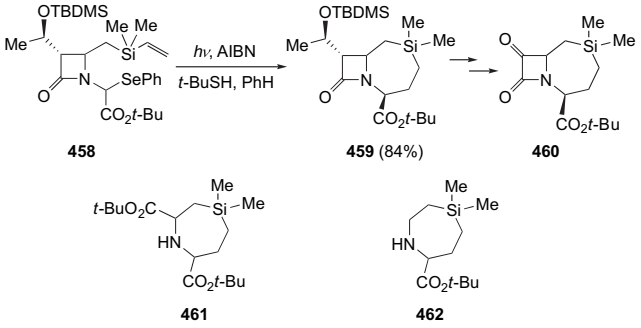
A quantitative formation of oxasilepane **457** was observed when alcohol **456** was mixed with acidic alumina (Scheme 114).[181] This interesting reaction was not further examined.



Scheme 114.

5.3. Preparation by formation of carbon–carbon bonds

Taddei and co-workers obtained the bicyclic β-lactam **459** (Scheme 115) by intramolecular addition of a radical on the CC double bond of a vinylsilane **458**.[182] In this case, only one regioisomer and stereomer was obtained. Sila β-lactam **459** did not show any particular antibiotic activity. This result is not very surprising since the replacement of a methylene group by a $SiMe_2$ group induces steric constraints, which could prevent the entry of the molecule into the enzymatic sites. β-Lactam **459** was transformed into β-diketone **460** by oxidation of the corresponding ethylidene β-lactam. This latter ketolactam was unstable in the reaction conditions and gave, among various products, compounds **461** and **462**.



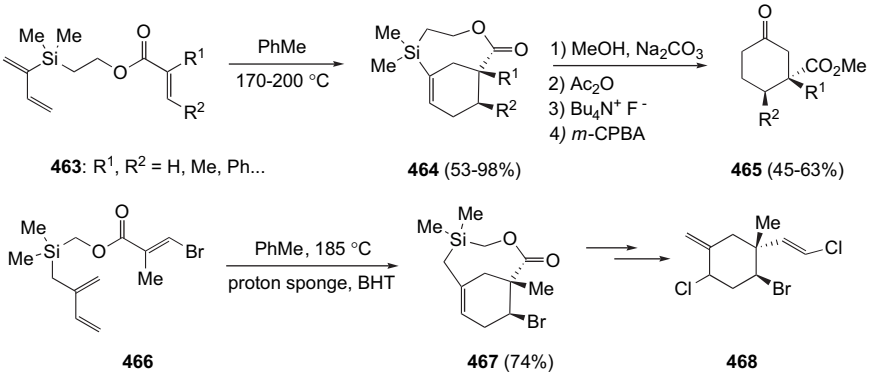
Scheme 115.

Shea et al. during their studies on intramolecular Diels–Alder reactions[183] examined the thermal behavior of butadienylsilanes **463**. At 170 °C, intramolecular cycloadditions occurred and bicyclic silalactones **464** were obtained in excellent yields (Scheme 116).[184] Only one diastereomer was obtained. Oxidative cleavage of the silicon part allowed the preparation of substituted cyclohexanones **465**. In a subsequent study, these authors showed that the position of the silicon in the carbon chain could be modified. Such an intramolecular Diels–Alder reaction was applied to the synthesis from **466** via **467** of the trihalogenated compound **468**, which is a metabolite of the red marine algae *Plocamium* sp.[185]

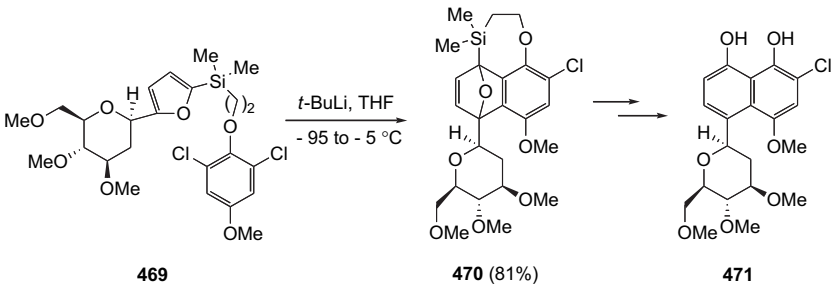
1,4-Oxasilepane **470** has been prepared from the sugar derivative **469** (Scheme 117) by an intramolecular Diels–Alder reaction of benzyne with the furan moiety.[142] The preparation of compound **470** was reported to be more efficient than the formation of the analogous six-membered heterocyclic compound **351** (see Scheme 88), and compound **470** was subsequently transformed into the C-glucoside **471**.

