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Synthesis, properties and reactivity of intramolecular hypercoordinate silicon complexes

A A Nikolin, V V Negrebetsky

N I Pirogov Russian National Research Medical University
ul. Ostrovityanova 1, 117997 Moscow, Russian Federation

The state of the art of the chemistry of hypercoordinate silicon compounds is analyzed. Published data on the current top-priority approaches to the preparative synthesis of these compounds and on their properties, structures and reactivity are summarized and generalized. Relying on the results obtained by modern physicochemical methods, the possible mechanisms of stereodynamic processes occurring in the coordination units of hypercoordinate silicon complexes are discussed.
The bibliography includes 157 references.

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I. Introduction

The structural features of hypercoordinate (hypervalent) silicon complexes dictated by the unusual coordination unit of the central atom, such as the reactivity, which is often higher than that of tetrahedral analogues,[1,2] high biological activity of many penta- and hexacoordinate organic derivatives[3–5] and the stereochemical non-rigidity of the coordination polyhedron,[6,7] are extensively investigated all over the world. Data on the possible use of certain silicon coordination compounds as drugs and catalysts, as well as in the synthesis of new polymer materials, are available in the literature.[8–11] It should be noted that some industrially important reactions (for example, the hydrolysis of chlorosilanes) are also associated with transformations in the coordination environment of the silicon atom.

A A Nikolin Candidate of Chemical Sciences, Lecturer of the Chair of Chemistry, RNRMU
Tel. (7-495) 434 11 00, e-mail: nikson111@rambler.ru
V V Negrebetsky Doctor of Chemical Sciences, Associate Professor, Head of the Chair of Chemistry and the Department of Medicinal Chemistry and Toxicology, RNRMU
Tel. (7-495) 434 04 65, e-mail: negrebetsky1@rsmu.ru
Current research interests: organic and heteroorganic chemistry, stereochemical non-rigidity of organic derivatives of hypercoordinate Group 14 elements.

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Despite considerable progress, many problems in the chemistry of hypercoordinate silicon derivatives are far from being solved. This primarily refers to chelate compounds. Thus, the possibilities of searching for new chelating ligands, the coordinating atoms of which can serve as intramolecular donors, are not exhausted. Investigations with the view of revealing and estimating (at least qualitatively) the factors responsible for the strength of the intramolecular coordination bond (ICB) D → Si (D is the donor atom in the ligand) and of evaluating the degree of deviation of the configuration of the central coordination unit in such complexes from trigonal bipyramidal (TBP) or octahedral geometry are being continued. The nature of coordinating atoms in the ligand, the type of substituents at the D and Si atoms and the size of the chelate ring are among the main factors which should be taken into account.

The model of the three-centre four-electron (3c – 4e) hypervalent bonding[12–18] and the applicability of this model to different coordination units (hard and soft)[14] are still debated (rejected or refined).

High-precision X-ray diffraction studies of such compounds have started in recent years. These studies combined with results of quantum chemical calculations provide an estimate of the character of electron density distribution in the central coordination unit of hypercoordinate complexes and allow researchers to draw conclusions about the absence or presence of the D → Si coordination bond and its strength.[19–23]

In a number of comprehensive reviews (see, for example, Ref. 24) published by 2007, the structures, reactivity and dynamic stereochemistry of hypervalent Group 14 elements, including silicon, germanium and tin, were considered in detail. For this reason, the present review on the structures

and reactivities of hypercoordinate silicon complexes summarizes the data published in the period of 2007 – 2013. Publications on silatranes and related compounds, the synthesis and structures of which have been reviewed in detail earlier,[25] are beyond the scope of the present review.

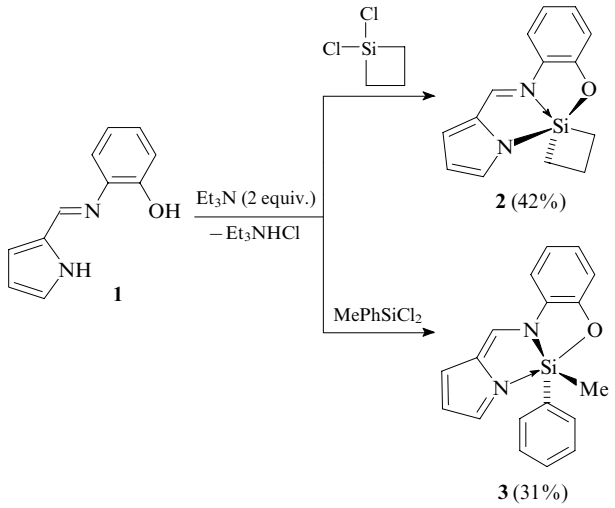
Emphasis is given to the results of studies of hypercoordinate silicon complexes by multinuclear NMR spectroscopy, including solid-state CP/MAS NMR spectroscopy, which is a relatively new and informative method extensively developed in recent years, and the results of X-ray diffraction (XRD) studies, as well as data on stereochemical non-rigidity of such compounds obtained by dynamic NMR spectroscopy at different nuclei.

II. Neutral pentacoordinate tetravalent silicon complexes

1. Complexes with an intramolecular N → Si coordination bond

The reactions of imine **1** with 1,1-dichlorosilacyclobutane and methylphenyldichlorosilane afforded complexes **2** and **3**, respectively, in which three donor atoms of the tridentate ligand are involved in the pentacoordinate unit (Scheme 1).[26]

Scheme 1



It was shown that a tridentate ligand can occupy different positions in the coordination unit depending on the nature of the substituent at the silicon atom: $N_{pyrrole}N_{imine}O_{phenolate} = N_{eq}N_{ax}O_{eq}$ or $N_{ax}N_{eq}O_{ax}$. The structures of two types of coordination units, $(N_{eq}N_{ax}O_{eq})Si(CH_2)_3$-cyclo and $(N_{ax}N_{eq}O_{ax})SiPhMe$, were determined in the solid state by XRD and ^{29}Si CP/MAS NMR methods.

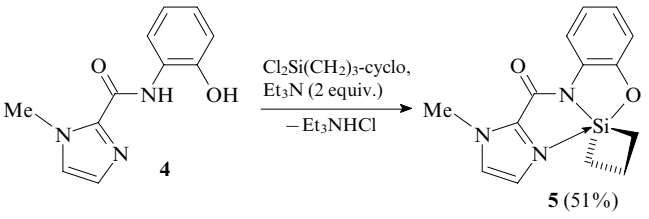
In solution, complex **2** undergoes a fast (on the NMR time scale) conformational inversion, as evidenced by the fact that the ^{13}C NMR spectra show only two signals of the silacyclobutane moiety with an intensity ratio of 2 : 1 at δ 23.2 and 13.0 ppm, respectively.

According to the XRD data, there are two independent molecules in the crystals of compounds **2** and **3**. Hence, two signals should be observed in the ^{29}Si CP/MAS NMR spectra. However, due to the structural similarity of independent molecules, the spectrum of complex **2** exhibits only one signal (−62 ppm), whereas the spectrum of complex **3** shows two strongly overlapping signals around −90 ppm.

In the authors' opinion, the silacyclobutane moiety is the main factor responsible for the differences in the structure and coordination mode of the tridentate NNO ligand in complexes **2** and **3** (see Scheme 1). Relying on the experimental data, it was suggested that the silacyclobutane moiety can exist only in a TBP polyhedron, in which one carbon atom takes up an axial position, whereas another carbon atom is in an equatorial position. Actually, according to the results of quantum chemical calculations, the equatorial arrangement of two carbon atoms of the silacyclobutane moiety contributes to an increase in the steric strain of the four-membered ring.

The replacement of ligand **1** with amide **4** (Scheme 2) by the reaction with 1,1-dichlorosilacyclobutane also results in the formation of pentacoordinate (XRD and NMR data) complex **5**.[27] The quantum chemical calculations using the B3LYP basis set showed that the transition of one of the Si—C bonds in this complex to the axial position has a low activation energy (< 3 kcal mol^{-1}).

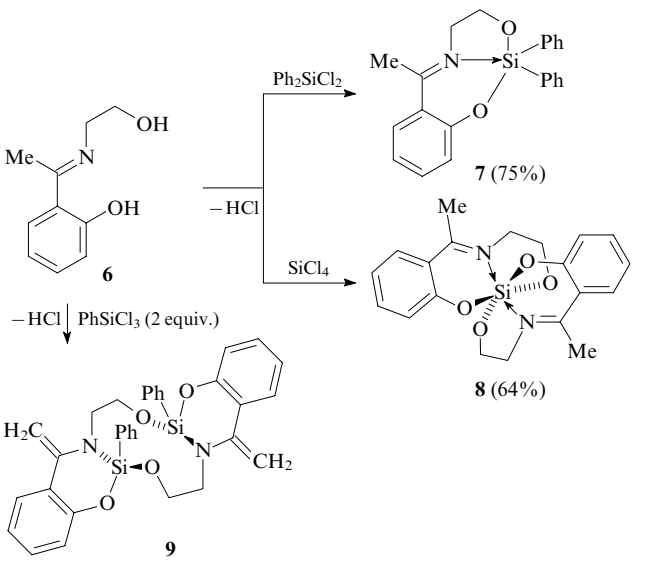
Scheme 2



The reactions of Schiff's base, *N*-(2-hydroxyethyl)-*o*-hydroxyacetophenone imine (**6**), with diphenyldichlorosilane and tetrachlorosilane in the presence of triethylamine gave penta- and hexacoordinate complexes **7** and **8**, respectively (Scheme 3).[28] According to the XRD data, the coordination unit in complex **7** has a distorted TBP structure, in which both oxygen atoms of the tridentate ligand and a carbon atom of one of the phenyl substituents are in equatorial positions. Complex **8** containing the distorted octahedral coordination unit is a chloroform monosolvate.

The hypercoordinate structure of both complexes is retained in solution. According to the ^{29}Si NMR data ($CDCl_3$), the strengthening of the coordination interaction

Scheme 3

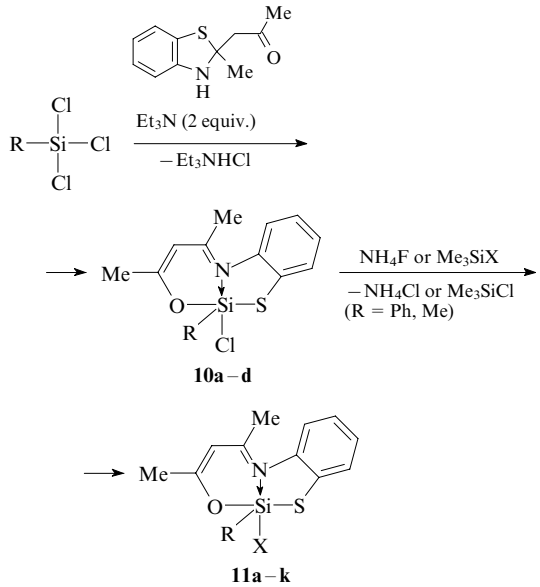


in complex **8** compared to complex **7** is accompanied by the upfield shift of the signal in the ^{29}Si NMR spectrum (−172.3 and −90.1 ppm, respectively).[29, 30]

It should be noted that the reaction of compound **6** with an excess of phenyltrichlorosilane produced heterocycle **9** containing two (XRD and NMR data) tetracoordinate silicon atoms (see Scheme 3) rather than the expected pentacoordinate complex.[31]

An unusual example of silicon complexes containing five different atoms in the coordination unit was described for the first time by Metz *et al.*[32] (Scheme 4).

Scheme 4



10: R = Ph (**a**), Me (**b**), 4-$F_3CC_6H_4$ (**c**), C_6F_5 (**d**)

Compounds **11**	R	X	Yield (%)
a	Ph	I	66
b	Ph	OSO_2CF_3	78
c	Ph	ONO_2	74
d	Ph	F	57
e	Ph	Br	71
f	Ph	NCS	86
g	Ph	N_3	78
h	Ph	CN	61
i	Me	F	13
j	Me	Br	68
k	Me	I	55

Complex **10a** was synthesized in 82% yield by the reaction of $PhSiCl_3$ with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one in the presence of triethylamine. The subsequent reaction of compound **10a** with iodotrimethylsilane or trimethylsilyl trifluoromethanesulfonate afforded complexes **11a**,**b**. It is noteworthy that these compounds have high hydrolytic stability.

According to the ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR and ^{29}Si CP/MAS NMR data and the results of X-ray diffraction studies, the synthesized complexes have a pentacoordinate structure both in the solid and liquid phases. The coordination polyhedra of compounds **10a** and **11a**,**b** (SiClSONC, SiISONC and $SiSO_2NC$, respectively) can be described as distorted TBP, in which carbon, oxygen and sulfur atoms are in the equatorial plane, and the axial positions are occupied by the nitrogen atom and the donor atom of the ligand X.

It should be noted that the enhancement of donor properties of the solvent is accompanied by an increase in the degree of coordination interaction, which is manifested in the upfield shift of the signal in the ^{29}Si NMR spectrum.[31, 32] This effect may be associated with the additional coordination of the central atom by solvent molecules. Interesting results were obtained by Metz *et al.*[32] Thus, the stronger donor properties of the solvents $CDCl_3$ and CD_3CN compared to CD_2Cl_2 result, on the contrary, in the downfield shift of the ^{29}Si NMR signal (Table 1). In our opinion, this is indicative of a weakening of the intramolecular coordination interaction under the experimental conditions due, apparently, to high steric crowding of the coordination unit in complex **11a** resulting from the presence of two bulky substituents (Ph and I), which hinder the approach of solvent molecules. As can be seen from Table 1, the chemical shift of the signal in the solid state differs only slightly from those observed in low-polarity solvents (CD_2Cl_2, $CDCl_3$), which may be evidence that the coordination number of the silicon atom in the condensed phase remains unchanged.

More recently, neutral pentacoordinate complex **11c** was synthesized in 74% yield by the reaction of chloride **10a** with freshly prepared trimethylsilyl nitrate in dichloromethane (see Scheme 4).[33] According to the XRD data, the coordination polyhedron in this complex is structurally similar to those in complexes **10a** and **11a**,**b**. The absence of substantial changes in the shifts δ^{29}Si in the solid state (−89.1 ppm) and in solution (−86.2 ppm, CD_2Cl_2) attests to the retention of the pentacoordinate state of the silicon atom. It should be noted that compound **11c** is the first complex with a Si−ONO_2 bond that was fully characterized by both solution and solid-state NMR spectroscopy.

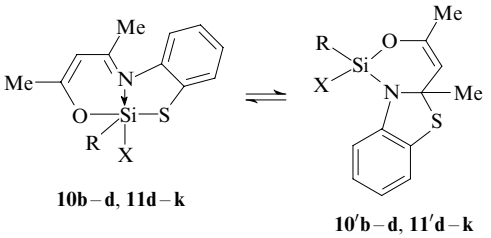
In the continuation of studies of pentacoordinate silicon compounds containing the SiSONCX unit (X = F, Cl, Br, I, N, C), complexes **10b**–**d** and **11d**–**k** were synthesized (see Scheme 4) in yields from 13% for compound **11i** to 78% for compound **11g**.[34] These complexes were characterized by elemental analysis. The structures of the complexes were determined by multinuclear ^{1}H, ^{13}C, ^{15}F and ^{29}Si NMR spectroscopy in solution and by ^{29}Si CP/MAS NMR and X-ray diffraction in the solid state. The pentacoordination of the silicon atom in solution (CD_2Cl_2) is evidenced by the

Table 1. Chemical shifts (δ /ppm) of complexes **10a** and **11a**,**b** in the solid (CP/MAS) and liquid phases.[32]

Complex	^{15}N CP/MAS	^{29}Si CP/MAS	δ^{29}Si (CD_2Cl_2)	δ^{29}Si ($CDCl_3$)	δ^{29}Si (CD_3CN)
10a	−149.4	−83	−82.1	–	–
11a	−163.8	−91	−92.5	−92.8	−85.2
11b	−156.4	−81.7	−83.7	–	–

upfield shifts of the signals in the ^{29}Si NMR spectra (in the range from −71.4 ppm for complex **10b** to −99.9 ppm for complex **11h**). The ^{29}Si NMR spectra show, along with the above-mentioned signals, signals at lower field (in the range from −19.2 ppm for complex **10b** to −53.7 ppm for complex **11d**). In the authors' opinion, this is indicative of the equilibrium in solution between the structures, with silicon atoms in the tetra- (designated with primed numbers) and pentacoordinate states (Scheme 5).

Scheme 5



10b–d, 11d–k **10′b–d, 11′d–k**

Compound **12** was prepared by the reaction of $PhSiCl_3$ with an equimolar amount of 4-[(2-hydroxyphenyl)amino]-pent-3-en-2-one in the presence of a twofold excess of triethylamine in THF (Scheme 6).[35] Then pentacoordinate complexes **13a**,**b** were synthesized by the reaction of compound **12** with trimethylsilyl trifluoromethanesulfonate and isocyanate in acetonitrile. Complex **14** was prepared by the reaction of $PhSiCl_3$ with 4-{[2-(methylamino)phenyl)]amino}pent-3-en-2-one by analogy with compound **12**. In all cases, the yields of the products were >55%.

The structures of complexes **12–14** in solution were determined by elemental analysis and ^{1}H, ^{13}C, ^{15}N, ^{19}F and ^{29}Si NMR spectroscopy; in the solid state, by ^{13}C, ^{15}N and ^{29}Si CP/MAS NMR spectroscopy and X-ray diffraction. According to the XRD data, the silicon atom in these compounds has coordination number 5 and is in a TBP environment, with the imine nitrogen atom of the tridentate ligand and the monodentate ligand in axial positions. It should be noted that the shifts $\delta^{29}Si$ in solution and in the crystals are only slightly different, thus indicating that the silicon atom has the coordination number 5 in solution as well (Table 2).

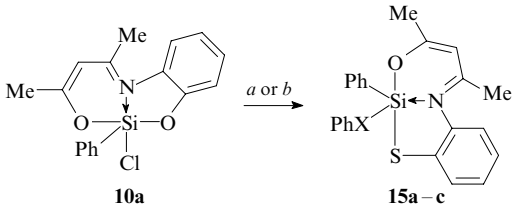
As can be seen from Table 2, the value of $\delta^{29}Si$ depends on the nature of the monodentate ligand and is virtually independent of the nature of the tridentate ligand. The replacement of the tridentate ONO or ONN ligand containing donor atoms (compounds **12–14**) by the ONS ligand (compounds **10a** and **11b**) is accompanied by a substantial downfield shift of the ^{29}Si NMR signal (see Tables 1 and 2).

Table 2. Chemical shifts (δ/ppm) of complexes **12–14** in the solid (CP/MAS) and liquid phases.[35]

Complex	^{29}Si CP/MAS	$\delta^{29}Si$ (CD_2Cl_2)
12	−97	−95.5
13a	−104.4	−106.1
13b	−114	−111.5
14	−96	−94.8

The reactions of complex **10a** with benzenethiol and benzeneselenol produced complexes **15a**,**b** in yields >75% (Scheme 7).[36] An alternative approach to the synthesis of compound **15a** is based on the reaction of complex **10a** with trimethylsilyl phenyl sulfide; however, the yield of the target product was somewhat lower (60%). Complex **15c** was synthesized by the reaction of compound **10a** with trimethylsilyl phenyl telluride. According to the XRD data, the coordination polyhedron in compounds **15a–c** can be described as a distorted trigonal bipyramid, with the oxygen and sulfur atoms of the tridentate ONS ligand in axial positions.

