Five- and six-membered silicon–carbon heterocycles. Part 1. Synthetic methods for the construction of silacycles

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Covering up to December 1997

1 Introduction

There has been a considerable interest in organosilicon chemistry over many years from several different points of view.[1a] Organic chemists discovered the synthetic potential of organo silicon compounds in various transformations (Sakurai-reaction,[1b] Tamao–Kumada-oxidation,[1c] Hiyama-cross-coupling,[1d] silicon-mediated aldol reactions[1e]). Topics in organosilicon chemistry which are especially attractive for inorganic and organometallic chemists are pentacoordination of silicon,[1f] low-valent silicon species (silylenes)[1g] and species where silicon is involved in multiple bonding.[2,3] Organosilanes have also been of interest for materials science as some of them seem to be promising precursors for electrically conducting polymers or materials with certain physical properties.[1h] Finally, there has been interest in the preparation of silicon compounds with physiological and biological activity, such as drugs or compounds with olfactory properties.[1i]

This review will cover the chemistry of five- and six-membered silicon-carbon heterocycles with one silicon atom in the ring. We will focus on contributions published during the last ten years, although in a few cases, older literature has been considered. The chemistry of silicon–carbon heterocycles with an endocyclic silicon–oxygen bond has recently been reviewed[1j] and will therefore not be discussed herein. Some aspects of the chemistry of silaheterocycles, including systems with more than one ring silicon atom, have previously been reviewed.[1k] A review on group 14 metalloles also covers the chemistry of silacyclopentadienes.[1l]

The first part of this review will deal with methods for the preparation of silicon–carbon heterocycles. We will focus on those reactions, which are useful for preparative purposes. This implies that some transformations, though mechanistically interesting, will only be briefly mentioned. The material is organized according to the different synthetic methods, not according to the structure of the products. Five different classes of syntheses may be distinguished: a) cycloaddition of reactive intermediates to dienes, b) ring enlargement reactions of three- and four-membered silacycles, c) ring closure of acyclic silanes by C–C bond formation, d) ring closure of acyclic silanes by Si–C bond formation and e) ring closure by simultaneous formation of two Si–C bonds.

Part 2 will deal with synthetic transformations and applications of silicon–carbon heterocycles.

2 Ring closure by cycloaddition of reactive intermediates to dienes

Silenes **1** and silylenes **2** both react with conjugated dienes to give silacyclohexenes **3** or silacyclopentenes **4** respectively (**Scheme 1**). These reactions have been exploited not only for the preparation of the heterocycles, but also for the indirect detection of these reactive intermediates.
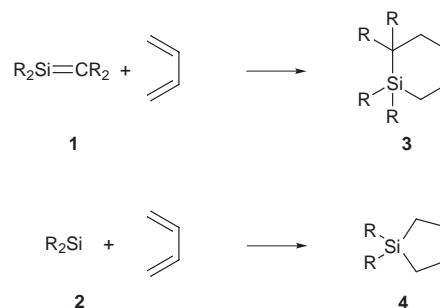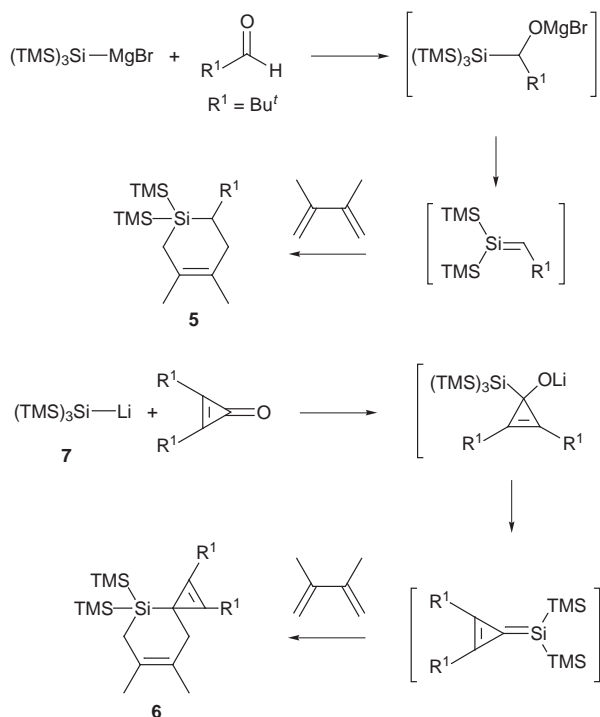

Scheme 1

In this section we will first discuss generation and cyclo-additions of silenes and then the generation of silylenes and their reaction with dienes.

2.1 Silenes in [4 + 2] cycloaddition reactions[2,3]
### a) Modified Peterson reaction
Several different methods for the generation of silenes have been reported. One approach utilizes a modified Peterson reaction, where a magnesium[4] or lithium[5] silanide is added to a ketone or an aldehyde followed by elimination of a magnesium or lithium silanolate. A trapping reaction with dimethylbutadiene leads to the silaheterocycles **5** and **6** respectively (**Scheme 2**).

When the carbonyl function of an aldehyde or ketone is sterically highly hindered, magnesium silanides are not reactive enough to add to the carbonyl carbon. In these cases the more reactive lithium silanides may give satisfactory results. For example, silaethene **9** could only be generated by addition of

Scheme 2

TMS₃SiLi **7** to the heavily shielded aldehyde **8**.[6] In this case intramolecular cyclization *via* insertion of a silene into a C–H bond occurs to give silacyclohexane **10** (**Scheme 3**).
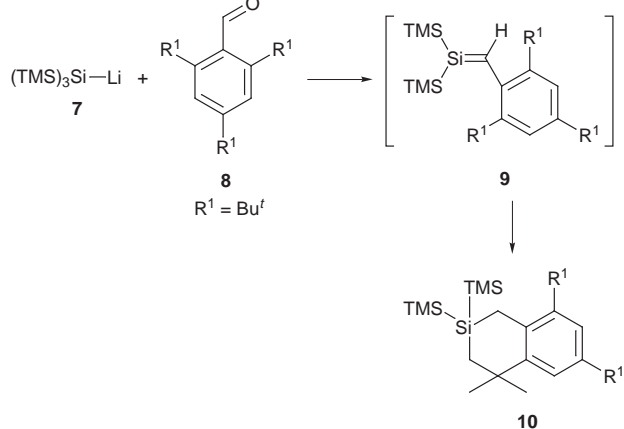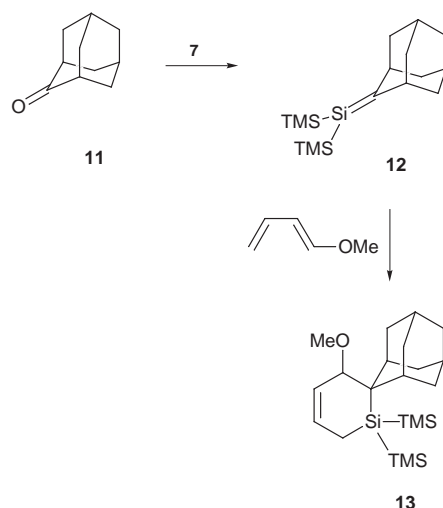

Scheme 3

Whereas in most cases the silene is only a reactive intermediate, Apeloig *et al.*[7] describe a stable silene **12** starting from **7** and adamantanone **11**. Despite being stable at room temperature, **12** readily adds to methoxybutadiene to give the silaheterocycle **13** (**Scheme 4**).

b) Silenes by elimination of lithium halide

Elimination of a salt from α-lithiated silanes with a Si–halogen bond represents a different approach to silenes. In an early report from Jones[8] a silene **16** is generated by addition of Bu'Li to a vinylchlorosilane **14** and elimination of LiCl from the intermediate **15**. Trapping with 2,3-dimethylbutadiene (DMB) leads to the two diastereomeric heterocycles **17a** (resulting from the *Z*-silene) and **17b** (resulting from the *E*-silene) and a side product **17c**, resulting from an ene reaction (**Scheme 5**).

The addition of Bu'Li to vinylchlorosilanes has been used in the following years to prepare a variety of silaheterocycles. Especially work by Auner *et al.* gives insight into the scope and limitations of the method and allows for some general statements:
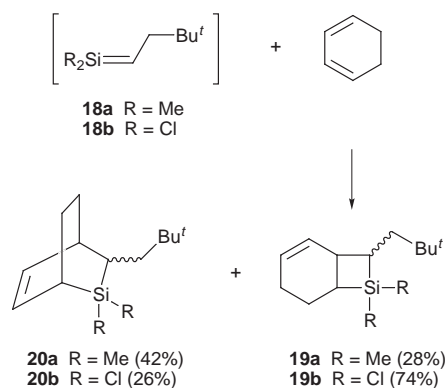

Scheme 4
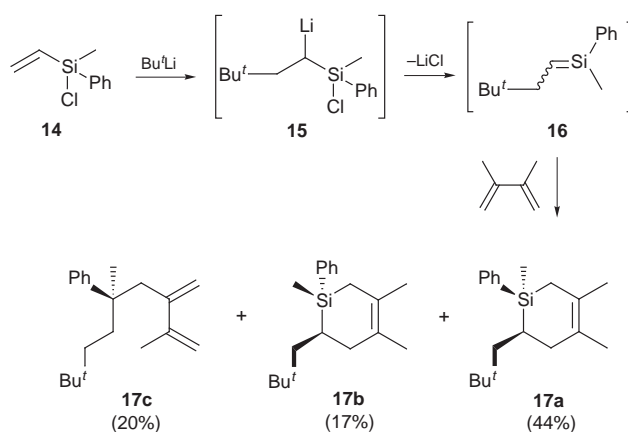
Scheme 5

—Silenes Cl₂Si=CHBu' are more reactive in [4 + 2]-cyclo-addition reactions than silylated alkenes Cl₃SiC=CH₂.[9]

—The [4 + 2] cycloaddition reaction competes with an ene reaction. The Diels–Alder reaction is preferred for dienes with higher π-electron densities.[10,11]

—In some cases, especially with cyclohexadiene, a [2 + 2] (leading to products of type **19**) rather than a [4 + 2] cyclo-addition (leading to products of type **20**) becomes the main reaction path.[12] In general, silenes **18** with a low lying LUMO (alkyl substituents at silicon) react preferentially in a [4 + 2] cycloaddition, whereas silenes with a higher LUMO (Cl[13] or OMe[14] at silicon) react preferably in a [2 + 2] cycloaddition (**Scheme 6**).[15]

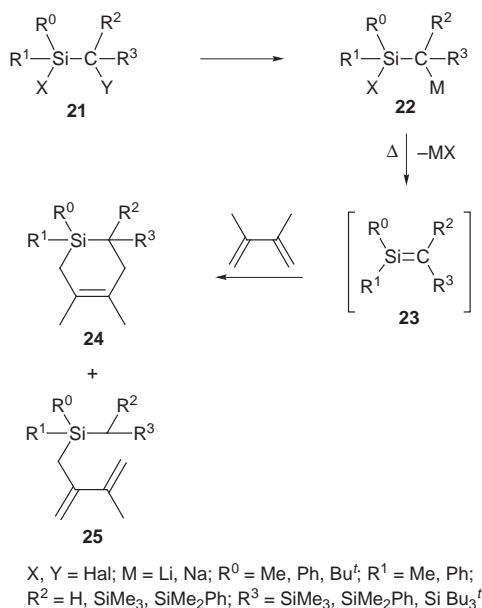**Scheme 6**

Very recently the addition of Bu'Li to divinyldichlorosilane has been used to generate a silaallene, an intermediate for a

spirocyclic compound.[16] A stable silene has also been prepared by this method.[17]

A selective halogen–metal exchange allows an alternative approach to α-metallated halosilanes.[18] Starting from the dihalogenated compounds **21** halogen–metal exchange proceeds selectively to give the metallated compounds **22**, which undergo elimination of MX.[19,20] Trapping with dienes yields silacyclohexenes **24** together with the ene products **25**. In some cases, **25** even becomes the major product (**Scheme 7**).[21]

X, Y = Hal; M = Li, Na; R^0 = Me, Ph, Bu^t; R^1 = Me, Ph; R^2 = H, $SiMe_3$, $SiMe_2Ph$; R^3 = $SiMe_3$, $SiMe_2Ph$, $Si Bu_3^t$

Scheme 7

### c) Silicon analogs of enolates

Ohshita *et al.* described the synthesis of silenolates, silicon analogs of enolates, by desilylation of acylsilanes **26** with TMS_3SiLi (**7**). Subsequent reaction with Et_3SiCl gives the intermediate **27** which undergoes a Diels–Alder reaction with DMB (**Scheme 8**).[22,23]

R = Mes
R^1 = Et
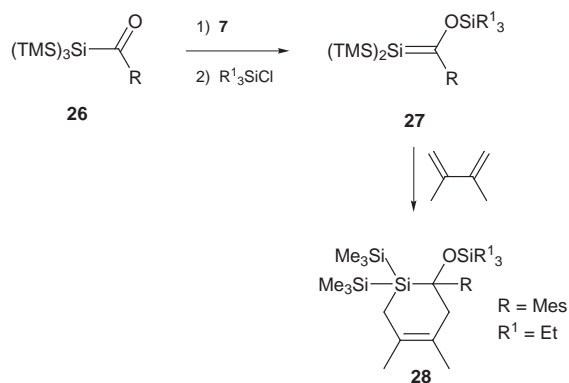
Scheme 8

A thermally or photochemically induced isomerization of acylsilanes represents an alternative pathway to silylenol ethers of type **27**.[24] For example, reaction of **27** with diene **29** leads to the formation of silacyclohexenes **30** as a 9:1 mixture of diastereomers in good yield (**Scheme 9**).