5.4. Formation by ring expansion

Corey and co-workers have intensively studied the ring expansion of phenoazasilinines and phenoxasilinines. Contrary to dibenzosiline **472**, for which the ring expansion to **473** was shown to be possible using Lewis acids such as $AlCl_3$,[186] utilization of these conditions was not adapted to the heterocyclic analogues with oxygen or nitrogen atoms. It was found that the ring enlargement occurred efficiently using fluoride ions. Treatment of compounds **474a**,**b** with KF in MeCN at reflux (1–2 days) led to the seven-membered ring products **475a**,**b**.[187] The reactions were accelerated in the presence of 18-crown-6. In the case of sulfone **476**, the ring expansion took place, but the product **477** appeared unstable in the reaction conditions and the ring-cleavage product **478** was isolated in good yield when 2 equiv of KF were used. Different fluorine sources were tested, without great



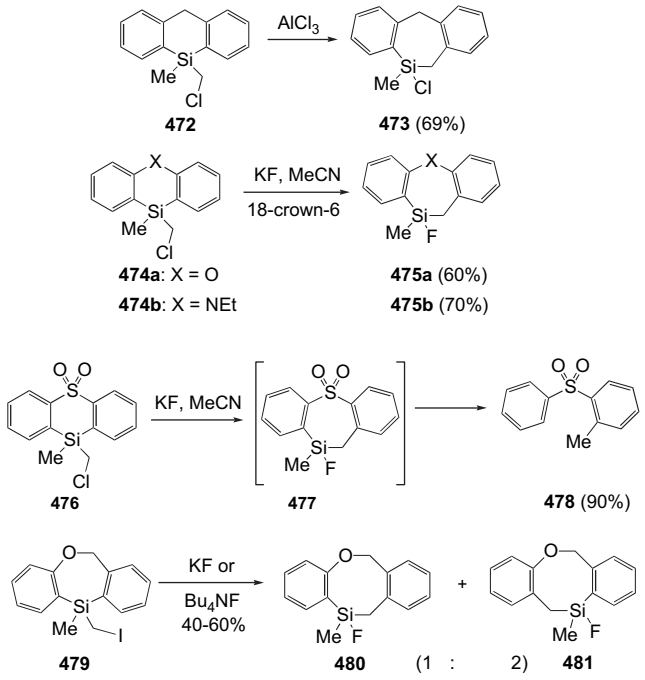
Scheme 116.



469 **470** (81%) **471**

Scheme 117.

success, to improve these reactions.[188] This transformation occurred only if a halomethyl group was fixed on the silicon atom. With α-chloroethyl and β-chloroethyl as substituents, no rearrangement was observed. Transformation of oxasilepine **479** into a mixture of regioisomer oxasilocines **480** and **481** was also reported. In this case, the iodomethyl derivative led to a better result than the chloromethyl derivative (Scheme 118).[189]

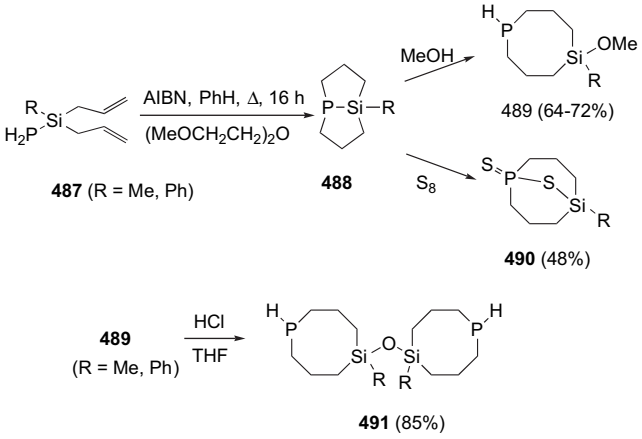


472 **473** (69%) **476** **477** **478** (90%) **479** **480** (1 : 2) **481**

Scheme 118.