Scheme 7



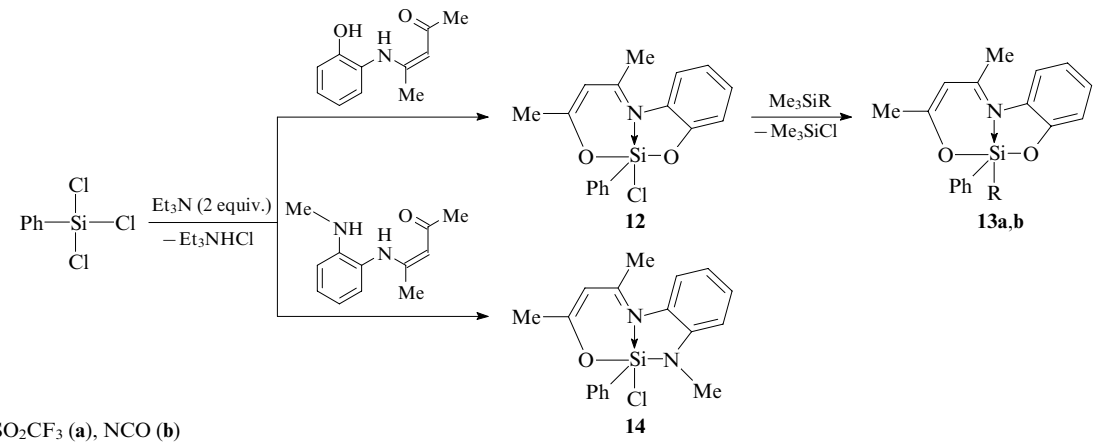
10a **15a–c**

(*a*) PhXH, Et_3N, $-Et_3NHCl$ (for **15a**,**b**);
(*b*) $PhXSiMe_3$, $-Me_3SiCl$ (for **15a**,**c**);
15: X = S (**a**), Se (**b**), Te (**c**)

Disilanes which contain tetra- and pentacoordinate silicon atoms and are not prone to reactions accompanied by the Si–Si bond cleavage were characterized.[37]

The reaction of imine **16** considered as the potentially tridentate ligand with disilane $(PhNCH_2CH_2NPh)Si(Me)SiMeCl_2$ (**17**) containing two tetracoordinate silicon atoms affords disilane **18** containing

Scheme 6

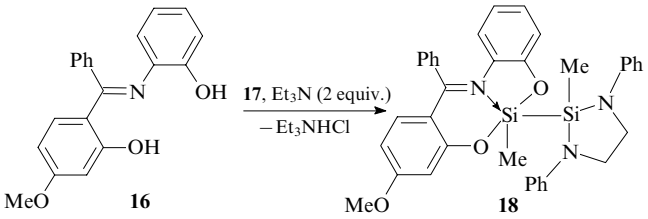


12 **13a**,**b** **14**

R = OSO_2CF_3 (**a**), NCO (**b**)

tetra- and pentacoordinate silicon atoms, the Si–Si bond remaining unchanged (Scheme 8).

Scheme 8



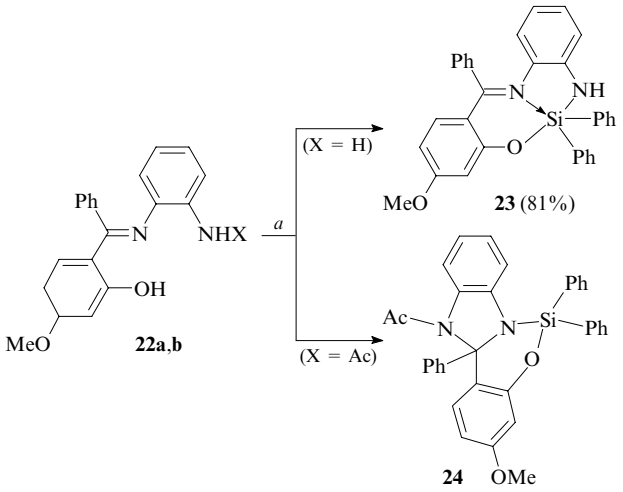
According to the XRD data, the pentacoordinate unit of complex **18** has a distorted TBP structure, with the oxygen atoms of the tridentate ligand in axial positions. It should be noted that the Si–Si bond length in complex **18** [2.3532(6) Å] is almost equal to the length of the corresponding bond in compound **17** [2.358(1) Å]. The ^{29}Si NMR spectrum of compound **18** in $CDCl_3$ shows two signals at δ 1.5 and −71.2 ppm assigned to tetra- and pentacoordinate Si atoms, respectively.[37]

Other disilanes containing one or two pentacoordinate Si atoms were synthesized by the reaction of dimethyltetrachlorodisilane with an equimolar amount or a twofold excess of imine **16** in THF upon cooling.[37] However, attempts to prepare target disilanes **19** and **20** failed. Monosilane **21** was isolated in both cases (Scheme 9). The pentacoordination of the Si atom in the latter compound in solution was established based on the high-field signal in the ^{29}Si NMR spectrum (−81.5 ppm) and the XRD data (distorted TBP).

The ^{29}Si NMR spectra of the reaction mixture show additional signals in a broad range from 36 to −94 ppm, which is indicative, in Wagler's opinion, of the formation of disilane followed by the Si–Si bond cleavage in this compound.[37]

The reaction of ligand **22a** with diphenyldichlorosilane in the presence of triethylamine gave compound **23** containing a pentacoordinate silicon atom (XRD data) (Scheme 10).[38] The pentacoordinate structure of complex **23** in the liquid phase was confirmed by the fact that the position of the high-field signal in the solid-state ^{29}Si NMR spectrum (−73.5 ppm) is close to that in the solution NMR spectrum (−79.3 ppm).

Scheme 10



X = H (**a**), Ac (**b**); (*a*) Ph_2SiCl_2, Et_3N (2 equiv.), $-Et_3NHCl$

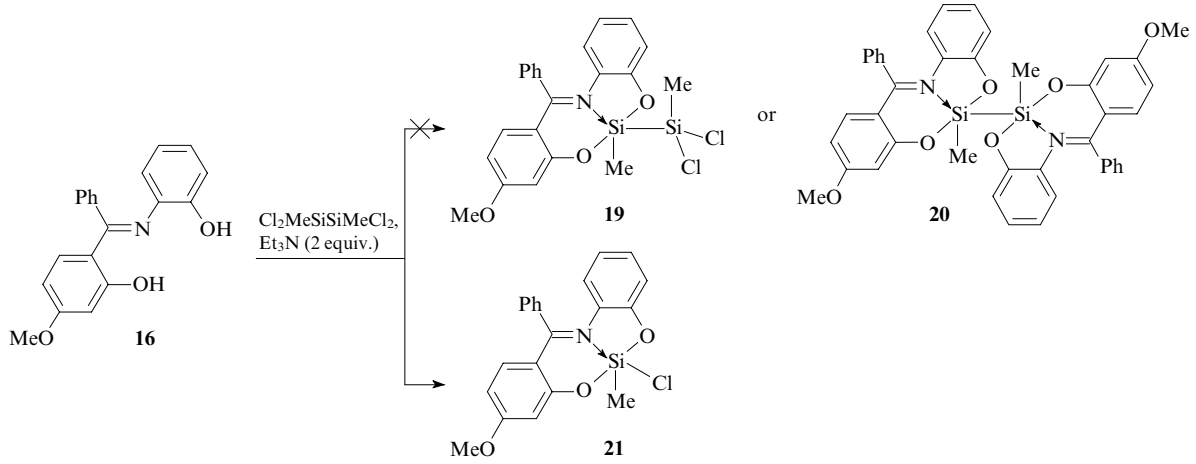
The ^{29}Si NMR spectrum of the reaction mixture, which was obtained by the corresponding reaction of compound **22b** containing the acetylated amino group, shows the major signal at δ −25.4 ppm,[38] which attests to the presence of a tetracoordinate silicon atom in the O,N-$SiPh_2$ coordination environment in product **24** (see Scheme 10).[39]

More recently, the synthesis of pentacoordinate chlorosilanes **25a**,**b** by the reaction of related imines **22c**,**d**, which are potential tridentate ligands, with $PhSiCl_3$ in the presence of triethylamine (Scheme 11) was documented.[40] The chlorine atom was then replaced with fluorine by the reaction of chloride **25b** with zinc fluoride to preprare fluoride **26**.

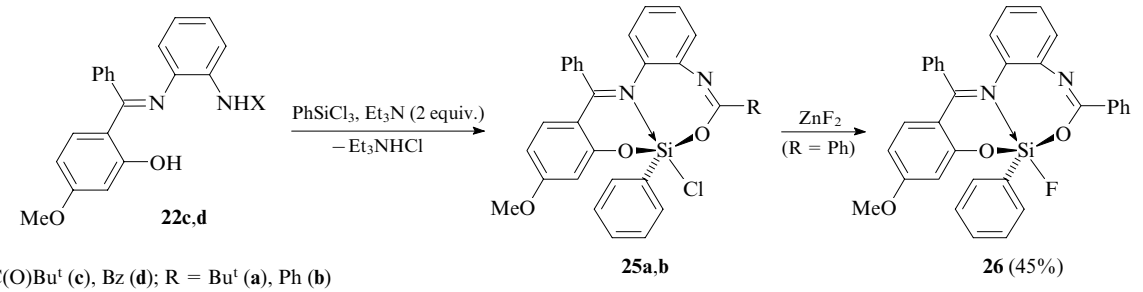
According to the XRD data, the coordination unit in halides **25b** and **26** has a TBP structure, with the equatorial plane formed by the carbon atom and two oxygen atoms. The Si–F bond (1.64 Å) in complex **26** is much shorter than the Si–Cl bond (1.980 Å) in compound **25b**, whereas the Si–N bond is longer (2.026 and 1.980 Å in complexes **26** and **25b**, respectively).

The reaction of bisimine **27** (the potentially tetradentate ligand) with diphenyldichlorosilane gave hexacoordinate complex **28** (Scheme 12).[41] Under UV irradiation of a suspension of complex **28** in THF, the latter undergoes a rearrangement involving the phenyl group to give penta-

Scheme 9

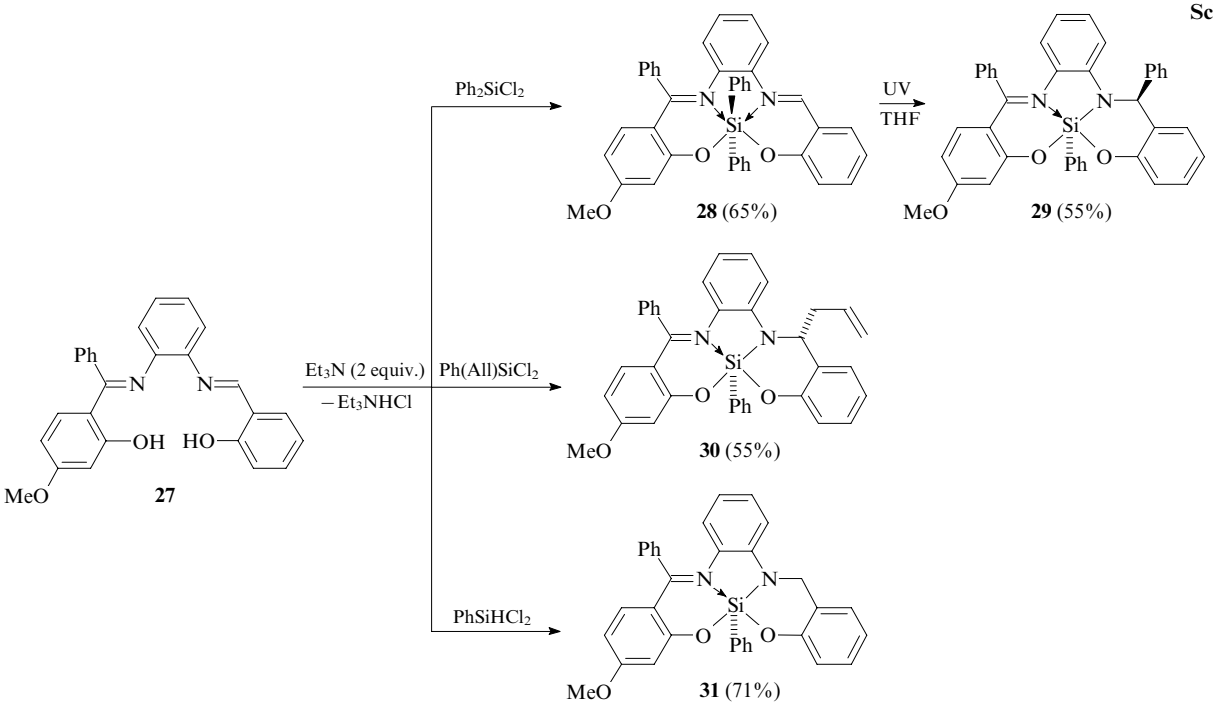


Scheme 11



X = C(O)Bu^t (**c**), Bz (**d**); R = Bu^t (**a**), Ph (**b**)

Scheme 12



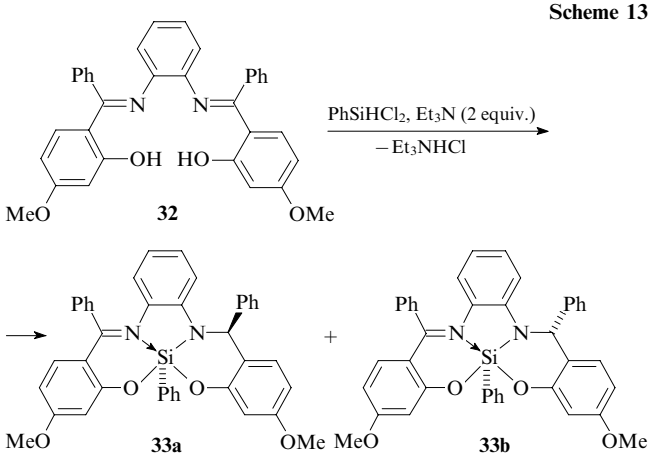
coordinate complex **29** (see Scheme 12). The structure of the latter in solution ($CDCl_3$) and in the solid state was confirmed by ^{29}Si NMR spectroscopy (−104.2 ppm) and X-ray diffraction.

The reactions of bisimine **27** with allylphenyldichlorosilane and phenyldichlorosilane give complexes **30** and **31**, respectively, as rearrangement products (see Scheme 12). According to the ^{29}Si NMR (−104.3 and −104.4 ppm, respectively, in $CDCl_3$) and XRD data, these complexes contain a pentacoordinate silicon atom. It should be noted that, as opposed to silane **29**, the allyl group in compound **30** is in the *syn* position with respect to the phenyl substituent at the silicon atom.

The reaction of bisimine **32** with phenyldichlorosilane affords a mixture of two stereoisomers **33a**,**b** containing a pentacoordinate silicon atom ($\delta^{29}Si$ −104.4 and −105.1 ppm, respectively, in $CDCl_3$) in a ratio of 10 : 1 (Scheme 13).[41]

The reaction of compound **34**, which was prepared by the silylation of bisimine **27** with trimethylchlorosilane, with $PhSiCl_3$ afforded hexacoordinate complex **35** (Scheme 14).[41] The addition of tetrachlorostannane to a solution of chloride **35** in $CHCl_3$ results in the Si−Cl bond cleavage to form ionic compound **36**. According to the XRD and ^{29}Si NMR data, the latter has pentacoordinate

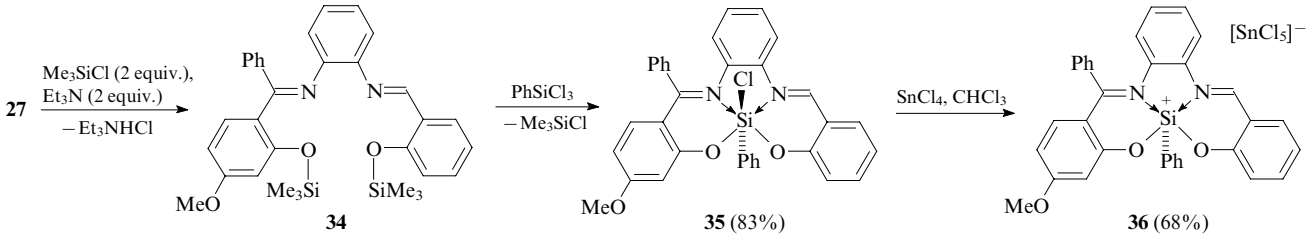
Scheme 13



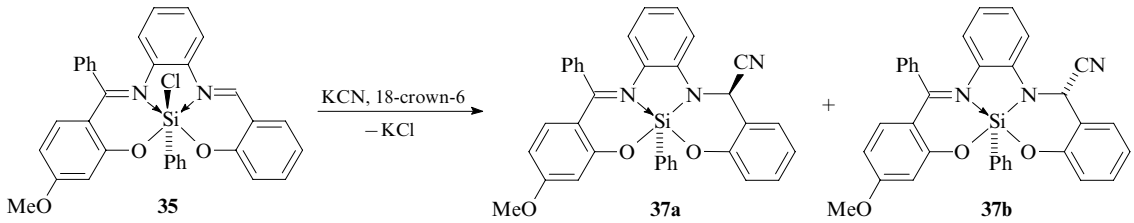
geometry both in the solid state and in solution ($\delta^{29}Si$ −111.3 ppm, $CDCl_3$).

As evidenced by the ^{29}Si NMR spectrum, the reaction of complex **35** with KCN in the presence of 18-crown-6 produces a mixture of two diastereomers **37a**,**b** containing a pentacoordinate silicon atom ($\delta^{29}Si$ −105.1 and −105.9 ppm, respectively) in a ratio of 2 : 1 (Scheme 15).

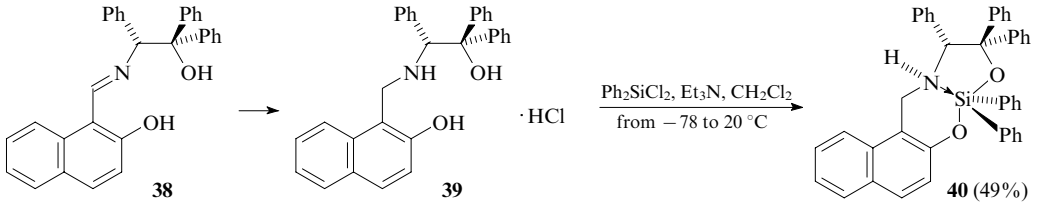
Scheme 14



Scheme 15



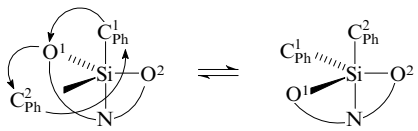
Scheme 16



The results of the above-considered studies of silicon complexes with O,N,O ligands containing the imine group opened up the possibility of the synthesis of the desired compounds and more detailed investigation of such ligands. Thus, imine **38** was prepared by the condensation of 2-hydroxynaphthaldehyde with (*R*)-2-amino-1,1,2-triphenylethanol and was then reduced with cyanoborohydride to aminodiol **39** isolated as hydrochloride (Scheme 16).[42] The reaction of the latter with diphenyldichlorosilane in the presence of triethylamine gave complex **40**. Its pentacoordinate structure in solution is evidenced by a high-field signal in the ^{29}Si NMR spectrum (–82.7 ppm, $CDCl_3$). It should be noted that the ^{1}H, ^{13}C and ^{29}Si NMR spectra of complex **40** at room temperature in solutions show signals belonging to only one structure. By contrast, two diastereomers (**40a**,**b**, 1 : 1) having TBP geometry (Scheme 17) were found in the crystals (XRD data).

The geometry of diastereomers was determined by quantum chemical calculations in the framework of the density functional theory (DFT). According to the calculations, both diastereomers are characterized by similar energies (ΔG_{298} < 9 kcal mol^{-1}).

Scheme 17

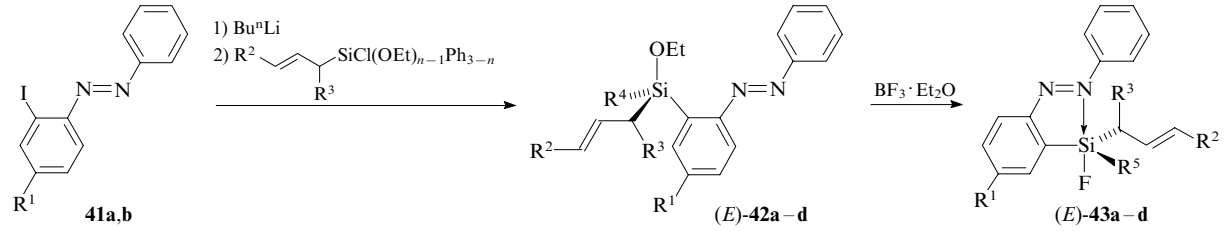


The interconversion of the diastereomers can take place as a result of the permutation isomerization through the Berry pseudorotation mechanism or *via* a turnstile rotation.[6, 7, 42] Other possible mechanisms of the permutation, in particular, the dissociative mechanism involving the reversible Si–N bond cleavage followed by the reorganization of the TBP structure, were also considered. However, the predominant mechanism of the stereodynamic process cannot be reliably established based on the available experimental data.

