

# Higher-Coordinated Molecular Silicon Compounds

Jörg Wagler, Uwe Böhme, and Edwin Kroke

**Abstract** In silicon compounds the Si atoms are known to be fourfold coordinated in most cases. However, there are several cationic, anionic, and neutral molecular species containing hypercoordinated – i.e., five- and sixfold coordinated (and in few cases even higher coordinated) – silicon atoms. This class of compounds ranges from long known stable inorganic species such as  $\text{SiF}_6^{2-}$  to many different organometallic compounds with multidentate chelate ligands. Although this field has been known since the early nineteenth century and expanded significantly in the twentieth century, very interesting advances have been developed in the past decade. These include the extension of established synthesis routes to novel ligand systems via substitution, addition, and oxidative addition, among others. A number of new organic ligand systems have been successfully applied leading to unprecedented coordination modes of the silicon atoms. The structures of the obtained compounds have been analyzed thoroughly in many cases providing detailed insights into structure and bonding situations in hypercoordinated silicon complexes. Besides the classical silicon compounds with donor atoms such as H, C, Cl, F, O, and N, many novel examples with main group metal as well as transition metal atoms in the coordination sphere of silicon have been reported.

**Keywords** Chelate ligand · Donor atom · Hypercoordination · Silicon complex · Structure · Synthesis

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J. Wagler, U. Böhme, and E. Kroke (✉)  
TU Bergakademie Freiberg, Institut für Anorganische Chemie, Leipziger Str. 29, 09596,  
Freiberg, Germany  
e-mail: [kroke@tu-freiberg.de](mailto:kroke@tu-freiberg.de)

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## Abbreviations

AIM	Atoms in molecules (see also QTAIM)
Ar	Aryl
bipy	2,2'-Bipyridyl
Bn	Benzyl
Bu	Butyl
<i>t</i> -Bu	<i>Tert</i> -butyl
cat	Catalyst
CN	Coordination number
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CSD	Cambridge Structural Database
Cy	Cyclohexyl

Dip	2,6-Diisopropylphenyl
DMAP	4-(Dimethylamino)pyridine
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Et	Ethyl
HMPA	Hexamethylphosphorictriamide
L	Ligand
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl (not methanesulfonyl)
mt	Methimazolyl (1-methyl-2-mercaptoimidazolyl)
NBO	Natural bond order
NHC	<i>N</i> -heterocyclic carbene
NHS	<i>N</i> -heterocyclic silylene
Nu	Nucleophile
Ph	Phenyl
phen	1,10-Phenantroline
Pr	Propyl
<i>i</i> -Pr	Isopropyl
py	Pyridine
pz	Pyrazolyl
pz*	3,5-Dimethylpyrazolyl
QTAIM	Quantum theory of atoms in molecules
SP	Square pyramid (or square pyramidal)
TBP	Trigonal bipyramid (or trigonal-bipyramidal)
Tf	Trifluoromethanesulfonyl (triflyl)
THF	Tetrahydrofuran
tmeda	<i>N,N,N',N'</i> -tetramethyl-1,2-ethylenediamine

## 1 Introduction

Silicon, as the heavier homolog of carbon, is fourfold coordinated in its compounds in most cases. This is, for example, reflected by the chemistry of silicates [1]. In these naturally occurring compounds, the silicon atoms are almost exclusively found in SiO<sub>4</sub>-coordination. The situation is similar for synthetic solids, such as extended binary phases like pure silica zeolite-type frameworks [2], SiS<sub>2</sub>, SiC or Si<sub>3</sub>N<sub>4</sub>, and related more complex ternary and multinary solids [3]. This is also valid for molecular silicon halides, hydrides, and metal organic (e.g., silicon alkoxides) as well as organometallic silicon compounds [3, 4].

Interestingly, for almost all mentioned classes of silicon compounds, there are also well-known examples containing higher-coordinated silicon atoms. For the silicates and silica phases, there are some naturally occurring minerals with SiO<sub>6</sub> moieties such as thaumasite [5] or the SiO<sub>2</sub> high-pressure phase stishovite [6]. Similarly, a high-pressure modification of silicon nitride (spinel-Si<sub>3</sub>N<sub>4</sub>) [7],

selected nitridosilicates, and so-called sialons (silicon aluminum nitride oxides), which contain sixfold-coordinated silicon atoms, have been reported [8–10]. An even larger variety of *molecular* compounds containing higher-coordinated silicon atoms are known. These include neutral, anionic, as well as cationic species with mono-, bi-, and multidentate ligands. The probably best-known representative of this class of species is  $[\text{SiF}_6]^{2-}$ , its salts and its acid  $\text{H}_2\text{SiF}_6$ . In fact, for the first synthesis of elemental silicon in pure form,  $\text{K}_2[\text{SiF}_6]$  was used as a starting material in 1825 [11], and the di-ammonia adduct of  $\text{SiF}_4$  was reported as early as in 1811 [12].

The chemistry of higher-coordinated – sometimes also called hypercoordinated and/or hypervalent silicon compounds – has been reviewed in several publications in the past. These references provided general overviews in the 1960s [13, 14], 1970s [15], 1980s [16], and the 1990s [17, 18]. More recently, i.e., since the year 2000, additional review-papers appeared. Some are of general nature covering most classes of molecular higher-coordinated silicon compounds [19]. Many others of these newer reviews are focused on certain more specific topics, i.e., groups of compounds such as organosilicon derivatives containing nitrogen heterocycles [20], higher-coordinated silicon(IV) compounds with  $\text{SiO}_5$  and  $\text{SiO}_6$  units [21], silicon (IV) complexes with  $\text{SiO}_2\text{N}_4$  units, zwitterionic compounds with pentacoordinated silicon atoms [22], applications of higher-coordinated silicon compounds as a reactive site in (stereoselective) organic synthesis [23–26], pentacoordinated sili-conium ion salts [27], pentaorganosilicates [28], silatranes and closely related compounds [29], silicon complexes with hydrazine derived N–O-donor ligands [30, 31], and silicon halides coordinated with neutral ligands [32]. Furthermore, a review is available on the role, properties, and fate of higher-coordinated fluoro-silicates which are frequently used as additives for drinking water [33]. Another example of a class of compounds containing sixfold-coordinated silicon, which has been extensively studied over the past decades, is phthalocyanine derivatives with photosensitizing behavior which can be used for photodynamic therapies [34] or as electron acceptor components for the development of supramolecular solar cells [35].

Compounds which accommodate agostic interactions of Si–H moieties with transition metals may also be considered as a special type of higher-coordinated silicon compounds. A few reviews on this matter are also available [36]. These include a recent general overview [37] and further publications on selected sub-topics such as platinum compounds [38] or niobium and tantalum complexes [39]. Complexes of this type are also discussed in comparison to C–H and H–H interactions with lanthanides [40].

In general, detailed explanations as to why and when higher-coordinated silicon atoms are formed remain limited, thus leaving the origin of silicon hypercoordination a matter of discussion. This holds also true for related heavier main group elements such as germanium, phosphorus or sulfur. There are many species which formally exceed the number of eight valence shell electrons and/or possess five, six, or more neighboring atoms with bonding interactions, i.e., distances below the sum of the van der Waals radii of the corresponding atoms.

For octahedral compounds a description using a  $sp^3d^2$  hybridization was frequently discussed. However, due to the relatively high energy of the 3d orbitals of silicon, it is usually accepted that their role is not significant. Thus, two-electron–two-center bonds are not considered as the appropriate description for these “hypervalent” compounds.

Another well-accepted interpretation of hypercoordination of silicon is based on the ionicity of their bonding situations, which in general is very high. It can be stated that the ionicity increases with the coordination number. However, it is obvious that in higher-coordinated silicon compounds with different ligands such as  $SiXYZ$ , the bonding situation including its ionicity to the different atoms X, Y, and Z is different and depends on several factors. This can be related to the Lewis acidity of silicon atoms bound to electronegative atoms.

Due to the numerous overviews on the chemistry of hypercoordinated silicon compounds, the present review is primarily focused on the structural and synthetic aspects. Spectroscopic and other properties as well as (potential) applications are only briefly mentioned in selected cases. Nevertheless, the literature on higher-coordinated silicon complexes published in the past 5 years should be covered comprehensively, while relevant older literature is also considered.

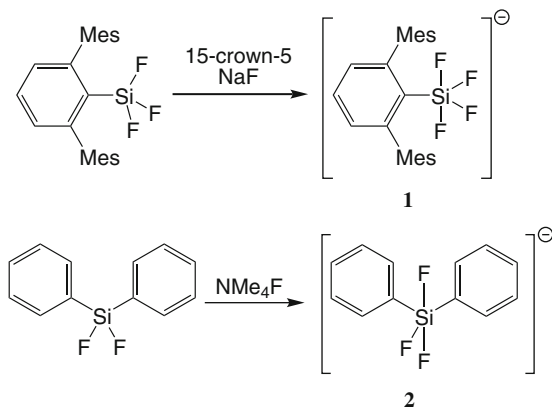
## 2 Synthesis of Hypercoordinated Silicon Compounds

Although a great variety of synthetic strategies is known to afford hypercoordinated silicon compounds, they can be classified as addition (and sometimes elimination), substitution, and rearrangement reactions or combinations thereof.

### 2.1 Addition of Anionic Nucleophiles

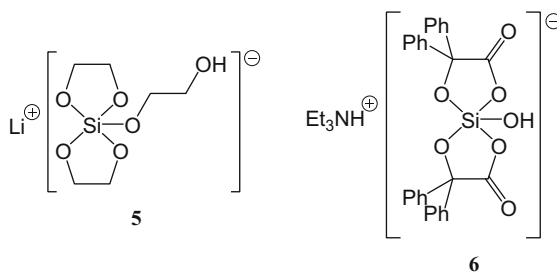
The most prominent examples of hexacoordinated silicon complexes –  $SiF_6^{2-}$ ,  $HSiF_6^-$  and  $H_2SiF_6$  – form instantly in an addition reaction of  $SiF_4$  and fluoride ions or HF in solution [11, 33] as well as in the gas phase [41]. In a similar manner, pentafluorosilicates ( $SiF_5^-$ ) can be obtained [42] and organofluorosilanes form organofluorosilicates (e.g., **1** and **2**, Scheme 1) upon reaction with suitable fluoride sources [42, 43]. This noticeable susceptibility to fluoride addition is made use of in fluoride-catalyzed nucleophilic substitution reactions at silicon, where  $F^-$  serves as the first nucleophile to increase the silicon coordination number to five, thus creating a reactive species prone to addition of a sixth donor moiety (i.e., the new substituent) [44]. Also due to the high fluoride susceptibility of fluorosilanes, in syntheses of fluorosilanes out of chlorosilanes by halide exchange, one has to avoid excess of easily available fluoride. Thus, fluoride sources such as  $SbF_3$  [45] and  $ZnF_2$  [46] proved useful reagents for this purpose.

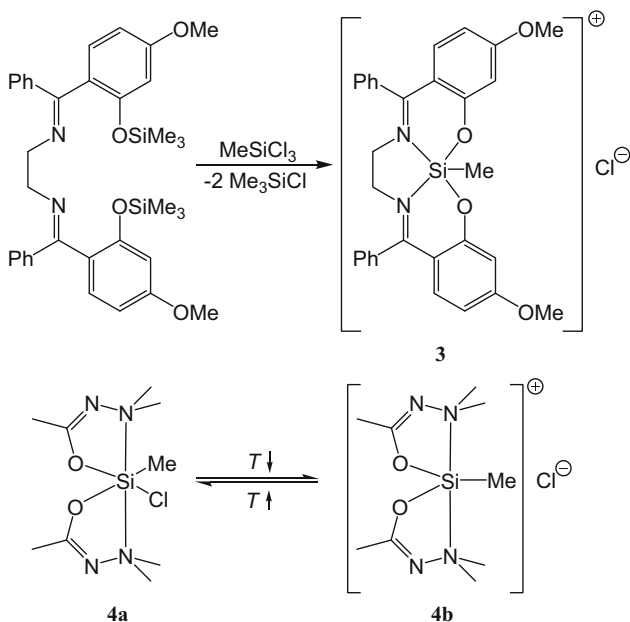
**Scheme 1** Formation of pentacoordinated fluorosilicates from di- and trifluorosilanes



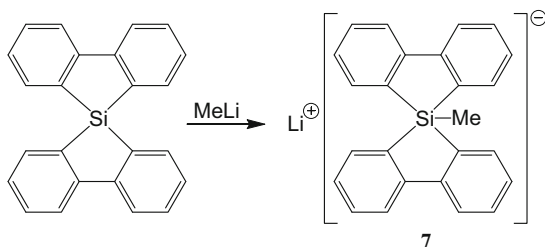
In sharp contrast, the anion  $\text{SiCl}_6^{2-}$  has not been isolated yet, whereas the related compound of the heavier congener ( $\text{GeCl}_6^{2-}$ ) is well known [47]. Even chlorosilicates with pentacoordinated Si atom are scarcely encountered, one of the rare exceptions being the anion  $(\text{Cl}_3\text{Si}-\text{SiMeCl}_2-\text{SiMeCl}_2)^-$  with a pentacoordinated central silicon atom [48]. Instead, hexacoordinated chlorosilicon complexes are frequently found to undergo ionic dissociation under release of chloride and formation of cationic complexes with pentacoordinated Si atom, either as isolable cationic Si complexes (e.g., **3**) or in dynamic equilibrium in solution (e.g., **4a** and **4b**), thus reflecting the weakening of Si–Cl bonds upon hypercoordination of the silicon atom (Scheme 2) [49–52].

Oxysilanes (such as silanes comprising hydroxy, alkoxy, aryloxy, or carboxy groups) were found to add further oxy-anionic ligands (thus yielding silicates with penta- or hexacoordinated Si atom) in case of selected silanes with small chelate rings (five-membered OSiO chelates, e.g., **5** and **6**) [53–60]. Crystal structures of pentaalkoxysilicates with exclusively monodentate ligand moieties have not been reported yet, but formation of such species in the gas phase has been proven by mass spectrometry [61]. Interestingly, in the solid state the silicate  $\text{Si}(\text{OH})_6^{2-}$  is stabilized and encountered in the mineral thaumasite [5].





**Scheme 2** Cationic pentacoordinated silicon complexes formed upon ionic dissociation of a Si–Cl bond



**Scheme 3** Formation of a pentacoordinated silicate with five Si–C bonds

Anionic nitrogen nucleophiles ( $X^-$ ), such as azide [62], cyanate [63, 64], thiocyanate [65, 66], and selenocyanate [67], are also well known to form hexacoordinated anionic silicon complexes of the type  $\text{SiX}_6^{2-}$  despite their monodentate nature.

Carbanions have also been shown to add to certain tetraorganosilanes. Even though this route is also supported by five-membered chelates in the silicon coordination sphere (formation of 7, Scheme 3) [28, 68–72], this structural feature

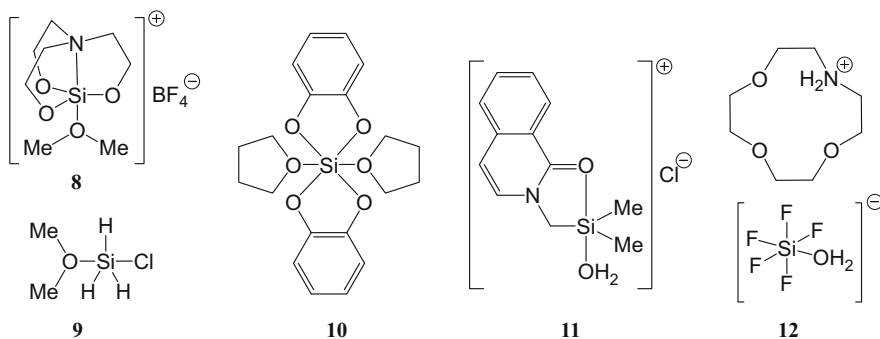
is not essential to achieve the formation of pentacoordinated Si complexes with five Si–C bonds, as proven by the anion  $[\text{SiMe}_3(\text{CF}_3)_2]^-$  [73].

Last but not least, hydridosilicates have been reported, which form upon addition of hydrides to hydridosilanes, e.g., formation of  $\text{K}^+[(i\text{PrO})_3\text{SiH}_2]^-$  out of KH and  $(i\text{PrO})_3\text{SiH}$  [74, 75].

## 2.2 Addition of Monodentate Charge-Neutral Nucleophiles

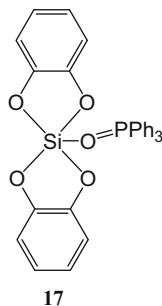
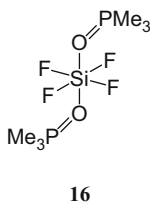
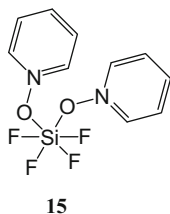
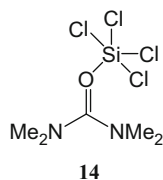
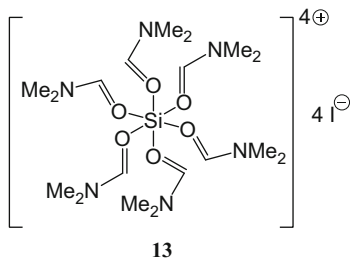
Basically, halocarbons should be capable of entering the silicon coordination sphere with a lone pair of one of their halogen atoms, as has been shown for the 1,2-dichlorobenzene solvate of a silicenium ion  $(i\text{Pr}_3\text{Si}^+ \dots \text{Cl}-o\text{-C}_6\text{H}_4\text{Cl})$  [76]. To the best of our knowledge, this kind of solvate formation has not been proven relevant in hypercoordinated silicon chemistry yet.

Ethers were shown to form adducts with silicon compounds (e.g., **8**, **9** and **10**), but literature reports on crystallographic evidence are limited to few examples [77–80]. In the same manner, alcohols and water should be capable of forming related adducts. Surprisingly, no example of an alcohol solvate can be found in the CSD [81], but adduct formation with alcohols has already been reported [82]. Water, however, has already been demonstrated by X-ray crystallography to act as a ligand in hypercoordinated Si complexes (e.g., **11** and **12**) [82–85].

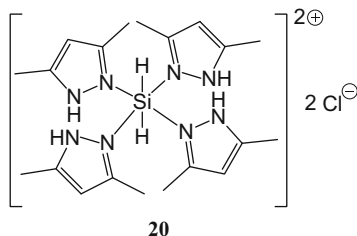
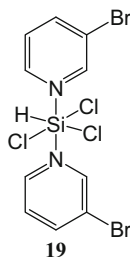
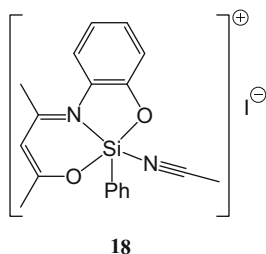


So far, no crystallographic evidence for adducts of silanes with aldehydes, ketones, esters, or acyl halides has been reported [81]. Dimethylformamide [86–88] and tetramethylurea [89], however, are known to enter the silicon coordination sphere (e.g., in **13** and **14**, respectively). In a similar manner amine-*N*-oxides (e.g., in **15**) [90], phosphine oxides (e.g., in **16** and **17**) [90, 91], and phosphoric amides [92–94] form hypercoordinated Si complexes. Although dimethyl sulfoxide (DMSO) increases the silicon coordination number (as shown  $^{29}\text{Si}$  NMR spectroscopy) [49], crystallographic evidence for a silicon complex with DMSO ligand(s) is still lacking [81].

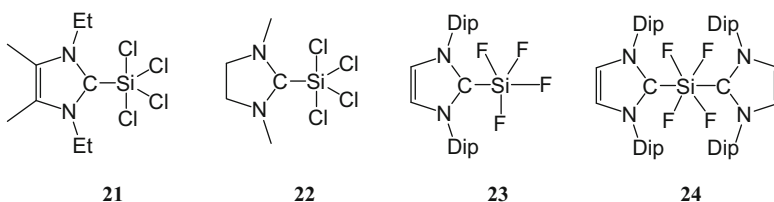




Only recently, nitriles were shown to increase the silicon coordination number to up to five in cationic complexes (**18**) [95], even though nitriles had already been shown to form adducts with silenium ions, thus functioning as a donor moiety in a tetrahedral Si coordination sphere [96]. Amines are scarcely encountered in silicon coordination compounds, only few examples of crystallographically evidenced silicon complexes with monodentate amines have been reported so far, which include the adduct  $\text{SiF}_4(\text{NH}_3)_2$  [97–100]. Imines, however, are well known to add to various halosilanes. Especially *N*-heterocycles with imine functionality, such as pyridines [101–103], imidazoles [104, 105], pyrazoles [106], and related compounds, can be found as ligands in various silicon complexes (e.g., in **19** and **20**).



Recently, the set of donor molecules for the synthesis of silicon complexes has been extended to *N*-heterocyclic carbenes (NHCs). Even though some first examples of NHC silane adducts were reported earlier [107], a noticeable number of NHC silicon complexes entered literature in the past 5 years [108–112]. Interestingly, in pentacoordinated silicon complexes of the type (NHC)SiX<sub>4</sub> (X=halide), the carbene ligand was found capable of binding in both the axial (in **21** and **22**) and the equatorial position (in **23**) of the trigonal-bipyramidal coordination sphere. Computational analyses of a set of different NHCs and silanes have shown that in some cases, the energetic difference between axial and equatorial coordination of the NHC ligand is marginal [113]. In octahedral silicon complexes with two NHC ligands (**24**), the carbenes are found *trans* to each other [108], which is in agreement with computational predictions [113].