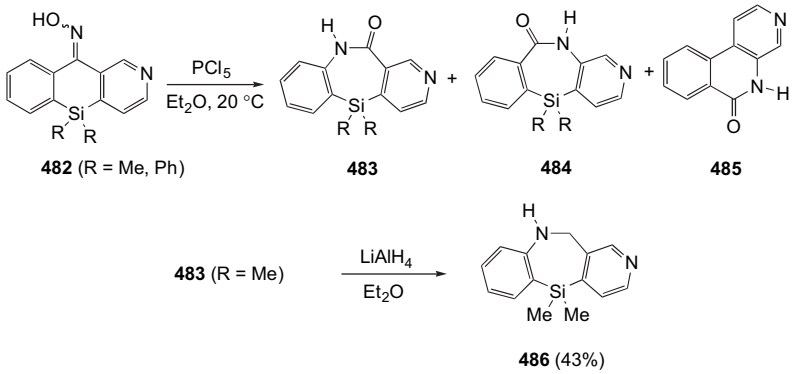
The Beckmann rearrangement was also used to obtain azasilepines. Reaction of oximes **482** with PCl_5 in ether led to a mixture of amides **483** and **484** (14–31%) and of the product of subsequent desilylation **485**. Compound **485** could be obtained in almost quantitative yield by heating amide **486** (R=Me) at 230 °C. $LiAlH_4$ reduction of amides **483** (R=Me) and **484** (R=Me) led to the corresponding amines, e.g., **486** (Scheme 119).[190]

Kuehne et al., during their work concerning the reactivity of P–H bonds,[128] examined the intramolecular cyclization of compounds **487**. In benzene in the presence AIBN, the stable bicyclic compounds **488** were obtained. Addition of methanol induced cleavage of the P–Si bond and phosphasilocanes **489** were isolated in good yields.[191] The bicyclo[3.3.1]nonanic compounds **490** were obtained by insertion of sulfur into the P–Si bond of compounds **488** (Scheme 120).



487 (R = Me, Ph) **488** **489** (R = Me, Ph) **491** (85%)

Scheme 120.



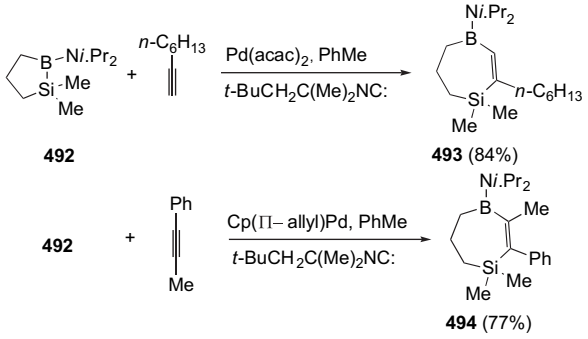
482 (R = Me, Ph) **483** **484** **485**

483 (R = Me) **486** (43%)

Scheme 119.

Phosphasilocanes **489** were stable in acidic conditions and gave disiloxanes **491** as expected.

Recently Suginome and co-workers have reported a study on the reactivity of silaborane **492** with alkynes. In the presence of palladium catalysts, cleavage of the Si–B bond allowed the regioselective insertion of an alkyne unit giving the 1,4-silaborepenes **493** and **494** in good yields (Scheme 121).[192]



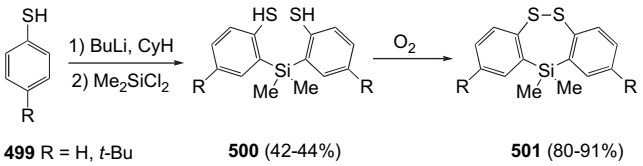
Scheme 121.