Table 3. Experimental and calculated (B3LYP/6-31 + + G(d) DFT-GIAO) ^{29}Si, ^{15}N and ^{13}C NMR chemical shifts (δ /ppm) of diastereomers **40**.[42]

Parameter	Solution in $CDCl_3$	Crystal		Ratio	Calculation	
		40a	**40b**		**40a**	**40b**
δ^{29}Si	–82.7	–88.1	–72.0	2.3 : 1.0	–83.0	–68.9
δ^{15}N	–	–313.1	–326.3	1.7 : 1.0	–290.9	–306.2
δ^{13}C (C-11)	42.6	43.6	40.8	1.3 : 1.0	47.9	42.3
δ^{13}C (C-12)	67.8	83.0	78.8	1.3 : 1.0	74.3	74.8
δ^{13}C (C-2)	153.6	154.8	153.4	1.2 : 1.0	163.4	163.1

Scheme 18



41a,**b** (*E*)-**42a**–**d** (*E*)-**43a**–**d**

R^1 = H (**a**), Me (**b**); n = 2, 3

Compounds **42**, **43**	R^1	R^2	R^3	R^4	R^5	Yield of **43** (%)
a	H	H	H	OEt	F	63
b	Me	Me	H	OEt	F	87
c	H	$(CH_2)_3$		OEt	F	31
d	H	H	H	Ph	Ph	90

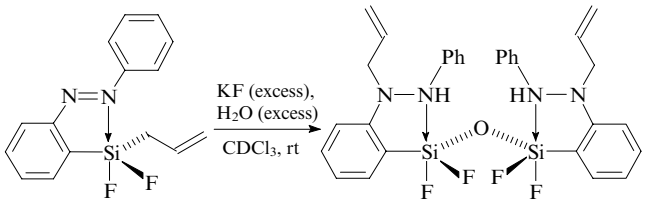
It should be noted that, as opposed to the high-resolution solution NMR spectra, the ^{29}Si and ^{15}N CP/MAS NMR spectra show two signals, which is consistent with the XRD data.[42] Besides, the experimental chemical shifts are in agreement with the calculated values, which made it possible to assign these shifts to the corresponding diastereomers (Table 3).

Allylsilanes (*E*)-**42a**–**d** containing a tetracoordinate silicon atom were prepared starting from azobenzenes **41a**,**b** and allylchlorosilanes and were then transformed into pentacoordinate allylsilanes (*E*)-**43a**–**d** by the treatment with boron trifluoride diethyl etherate (Scheme 18).[43]

The complexes were characterized by elemental analysis. Their structures were determined by multinuclear (^{1}H, ^{13}C, ^{19}F and ^{29}Si) NMR spectroscopy. The pentacoordination of the silicon atom in compounds (*E*)-**43a**–**d** in solution (CD_2Cl_2, $CDCl_3$) is evidenced by the fact that the ^{29}Si NMR spectra dispaly signals at higher field (at δ ~ -38 ppm) compared to the starting tetracoordinate allylsilanes (*E*)-**42a**–**d** (~ -24 ppm, CD_2Cl_2, $CDCl_3$). The ^{19}F NMR spectra of difluoride (*E*)-**43a** at room temperature shows a broadened singlet at δ^{19}F ~ -140.4 ppm (CD_2Cl_2, $CDCl_3$), which is split into two broadened singlets at δ^{19}F -141.3 and -127.2 ppm (CD_2Cl_2) as the temperature is reduced to -90 °C. The observed spectral pattern indicates that two fluorine atoms are nonequivalent. The XRD data confirm this conclusion. Thus, complex (*E*)-**43a** contains the $SiNF_2C_2$ coordination unit having distorted TBP geometry, with the nitrogen atom and one of the fluorine atoms in axial positions and the second fluorine atom in the equatorial plane.

The reaction of complex (*E*)-**43a** with an excess of potassium fluoride in the presence of water results in the intramolecular allylation of the azobenzene moiety at the nitrogen atom to give tetrafluorodisiloxane (*E*)-**44a** in 84% yield (Scheme 19).[43]

Scheme 19

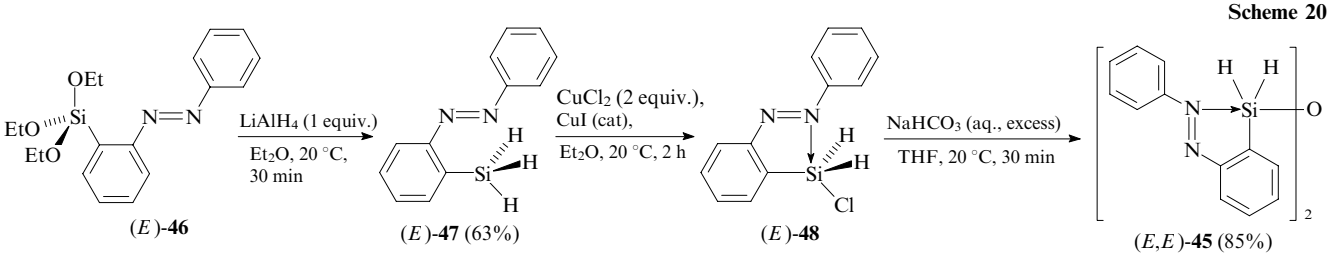


(*E*)-**43a** (*E*)-**44a** (84%)

The pentacoordination of the silicon atom in compound (*E*)-**44a** in solution is evidenced by the presence of a high-field signal in the ^{29}Si NMR spectrum (-87.3 ppm, $CDCl_3$). It should be noted that, since disiloxane (*E*)-**44a** has two asymmetric silicon atoms, the NMR spectra should exhibit signals of four diastereomers. In actuality, two sets of signals with equal intensity are observed in the ^{19}F NMR spectrum at -60 °C; these signals become broader and coalesce to a singlet (-136.78 ppm) as the temperature is raised to 60 °C. This may attest to the similarity of the chemical shifts of the signals of the diastereomers and the occurrence of a stereodynamic process involving two diastereomers in solution.

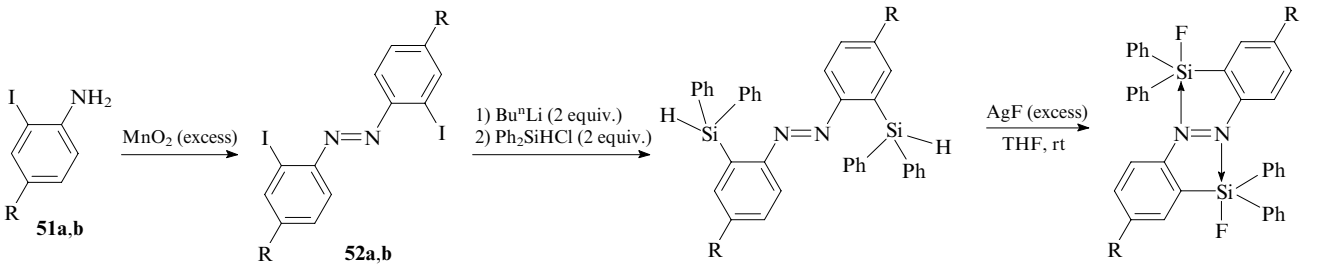
More recently, the same authors prepared disiloxane (*E*,*E*)-**45**, in which both silicon atoms are in the pentacoordinate state (Scheme 20).[44] The reaction of triethoxysilane (*E*)-**46** with $LiAlH_4$ in diethyl ether at room temperature afforded trihydrosilane (*E*)-**47**. The chlorination of the latter with $CuCl_2$ in the presence of catalytic amounts of CuI gave dihydrochlorosilane (*E*)-**48** in quantitative yield.[45] Compound (*E*)-**48** was then transformed into disiloxane

Scheme 20



(*E*)-**46** (*E*)-**47** (63%) (*E*)-**48** (*E*,*E*)-**45** (85%)

Scheme 21



51a,**b** **52a**,**b** **50a**,**b** [70% (**a**), 82% (**b**)] **49a**,**b** [40% (**a**), 79% (**b**)]

R = Me (**a**), Bu^n (**b**)

(*E*,*E*)-**45** by the hydrolysis in the presence of sodium hydrocarbonate.

The pentacoordination of the silicon atom in complex (*E*,*E*)-**45** is evidenced by the presence of the signal in the ^{29}Si NMR spectrum at higher field compared to that of 1,1,3,3-tetrahydro-1,3-diphenyldisiloxane (−58.9 and −25.4 ppm, respectively).[46] The pentacoordinate structure of disiloxane (*E*,*E*)-**45** in the solid state was confirmed by X-ray diffraction.[47]

It should be noted that the irradiation of tetrahydrosiloxane (*E*,*E*)-**45** using a high-pressure mercury lamp causes its quantitative isomerization to the *Z*,*Z* form. The ^{29}Si NMR spectrum of the reaction mixture shows only one triplet (−28.3 ppm, $^1J_{SiH}$ 230 Hz), the chemical shift of which is indicative of the tetracoordination of the Si atom.[44]

Pentacoordinate 2,2′-bis(fluorodiphenylsilyl)azobenzenes **49a**,**b** were synthesized by the reaction of tetracoordinate silanes **50a**,**b** (which were prepared in two steps from anilines **51a**,**b** through intermediates **52a**,**b**) with an excess of silver fluoride in THF at room temperature (Scheme 21).[48]

The resulting complexes were identified in solution and in the solid state by elemental analysis, multinuclear (^{1}H, ^{13}C, ^{19}F, ^{29}Si) NMR spectroscopy, ^{29}Si CP/MAS NMR and X-ray diffraction. The pentacoordination of the Si atom in complexes **49** in $CDCl_3$ is evidenced by the high-field signals in the ^{29}Si NMR spectra at δ −21.0 and −20.3 ppm, respectively. It should be noted that the ^{29}Si CP/MAS NMR spectrum of compound **49a** shows a signal at δ^{29}Si −4.7 ppm characteristic of tetracoordinate fluorosilanes,[25,26] whereas a high-field signal at δ^{29}Si −29.0 ppm is recorded under the same conditions for complex **49b**.

The difference in the structure of the complexes in the solid state was confirmed by XRD data. Thus, both Si atoms in compound **49a** have the coordination number 4, whereas silane **49b** contains two $SiNFC_3$ coordination units having distorted TBP geometry.

The reaction of di(isothiocyanato)methylsilane with compound **53** affords pentacoordinate complex **54** (^{29}Si CP/MAS NMR −107 ppm; δ^{29}Si −105.7 ppm in $CDCl_3$) (Scheme 22).[49] The reaction was performed at 20 °C in dichloromethane in the presence of triethylamine.

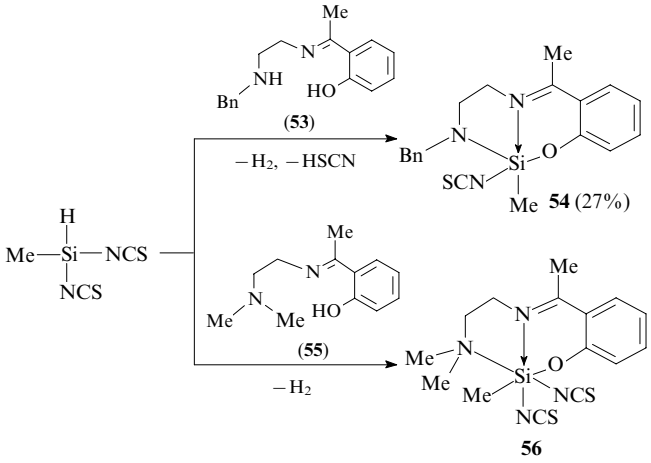
The reaction of di(isothiocyanato)methylsilane with compound **55** gives hexacoordinate complex **56** (^{29}Si CP/MAS NMR, δ −172.9; δ^{29}Si −172 in $CDCl_3$) (see Scheme 22).

Pentacoordinate complex **57** reacts with salicylic, glycolic and (*S*)-lactic acids to form compounds **58** and **59a**,**b**, respectively (Scheme 23).[50] The chemical shifts of the signals in the solution and solid-state ^{29}Si NMR spectra of complexes **58** and **59a**,**b** are given in Table 4.

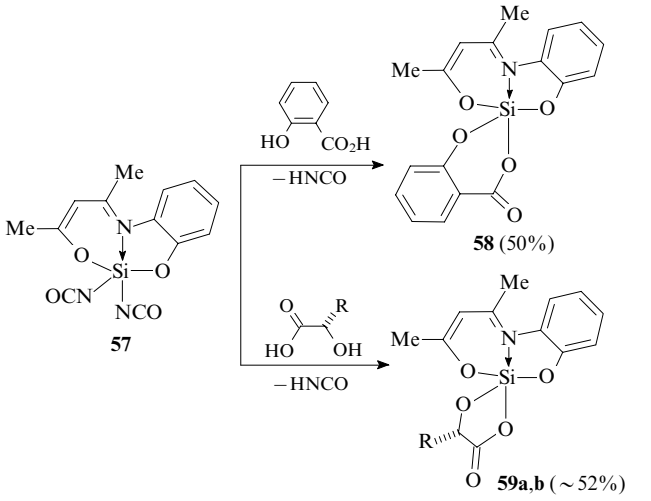
Table 4. Chemical shifts (δ/ppm) of complexes **58** and **59a**,**b** in the solid (CP/MAS) and liquid phases.[50]

Complex	^{29}Si CP/MAS	δ^{29}Si (CD_2Cl_2)
58	−126.1	−128.3
59a	−111.0	−111.3
59b	−113.3, −114.3	−113.6, −113.7

Scheme 22



Scheme 23



R = H (**a**), Me (**b**)

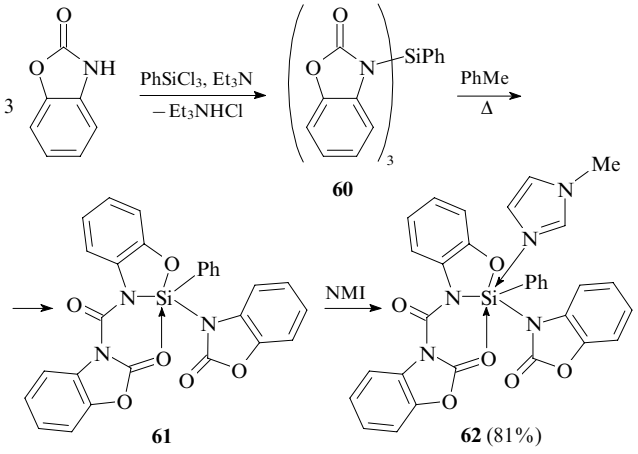
Compound **58** proved to be unstable in solution, as indicated by the fact that additional signals appear in a few hours in the ^{29}Si NMR spectrum at δ^{29}Si −188.8 and −164.7 ppm. Based on the published data, these signals were assigned to the tris[salicylato(2−)-*O*1,*O*3]silicate dianion [51] and the neutral tetracoordinate compound with two tridentate ligands.[52] Compound **59a** was isolated as a solvate with 1/2 THF molecule.

Unlike complex **59a**, the crystals of compound **59b** consist of two diastereomers in a ratio of 1 : 1. The coordination polyhedron of these diastereomers has a distorted TBP structure, with the oxygen atoms of the tridentate ligand and the oxygen atom of the hydroxy group of the bidentate ligand in the equatorial plane.

The study of the stereodynamic properties of the complexes showed that the rise of the temperature to 48 °C leads to a coalescence of the proton signals of the CH_2 group of the glycolate moiety of compound **59a** due to the racemization of the SiO_4N skeleton.

The reaction of benzoxazolin-2-one with $PhSiCl_3$ in the presence of triethylamine gave silane **60** in 68% yield, and this compound was transformed under reflux in toluene into chelate complex **61** containing the tridentate O,N,O ligand and a pentacoordinate silicon atom (Scheme 24).[53] The pentacoordinate structure of complex **61** in solution was confirmed by ^{29}Si NMR spectroscopy (−96.0 ppm in $CDCl_3$) and in the solid state by X-ray diffraction. Complex **61** exhibits an almost ideal TBP coordination environment, with the tridentate ligand in the $O_{ax}N_{eq}O_{ax}$ position.

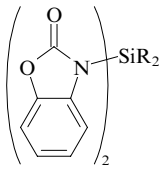
Scheme 24



The treatment of complex **61** with *N*-methylimidazole (NMI) affords adduct **62**. According to the XRD data, its coordination unit has an octahedral structure, in which the imidazole nitrogen atom is in the *trans* position with respect to the benzoxazolinone nitrogen atom. The chemical shift of the signal in the ^{29}Si NMR spectrum in $CDCl_3$ is −166.3 ppm

The prolonged heating of compounds **63a**,**b**, which were prepared by the reaction of benzoxazolin-2-one with diorganyldichlorosilanes, with NMI did not result in the formation of pentacoordinate silicon compounds related to complex **61**.[54] After the addition of NMI to the reaction mixture, the spectra show, along with the signals of the starting compounds (δ^{29}Si −22.5 and 5.7 ppm for silanes **63a**,**b**, respectively), signals of pentacoordinate silicon complexes (−82.2 and −59.2 ppm). However, after the heating under reflux, only compounds containing a tetracoordinate silicon atom were detected; the chemical shifts in the spectra of these signals (δ^{29}Si −32.9 and −0.2 ppm) are substantialylly shifted downfield compared with δ^{29}Si of compound **61** (see Scheme 24).

Structures 63

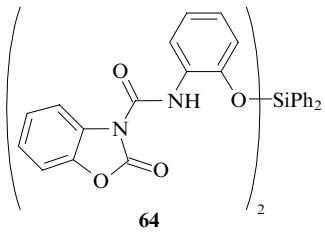


63a,**b** R = Ph (**a**), Me (**b**)

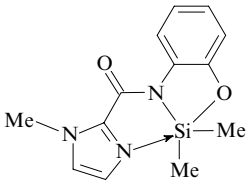
Crystalline compound **64** was isolated as the product of the reaction involving silane **63a**; in the case of silane **63b**, several crystals of complex **65** were obtained. Their structures were confirmed by X-ray diffraction.

The reaction of 1-methylimidazole-2-thione with dimethylchloro(chloromethyl)silane produced complex **66** (Scheme 25).[55] The presence of an intramolecular N → Si coordination bond in the crystals of this compound was established by X-ray diffraction.

Structures 64, 65

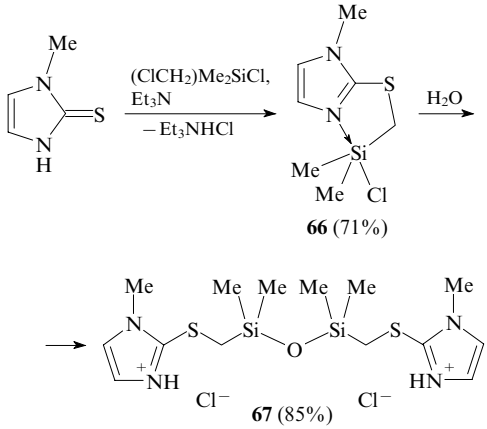


64



65

Scheme 25

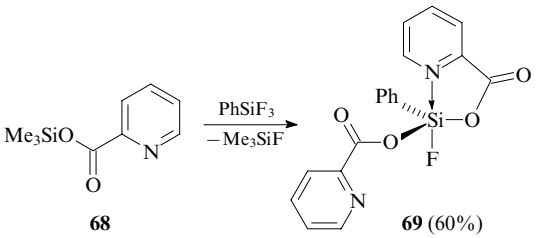


The pentacoordination of the Si atom in solution follows from the similarity of the chemical shifts of the signals in the ^{29}Si NMR spectrum (−35.2 ppm in $CDCl_3$) and in the ^{29}Si CP/MAS NMR (−34.7 ppm). According to these data, the Si atom is in a TBP coordination environment, with three carbon atoms in the equatorial plane and the nitrogen and chlorine atoms in the axial positions. The Si−Cl bond length is 2.51 Å. In our opinion, the abnormal elongation of the Si−Cl bond is attributed to the formation of a strong intramolecular N→Si coordination bond, as evidenced by the fact that the values of δ^{29}Si in solution differ only slightly from those in the solid state (see above). The hydrolysis of chlorosilane **66** in the absence of bases

afforded salt **67**, in which both silicon atoms of the disiloxane group are tetracoordinate. The structure of salt **67** was confirmed by elemental analysis, X-ray diffraction and high-resolution multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR spectroscopy in solution.