The [4 + 2] cycloaddition of silenolates doesn't necessarily require the formation of a silylenol ether of type **27**, even lithium enolates undergo Diels–Alder reactions. In the example outlined in **Scheme 10** a lithium silenolate **31** was generated by the Ohshita method from acylsilane **26** (R = Bu^t). The product of the cycloaddition, lithium alcoholate **32**, undergoes a Peterson-type elimination to give intermediate **33**, which
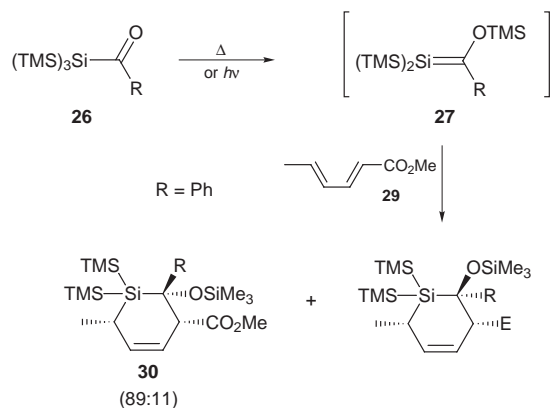
Scheme 9
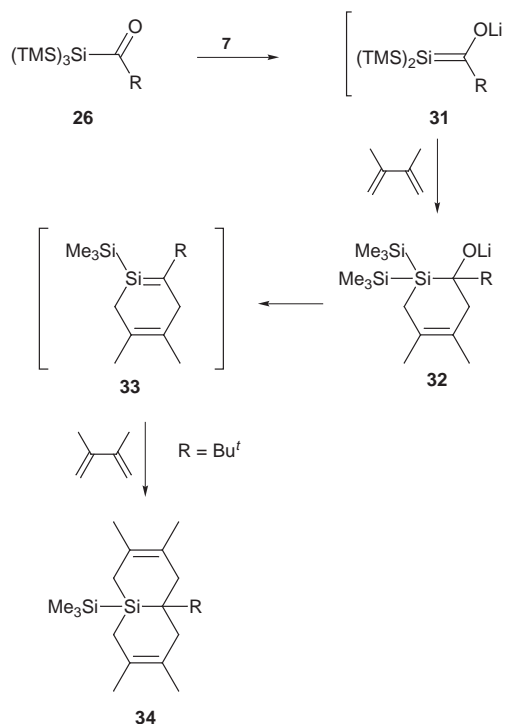
Scheme 10

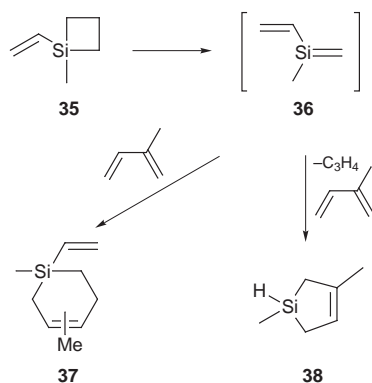reacts with a second equivalent of DMB to give the bicyclic compound **34**.[25]

Interestingly, no side-products resulting from ene reactions or [2 + 2] cycloadditions are found in the reaction of silenes of type **27** or **31** with dienes.

d) Silenes by cycloreversions

Cycloreversion of silacyclobutane **35** gives ethene and silene **36**, which can be trapped with isoprene to produce heterocycle **37**. However, vinylsilene **36** undergoes elimination of allene, resulting in the formation of a silylene, which was trapped as a silacyclopentene **38** (**Scheme 11**).[26]

The cycloreversion of a symmetrically substituted disilaheterocycle to yield two equivalents of a silene has also been reported.[27]

Silabutadienes **40** have been postulated as reactive intermediates in gas phase flow pyrolyses of silacyclobutenes **39**. The reactive intermediates can be trapped by alkenes leading to silacyclohexenes.[28] The reaction is stereospecific, as from (*E*)-butene predominantly *trans*-substituted silacyclohexenes **41** and **42** are formed, whereas from (*Z*)-butene under the same conditions mainly *cis*-silacyclohexenes **41** and **42** are formed (**Scheme 12**). If the pyrolysis of silacyclobutene is carried out in the absence of a dienophile, a mixture of formal dimers of silabutadienes results.[29]

35   **36**

−C$_3$H$_4$

37   **38**

Scheme 11

39   350 °C   **40**

(39%)   (39%)   (44%)   (44%)

cis-**41**   *cis*-**42**   *trans*-**41**   *trans*-**42**
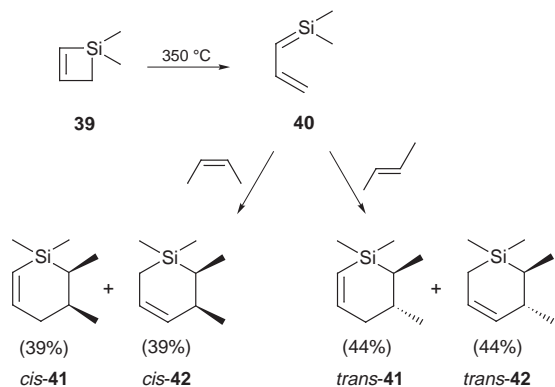
Scheme 12

2.2 Silylenes in cycloaddition reactions

Silylenes have been postulated as short-lived reactive intermediates in a number of processes. An often used method for the indirect detection of silylenes is the trapping reaction with butadiene or dimethylbutadiene (for recent examples, see: refs. 30–38). Investigations into the mechanism [39] suggest that in a first step a [2 + 1] addition occurs, leading to a vinylsilacyclopropane **43**, which rearranges to the silacyclopentene **4**. The isolation of stable vinylsilacyclopropanes by Zhang and Conlin is additional proof for this mechanism.[40] The formation of divinylsilacyclopentanes **44** can also be explained when a vinylsilacyclopropane **43** is assumed as an intermediate (**Scheme 13**).[41]

R$_2$Si **2**   →   R$_2$Si **44**

R$_2$Si **43**   →   R$_2$Si·

R$_2$Si **4**
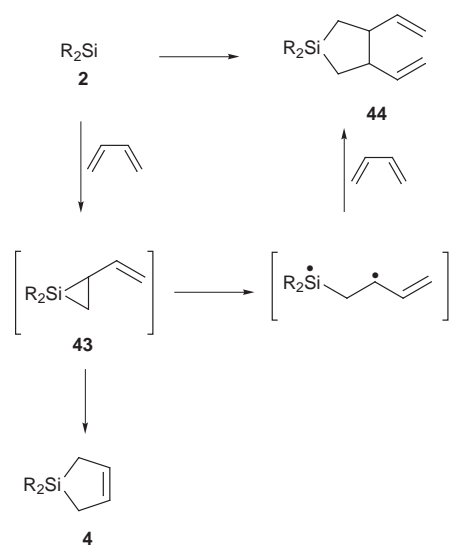
Scheme 13

The addition of silylenes to dienes is reversible, this was demonstrated for 1,1-dichlorosilacyclopentene by co-pyrolysis with other dienes.[42,43] Using the trapping reaction with buta-

diene, dichlorosilylene and methylchlorosilylene were detected as surface intermediates in the direct synthesis of methylchlorosilanes (Müller–Rochow process).[44,45] Some reactions involving silylenes can be used for the preparation of silaheterocycles. However, yields are sometimes poor. In this chapter we will only discuss those contributions where silaheterocycles are formed in preparatively useful quantities. This section will be subdivided according to the different methods for the generation of silylenes. It will include heterocycle formation *via* transition metal stabilized silylenes and catalytic processes where a transition metal stabilized silylene is postulated as an intermediate.

a) Dehalogenation of dihalosilanes in the presence of dienes

The reductive dehalogenation of dichlorosilanes in the presence of dienes leads to the formation of silacyclopentenes. Typically, harsh conditions are employed (Na/K vapour at 300 °C and low pressure) and yields are low (around 30%). This method has been used for the preparation of spirocycles **45** as outlined in **Scheme 14**.[46,47]
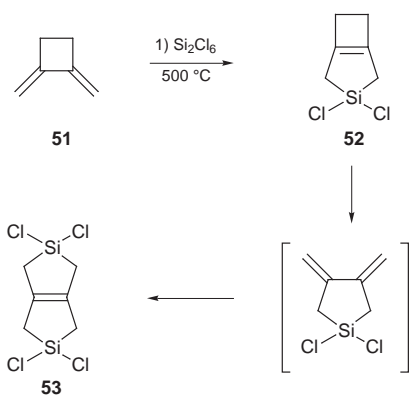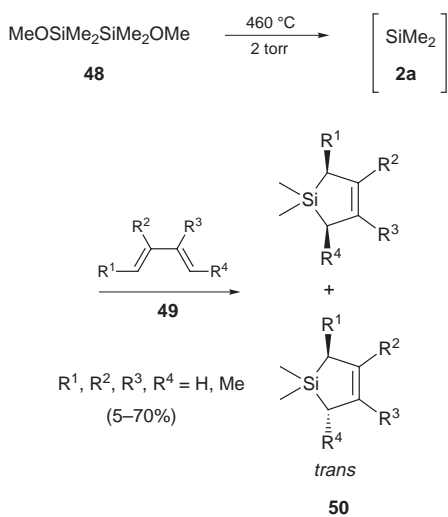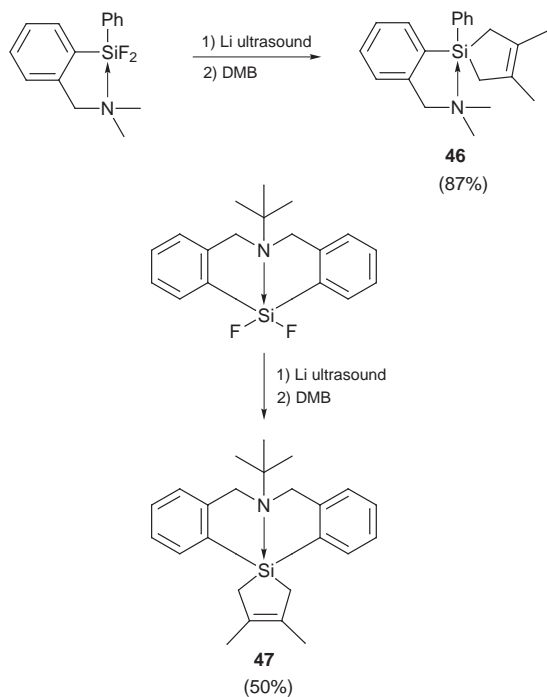
Na/K
300 °C
1 torr

45

(26%)
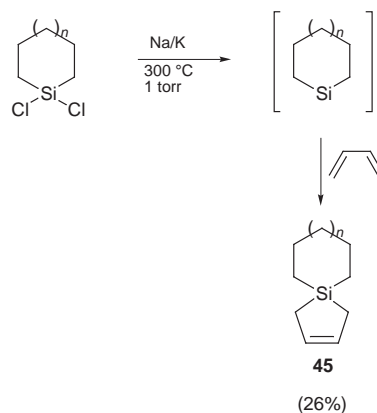
Scheme 14

Recently, dichlorosilanes have been reduced in the presence of dienes in ether–THF solution under sonication to give silaheterocycles in comparable yield.[48] Whilst for these reactions a mechanism involving the intermediate formation of silylenes is generally accepted, a different mechanism has been proposed for the electrochemical reduction of dichlorosilanes in the presence of DMB on the basis of cyclovoltammetry.[49] Here silacyclopentenes are isolated in up to 28% yield along with polymers.

Corriu *et al.* report a remarkable improvement of the yield when the intermediate silylenes are stabilized by intramolecular coordination (**Scheme 15**). This can either be achieved *via* a donor substituted side chain (**46**)[50] or by introduction of a donor atom into a silicon containing macrocycle (**47**).[51] Although stabilization of the low valent silicon species is not sufficient to allow the isolation of monomeric silylenes, the formation of undesired by-products is suppressed.

b) Decomposition of di- or oligo-silanes in the presence of dienes

Gaspar *et al.* studied the reaction of disilane **48** and various butadienes.[52] **48** serves as a source of dimethylsilylene (**2a**) which reacts with butadienes **49** to give 1,1-dimethylsilylcyclopentenes **50**. However, satisfactory results are only obtained for dienes without substituents at the 1- and 4-positions (65–70%). Pentadienes and hexadienes give the desired heterocycles only in poor to moderate yield (5–35%) (**Scheme 16**).

Formation of 1-heterosubstituted silaheterocycles *via* silylene insertion into dienes is also possible. Chernyshev *et al.* reported the formation of a bicycle **53** on a multi-gram scale by co-pyrolysis of *exo*-methylene butane **51** and hexachlorodisilane. An intermediate product **52** has also been isolated (**Scheme 17**).[53]

Scheme 15

46 (87%)

47 (50%)

Scheme 16

R¹, R², R³, R⁴ = H, Me
(5–70%)

49

50

trans

Scheme 17

MeOSiMe₂SiMe₂OMe
48

$\xrightarrow[\text{2 torr}]{460\ °C}$

[SiMe₂]
2a

51

1) Si₂Cl₆
500 °C

52

53

More recently, Heinicke *et al.* used the co-pyrolysis of Si₂Me₂X₄ (**54**) [**54a** (X = Cl): obtained as a by-product from the direct synthesis of chlorosilanes; **54b,c**: X = OMe, NMe₂: obtained from **54a**] and dienes to prepare silacyclopentenes with two different substituents at silicon on a multigram scale (**Scheme 18**).[54] In mos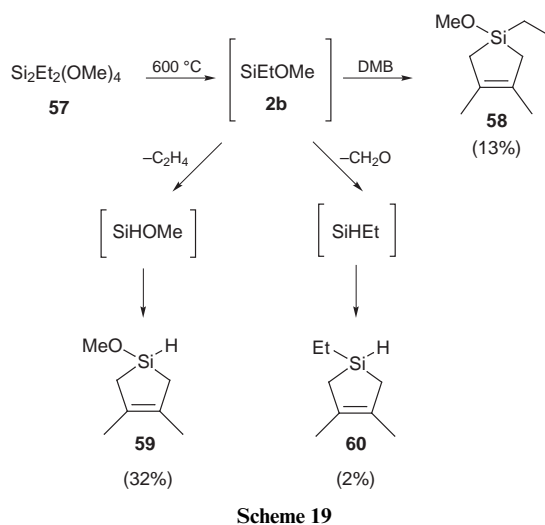t cases, mixtures of the 2- (**56**) and 3-isomer (**55**) were isolated. **56** seems to be a secondary product of the initially formed silacyclopent-3-ene **55**. The amount of the 2-isomers (**56**) is up to 12% and depends on the temperature required for pyrolysis. In general, substituents with lower donor ability (OMe < Me₂N < Cl) make lower reaction temperatures possible which suppresses isomerization to the 2-isomer. With 2,3-DMB, instead of butadiene, the silacyclopent-2-ene was not detected in any case.
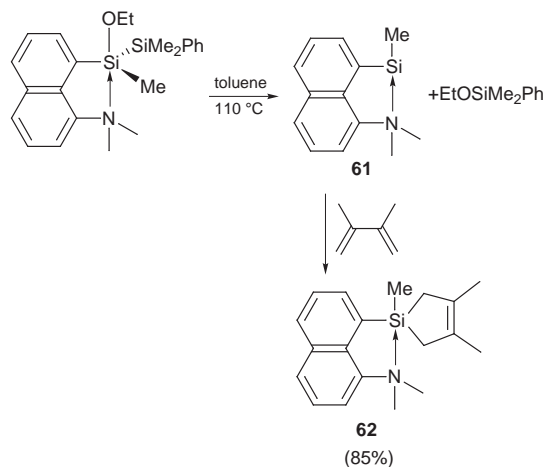
Si₂Me₂X₄
54

$\xrightarrow{400–550\ °C}$

[SiMeX]

56 + 55

a X = Cl (60%)
b X = OMe (66%)
c X = NMe₂ (76%)

Scheme 18
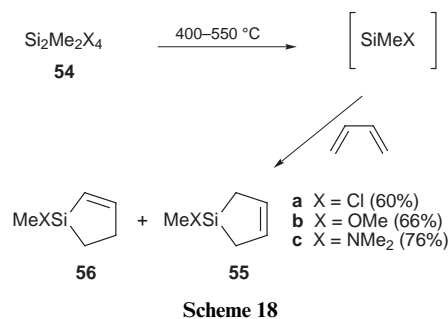
The formation of a dimethoxysilacyclopentene from dimethoxysilylene [obtained from Si₂(OMe)₆ by pyrolysis] and DMB is possible.[55] However, the synthetic utility of this particular silylene seems to be limited. Recent reports by Kwak demonstrate that syntheses using mixed alkyl/alkoxy silylenes may suffer from undesired side reactions leading to other silylene species.[56] For example, co-pyrolysis of compound **57** in the presence of DMB yields three different silacyclopentenes **58**–**60**, indicating elimination of ethylene or formaldehyde from the initially formed silylene **2b** (**Scheme 19**).[57]

Si₂Et₂(OMe)₄
57

$\xrightarrow{600\ °C}$

[SiEtOMe]
2b

$\xrightarrow{DMB}$

58 (13%)

−C₂H₄

[SiHOMe]

59 (32%)

−CH₂O

[SiHEt]

60 (2%)

Scheme 19

In the last few years methods for remarkably facile generation of silylenes and insertion into dienes have been published. Intramolecular stabilization of a transient silylene **61** by a dimethylamino group allows the synthesis of silacyclopentene **62** in excellent yield in refluxing toluene (**Scheme 20**).[58]

Formation of silaheterocycles under even milder conditions occurs when cyclic trisilanes **63** are heated[59] or irradiated[60] in the presence of alkenes. Irradiation of **63b** in the presence of cyclopentadiene leads to **64**, which upon heating isomerizes to the six-membered heterocycles **65**. Reaction of **63a** with cyclohexadiene gives the bicyclic system **66** (**Scheme 21**).[61]

Stable disilenes, which have been obtained from reductive dehalogenation of sterically extremely hindered dibromosilanes, dissociate upon heating to 60 °C and can be trapped with dienes to give silacyclopentenes in fair yield.[62–65]

Scheme 20

+EtOSiMe₂Ph

toluene
110 °C

61

62
(85%)

Scheme 21

40 °C

63a,b

66

64

65

a) R = 2-(Me₂NCH₂)C₆H₄

85 °C

b) R = Buᵗ

Ph₂SiH₂ +

67

(DMI)

+ Fe(CO)₅ ⟶

Ph—Si=Fe(CO)₄

DMI   68

Hex-3-yne | hν

hν

Ph₂Si

69

(62%)

Ph₂Si

70
(31 %)

Scheme 22

Ni(acac)₂ (5 mol %)
PPh₃ (10 mol %)

DIBAL–H (10 mol %)
toluene, 110 °C

Ph———Ph (5 equiv.)