Tamao and co-workers have reported the formation of phosphasilinene (six-membered ring compound) by thermal decomposition of the silylated phosphine **223** in the presence of diphenylacetylene, via silylene **224** (Scheme 58).[95] When two phenyl substituents were present on phosphorus atom (**495**), the seven-membered heterocyclic compound **498** was obtained (Scheme 122). The intermediate phosphasilete **497** should be formed by the reaction of silylene **496** with the acetylenic reagent and a P→Si phenyl migration could induce a ring opening of the four-membered ring.

5.5. Other methods

Reaction of thiophenols **499** with 2 equiv of butyllithium in the presence of TMEDA was also reported to lead to dilithiated intermediates. Subsequent reaction with dichlorodimethylsilane led to the silylated compounds **500**, which, by heating or in the presence of oxygen, gave dithiasilepins **501** in good yields (Scheme 123).[193]

Le Floch and co-workers have reported the preparation of compound **504** by heating phosphinine **502** bearing two phosphazinylsilyl groups with diethynylsilane **503**. Compound **504** was stable and was purified by liquid chromatography (Scheme 124).[194] The same substrate **502** led, by reaction with the heterocyclic compound **505**, to the



Scheme 123.

formation of the air-sensitive polycyclic compound **506**. Such cycloadditions were also possible using thiophene and furan derivatives **507** with diacetylenic reagents **508**, to give rise to the mixed polyaromatic compounds **509**. Silaheterocyclic compounds **504**, **506**, and **509** possess holes of different radii and can probably be used to encapsulate metal ions with coordination spheres of different sizes.

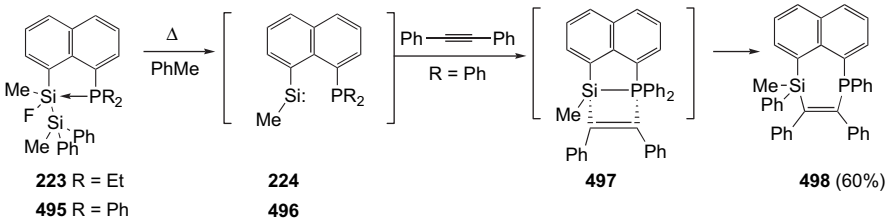
Reactions of siloles **510** with dimethyl acetylenedicarboxylate in toluene were found to give mainly the seven-membered ring heterocycles **512** (Scheme 125), and minor amounts of the bicyclic silalactones **513**. Cleavage of the bicyclo[2.2.1]silaheptane intermediate **511** was postulated to occur by a radical pathway, and the postulated diradical should give the bicyclic products **512** by reaction with a second molecule of dimethyl acetylenedicarboxylate.[195]

5.6. Reactivity and applications

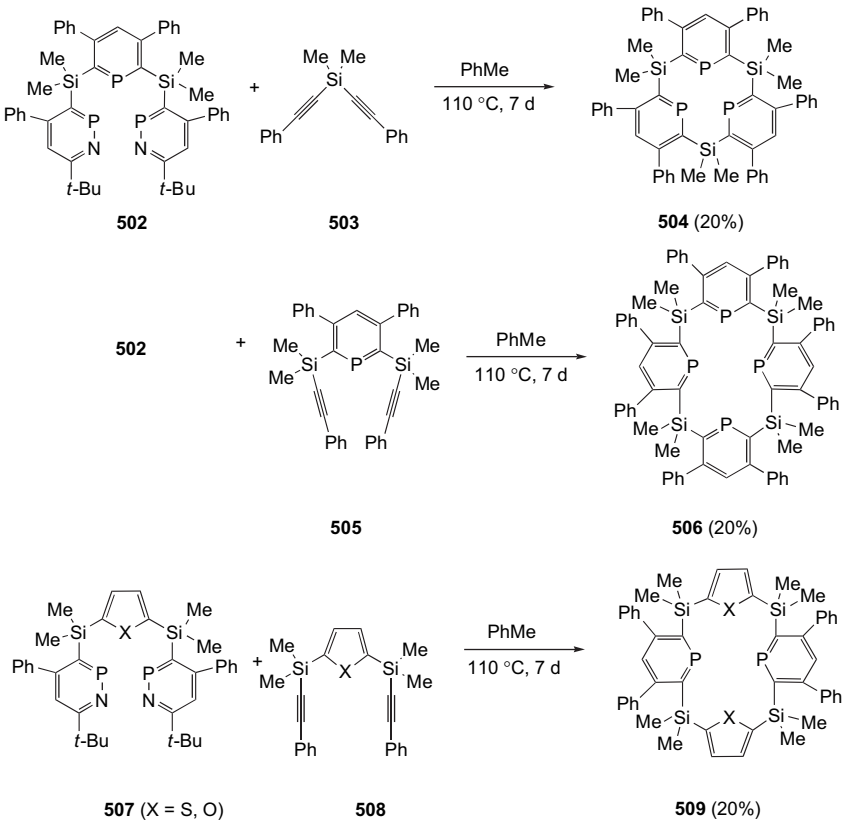
It has been found that 7- and 8- membered heterocyclic compounds may be used in various reactions without transformation of their heterocyclic cores. Oxasilepine **475a** was reduced using $LiAlH_4$ to provide hydrosilane **514**, which could add to allylamine to give the carbo-functionalized silane **515**. Reaction of compound **514** with methylmagnesium bromide afforded dimethylsilane **516**. This latter compound reacted with NBS to lead to the dibromo derivative **517** (Scheme 126).[64]