The reaction of phenyltrifluorosilane with the trimethylsilyl derivative of α-picolinic acid **68** gave fluorosilane **69** (Scheme 26).[56] The ^{19}F and ^{29}Si NMR spectra of complex **69** in $CDCl_3$ show signals at δ −130.56 and −75.1 ppm, respectively, which attests to the pentacoordination of the silicon atom.[25,26]

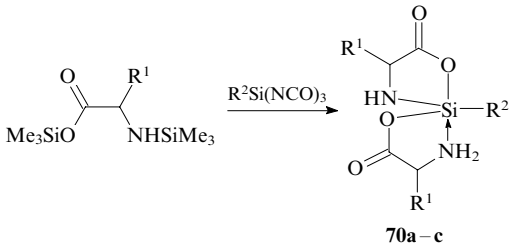
Scheme 26



68 **69** (60%)

Compounds **70a–c** were synthesized by the reactions of various tris(isocyanato)silanes with a twofold excess of *O*,*N*-bis(trimethylsilyl) derivatives of alanine, phenylalanine and leucine (Scheme 27).[57] The reactions were performed in acetonitrile at temperatures < −20 °C. The target compounds were isolated in yields of ~ 50%. The moderate yields were attributed to the possible formation of oligopeptides as by-products, which is accompanied by the elimination of trimethylsilanol. The latter is transformed into hexamethyldisiloxane with the water abstraction. According to the ^{13}C, ^{15}N and ^{29}Si CP/MAS NMR data and the results of X-ray diffraction, the coordination number of the silicon atom in compounds **70a–c** in the solid state is 5. It should be noted that the authors succeeded in studying the ^{1}H, ^{13}C and ^{29}Si NMR spectra in DMSO only for complex **70b**. According to the XRD data, the coordination polyhedron of complexes **70** has distorted TBP geometry, with the oxygen atom and the nitrogen atom of the NH_2 group in the axial positions; the carbon atom, the second oxygen atom and the nitrogen atom of the NH group are in the equatorial plane. The strongest upfield shift of the ^{29}Si NMR signal in the solid state was observed for complex **70b** (δ^{29}Si −98.5 ppm).

Scheme 27

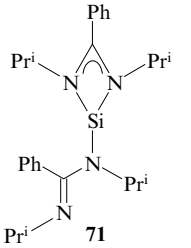


70a–c

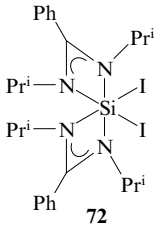
$R^1 = R^2$ = Me (**a**); R^2 = Ph: R^1 = Bn (**b**), Bu^t (**c**)

The synthesis of compound **71** (in 86% yield) containing a tricoordinate silicon atom in the coordination environment, which is formed by mono- and bidentate ligands, was documented.[58] The reaction of derivative **71** with iodine produced hexacoordinate silicon(IV) complex **72** in 89% yield.[58] It should be noted that the syntheses of a number of stable silicon(IV) compounds containing a Si=X bond (X is chalcogen) have been published earlier: **73a–c**,[59] **74a–d**,[60–62] **75a–c**,[63] **76a**,[64] **76b**,[65] **77**,[65] **78**,[66] **79a–f**,[67] **80a–c**.[68,69] However, all these complexes contain a tri- or tetracoordinate silicon(IV) atom. By contrast, the reactions

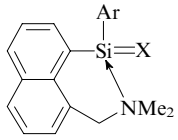
Structures 71–80



71

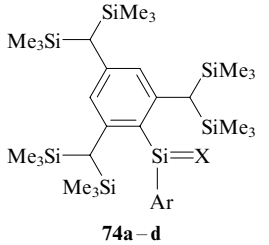


72



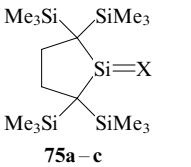
73a–c

X = S: Ar = Ph (**a**), 1-Naph (**b**); X = Se, Ar = Ph (**c**); Naph is naphthyl



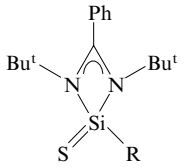
74a–d

Ar = 2,4,6-$Me_3C_6H_2$, X = S (**a**);
Ar = 2,4,6-$Pr^i_3C_6H_2$: X = S (**b**), Se (**c**), Te (**d**)



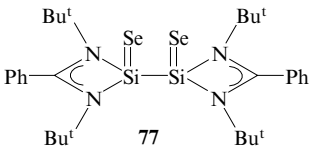
75a–c

X = S (**a**), Se (**b**), Te (**c**)

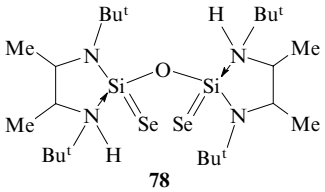


76a,b

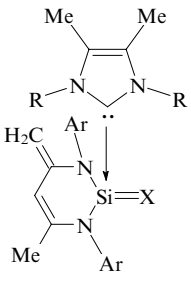
R = SBu^t (**a**), Cl (**b**)



77

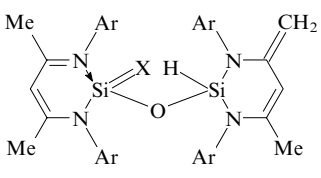


78



79a–f

X = S: R = Me (**a**), Pr^i (**b**);
X = Se: R = Me (**c**), Pr^i (**d**);
X = Te: R = Me (**e**), Pr^i (**f**);
Ar = 2,6-$Pr^i_2C_6H_3$

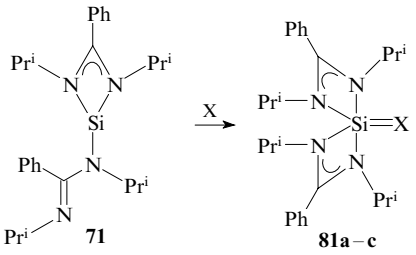


80a–c

X = S (**a**), Se (**b**), Te (**c**);
Ar = 2,6-$Pr^i_2C_6H_3$

of compound **71** with elemental sulfur, selenium and tellurium in toluene at 20 °C afforded compounds **81a–c** in 51%, 46% and 72% yields, respectively (Scheme 28).[70]

Scheme 28



X = S (**a**), Se (**b**), Te (**c**)

Compounds **81** were characterized by elemental analysis. Their TBP structure was established by solution and solid-state NMR spectroscopy, as well as by X-ray diffraction. The similarity of the chemical shifts of the signals in the solution and solid-state ^{29}Si NMR spectra of complexes **81** indicates that the coordination units have similar structures.

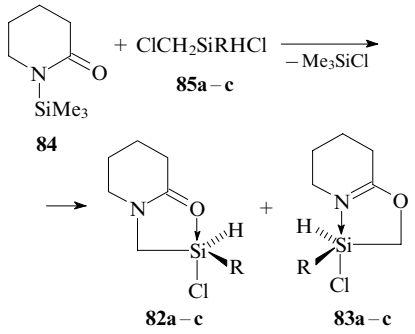
Compounds **81**	δ /ppm	
	CP/MAS	solution in C_6D_6
a	−74.7	−70.7
b	−85.0	−80.8
c	−111.4	−116.5

It should be noted that Junold *et al.* failed to prepare oxygen-containing analogues of complexes **81**.[58]

2. Complexes with an intramolecular O → Si coordination bond

Pentacoordinate silanes **82a–c**, **83a–c** were synthesized by the transsilylation of *N*-trimethylsilylpiperidin-2-one (**84**) with different chloromethylsilanes $ClCH_2SiRHCl$ (**85a–c**) (Scheme 29).[71] Thus, the reaction of N-TMS derivative **84** with silane **85b** affords a mixture of isomeric pentacoordinate chelates **82b** and **83b** in a ratio of 4.5 : 1 in a total yield of 87%. The ratio of the isomers was calculated based on the analysis of the ^{1}H NMR spectra of the reaction mixture, which show two sets of signals of the CH_2 group at δ 2.93 and 4.08 ppm assigned to the $SiCH_2N$ and $SiCH_2O$ groups of compounds **82b** and **83b**, respectively.

Scheme 29

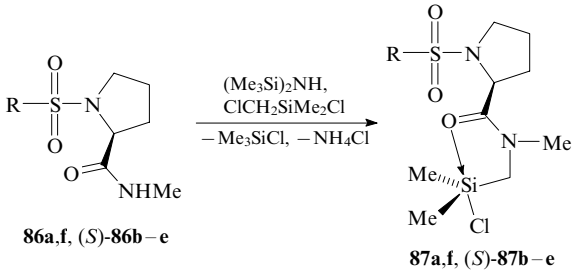


R = Me (**a**), Ph (**b**), Bn (**c**)

It should be noted that chloride **83b** was the first example of pentacoordinate complexes having a lactim structure, which is stable at room temperature. The chemical shifts of the signals in the ^{29}Si NMR spectra of complexes **82b** and **83b** are −74.35 and −83.30 ppm, respectively.

Among the known types of organic derivatives of pentacoordinate silicon, no C,O- and O,O-chelates containing amino acid moieties involved in the substituent at the amide carbon atom were described. Hence, the data on the synthesis of such complexes by the direct N-dimethylchlorosilylmethylation of amides **86a–f** with the system $ClCH_2SiMe_2Cl-(Me_3Si)_2NH$ (Scheme 30) are of interest.[72] (Scheme 30 shows the *S* isomers, although compounds **86a**,**f** and **87a**,**f** existed as racemates.)

Scheme 30



86a,**f**, (*S*)-**86b–e** **87a**,**f**, (*S*)-**87b–e**

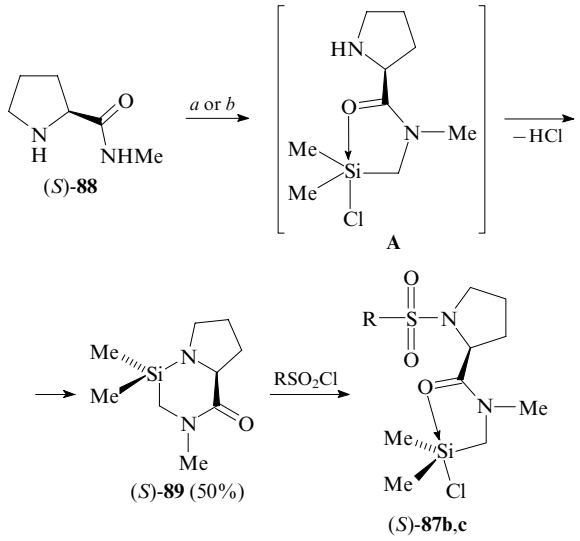
R = Me (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-$O_2NC_6H_4$ (**f**)

The optimal ratio (1 : 2) of the starting amides to the $ClCH_2SiMe_2Cl-(Me_3Si)_2NH$ system for the preparative isolation of chlorosilanes **87a–f** was chosen based on the results of IR spectroscopy monitoring. It was found that the reaction of methylamide (*S*)-**86c** with $ClCH_2SiMe_2Cl$ in the presence of Et_3N in boiling benzene is completed in 3 h at the ratio methylamide : $ClCH_2SiMe_2Cl$ = 1 : 1. However, product (*S*)-**87c** was obtained in a substantially lower yield (65%) compared with that obtained with the use of the $ClCH_2SiMe_2Cl-(Me_3Si)_2NH$ system (88%).

Yet another route to C,O-chelates **87** was examined as an alternative method. This approach was accomplished to prepare compound (*S*)-**88**, the pyrrolidine ring of which, as opposed to prolinamides **86**, contains the free NH group. It was found that the silylmethylation of amide (*S*)-**88** with the $ClCH_2SiMe_2Cl-(Me_3Si)_2NH$ system or its treatment with $ClCH_2SiMe_2Cl$ in the presence of Et_3N produces the previously unknown bicyclic silacyclane (*S*)-**89** (Scheme 31).[73]

According to the proposed scheme, the first step results in the formation of the N-dimethylchlorosilylmethylation product at the amide nitrogen atom, *viz.*, chlorosilane **A** [or(and) its *N*′-TMS derivative in the reactions with the use of hexamethyldisilazane], which undergoes thermal decomposition accompanied by the elimination of HCl (or, respectively, Me_3SiCl) in the course of the fractionation to form the target silacyclane. The IR spectrum of compound (*S*)-**89** shows a stretching band at ~1650 cm^{-1} (NCO), and its ^{29}Si NMR spectrum exhibits a signal at δ^{29}Si ~5 ppm typical of a tetracoordinate Si atom in a comparable coordination environment. The subsequent reactions of silacyclane (*S*)-**89** with sulfochlorides $PhSO_2Cl$ and 4-$MeC_6H_4SO_2Cl$ gave (O → Si)-chelate chlorosilanes (*S*)-**87b**,**c** in 75% and 81% yields, respectively. The advantage of this method is that it can be used to synthesize

Scheme 31

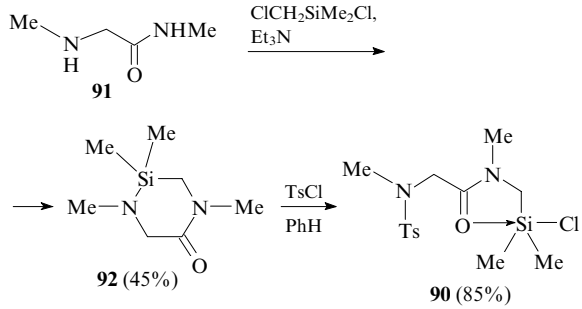


(*a*) $ClCH_2SiMe_2Cl$, $(Me_3Si)_2NH$, $-Me_3SiCl$, $-NH_4Cl$;
(*b*) $ClCH_2SiMe_2Cl$, Et_3N, $-Et_3NHCl$;
R = Ph (**b**), 4-MeC_6H_4 (**c**)

chlorosilanes **87** containing different substituents in the sulfonamide group and does not require the multi-step preparation of the corresponding starting amides **86**.

The same approach can be applied to the synthesis of chlorosilane **90**. In the first step, the reaction of amide **91** with $ClCH_2SiMe_2Cl$ in the presence of Et_3N affords 2-sila-piperazin-5-one **92** isolated in a moderate yield as a readily hydrolyzable oil (Scheme 32). The formation of compound **92** was confirmed by mass spectrometry.[72–74] In the second step, the Si–N bond cleavage in compound **92** gave C,O-chelate chlorosilane **90**.

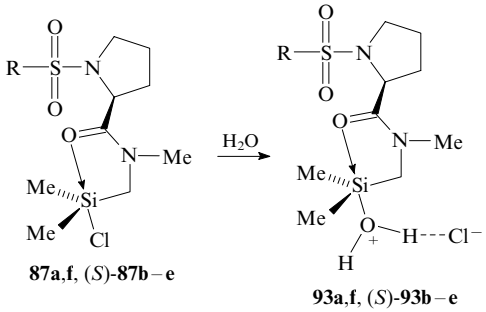
Scheme 32



Ts = 4-$MeC_6H_4SO_2$

Sarcosine derivative **90** proved to be unstable and is very readily hydrolyzed. Nevertheless, compound **90** was characterized by elemental analysis and IR spectroscopy. The proposed structure of complex **90** in the crystal was confirmed by X-ray diffraction. The conclusion that the resulting chlorosilanes are hydrolyzed in solutions to form silyloxonium chlorides was made based on ^1H, ^{13}C and ^{29}Si NMR spectroscopic data and was confirmed by X-ray diffraction study of the crystals of these compounds. Thus, the recrystallization of chlorosilanes **87** under conditions, which do not prevent the contact with moisture,[73] gave complexes **93** (Scheme 33).

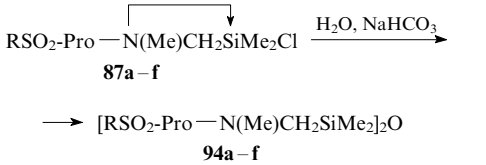
Scheme 33



The solid-state ^{29}Si CP/MAS NMR spectra of silyloxonium chlorides were measured for the first time. In the solid state, complexes **93a**,**f** and (*S*)-**93c** are characterized by a signal $\delta^{29}Si$ at an even higher field (−40.2, −42.2 and −43.4 ppm, respectively) compared with the position of the signal in solution (from −30 to −35 ppm). The changes in $\delta^{29}Si$ are indicative of the weakening of the intramolecular O → Si coordination bond due to the solvation of the Si atom in the pentacoordinate complexes by solvent molecules.

The high lability of the chlorine atom in monochlorosilanes **87** facilitates the abstraction of this atom as a result of the hydrolysis in the presence of a base to form disiloxanes **94** (Scheme 34, the intramolecular hydrogen bond is indicated by a broken line).[72–74] Their compositions and structures were determined by elemental analysis and spectroscopic methods (IR and ^1H, ^{13}C, ^{29}Si NMR). The IR spectra of disiloxanes **94** show an intense absorption band of the free amide group at 1650 cm^{-1}. The signal of the tetracoordinate Si atom in the ^{29}Si NMR spectra appears in the narrow range characteristic of disiloxanes (4–5 ppm).

Scheme 34

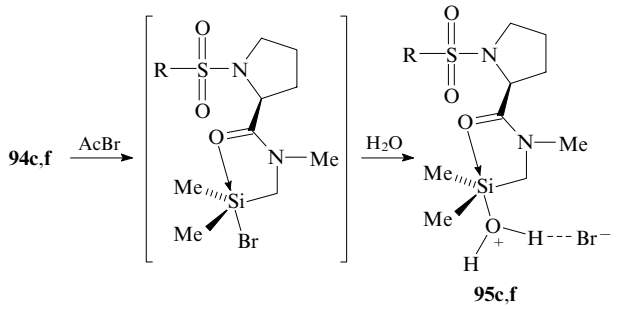


R = Me (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-$O_2NC_6H_4$ (**f**); Pro is the proline moiety

The reactions of compounds (*S*,*S*)-**94c** and **94f** with $SOCl_2$ take place even at room temperature to give chlorosilanes (*S*)-**87c** and **87f** in high yields (83% and 90%, respectively).[72–74]

In the study of complexes **94c**,**f**, it was shows that the Si–O–Si bond activated by amide groups can be cleaved using an excess of acetyl bromide. Silyloxonium bromides **95c**,**f** were obtained in the presence of moisture at room temperature (Scheme 35).[72–74] According to the XRD data, the silicon atom in compound **95f** is pentacoordinate and has TBP coordination geometry; three carbon atoms form the equatorial plane, and the amide oxygen atom and the oxygen atom of the $^+OH_2$ group are in the axial positions.

Scheme 35

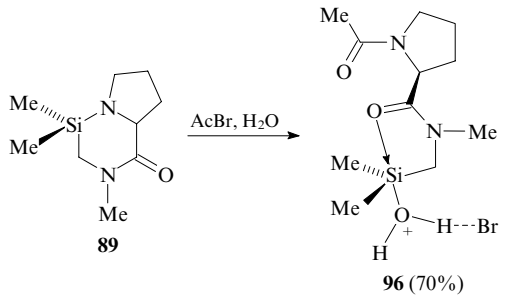


R = 4-MeC_6H_4 (**c**), 4-$O_2NC_6H_4$ (**f**)

Therefore, disiloxanes **94** readily react with electrophilic reagents ($SOCl_2$, AcBr). It should be noted that these reactions can be performed on a preparative scale. This is evidence of high reactivity of disiloxanes. These reactions provide additional possibilities for the synthesis of new pentacoordinate silicon compounds.

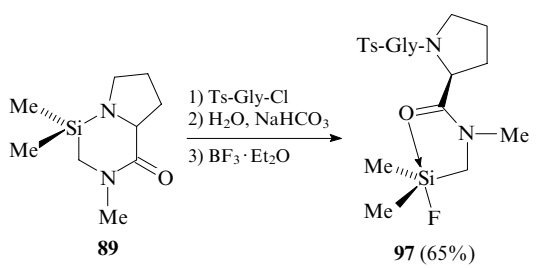
The synthesis of new chelate silicon compounds containing a proline moiety was based on the fact that the Si – N bond can be easily cleaved with electrophilic reagents. For example, the reaction of heterocycle **89** with acetyl bromide in the presence of atmospheric moisture afforded the ring opening product, (O → Si)-chelate **96** (Scheme 36).[72, 73]

Scheme 36



The ring opening in compound **89** with tosylglycine acid chloride followed by the hydrolysis of the resulting chlorosilane in the presence of a base and the treatment of disiloxane with $BF_3 \cdot Et_2O$ in the last step afforded fluorosilane **97** containing a dipeptide moiety (Scheme 37).[73, 74] As opposed to chlorosilanes, which are readily hydrolyzed in solution to form the corresponding silyloxonium chlorides due to high reactivity of the Si – Cl bond, the Si – F bond proved to be much more stable and is resistant to the hydrolysis in such solvents as $CDCl_3$ or CD_2Cl_2 commonly used in NMR spectroscopy. Therefore, fluorosilanes are very convenient models for studying equilibrium processes in solution.