71

72
(27 %)

Scheme 23

2 R———R +
HSiR₂-SiR₃

Ni (0)

A

B

C

D

H–SiR₃
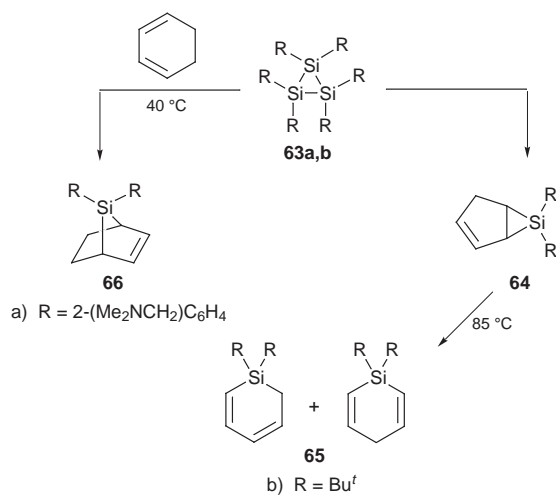
Scheme 24

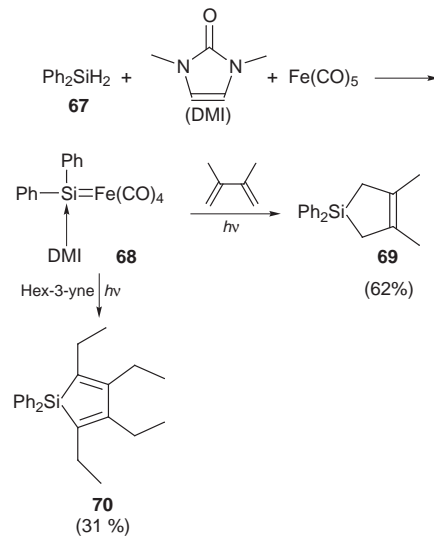**c) Silaheterocycles from transition metal stabilized silylenes**

Transition metal mediated reactions of silanes with unsaturated hydrocarbons belong to the most important methods for the preparation of organosilicon compounds. This chapter summarizes transformations where silylenes bound to metal complexes are involved. Complex **68**, prepared from diphenylsilane (**67**), Fe(CO)₅ and dimethylimidazolidinone (DMI) reacts with an equimolar amount of DMB or two equivalents of hex-3-yne to yield silacyclopentene **69** or silole **70** respectively (**Scheme 22**).[66]

Tamao *et al.* investigated the potential of a catalytic version of the latter transformation.[67] Diphenylacetylene and disilane **71** react in the presence of a Ni⁰ catalyst (formed *in situ* from a Ni^II complex) to the intramolecularly stabilized silole **72** (**Scheme 23**). Without intramolecular stabilization only hydrosilation of the acetylene occurs.
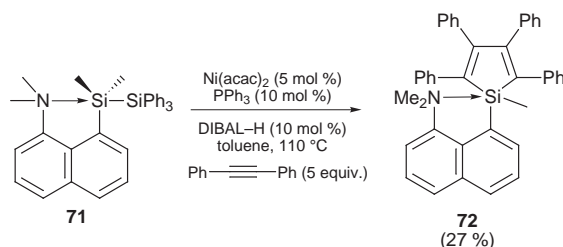
Scheme 24 presents a mechanistic proposal.[67] Key steps are an oxidative addition of the silane to the Ni⁰ species (**A**), reductive elimination of a silane to form a nickel-silylene complex (**B**), subsequent insertion of the two acetylene ligands to form intermediates **C** and **D** respectively and finally reductive elimination of the silole and regeneration of the Ni⁰ species.

Yields are better for intramolecular cyclizations. Under the conditions given in Scheme 23 for the cyclization of tolane, diynes **73** react to siloles **74** in good yields without any intramolecular stabilization of the low valent silicon species (**Scheme 25**).[68,69]

Pd catalyzed reactions should also be summarized in this context as similar mechanistic proposals have been made. The Pd⁰ catalyzed reaction of a linear trisilane **75** with phenylacetylene mainly leads to a disilacyclohexadiene **76**, whereas the silole

+ Si₂HMe₃Ph₂
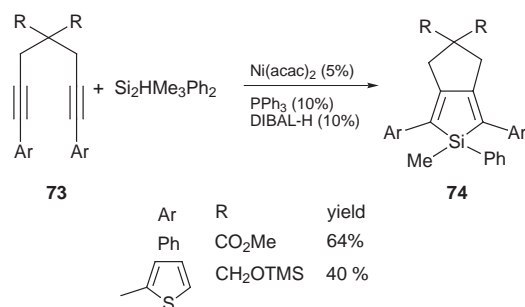
Ni(acac)₂ (5%)

PPh₃ (10%)
DIBAL-H (10%)

73

74

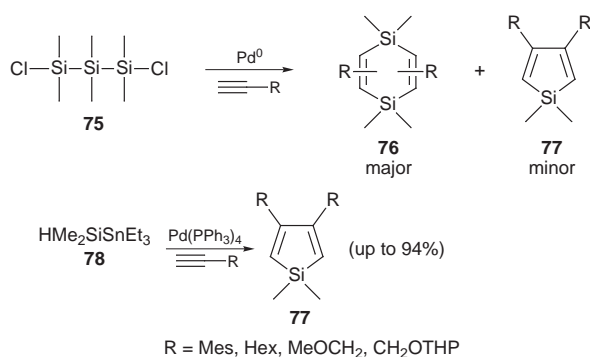| Ar	R	yield
Ph	CO₂Me	64%
(2-thienyl)	CH₂OTMS	40 %
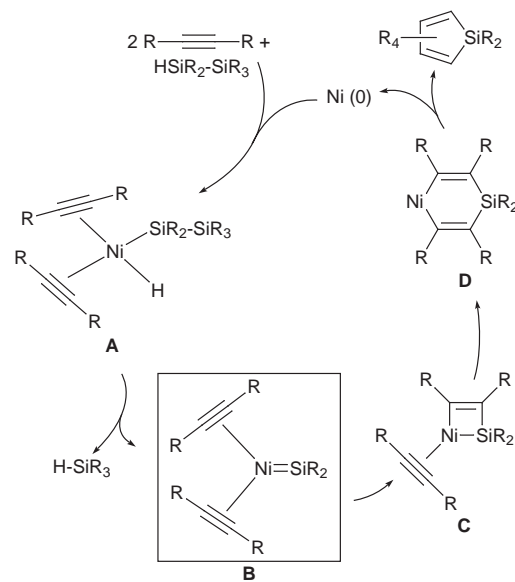
Scheme 25

77 is only formed as a minor product.[70] However, siloles become the major products and can be isolated in yields up to 94% when silylstannanes **78** are used as sources for silylene (**Scheme 26**).[71]

Cl–Si–Si–Si–Cl →[Pd⁰, ≡R] **76** major + **77** minor

75

HMe₂SiSnEt₃ →[Pd(PPh₃)₄, ≡R] **77** (up to 94%)
78

R = Mes, Hex, MeOCH₂, CH₂OTHP

Scheme 26

The results presented so far suggest that the formation of the metal bound silylene (**B** in Scheme 24) is a crucial step in the catalytic cycle. In those cases, where the formation of **B** is facilitated, heterocycle formation occurs readily. Therefore the formation of silole **80** from diyne **79** under Rh catalysis is surprising, as it obviously includes activation of a C–Si bond under loss of methane (**Scheme 27**).[72]

79 + Bu^tMe₂SiH →[Rh(acac)(CO)₂, CO (10 bar), 50 °C, 48 h] **80** (66%)
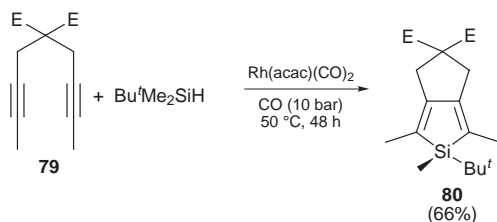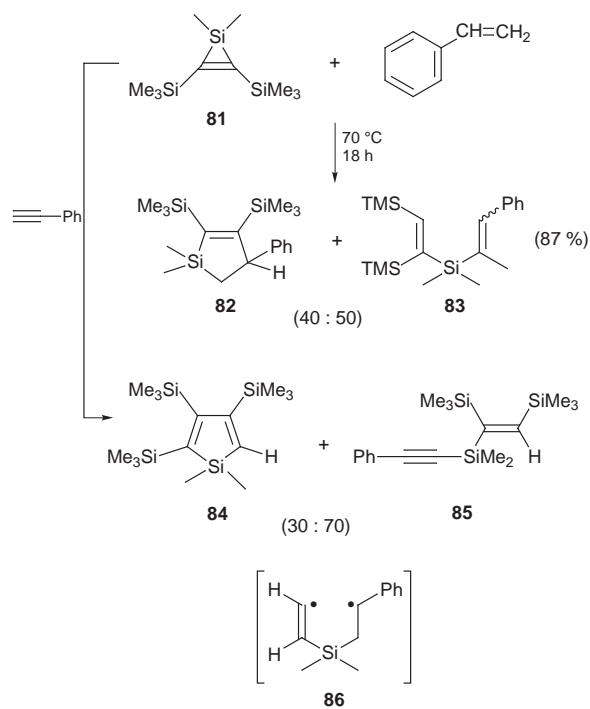
Scheme 27

It should be mentioned that intermediates closely related to those in the catalytic cycle have also been discussed for Ni catalyzed transformations of alkynyltrisilanes.[73,74] Though mechanistically interesting, these processes are only of limited synthetic use and will not be discussed in detail.

## 3 Ring enlargement reactions of small silaheterocycles

3.1 Ring enlargement starting from three-membered silaheterocycles

It has been known for several years that unsaturated compounds tend to undergo insertion reactions into strained carbon–silicon bonds. In an early report on this field, Seyferth *et al.* investigated the thermally or photochemically induced insertion of alkynes and alkenes into silacyclopropenes.[75] Under the conditions employed, normally two types of products are observed: a ring enlargement product and an acyclic product, the latter one normally being preferred. For example, silirene **81** reacts with styrene to the silacyclopentene **82** and acyclic compound **83**. The reaction with phenylacetylene yields silole **84** and the acyclic silane **85** as the major product. From these observations it was concluded, that the reaction proceeds *via* a radical mechanism with the diradical **86** being an intermediate for both types of products. Thus, cyclic products result from a radical coupling whereas acyclic products are formed *via* hydrogen atom transfer (**Scheme 28**).

More recently, Kunai *et al.* found that in the absence of an alkyne or alkene thermolysis of a silacyclopropene **87** leads to a variety of intramolecular cyclization products, depending on the conditions employed and on the substitution pattern. Thus, formation of the products depicted in **Scheme 29** illustrates that C–H bond activation of phenyl groups or silicon bound methyl
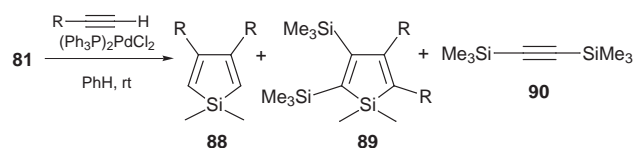
Scheme 28
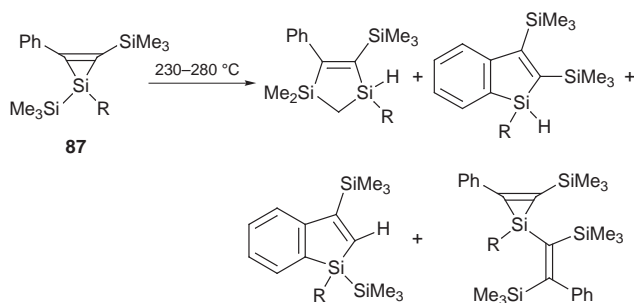
Scheme 29

groups may occur. In this particular case addition of an acetylene causes addition of the Si–Si bond across the triple bond rather than ring enlargement.[76]
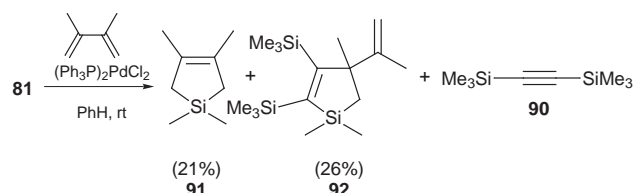
When Seyferth *et al.* repeated their experiments illustrated in Scheme 28 in the presence of a Pd catalyst, they found completely different products.[77] From silirene **81** and phenylacetylene the diphenylsilole **88a** was formed in good yield, together with approximately the same amount of bis(trimethylsilyl)-acetylene (**90**). *tert*-Butylacetylene reacted with silirene **81** under the same conditions to give a mixture of two siloles **88c** and **89c**. Reactions with allene or conjugated dienes gives mixtures of different silacyclopentenes **91** and **92** (**Scheme 30**).

Obviously, a mechanism similar to the one discussed in Scheme 23 for the formation of siloles under nickel catalysis is working here. The initiating step is the reduction of the Pd^II complex to a coordinatively unsaturated Pd⁰ species which undergoes insertion into the strained Si–C bond of the silirene, leading to the formation of a palladasilacyclobutene analog of intermediate **C** in Scheme 23.[77]

A similar mechanism has been proposed by Ishikawa for tungsten catalyzed transformations of a silirene **93a,b**.[78] Thus, in the presence of dimethylbutadiene as a silylene trapping agent silacyclopentenes **94a,b** were found together with a comparable amount of an acetylene. In the absence of a diene trapping agent, C–H bond activation of a silicon bound methyl group occurs. The formation of **95** can also be explained if a tungsten–silylene complex is assumed as an intermediate in the catalytic cycle (**Scheme 31**).