Reaction of silaheterocyclic compound **404b** with $BF_3 \cdot Et_2O$ led to difluorosilane **518**, while reaction with $LiAlH_4$ gave dihydrosilane **519** (Scheme 127).[164] Treatment of compound **518** with Li metal, in the presence of 2,3-dimethylbuta-1,3-diene, gave rise to the formation of the silacyclopentenyl compound **520**, via a silylene intermediate. Monosubstitution of dihydrosilane **519** was also reported to lead to useful unsymmetrical difunctionalized silanes **521** (60–90% yields).[163]

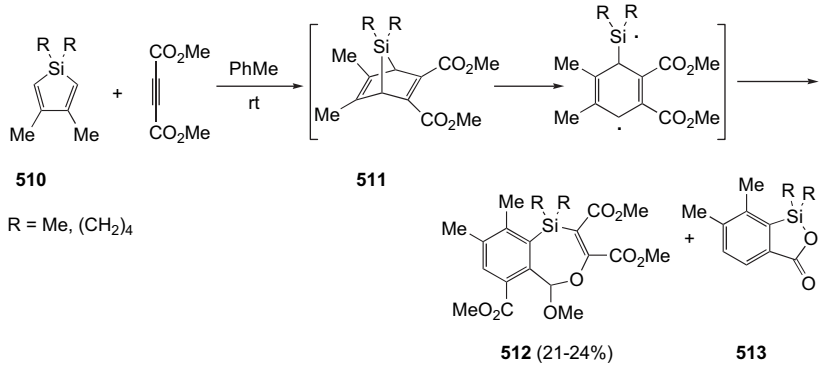
Regioselective metallation of thiasilepin **402** occurred using phenyllithium, and subsequent addition of a chloroalkylamine allowed the formation of the alkylated compound **522** (Scheme 128).[84]



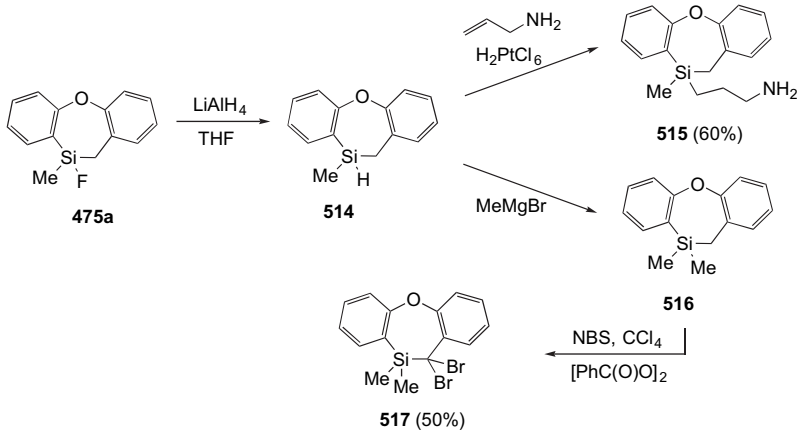
Scheme 122.