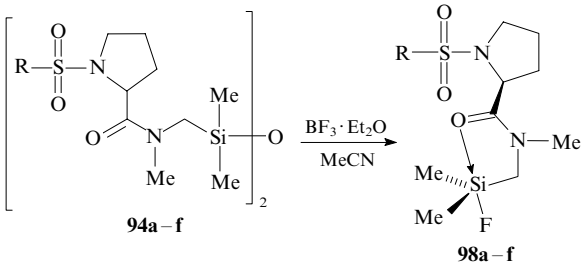
Scheme 37



The activation of the siloxane bond through the effect of adjacent amide groups facilitates the reaction of disiloxanes **94** with BF_3 etherate, which proceeds under relatively mild conditions; the yields (80% – 90%) and purity of the reaction products are such that this method can be considered to be suitable for the preparative synthesis of pure fluorosilanes **98a – f** (Scheme 38).[74, 75] The position of the absorption band (~1611 – 1615 cm^{-1}) of the NCO group in the solid-state attenuated total internal reflectance infrared spectra of fluorosilanes **98a – f** is characteristic of pentacoordinate compounds.[75]

Investigations of the character of changes in the spectral parameters (IR and NMR) depending on the concentration and the aggregation state revealed a considerable contribution of the solvation effects to the stabilization of the molecule in solution. Taking into account that variations in the concentration in the range of 0.01 – 0.5 mol $litre^{-1}$ cause only slight changes in the frequency of NCO bending vibrations in the IR spectrum, it was concluded that a solution in chloroform contains dimeric forms of fluorosilanes **98** in a low concentration.[72]

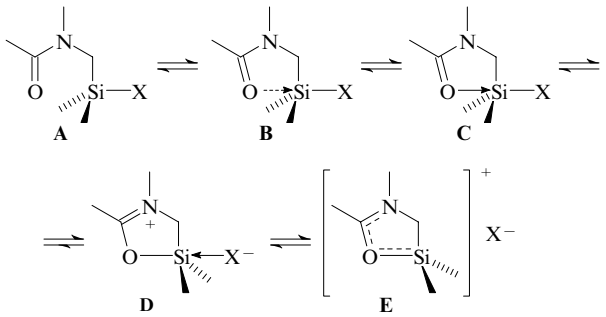
Scheme 38



R = Me (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-$O_2NC_6H_4$ (**f**)

Depending on the nature of the monodentate ligand X (X = F, Cl, Br, I, OTf), pentacoordinate derivatives of silicon can be arbitrarily divided into several groups based on the similarity of their structures to one of the resonance forms **B – E** (Scheme 39).[7, 75] In the series of the structures **D** → **C** → **B**, the Si – O covalent bond is transformed into a strong coordination bond (form **C**) and a weak coordination bond (form **B**). Scheme 39 also includes the tetracoordinate structure **A**. The latter can be considered as the limiting structure, in which an intramolecular Si → O hydrogen bond is absent. In the case of compounds containing the $XSiC_3O$ coordination unit, fluorides are characterized by the largest contribution of the structures **A** and **B**; chlorides, of the form **C**; bromides, of the form **D**, iodides and triflates, of the form **E**.

Scheme 39



An analysis of the temperature-dependent ^{1}H, ^{19}F and ^{29}Si NMR spectra of fluorosilanes **98** showed that the ratio of the contributions of the forms **A**–**E** to the equilibrium presented in Scheme 39 changes with temperature.[72–75] Thus, the lowering of the temperature to −60 °C leads to the shift of the equilibrium towards the pentacoordinate structure **B**, whereas the rise of the temperature shifts the equilibrium towards the tetracoordinate structure **A**.

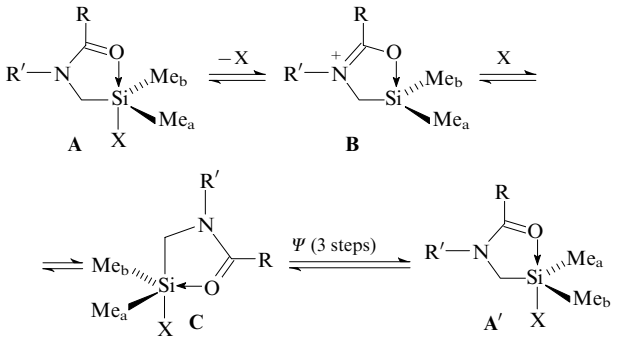
In the study of complexes **98b**,**e**, it was found for the first time that temperature-dependent changes in $\delta^{19}F$ in the ^{19}F NMR spectra are accompanied by changes in the multiplicity of the signal. These observations made it possible to determine the character of transformations in the coordination unit depending on the temperature and the nature of the solvent.[74,75]

In the ^{1}H NMR spectra of chlorosilanes **87**, silyloxonium chlorides **93** and fluorosilanes **98**, the signal of the $SiMe_2$ group appears as a symmetric doublet, an additional splitting of each component of the doublet being observed for fluorosilanes due to the spin–spin coupling (SSC) with the axial fluorine atom.[72–75] The reversibility of the temperature dependence of the line shape of the signals was revealed by dynamic ^{1}H NMR (DNMR) spectroscopy, and the activation parameters of the slow (on the NMR time scale) exchange between the positions of equatorial methyl groups in the coordination polyhedron were calculated. It was found that the nature of the substituent in the aromatic ring (group R) has only a slight effect on the Gibbs free energy of activation of the permutation isomerization ($\Delta G^{\neq}_{298}$): ~11 kcal mol^{-1} for chlorosilanes and silyloxonium chlorides, >20 kcal mol^{-1} for fluorosilanes. In all cases, the entropies of activation are characterized by larger (in magnitude) negative values (from −14 cal mol^{-1} K^{-1} to −24 cal mol^{-1} K^{-1}).

The stereodynamic behaviour of pentacoordinate silicon complexes in the presence of an external nucleophile was studied by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy for compounds **98b**,**d**. It was shown that the addition of 10 mol.% $Bu^{n}_{4}NF$ to solutions of fluorosilanes in $CDCl_3$ is accompanied by a substantial broadening of the signals of the $SiMe_2$ group in the ^{1}H NMR spectra, whereas the ^{1}H NMR signals of the other groups remain almost unchanged. For complex **98e**, the addition of $Bu^{n}_{4}NF$ leads to the disappearance of SSC ($^{3}J_{HF}$) and the collapse of the ^{19}F NMR multiplet into a broadened singlet. It should be noted that the presence of an external nucleophile has no noticeable effect on the position of the signal in the ^{29}Si NMR spectrum of fluorosilanes **98d**,**e**, which indicates that the coordination number 5 of the silicon atom remains unchanged.

The mechanism of the polytopic rearrangement in the coordination unit was proposed[73,74] based on the experimental data and quantum chemical calculations by the DFT method using the PBE0/6-311G(d,p) basis set for complex **98a**. The rearrangement occurs through the formation of an ionic tetracoordinate topomer (**B**), which is formed as a result of the elimination of the monodentate ligand X (Scheme 40). The subsequent nucleophilic attack of X occurs from the rear with respect to the $Si-CH_2$ bond to form the pentacoordinate intermediate **C**. The topomer **A′** is formed after the three-step Berry pseudorotation (Ψ) in the intermediate **C**. A large negative entropy of activation is indicative of the stabilization of the topomer **B** by solvent molecules due to solvation. An increase in the barrier to the activation for fluorosilanes compared to silyloxonium halides and chlorosilanes is apparently associated with the hindered removal of the fluorine atom in the first step (see Scheme 40).

Scheme 40

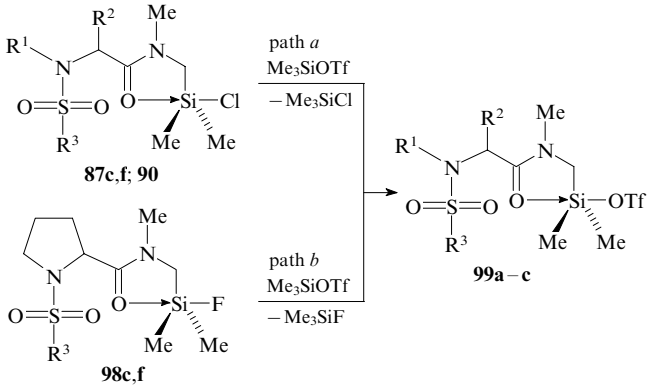


X = F^-, OH_2

The NMR spectra of a series of C,O-monochelate *N′*-(dimethylfluorosilylmethyl)-*N′*-methyl-*N*-(organylsulfonyl)prolinamides **98** were studied in the solid state and in solutions in chloroform, pyridine and acetone.[76] The spectroscopic data were interpreted using quantum chemical calculations. It was found that the molecular conformation observed in the crystals is the same as in solution. The coordination bonds of the silicon atom with acetone and pyridine are very weak and cannot stabilize the acyclic form (without the O → Si coordination bond). The ^{29}Si NMR chemical shift was found to directly depend on the Si–O bond length. The mutual effect of the organylsulfonyl group and the chelate ring was described in terms of polarization effects.

Halosilanes **87c**,**f**, **90** and **98c**,**f** based on proline and sarcosine were transformed into C,O-chelate triflates **99a**–**c** in yields >80% by the reaction with trimethylsilyl triflate (Scheme 41).[72]

Scheme 41



99: R^1 = Me, R^2 = H, R^3 = 4-MeC_6H_4 (**a**);
R^1-R^2 = $(CH_2)_3$: R^3 = 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**)

The reaction with the use of fluorosilanes as the starting compounds (path *b*) was shown to be preparatively more convenient because low-boiling point trimethylfluorosilane that is formed can be easily removed from the reaction mixture in the course of the synthesis.

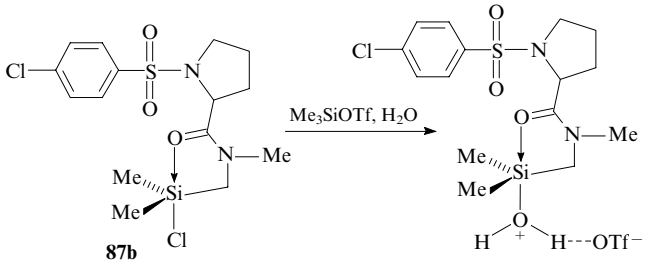
The ^{1}H NMR spectra of triflates **99** in CD_3CN show an additional broadened signal in the range of 6–8 ppm assigned to the $^{+}OH_2$ group. This is indicative of the

rapid hydrolysis of the resulting complexes to form silyloxonium triflates.

The pentacoordinate structure of the latter compounds in solution is evidenced by the ^{29}Si NMR spectra, which show signals at δ −18 and −10 ppm for compounds **99b** and **99c**, respectively.[73] According to the XRD data, the coordination polyhedron of the silicon atom in complexes **99a**,**b** has distorted TBP geometry.

The reaction of chlorosilane **87b** with trimethylsilyl triflate in the presence of atmospheric moisture afforded complex **100**, the ionic structure of which and the pentacoordination of the silicon atom both in the solid state and in solution were confirmed by X-ray diffraction and ^{29}Si NMR spectroscopy (Scheme 42).[73]

Scheme 42



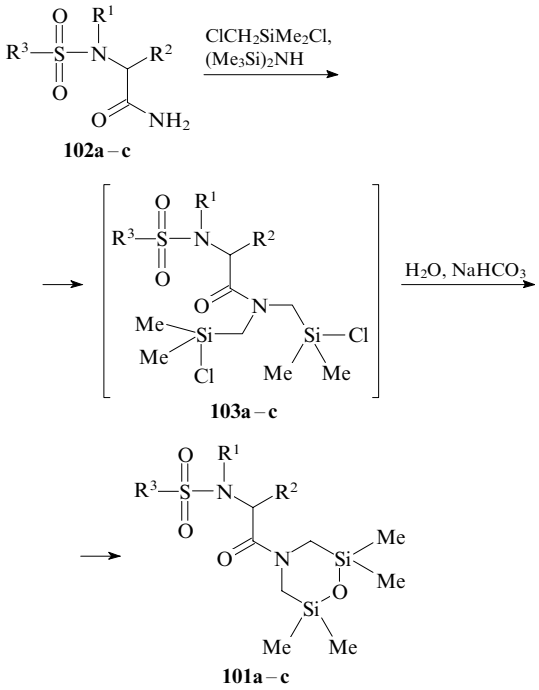
The synthesis of pentacoordinate silicon compounds containing two $SiMe_2X$ groups, which can coordinate the oxygen atom of the C=O group, is not only of experimental but also of theoretical importance. For example, the available results can be used for the modelling of S_N2 reactions, the estimation of the degree of the coordination contributions of each group potentially capable of being involved in the coordination, investigation of the relative reactivity of $SiMe_2F$ groups containing silicon atoms in different coordination environment (coordination numbers 4 or 5) in one molecule, *etc*. The two-step synthesis of bisfluorides based on two α-amino acids, proline and sarcosine, through the formation of 2,6-disilamorpholines, is worthy of notice.[75]

2,6-Disilamorpholines **101a**–**c** containing amino acid groups were synthesized by the reaction of amides **102a**–**c** with the $ClCH_2SiMe_2Cl-(Me_3Si)_2NH$ system followed by the treatment of the reaction mixture with an aqueous $NaHCO_3$ solution (Scheme 43). The monitoring of the reaction of amide **102a** with dimethylchloromethylchlorosilane in a ratio of 1 : 3 (under reflux in benzene or toluene for 4 h) by IR spectroscopy revealed the formation of the intermediate, pentacoordinate *N*,*N*-bis(dimethylchlorosilylmethyl)amide **103a** (see Scheme 43).[73]

In the IR spectra, the C=O absorption band of amide **102a** is shifted from 1680 to 1590 cm^{-1}, which corresponds to C=O vibrations of pentacoordinate silicon compounds. It is known that such chlorosilanes are very easily subjected to hydrolysis. Hence, compounds **103** were not isolated in the individual state. The hydrolysis of *in situ* prepared dichlorides **103** gave previously unknown 2,6-disilamorpholines **101** in yields >75%.

(O → Si)-Chelate *N*′,*N*′-bis(dimethylfluorosilylmethyl)-*N*-organylsulfonyl-(*S*)-prolinamides **104a**,**b** and *N*′,*N*′-bis(dimethylfluorosilylmethyl)-*N*-mesylsarcosinamide (**104c**) were synthesized in yields >80% by heating disilamorpholines **101a**–**c** with $BF_3\cdot Et_2O$ in refluxing acetonitrile (Scheme 44).

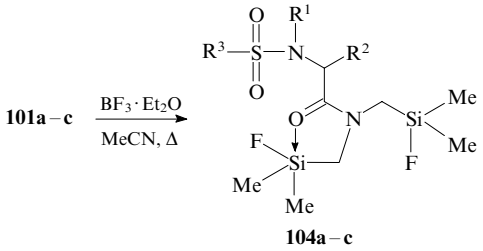
Scheme 43



$R^1-R^2 = (CH_2)_3$: R^3 = Me (**a**), 4-MeC_6H_4 (**b**);
R^1 = R^3 = Me, R^2 = H (**c**)

The pentacoordination of one of the silicon atoms in difluorides **104** in the solid state and in solution was established by single-crystal X-ray diffraction and ^{29}Si NMR spectroscopy.

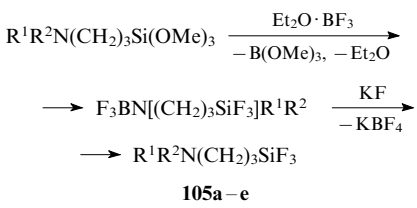
Scheme 44



$R^1-R^2 = (CH_2)_3$: R^3 = Me (**a**), 4-MeC_6H_4 (**b**);
R^1 = R^3 = Me, R^2 = H (**c**)

Trifluorosilanes **105a**–**e** were synthesized in two steps. In the first step, the fluorination of (3-aminopropyl)trimethoxysilanes with boron trifluoride diethyl etherate gave the complexes $F_3B(NCH_2CH_2CH_2SiF_3)R^1R^2$. In the second step, the latter were treated with an excess of KF to prepare

Scheme 45



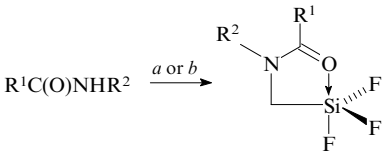
R^1 = R^2 = H (**a**), Me (**b**); R^1 = Ph, R^2 = H (**c**);
$R^1R^2N = O(CH_2CH_2)_2N$ (**d**), $(CH_2)_5N$ (**e**)

the target products (yields >70%) as moisture-sensitive coloured oils (Scheme 45).[77] The resulting complexes were characterized by elemental analysis, IR spectroscopy and ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy. The pentacoordination of the silicon atom in fluorosilanes **105a**,**b** in $CDCl_3$ is evidenced by the presence of ^{29}Si NMR signals at higher field (−90.1 and −88.8 ppm, respectively) compared to the model trifluorosilane $Cl(CH_2)_3SiF_3$ (−59.0 ppm).[78]

At room temperature, the ^{19}F NMR signal of trifluorides **105a**,**b** appears as a broadened singlet, which attests to the fast (on the NMR time scale) positional exchange in the coordination unit involving three fluorine atoms. A decrease in the temperature is accompanied by broadening of the signals. At temperatures < −100 °C, one axial and two equatorial fluorine atoms in the ^{19}F NMR spectra of complexes **105a**,**b** are nonequivalent. Thus, the signal of F_{ax} appears as a triplet ($\delta^{19}F$ −115.4 and −113.8 ppm, respectively), whereas two signals of F_{eq} are observed as two doublets −131.4 ppm [$J(^{19}F_{ax},^{19}F_{eq})$ 30.1 Hz] and −146.6 ppm [$J(^{19}F_{ax},^{19}F_{eq})$ 33.0 Hz]. The activation barriers of the interconversion of diastereomers determined at the coalescence temperature (−40 °C) are 9.2 and 8.8 kcal mol^{-1} for trifluorides **105a**,**b**, respectively.

N-(Trifluorosilylmethyl)-[*N*-(*S*)-(1-phenylethyl)]acetamide (**106a**) and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine (**106b**) were synthesized in yields of >50% by the reactions of the corresponding amides with $ClCH_2SiCl_3$ and Et_3N or the $ClCH_2SiCl_3$–$(Me_3Si)_2NH$ system followed by the methanolysis or hydrolysis of the reaction mixture in the presence of bases and the subsequent treatment of intermediate trimethoxysilanes or oligosiloxanes (without their isolation) with BF_3 diethyl etherate (Scheme 46).[79]

Scheme 46

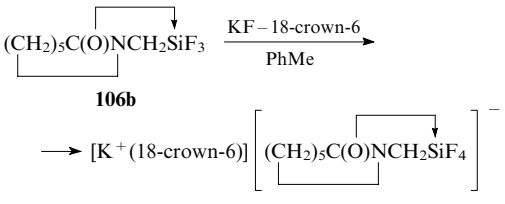


106a,**b**

(*a*) 1) $ClCH_2SiCl_3$, $(Me_3Si)_2NH$; 2) H_2O, $NaHCO_3$; 3) $BF_3 \cdot Et_2O$; (*b*) 1) $ClCH_2SiCl_3$, Et_3N or $(Me_3Si)_2NH$; 2) MeOH, Et_3N or $(Me_3Si)_2NH$; 3) $BF_3 \cdot Et_2O$; R^1 = Me, R^2 = CH(Ph)Me (**a**); R^1–R^2 = $(CH_2)_5$ (**b**)

The reaction of trifluoride **106b** with KF in the presence of 18-crown-6 produced (2-oxoperhydroazepinomethyl) tetrafluorosilicate **107** (Scheme 47).[79] According to the ^{19}F and ^{29}Si NMR spectroscopic and XRD data, the silicon atom is pentacoordinate in trifluorides **106a**,**b** and hexacoordinate in adduct **107**. Therefore, the intramolecular O → Si coordination bond that is present in trifluorides **106** is retained in adduct **107**.