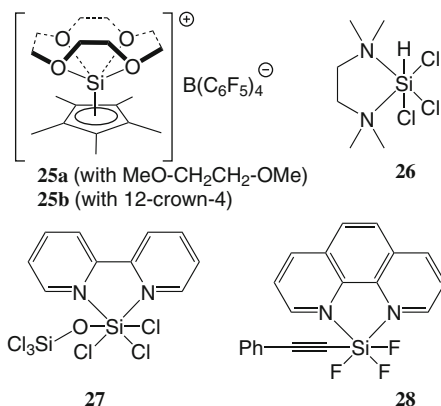


The above-listed monodentate donor moieties clearly demonstrate that, in addition to hydrocarbons (pentane, hexane, benzene, toluene, etc.), halogenated hydrocarbons (dichloromethane, chloroform, chlorobenzene, etc.), ethers (diethyl ether, tetrahydrofuran (THF), 1,4-dioxane, etc.), and nitriles (e.g., acetonitrile) should be suitable “innocent” solvents for syntheses and reactions of silicon complexes, as far as competitive solvent coordination has to be circumvented. The same holds true for trialkylamines as sacrificial bases (if required), as they appear least likely to compete in complex formation with other ligands. Nonetheless, care has to be taken when other side reactions appear likely. Solvolysis of Si–Cl, Si–OR (R=aryl, alkyl), or Si–N bonds by protic solvents such as alcohols or water is a well-known reaction in silicon chemistry [44, 114, 115] and may thus also apply to hypercoordinated silicon complexes [116, 117]. Although many reports can be found that deal with the syntheses of chlorosilicon complexes in alcohols as solvents, none of the resulting complexes has been confirmed crystallographically so far (to the best of our knowledge) [118–124]. Ether and ester cleavage represents another competitive reaction pathway and has to be considered in reactions of halosilanes (especially bromo and iodosilanes) in solvents of that kind [125, 126]. Enolization of carbonyl compounds (e.g., acetone), which may result in silylation of the enol, is another noteworthy competitor [127], whereas enols may also serve as the desired ligands, e.g., in compounds with acetylacetonato-derived ligand systems [128–130]. Dimethylformamide is known to transfer oxide to hydrosilanes, thus yielding siloxanes [131], and similarly dimethyl sulfoxide reacts with chlorosilanes under formation of siloxanes [132]. In some cases the solvent molecules participate in the formation of novel hypercoordinated silicon compounds in different ways than just

acting as neutral donor ligands. Acetonitrile has been shown to undergo addition reactions with silicon-bound ligands, thus creating entirely new ligand systems [133, 134]. Recrystallization of a bromosilicon complex from 1,2-dichloroethane afforded a chlorosilicon complex upon halide exchange with the solvent [135].

### 2.3 Addition of Oligodentate Charge-Neutral Ligands

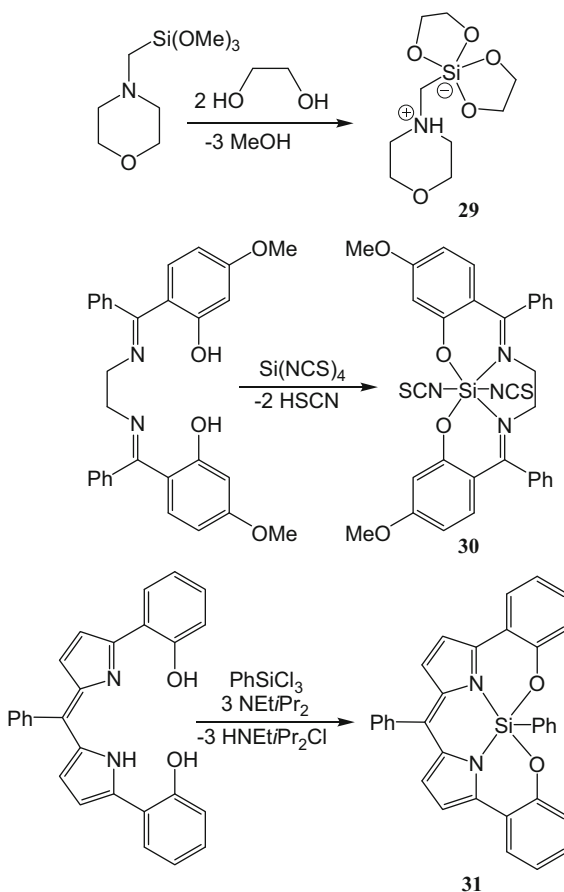
In general, silicon complex formation is favored when using chelating ligands. Thus, various kinds of chelators will be dealt with in the following sections, and just few examples are listed here. To the abovementioned monodentate ligands (from Sect. 2.2), various chelating combinations of one or more kinds of donor functions can be used to enhance the coordination number of silicon. Thus, 1,2-dimethoxyethane (**25a**) and 12-crown-4 (**25b**) [136] have also been successfully utilized as ligands at silicon (in this particular case in a silicon(II) compound). Many examples of N-donor chelates such as tetramethylethylenediamine (tmeda, e.g., in **26**) [137] and related amines [138, 139] as well as 2,2'-bipyridyl (bipy, e.g., in **27**) [140–143], 1,10-phenanthroline (phen, e.g., in **28**) [142, 143], and N-oxides thereof [144] were shown to form hypercoordinated silicon complexes.



### 2.4 Metathesis with Anionic Chelating Ligands

A very successful strategy of anchoring charge neutral donor moieties is the substitution of anionic monodentate substituents by anionic chelators. In the same way, additional anionic donor moieties can be introduced in the Si coordination sphere, which are less likely to bind to Si if of monodentate nature. Various routes

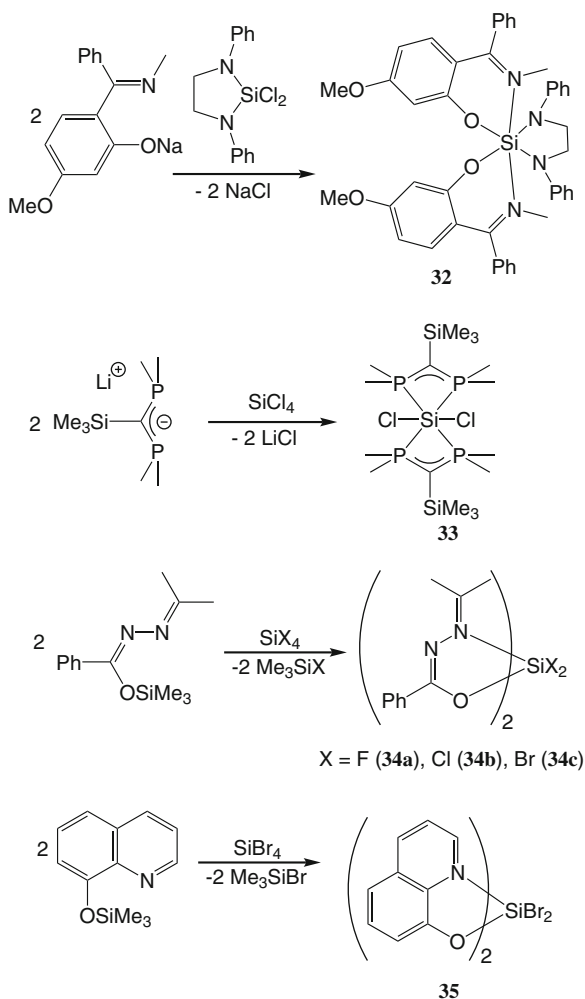
**Scheme 4** Syntheses of penta- and hexacoordinated silicon complexes from ligand acids and alkoxy-, thiocyanato-, and chlorosilanes



have been developed for introducing new ligands in the silicon coordination sphere by metathesis, which include reaction of a ligand acid with an alkoxyasilane (e.g., synthesis of **29**, Scheme 4) [145, 146], a cyanato- or thiocyanatosilane (e.g., synthesis of **30**, Scheme 4) [66, 128, 147], or a halosilane [148, 149], base-supported substitution of a ligand acid with a halosilane (e.g., synthesis of **31**, Scheme 4) [150–153], salt elimination from a ligand alkali metal salt and a halosilane (e.g., synthesis of **32** and **33**, Scheme 5) [153–155], and transsilylation between a trimethylsilylated ligand and a halosilane (e.g., synthesis of **34** and **35**, Scheme 5) [49, 156–158].

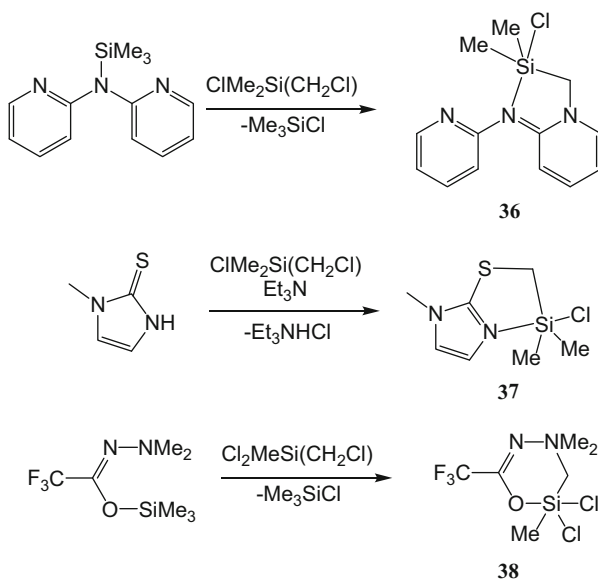
In addition to metathesis reactions at silicon, a substitution reaction in close proximity to the Si atom is also suitable for introducing chelators in the Si coordination sphere (Scheme 6). In this context, chloromethyl-substituted silanes have successfully been modified at the  $\alpha$ -C-atom with amides (**36**) [84, 159–162],

**Scheme 5** Syntheses of pentacoordinated silicon complexes from metalated and silylated ligands and halosilanes

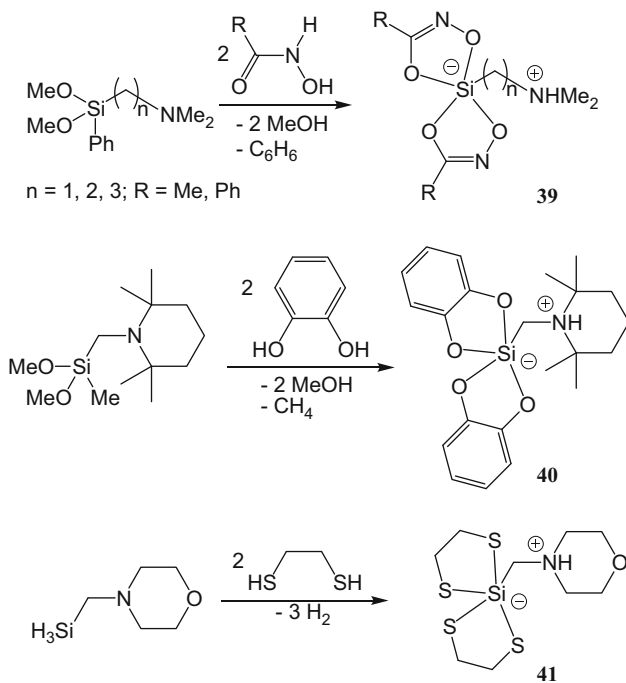


thiolates (**37**) [163], and other nucleophiles (**38**) [52, 164] to furnish new chelators anchored to silicon via Si–C bond. These nucleophilic substitution reactions again may be performed along various routes, which include base-supported reaction with a ligand acid and transsilylation with a trimethylsilylated ligand.

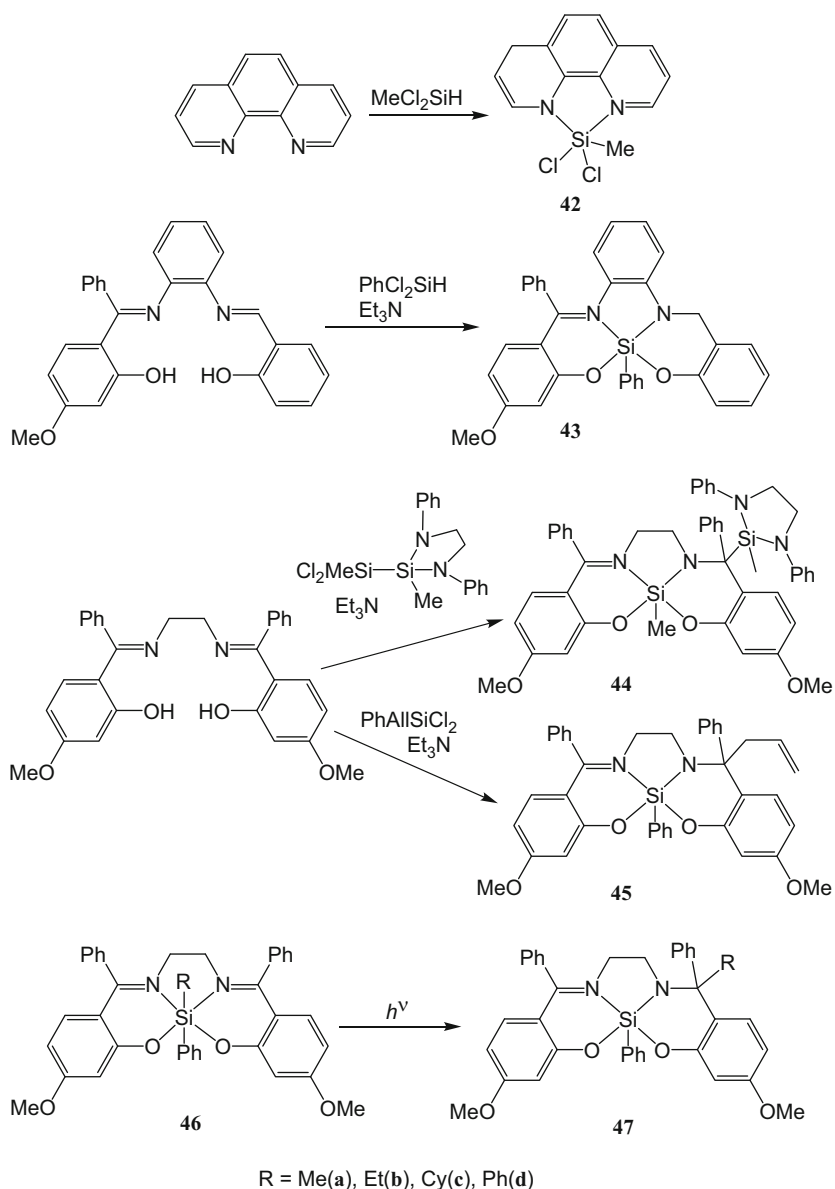
Last but not least, reactions of some organosilanes or hydrosilanes with ligand acids proceed under release of a hydrocarbon (e.g., **39** and **40**, Scheme 7) [165, 166] or hydrogen (e.g., **41**, Scheme 7) [145, 167], respectively, as very benign leaving groups.



**Scheme 6** Syntheses of pentacoordinated silicon complexes from (chloromethyl)silanes



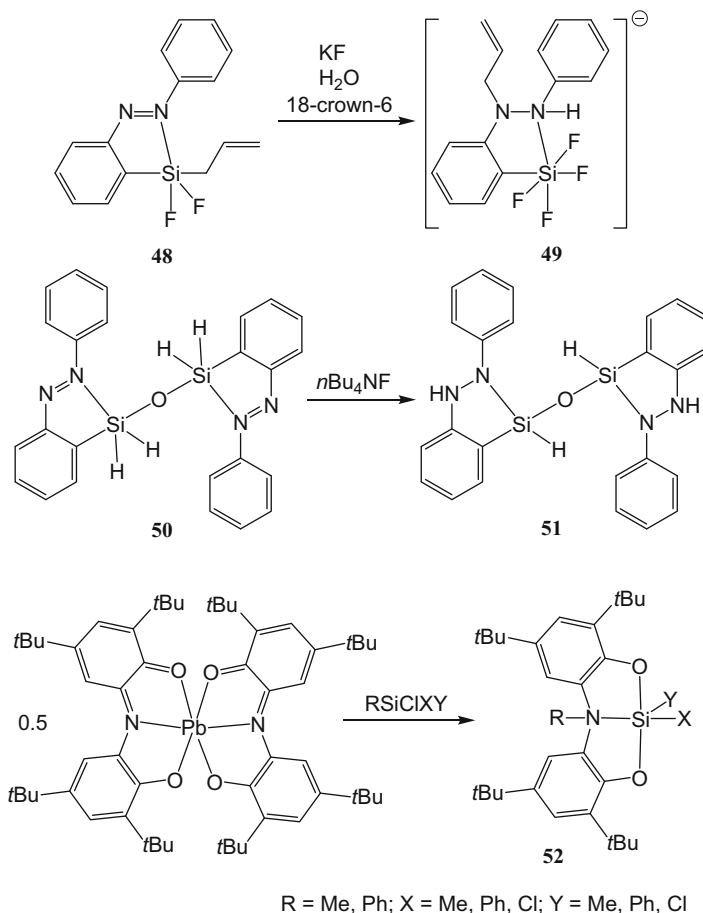
**Scheme 7** Syntheses of pentacoordinated silicon complexes under release of hydrocarbons or hydrogen



**Scheme 8** Syntheses of pentacoordinated silicon complexes under migration of a silicon-bound substituent to the chelating ligand

## 2.5 Rearrangement Reactions

The abovementioned routes can include molecular rearrangement (Scheme 8). Addition of 1,10-phenanthroline to methylchlorosilane was shown to result in hydride migration, thus producing a pentacoordinated silicon complex (42) [168].



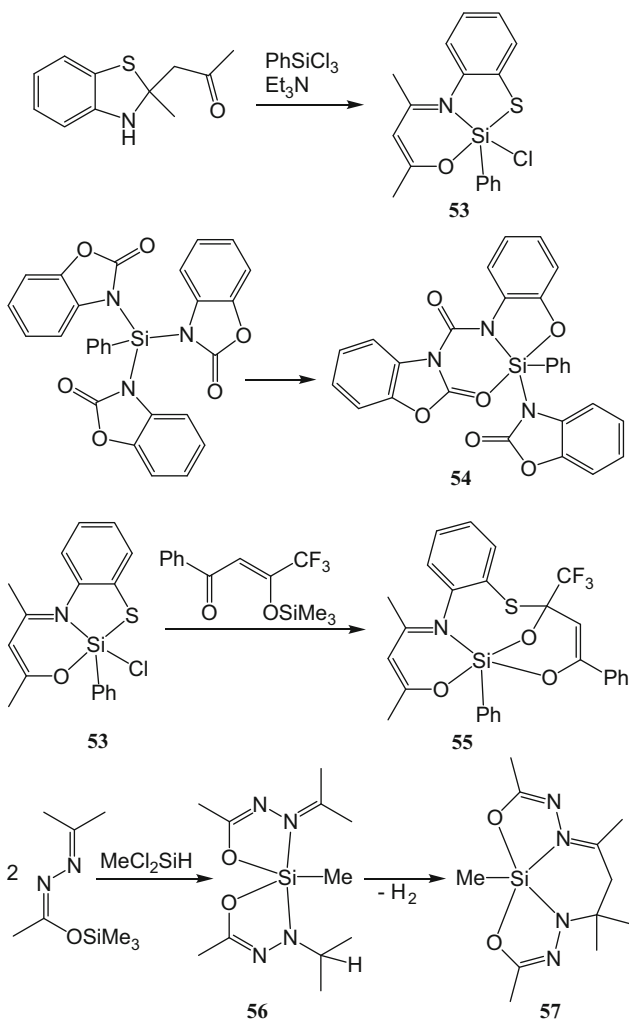
**Scheme 9** Examples for migration of hydride and hydrocarbyl groups from silicon to an N atom of the chelating ligand

In a similar manner, hydride (**43**) [169, 170], silyl groups (**44**) [171], allyl groups (**45**) [169, 172], as well as alkyl (**47a-c**) and aryl groups (**47d**) [173–176] can migrate to imine carbon atoms of the ligand, either during the metathesis reaction or upon thermal or photochemical activation of an intermediate hypercoordinated silicon complex (**46a-d**).

Related shift reactions were also observed in complexes with diazobenzene derived ligands (**48–51**) [177–179] and upon complex formation with aryloxyiminoquinones (**52**), as shown in Scheme 9 [180]. The allyl migration in particular, which is facilitated by silicon hexacoordination, is utilized for syntheses of various allylmethanols from aldehydes (or ketones) and allylsilanes [181–187].

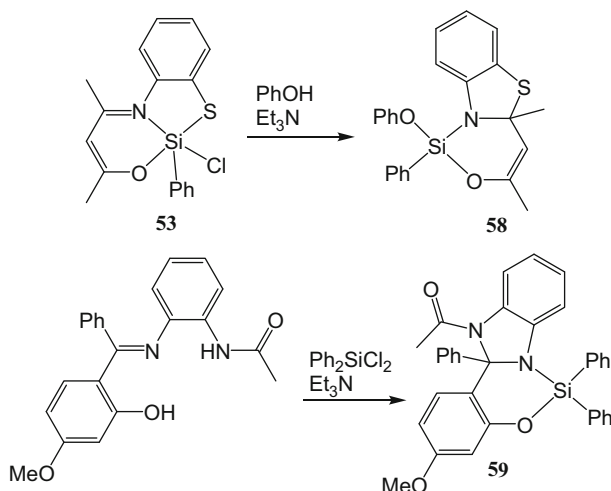
Further examples of formation of hypercoordinated silicon complex by rearrangement reactions include silicon-templated ring opening reactions, which give rise





**Scheme 10** Examples for Si-templated formation of multidentate chelators

to the installation of the chelator in the silicon coordination sphere (**53** and **54**, Scheme 10). The precursor may include all donor atoms in one molecule, as in case of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one [188–190], or two precursor ligands may rearrange to the new chelator, as shown in case of silylated benzoxazolone [191, 192]. In a related rearrangement reaction, an ONS-chelator (in **53**) combined with an acetylacetone derivative to yield complex **55** [193]. Another type of Si-templated ligand rearrangement involves bidentate Si-bound hydrazide derivatives and a hydride shift from Si to one of these ligands (**56**) followed by condensation of the two ligand moieties (**57**) [170].



**Scheme 11** Examples for rearrangement reactions of multidentate chelators in the Si coordination sphere

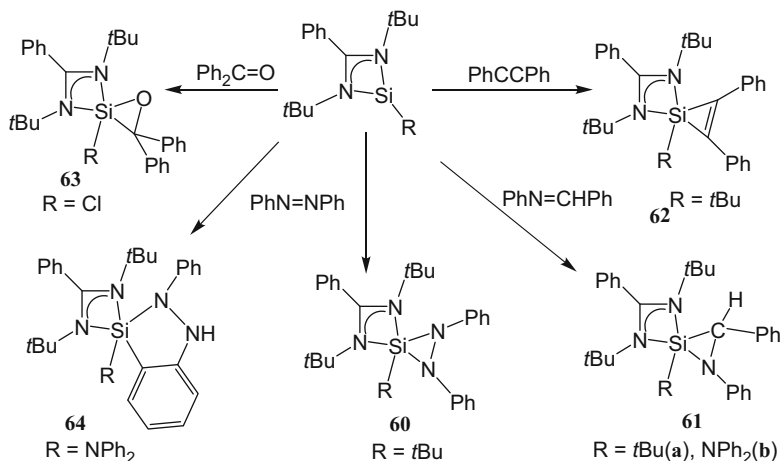
The opposite route, i.e., the withdrawal of a potential donor moiety by rearrangement and formation of a heterocycle, may also occur (Scheme 11), as shown for the formation of Si-bound 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one (in **58**) [194] and Si-bound benzimidazoline (in **59**) [195] out of tridentate chelators.