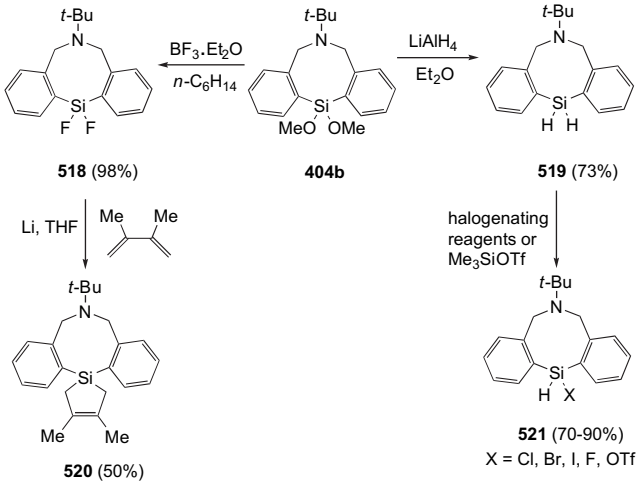
Scheme 124.



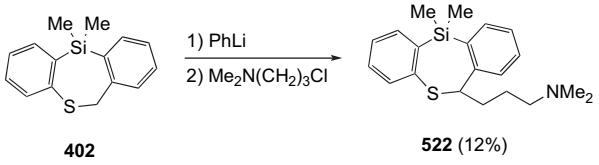
Scheme 125.



Scheme 126.

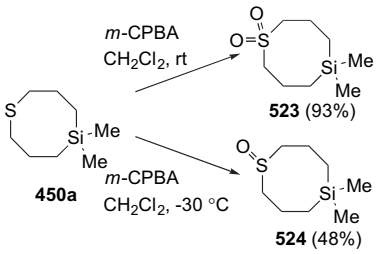


Scheme 127.



Scheme 128.

The oxidation of thiasilocane **450a** has been studied in detail. At −30 °C, sulfoxide **524** could be obtained, while, at room temperature, sulfone **523** was formed, without any cleavage products (Scheme 129).[196] Similar results were obtained using thiasilepane **303**.



Scheme 129.

6. Conclusions

We have seen in this review that numerous methods have been reported concerning the preparation of sila–heterocyclic compounds in which the silicon atom and the heteroatom are separated by at least one carbon atom. These results show that the preparation of new compounds in which a silicon atom replaces one carbon atom becomes possible and these compounds can be planned in strategies to obtain various heterocyclic compounds. Interesting properties can be anticipated for these compounds, as already reported for some products possessing biological activities or others as new materials.[1,2]

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Biographical sketch

Dr. Gérard Rousseau was born in 1946 in Versailles, France. He obtained his PhD at the Université Paris-Sud, Orsay, France, under the supervision of Professor J. M. Conia in 1976 on the reaction of singlet oxygen with cyclopropanic derivatives. Then he carried out a post-doctoral research with Professor R. B. Woodward on the total synthesis of erythromycin A. After his return to France, he worked principally on the chemistry of ketene acetals, the utilization of enzymes in organic chemistry, the chemistry of medium-ring compounds and more recently on electrophilic cyclizations. His present interest concerns the preparation of silaheterocycles. He is director of research at the CNRS.

Luis Blanco was born in 1948 in Paris, France. After a previous study of Conia-ene reactions, he completed his PhD in 1982 under the supervision of Professor Jean-Marie Conia at the Université Paris-Sud, Orsay, France, where he worked on the synthesis and the transformations of halosilyloxycylopropanes. He entered the Centre National de Recherche Scientifique in 1973. In 1985, he joined for one year Professor K. P. C. Vollhardt's group at University of Berkeley, California, as a post-doctoral fellow to work on the synthesis of multiphenylenes. His research interests concentrated on silyl enol ethers and on cyclopropanic compounds as synthetic tools, using ionic, radical, and oxidative methods to open the cyclopropanic rings, and on the use of enzymes in organic synthesis. More recently, he was involved in the enantio- and diastereoselective synthesis of sila-substituted organic compounds and he works to obtain sila drugs.