Scheme 47



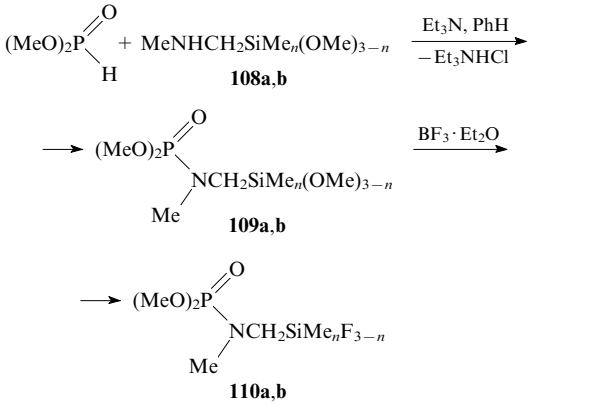
106b

107 (70%)

Stereochemical non-rigidity of thrifluorides **106a**,**b** was studied by ^{19}F DNMR.[79] The activation barriers of the permutation isomerization vary from 9.5 to ~10 kcal mol^{-1} and are similar to those for trifluorides **105a**,**b**. It was suggested[79] that the lower values of $\Delta G^{\#}$ for the permutation of trifluorides **106a**,**b** compared with those for monofluorides with the $OSiC_3F$ coordination unit (>20 kcal mol^{-1}), as well as the small (in magnitude) negative activation entropies, correspond to the non-dissociative (regulatory) mechanism of the permutation isomerization.[7]

The reaction of α-silylmethylamines $MeNHCH_2SiMe_n(OMe)_{3-n}$ (**108a**,**b**) with dimethyl phosphite in the presence of triethylamine afforded dimethyl phosphoric acid *N*-methyl-*N*-trimethoxysilylmethyl- (**109a**) and *N*-methyl-*N*-dimethyl(methoxy)silylmethylamides (**109b**) in 75% and 82% yields, respectively (Scheme 48).[80] The structures of the latter compounds in solution were determined by multinuclear NMR spectroscopy. The subsequent reaction of compounds **109a**,**b** with boron trifluoride diethyl etherate gave the corresponding dimethyl phosphoric acid *N*-methyl-*N*-fluorosilylmethylamides **110a**,**b**. The following data indicative of the pentacoordination of the silicon atom in complex **110a** were obtained: $\delta^{29}Si$ −107.2 ppm (for model $ClCH_2SiF_3$, −71 ppm), $^{1}J(^{29}Si,^{19}F)$ is 221.1 Hz, which is 46 Hz smaller than the corresponding value for $ClCH_2SiF_3$ [$^{1}J(^{29}Si,^{19}F)$ 267 Hz]; $\delta^{19}F$ −131.29 ppm *versus* $\delta^{19}F$ −143.99 ppm for model trifluoride.

Scheme 48



108a,**b**

109a,**b**

110a,**b**

n = 0 (**a**), 2 (**b**)

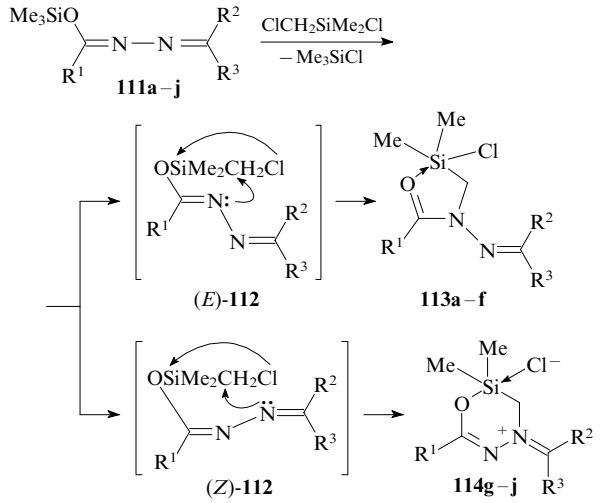
It was found that hydrazine derivatives **111a**–**j** react with dimethylchloro(chloromethyl)silane through the formation of intermediates **112** resulting in the regioselective formation of products of two types containing, depending on the nature (bulkiness) of the substituent R^1, either five-membered (compounds **113**) or six-membered (**114**) chelate rings (Scheme 49) (yields >75%).[81]

The ^{29}Si NMR spectra in $CDCl_3$ at 25 °C show signals in the range from −30.6 to −36.3 ppm for complexes **113** and in the range from −6.3 to 10.3 ppm for compounds **114**. An increase in the temperature leads to a slight downfield shift of the signals in the ^{29}Si NMR spectra of compounds **113b**,**d**. The effect of the temperature on the ratio of resonance structures **I**–**IV** was exemplified by complexes **114** (Scheme 50).

The dissociation into ions in the final step **IV** → **V** is evidenced by the downfield shift of the ^{29}Si NMR signal, which attests to the change from the pentacoordination to

tetracoordination. An analysis of the experimental data led to the conclusion that the role of the solvent ($CDCl_3$) is to stabilize the chloride ion at low temperature (see Scheme 50).[81]

Scheme 49

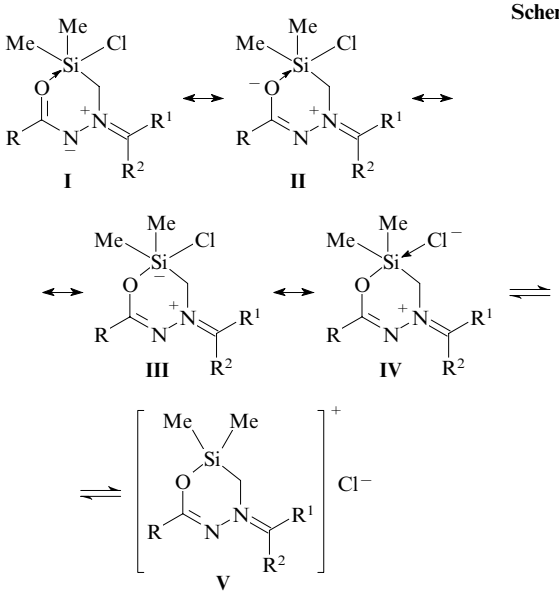


Compounds			R^1	R^2		R^3
111	**113**	**114**				
a	**a**		Me	Me		Me
b	**b**		Me		$(CH_2)_4$	
c	**c**		Me	Ph		H
d	**d**		Bn	Me		Me
e	**e**		Bn	Et		Et
f	**f**		Bn		$(CH_2)_6$	
g		**g**	Ph		$(CH_2)_4$	
h		**h**	Ph		$(CH_2)_5$	
i		**i**	Ph		$(CH_2)_6$	
j		**j**	Bu^t	Me		Me

According to the XRD data, the Si atom in compounds **113c**,**d** and **114i** has a TBP coordination environment, with three carbon atoms in the equatorial plane and the chlorine and oxygen atoms in the axial positions. A comparison of the Si – Cl and Si – O bond lengths showed that the former bond in complex **114i** is longer, whereas the latter bond is shorted compared with those in structure **113c**. In both cases, the changes in the bond lengths are small (0.114 – 0.115 Å).

Starting from heterocycle **115** (BonH) through the formation of its TMS derivative **116**, the first representative of monochelate pentacoordinate Si complexes with the

Scheme 50

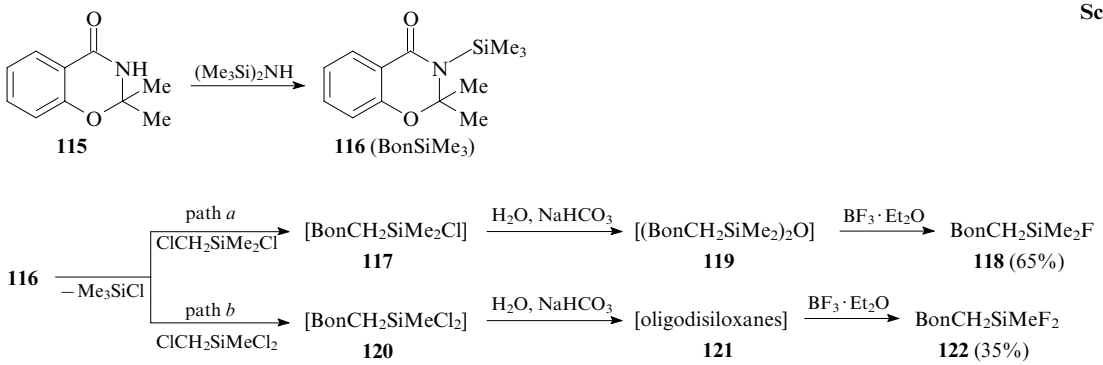


$BonCH_2$ ligand, chloride $BonCH_2SiMe_2Cl$ (**117**), was synthesized by the reaction of the **116** with $ClCH_2SiMe_2Cl$ (Scheme 51).[82] Fluoride $BonCH_2SiMe_2F$ (**118**) was prepared by the one-pot synthesis from TMS derivative **116** and dimethyl(chloromethyl)chlorosilane $ClCH_2SiMe_2Cl$ followed by the hydrolysis of intermediate chloride **117** in the presence of $NaHCO_3$ to give disiloxane **119** and the treatment of the latter with $BF_3 \cdot Et_2O$ (see Scheme 51, path *a*). Difluoride $BonCH_2SiMeF_2$ (**122**) was synthesized in a similar way, also in a one-pot fashion, using $ClCH_2SiMeCl_2$ as the dichlorosilylmethylation reagent through intermediate dichloride **120** and a mixture of oligodisiloxanes **121** without their isolation (path *b*).

A lower-field position of the signal in the ^{19}F NMR spectra of monochelates **118** and **122** (δ −120.7 and −123.7 ppm, respectively) compared with the signal of tetrahedral Me_3SiF (−158 ppm) and the upfield shift of the signal in the ^{29}Si NMR spectra of **118** and **122** (δ −12.9 and −51.3 ppm) with respect to the same model fluorosilane (28.1 ppm) are indicative of the formation of an intramolecular O → Si coordination bond in solution. It should be noted that this interaction of difluoride **122** is stronger, as was expected based on an increase in the number of electronegative monodentate ligands (F).

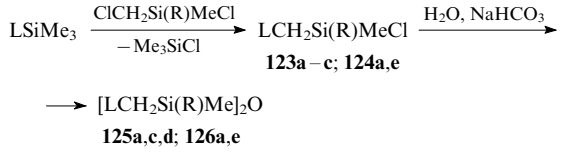
The hydrolysis of monochelate pentacoordinate chlorosilanes LCH_2SiMe_2Cl (**123**) and $LCH_2SiMePhCl$ (**124**) containing the monoanionic C,O-chelating ligand LCH_2 [where L is a residue of amide, *n*-membered lactam (Lc^n), succinic acid amide (Im^5) or phthalimide (PhtIm)], which were

Scheme 51



synthesized in the study,[84] was investigated in detail.[83] In the presence of bases, disiloxanes **125** and **126**, respectively, were obtained as the final products (Scheme 52). An attempt to synthesize chlorosilane **123d** resulted in the isolation of only its hydrolysis product **125d**.

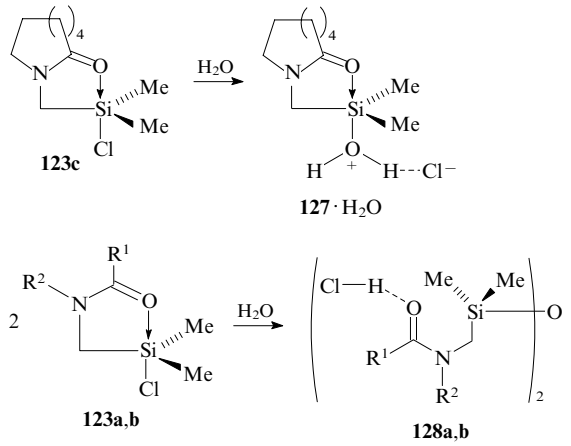
Scheme 52



R = Me (**123**, **125**), Ph (**124**, **126**); L = AcNMe (**a**), Lc[7] (**b**), Lc[8] (**c**), PhtIm (**d**), Im[5] (**e**)

The structures of chlorides **123a**,**c** and **124a**, hydrolysis products of chlorides **123a**,**c** in the absence of bases, such as silyloxonium chloride $[Lc^8CH_2SiMe_2OH_2]Cl$ (**127**·H_2O), disiloxane dihydrochloride $[AcN(Me)CH_2SiMe_2]_2O \cdot 2\,HCl$ (**128a**) (Scheme 53) and disiloxanes $(PhtImCH_2SiMe_2)_2O$ (**125d**) and $(Im^5CH_2SiMePh)_2O$ (**126e**), were determined by X-ray diffraction.

Scheme 53



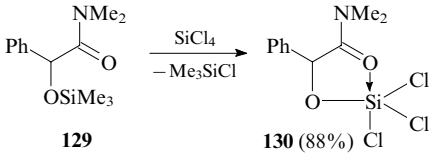
$R^1 = R^2 =$ Me (**a**), $R^1 - R^2 = (CH_2)_5$ (**b**)

According to the XRD data, the silicon atom in chlorides **123a**,**c** and **124a** and in silyloxonium chloride hydrate **127**·H_2O is pentacoordinate through the formation of an intramolecular O → Si coordination bond, whereas the silicon atom in dihydrochloride **128a** and disiloxanes **125d** and **126e** is tetracoordinate. The general scheme was proposed for the hydrolysis of mono-C,O-chelate chlorosilanes based on the experimental data obtained in the cited study and the data published in the literature. This scheme involves the formation of silyloxonium chlorides **127** in the first step followed by the generation of disiloxane di(hydrochlorides) **128**. The formation of the final hydrolysis products, disiloxanes **125** and **126**, is usually observed in the presence of bases acting as acceptors of HCl (see Scheme 52).

The reaction of silicon tetrachloride with L-amygdalic acid *N*,*N*-dimethyl-*O*-trimethylsilylamide (**129**) produced new hypercoordinate silicon complex **130** with the monoanionic O,O-chelating ligand (Scheme 54).[85]

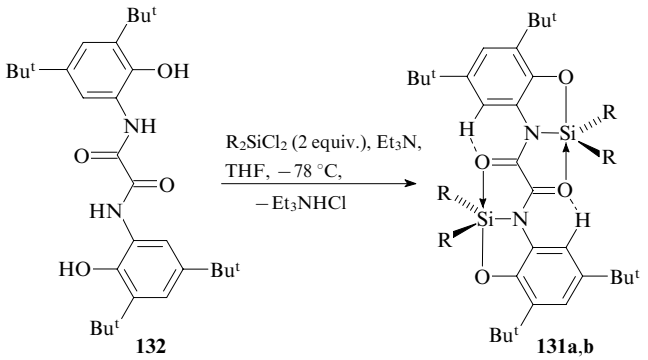
The reaction is accomplished by stirring the reactants (in a ratio of 1 : 1) in hexane at room temperature for 5 h. The structure of compound **130** was confirmed by IR spectroscopy, ^1H, ^{13}C and ^{29}Si NMR spectroscopy and elemental analysis. The high-field signal of the silicon atom in complex **130** ($\delta^{29}Si$ −93.84 ppm) is indicative of its hypercoordinate state as a result of the additional binding to the amide oxygen atom and solvent molecules. According to the XRD data, the silicon atom in the crystals of complex **130** has somewhat distorted TBP geometry, with the amide oxygen atom and one of the chlorine atoms in the axial positions.

Scheme 54



Neutral binuclear complexes **131a**,**b** containing a pentacoordinate silicon atom were synthesized in 92% and 95% yields, respectively, by the reaction of compound **132** with dichlorosilanes R_2SiCl_2 (R = Me, Ph) in THF (Scheme 55).[86]

Scheme 55



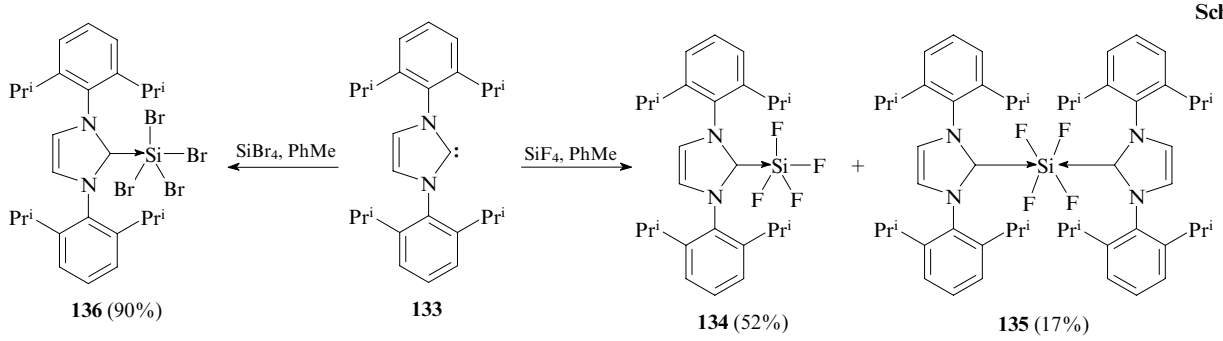
131: R = Me (**a**), Ph (**b**)

According to the XRD data, TBP complex **131b** also has a distorted structure, with the nitrogen atom and two carbon atoms in the equatorial plane. The C(3)−H···O=C distance is 2.45 Å. The signals in the ^{29}Si NMR spectra of complexes **131a**,**b** in $CDCl_3$ are observed at δ −21.6 and −60.9 ppm, respectively. The upfield shifts of the signals are indicative of the retention of the pentacoordinate unit in solution. The IR spectra of complexes **131a**,**b** in KBr pellets show a C=O band at 1664 and 1666 cm^{-1}, respectively. It should be noted that in both spectra, the positions of the bands differ only slightly from the corresponding value for the starting amide (1662 cm^{-1}), which is quite unexpected. Actually, in most complexes described in the literature, the formation of a coordination bond is accompanied by the shift of the C=O absorption band to lower frequencies compared to the model tetracoordinate silicon compound.[87] The factors responsible for the abnormal behaviour of complexes **131a**,**b** were not discussed.

3. Carbene-based syntheses

The reaction of N-heterocyclic carbene **133** with tetrafluorosilane in toluene affords neutral penta- (**134**) and hexacoordinate (**135**) silicon complexes (Scheme 56).[88] Due to low solubility of compound **134** in toluene, the reaction

Scheme 56



products were separated by the recrystallization. Complex **136** was prepared in high yield by the reaction of tetrabromosilane with an equimolar amount of carbene **133**. The synthesized compounds were identified by elemental analysis, ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy and X-ray diffraction. The pentacoordination of the Si atom in complexes **134** and **136** in solution is evidenced by the high-field signals in the ^{29}Si NMR spectra (C_6D_6) at δ −141.01 and −89.62 ppm, respectively. The ^{29}Si NMR spectra of hexacoordinate complex **135** in the same solvent display a signal at a much higher field (−184.01 ppm).

The ^{19}F NMR spectrum of tetrafluoride **134** at room temperature exhibits a narrow singlet at δ −119.62 ppm. The shape and position of the signal are independent of the temperature. This fact indicates that fast (on the NMR time scale) exchange processes take place in the coordination unit of the complex.

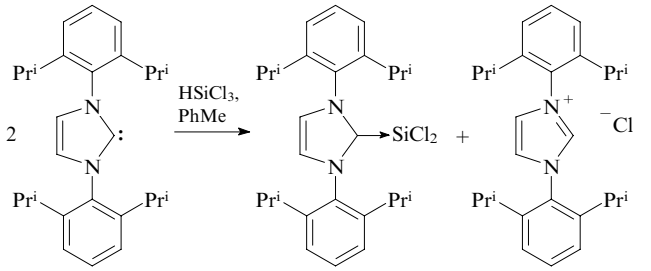
According to the XRD data, the Si atom in complexes **134** and **136** is pentacoordinate and has a distorted TBP coordination environment. In tetrabromide **136**, the carbon atom of the ligand is in the equatorial plane, as in the complexes based on $SiCl_4$ synthesized earlier.[89] The Si—Br bond length for the axial bromine atoms [2.3936(7) Å] in complex **136** is somewhat larger compared to the equatorial Si—Br bond lengths [2.2360(4) Å)]. The coordination unit of fluoride **134** has distorted TBP geometry. However, the carbon atom is in the axial position. According to the quantum chemical calculations, this structure is due to a small energy difference between the states with the axial and equatorial arrangement of the carbon atoms in compound **134**.[90] The axial Si—F bonds [1.6462(13) Å] are longer than the equatorial Si—F bonds [1.5767(17) Å].

The reaction of tetrabromosilane with carbene **133** in hexane followed by the recrystallization of the product from dichloromethane afforded the ionic complex [$SiBr_3$IPr]Br [IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] containing a tetracoordinate silicon atom.[91] Its structure was determined by elemental analysis, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy (−63.9 ppm) and X-ray diffraction.