## 2.6 Oxidative Addition

In the past 5 years, much effort was dedicated to the exploration of the chemistry of amidinate-functionalized silylenes (Scheme 12). As the starting silylene already comprises a tricoordinated silicon atom, various oxidative addition reactions furnished silicon(IV) complexes with pentacoordinated Si atoms. Some of them comprise the striking features of three-membered SiNN (**60**) [196], SiNC (**61**) [196], SiCC (**62**) [196], or SiOC (**63**) [110] heterocycles, which are genuine novelties in silicon coordination chemistry. *o*-CH-activation of diazobenzene has also been observed (formation of **64**) [197].

Some related reactions (Scheme 13) have also been investigated for a disilylene (to afford **65**) [198], a related disilicon(I,III) system (to yield **66** and **67**) [199], and for a mononuclear silylene the oxidative addition of diphenylacetylene was found to proceed under formation of an Si–Si bond (formation of **68**) [200].

Further related reactions (Scheme 14) were found to result in cyclodimerization upon addition of diazomethane derivatives (**69**) [201], formation of cyclodisiloxane motifs with pentacoordinated Si atoms upon oxidation with N<sub>2</sub>O (**70**), and insertion into the C–Cl bonds of dichloromethane (**71**) [202].



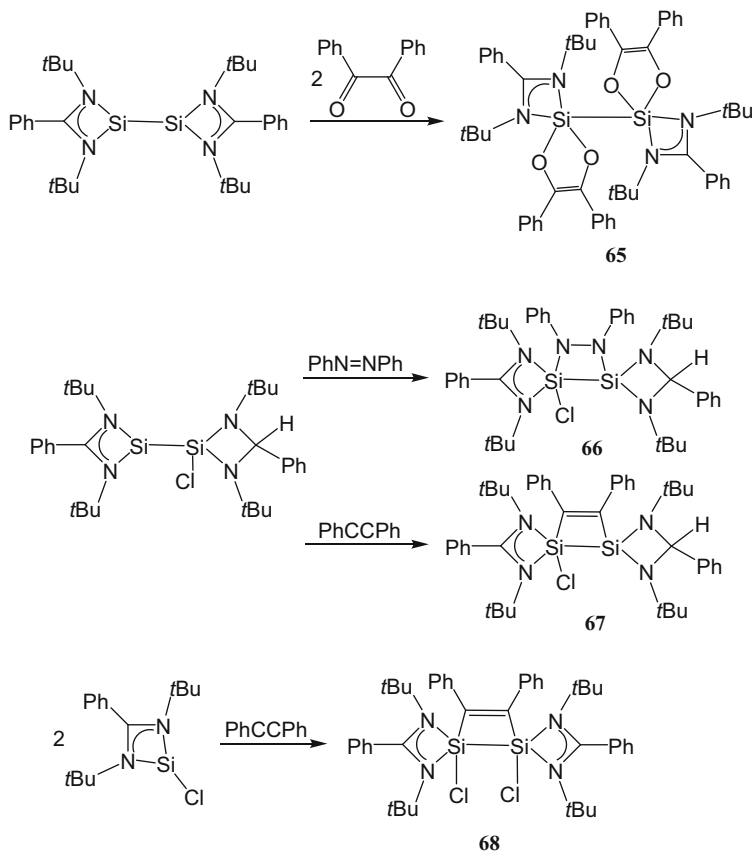
**Scheme 12** Oxidative addition reactions of an amidinate stabilized silylene with various unsaturated compounds

Oxidative addition to a related silylene (Scheme 15) afforded a hexacoordinated silicon complex with two Si–I bonds (**72**), the first crystallographically evidenced hexacoordinated iodosilicon complex so far [203]. Furthermore, addition of chalcogens E (S, Se, Te) afforded pentacoordinated Si compounds with Si=E bonds (**73**) [204].

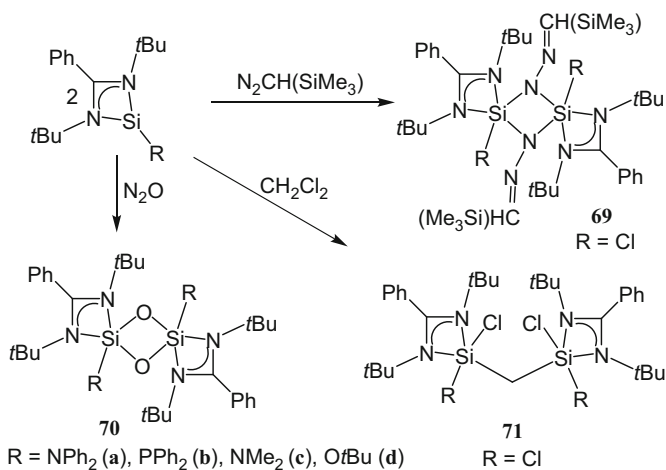
NHC-stabilized dichlorosilylene was shown to exhibit similar behavior in oxidative addition reactions (Scheme 16), i.e., formation of a SiOC three-membered heterocycle upon addition of benzophenone (**74**), whereas in the reaction with benzil, the formation of a five-membered heterocycle is favored (**75**) [110]. The reaction with diphenylacetylene involves silylene oligomerization to also yield a compound with five-membered silacycle (**76**) [109].

N-heterocyclic silylenes (NHSis) with acetylacetonate diimine dianions as backbone were also shown to undergo oxidative addition which involves formation of hypercoordinated silicon complexes (Scheme 17). Particularly noteworthy appears the formation of a compound with SiOO three-membered heterocycle (**77**), which could be isolated on its way of rearranging into a urea-stabilized silanone [111]. Oxidative addition of a phenol to a similar NHSi followed by addition of another phenol to the resultant silyl enamine also afforded a pentacoordinated silicon complex (**78**) [205], and the addition of a carboxylic acid hydrazide proceeds in a similar manner (to afford **79**) [206]. The second step in these addition sequences, the addition reactions between silyl enamines and various Brønsted acids, has already been shown capable of augmenting the silicon coordination number [207–209].

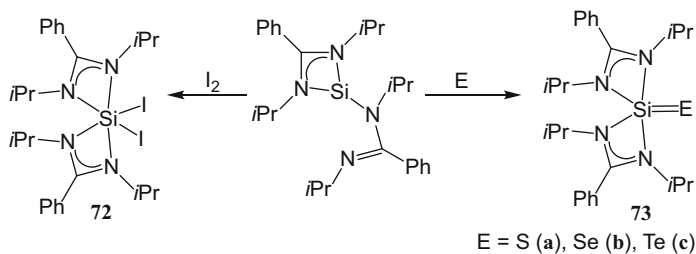
For structurally different P-donor-stabilized silylenes (Scheme 18) a related formation of a SiCO three-membered heterocycle (upon oxidative addition of mesityl carbaldehyde) was reported (formation of **80**) [210], and an oxidative addition of CO<sub>2</sub> (under release of CO) to a P-donor-stabilized disilylene afforded a bridged disiloxane motif with pentacoordinated Si atoms and a bridging carbonate ligand (**81**) [211].



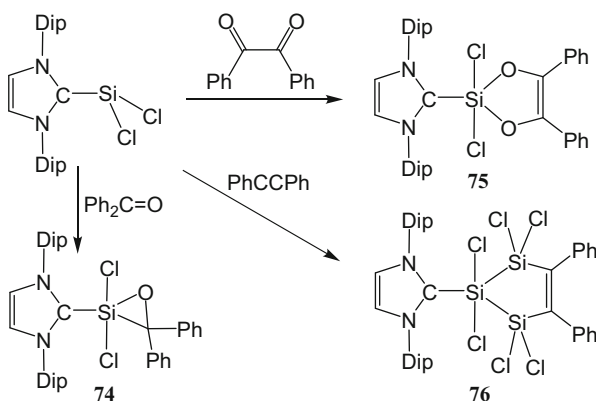
**Scheme 13** Further oxidative addition reactions with amidinate stabilized silylenes



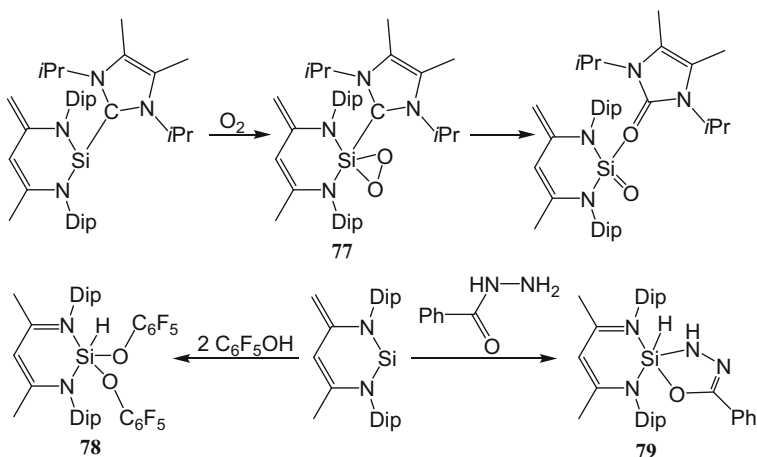
**Scheme 14** Further oxidative addition reactions with amidinate stabilized silylenes



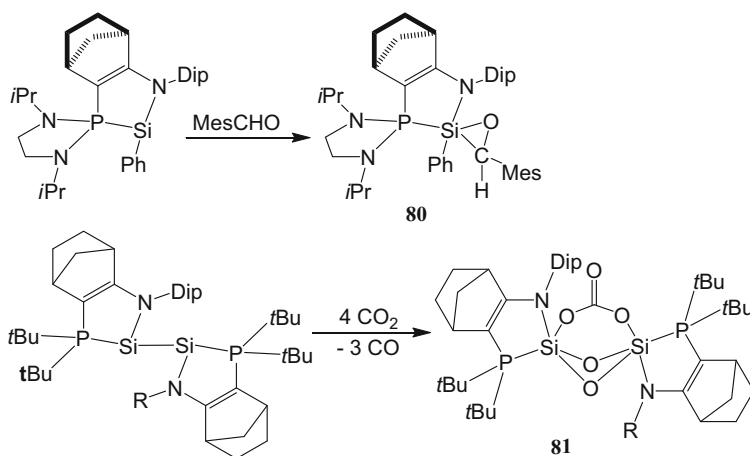
**Scheme 15** Formation of a hexacoordinated iodosilicon complex and pentacoordinated silachalcogenones by oxidative addition reactions with an amidinate stabilized silylene



**Scheme 16** Oxidative addition reactions with an NHC-stabilized silylene



**Scheme 17** Oxidative addition reactions with six-membered *N*-heterocyclic silylenes

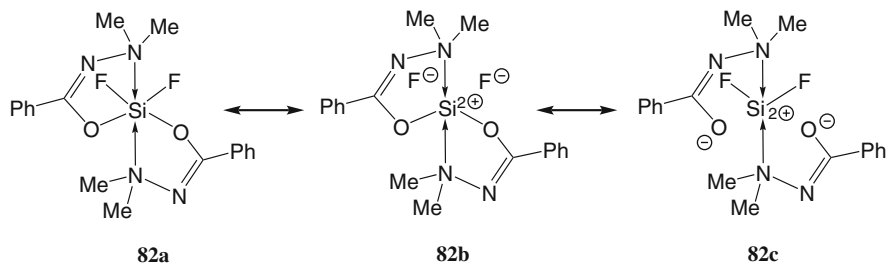


**Scheme 18** Oxidative addition reactions with P-donor-stabilized silylenes

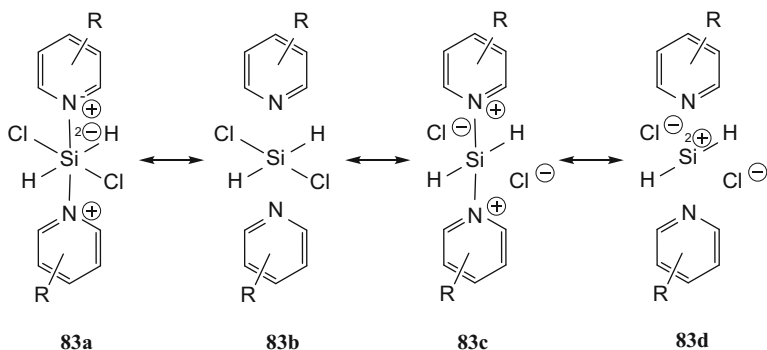
### 3 General Aspects of Structure

In a landmark paper Stalke et al. demonstrated with experimental and theoretical charge density studies on the molecule **82** (Scheme 19) that the silicon atom in this molecule is definitely not hypervalent (by means of more than four covalent bonds, thus exceeding the valence shell electron octet of silicon) [212]. Two different kinds of bonds around the hexacoordinated silicon atom are present. The Si–N bonds in **82** clearly are dative bonds with completely different properties than shorter nondative Si–N bonds. The question of whether dative bonds are to be classified as covalent or ionic remains controversial. Almost all properties in this molecule derived from both experiment and theory suggest ionic domination, and it is just the deformation of the lone pair charge concentration that might introduce a notable covalent contribution. The four remaining Si–O and Si–F bonds indicate predominantly ionic contributions and just a small covalent augmentation [212]. It was pointed out by the authors that “... all the electronic properties emphasize the dominance of the Lewis structures **82b** and **82c** in Scheme 19 to the appropriate bond description, and the covalent contribution obviously is much lower than commonly anticipated.” A short summary of these results can also be found in [213].

A high degree of ionic bonding was also observed in adducts of dichlorosilane, trichlorosilane, and dichloromethylsilane with substituted pyridines [101, 103]. For example, four possible valence structures **a–d** (Scheme 20) have been investigated with the NBO method for compound **83**, with the valence structures **b**, **c**, and **d** being equally good descriptions of the bonding situation. The analysis of the topological properties of the electron density distribution (AIM) suggests that the Lewis structure **c** represents best the bonding situation in molecules of this type [101].

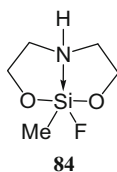


**Scheme 19** Proposed Lewis structures for compound **82**

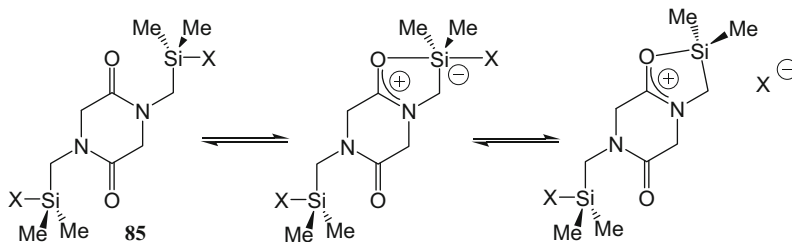


**Scheme 20** Proposed Lewis structures for compound **83**

Experimentally determined and theoretically calculated electron density distribution functions of the fluoroquasisilatrane **84** have been investigated [214].



The quantum theory of atoms in molecules (QTAIM or AIM) [215–217] is now often used for the analysis of the electron density distribution in higher-coordinated silicon complexes. There are further works dealing with the properties of chemical bonding in 1-hydrosilatrane [218], 1-fluorosilatrane [219], several complexes of tris(pentafluorophenyl)silanes with neutral Lewis bases [92], and chlorosilanes of the composition  $\text{Cl}_{3-n}\text{H}_n\text{SiOCH}_2\text{CH}_2\text{NMe}_2$  ( $n = 1-3$ ) [220].



**Scheme 21**  $S_N2$  Profile at the silicon atom of compound **85** (X=F, Cl, OTf, Br, I)

### 3.1 Compounds with Pentacoordinated Silicon Atoms

Pentacoordinated silicon compounds might form a trigonal bipyramid (TBP), a square pyramid (SP, or more generally rectangular pyramid), or all possible geometries in between. The coordination sphere in pentacoordinated silicon compounds is generally very flexible with low energy differences between TBP and SP structures [221]. Several methods have been applied to quantify the degree of deformation of a TBP towards a SP [222–224]. The geometric features of compounds with pentacoordinated main group and transition metal element atoms have been reviewed comprehensively by Holmes [225]. Only recently reported aspects of geometry in pentacoordinated silicon compounds will be briefly discussed here.

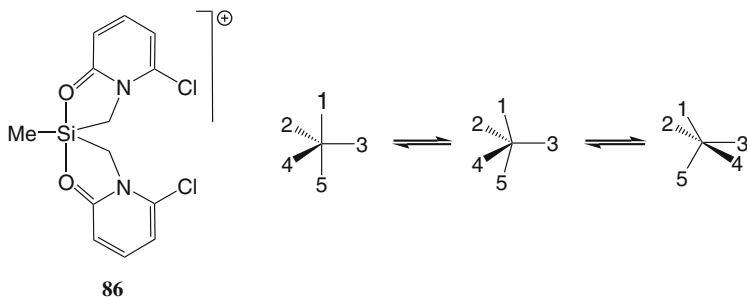
A series of binuclear pentacoordinated silicon complexes **85** of diketopiperazine have been synthesized and substituent (or leaving group) effects on the Si-O coordination have been studied for five analogues with X=F, Cl, OTf, Br, and I [226]. Variable-temperature NMR spectroscopy (supported by X-ray crystallography) shows, for the first time in binuclear pentacoordinated silicon complexes, a complex equilibrium with both nonionic (O–Si) and ionic (Si–X) dissociation of the axial bonds in the silicon-centered trigonal bipyramids. The two dissociation pathways are consistent with a model for nucleophilic substitution at the silicon atom in a binuclear pentacoordinated silicon compound (Scheme 21) [226].

The conformations of four independent cations of the compound **86** correspond to different points on the Berry pseudorotation pathway (Scheme 22) [221]. The percentage of square planar character varies between 19% and 40%.

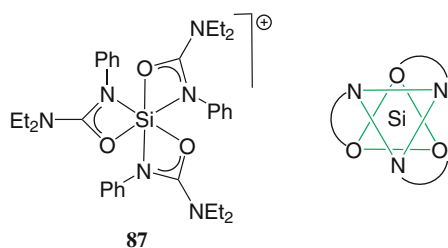
### 3.2 Compounds with Hexacoordinated Silicon Atoms

Hexacoordinated silicon complexes form octahedra in most cases, or with different ligands distorted octahedra. Deviations from this rule of thumb are seldom observed. One exception in the last 5 years was the distorted trigonal antiprismatic cationic silicon complex **87** with ureato ligands (Scheme 23) [227].





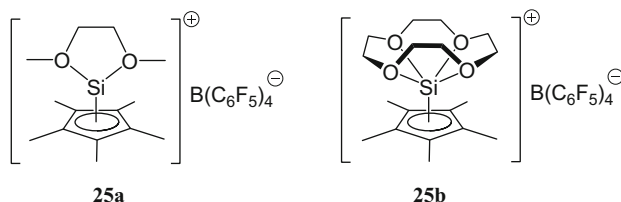
**Scheme 22**  $S_N2$  Cationic pentacoordinated silicon complex **86** (left) and schematic representation of a Berry pseudorotation process (right) [221]



**Scheme 23** Cationic silicon complex **87** with ureato ligands (left) and schematic representation of a trigonal antiprismatic coordination geometry (right)

### 3.3 Coordination Numbers Higher than Six

Whereas Si-hypercoordination is most frequently observed with five or six formal electron pair donors, silicon coordination numbers higher than six have also been realized. However, examples for such higher-coordinated silicon compounds bearing more than six formal lone pair donors in the coordination sphere are rare. Thus, only a few but quite fascinating compounds with Si coordination numbers higher than six have been reported during the last 5 years. Among these were ionic silicon(II) compounds derived from  $[Cp^*Si]^+$ . This highly reactive ion is stabilized by complexation with dimethoxyethane (DME) (in **25a**) and 12-crown-4 (in **25b**) [136]. Considering the  $Cp^*$  anion a formal three-electron-pair donor, the hepta- and nona-coordinated Si atoms of **25a** and **25b**, respectively, are surrounded by five and seven formal electron pair donors, respectively.



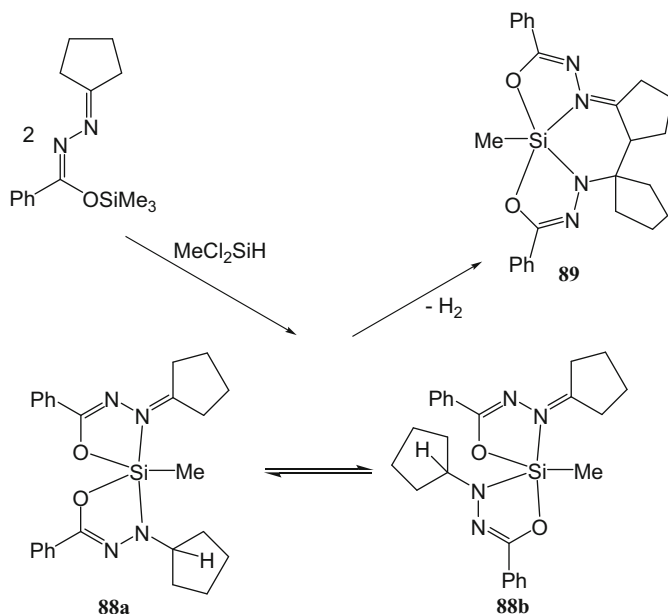
Further examples with Si coordination numbers greater than six are encountered with oligometallic (or oligometalloidic) clusters. The preparation and X-ray structures of  $\text{Si}@\text{Al}_{14}\text{R}_6$  ( $\text{R} = \text{Cp}^*$ ,  $\text{N}(\text{dip})\text{SiMe}_3$ ;  $\text{dip} = 2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3$ ) are described via the disproportionation and substitution reaction of a metastable  $\text{AlCl}$  solution [228]. The silicon atom in these compounds occupies the center of an  $\text{Al}_8$  cube. This central unit is stabilized through capping of six faces of the cube by  $\text{AlR}$  moieties.