Scheme 30

a R = Ph   80%   0%   76%

b R = CH₂C(Me)H₂ 42%   0%

c R = Bu^t   22%   30%

(21%) **91**   (26%) **92**   **90**

Scheme 30

R = Mes, SiMe₃

R = Mes (22%)
R = SiMe₃ (25%)

93a, b   **94a, b**

93a   W(CO)₆, 190 °C, 20 h   **95** (33%) + byproducts
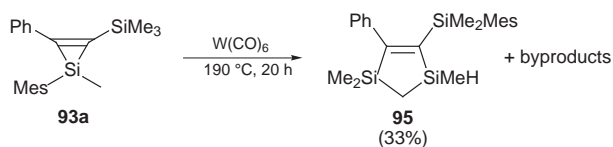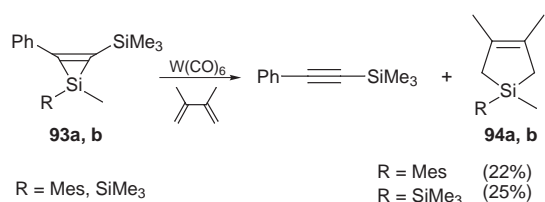
Scheme 31

Reports on the selective formation of unsymmetrically substituted siloles are rare. One example was published by Belzner *et al.*[79] and two further examples were published recently by Woerpel *et al.* (**Scheme 32**).[80]

R = Ph, Et; R¹ = Bu^t (81–86%)

Ph——H, PdCl₂(PPh₃)₂, 100–110 °C   (78–99%)

Scheme 32

Ring enlargement reactions of silacyclopropanes have also been investigated. When acetylenes are employed under Pd catalysis, forma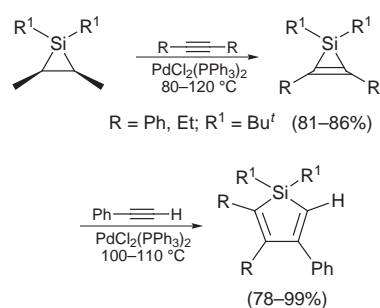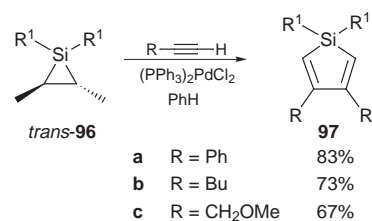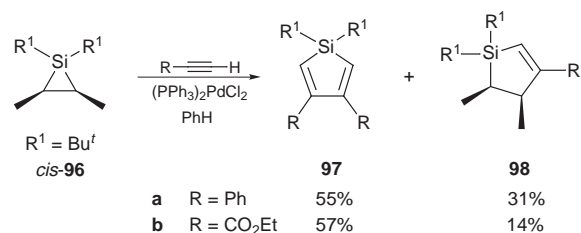l silylene extrusion leading to the formation of siloles as described above also occurs under certain conditions. However, the product distribution significantly depends on the structure of the silacyclopropane. For example, Woerpel *et al.* investigated the product distribution of the reaction of *cis*- and *trans*-silacyclopropanes **96** with a variety of terminal acetylenes under Pd-catalysis.[81] The symmetrically substituted siloles **97** become the sole products when *trans*-**96** is used as a starting material, whereas from the *cis*-isomer a mixture of siloles **97**

and **98** results. The extrusion of silylene from *cis*- or *trans*-silacyclopropane **96** occurs stereospecifically, leading to *Z*- or *E*-but-2-ene respectively. The formal acetylene insertion into the Si–C bond also occurs stereospecifically, since *cis*-**98** exclusively results from *cis*-**96** (**Scheme 33**).

cis-**96** R¹ = Bu^t   **97**   **98**

a R = Ph   55%   31%

b R = CO₂Et   57%   14%

trans-**96**   **97**

a R = Ph   83%

b R = Bu   73%

c R = CH₂OMe 67%

Scheme 33

For ring enlargement reactions with unsymmetrical silacyclopropanes not only side-products from formal silylene extrusion may occur, but regioselectivity of the insertion is also a problem. This question was addressed by Ando *et al.* who investigated the reactivity of *exo*-methylenesiliranes **99** in Pd catalyzed ring enlargement reactions.[82,83] As the Si–C bonds are no longer equivalent, two regioisomeric products **100** and **101** can be formed. If acetylenedicarboxylate is employed, the regioselectivity can be determined by the choice of the catalyst as outlined in **Scheme 34**. Regioselectivity is completely reversed for acetylene, which reacts by insertion into the more reactive Si–C2 bond.

(*Z*)-**99** + MeO₂C——CO₂Me   cat., PhH, 80 °C

100   **101**

Pd(PPh₃)₄   86%   trace

PdCl₂(PhCN)₂   trace   87%
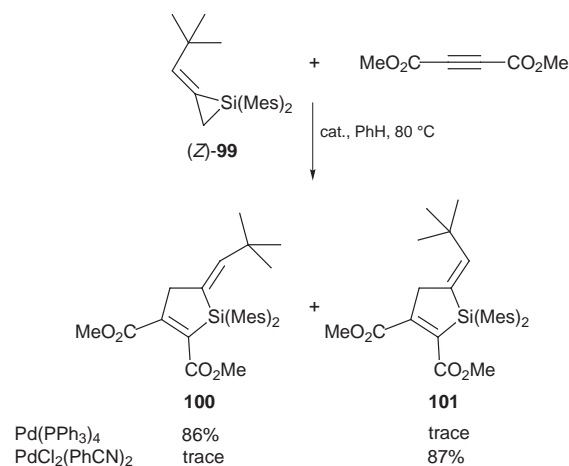
Scheme 34

If the *E*-isomer of silacyclopropane **99** is reacted with acetylenedicarboxylate under identical conditions, silole formation (**102**), which was not observed for (*Z*)-**99**, occurs. If (*E*)-**99** is reacted with methyl acrylate, an insertion product, **103**, is isolated as a single regioisomer in good yield (**Scheme 35**).[82]

It seems to be difficult to make reliable predictions on the outcome of a ring enlargement reaction starting from three-membered silacycles, which is a serious drawback for the use of these reactions in synthesis. However, some transformations occur with high regio-, stereo- and chemo-selectivity that makes them interesting for special applications.

Scheme 35

E-99
+
MeO₂C——CO₂Me

Pd(PPh₃)₄
PhH, rt
12 h

102
(31%)

E-99 +

103
(61%)
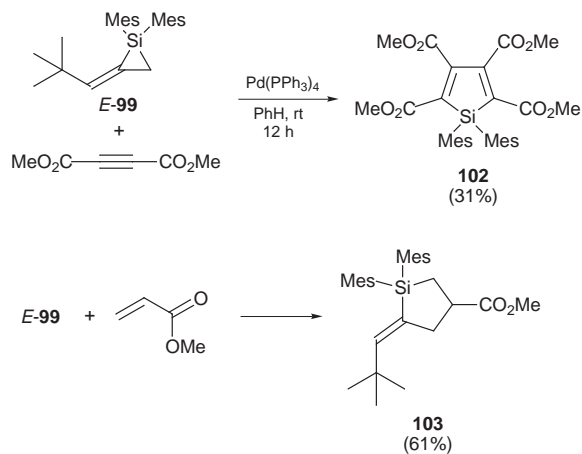
Scheme 35

3.2 Ring enlargement reactions starting from four-membered silacycles

The insertion of carbenes into single bonds appears to be an interesting process both from the mechanistic and from the synthetic point of view. However, synthetic use of carbene insertion for the formation of silacycles has been limited. Such a process can in principle occur by intramolecular insertion of a carbene into a C–H bond or a Si–C bond or by intermolecular insertion of a carbene into a C–C bond or a Si–C bond. Usually, insertion into a C–H bond is strongly preferred.[84,85] However, ring enlargement products resulting from an intermolecular[86] and from an intramolecular[87,88] insertion of a carbene into a strained Si–C bond of a silacyclobutane have been identified along with other reaction products. At present no synthetically useful carbene insertion reactions for the preparation of silaheterocycles seem to be available.

Consequently, other attempts were made to activate the Si–C bond in silacyclobutanes. The use of Pd catalysis seems to be obvious. In an early report on this field, Sakurai *et al.* described the clean formation of silacyclohexenes **105** from silacyclobutane **104** by Pd catalyzed insertion of acetylene dicarboxylate in 65% to 95% yield.[89] When this transformation was reinvestigated by Oshima *et al.* several years later in more detail, the formation of a considerable amount of a by-product **106** was discovered, which results from β-hydride elimination during the catalytic cycle. Under certain conditions, especially if phenylacetylene is employed, allylvinylsilane **106** may even become the preferred product (**Scheme 36**).[90]

104a   +   R¹——R²

R¹, R² = H, Ph, CO₂Me

PdCl₂(PPh₃)₂

**105**   +   **106**
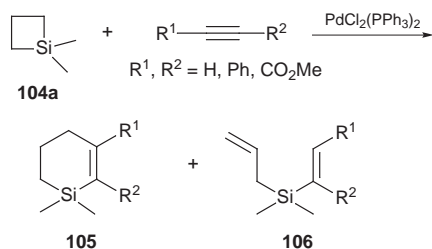
Scheme 36

Inspired by reports on the insertion of carbenes into the Si–C bond of silacyclobutanes, the behaviour of lithium carbenoids towards strained Si–C bonds was investigated.[91] Thus, addition of LDA to a mixture of silacyclobutane **104a** (R = Me; R¹ = H) and diiodomethane provided silacyclopentane **106a** (R = Me, R¹ = H; R² = I) in 83% yield on a 3 gram scale. The reaction is thought to proceed *via* a nucleophilic addition of lithiated diiodomethane to give a pentacoordinate intermediate **105** which then undergoes ring enlargement and substitution of one iodide.[92] Stereoselectivity of the carbene insertion was investigated starting from methyl substituted silacyclobutanes **104**

(R¹ = Me). Thus, symmetrical silacyclobutanes **104** were converted under the conditions described for the unsubstituted compound to mixtures of two diastereomeric silacyclopentanes *cis*-**106** and *trans*-**106**. In most cases *cis/trans* ratios of 9:1 were found, except for R = R² = Ph, where the *trans*-isomer is slightly preferred (**Scheme 37**).
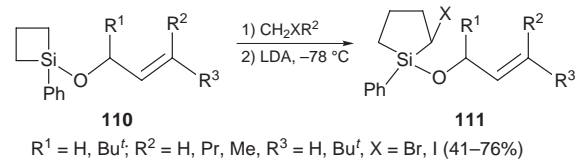
104

1) CH₂XR²
2) LDA, –78 °C

105

–LiX

cis-**106**   +   *trans*-**106**
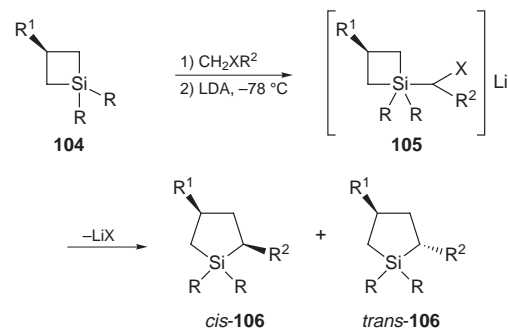
For R¹ = H: R = Me, Bu, Ph, OPr; X = Cl, Br, I;
R² = Cl, Br, I, Ph, SiMe₃. Yield: 46–88%

For R¹ = Me: R = Me, Bu; Y = Br, I; R² = Br, I Ph.
Yield: 40–97%. *cis* : *trans* = 33 : 67 (R = R² = Ph)
all other examples: *cis* : *trans* = 89 : 11 up to 93 : 7.

107

1) CH₂XR²
2) LDA, –78 °C

cis-**108**   +   *cis/trans*-**109**
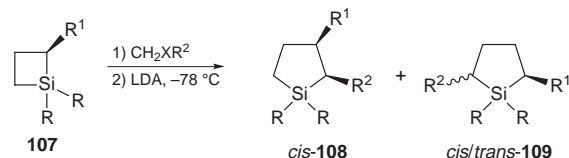
R = Me, Ph; R¹ = Me, Ph; R² = Br, I, Ph.

110

1) CH₂XR²
2) LDA, –78 °C

111

R¹ = H, Buᵗ; R² = H, Pr, Me, R³ = H, Buᵗ, X = Br, I (41–76%)

Scheme 37

When unsymmetrically substituted silacyclobutanes **107** were employed in the reaction, two regioisomers **108** and **109** became available. In most cases the 2,5-isomer **109** is preferred over the 2,3-isomer **108**, however, regioselectivity is poor in most cases. The 2,3-disubstituted silacyclopentane is exclusively obtained as the *cis*-diastereomer, whereas the 2,5-isomer is formed less stereoselectively in *cis/trans* ratios of 2:1 up to 9:1.[91]

Silacyclopentanes **111** with different substituents at the silicon atom can also be prepared by this method, as was demonstrated for a variety of silacyclopentanes with one allyloxy substituent and one phenyl at the silicon center and a halogen atom in the 2-position.[93] The reaction proceeds stereoselectively, however, no assignment of the relative configuration has been made for the silacycles (Scheme 37).[94]

A similar ring enlargement reaction was observed, when a mixture of epoxides **112** and 1,1-dimethylsilacyclobutane (**104a**) was treated with LDA. Here again a pentacoordinate intermediate **113** is assumed which undergoes ring enlargement under nucleophilic attack of the epoxide. Acyclic silanole **115**, obviously resulting from an intramolecular Peterson elimination, is isolated from the reaction in 15% yield. Silacyclopentanes **114** can be converted to the acyclic silanol by elimination with KH. If R¹ = SiPh₃, only the acyclic product **115** is isolable (**Scheme 38**).[95]

Based on the assumption that pentacoordinated species **105** and **113** are intermediates for this type of ring enlargement, Oshima *et al.* developed a different strategy for the synthesis
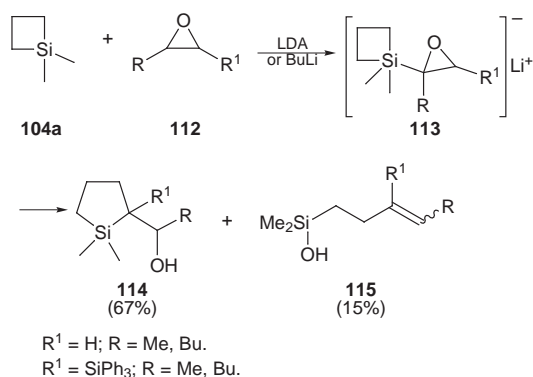
Scheme 38

of silacyclopentanes from silacyclobutanes. Starting from 1-vinylsilacyclobutane **116**, radical addition of an alkyl iodide yields the iodo compound **117**, which undergoes an intramolecular substitution of iodide, induced by nucleophilic attack at the silicon. A pentacoordinate species similar to **105** is again proposed as an intermediate. Treatment with KOBu^t or AgOAc gives silacyclopentanes **118** in good yields but poor diastereoselectivities (**Scheme 39**).[96]
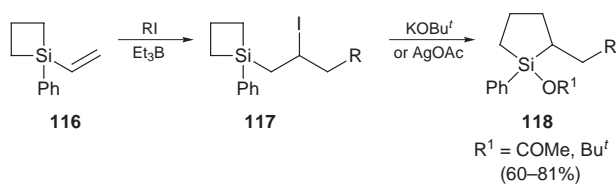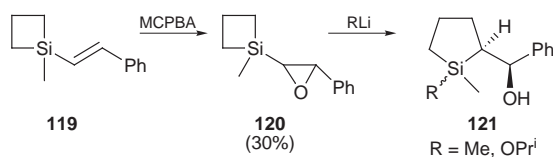

Scheme 39

1-Vinylsilacyclobutanes have also been used as starting materials in an analogous ring enlargement reaction by intramolecular epoxide opening.[97] **Scheme 40** shows a representative example: Treatment of (*E*)-vinylsilane **119** with MCPBA provides the *trans*-epoxide **120**, which undergoes ring enlargement to silacyclopentanes **121** induced by methyllithium or lithium isopropoxide with high stereoselectivity.[98] Starting from (*Z*)-vinylsilane (*Z*)-**119**, the other diastereoisomer is accessible.

Scheme 40

4 Ring closure by C–C bond formation

This chapter deals with ring closure reactions where a carbon–carbon bond is formed. The newly formed bond may either be a single or a double bond. Starting materials are usually tetraorganosilanes where at least two substituents at silicon display appropriate functionality, very often carbon–carbon multiple bonds, which allow cyclization reactions.