The reaction of carbene **133** with trichlorosilane in toluene gave dichlorosilylene **137**, which is stable at room temperature, and insoluble salt **138** as a by-product (Scheme 57).[92]

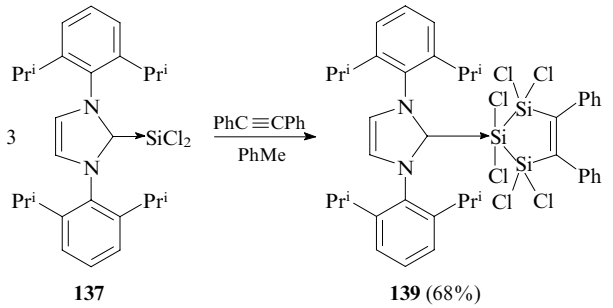
Dichlorosilylene **137** reacts with diphenylacetylene at room temperature to form complex **139** (Scheme 58).[92] The ^{29}Si NMR spectrum of the latter shows signals at δ −142.47 and −2.84 ppm assigned to cyclic silicon compounds.[93] According to the XRD data, the synthesized complex contains one pentacoordinate and two tetracoordinate silicon atoms.

Scheme 57



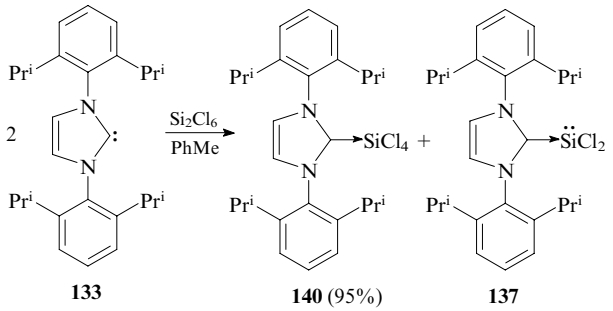
The central coordination unit has distorted TBP geometry. The axial positions are occupied by chlorine atoms and the equatorial plane is formed by tetracoordinate silicon atoms and one carbon atom.

Scheme 58



Complex **140**, the coordination unit of which is structurally similar to that of complex **134**, was synthesized by the reaction of carbene **133** with Si_2Cl_6 in toluene; low-valent silicon complex **137** was obtained as the second product (Scheme 59).[94]

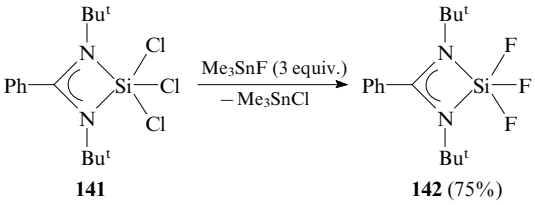
Scheme 59



The reaction of trichloride **141** with Me_3SnF in THF at room temperature produced trifluoride **142**, in which the Si

atom is pentacoordinate, like that in the starting trichloride (Scheme 60).[94]

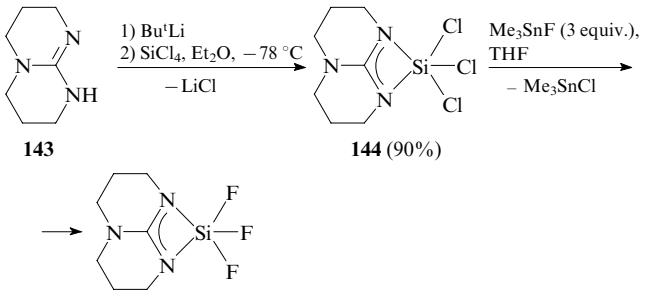
Scheme 60



141 **142** (75%)

The deprotonation of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (**143**) with *tert*-butyllithium followed by the treatment of the reaction product with $SiCl_4$ gave complex **144**, and the reaction of the latter with Me_3SnF in THF afforded complex **145** (Scheme 61).[94]

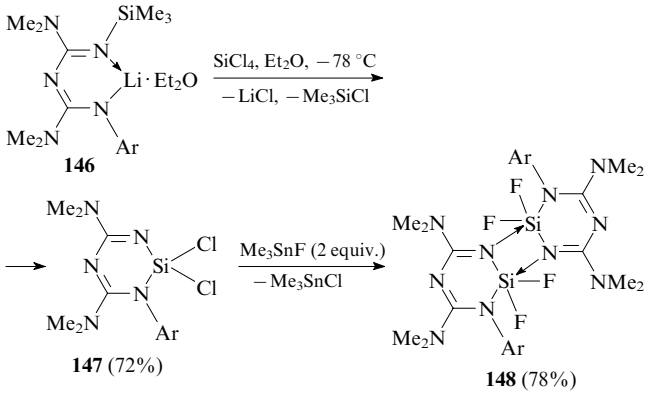
Scheme 61



143 **144** (90%) **145** (79%)

The treatment of lithium derivative **146** with $SiCl_4$ produced chlorosilane **147**, and the reaction of the latter with Me_3SnF gave fluorosilane **148** containing two pentacoordinate silicon atoms (Scheme 62).[94]

Scheme 62



146 **147** (72%) **148** (78%)

Ar = 2,6-$Pr^i_2C_6H_3$

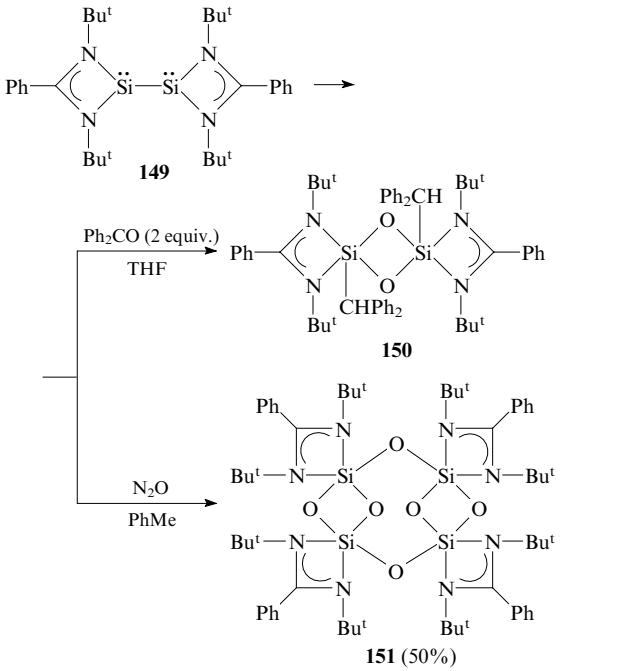
Complexes **142**, **144**, **147** and **148** were identified by elemental analysis, ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy and X-ray diffraction. The ^{29}Si NMR spectra of these complexes show characteristic high-field signals in the range from –103.42 to –132.03 ppm, which attest to the pentacoordination of the silicon atom in solution.

4. Syntheses based on N-heterocyclic silylenes

In the last two decades, impressive progress has been achieved in synthetic organosilicon chemistry. For instance, stable silylenes, persilaallenes and disilylenes were isolated.[95] The synthesis of disylene $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) and sylene $(Me_3Si)_2Si{=}C(OSiMe_3)(2\text{-Ad})$ (Ad is adamantyl) accomplished at the end of the 20th century gave a powerful impetus to the development of the chemistry of low-valent silicon compounds.[96, 97]

High reactivity of low-valent silicon compounds can be illustrated by the reaction of bis(silylene) $PhC(NBu^t)_2SiSi(NBu^t)_2CPh$ (**149**) with benzophenone (2 equiv.) in THF (Scheme 63).[98] The oxidative addition of benzophenone followed by the C=O bond cleavage gave, in a moderate yield, complex **150** containing pentacoordinate Si atoms in the four-membered ring Si_2O_2. Compound **151** containing two four-membered rings Si_2O_2 was synthesized by the reaction of complex **149** with nitrogen(I) oxide (see Scheme 63).

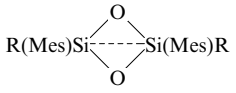
Scheme 63



149 **150** **151** (50%)

The composition and structures of compounds **150** and **151** were determined by NMR spectroscopy, mass spectrometry and X-ray diffraction. The values of $\delta^{29}Si$ for compounds **150** and **151** are –86.25 and –111.02 ppm, respectively, which are indicative of the pentacoordination of the Si atom in solution. These chemical shifts were found at higher field compared with the values determined by West and co-workers[99] for cyclic disiloxanes **152** (~ –22 ppm).

Structures 152

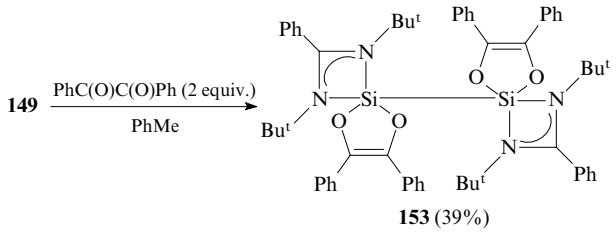


152 R = Bu^n, N(SiMe$_3$)$_2$

Complex **153** containing two siladioxolene rings linked by a Si–Si bond was synthesized by the reaction of bis(silylene) **149** with PhC(O)C(O)Ph in toluene (Scheme 64).[100] The ^{29}Si NMR spectrum of compound **153** shows a signal at δ –79.75 ppm, whereas the signal of the starting bis(silylene)**149** is observed at a much lower field

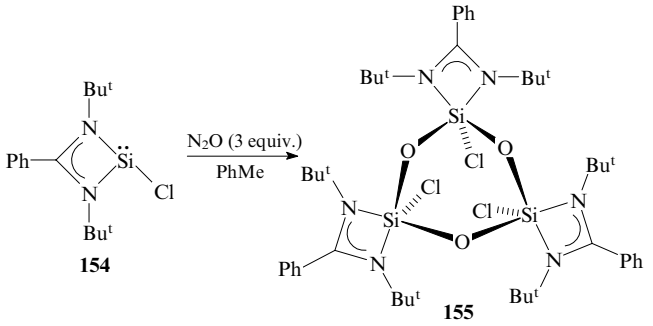
(δ^{29}Si 76.15 ppm).[101] The structure of complex **153** in the crystalline state was confirmed by X-ray diffraction.

Scheme 64



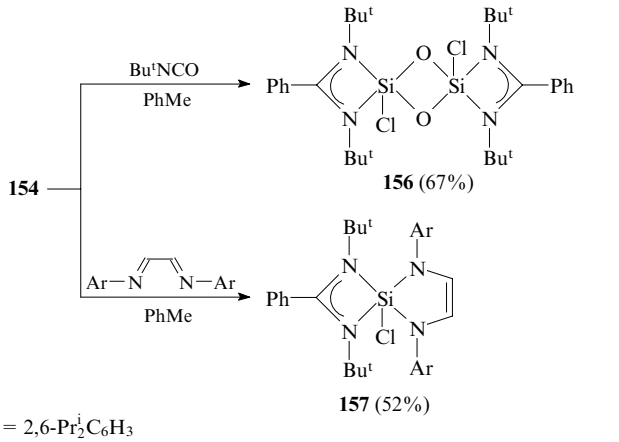
More recently, Jana *et al.*[102] synthesized the trimer $[PhC(NBu^t)_2Si(O)Cl]_3$ (**155**) containing the six-membered ring Si_3O_3 by the treatment of silylene **154** with nitrogen(I) oxide in toluene (Scheme 65). The pentacoordination of the silicon atom in complex **155** in solution is evidenced by the high-field signal in the ^{29}Si NMR spectrum (−114.51 ppm). The ^{1}H NMR spectrum at room temperature displays a broadened signal of the Bu^t group, which is indicative of a fast (on the NMR time scale) stereodynamic process.

Scheme 65



Due to high reactivity of chlorosilylene **154**, it became possible to prepare two new silicon-containing heterocycles **156** and **157** (Scheme 66).[103] Compound **154** reacts with *tert*-butyl isocyanate to form complex **156**, in which two pentacoordinate silicon atoms are linked by two bridging oxygen atoms. The pentacoordination of the Si atoms in solution and in the solid state was established by ^{29}Si NMR spectroscopy (−113.54 ppm) and X-ray diffraction, respectively. It should be noted that complex **156** was synthesized also according to an alternative procedure using trimethylamine *N*-oxide as the ligand.[103] The reaction of compound **154** with diimine ArN=CHCH=NAr (Ar = 2,6-$Pr^i_2C_6H_3$) produced complex **157** (see Scheme 66). The pentacoordination of the silicon atom in complex **157** in solution is evidenced by the high-field signal in the ^{29}Si NMR spectrum (−101.89 ppm).[103] The trigonal-bipyramidal structure of complex **157** in the solid state was confirmed by X-ray diffraction.

Scheme 66

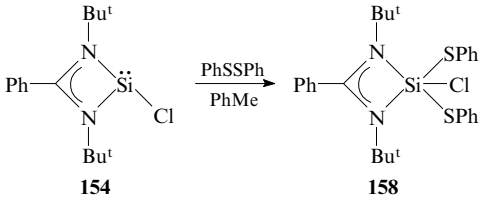


Ar = 2,6-$Pr^i_2C_6H_3$

In the authors' opinion, compound **154** is readily involved in the oxidative addition due to the presence of lone-pair electrons on the silicon atom.

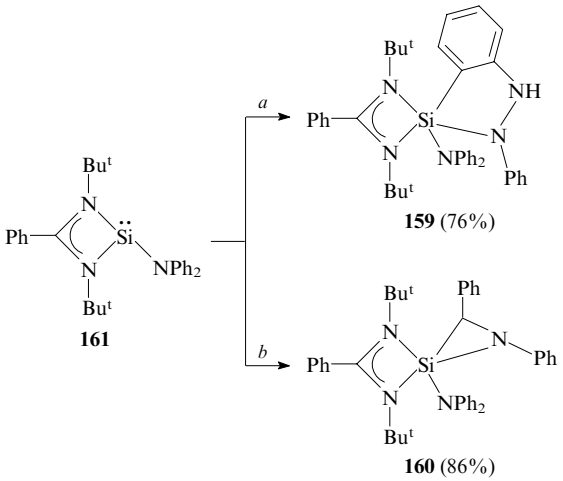
The reactions of silylenes with sulfur-containing compounds, for example, with CS_2, S_8 and PhNCS, were studied in sufficient detail.[60, 104 – 106] However, data on the use of disulfides as reactants in reactions with silylenes are virtually absent in the literature published in 2007 – 2012. This is rather surprising since the S−S bond is weaker than the C−C bond and is characterized by the dissociation energy of ~60 kcal mol^{-1} (Ref. 107). Therefore, the reported[103] synthesis with the use of silylene **154** and diphenyl disulfide is not only of practical but also of theoretical interest (Scheme 67). The formation of complex **158** is accompanied by a considerable upfield shift of the signal in the ^{29}Si NMR spectrum (−83.26 ppm), which is indicative of its pentacoordinate structure in solution.

Scheme 67



It should be noted that all pentacoordinate complexes, which are formed in the reactions with silylene **154**, contain the four-membered ring CN_2Si.[103] In the authors' opinion, unusual stability of this moiety may be due to the stabilizing role of the lone pairs of two nitrogen atoms involved in the coordination unit.

Scheme 68



(*a*) PhN=NPh, PhMe; (*b*) PhN=CHPh, PhMe

Compounds **159** and **160** were synthesized by the reactions of silylene **161** with PhN=NPh and PhN=CHPh, respectively, taken in a molar ratio of 1 : 1 (Scheme 68).[108] The complexes were completely characterized by spectroscopic methods, and their molecular structures were determined by X-ray diffraction. The ^{29}Si NMR spectra of compounds **159** and **160** show signals at higher field (−88.2 and −133.1 ppm) compared with the signal of the starting compound **161** (−20.5 ppm).

III. Neutral hexacoordinate tetravalent silicon complexes

Past decades have witnessed the active development of the chemistry of hexacoordinate silicon compounds. The creation of the modern theoretical basis of quantum chemistry has played a great role in this process. These methods include DFT approaches at different levels, Bader's atoms in molecules theory, *etc*. The complex application of these approaches made it possible to perform for the first time a comparative analysis of the structures, energies, geometric parameters and the aromaticity of hexacoordinate silicon complexes containing the phthalocyanine group compared to their tetracoordinate analogues.[109] The synthesis of hexacoordinate silicon compounds was also documented; in these complexes an intramolecular coordination bond is present between the silicon atom and heavy metal atoms (Pd^{II}, Pt^{II}, Ge^{II}, Sn^{II}).[109–112]

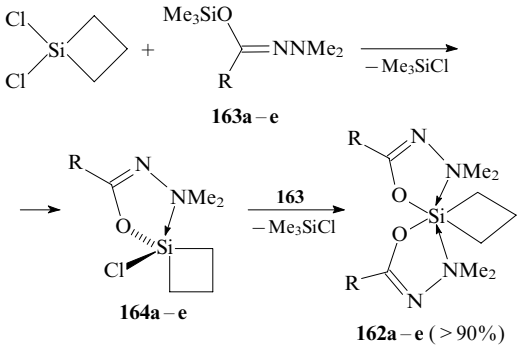
The progress in studies is related to the improvement of available synthetic methods and the development of new approaches, as well as to the extension of the range of potential ligands employed in reactions giving hexacoordinate products.

It is well known that compounds containing penta- or hexacoordinate silicon atoms may be either mono- or bischelate. Moreover, trischelate complexes of hexacoordinate silicon have been synthesized by the end of the 20th century.[113–115]

1. Mono- and bischelate complexes with a N → Si coordination bond

Hexacoordinate bischelate complexes **162a–e** were synthesized in high yields starting from dichlorosilacyclobutane and trimethylsilyl derivatives of hydrazides **163a–e** by the transsilylation through the formation of intermediate pentacoordinate compounds **164a–e** (Scheme 69).[116]

Scheme 69



R = CF_3 (**a**), Bu^t (**b**), Ph (**c**), NMe_2 (**d**), CH_2CN (**e**)

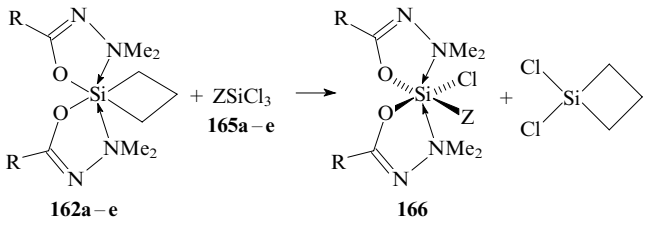
It was noted that the ^{1}H and ^{13}C NMR spectra of complexes **162** in $CDCl_3$ show signals of N-methyl groups as one singlet despite the fact that two singlets should appear according to the symmetry (C_2). The signals of complexes **162b,d** are split into two signals only upon a decrease in the temperature to −13 °C.

This attests to a slow (on the NMR time scale) dynamic process, resulting in the equivalence of two diastereotopic N-methyl groups. Yakubovich *et al*. believed[116] that the only possible mechanism of the process resulting in the observed spectral pattern involves the interexchange of oxygen-containing ligands due to the twist in the O–Si–O plane through the bicapped tetrahedral transition state or the intermediate. The same authors considered this mechanism in detail in the earlier study.[117] More recently, the observed dynamic equilibrium was studied by the DFT method using the B1PW91/TZP basis set.[118]

It should be noted that the ^{1}H and ^{13}C NMR spectra of complexes **162a,c** containing electron-withdrawing substituents (CF_3, Ph) measured under the same conditions show only one set of signals. This is indicative of the lower barrier to the isomerization compared to complexes **162b,d** containing electron-donating substituents. Based on these data, it was concluded that electron-withdrawing substituents cause a weakening of the coordination bond between the donor nitrogen atom and the silicon atom, which is consistent with the results obtained earlier.[119, 120]

The reaction of complexes **162a–e** with silanes $ZSiCl_3$ (**165a–e**) affords hexacoordinate products **166** (Scheme 70).[116] Hexacoordinate germanium compounds structurally similar to complexes **166** were prepared by the replacement of $ZSiCl_3$ with $ZGeCl_3$.[121]

Scheme 70



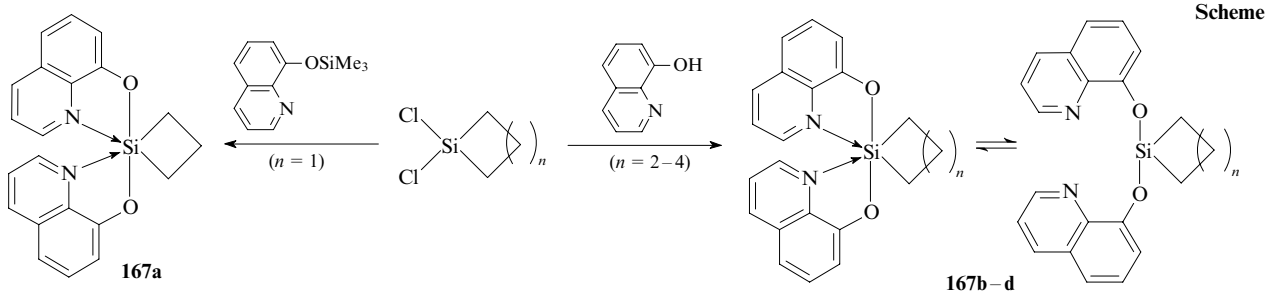
Z = Bu^i (**a**), Et (**b**), Ph (**c**), Cl (**d**), H (**e**)

It was found that in the case of Z = Ph, Cl or H, the transformation is completed in a few minutes even at room temperature. The reaction rate substantially decreases in the presence of an alkyl substituent (Z = Bu^i, Et); in the latter case, the reaction is completed in 1 h upon heating to 80 °C.