Some new Zintl anions containing silicon atoms in high coordination numbers have been reported since 2008. Among these were  $[\text{Rb}(18\text{-crown-6})]\text{Rb}_3\text{Si}_9\cdot 4\text{NH}_3$ ,  $\text{Rb}_4\text{Si}_9\cdot 4.75\text{NH}_3$ , and  $\text{Rb}_4\text{Si}_9\cdot 5\text{NH}_3$  [229, 230]. Single-crystal X-ray diffraction analysis reveals the presence of  $\text{Si}_9^{4-}$  anions. The nonasilicide anions are coordinated by rubidium cations, thus expanding the coordination number of the silicon atoms above six. The reaction of  $\text{K}_6\text{Rb}_6\text{Si}_{17}$ ,  $\text{MesCu}$ , and 18-crown-6 in liquid ammonia yielded crystals of  $[\text{Rb}(18\text{-crown-6})]_2\text{Rb}_{1.54}\text{K}_{0.46}[(\text{MesCu})_2\text{Si}_4](\text{NH}_3)_{12}$  [230]. This compound contains a tetrahedral tetrasilicide(4−) anion which is stabilized by mesityl-copper units and rubidium cations thus yielding coordination numbers higher than six for the silicon atoms involved in this tetrasilicide. In a similar way the isotopic compound  $[\text{Rb}(18\text{-crown-6})]_2\text{Rb}_2[(\text{MesCu})_2(\text{Si}_{3.3}\text{Ge}_{0.7})](\text{NH}_3)_{12}$  has been synthesized [231].

Some recent publications deal with Keggin-type polyoxo-tungstates and polyoxo-molybdates featuring central silicon atoms [232–234]. In CSD and CA registry database searches these compounds might appear as higher-coordinated silicon species probably due to complex nature of these anions. However, the central silicon atom in anions of composition  $[\text{SiM}_{12}\text{O}_{40}]^{4-}$  ( $\text{M} = \text{Mo}, \text{W}$ ) is tetracoordinated. These Keggin-type polyoxometalates therefore do not belong to the class of higher-coordinated silicon compounds considered here.

### 3.4 Equilibria Between Complexes with Different Coordination Numbers

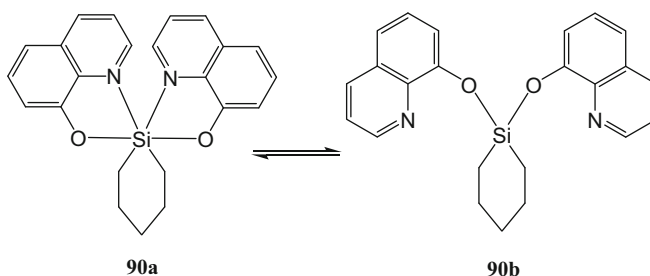
Equilibria between hexa- and pentacoordinated silicon complexes have been examined carefully by Kost et al. Exemplarily the following works might be cited here: Neutral hexacoordinated silicon complexes derived from hydrazide chelating ligands with imino-donor groups form pentacoordinated Si complexes in the course of ionic dissociation reactions. Such complexes were shown to undergo facile intramolecular aldol-type condensation [176]. In a related system



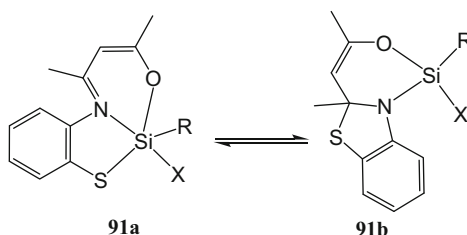
**Scheme 24** Equilibrium between two isomeric silicon complexes (**88a** and **88b**) with penta-coordinated Si atom

(Scheme 24), the hydride migration from silicon to an adjacent unsaturated imino carbon atom leads to a pentacoordinated silicon complex **89** as final product [170]. For the intermediate **88** a dynamic equilibrium between two conformers **88a** and **88b** with pentacoordinated Si atom was observed by NMR spectroscopy. For related compounds with hexacoordinated Si atom within a  $(\text{O},\text{N})_2\text{SiMe}(\text{H})$  coordination sphere, the authors observed reversible neutral dissociation of the N–Si dative bond, i.e., an equilibrium between hexa- and pentacoordinated hydrido complexes of silicon [235].

In several cases it was possible to observe equilibria or to isolate crystalline derivatives containing tetra- and hexacoordinated silicon atoms with the same ligand system. Some examples are listed here: A bicapped tetrahedral intermediate or transition state has been postulated in neutral hexacoordinated mixed trichelate silicon complexes on the basis of the temperature dependence of the  $^1\text{H}$  NMR spectra and coalescence of signals due to diastereotopic *N*-methyl- and  $\text{CH}_2$  groups [156]. The silacycloalkanes  $(8\text{-oxyquinolate})_2\text{Si}(\text{CH}_2)_n$  ( $n = 3, 4, 5, 6$ ) (for  $n = 5$  see Scheme 25) reveal stepwise decreasing NSi coordination with increasing ring size. Whereas for  $n = 3$  and 4 hexacoordinated silicon compounds were found at room temperature,  $n = 5$  supports an equilibrium that allowed for the isolation of two coordination isomers (CN 4 and 6, compounds **90b** and **90a**, respectively) as crystalline solids, and  $n = 6$  causes the equilibrium to shift towards the tetracoordinated Si compound [175].



**Scheme 25** Equilibrium between two isomeric silicon complexes (**90a** and **90b**) with hexa- and tetracoordinated Si atom

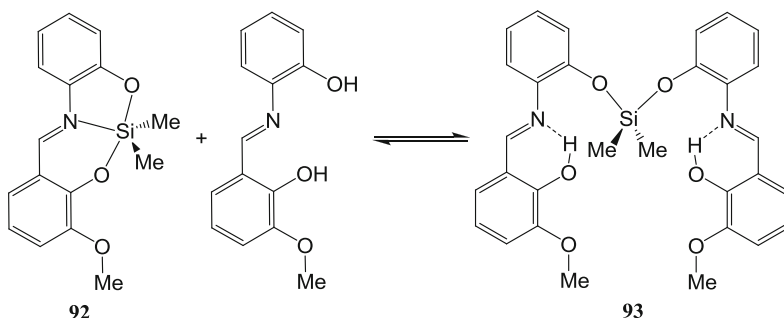


**Scheme 26** Dynamic equilibrium between penta-(**91a**) and tetracoordination (**91b**) in solution

Solution-state NMR studies of silicon complexes with tridentate O,N,S-ligands (Scheme 26) revealed the existence of dynamic equilibria between pentacoordinated silicon complexes (**91a**) and isomeric tetracoordinated species (**91b**) [190]. The ratio between tetra- and pentacoordinated complexes depends on the nature of the (pseudo) halogeno and organyl ligands and on the solvent. These effects are not yet fully understood. In the series of the halogenosilicon complexes, the halogeno ligands favor pentacoordination in the following rank order:  $I \approx Br > Cl > F$ . This is contrary to expectations if it is assumed that hard ligand atoms should favor pentacoordination of the hard silicon(IV) center [190].

A pentacoordinated (**92**) and a tetracoordinated silicon complex (**93**) were isolated from the reaction of 2-(2-hydroxy-3-methoxybenzylideneamino)phenol with dichlorodimethylsilane [236]. These complexes are related to one another via addition and elimination of one ligand molecule (Scheme 27). According to quantum chemical calculations, **93** is the thermodynamically stable product and **92** is the kinetically favored product.

Hexamethylphosphoramide (HMPA) adducts of tetrachlorosilane ( $\text{SiCl}_4$ ) were investigated with NMR spectroscopy in solution and solid-state structures [93]. In solution, the meridional and facial isomers of the hexacoordinated cationic silicon complex  $[\text{SiCl}_3(\text{HMPA})_3]^+\text{Cl}^-$  predominate at all HMPA concentrations and are in equilibrium with the hexacoordinated neutral *trans*- and *cis*- $[\text{SiCl}_4(\text{HMPA})_2]$  complexes, as well as the pentacoordinated cationic Si-complex *cis*- $[\text{SiCl}_3(\text{HMPA})_2]^+\text{Cl}^-$  [93].



**Scheme 27** Equilibrium between penta- (**92**) and tetracoordination (**93**) via addition and elimination of a ligand acid

## 4 Frequently Used Ligands and Donor Atoms

There are several types of ligand systems which have often been used to generate higher-coordinated silicon complexes within the last 5 years. These are:

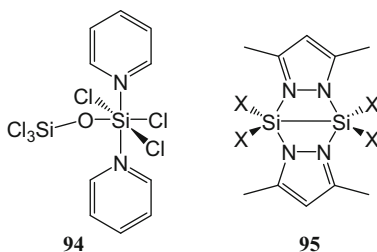
1. Neutral mono- and bidentate nitrogen bases
2. Bidentate ionic ligands with oxygen and nitrogen as donor atoms
3. Bidentate ligands forming four-membered rings with silicon
4. Bidentate ligands derived from carboxylic acids
5. Tridentate chelate ligands
6. Triethanolamines forming silatranes
7. Tetradentate chelate ligands of “salen”-type
8. Phthalocyanines

These classes of silicon complexes will be discussed in the following sections.

### 4.1 Neutral Mono- and Bidentate Nitrogen Bases

Adducts of chlorosilanes with neutral nitrogen bases are known since more than 40 years [237–239]. Recently a series of new compounds of this type involving hydrido-chlorosilanes has been synthesized, characterized by X-ray structure analysis, and investigated under different aspects. These compounds are hexacoordinated adducts of trichlorosilane, dichloromethylsilane, and dichlorosilane with substituted pyridines [101–103]. The main focus of these articles was the structural and spectroscopic characterization of the new compounds, including  $^{29}\text{Si}$  CP/MAS NMR investigation for experimental and theoretical evaluation of the tensor components of the  $^{29}\text{Si}$  NMR shift anisotropy. These complexes prefer a *trans* arrangement of the nitrogen ligands. This is not possible in complexes bearing chelating ligands like 2,2'-bipyridine or 1,10-phenanthroline. Various hexacoordinated silicon complexes

have also been prepared with these two nitrogen donor ligands, i.e., by complexation with  $\text{H}_2\text{SiCl}_2$ ,  $\text{HSiCl}_3$ ,  $\text{RSiCl}_3$  ( $\text{R} = \text{Me}, \text{Ph}$ ), and  $[\text{Na}(\text{CH}_3\text{CN})_n]^+_2 (\text{Si}(\text{N}_3)_6)^{2-}$  [142, 168]. Possible applications of silicon complexes with neutral nitrogen donor ligands have been outlined in a paper dealing with the preparation of sol–gel-derived Si/C/O/N materials. Therein the reactions of hexachlorodisiloxane ( $\text{Cl}_3\text{Si}-\text{O}-\text{SiCl}_3$ ) with bis(trimethylsilyl)carbodiimide ( $\text{Me}_3\text{Si}-\text{NCN}-\text{SiMe}_3$ ) were catalyzed with pyridine. The crystal structure of  $\text{Cl}_3\text{Si}-\text{O}-\text{SiCl}_3(\text{pyridine})_2$  **94** was determined and it was concluded that this compound is a potential intermediate in the pyridine catalyzed sol–gel process [240].

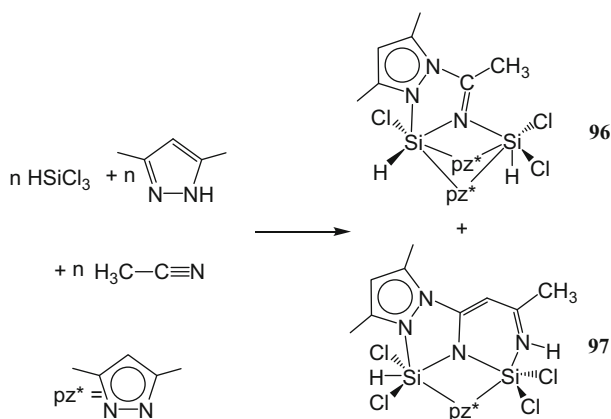


The reaction conditions for the synthesis of  $[\text{Si}_2(\text{pz}^*)_6]$  and  $[\text{Si}(\text{pz}^*)_4]$  have been investigated in detail in order to obtain suitable precursor compounds for the synthesis of the hitherto unknown Janus-head ligand tris(3,5-dimethylpyrazolyl)silanide ( $[\text{Si}(\text{pz}^*)_3]^-$  [241]. The X-ray structures of several pentacoordinated disilanes of type **95** with  $\text{X} = \text{Cl}$  or 3,5-dimethylpyrazolyl have been presented in this work. The chemistry of 3,5-dimethylpyrazolyl silicon complexes has been further explored. Although pyrazolide is an anionic substituent, its second N atom (the imine N atom of N-silylated pyrazole) also coordinates to silicon, thus exhibiting features of a neutral nitrogen donor as well.

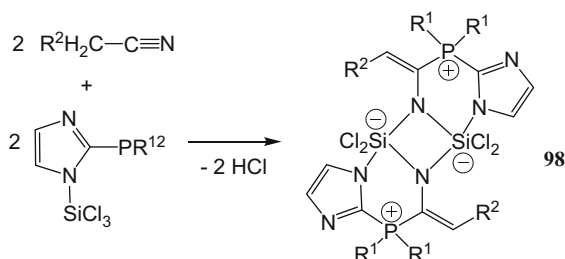
A complex system of equilibria of both Si–Cl vs. Si–N dismutation and intramolecular Si–N exchange was observed with NMR spectroscopy in  $\text{Si}(\text{pz}^*)_4$  and  $\text{Si}(\text{pz}^*)_3\text{Cl}$  [106]. The reaction of  $\text{Me}_3\text{Si}(\text{pz}^*)$  with  $\text{H}_2\text{SiCl}_2$  leads to the unexpected formation of a silicon complex with three silicon atoms [134]. The lateral silicon atoms are pentacoordinated; the central silicon atom is hexacoordinated. Furthermore, it was found that the reaction of  $\text{HSiCl}_3$  with 3,5-dimethylpyrazole in acetonitrile gives 3,5-dimethylpyrazolyl silicon complexes where one (**96**) or two molecules acetonitrile (**97**) have been inserted into the bond between silicon and the 3,5-dimethylpyrazolyl ligand (see Scheme 28) [134].

Silicon-mediated nitrile activation has also been observed in trichloro [2-(dialkylphosphanyl)imidazol-1-yl]silanes (Scheme 29) [133]. These react with aceto- or propionitrile to yield the dinuclear pentacoordinated silicon complexes **98**. The reactions leading to **96**, **97**, and **98** hint to new pathways of catalytic activation mediated by dinuclear silicon complexes.

An unusual hydrolysis product **99**, which contains three hexacoordinated silicon atoms, was observed in reactions between  $\text{HSiCl}_3$  and 3,5-dimethylpyrazole ( $\text{Hpz}^*$ ) [134]. The cationic complex consists of three  $\text{pz}^*$  bridged Si–H units

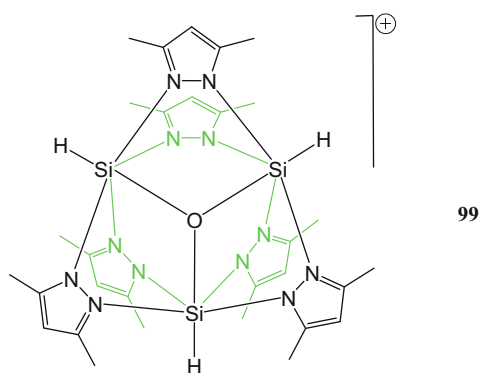


**Scheme 28** Formation of binuclear silicon complexes as formal products of acetonitrile insertion



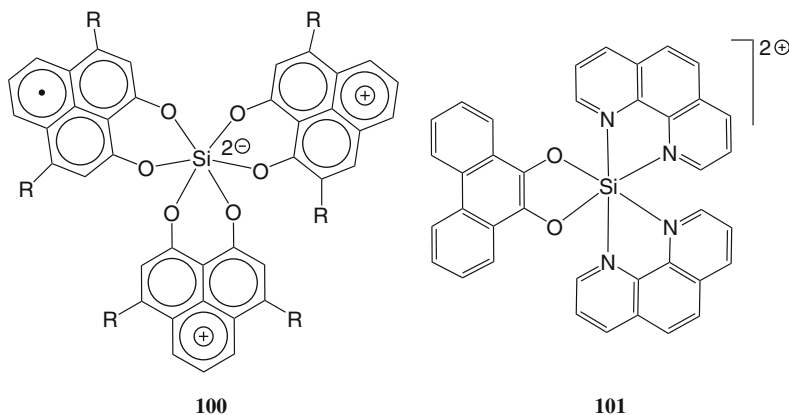
**Scheme 29** Insertion of nitriles in trichloro[2-(dialkylphosphanyl)imidazol-1-yl]silanes ( $\text{R}^1 = \text{Et}$ ,  $i\text{-Pr}$ ;  $\text{R}^2 = \text{H}$ ,  $\text{Me}$ )

and one oxo ligand in the center. Three crystal structures obtained from different reaction batches hint to the fact that this hydrolysis product might be exceptionally stable.



## 4.2 Bidentate Ionic Ligands with Oxygen and Nitrogen as Donor Atoms

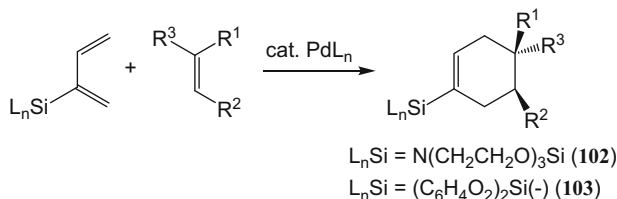
Bidentate O,O-ligands like phenolates, glycolates, tartrates, and compounds bearing simple O,N and N,N chelating ligands are in the focus of this section. Trisphenalenyl-silicon neutral radicals **100** (R=H, OMe) have been synthesized, characterized, and their solid-state properties have been investigated [242, 243]. Such compounds were proposed as building blocks for molecular conductors and provide an alternative approach to the conventional charge-transfer organic conductors and superconductors, in which the unpaired electrons of the neutral radicals serve as charge carriers. Several substituted catechols and sterically bulky natural flavones were used as 1,2-diolate anionic ligands to encapsulate silicon in an O<sub>6</sub> coordination sphere [244]. Electron-withdrawing groups at the aromatic ring favor a greater stability and better yields of the complexes. Octahedral silicon complexes bearing two 1,10-phenanthroline ligands and one arenediolate ligand as **101** were investigated as a structural motif for the design of hydrolytically stable bioactive complexes as demonstrated with the generation of silicon-based high-affinity DNA binders [245]. This proof-of-principle study suggests that octahedral silicon complexes are promising structural templates for widespread applications in chemical biology and medicinal chemistry.



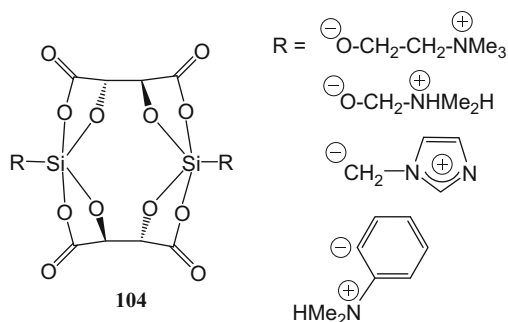
The use of 2-silyl-substituted 1,3-dienes in Diels–Alder and cross-coupling reactions was reported in [246]. Among other silicon compounds the authors utilized silatranyl (**102**) and catecholato-chelated silyl derivatives (**103**) with penta-coordinated Si atoms for the reactions shown in Scheme 30.

A series of zwitterionic and anionic dinuclear pentacoordinated silicon complexes with bridging (R,R)-tartrato ligands have been prepared and characterized [117, 247]. Common structural features of these compounds are two bridging tartrate ligands forming a cage-like unit with two silicon atoms. This leaves space for the coordination of a fifth ligand. For this purpose often zwitterionic groups are used, which





**Scheme 30** Diels–Alder reactions of 2-silyl-substituted 1,3-dienes with pentacoordinated silicon atoms



**Scheme 31** Examples for zwitterionic dinuclear pentacoordinated silicon complexes with bridging (*R,R*)-tartarato ligands

render the complexes **104** charge neutral. Examples of such compounds are shown in Scheme 31. They were thoroughly characterized and their hydrolytic stability was investigated with respect to the role such complexes (or related compounds) might play in the biochemistry of silicon. Tartaric acid has been used in combination with (2-oxopiperidin-1-yl)methyl to prepare similar dinuclear silicon complexes such as **104**. Since the (2-oxopiperidin-1-yl)methyl ligand is a monoanion, dianionic complexes are obtained, which are stabilized by dicyclohexylammonium cations [248].

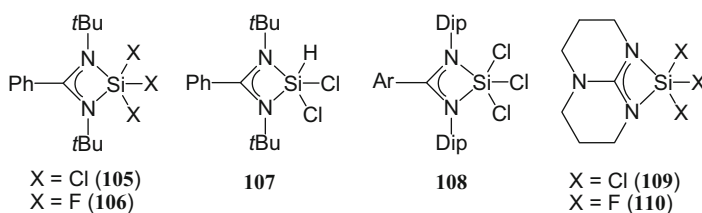
Simple  $\alpha$ -amino acids have been utilized as dianionic and monoanionic chelating ligands to stabilize hexa- and pentacoordinated silicon complexes [249]. The hydrolysis reactions of these compounds lead to the formation of free  $\alpha$ -amino acids and alkylsilanetriol  $\text{RSi}(\text{OH})_3$ . In case of  $\text{R}=\text{Me}$ , methylsilanetriol is generated. This species is considered as a “silicon food supplement” for use in humans and is currently being discussed as a potential drug for the improvement of bone and other connective tissue health. Therefore, such silicon complexes might serve as silicon food supplements or as pro-drugs for methylsilanetriol. The reaction of *O*-trimethylsilyl-*L*-mandelic *N,N*-dimethylamide with tetrachlorosilane leads to a new complex with pentacoordinated silicon and a monoanionic (O,O) chelating ligand [250].

Penta- and hexacoordinated silicon complexes have been prepared with  $\beta$ -diketonato ligands generated from 1,3-diphenylpropane-1,3-dione and 1-phenylbutane-1,3-dione [128]. Several bidentate O,O-ligands and one O,N-ligand have been used to synthesize pentacoordinated silicon complexes containing the tris(pentafluorophenyl)silyl unit [92]. These bidentate ligands have been generated from salicyl aldehyde, *N*-(2-hydroxybenzoyl)pyrrolidine, *N*-methyl-*N*-(2-hydroxybenzylidene)amine, succindicyclopentylamide, and by aldol coupling of 1-tris(pentafluorophenyl)silyloxycyclopentene with isobutyraldehyde.