4.1 Ring closure through cascade reactions of acyclic silanes

Over the past few years some examples for the formation of functionalized silicon carbon heterocycles *via* cascade reactions have been published. In this section we will focus on those where the first step of the cascade is the formation of a carbon–carbon bond.

a) Zirconium mediated carbocyclization

The cyclization of non-conjugated α,ω-dienes in the presence of a stoichiometric amount of Cp$_2$ZrCl$_2$ and two equivalents of

BuLi was first investigated nearly ten years ago by Nugent.[99] The reaction proceeds *via* the intermediate formation of Cp$_2$ZrBu$_2$ which serves as a source for coordinatively unsaturated (and hence unstable) Cp$_2$Zr. In the first step a bicyclic zirconacycle is formed which is prone to subsequent reaction with electrophiles, leading to substituted cycloalkanes (**Scheme 41**).
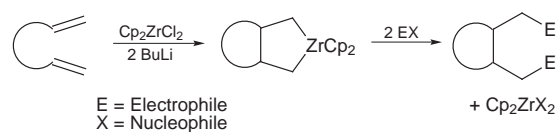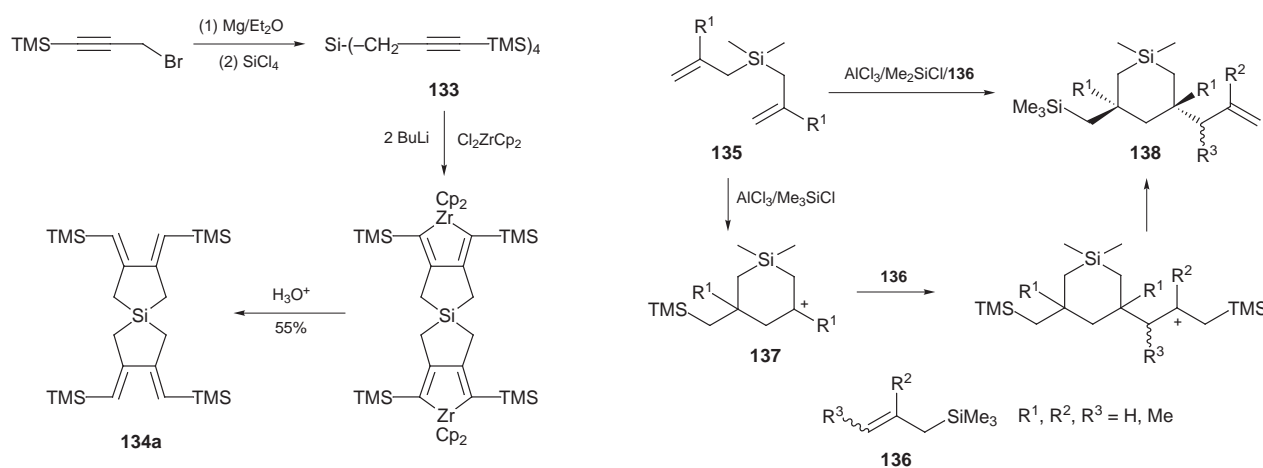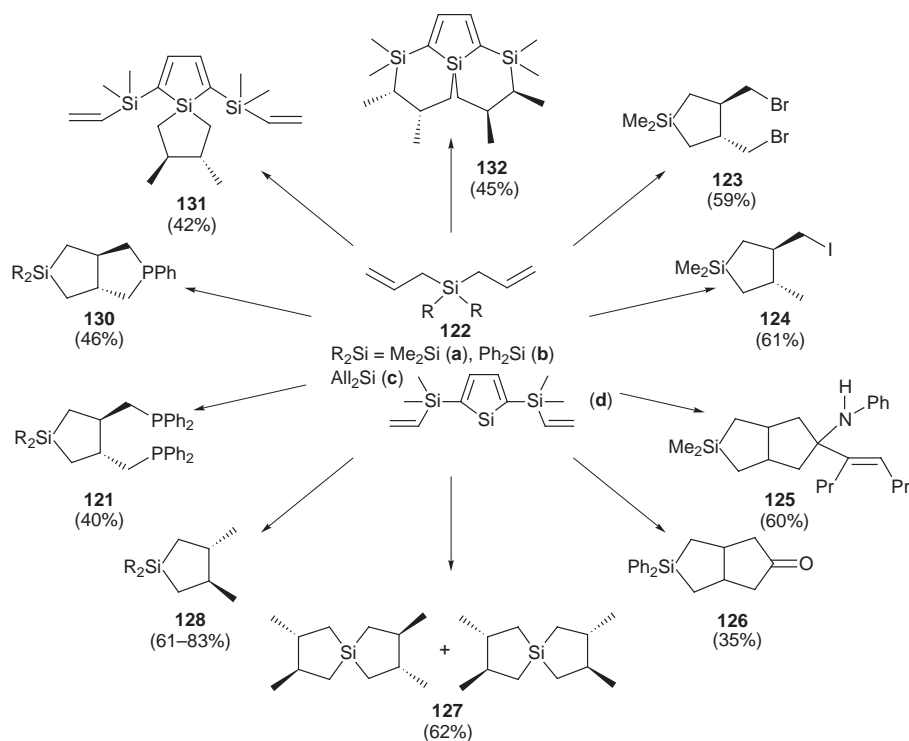

Scheme 41

If the α,ω-diene contains a SiR$_2$ group instead of a methylene group, silicon–carbon heterocycles result. The first example for the preparation of a silacyclopentane using this method was described in the original publication by Nugent. Dimethyldiallylsilane (**122a**) reacts to give the zirconacycle as described above. Subsequent treatment of the reaction mixture with bromine gives the silacyclopentane **123** (**Scheme 42**).[99,100] The selective introduction of one halogen into the side chain was achieved by Takahashi *et al.* with their cleavage procedure using MeOH–I$_2$ leading to **124**.[101,102] If the second step of the cascade is an acid catalyzed hydrolysis, 3,4-dimethylsilacyclopentane **128** is the product.[100] Starting from tetraallylsilane (**122c**), spirocycles **127** become accessible *via* this sequence as a mixture of diastereomers.[103] From diallylsilole **122d**, spirocycle **131** is accessible by essentially the same methodology, however, a different cyclization mode leading to the tricyclic system **132** is observed when a threefold excess of 'Cp$_2$Zr' is employed.[103] The cleavage of the Zr–C bonds using P-electrophiles was investigated by Manuel *et al.* during their studies directed towards new phosphorous containing ligands. Thus, **129** and **130** have been prepared by reaction of the intermediate zirconacycle with two equivalents of a chlorophosphine or one equivalent of a dichlorophosphine.[100] The formation of **130** is an example where the bicyclic structure of the intermediate is maintained in the final product. Another example where this is the case is the formation of bicyclic cyclopentanone **126**, which results from cleavage of the zirconacycle under 1 atm of CO.[103] Whitby's elegant synthesis of a bicyclic silacyclopentane **125** contains a cascade of three reactions. The first step is the formation of the zirconacycle, followed by insertion of PhNC into one Zr–C bond, rearrangement of the six-membered intermediate and finally insertion of an alkyne. Hydrolysis completes the synthesis.[104]

A striking feature of these transformations is the high *trans*-selectivity which is observed for all examples. Diastereomeric ratios of up to 96:4 are described. Scheme 42 summarizes the transformations discussed above.

Two reports dealing with the closely related cyclization of propargylsilanes have appeared recently. Products are *exo*-dimethylenesilacyclopentanes.[100] With a view towards the synthesis of electronic devices on a molecular scale the Zr-mediated cyclization of tetrapropargylsilanes **133** has been exploited by Tour *et al.* for the preparation of silaheterocycles **134** with the silicon as the spirocyclic centre (**Scheme 43**).[105] Hydrolysis or treatment with S$_2$Cl$_2$ (leading to thiophenes **134b**) are two different possibilities to terminate the sequence.

b) Cascade reactions with ionic or radical intermediates

Quite recently an example for a Lewis-acid catalyzed cascade reaction leading to six-membered silicon–carbon heterocycles was published.[106] In this reaction, a diallylsilane **135** cyclizes in the presence of AlCl$_3$ and Me$_3$SiCl. The intermediate carbenium ion **137** is quenched by an allyltrimethylsilane **136** in a Sakurai-type reaction yielding a 3,5-disubstituted silahetero-

Scheme 42

Scheme 43

Scheme 44

$R^1, R^2, R^3 =$ H, OMe

Scheme 45

cycle **138** (**Scheme 44**). Depending on the substitution pattern, yields vary between 45% and 76% and diastereomeric ratios up to 92:8 have been obtained.

A related AlCl$_3$-mediated cyclization of vinylbenzylsilanes **139** leads, after subsequent methanolysis, to silatetralins **140** (**Scheme 45**).[107]

Sieburth *et al.* described an asymmetric cascade reaction *via* anionic intermediates. The chirally modified silane **141** was deprotonated with LDA followed by alkylation and subsequent Dieckmann condensation. Heterocycle **142** was isolated as a single (*cis*)-isomer. If a different base is used, the alkylation step does not occur, leading to **143** as a 1:1 mixture of diastereomers (**Scheme 46**).[108]

The Tamao synthesis of siloles by reductive cyclization of dialkynylsilanes **144** represents the first example for an *endo-endo*-mode cyclization.[109] The ring closure reaction is a radical coupling and the second step an anionic reaction.[110] For example, diphenylethynylsilanes **144a**–**e** react in the presence of an excess amount of lithium naphthalenide as a one electron reducing agent to a dianion–diradical intermediate **145a**–**e**, which cyclizes through C3–C4 radical coupling. The dilithiated intermediate **146a**–**e** can be treated with a variety of electrophiles to yield 2,5-difunctionalized siloles **147** to **150**.[110] **152a** and **153a** are examples of 2,5-diarylsubstituted siloles which are accessible *via* transmetallation with ZnCl$_2$ followed by Pd-catalyzed cross-coupling of silole **151** with aryl bromides.[111]

Scheme 46

Scheme 48
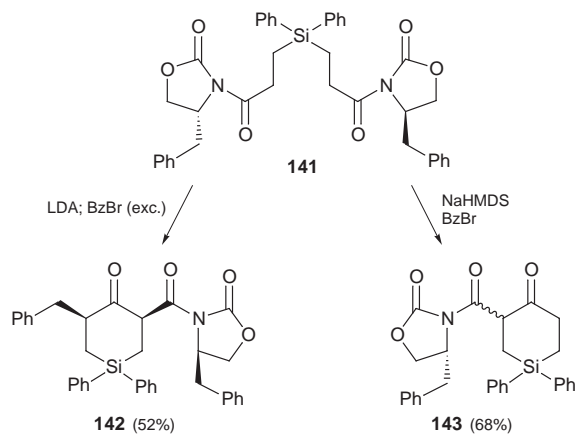
Diethynylsilanes with amino substituents at the silicon can also be employed in this reaction, which was demonstrated by the formation of **147e**.[112] The latter transformation is particularly interesting, as it gives access to siloles prone to substitution reaction at the silicon atom. The enormous scope of the Tamao synthesis is illustrated in **Scheme 47**.
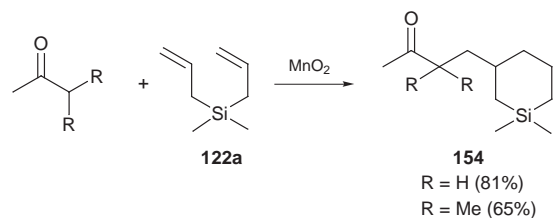

Scheme 47
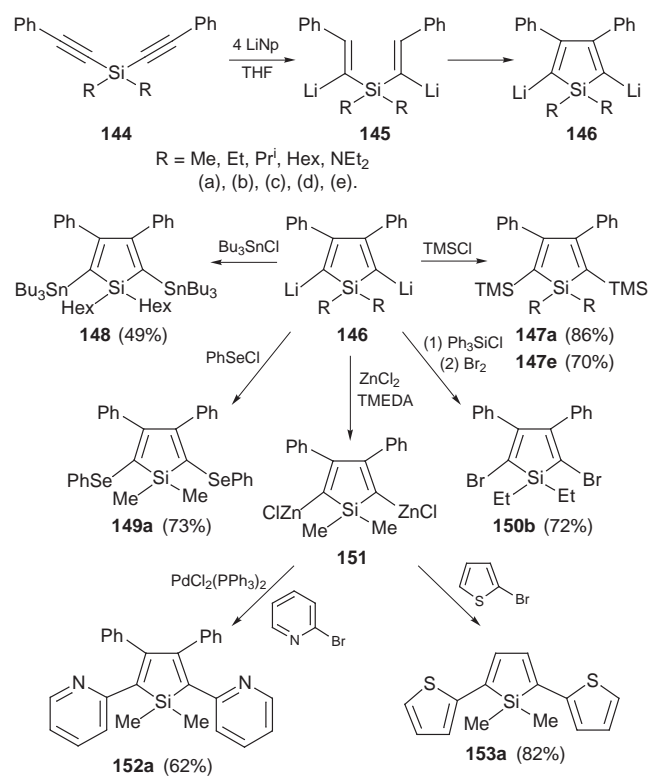
While in the Tamao-synthesis the C–C bond forming step is a radical coupling leading to a dianionic intermediate, addition of a radical species to diallylsilanes induces a ring closure with intermediate formation of a cyclic radical.[113] Recently, it was demonstrated that a radical cyclization of **122a** in the presence of acetone or 3-methylbutanone and MnO$_2$ as an oxidizing agent leads to the formation of silacyclohexanes **154** with a butan-2-one side chain in the 3-position (**Scheme 48**).[114]

4.2   Ring closure reactions induced by carboboration or carboalumination
#### a) Ring closure reactions induced by carboboration
Diethinylsilanes have previously been used as starting materials for siloles.[115] Thus, 2,5-distannylated silole **156a** is accessible from diethynylsilane **155a** by an alkylboration procedure. For

this reaction a mechanism has been postulated[116] which involves *gem*-addition of a trialkylborane (giving intermediate **157**), cyclization to a six-membered intermediate **158** followed by ring contraction to the silole **156a** (**Scheme 49**).
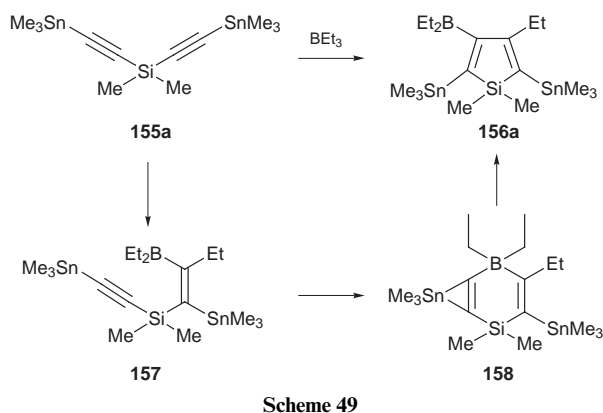
Scheme 49

The scope of this reaction has been broadened by using silanes **155b–f** with different alkynyl groups. In the examples given in **Scheme 50** the different reactivity of the alkynyl groups towards BEt$_3$ was exploited for the selective formation of siloles with different substituents in the 2- and 5-position: due to the ability of the tin moiety to stabilize positive charge in the β-position, the initial ethylboration occurs much faster at this alkynyl group leading to siloles **156b–f**. Hydrolysis selectively removes the boron, whereas protonolysis with acetylacetone removes the boron and tin substituent.[117] Acetic acid or aminoethanol are other reagents for removal of the boron.[118]
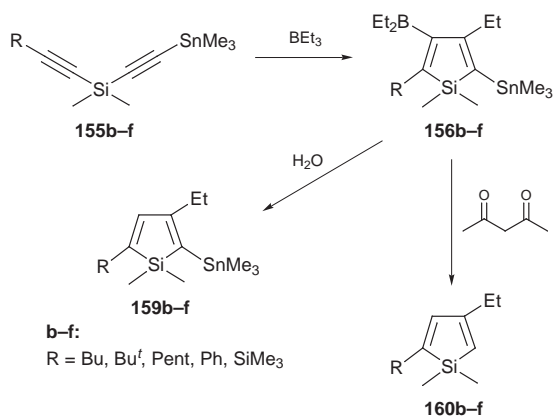
Scheme 50

Starting from tetralkynylsilane **155g** the spirocycle **161** was obtained after deborylation.[119] For the sterically more demanding derivative **155h** only one cyclization occurs and two alkynyl groups are left unchanged (**Scheme 51**).[120]