With 8-oxyquinolate as an O,N-ligand it was shown that the donor–acceptor interaction between the nitrogen atom of the 8-oxoquinolate ligand and the central silicon atom can be tuned by a stepwise increase of the ring size of a cycloalkyl group in the silacycloalkane series (8-oxyquinolate)<sub>2</sub>Si(CH<sub>2</sub>)<sub>*n*</sub> (*n* = 3, 4, 5, 6) (see Scheme 25) [175]. Strong intramolecular Si–N interactions have been proven to exist in the chlorosilanes Cl<sub>3–*n*</sub>H<sub>*n*</sub>SiOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (*n* = 1–3) [220]. Further work by the same group of Mitzel et al. shows that geminal Si–N interactions exist in compounds of the type C<sub>6</sub>F<sub>5</sub>SiF<sub>2</sub>–X–NMe<sub>2</sub> with X = NSiMe<sub>3</sub> and X = O but not with X = CH<sub>2</sub> [251].

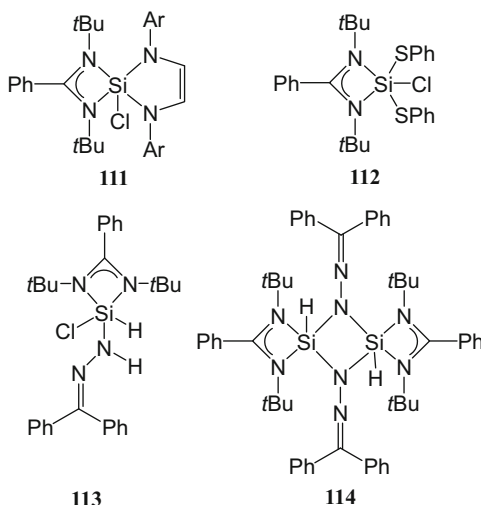
### 4.3 Bidentate Ligands Forming Four-Membered Rings with Silicon

Benzamidinates (and guanidines) are able to stabilize pentacoordinated silicon complexes. The amidinate ligand coordinates via both nitrogen atoms to the central silicon atom, which is further supplemented by three other anionic ligands as it is shown exemplarily by the compounds **105–110** [200, 252–254].



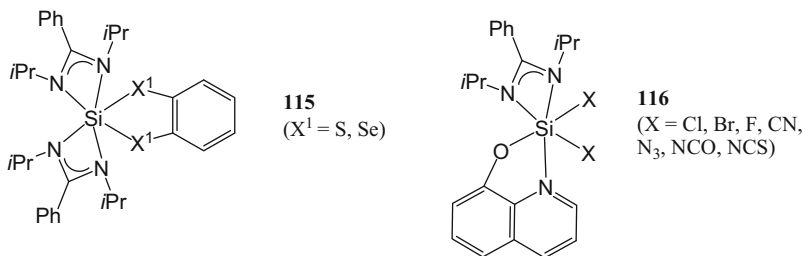
Starting from **107**, the heteroleptic chlorosilylene PhC(NtBu)<sub>2</sub>SiCl is accessible [200]. This silylene has been utilized as a substrate to prepare various higher-coordinated silicon compounds. In a series of publications a rich chemistry was developed with several oxidative addition reactions and has therefore already been addressed in Sect. 2.6 (see Schemes 12, 13, and 14). Further reactions of

this silylene include oxidative addition of a glyoxaldiimine to afford a formal [1+4]-cycloaddition product **111**. When treated with diphenyl disulfide, cleavage of the S–S bond occurs to form **112** [255].



The reaction of chlorosilylene  $\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}$  with diphenylhydrazone leads to a diphenylhydrazone derivative **113** with pentacoordinated silicon atom. Therefrom a disilicon compound **114** with a  $\text{Si}_2\text{N}_2$  core is prepared under  $\text{HCl}$  elimination [256]. The reaction of  $\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}$  with  $\text{N}_2\text{O}$  afforded a trimer which contains a  $\text{Si}_3\text{O}_3$  six-membered ring with pentacoordinated silicon atoms [257]. The reaction of  $\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}$  with 2-adamantanone furnishes a [1+2]-cycloaddition product, whereas treatment with 3,5-di-tert-butyl-*o*-benzoquinone leads to the [1+4]-cycloaddition product [258]. Both compounds contain pentacoordinated silicon atoms. The reaction of this silylene with diazobenzene afforded an unsymmetrical polycyclic product via chlorosilylene-mediated aromatic C–H bond activation. The reaction proceeds without the cleavage of the N–N bond of diazobenzene [259]. Another example of bond activation was demonstrated to occur in the reactions of  $\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}$  with hexafluorobenzene and other fluorinated arenes, which afford silicon(IV) fluorides with pentacoordinated silicon atoms [260]. This chemistry was further explored recently by investigating the reactivity of  $\text{LSi-SiL}$  [198],  $\text{LSi-Si(Cl)HL}$  [199],  $\text{LSi}(t\text{-Bu})$  [196], and  $\text{LSi}[\text{C}(\text{SiMe}_3)_3]$  [261]  $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$ . Cycloaddition and oxidative addition reactions with these silylenes and bis-silylenes give access to a steadily growing number of unusual silicon complexes with pentacoordinated silicon atoms (see also Sect. 2.6).

A number of hexacoordinated silicon complexes have been prepared by using benzamidinato ligands mainly in combination with other chelating ligands [154, 262]. Examples are compound **72** (Scheme 15) and the compound classes **115** and **116**.

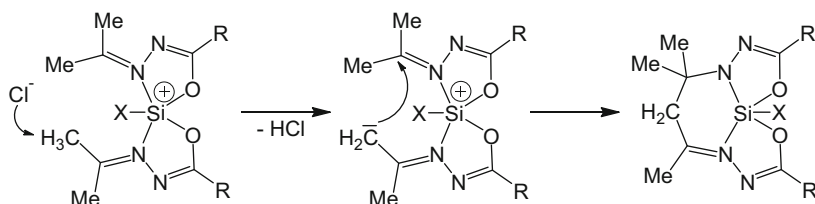


Ureato ligands with coordination ability via one carbonyl oxygen and a nitrogen atom represent an alternative to the benzamidinato ligands discussed above. They form also four-membered cycles with the silicon atom. Only one publication appeared in the past 5 years using this ligand system to prepare higher-coordinated silicon complexes. The distorted trigonal antiprismatic cationic silicon complex **87** (Scheme 23) with ureato ligands was characterized by X-ray structure analysis and <sup>29</sup>Si CP/MAS NMR spectroscopy [227].

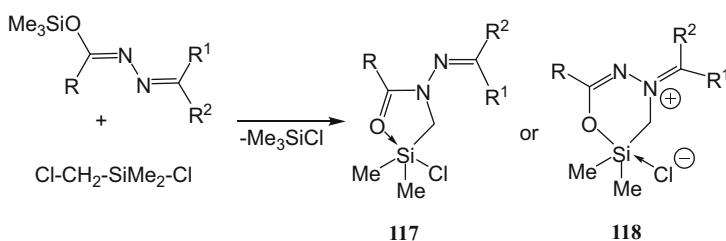
#### 4.4 Bidentate Ligands Derived from Carboxylic Acids

A multifaceted chemistry of higher-coordinated silicon complexes has been developed utilizing hydrazide chelating ligands with imino-donor groups. Neutral hexacoordinated silicon complexes derived from these ligands and their penta-coordinated ionic dissociation products undergo facile intramolecular aldol-type condensation catalyzed by their chloride counterion leading to formation of a third chelate ring (Scheme 32) [176]. Furthermore, rearrangements involving silicon-bonded cyanide and *t*-Bu groups [176], hydride migration from silicon to an adjacent unsaturated imino carbon [170], reversible neutral dissociation of the N–Si dative bond [235], dynamic stereochemistry [156], and both chelate ligand exchange and central-element exchange [263] have been observed with complexes of this type.

Another effective route to pentacoordinated silicon complexes with ligand systems derived from carboxylic hydrazides is the reaction of *O*-trimethylsilylated hydrazide Schiff-base derivatives (at the terminal nitrogen atoms) [RC(OSiMe<sub>3</sub>)=NN=CR'R''] with chloro(chloromethyl)dimethylsilane [ClCH<sub>2</sub>SiMe<sub>2</sub>Cl] (Scheme 33) [264]. This reaction proceeds in a regioselective manner, forming either five-membered (**117**) or zwitterionic six-membered chelate complexes (**118**) with pentacoordinated silicon. The type of product is determined by the size of the substituent R. Bulky groups (R=Ph, *t*-Bu) lead to exclusive formation of complexes with six-membered chelate, whereas with the less bulky groups (Me, PhCH<sub>2</sub>), only the five-membered



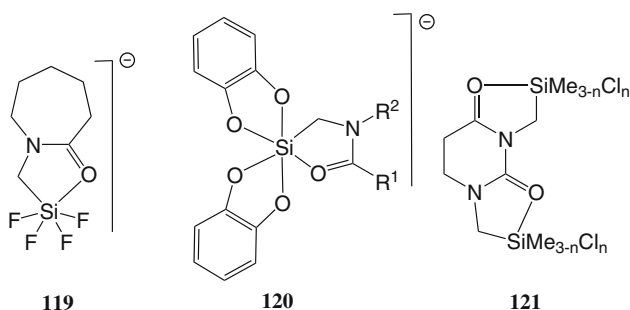
**Scheme 32** Intramolecular aldol-type condensation catalyzed by a chloride counterion



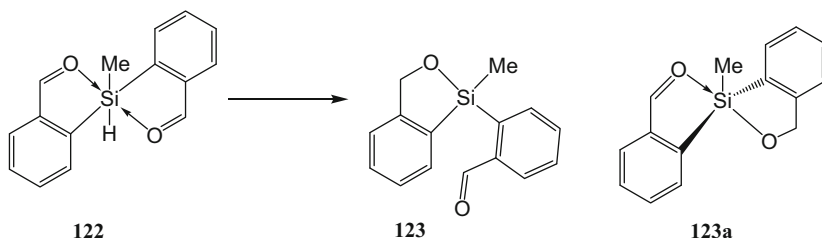
**Scheme 33** Reaction of *O*-trimethylsilylated hydrazides with chloro(chloromethyl)dimethylsilane

chelate is obtained. Upon mild heating, the six-membered chelate complex **118** transforms into its five-membered isomer **117** [264].

Amides and hydrazides of carboxylic acids have been also used successfully by other groups to stabilize penta- and hexacoordinated silicon. The compounds **119** [265], **120** [266], and **79** [206] serve as examples.



Compound **119** involves a cyclic amide of an  $\omega$ -amino acid as ligand. Related to this are complexes containing cyclic amides like uracil (**121**), barbituric acid, 5,5-dimethylbarbituric acid [116], 2,5-piperazinedione (**85**) [226], and 2-chloro-6-hydroxypyridine (**86**) [221], respectively, to accomplish pentacoordination at silicon.



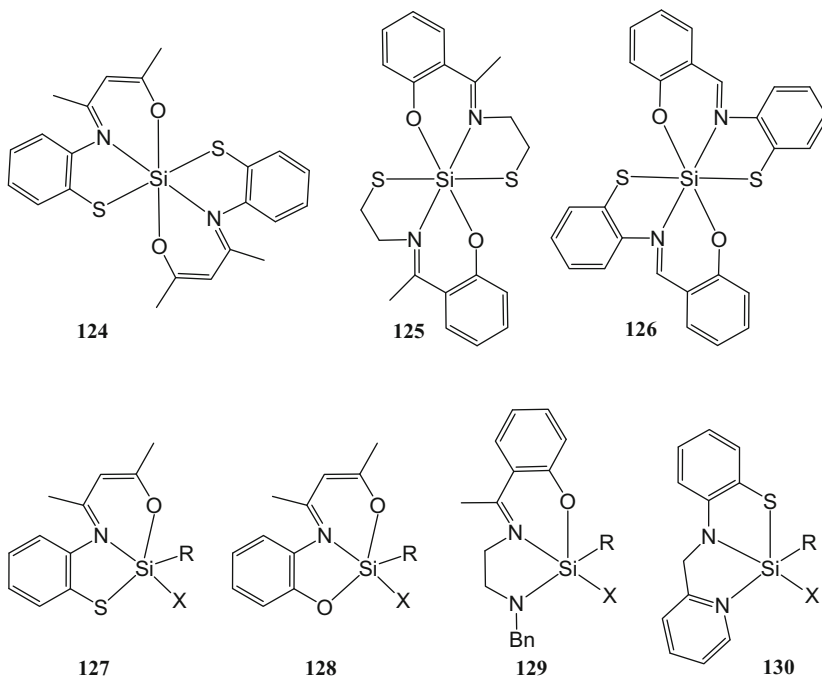
**Scheme 34** Hydride migration from Si to an aldehyde C atom

These compounds were investigated with variable-temperature NMR spectroscopy supported by X-ray crystallography. It was shown that a complex equilibrium with both nonionic (O–Si) and ionic (Si–X) dissociation of the axial bonds in the silicon-centered trigonal bipyramids exists (*vide supra*) [226].

A hexacoordinated silicon complex with two ortho-silylated benzaldehyde ligands **122** has been proposed as an intermediate in the formation of compound **123** (Scheme 34) [267]. Notably, the authors have published a crystal structure and interpreted the molecule as compound **122**, but a closer inspection of the X-ray structure data shows (1) the silicon coordination sphere is trigonal-bipyramidal (equatorial situation of three Si–C bonds, axial situation of two Si–O bonds), (2) the Si-bound hydrogen atom has been refined in an unreasonable position (very close to one Si–O bond), (3) the quality of the structure is poor (R-factor 7.8%), (4) the thermal displacement ellipsoids of the Si and O atoms are unusually large, and (5) the C=O bond lengths are refined to 1.30 Å. Thus, we suspect that the crystal structure reported had been determined from compound **123a**, an isomer of the proposed compound **123** with pentacoordinated Si atom, and disorder of the two chelating ligands causes the unusually large ellipsoids of Si and O atoms and the C=O bond length which lies between the values expected for C=O and C–O bonds.

## 4.5 Tridentate Chelate Ligands

A large number of papers have been published in the last 5 years dealing with penta- and hexacoordinated silicon complexes stabilized by tridentate O,N,O-, O,N,S-, N,N,S-, and O,N,N-chelate ligands. A substantial part of these were produced by Tacke et al. [189, 190, 193, 194, 268–272]. Most of the tridentate ligand systems used in their investigations are Schiff bases of aromatic *o*-hydroxy- or *o*-mercaptoaniline derivatives. These were used to prepare penta- and hexacoordinated silicon complexes **124–130**.

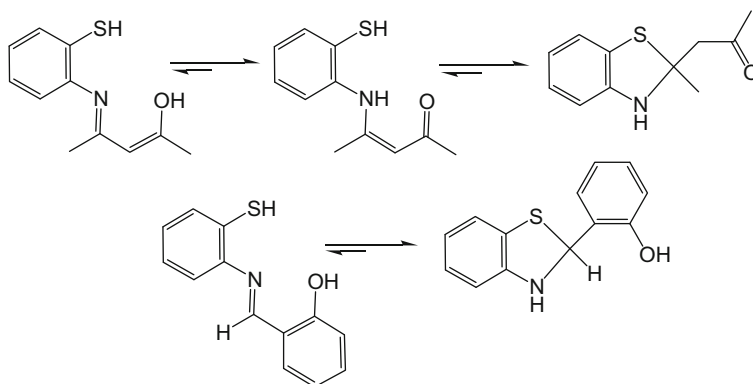


Ligands containing imine nitrogen and thiol groups in vicinal position can exist in a ring-opened form or in a ring-closed thiazol form (Scheme 35). It is difficult to predict which isomer will coordinate to silicon, as both coordination modes have been observed (e.g., compounds **53** and **58**, Scheme 11). Furthermore, one of these ligands was shown to react under formal loss of hydrogen ( $H_2$ ) as a bidentate ligand and coordinates via the oxygen and nitrogen atom [269] to form the hexacoordinated silicon complex **131** (Scheme 36).

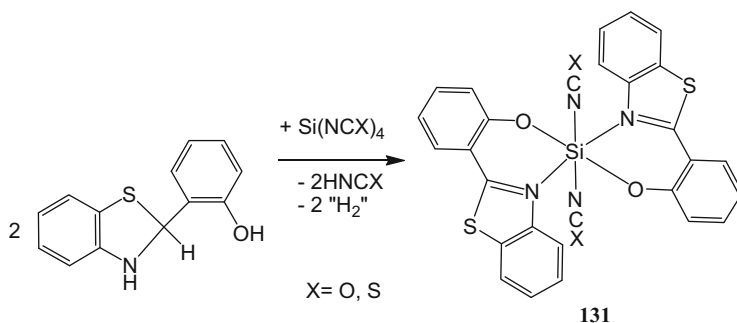
In a similar way the ring opening of organosilicon-substituted benzoxazolinone has been used as a convenient route to chelating ureato and carbamido ligands [192]. It was even possible to obtain three different coordination modes to silicon with the ligand *N*-(*o*-aminophenyl)-2-oxy-4-methoxybenzophenoneimine and its *N*-acylated derivatives, respectively (Scheme 37) [195, 273].

Further aspects which have been dealt with were the question whether ring-strain-formation Lewis acidity plays a role in pentacoordinated silacyclobutane derivatives [274]; intra-ligand  $\pi$ - $\pi^*$  transitions within a tridentate O,N,N-ligand [275]; dynamic disorder in a pentacoordinated silicon complex with 2,2'-diazenediylldiphenol [276]; pentacoordination vs. tetracoordination in silicon derivatives of an O,N,O-tridentate ligand [236] and the coordination of the pyridine moiety of an ONN-ligand in diorganosilicon complexes [277].

A few publications deal with silicon complexes of chiral O,N,O-ligands. Tridentate imine ligands were obtained from chiral amino alcohols by Schlecht et al. [278]. These ligands serve for the formation of bis-chelated silicon complexes. Whereas the complex based on 2-amino-1,1,2-triphenylethanol is obtained as a diastereomeric



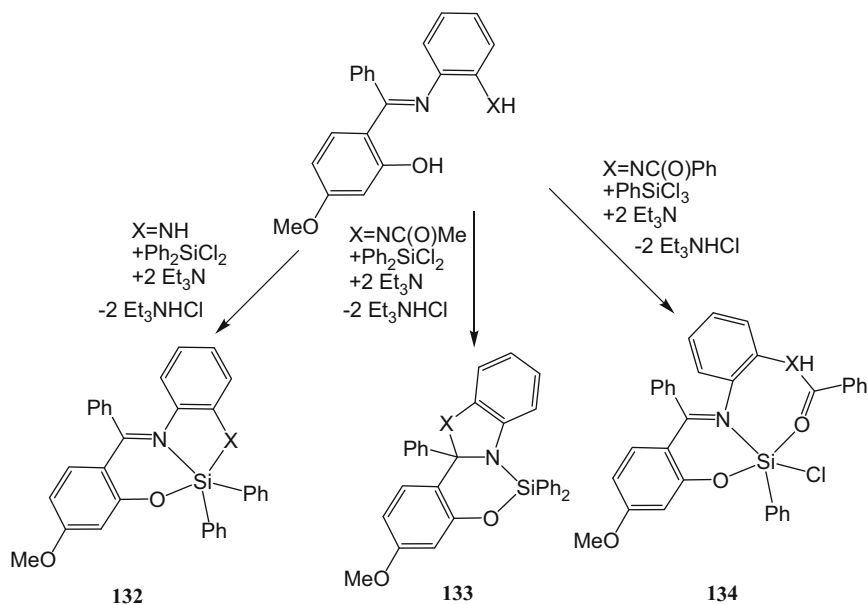
**Scheme 35** Ring-opened (*left*) and ring-closed isomers (*right*) of potential tridentate ligands with O,N,S-coordination ability



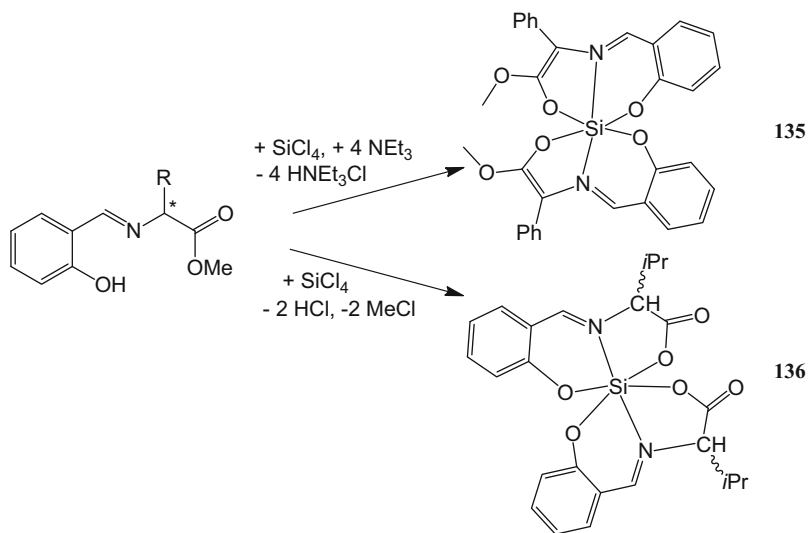
**Scheme 36** Formation of a hexacoordinated silicon complex under loss of hydrogen

mixture, the complex that is derived from 1-amino-1,2,2-triphenylethanol forms in a completely diastereoselective manner. The new silicon complexes are found to be efficient dopants for the conversion of nematic liquid crystals into cholesteric phases [278]. Two turnstile rotamers of a pentacoordinated silicon complex with a chiral backbone derived from 2-amino-1,1,2-triphenylethanol have been confirmed by crystal structure analysis. In addition, the coexistence of two rotamers, which readily interconvert in solution, was demonstrated by NMR spectroscopy. A 120° turnstile rotation of three ligands at the silicon atom is assumed as the preferred path of the observed stereomutation [279]. Chiral Schiff-base ligands with O,N,O-coordination ability have been prepared with amino acid esters from the chiral pool [280]. The chiral information is lost during the formation of complexes with these chiral ligands with silicon tetrachloride (Scheme 38). The Schiff-base ligand yields a ketene acetal structure (**135**) or a racemized ligand system (**136**) depending on the reaction conditions and the nature of the amino acid group. The surprising structural features of **135** and **136** allowed to develop a uniform concept explaining the racemization of the ligand system during complex formation.