In this context an example where hydroboration plays a key role for the cyclization reaction should be mentioned. Mignani *et al.* use a cyclic hydroboration of divinylsilane **162a** with BH$_3$–DMS followed by the dichloromethyl methyl ether (DCME) cleavage of the isolable boron heterocycle **163** to prepare a cyclic ketone **164** (**Scheme 52**).[121]
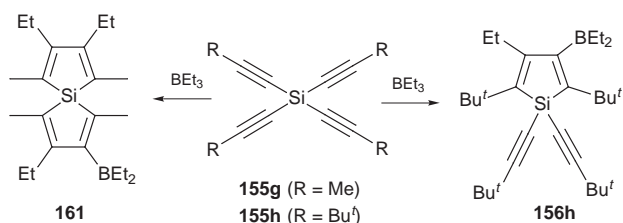
Scheme 51
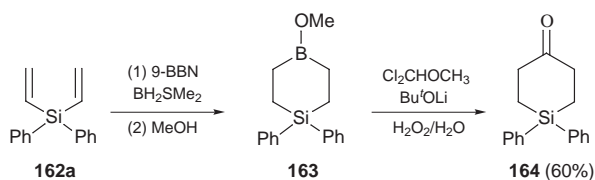
Scheme 52

b) Carboalumination reactions

Zr- or Ti-catalyzed carboalumination reactions have been investigated in more detail because of their importance for Ziegler–Natta-type polymerization reactions. Over the past few years these processes have also been used for the stereoselective preparation of organic molecules with low molecular weight. For example, functionalized five- and six-membered rings are accessible by this method starting from α,ω-dienes. The first report in this field by Negishi *et al.* describes the cyclization of dimethyldiallylsilane (**122a**) in the presence of a catalytic amount of Ti(OPr^i)$_4$ and 0.6 equivalents of Et$_2$AlCl.[122] The sequence is terminated by reaction with molecular oxygen to yield the heterocycle **165** and thus displays the features of a cascade process (**Scheme 53**). While for this example the *cis*-isomer is the major one, Waymouth *et al.* describe the exclusive formation of the analogous methyl substituted *cis*-silaheterocycle *rac*-**166** using Cp$_2$ZrMe$_2$–B(C$_6$F$_5$)$_3$ as a catalyst and AlMe$_3$ as carboalumination reagent.[123] Negishi *et al.* reported the synthesis of (*S*,*S*)-**165**[124] and (*S*,*S*)-**166**[125] in 96% ee and 74% ee respectively using an enantiomerically pure Zr catalyst **167**. The good enantioselectivity reported for (*S*,*S*)-**165** compared to (*S*,*S*)-**166** is probably not caused by the different substituent, but seems to be due to a solvent effect. Obviously, more polar solvents are beneficial for the enantioselectivity (Scheme 53).[124]
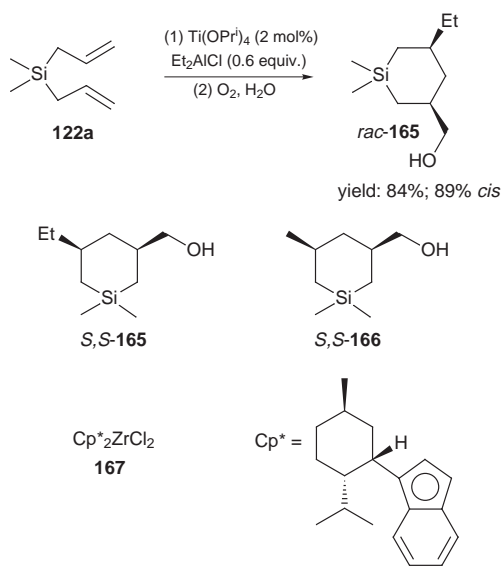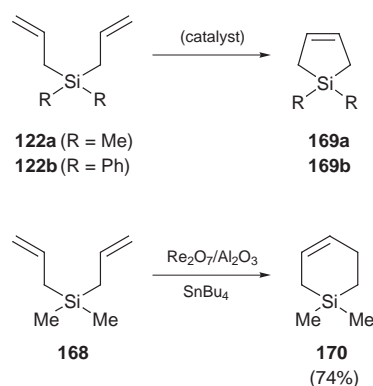

Scheme 53

4.3 Other transition metal catalyzed C–C bond forming processes

Ring closing metathesis, dehydrogenative cyclization at hetero-

geneous catalysts and Pd-mediated coupling reactions are other C–C bond forming reactions which have been used for the preparation of silaheterocycles.

Though ring closing metathesis has become a very important synthetic tool over the past few years, only few examples for the formation of silicon–carbon heterocycles using this method have been published up to now (for the formation and use of cyclic siloxanes obtained by ring closing metathesis see ref. 126). An early report by Finkel'shtein *et al.* describes the use of a heterogeneous catalyst system based on Re$_2$O$_7$–Al$_2$O$_3$ and SnBu$_4$ for the metathesis of allylsilanes **122a** and **168**.[127] Whereas for this catalyst system only poor yields are observed for the formation of five-membered rings **169**, six-membered rings **170** are obtained in much better yields. Intermolecular metathesis leading to polymers is usually the preferred reaction path.[128] Tungsten catalysts seem to be suited for the ring closing metathesis of **122a**. Thus, the simple inorganic compound WOCl$_4$ catalyzes the cyclization of **122a**.[129] A more advanced tungsten carbene complex was employed as a catalyst by Basset *et al.* for the cyclization of **122a** and **122b**. In the case of **122a** good yields are obtained with 2 mol% of catalyst. However, for the sterically more demanding system **122b** the yield of **169b** is only 8% (**Scheme 54**).[130] Interaction of Schrock's MoF$_6$ catalyst and diallylsilane **122a** leads to the formation of silicon containing polymers, a ten-membered ring and **169a** in an equilibrium mixture.[131]

Scheme 54

Dehydrogenative cyclizations with heterogeneous catalysts at high temperatures have been used for the preparation of silaazaanthracenes[132,133] and silathiophenes.[134,135] These methods suffer from harsh reaction conditions and sometimes low isolated yields. No detailed information concerning the catalysts employed in these reactions is given in the literature. More recently Pd-catalyzed reactions were used to achieve C–C bond formation. For example, Pd catalyzed coupling reactions of dibromides **171** or **173** lead to the silaheterocycles **172** and **174** respectively.[136] Pd catalyzed cross-coupling reaction of an α,ω-diboronated compound, generated *in situ* by hydroboration of divinylsilane **162b**, and a *gem*-dibromide gives the six-membered heterocycle **175** (**Scheme 55**).[137]

4.4 Ring closure through concerted reactions

Few reactions have been reported where the formation of a carbon–carbon bond proceeds *via* a concerted mechanism. Among these are intramolecular [2 + 2]-photocycloadditions of diallylsilanes **122** leading to silacyclopentanes **176** with an annellated cyclobutane ring.[138] Metaphotocycloadditions of benzylallylsilanes **177** allow the construction of complex molecules such as **178**. In these reactions the silicon group exerts a strong directing effect which is explained by the β-effect of silicon (**Scheme 56**).[139]

Robertson *et al.* report on an ene-type reaction used for the cyclization of aldehydes **179**, which react in the presence of a

Pd(PPh₃)₄ (20 mol%) — Sn₂Me₆ (0.9 equiv) / PPh₃ (0.5 equiv)

171

172
(72%)

Pd(PPh₃)₄ (20 mol%) — Sn₂Me₆ (0.9 equiv) / PPh₃ (0.5 equiv)

173

174
(69%)

(1) 9 - BBN
(2) R Br / Br
Pd(PPh₃)₄
R = Ph, Fu, Biphenyl

162b

175
(25–60%)

Scheme 55

$h\nu$

122

176
(47–75%)

$h\nu$

177

178
(60%)
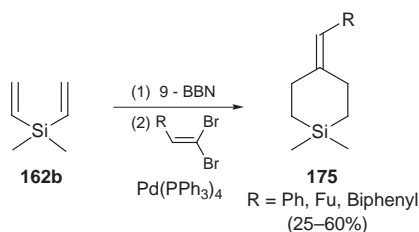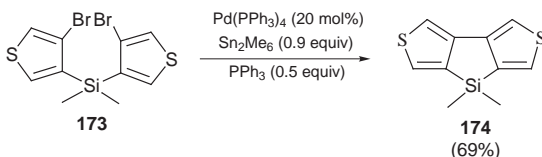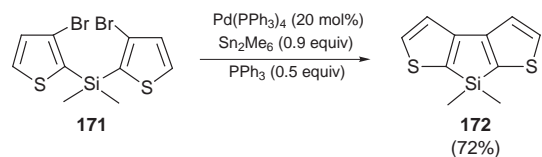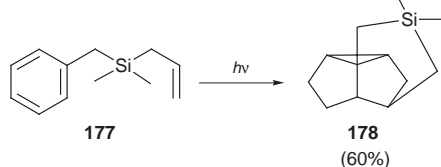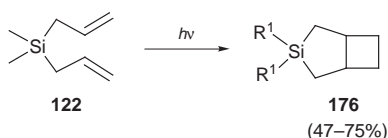
Scheme 56

Lewis-acid to the silacyclohexanes **180** in good yield and with good diastereoselectivities.[140]

Quite recently the formation of bicyclic system **181** by an intramolecular Diels–Alder reaction has been reported (**Scheme 57**).[141]

5   Ring closure by C–Si bond formation

Hydrosilation of acetylenes or alkenes represents one of the most powerful methods for C–Si bond formation. The reaction may proceed *via* a radical mechanism or catalyzed by transition metal complexes. For the formation of monocyclic compounds by hydrosilation mainly transition metal catalyzed processes have been reported. Hexachloroplatinic acid has been used as a catalyst for the intramolecular hydrosilation of acetylene **182**.[142] In contrast to observations made for the hydrosilation of acyclic acetylenes,[143] the intramolecular process proceeds predominantly in a Markownikoff fashion leading to a five-membered heterocycle **183** with an *exo*-methylenic double bond. The same regiochemistry had previously been observed by Tamao *et al.* for the intramolecular hydro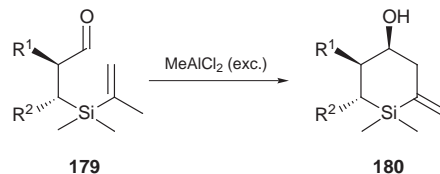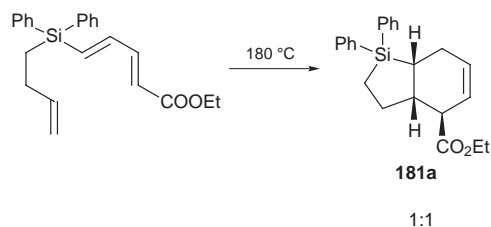silation of acetylenic ethers **184**[144] which results in the formation of cyclic siloxanes **185** (**Scheme 58**). Acetylenic silanes with an additional SiMe₂ group in the chain also undergo intramolecular hydrosilation with the same regiochemistry, leading to disilaheterocycles with an exocyclic double bond.[142]

A preparation of silaindenes **187** by hydrosilation of silylated tolanes **186** apparently displays different regioselectivity.[145] In fact, this reaction proceeds *via* a two step mechanism, where the first step is the formation of a polymer by intermolecular hydrosilation of **186** followed by a thermal decomposition at low pressure in the second step to yield substituted silaindenes **187** (**Scheme 59**).

MeAlCl₂ (exc.)

179

180

$R^1 = R^2 = H$ (80%); $R^1 = H$, $R^2 = Me$ (80%, *trans:cis* > 95:5); $R^1 = Me$, $R^2 = H$ (69%, *trans:cis* > 31:1)

180 °C

181a

1:1

181b

Scheme 57

H₂PtCl₆

182

183
(67%)

H₂PtCl₆

184

185

Scheme 58

H₂PtCl₆ / DCM → [Polymer]

186   R, R¹ = H, OMe

1 torr | 350–380 °C
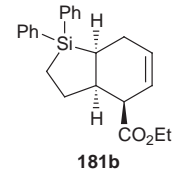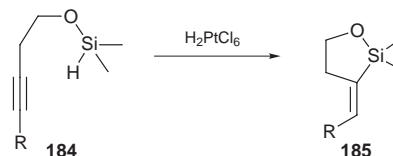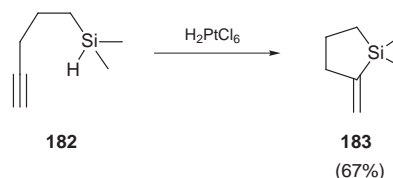
187 (30–38%)
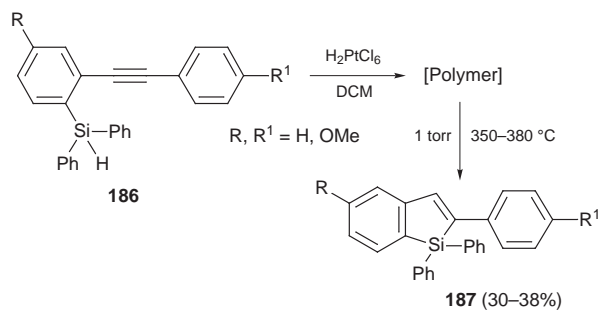
Scheme 59

Intramolecular hydrosilation of acetylenes as the first step of a cascade reaction has been reported recently.[146] Rhodium catalyzed hydrosilation under 20 atm of CO leads to the formation of α,β-unsaturated aldehydes. Thus, from acetylenic silanes **188** five-membered silaheterocycles **189** are accessible (**Scheme 60** and **Table 1**).

Similarly, silanes **190** are starting materials for six-membered silaheterocycles **191**. Internal acetylenes generally seem to give better yields than terminal ones (**Scheme 61** and **Table 2**).

Alkenes are in general considered to be less reactive in transition metal catalyzed hydrosilations.[147] Over the past few years, however, numerous reports on the catalyzed intramolecular hydrosilation of alkenes have appeared. In most examples the hydrosilation of an allyl or homoallyl ether is described which results in the formation of cyclic siloxanes.[1j,148] Here we wish to

Table 1 Silacyclopentanes by silylformylation (Scheme 60)

A: [Rh$_4$(CO)$_{12}$] **B**: [Rh(1,5-COD)(η^6-C$_6$H$_5$BPh$_3$)]

R^1	R^2	R^3	R^4	Yield	Catalyst	Mol%-Cat.
Me	Ph	H	H	56%	**A**	0.5
Ph	Ph	H	H	37%	**B**	1.0
Me	Me	Et	H	83%	**B**	0.5
Me	Me	Bu	Me	71%	**B**	0.5
Me	Me	Ph	H	79%	**B**	0.5

Table 2 Silacyclohexanes by silylformylation (Scheme 61)

A: [Rh$_4$(CO)$_{12}$] **B**: [Rh(1,5-COD)(η^6-C$_6$H$_5$BPh$_3$)]

R^1	R^2	R^3	Yield	Catalyst	Mol%-Cat.
Me	Ph	H	56%	**B**	1.0
Ph	Ph	H	49%	**B**	1.0
Me	Me	Ph	69%	**A**	0.5

Scheme 60

Scheme 61

focus on those hydrosilations where a silicon–carbon heterocycle results. For example, a silanorbornane **193** results from the platinum catalyzed hydrosilation of cyclopentene **192** (**Scheme 62**).[149]
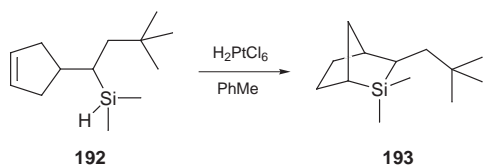
Scheme 62

In Bosnich's investigation on asymmetric rhodium-catalyzed hydrosilations mostly silyl ethers were employed.[150] Only two homoallylsilanes were investigated: silicon–carbon heterocycles **195a,b** a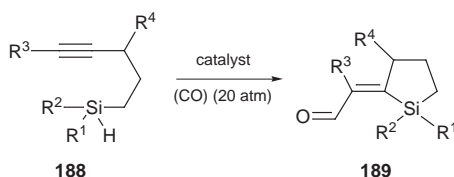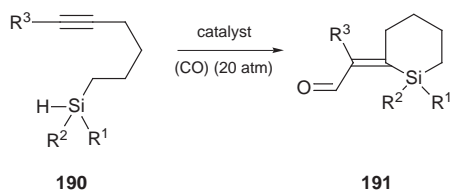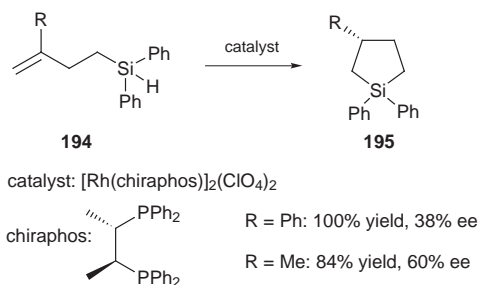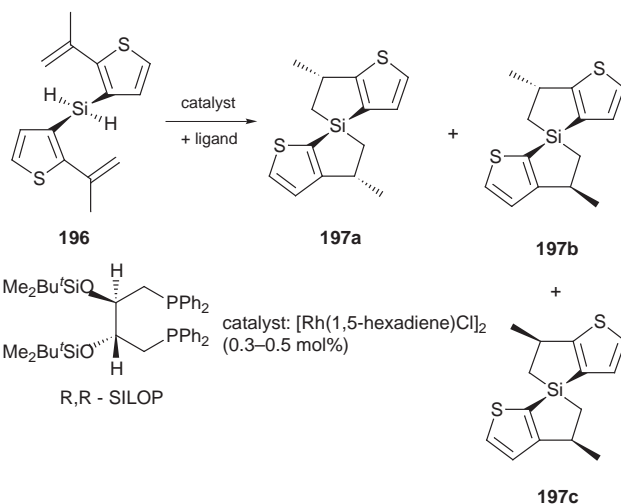re formed in good yield but moderate ees from **194a,b** when the catalyst [Rh{(*S,S*)-chiraphos}]$^+_2$(ClO$_4^-$)$_2$ was used (**Scheme 63**).