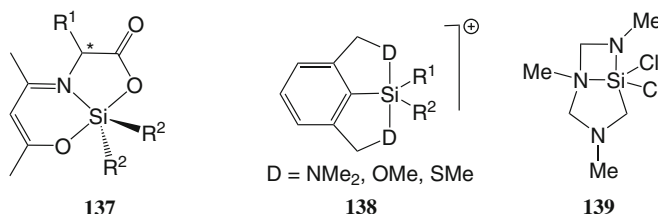


**Scheme 37** Three different coordination modes to silicon with the ligand *N*-(*o*-aminophenyl)-2-oxy-4-methoxybenzophenoneimine and its acylated derivatives



**Scheme 38** Formation of a ketene acetal structure (**135**) or a racemized ligand system (**136**) in the complex formation of SiCl<sub>4</sub> with chiral Schiff-base ligands

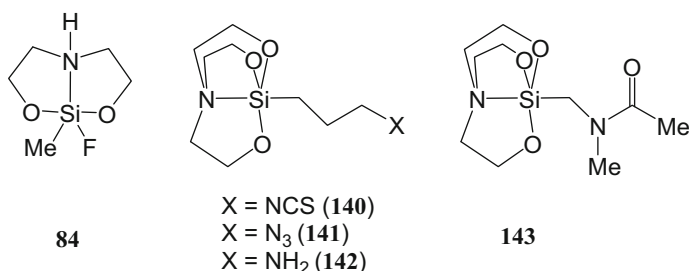
A new type of chiral silicon complexes have been developed recently. By preparation of a Schiff-base from acetylacetone and amino acids from the chiral pool a ligand system is available which allows the preparation of chiral penta-coordinated silicon complexes of type **137** [281]. No racemization has been observed during complex formation with dichlorodiorganosilanes.



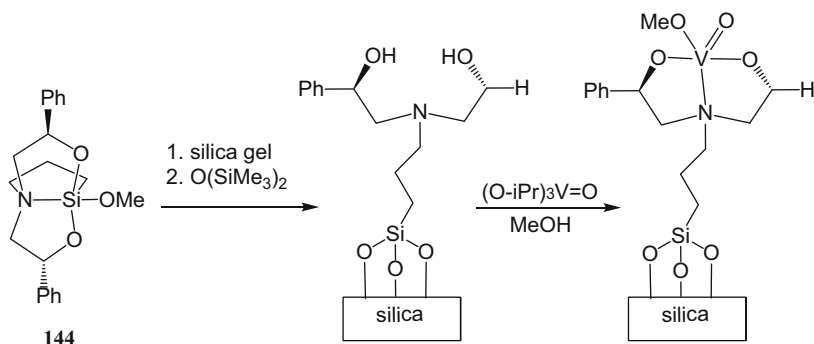
Only one investigation during the last 5 years employed pincer ligands (in this case to generate cationic higher-coordinated silicon complexes of type **138**) [282]. Pincer ligands are far more often used in transition metal chemistry, as it is reflected by numerous review articles published in the last years [283–285]. The molecule **139** was identified by X-ray structure analysis. It represents the formal insertion product of SiCl<sub>2</sub> into a C–N bond of 2,4,6-trimethyl-2,4,6-triaza-1,1-dichloro-1-sila-cycloheptane [286].

#### 4.6 Triethanolamines Forming Silatranes

Silatranes are known since more than 50 years [287, 288] but are still fascinating molecules in the focus of an ongoing scientific interest. Fluoro-substituted quasisilatranes have been synthesized [214, 289–291]. Experimental and theoretically calculated electron density distribution functions in the crystal structure of **84** have been investigated [214]. Properties of chemical bonding in silatranes have also been studied in 1-hydrosilatrane [218] and 1-fluorosilatrane [219].



One aspect of recent interest is the functionalization of silatranes via a silicon-bound alkyl group. Examples for such compounds are 3-isothiocyanatopropylsilatrane



**Scheme 39** Example for a carbasilatrane (**144**) as precursor to link the optically active ligand system to silica gel and to prepare vanadium(V) complexes

**140** [292], 3-azidopropylsilatrane **141** [293], 3-aminopropylsilatrane **142** [294], 1-(2-pyridyloxy)silatrane [295], and *N*-(1-silatranylmethyl)succinimide and glutarimide [296], as well as urea and Schiff-base-functionalized propylsilatrane [297, 298]. These compounds offer opportunities, for instance, to build up larger ligand systems and to coordinate transition metals. Along these lines, a 1,3,2-dioxaphosphorinane unit was coupled to  $\gamma$ -aminopropylsilatrane to yield a compound which might have interesting biological properties [299]. The functionalization with *N*-methylacetamide (**143**) and *N*-(2-hydroxyethyl)acetamide delivers silatrane, which are partial muscarinic agonists and mimic the effect of acetylcholine by binding directly to cholinergic receptors of the ileal smooth muscle [300]. (Buta-1,3-dien-2-yl)silatrane has been used in Diels–Alder and cross-coupling reactions (Scheme 30 in Sect. 4.2) [246].

Carbasilatrane is another variation of the silatrane structure. The carbasilatrane **144** has been used as a precursor to fix the optically active ligand system via the incorporated silicon atom on silica gel or mesoporous silicas (Scheme 39) and to prepare vanadium(V) complexes therefrom, which act as functional models for the sulfide-peroxidase [301]. Several 3,7,10-trimethylsilatrane and carbasilatrane have been synthesized and investigated by NMR spectroscopy [302].

#### 4.7 Tetradentate Chelate Ligands of “Salen”-Type

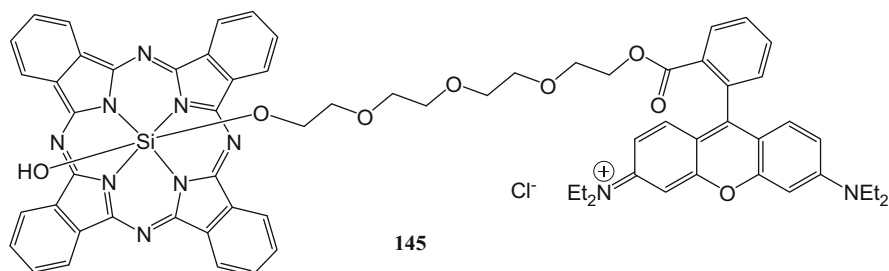
Salen-silicon complexes have been first crystallographically characterized in 1998 [148]. The studies on penta- and hexacoordinated silicon complexes containing salen-type ligands led to new insights in the field of silicon coordination chemistry; for instance, unusual activation of Si–C [173] and Si–Si [171] and other bonds (Schemes 2 and 8) or intramolecular ligand charge transfer promoted by hexacoordinated silicon(IV) complexes [153] has been observed in these compounds [147]. In continuation of this work, photo-driven Si–C bond cleavage in hexacoordinated silicon complexes [174] and the regio- and diastereoselectivity of rearrangement reactions in silicon–salphen complexes [169] have been investigated.

Hexacoordinated salen–silicon complexes can undergo Wurtz-type coupling reactions to produce the first examples of oligosilanes and polysilanes containing hexacoordinated silicon backbones [149]. This principle has been utilized to couple salen-type complexes containing thiocyanato ligands  $[\text{Si}(\text{salen}^*)(\text{NCS})_2]$  to a mixture of linear oligosilanes with a hexacoordinated silicon backbone  $\text{SCN}[\text{Si}(\text{salen}^*)]_n\text{NCS}$  with  $n = 2\text{--}8$  [147].

The structure of the salen ligand system has been modified by using a dipyrin – instead of the ethylenediamine-unit. The novel pentacoordinated dipyrin-silicon complexes (**31**, see Scheme 4, and some of its derivatives) showed efficient red or near-IR fluorescence, and the structural interconversion between silanol and siloxane derivatives resulted in significant changes in the optical properties [150].

## 4.8 Phthalocyanines

Metal phthalocyanines have a long-standing history as dyes and catalysts and are since recently being used in the manufacture of compact discs [303]. Only a few, but promising papers on silicon phthalocyanines, have been published in the last 5 years. Two new axially disubstituted silicon(IV) phthalocyanines containing adamantane moieties have been synthesized [304]. Both compounds are efficient singlet-oxygen generators with a quantum yield of 0.40–0.43. With two rigid bulky adamantane moieties at the axial positions, these phthalocyanines are essentially non-aggregated in common solvents but also exhibit a high photo stability. They are about 100 times more stable than zinc phthalocyanine under the same irradiation conditions [304]. Two axially ligated rhodamine-silicon(IV)-phthalocyanine complexes, bearing one (**145**) and two rhodamine B units, were synthesized and their photophysical, subcellular localization, and photocytotoxic properties were studied [305]. These phthalocyanine complexes exhibit an almost exclusive mitochondrial localizing property in human nasopharyngeal carcinoma (HK-1) cells and human cervical carcinoma (HeLa) cells. Strong photocytotoxic but low dark cytotoxic properties were also observed [305].



Three publications deal with the synthesis of  $\mu$ -oxo-linked silicon phthalocyanine and porphyrin derivatives. The stepwise syntheses of  $\mu$ -oxo-linked heterochromophore arrays containing phthalocyanine, porphyrin, and sub phthalocyanine silicon and germanium complexes have been described [306, 307]. The  $\mu$ -oxo

linkage between the central group 14 metalloid atoms ensures  $\pi$ -overlap between the macrocycles, and an extension of the absorption profile to provide arrays that absorb across the whole UV-visible spectrum and into the near-IR. The strategy is sufficiently versatile to be extended to synthesis of higher defined oligomers and subsequent functionalization or attachment at either or both ends of the stack [307]. Similarly structured oxygen-bridged silicon phthalocyanine oligomers with  $(\text{Me}_3\text{SiO})_2\text{MeSiO}$ -end groups give structural parameters for a matching set of three cofacial, oxygen-bridged silicon phthalocyanine oligomers for the first time [308]. The staggering angles between the six adjacent cofacial ring pairs in the three oligomers are neither in a random distribution nor in a cluster at the intuitively expected angle of  $45^\circ$  but rather are in two clusters, one at an angle of  $15^\circ$  and the other at an angle of  $41^\circ$ . These two clusters lead to the conclusion that long, directional interactions (LDI) exist between the adjacent ring pairs. An understanding of these interactions is provided by quantum chemical calculations [308].

## 5 Heavy Donor Atoms in the Silicon Coordination Sphere

A large number of penta- and hexacoordinated silicon compounds are known which comprise hydrogen, 2nd row elements (especially C, N, O, F), and/or chlorine in the silicon coordination sphere (as one can easily conclude from the contents of the previous sections).

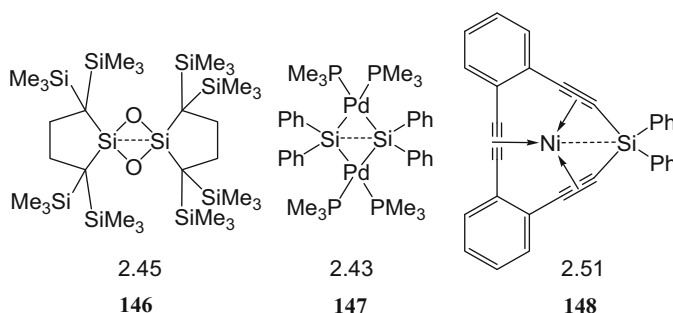
Far less compounds have been reported which comprise heavier elements in the coordination sphere of their penta- or hexacoordinated silicon atom. During the past decade significant contributions emerged on the field of silicon coordination chemistry with heavier lone pair donor atoms, and therefore this section will be dedicated to highlight these compounds.

As the silicon coordination number can be understood as the number of atoms located in proximity of the Si atom within the sum of the van der Waals radii and a large number of compounds without lone pair donation from atoms within this kind of coordination shell would fall into this section (such as those listed in Sect. 5.1), we focus on silicon compounds with five or six formal lone pair donors in the Si coordination sphere (Sects. 5.2–5.7).

### 5.1 *Compounds with Si Coordination Number >4 but less than 5 Formal Lone Pair Donors*

#### 5.1.1 Silicon Hypercoordination due to Non-lone Pair Donors in Close Proximity, Apparent Absence of a Bond

This is encountered, e.g., with atoms in four-membered cycles (146–148, Scheme 40) [309–313]. Upon omission of the fifth atom in the silicon coordination sphere (omission of the coordination along the dashed line in Scheme 40), the almost tetrahedral coordination environment about silicon in these compounds is in support of the absence of significant  $\text{M}^{\cdots}\text{Si}$  electronic interaction ( $\text{M} = \text{Si}, \text{Ni}$ ).



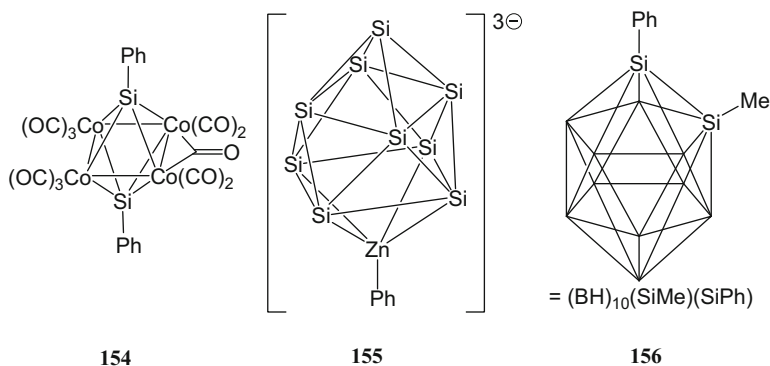
**Scheme 40** The dashed lines indicate close interatomic contacts in the four-membered cycles. The interatomic separations in Å ( $\text{Si} \cdots \text{Si}$  or  $\text{Ni} \cdots \text{Si}$ , respectively) are given below the formula

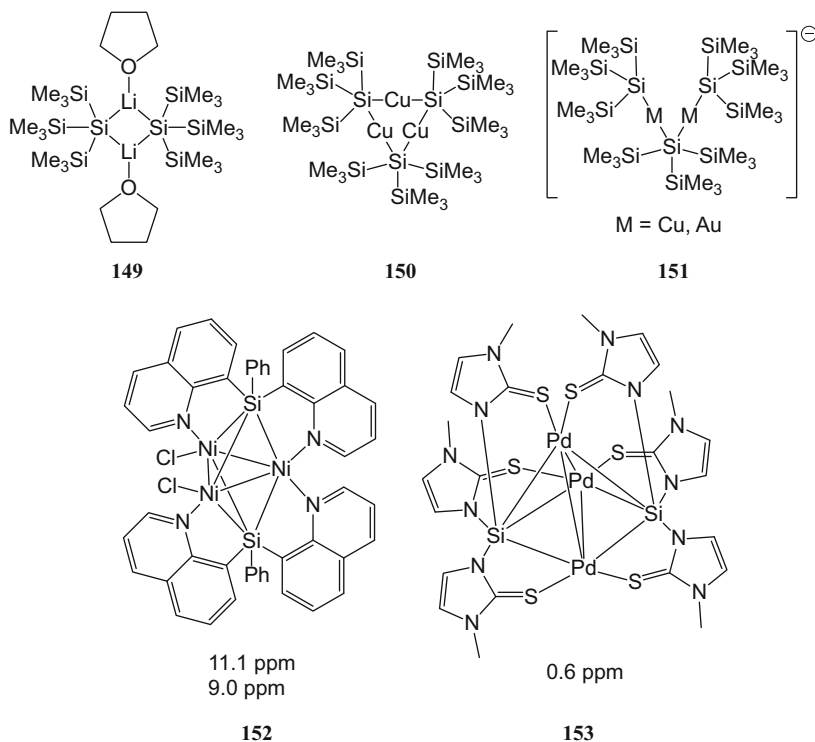
### 5.1.2 Silicon Hypercoordination due to Lone Pair Acceptors in Close Proximity

This is encountered with various silanides, which can bridge two or more counter-cations with their Si-located lone pair (e.g., in compounds **149–151**) [314–317]. In a similar fashion, some silanides can  $\mu^3$ -bridge assemblies of three transition metals (compounds **152** and **153**), which are stabilized by the additional ligand functionalities of the silanide, thus rendering the silanide Si atom formally hexacoordinated (Scheme 41) [318, 319]. The  $^{29}\text{Si}$  NMR shifts of **152** and **153** clearly distinguish them from hexacoordinated Si complexes with six lone pair donors in the coordination sphere.

### 5.1.3 Silicon Within Oligoatomic (e.g., Oligometallic) Clusters

In these compounds the Si atom is constituent of a multicenter bonding system and the number of interatomic bonds drawn exceeds the number of electron pairs available for bonding. Some representative examples are compounds **154–156** [320–323].

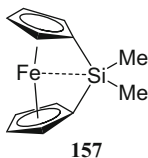




**Scheme 41** Compounds with penta- and hexacoordinated Si atoms due to the presence of lone pair acceptors around the silanide Si atom. For compounds (**152**) and (**153**) the  $^{29}\text{Si}$  NMR shifts are listed below the molecular formula

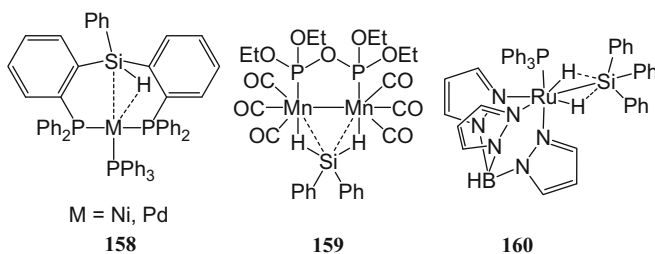
#### 5.1.4 Silicon Atoms in Metallocenophane Bridge Positions

In these compounds the Si atom is sterically constrained to a position in close proximity to the metal atom, thus exhibiting an unusually short metal–silicon contact (dashed line in the structure of compound **157**), but the otherwise almost tetrahedral coordination sphere about silicon and the coordination geometry about the transition metal suggests absence of lone pair donation from the metal to silicon [324–326].



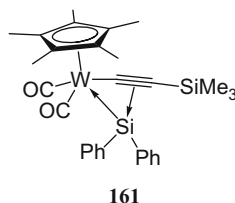
### 5.1.5 Silicon in Close Proximity to Transition Metal Atom via H-Bridge(s)

In these compounds the Si–H bond is likely to act as a  $\sigma$ -donor to the transition metal (agostic interaction), or the Si-bound hydrogen atoms act as  $\sigma$ -donors towards the transition metal, thus constraining the Si atom in close proximity to the transition metal even without  $\sigma$ -donor action from the latter to the Si atom. Besides, there are review articles on this topic, as mentioned in the introduction [36–40]. Hence, compounds such as **158** and **159** will not be discussed in detail here [327, 328]. Also, the same applies to compounds with Si transition metal bond which only achieve Si-hypercoordination by the presence of metal-bonded hydrogen atoms in closer proximity of the Si atom, while the rest of the Si coordination sphere is almost tetrahedral, thus less indicative of  $\text{H} \rightarrow \text{Si}$  donor action (e.g., **160**) [329].



### 5.1.6 Multi-atomic Single- $\sigma$ -Donor Stabilization of Silylene (Complexes)

Compound **161** represents a silylene ( $\text{SiPh}_2$ ) complex of tungsten, the silylene ligand of which is stabilized by  $\sigma$ -donor action of the neighboring acetylene. Formally, the bonding environment of Si is comprised of only four electron pairs, even though the presence of the two acetylene carbon atoms in the coordination shell of Si accounts for the formal coordination number five [330].



These classes of compounds are briefly mentioned here (in Sect. 5.1), as their Si atoms are surrounded by more than four atoms, but in the following Sects. 5.2–5.7 we will only focus on compounds which are devoid of these features,



i.e., compounds which, in addition to the presence of more than four atoms in the Si coordination sphere, comprise more than four formal  $\sigma$ -electron pairs in the Si valence shell, and if hydrogen atoms contribute to the enhanced coordination number, only compounds without Si transition metal bridging hydrogen are considered.

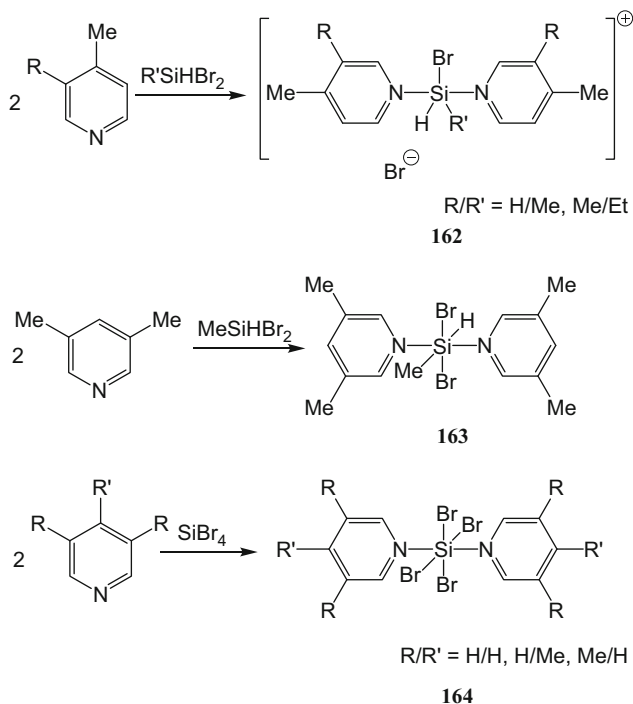
## 5.2 *Penta- and Hexacoordinated Si Compounds with Heavier Halides (Br, I)*

Alkylbromosilanes were shown to form pyridine adducts under ionic dissociation of an Si–Br bond (Scheme 42) [331, 332]. Thus, pentacoordinated Si complexes of the type **162** were isolated in which one out of two Si–Br bonds has been retained. Notably, this Si–Br bond occupies an equatorial position in the distorted trigonal-bipyramidal silicon coordination sphere (with bond lengths of 2.27 and 2.28 Å for the ethyl- and methylsilicon compound, respectively). In addition, a related compound with hexacoordinated Si atom and two Si–Br bonds (**163**) was characterized crystallographically [333]. The long Si–Br bonds (2.52 Å) already indicate the progress of Si–Br bond dissociation. Bromosilanes without electron-releasing alkyl groups (which most likely stabilize the cationic complex) form analogous pyridine adducts with hexacoordinated Si atom (compounds of type **164**) [334, 335]. The Si–Br bond lengths in the  $\text{SiBr}_4$  adducts (ca. 2.38 Å) indicate the strengthening of this bond in these complexes. In the series of 4-methylpyridine complexes of the silicon tetrahalides  $\text{SiBr}_n\text{Cl}_{4-n}$  ( $n = 0\text{--}4$ ), it was shown that the N–Si bond lengths are very similar despite the different number of Si-bonded Br vs. Cl atoms [335].

Monoanionic bidentate chelators have also been shown useful to achieve hexacoordination of silicon under retention of Si–Br bonds (Scheme 43) [135, 154, 157, 262, 336, 337]. Although the Si atoms were shown to be hexacoordinated in the solid state, for some of those compounds (e.g., **168**, **169**) ionic dissociation of the Si–Br bond was found to occur in solution. As for the above pyridine adducts, the Si–Br bond lengths exhibit noticeable variability (ranging between 2.33 and 2.45 Å).

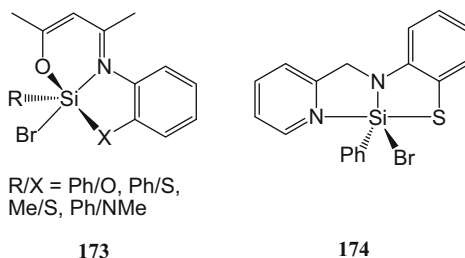
The weakness of the Si–Br bond, which is reflected by its ionic dissociation upon silicon hexacoordination, is also manifested in neutral pentacoordinated Si complexes. As shown by the related compounds in Scheme 44, the gradual approach of the additional donor moiety (O atom) causes a stepwise dissociation of the Si–X bond, which is reflected in the “umbrella inversion” of the equatorial Si-bound alkyl groups [338, 339]. In this course, a very long Si–Br bond (3.12 Å) has been observed for **172**.

In the compounds **170–172**, the halide (e.g., the Si–Br bond) occupies an axial position in the distorted trigonal-bipyramidal Si coordination sphere (cf. compounds in Scheme 42). The features of both axial [95, 190] and equatorial Si–Br bond situation [270] in pentacoordinated bromosilicon complexes have recently been

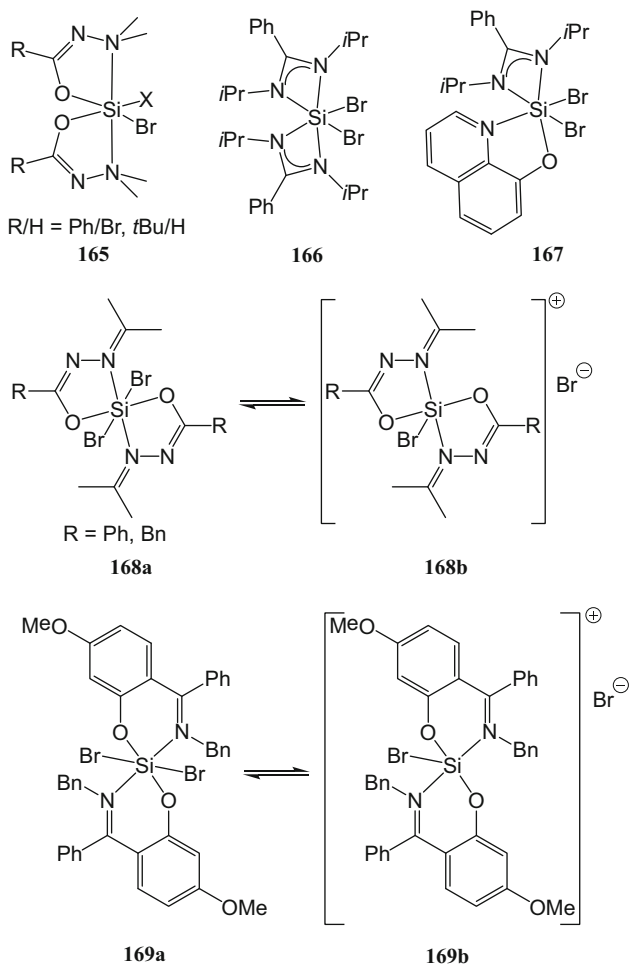
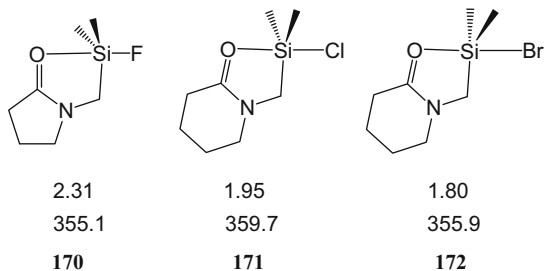


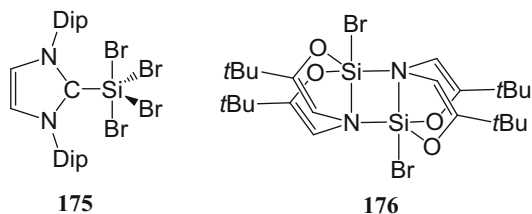
**Scheme 42** Syntheses of bromosilane pyridine adducts

encountered with some tridentate chelates (compounds **173** and compound **174**). Apparently, the nature of the chelating ligand exerts great impact on the situation of the Si–Br bond (the same was observed for the related Si–Cl bearing compounds) in the silicon coordination sphere. The length of the Si–Br bond responds to the position within the trigonal-bipyramidal coordination sphere, i.e., 2.39–2.45 Å for axial positions and 2.33 Å for Br in an equatorial position.

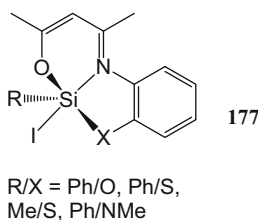


Last but not least, a carbene adduct of  $\text{SiBr}_4$  (**175**) with pentacoordinated Si atom (with carbene ligand in equatorial position and Si–Br bond lengths of 2.24 and 2.38/2.41 Å for equatorial and axial sites, respectively) [108] and a dinuclear pentacoordinated bromosilicon compound (**176**) with a central  $\text{Si}_2\text{N}_2$  four-membered cycle and rather short axial Si–Br bonds (ca. 2.28 Å) [340] have been reported.

**Scheme 43** Syntheses of chelated bromosilicon complexes**Scheme 44** Model compounds for steps along an  $S_N2$  reaction coordinate. Si–O bond lengths (in Å) and the sum of the equatorial C–Si–C angles (in °) are listed under each compound

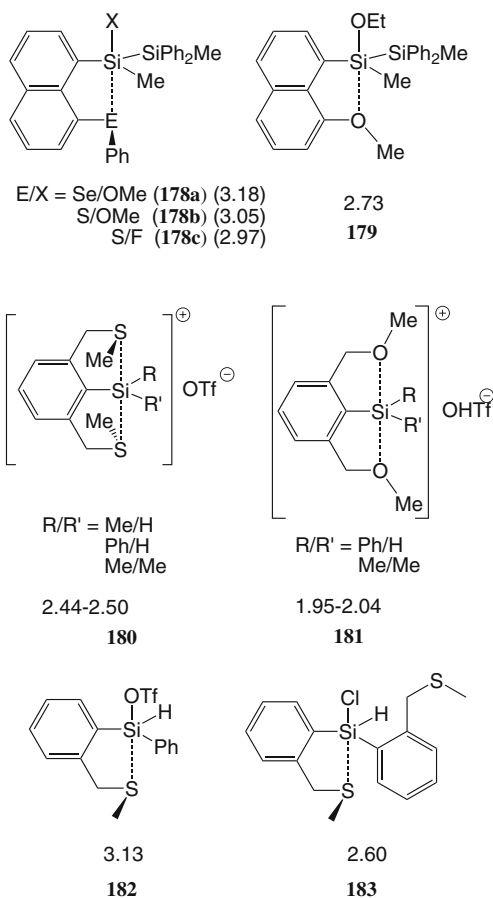


This variety of hypercoordinated bromosilicon compounds is in sharp contrast to hypercoordinated iodosilicon compounds, which are represented by far less crystallographically evidenced examples. In addition to some pentacoordinated monoiodosilicon compounds with tridentate chelators (compound **177**, Si—I bond lengths ranging between 2.74 and 2.82 Å) [95, 188, 190], the first crystallographically characterized hexacoordinated iodosilicon compound (with two Si—I bonds, 2.64 and 2.66 Å) [203] has been reported very recently (compound **72**, Scheme 15).



### 5.3 Penta- and Hexacoordination of Silicon with Heavier Chalcogens (S, Se, Te)

In case of silicon compounds with chalcogen donor moieties, we need to distinguish between chalcogenides and chalcogenolates as anionic ligands on the one hand and chalcogenoethers and chalcocarbonyl compounds as neutral donor moieties on the other hand. Only few examples of crystallographically characterized pentacoordinated Si complexes with chalcogenoether donor moieties have been reported to date (Scheme 45) [282, 341–343], but their characteristic features already allow deeper insights into the difference between ether and heavier chalcogenoether donor action towards silicon. Even though the particular kind of silicon hypercoordination which is forced by the short peri-distance of the naphthalene-1,8-diyl backbone can often be interpreted in terms of minimization of repulsive forces rather than deliberate attraction of silicon and its peri-situated additional donor atom [344, 345], the behavior of chalcogenoether S or Se atoms in compounds **178** systematically resembles that of related interactions in a much more flexible 2-methylthiomethyl substituted aryl group (compounds **180**, **182**, **183**). In detail, the methoxy O atom (in compounds **179** and **181**) approaches the Si atom in a  $sp^2$ -like fashion (Si atom located within the C—O—C plane). For compound **179**



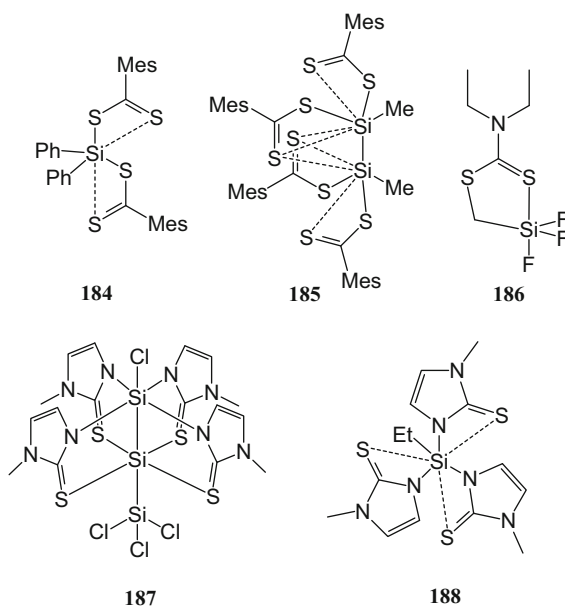
**Scheme 45** Chalcogenoether coordination at silicon. The interatomic separations of Si and the chalcogen atom (*dashed line*) are given below the formula

the angles about the methoxy O atom sum up to  $356.6^\circ$ . For the related seleno- or thioether compounds **178** a non-hybrid approach of the chalcogen atom towards the Si atom is observed (both the E–C bonds and the E...Si interaction being aligned along the axes of p-orbitals). Thus, for compounds **178** the angles about the heavy chalcogen atom sum up to  $309.6^\circ$ ,  $310.6^\circ$ , and  $303.4^\circ$  (for **178a–c**, respectively). Similar features are observed with the *o*-methylthiomethylphenyl-substituted compound **180** vs. their *o*-methoxymethylphenyl analogue **181**.

To our best knowledge, there is no crystallographic evidence for telluroether silicon coordination compounds to date.

Thiocarbonyl compounds as ligands in the Si coordination sphere are encountered with thiocarboxylate (**184**, **185**), thiocarbamate (**186**), and thiourea (**187**, **188**) derivatives [346–348]. Whereas in the first case (**184**, **185**) only capped tetrahedral

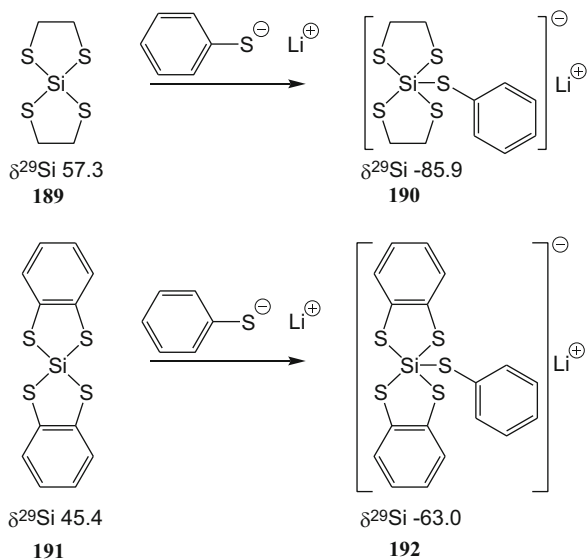
Si coordination spheres have been reported (with weak  $\text{S} \cdots \text{Si}$  interactions indicated by interatomic separations of 3.05–3.48 Å), thiocarbamate was shown to form a noticeably shorter Si–S bond in **186** (2.70 Å) and the anion of the thiourea derivative methimazole was shown to be capable of forming a trisilane (**187**) with two adjacent octahedral Si coordination spheres, one of which comprises four Si–S bonds (with separations ranging between 2.35 and 2.48 Å). Notably, this trisilane with a central  $\text{Si}(\text{Si}_2\text{S}_4)$  skeleton is one out of only few crystallographically characterized hexacoordinated Si compounds which are devoid of first and second row elements in the octahedral Si coordination sphere of one of their Si atoms (further examples can be found with P and Cl in the coordination sphere, *vide infra*). The kind of tetrahedral capping by rather long  $\text{Si} \cdots \text{S}$  separations of about 3.17–3.50 Å is encountered with various methimazolyl-substituted silanes such as **188** [349].



Apparently, silicon hypercoordination can be achieved more readily by utilizing anionic chelating S-donor ligands. Even though a hexacoordinated silicon compound with  $\text{SiS}_6$  skeleton has not been reported yet, its left neighbor has already been shown to form compounds with  $\text{AlS}_6$  skeleton [350–352]. Pentacoordinated Si compounds with  $\text{SiS}_5$  skeleton have at least been evidenced by  $^{29}\text{Si}$  NMR spectroscopy, as the spiro compounds **189** and **191** with  $\text{SiS}_4$  skeleton (shown in Scheme 46) have been extensively characterized by crystallography, NMR spectroscopy, and quantum chemical calculations and a significant high-field shift of their  $^{29}\text{Si}$  resonance has been observed upon addition of thiolates, wherefrom the formation of **190** and **192** has been concluded [353, 354].

In further studies this strategy of including thiolate donor moieties in chelating ligands (see compounds **41**, **124–127**, **130**, and **193–199**) proved successful to

**Scheme 46** Formation of compounds with  $\text{SiS}_5^-$  skeleton ( $^{29}\text{Si}$  NMR shifts are given below the molecular formulae)



create a larger set of penta- and hexacoordinated Si compounds. Some related selenolato silicon compounds with heavier chalcocatecholate type ligands have also been reported [145, 154, 167, 188–190, 193, 194, 268, 270, 355–357]. In these compounds the chelators' S atoms can be found in axial and equatorial positions in the pentacoordinated Si compounds with equatorial and axial Si–S bonds in the ranges 2.13–2.18 Å and 2.23–2.39 Å, respectively (and in a particular case four S atoms were found to occupy the basal positions of a square pyramidal Si coordination sphere with Si–S separations of 2.23–2.26 Å [167]). In the hexacoordinated Si compounds of this class the Si–S bond lengths range between 2.26 and 2.31 Å. Si–Se bond lengths were found in the ranges 2.40–2.41, 2.46–2.58, and 2.29–2.32 Å for the hexacoordinated and the axial and equatorial positions in the almost trigonal-bipyramidal pentacoordinated Si compounds, respectively.

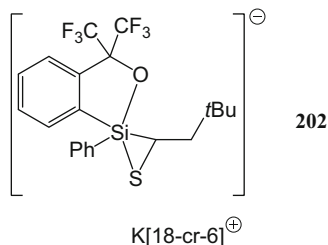
Some related monodentate chalcogenolates have also been successfully introduced in the coordination spheres of pentacoordinated Si compounds (Scheme 47) [190, 194, 270]. In these compounds the monodentate chalcogenolates occupy equatorial sites in the distorted trigonal-bipyramidal Si coordination spheres, and the Si–E bond lengths slightly exceed the ranges mentioned above (Si–S 2.19 and 2.21 Å, Si–Se 2.32 and 2.35 Å). Furthermore, equatorial Si–Te bonds with lengths of 2.52 and 2.56 Å have been reported. Interestingly, the equilibrium between isomeric tetra- and pentacoordinated Si compounds (**200b** and **200a**, respectively) was found to be shifted to the latter in case of the heavier chalcogenolates, whereas the phenoxy substituent promotes the formation of the compound with tetracoordinated Si atom (see also compound **58** Scheme 11) [194].

Finally, a pentacoordinated Si compound **202** with a thiolate type ligand as a 1,2-bidentate chelator (thus forming a thiasilirane, a three-membered Si,C,S heterocycle) is highly noteworthy [358]. In this compound the S atom occupies





an axial position (*trans* to O) in the distorted trigonal-bipyramidal Si coordination sphere. The Si–S bond (2.57 Å) is notably longer than those in the abovementioned compounds with axial thiolate ligands, most likely due to its S $\cdots$ K coordination (3.12 Å) in the crystal packing.

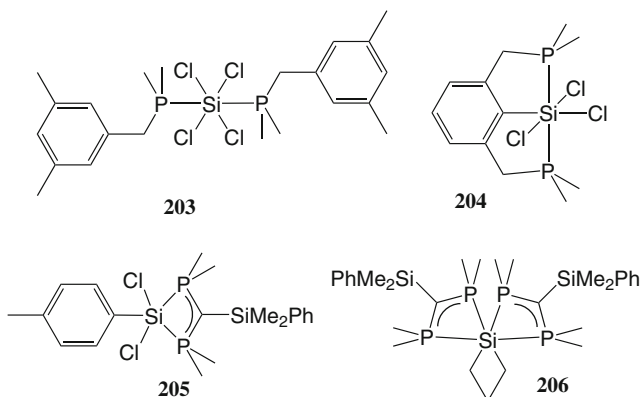


Last but not least, formally dianionic heavy chalcogeno ligands (i.e., chalcogenides) have recently been introduced in the Si coordination sphere (compounds **73**, Scheme 15) [204]. The Si=E bond lengths for the equatorially situated “chalcosilanone” bonds (2.02, 2.16, 2.40 Å for S, Se, Te, respectively) are noticeably shorter than those reported for the corresponding equatorially bonded chalcogenolates, as one would expect due to the lower coordination number of the chalcogen atom and the formally higher bond order.

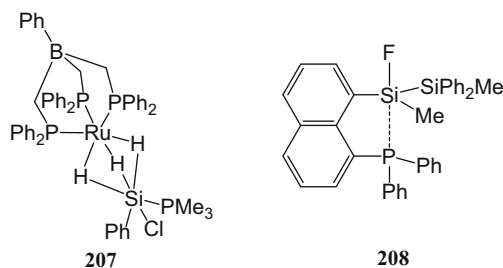
### 5.4 Penta- and Hexacoordinated Si Compounds with Heavier Pnictogens (P)

To date hypercoordinated Si compounds with As, Sb, or Bi in the silicon coordination sphere have not been reported with any crystallographic evidence of their bonding situation. Phosphorus atoms in the coordination shell of such Si compounds, however, have been reported and the P-donor moieties cover the two classes of neutral (phosphane) and anionic (phosphanide) ligands.

In an earlier review it has already been pointed out that phosphane coordination at silicon is rarely encountered in the literature [359]. With the trialkylphosphane adduct of SiCl<sub>4</sub> (**203**), crystallographic evidence for the feasibility of the synthesis of this class of compounds from SiCl<sub>4</sub> and a phosphane has been delivered and the Si–P bond length was found to be 2.36 Å. The use of a chelating ligand (**204**) resulted in slightly stronger Si–P coordination (bond lengths 2.31 Å). In addition to the use of trialkylphosphanes, diphosphinomethanides proved suitable to enhance the silicon coordination number to five and six (**205**, **206**, and **33**) [155, 360]. The Si–P bond lengths in these compounds range between 2.30 and 2.48 Å.

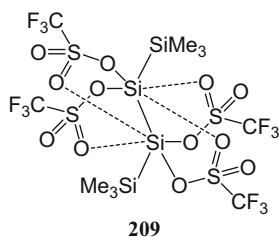


Recently, some further hypercoordinated Si compounds with crystallographically evidenced phosphane donor action have been published (**80**, **81**, **207**) [210, 211, 361]. Even though the overall coordination mode of the silicon atom in the Ru complex **207** does not fall into this class of hypercoordinated Si compounds (because of the  $\text{Ru} \cdots \text{Si}$  bridging hydrogen atoms and furthermore its  $^{29}\text{Si}$  NMR shift of 9 ppm, which is far downfield from the ranges expected for “ordinary” penta- and hexacoordinated Si compounds), the silicon coordination of trimethylphosphane in this compound is still noteworthy, and the Si–P bond length of 2.34 Å matches the ranges reported for the abovementioned trialkylphosphane silicon complexes. Furthermore, the angles Cl–Si–C, Cl–Si–P, and P–Si–C sum up to 288.6°, which is much closer to the expected sum of three *cis* angles in an octahedron (270°) than three tetrahedral angles (328.5°). In the compounds **80** and **81** Si–P bond lengths of 2.50 and 2.49 Å have been found. These compounds constitute additional classes of phosphanes suitable for lone pair donation towards silicon. Silicon hypercoordination with the aid of triarylphosphanes has also been reported, but the crystallographically characterized example of a naphthalene-1,8-diyl bridged phosphorus silicon interaction (**208**) hints at rather repulsive forces with the Si–P separation of 2.99 Å [362]. As a diarylphosphanide, however, phosphorus has entered the trigonal-bipyramidal Si coordination sphere (in equatorial position) of the compound **70b** (Scheme 14) [202]. Surprisingly, the formally covalent Si–P bond in this compound (2.29 Å) is only little shorter than the formally dative Si–P bonds in the earlier mentioned trialkylphosphane adducts.