Tamao *et al.* screened a variety of different chiral ligands for the double hydrosilation of **196**.[151] Upon hydrosilation, three new stereogenic centers are created. Thus, the appropriate ligand system must ensure control of enantioselectivity and diastereoselectivity. In **Scheme 64** the different possible diastereomers of the product **197** are shown. Best results were obtained when a rhodium catalyst was used in the presence of the (*R,R*)-TBDM–SILOP ligand. In this case, **197a** was formed in 96% de, 99% ee and 83% yield. Other commonly used chiral diphosphanes such as (*R*)-BINAP, (*R,R*)-DIOP or ferrocene derived ligands gave less satisfactory results (Scheme 64).

catalyst: [Rh(chiraphos)]$_2$(ClO$_4$)$_2$

chiraphos:

R = Ph: 100% yield, 38% ee

R = Me: 84% yield, 60% ee

Scheme 63

catalyst: [Rh(1,5-hexadiene)Cl]$_2$ (0.3–0.5 mol%)

R,R - SILOP

Scheme 64

Pd(OAc)$_2$ in the presence of an isonitrile has been used as a catalyst for the intramolecular silylsilylation of alkenes **198**.[152] Addition of the Si–Si bond across the double bond results in the formation of silacyclopentanes **199** with an additional exo-cyclic silicon functionality. The reaction proceeds with *trans*-diastereoselectivities up to 99:1 for 2,3- or 2,4-disubstituted heterocycles. For the 2,5-disubstitution pattern diastereoselectivity is poor. Diastereoselectivity of the ring closure improves when the endocyclic silicon atom carries two phenyl substituents rather than two methyl groups. **Scheme 65** shows one example for a highly diastereoselective silylsilylation.
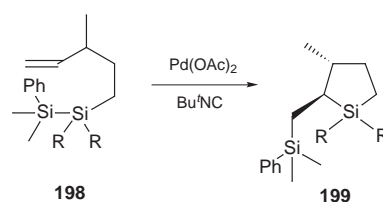
R = Ph: *trans* : *cis* 91 : 1 yield 99%
R = Me: *trans* : *cis* 86 : 14 yield 87%

Scheme 65

As noted above, hydrosilations can also proceed *via* a radical mechanism. One silane that has gained much attention over the past ten years is tris(trimethylsilyl)silane (TTMSS) (**200**). An early report[153] describes the use of TTMSS as a substitute for Bu$_3$SnH in the reduction of organic halides. However, the TTMSS-group can also be attacked by carbon centered radicals resulting in the release of a trimethylsilyl radical from the molecule. If the TTMSS group is attached to the same molecule as the radical center, this results in the formation of a hetero-cycle, an observation first made by Giese and co-workers.[154] A simple experiment (**Scheme 66**) illustrates that Si–Si bond fission readily occurs in the presence of carbon centered

Scheme 66

Table 3 Radical cyclization of dienes with TTMSS (Scheme 69)

Diene No.	X	Product No.	Yield	*cis*:*trans*
208	CH$_2$	**205**	62%	6:1
214	O	**216**	53%	only *cis*
215	C(CO$_2$Me)$_2$	**217**	71%	15:1
218	CH$_2$-CH$_2$	**219**	52%	1.7:1

Table 4 Barbier-type cyclization of chlorosilanes (Scheme 70)

220	R	**221** (Yield)	**222** (Yield)
a	H	60%	60%
b	SiEt$_3$	81%	86%
c	GeEt$_3$	65%	72%
d	SiCl$_2$Me	80%	72%
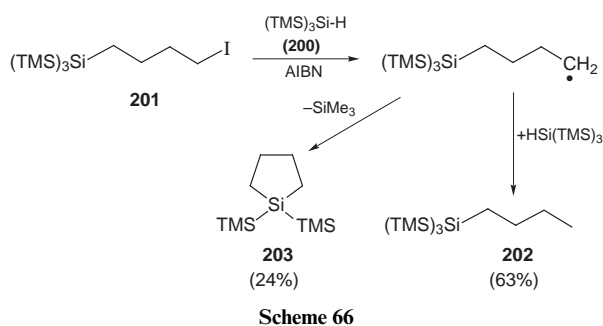
radicals.[155] Reduction of iodide **201** with a stoichiometric amount of **200** in the presence of AIBN leads to two products: **202**, resulting from hydrogen abstraction of the intermediate radical from **200**, and **203**, resulting from intramolecular attack of the radical at the silicon atom.

If the reaction outlined in Scheme 66 is run in the presence of a catalytic rather than a stoichiometric amount of **200**, formation of a cyclized product should be favored: reaction of bromide **204** in the presence of a catalytic amount of **200** and AIBN gave the bicyclic product **205** in excellent yield.[154] Starting from vinyl bromide **206**, cyclization is so fast that even in the presence of a stoichiometric amount of **200** no reduction product is observed (**Scheme 67**).[156]

Scheme 67

Scheme 68

Scheme 69
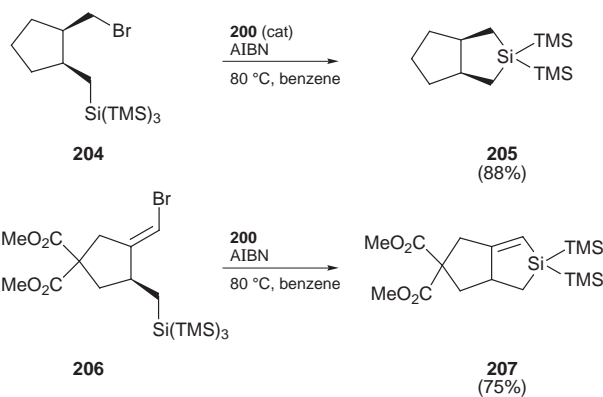
The same products that result from the radical cyclizations of bromides **204** and **206** can in principle be obtained by cyclization of diene **208** and enyne **209**, however in lower yields and lower selectivities. Thus, **208** reacts with **200** in the presence of AIBN to give a mixture of three products **205**, **210** and **211** which are formed in 35, 15 and 21% yield.[154] Enyne **209** reacts under similar conditions to **207** (48%) along with carbocycles **212** (6%) and **213** (39%) (**Scheme 68**).[156]

The selectivity significantly improves when the hydrosilation is run at lower concentrations. For example, dienes **208**, **214** and **215** were transformed to the corresponding bicyclic systems **205**, **216** and **217** in preparatively useful yields and *cis/trans* selectivities when the concentration of substrate was 0.02 M.[156] For the cyclization of 1,7-diene **218** to a heterocycle with a fused six-membered ring **219** *cis/trans* selectivity was only 1.7:1 (**Scheme 69** and **Table 3**).[155]

If internal dienes or enynes are employed in the reaction, the cyclization is usually fully or partially suppressed.[155]

A completely different method for intramolecular carbon–silicon bond formation is a Barbier-type reaction of a chlorosilane. Based on this transformation a sequence for the preparation of functionalized silacyclopentenes has been developed by Manuel *et al.*[157] For example, starting from 1,4-dichlorobut-2-ene (**220a**), trichlorosilane **221a** is accessible in a CuCl catalyzed coupling reaction with trichlorosilane. Subsequent treatment of **221a** with Mg gives 1,1-dichlorosilacyclopentene

222a. The functionalized derivatives **222b**,[157] **222c**[158] and **222d**[159] can be prepared by similar methodology. In these cases, however, the copper catalyzed coupling reaction yields structural isomers of **221b,c,d** as by-products, which do not undergo cyclization to silacyclopentenes **222b,c,d**. The starting materials **220b,c,d** can be obtained by hydrosilation of 1,4-dichlorobutyne catalyzed by hexachloroplatinic acid (**Scheme 70** and **Table 4**).

A reductive coupling of a trichlorosilane **223** has recently been reported by West *et al.* The product of its reaction with Li and TMSCl is a silafluorene **224**. A radical mechanism has been proposed for this transformation (**Scheme 71**).[160]

6 Ring closure by silylation of α,ω-dimetallic compounds

The reaction of a dihalide with an α,ω-dimetallic compound is one of the most common methods not only for the preparation of silaheterocycles but for the preparation of heterocycles of

220   **221**   **222**

Scheme 70

223   **224**
(35%)

Scheme 71

228   **229**   **230**

231a (R = Me, 70%)
231b (R = vinyl, 50%)
231c (R = allyl, 40%)

232   **233**
(R = Me, Ph; 50%)
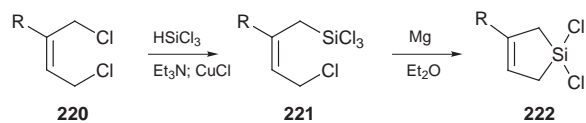
Scheme 73

main group elements in general.[161] In this chapter we will focus on more recent contributions to this field. In the first part, syntheses starting from dilithio compounds are discussed. The second part will summarize reactions where magnesium compounds are employed.

a) Dilithiocompounds as starting materials

It has been known for 30 years that diphenylacetylene reacts with lithium under the formation of a radical anion which dimerizes to give 1,4-dilithiotetraphenylbutadiene (**225**). Upon reaction with chlorosilanes **226** silacyclopentadienes (siloles) **227** are formed.[161] Joo *et al.* used this transformation to obtain siloles **227a**,**b**,**c** with one or two chlorine substituents at the silicon.[162] Using essentially the same methodology compounds **227d**–**g** where two siloles are bridged by a phenyl group have been prepared recently (**Scheme 72**).[163]

225   **226**   **227a–c**

R = Cl (a), Me (b), Ph (c)   (70%)

R = H, Me, Et, Cl   **227d–g**   (37–82%)

Scheme 72

Though the reductive coupling of tolane with lithium works well, the reaction does not seem to be generally applicable for other acetylenes. For example, 2,5-diphenylsilacyclopentadienes **231** have been prepared in two steps starting from 1,4-dibromo-1,4-diphenylbutadiene (**2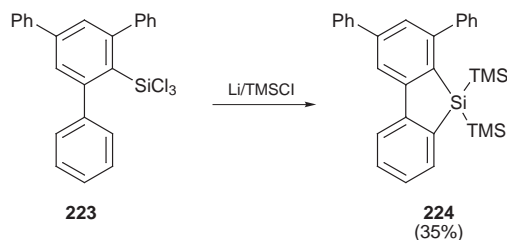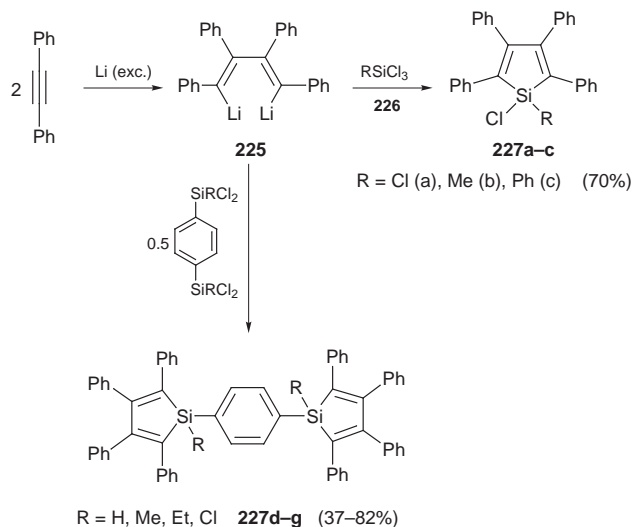28**).[164] Trimethoxysilanes **230** were found to be better silylating agents than the corresponding chlorosilanes in most cases.[164] It has also been demonstrated that pentavalent silanes derived from catechol (*e.g.* **232**) can be used as silylating agents for dilithio compound **229**. Thus, 1-hydrosiloles **233** can be obtained in a one pot procedure by treating **229** with **232** followed by reduction with LAH (**Scheme 73**).[165]

Over the past few years efforts were made to find more general methods for the preparation of siloles from α,ω-dimetallic
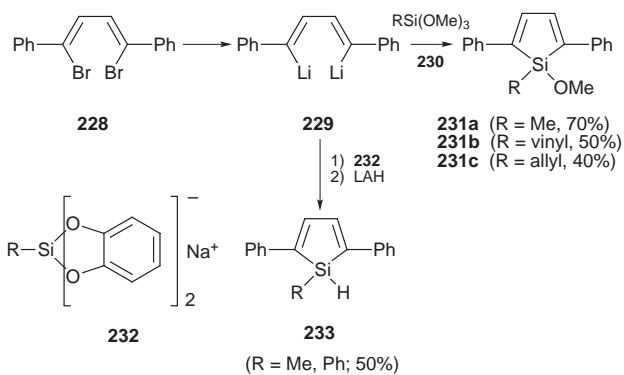
compounds. The Zr-mediated coupling of acetylenes (see Section 3) looked especially promising because a zirconacyclo-pentadiene is formed which should be amenable to transmetal-lation with dihalosilanes. However, when this synthetic path was investigated first it was found that the zirconacycle **234** can be transformed to silole **235a** with SiBr₄ only in poor yield and under harsh conditions.[166] **234** was also found to be completely inert towards neat SiCl₄ at elevated temperatures. These difficulties can be circumvented when zirconacycle **234** is first cleaved with iodine to give the diiodo compound **236**, followed by reaction with BuLi and SiCl₄ to yield **235b**.[167] Takahashi *et al.* recently published a procedure for the zirconium mediated cyclization of two different alkynes leading to unsymmetrically substituted zirconacycles **234**.[168] When the iodination–metallation sequence outlined above is applied to these zircona-cycles, unsymmetrically substituted siloles **235c**,**d**,**e** are accessible in excellent yields. The cleavage of the zirconacycle with iodine can be promoted by addition of a copper(I) salt (**Scheme 74**).[169]

234   R¹–R⁴ = Me   **235a** (28%)

235c (95%)   **236** (80–95%)   R¹–R⁴ = Me   **235b**

235d (98%)   **235e** (84%)
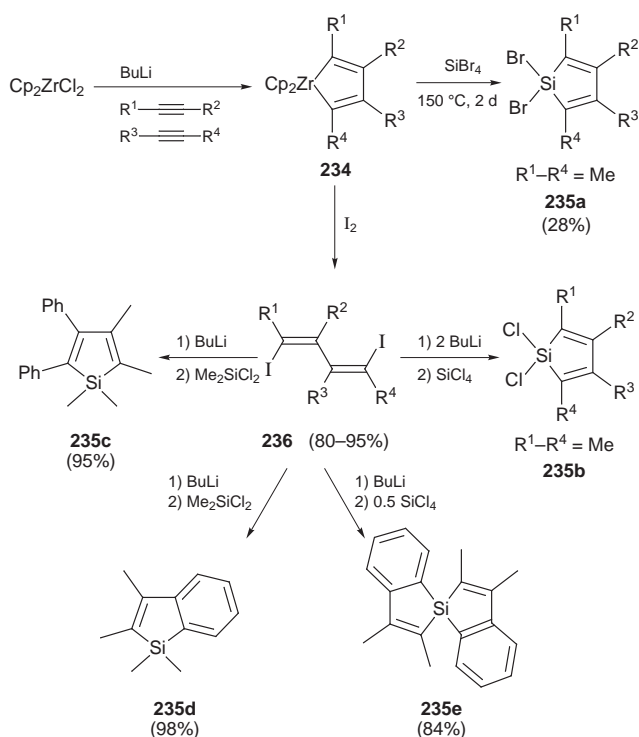
Scheme 74

Silaindene **235f** had previously been prepared by silylation of a dilithio compound obtained in two steps from acetyl-ene **237**.[170] Here the two lithium atoms were introduced by deprotonation and halogen–lithium exchange of intermediate **238** (**Scheme 75**).