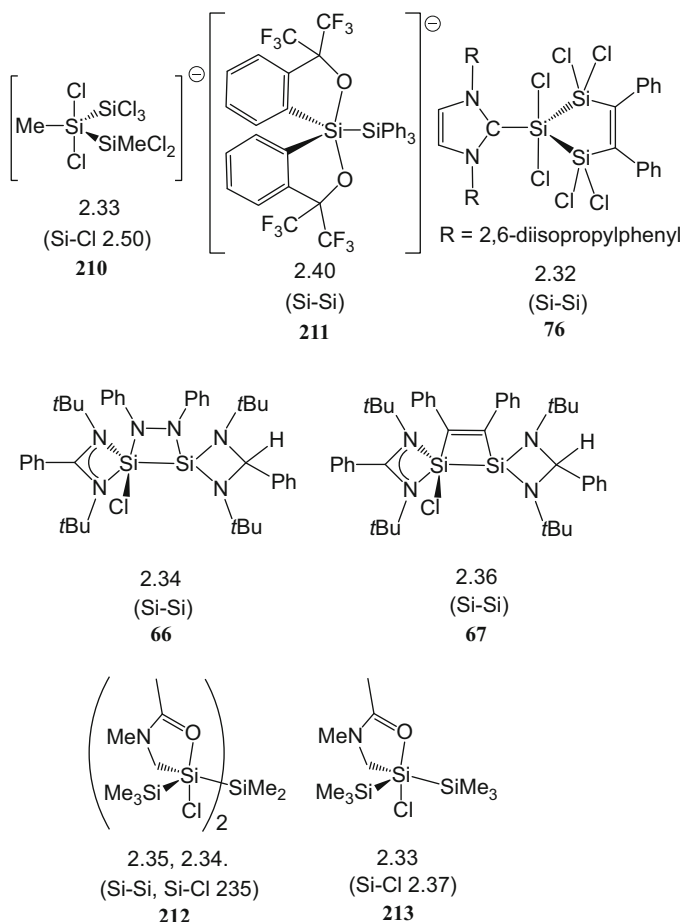


### 5.5 *Penta- and Hexacoordinated Si Compounds with Heavier Tetrels (Si, Ge, Sn)*

As di- and oligosilanes are a well-known class of silanes, which may bear a variety of functional groups (e.g., Si–Cl bonds) suitable for anchoring additional donor ligands, various oligosilanes with hypercoordinated Si atoms have already been reported in the literature. In order to assess the effect of hypercoordination on the Si–Si bond, we will only focus on crystallographically characterized compounds. Literature provides examples of some oligosilanes with relatively remote lone pair donor moieties in addition to four “regular” bonds in the Si coordination shell. This leads to capping of tetrahedral faces, but does not strongly distort the Si coordination spheres towards square-based pyramidal or trigonal-bipyramidal (for Si pentacoordination) or octahedral (for Si hexacoordination). Disilane **185** and tetrasilane **209** exhibit features of that kind [346, 363]. The interatomic separations between Si and the remote donor moieties are 3.05–3.48 Å (for S in **185**) and 2.72 and 2.84 Å (for O in **209**). The C–Si–Si and Si–Si–Si angles, which one would expect to be close to 180° or 90° in case of almost octahedral coordination, are 117.8/117.9° and 135.4°, respectively. The bond angles of the four noticeably shortest bonds around Si range between 97.5° and 117.9° in case of disilane **185** and between 96.9° and 135.4° in case of tetrasilane **209**. Thus, the particular geometrical parameters of these compounds do not match the expectations for octahedral coordination either, which would be  $1 \times 180^\circ$  and  $5 \times 90^\circ$  or  $2 \times 180^\circ$  and  $4 \times 90^\circ$ . The Si–Si bond lengths are 2.35 Å for the S-substituted disilane and 2.37 and 2.41 Å for the terminal and the central Si–Si bond in the O-substituted tetrasilane.

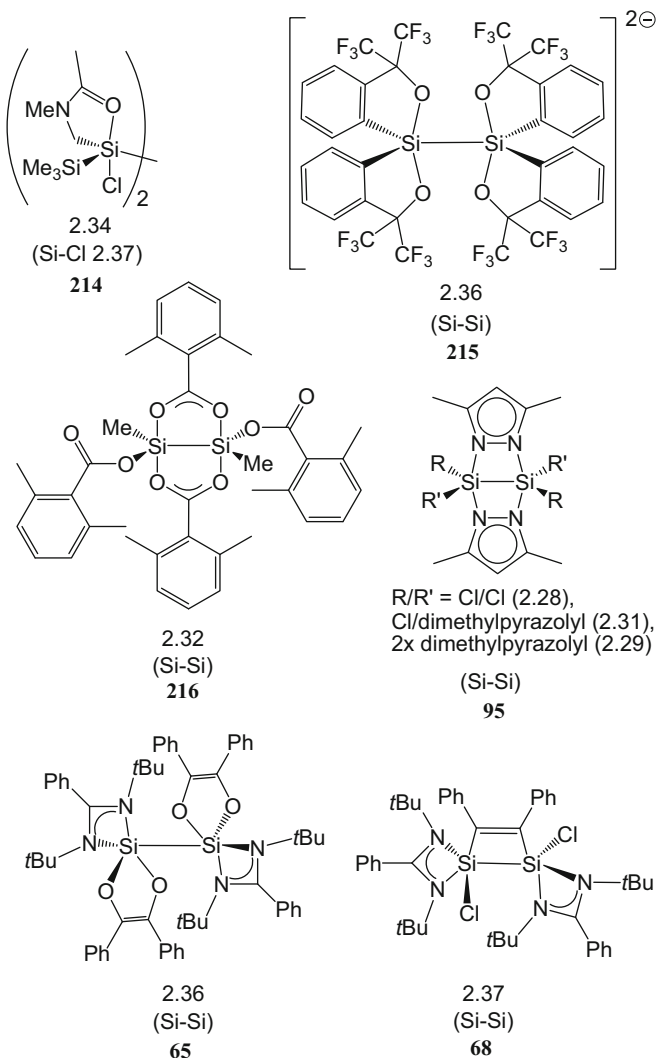


“Genuine” hypercoordination has been encountered with isolated and with adjacent hypercoordinated Si atoms within oligosilanes [48, 109, 134, 161, 162, 198–200, 241, 348, 364–368]. Schemes 48 and 49 show such compounds with isolated and with adjacent pentacoordinated Si atoms, respectively, and their Si–Si bond lengths (the value for the longest bond distance within the Si coordination sphere is given in the Schemes). Without exception, the Si–Si bonds are located in equatorial positions within the distorted trigonal-bipyramidal coordination spheres.



**Scheme 48** Compounds with pentacoordinated Si atoms within an oligosilicon skeleton. Si–Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses

Far less compounds with octahedrally coordinated Si atom(s) within an oligosilicon compound have been reported, which are shown in Scheme 50 (again, in combination with their Si–Si bond lengths and the longest bond in the Si coordination sphere). Surprisingly, their Si–Si bond lengths are very similar to those of pentacoordinated Si atoms in oligosilicon compounds despite the now *trans*-disposed bond. The two compounds **219a** and **219b** are currently the only examples of crystallographically confirmed hypercoordinated Si compounds with Ge or Sn in the silicon coordination sphere.

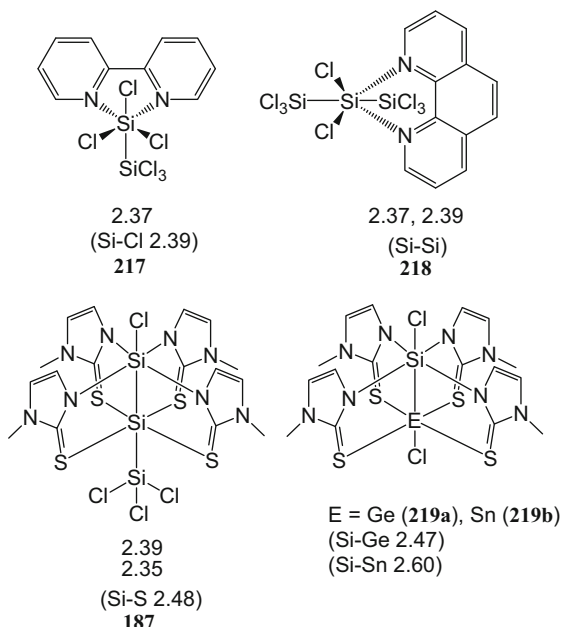


**Scheme 49** Compounds with adjacent pentacoordinated Si atoms within an oligosilicon skeleton. Si-Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses

## 5.6 Pentacoordinated Silicon Compounds with Coinage Metals (Cu, Ag, Au)

A phosphane-functionalized arylfluorosilane (**220**) has been shown to bind AuCl in almost linear P-Au-P arrangement and with an Au $\cdots$ Si separation of 3.09 Å (in **221**, Scheme 51) [369]. Although this interatomic distance is probably longer than one would expect for a strong Au $\rightarrow$ Si donor-acceptor interaction, the  $^{29}\text{Si}$

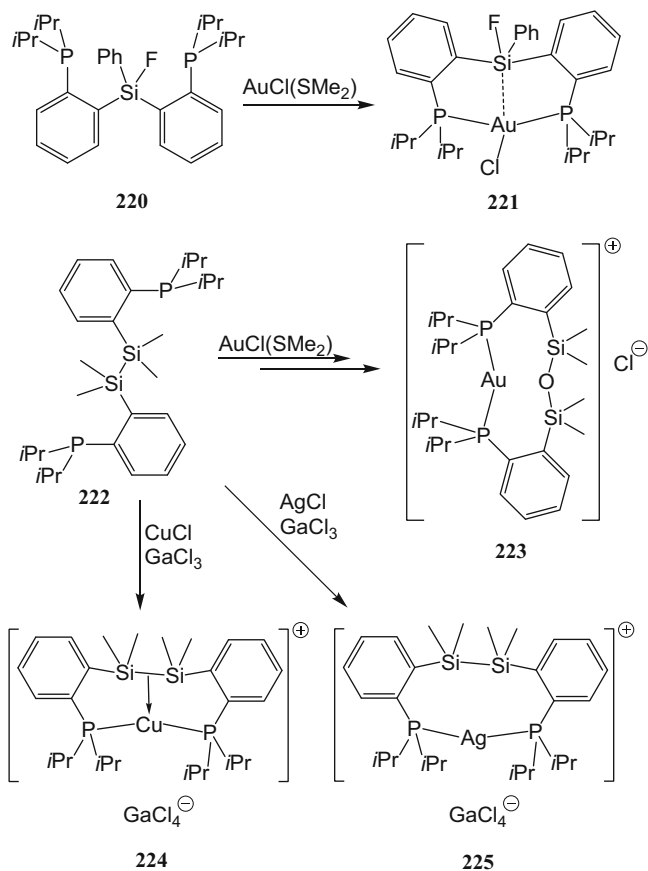
**Scheme 50** Compounds with octahedrally coordinated Si atoms within an oligosilicon or related skeleton. Si–Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses



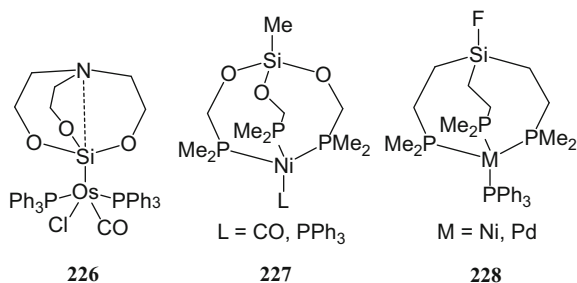
NMR shift of this compound ( $-21.4$  ppm) already indicates effects of an enhanced coordination number of silicon, as this shift is significantly upfield ( $\Delta\delta -23$  ppm) with respect to triphenylfluorosilane [370]. In a related phosphane-functionalized disilane (**222**), complexation of gold activates the Si–Si bond for oxidation to afford **223** [371]. In sharp contrast, the related complexation of Cu(I) leads to a metal–silicon interaction in **224** (Cu–Si separations  $2.72$  Å) that has been interpreted as the Si–Si  $\sigma$ -orbital acting as an electron pair donor towards Cu(I), and complexation of Ag(I) (**225**) leads to a compound with noticeably larger intermetallic separations ( $3.39$  and  $3.48$  Å) [372].

### 5.7 Penta- and Hexacoordinated Si Compounds with Transition Metals

An osmium-substituted silatrane (**226**) has been reported in 1998, which bears the transition metal atom as a formal covalently bonded substituent, whereas the silatrane N atom acts as the additional lone pair donor. In this particular compound, the transannular N→Si coordination is remarkably weak, which is reflected by the N–Si separation of  $3.00$  Å [373]. The use of electron rich transition metals as lone pair donors themselves to enhance the silicon coordination sphere has also been explored as early as 1994. The Ni(0) and Pd(0) centers in compounds **227** and **228**, however, exhibit poor  $\sigma$ -donor qualities, thus leading to transannular silicon metal separations of about  $4$  Å [373–378].



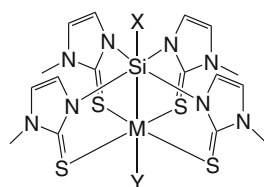
**Scheme 51** Coinage metal atoms in the silicon coordination sphere



In the past 3 years, Ni(II), Pd(II), and Pt(II) proved suitable  $\sigma$ -donors in the octahedral silicon coordination sphere (compounds **229**) [377–379]. With <sup>29</sup>Si NMR shifts ranging between –175 and –216 ppm, the metal atom clearly acts as one out of six bonding partners at silicon, and the metal silicon separations of

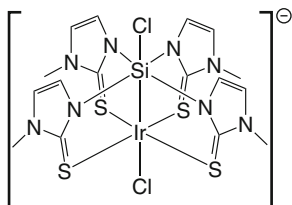
about 2.45–2.51 Å ( $M = \text{Pt}$ ), 2.53–2.57 Å ( $M = \text{Pd}$ ), and 2.56–2.61 Å ( $M = \text{Ni}$ ) are in support of this interaction. In a series of these compounds it was shown that the spin-orbit effects on the  $^{29}\text{Si}$  NMR shift are greater for  $M = \text{Ni}$  than for  $M = \text{Pd}$ , which appears unusual at first glance but can be rationalized as a result of the weaker ligand field splitting in case of  $M = \text{Ni}$ .

A related (hitherto not synthesized) Ir(I) compound (**230**) was predicted to exhibit similar structural features as the compound  $\text{ClSi}(\text{mt})_4\text{PtCl}$  ( $\text{mt}$  = methimazoly), i.e., to accommodate a metal silicon bond [380].

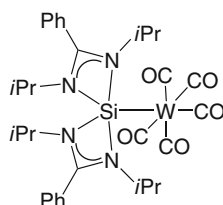


various combinations of  
 $X = \text{F}, \text{Cl}$   
 $M = \text{Ni}, \text{Pd}, \text{Pt}$   
 $Y = \text{Cl}, \text{Br}, \text{I}$

229



230



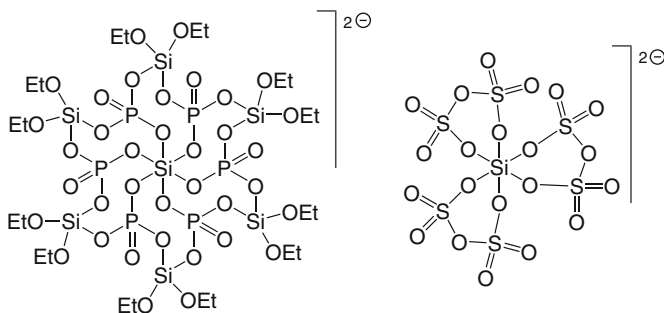
231

Last but not least, a pentacoordinated Si compound with Si–W bond (**231**) has been reported recently [203]. According to X-ray crystallographic results, the silicon coordination sphere in this compound is distorted trigonal-bipyramidal, with the Si–W bond (2.58 Å) in equatorial position. The  $^{29}\text{Si}$  NMR shift of  $-13.3$  ppm is noticeably downfield with respect to other pentacoordinated Si compounds with the same  $\text{SiN}_4$  (bis-amidinate) skeleton, e.g.,  $\text{N}_4\text{Si} = \text{S}$   $\delta^{29}\text{Si} = -70.7$  ppm [204]. This observation can probably be attributed to the silylene character of the silicon bis-amidinate moiety in this tungsten compound, which renders the  $\text{W}(\text{CO})_5$  moiety a  $\sigma$ -lone pair acceptor, not a donor, and thus clearly distinguishes this metal–silicon interaction from the abovementioned Si– $M$  ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ) bonding situations, which have been shown to be rather covalent ( $M = \text{Pt}$ ) or formally dative with the metal as lone pair donor ( $M = \text{Ni}, \text{Pd}$ ) [378].

## 6 Hexacoordination of Silicon with Anions of Mineral Acids

Surprisingly, very few compounds with higher-coordinated silicon atoms and mineral oxoacids such as carbonic, nitric, phosphoric, and sulfuric acids are known. These involve oxygen-coordination which is – on the other hand – very common. An example is compound **81** (Scheme 18) in which the carbonate ion is generated from carbon dioxide. Recently, an unusual higher-coordinated molecular silicon





**Scheme 52** Anions of **232** (left) and **233** (right) with hexacoordinated silicon atoms

compound has been prepared by the reaction of crystalline  $\text{H}_3\text{PO}_4$  and  $\text{Si}(\text{OEt})_4$  in the presence of triethylamine. After recrystallization from chloroform the X-ray structure of  $[\text{Et}_3\text{NH}]_2[\text{Si}(\text{PO}_4)_6(\text{SiO}_2\text{Et}_2)_6] \cdot 4(\text{CHCl}_3)$  (**232**) has been determined [381]. The silicophosphate anion contains a central hexacoordinated silicon atom which is surrounded by six  $\text{PO}_4$  tetrahedra. These are supplemented by six diethoxysilicate groups, each one linking two phosphate groups. The structure of the anion is shown in Scheme 52. This compound illustrates possible structural motifs in silicophosphate glasses.

Another example of a hexacoordinated silicon atom generated by coordination of an inorganic acid anion is  $\text{Na}_2[\text{Si}(\text{S}_2\text{O}_7)_3]$  (**233**) [382–384]. Herein the disulfate anion stabilizes the hexacoordinated silicon as a bidentate chelating ligand. Compounds like **232** and **233** might give insight into the possible genesis of naturally occurring silicates with hexacoordinated silicon [1, 385].

## 7 Conclusions

Although most of the known silicon compounds comprise tetracoordinated Si atoms, there are numerous and important classes of higher-coordinated silicon compounds. Some are long known such as the very stable hexafluorosilicate anion and its derivatives. Many more examples have been reported for (organometallic) higher-coordinated silicon compounds containing chelate ligands forming five- and six-membered silaheterocycles. The corresponding primary literature has been reviewed in the past decades. Nevertheless, similar to the field of lower-coordinated silicon compounds (silylenes, disilenes, etc.), the overall research in the field of higher-coordinated silicon compounds remains very active. This is indicated by the numerous publications on these topics that appeared in the past 5–10 years.

In this review we focused on the most recent literature, while at the same time trying to provide a comprehensive overview on the synthetic routes, structures, ligand types, and donor atoms in higher-coordinated silicon compounds. The

syntheses can be subdivided into various (oxidative) addition, metathesis, and rearrangement reactions. The structures of pentacoordinated silicon compounds are either derived from (distorted) trigonal-bipyramidal or square (rectangular) pyramidal motives. Hexacoordinated compounds are based on (distorted) octahedra, while purely trigonal prismatic species are seldom. Only a few examples of compounds with coordination numbers higher than six are known. These either involve special ligands such as  $\text{Cp}^*$ , or belong to cluster species (Zintl anions) or comprising donor moieties in greater distance (e.g., larger  $\text{Si}^{\cdots}\text{S}$  separations).

In most cases, bonding in higher-coordinated silicon compounds is significantly more ionic than in the corresponding tetrahedral or lower-coordinated species. However, the “nature” of a  $\text{Si}-\text{E}$  bond is strongly influenced by the type of atom E, the type of the other donor atoms at the silicon center, and steric and electronic constraints within the considered compound. The bonding “nature” may be roughly separated into covalent  $\sigma$ -bonds, ionic bonds, and dative interactions. The latter, however, may be considered as ionic as well, with some directionality, i.e., covalency. In many cases, bonding in the considered higher-coordinated silicon compounds can be described as  $4\text{e}3\text{c}$  bonds. Nevertheless, especially in the cases of weak (additional) donor interaction with a Lewis-acidic, fourfold coordinated silicon atom  $2\text{e}2\text{c}$  bonds are also present.

Apart from the well-known donor (or ligand) atoms such as C, N, O, F, and Cl, an increasing number of higher-coordinated silicon compounds with hydrogen, on the one hand, and heavy nonmetal as well as main group and transition metal donor atoms, on the other hand, have been reported. The latter may be separated into species without any bonding or donor–acceptor interaction (but distances below the sum of the van der Waals radii), compounds containing silicon atoms which act as electron pair acceptors as well as species where the Si is the Lewis donor.

Spectral and other properties and (potential) applications of higher-coordinated silicon compounds are not in the focus of this review. Nevertheless, interesting features and applications of selected subclasses of higher-coordinated silicon compounds include, for example, fluorination of drinking water involving fluorine complexes. It is well known that higher-coordinated silicon compounds act as reactive sites in (stereoselective) organic synthesis and in silicon chemistry in general. Octahedral silicon complexes bearing 1,10-phenanthroline and arenediolate ligands were investigated for the design of hydrolytically stable silicon-based high-affinity DNA binders, suggesting that similar silicon complexes are promising templates for applications in medicinal chemistry. Similarly, another class of compound containing hexacoordinated silicon, namely, phthalocyanine derivatives, is known to possess photosensitizing behavior, which can be used for photodynamic therapies. Zwitterionic and anionic (dinuclear) pentacoordinated silicon complexes with bridging tartrato ligands have been thoroughly characterized and their hydrolytic stability has been investigated with respect to the role of such complexes (or related compounds) in the biochemistry of silicon. Selected silatranes are partial muscarinic agonists and mimic the effect of acetylcholine, while others have been used in Diels–Alder and cross-coupling reactions, to name just a few examples.

Transition metal-containing compounds with higher-coordinated silicon atoms – especially those discussed in Sects. 5.6 and 5.7 – may be utilized as tunable homogeneous or heterogeneous catalysts. These (potential) applications and even more so the numerous fascinating fundamental results reported in the past few years, which have been summarized here, provide a promising and motivating basis for further research in the field of higher-coordinated molecular silicon compounds in the future.

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Regular Oxidation States

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