Scheme 75

237

238
(92%)

DIBAL-H
NBS

BuLi | Et₂O/Δ

Me₂SiCl₂

235f
(80%)
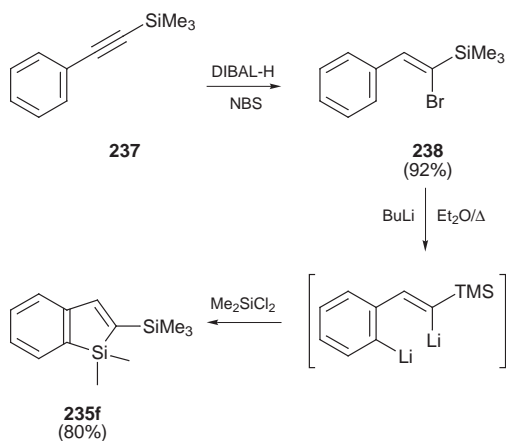
ortho-Dilithiated biphenyls are selectively prepared by halogen–lithium exchange. Subsequent reaction with a dichlorosilane is a commonly used method for the preparation of silafluorenes.[171,172] Silafluorenes also result from the direct synthesis of halogenated biphenyls with elemental silicon.[173] Formation of a silafluorene starting from 2,2′-dilithiated binaphthyl has recently been described.[174] Syntheses of various silaanthracene derivatives have been developed by Bickelhaupt *et al.* in the course of their studies towards silaaromatics.[175,176] Starting from dibromides **239** halogen–lithium exchange can either be achieved using elemental lithium or butyllithium. Cyclic products **241** result from subsequent treatment with dichlorosilanes **240** (**Scheme 76**).

239

1) Li or BuLi
2) R¹PhSiCl₂

240

241

(R = H, Ph; R¹ = Ph, Bz; 45–58%)

Scheme 76

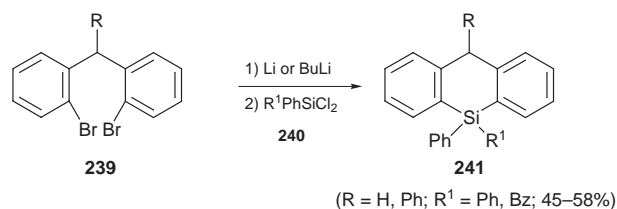So far mainly silacyclopentadienes and their benzoannellated derivatives were discussed in this chapter. However, silacyclopentanes and silacyclopentenes have also been prepared by silylation of dilithio-alkanes or -alkenes. A reductive coupling of a bis-silylated alkene **242** has been used for the preparation of fully saturated silaheterocycles **243**. This transformation is remarkable, as it leads to sterically crowded silacyclopentanes in comparatively good yield (**Scheme 77**).[177]

A silacyclopentene **245** fused to a cyclopentadiene has been isolated as the product of the reductive ring opening of a spiro-

242

Li

RR¹SiCl₂

243

R = H
R¹ = Me, Ph, H
(34–42%)
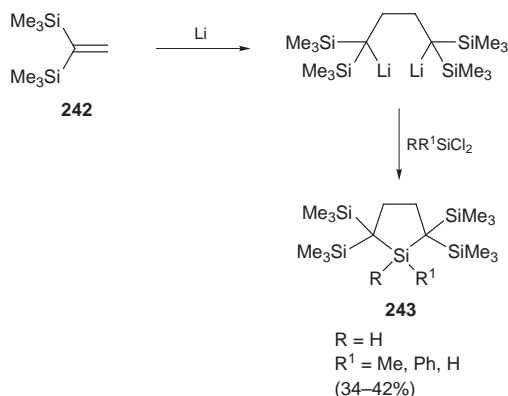
Scheme 77

heptadiene **244** followed by quenching with diphenyldichlorosilane. Compounds of this type could be of interest as prochiral ligands for transition metal complexes (**Scheme 78**).[178]

244

Li

Ph₂SiCl₂

245
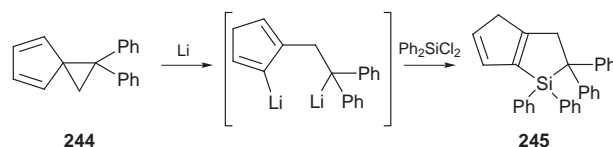
Scheme 78

While double halogen–metal exchange is a commonly used method for the preparation of 1,4-dilithiobutadienes (see above), difficulties occur when this method is applied for the preparation of 1,4-dilithiobutenes. For example, 1,4-dichlorobutene reacts with elemental lithium to give LiCl and butadiene, because elimination of LiCl from the intermediate monolithiated species is fast even at very low temperatures.[179] If, however, dichlorobutenes are treated with lithium and a dichlorosilane in the presence of a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB), a silacyclopentene **246a** is formed in a Barbier-type reaction. The three isomeric dichlorobutenes shown in **Scheme 79** all lead to the same product **246a** when employed in the reaction.[179] Similarly, a bicyclic system **248** has been prepared from tetrabromide **247** by reduction with lithium in the presence of a dichlorosilane.[180] The success of the latter transformation strongly depends on the solvent, with best results being obtained for ether–THF mixtures. Attempts to substitute lithium by sodium or potassium gave worse results.[181] These observations indicate that reduction of dihalobutenes by alkali metals is not a straightforward process.

Li (exc.)
DTBB (5 mol%)

Et₂SiCl₂

246a
(70–83%)

247

8 Li, Me₂SiCl₂

Et₂O/THF

248 (36%)
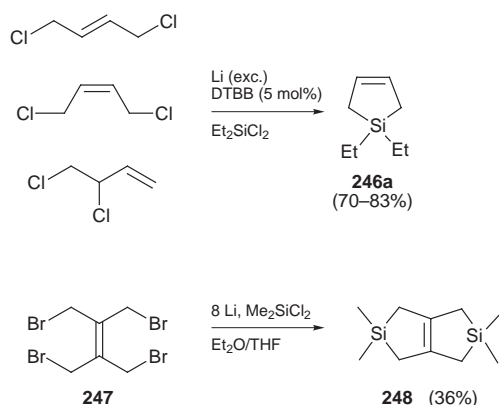
Scheme 79

b) Magnesium or zinc compounds as starting materials

While silacyclopentadienes are best prepared from 1,4-dilithiobutadienes as described above, Grignard reagents are commonly used for the preparation of saturated heterocycles. This chemistry has already been reviewed[182] and will therefore only be briefly mentioned here.

The stereochemistry in the formation of silacyclohexanes has been investigated by Cartledge *et al.*[183] Starting from piperidines **249**, they developed a convenient procedure for the preparation of a variety of silacyclohexanes **250** with different substitution patterns. Two points are worth mentioning: a) yields are significantly lower for 2-methyl substituted compounds and b) the *cis/trans* ratio depends on the substitution pattern at silicon and seems to be nearly independent of the other substituents (**Scheme 80** and **Table 5**).

Although no Grignard reagents are involved, a related electrochemical process should be mentioned in this context. By electrochemical reduction of a mixture of 1,4-dibromobutane or 1,5-dibromopentane and dichlorosilanes silacyclopentanes or silacyclohexanes can be prepared in approximately 90%

Table 5 Silacyclohexanes from piperidines (Scheme 80)

249	R¹	R²	R³	X	*cis* : *trans*	251 (Yield)
a	Me	H	H	Cl	30 : 70	44%
b	H	Me	H	Cl	70 : 30	60%
c	H	H	Me	Cl	32 : 68	60%
d	Me	H	H	H	55 : 45	43%
e	H	Me	H	H	50 : 50	53%
f	H	H	Me	H	52 : 48	60%
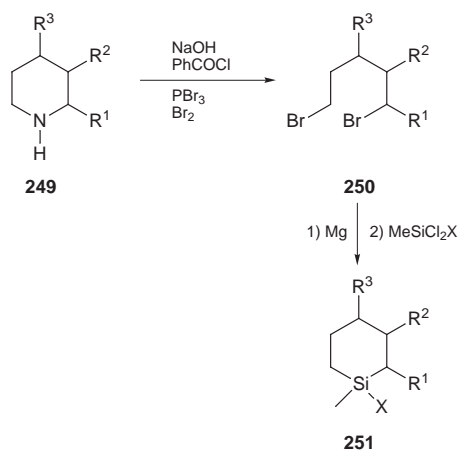
Scheme 80

yield. However, as for the reduction of dibromides with Mg, high dilution is required to obtain preparatively useful yields.[184]

A Zr catalyzed coupling reaction of two styrenes induced by a dialkylmagnesium compound is a method to obtain 1,4-dimagnesiobutanes **252**, which react with dimethyldichlorosilane to give a mixture of silacyclopentanes **253** (**Scheme 81**).[185]

Scheme 81

Zinc has been used as a reducing agent for a mixture of tetrabromide **247** and diphenyldichlorosilane. From this reaction heterocycle **254** results. The diene moiety in **254** is formed by reductive elimination of two bromides and can be used for further ring closure reactions, for example using GeI₂ to give the bicyclic compound **255** (**Scheme 82**).[181]
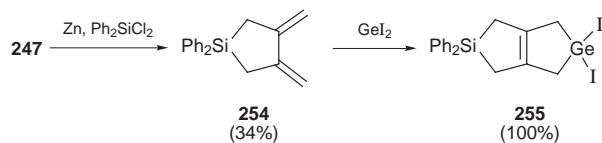
Scheme 82

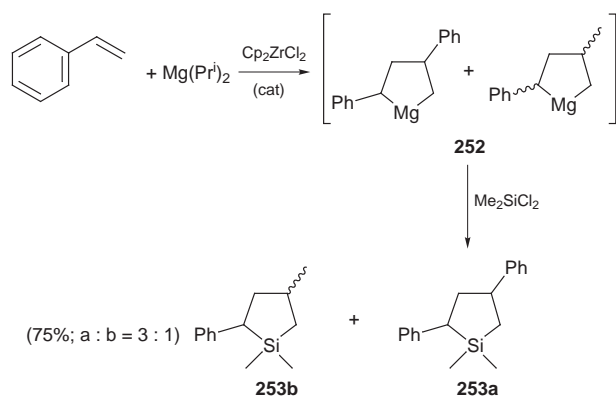From the examples given above it becomes clear that α-ω-dihalocompounds are the starting materials of choice for the preparation of saturated silaheterocycles. This is normally not the case for silacyclopentenes as the dihalobutenes required often undergo reductive elimination of halide to yield butadienes. This result was found, for example, by Manuel *et al.* when the dichlorobutadienes **256** were treated with activated zinc leading to metallated butadienes **257** in good yield.[158] These difficulties may be circumvented when butadienes are reduced with magnesium and the resulting magnesium butadiene is reacted with dichlorosilanes. Thus, dienes **257** can serve as starting materials for silacyclopentenes **246c,d** when they are treated with magnesium in the presence of dichloro-dimethylsilane (**Scheme 83**).[158]
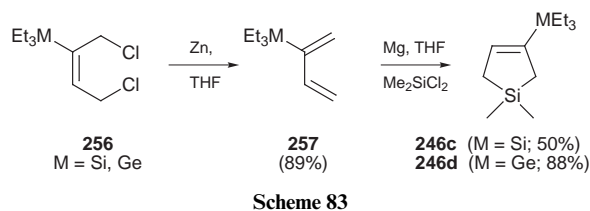
Scheme 83

This reaction has been used as a one-pot procedure by Manuel *et al.* who made a series of significant contributions to this field.[186,187] It should be pointed out that diphenyl-silacyclopentadiene (**246b**) is accessible *via* this method on a large scale.[188] Thus, from 8 moles of butadiene, 2 moles of dichlorosilane and 2 moles of Mg, 336 g (71%) of **246b** were prepared in a one pot procedure (**Scheme 84**).
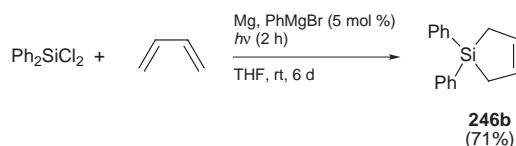
Scheme 84
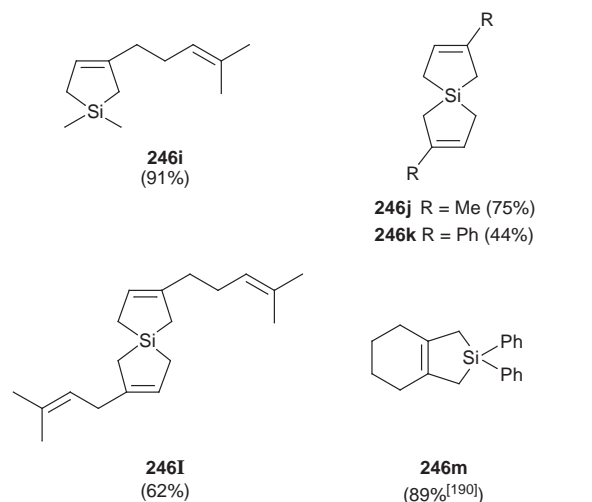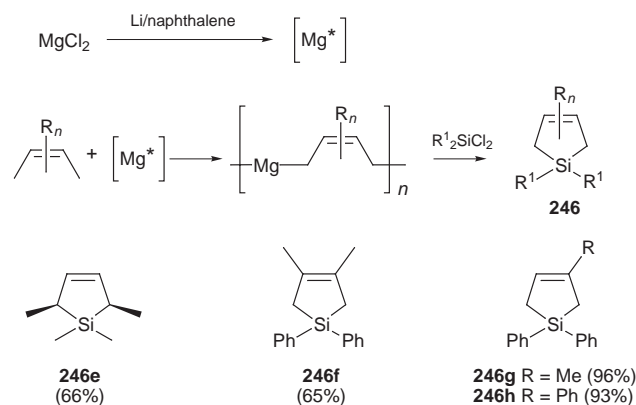
Scheme 85

Compound **246b** had previously been prepared *via* a two step procedure, involving the isolation of the pyrophoric magnesium butadiene which was subsequently treated with dichlorodiphenylsilane.[189] Though the reduction of butadiene with magnesium works well, other conjugated dienes often give oligomers with ordinary magnesium. Therefore, Rieke *et al.* employed highly reactive magnesium, obtained by reduction of magnesium chloride with lithium and naphthalene as an electron carrier, for the reduction of dienes other than butadiene.[190,191] *via* this method, a variety of functionalized silacyclopentenes **246e**–**m** become accessible in preparatively useful yield. It should be noted, that magnesium dienes do not always have the polymeric structure shown in **Scheme 85**. For the magnesium compound of 1,4-diphenylbutadiene a cyclic structure was found by crystal structure analysis, which may probably explain the high *cis*/*trans*-ratio of 15∶1 which is observed for **246e**.[192]

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