In the study of silacycloalkanes **167a–d**, it was shown that a weakening of the N → Si bond (a decrease in the degree of intramolecular coordination) occurs in parallel with an increase in the ring size (Scheme 71).[122] Complexes **167a,b** have a hexacoordinate structure as evidenced by the values of δ^{29}Si in the solid state (−129.9 and −103.3 ppm, respectively). As exemplified by complex **167b**, the variation of the solvent polarity leads to a slight downfield shift of the ^{29}Si NMR signal to −100.3 and −98.6 ppm in THF-d_8 and $CDCl_3$, respectively. The observed position of the signal in the ^{29}Si NMR spectrum of complex **167c** at δ −20.2 ppm ($CDCl_3$, 20 °C) is characteristic of a tetracoordinate silicon atom.

The chemical shift of the signal in the ^{29}Si NMR spectrum of complex **167c** in THF-d_8 was found to depend on the temperature. A decrease in the temperature from 20

Scheme 71



n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**)

to −45 °C is accompanied by the upfield shift of the signal (from −44 to −100.2 ppm). The character of changes observed with a decrease in the temperature is evidence in favour of the shift of the equilibrium shown in Scheme 71 towards the structure with a hexacoordinate silicon atom.

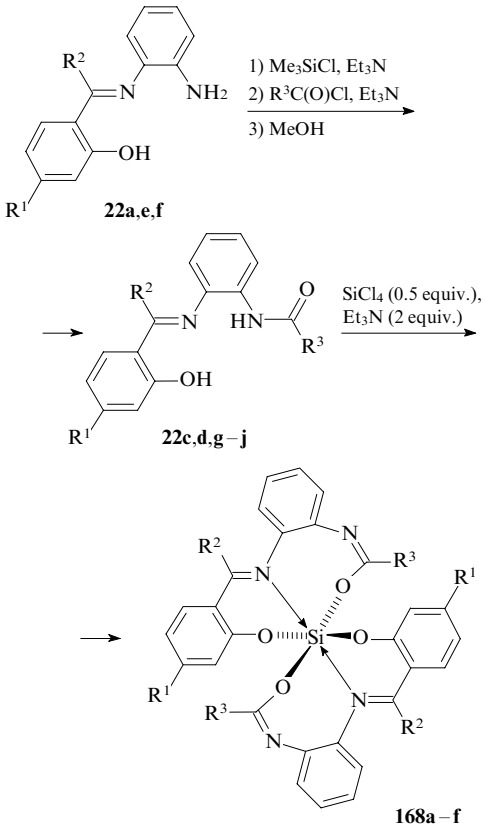
The thermodynamic parameters of the equilibrium between the structures with hexa- and tetracoordinate silicon atoms evaluated for compounds **167c**,**d** based on the analysis of the temperature-dependent spectra are as follows: $\Delta H^\circ = -23.5$ and −9 kJ mol, $\Delta S^\circ = -85.8$ and −55.7 J mol^{-1} K^{-1}, respectively. The formation of an intramolecular coordination bond between the silicon and nitrogen atoms in silacyclohexane is characterized by a lower exothermic effect compared with the corresponding process in compound **29** containing a Si−Ph group ($\Delta H^\circ = -31.5$ kJ mol^{-1}, $\Delta S^\circ = -116.7$ J mol^{-1} K^{-1})[41] or with related complexes containing two chelating imine N,O ligands and the Si−Ph group.[123] Despite the fact that the position of the signal of silacycloheptane **167d** in the ^{29}Si NMR spectrum is temperature-dependent. The tetracoordinate silicon compound makes the major contribution to the equilibrium shown in Scheme 71 even as the temperature was decreased to −50 °C.

Hexacoordinate silicon complexes with tridentate O,N,N ligands **22c**,**d**,**g**–**j** prepared by the acylation of the amino group in compounds **22a**,**e**,**f** was characterized.[40] The latter compounds were synthesized by the reaction of *o*-phenylenediamine with the corresponding ketone or aldehyde.[124] The reaction of compounds **22c**,**d**,**g**–**j** with $SiCl_4$ (2 : 1) gave target complexes **168a**–**f** in yields >70% (Scheme 72). The hexacoordination of the silicon atom in compounds **168a**–**f** in the solid state was confirmed by X-ray diffraction and ^{29}Si CP/MAS NMR spectroscopy. It should be noted that the chemical shifts of the signals in the latter spectra vary in a narrow range from −176 to −183 ppm.

The synthesis of new neutral hexacoordinate complexes with the central SiN_4O_2 (**169a**) and SiN_3O_2C (**169b**) coordination units in 68% and 51% yields, respectively (Scheme 73) was documented.[125] Complexes **169a**,**b** contain the dianionic tetradentate ligand in the equatorial plane of the coordination polyhedron (XRD data). It should be noted that ligand **170** used in this synthesis is similar to ligand **32** successfully employed in the synthesis of pentacoordinate compounds (see Scheme 13).[41]

The equilibrium involving hexacoordinate complex **28** and tetracoordinate silicon compound **171** was studied by the DNMR method (Scheme 74).[37] The thermodynamic parameters of the formation of two intramolecular N → Si coordination bonds are as follows: $\Delta H^\circ =$

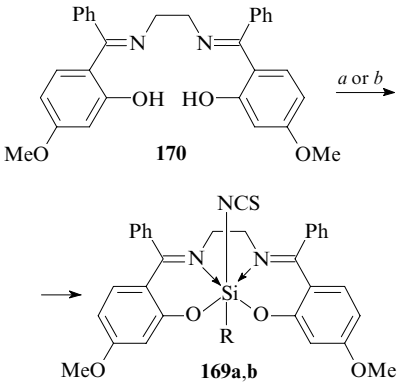
Scheme 72



Compounds **22**	R^1	R^2	R^3	Compounds **168**
a	MeO	Ph		
c	MeO	Ph	Bu^t	**a**
d	MeO	Ph	Ph	**b**
e	H	Me		
f	H	H		
g	H	Me	Bu^t	**c**
h	H	Me	Ph	**d**
i	H	H	Bu^t	**e**
j	H	H	Ph	**f**

−15.6 kcal mol^{-1}, $\Delta S^\circ = -50$ cal mol^{-1} K^{-1}. These data are similar to those published earlier,[123] according to which the formation of one intramolecular N → Si coordination bond is characterized by $\Delta H^\circ = -7.5$ kcal mol^{-1}, $\Delta S^\circ = -28$ cal mol^{-1} K^{-1}. In $CDCl_3$, the slow (on the NMR time scale) equilibrium is established as a result of the bond dissociation (see Scheme 74), which made it pos-

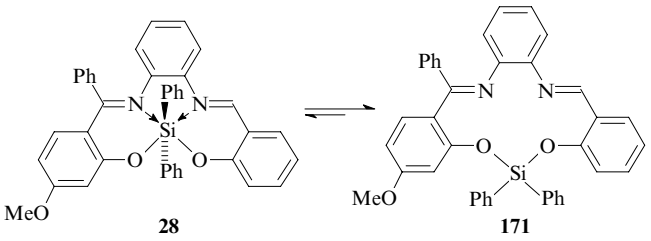
Scheme 73



(*a*) $Si(NCS)_4$, $-$ HSCN (for **169a**);
(*b*) $HMeSi(NCS)_2$, $-H_2$, $-$HSCN (for **169b**); R = NCS (**a**), Me (**b**)

sible to determine the activation parameters of the process: $\Delta H^{\#} = 38$ kcal mol^{-1}, $\Delta S^{\#} = 50$ cal mol^{-1} K^{-1}. The high positive entropy of the activation corresponds to processes accompanied by the cleavage of the coordination bond.[7]

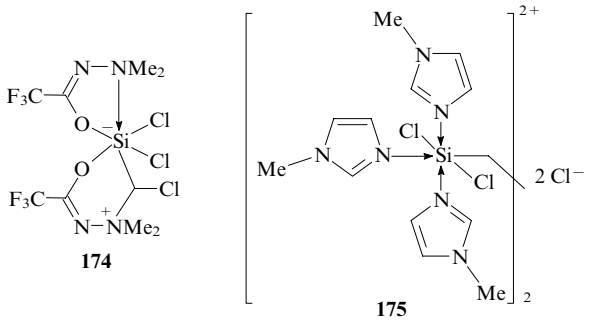
Scheme 74



It was found that the reaction of compound **172** with $PhSiCl_3$ in the presence of triethylamine affords hexacoordinate silane **173a** (Scheme 75).[126] According to the XRD data, the crystal structure of solvate **173a** · $CHCl_3$ contains a rather unusual coordination unit. Thus, despite the presence of two chlorine atoms, the sp^2-hybridized nitrogen atom of the tridentate ligand is in the *trans* position with respect to the phenyl group. It should be noted that only two similar complexes, *viz*., compounds **174** and **175**, have been characterized earlier.[126, 127]

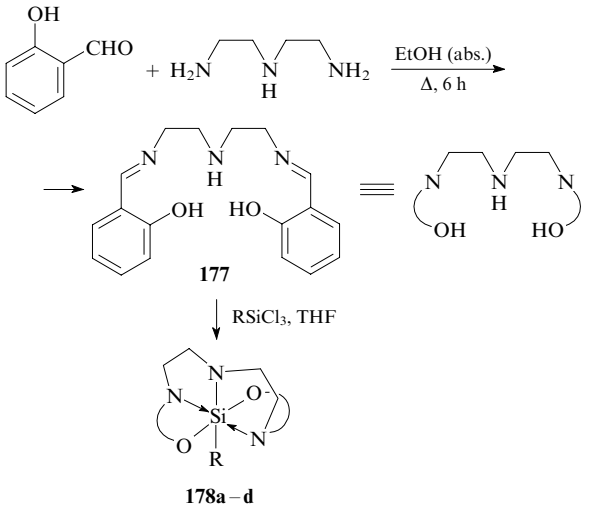
The silylation of ligand **172** with hexamethyldisilazane followed by the treatment of the reaction mixture with methyltrichlorosilane produces hexacoordinate cationic complex **176** (see Scheme 75). This reaction gave compound **173b** as the second product. The latter is the first structurally characterized complex of a Group 14 element with salicylaldimine.

Structures 174, 175



The reaction of the potentially pentadentate ligand *N*,*N*′-diethylenetriaminobis(salicylideneimine) (**177**) with $RSiCl_3$ in the presence of triethylamine (Scheme 76) produced a series of new hexacoordinate silicon complexes **178a**–**d** containing the SiO_2N_3C unit (yield > 60%).[128] In the solution ^{29}Si NMR spectra, the signals of complexes **178a**–**d** are observed in the range from -145 to -155 ppm, which is indicative of the hexacoordination of the silicon atom.

Scheme 76

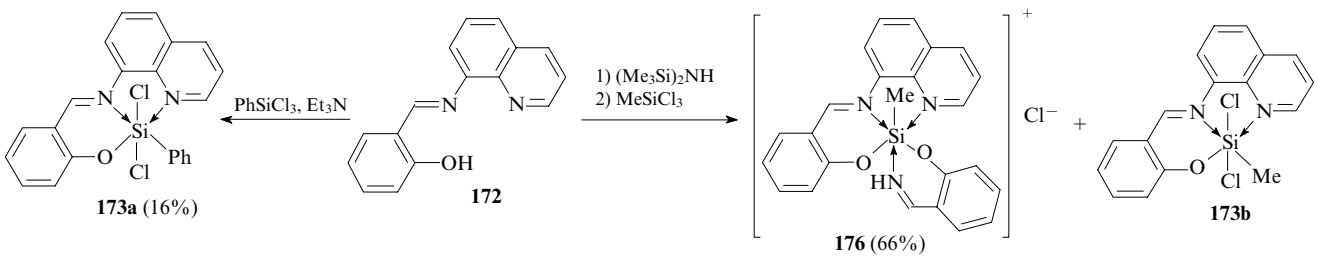


R = Me (**a**), Ph (**b**), Et (**c**), CH=CH$_2$ (**d**)

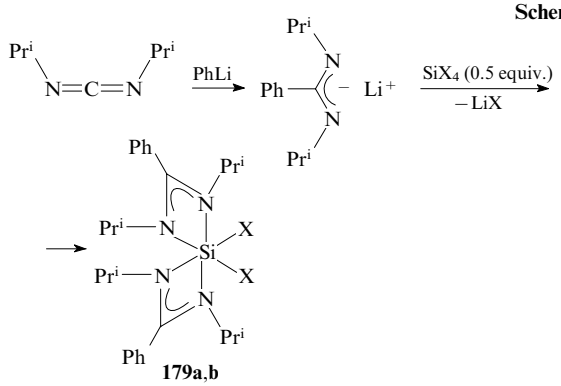
The synthesis of new hexacoordinate silicon complexes **179a**–**g** (Schemes 77 and 78) containing the SiN_4X_2 unit (X = F, Cl, Br, C, N, S, Se) was documented;[129] the yields were > 70% (except for compound **179b**, which was prepared in 40% yield). All complexes were studied in solution by multinuclear (^1H, ^{13}C, ^{19}F, ^{29}Si, ^{77}Se) NMR spectroscopy and in the solid state by ^{13}C, ^{15}N, ^{19}F, ^{29}Si and ^{77}Se CP/MAS NMR spectroscopy.

The ^1H NMR spectra of dichloride **179a** show a well-resolved septet and four doublets in the range from 20 to

Scheme 75

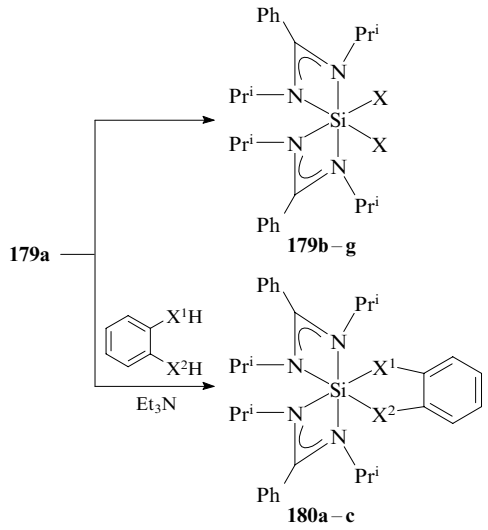


Scheme 77



X = Cl (**a**, 68%), Br (**b**, 40%)

Scheme 78



180: $X^1 = X^2 = S$ (**a**), Se (**c**); $X^1 = S$, $X^2 = Se$ (**b**)

Compounds **179**	X	Conditions
b	Br	Me_3SiBr, $-Me_3SiCl$
c	F	KF, $-$KCl or $AgBF_4$, Et_3N, $-BF_3 \cdot NEt_3$, $-$AgCl
d	CN	Me_3SiCN, $-Me_3SiCl$
e	N_3	Me_3SiN_3, $-Me_3SiCl$
f	NCO	KOCN, 18-crown-6, $-$KCl
g	NCS	NH_4SCN, 18-crown-6, $-NH_4Cl$

70 °C. The observed spectral pattern is consistent with the C_2 molecular symmetry.

The isotropic chemical shifts of the signals in the solid-state and solution ^{29}Si NMR spectra have similar values (Table 5), which indicates that the intramolecular coordination bonding in the complexes under consideration is retained in solution.

As can be seen from Table 5, the isotropic ^{29}Si NMR chemical shifts for compounds **179** and **180** depend on the type of the monodentate ligand and vary in a broad range from -216.6 (complex **179d**) to -156.1 ppm (**180a**) in the solid state and from -213.2 (**179d**) to -156.5 ppm (**180a**) in solution. It should be noted that the signals of complexes **179a**,**b**,**d** – **g** and **180b** in the ^{1}H NMR spectra are well-resolved at room temperature (23 °C), whereas broadened signals are observed under the same conditions in the spectrum of complex **179c**.

The broadening of the signals in the ^{1}H NMR spectrum of difluoride **179c** in the range from -20 to 20 °C indicates

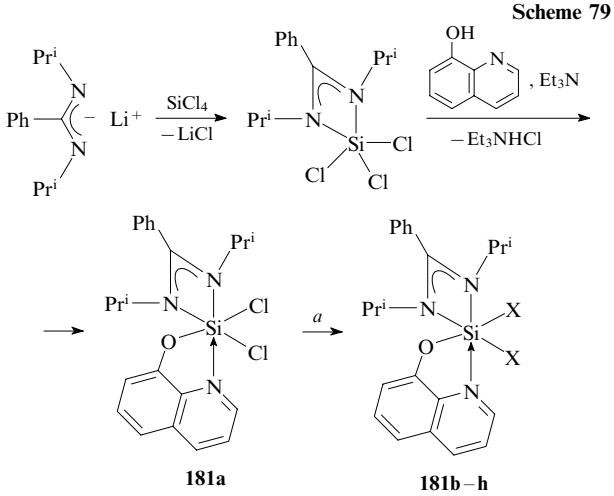
Table 5. The ^{29}Si NMR chemical shifts of complexes **179a** – **g** and **180a** – **c** in the solid state (22 °C) and in solution (23 °C).[129]

Complex	δ^{29}Si, ppm	
	in the solid state	in solution
179a	-170.4	-171.0
179b	-206	-199.4
179c	-161	-161.6
179d	-216.6	-213.2
179e	-176.5	-175.5
179f	-193.2	-192.3
179g	-195.7	-197.2
180a	-156.1	-156.5
180b	-164.0	-165.1
180c	-175.2	-173.6

that a stereodynamic process takes place in its coordination unit. This process results in the disappearance of the diastereotopicity of the methyl groups and, as a consequence, in the presence of one doublet for all eight methyl groups and one multiplet for all four protons of CH_3CHCH_3 in the spectrum recorded at 72 °C. The observed effect may be caused by the exchange of the positions of two nitrogen atoms in the bidentate ligands. The absence of dynamic processes in dichloride **179a** was attributed to the shortening of the Si – N bond compared to the bond in difluoride **179c**, which is responsible for an increase in the configurational stability of molecule **179a**.

The synthesis of hexacoordinate complexes **181a** – **h** with different coordination units (SiN_3OF_2, SiN_3OCl_2, SiN_3OBr_2, SiN_5O and SiN_3O_3) in yields from 41% (**181b**) to 93% (**181d**) (Scheme 79) was documented.[130]

Scheme 79



Compounds **181**	X	Conditions *a*
b	Br	Me_3SiBr, $-Me_3SiCl$
c	F	KF, $-$KF or $AgBF_4$, Et_3N, $-BF_3 \cdot NEt_3$, $-$AgCl
d	N_3	Me_3SiN_3, $-Me_3SiCl$
e	NCS	Me_3SiNCS, $-Me_3SiCl$
f	0.5(1,2-$O_2C_6H_4$)	1,2-$(HO)_2C_6H_4$, Et_3N, $-Et_3NHCl$
g	NCO	KOCN, 18-crown-6, $-$KCl
h	OTf	Me_3SiOTf, $-Me_3SiCl$

Complexes **181a–h** contain two bidentate monoanionic ligands, *N*,*N*′-diisopropylbenzamidinate and the 8-hydroxyquinoline moiety, as well as two identical monoanionic ligands (F, Cl, Br, N_3, NCO, NCS, OTf), or one bidentate dianionic ligand. The chemical shifts of the signals of the complexes in solid-state and solution ^{29}Si NMR spectra vary in a broad range: from −145.9 (complex **181f**) to −190.2 ppm (**181e**) in the solid state and from −146.6 (**181f**) to −189.3 ppm (**181e**) in solution, which indicates that these shifts depend on the nature of the silicon–ligand bond.[130]

Four methyl groups of the ligands in complexes **181a–h** are diastereotopic, resulting in the presence of four doublets (C_1 symmetry) in the ^{1}H NMR spectra. The ^{29}Si NMR signal in the NMR spectrum of difluoride **181c** at 23 °C appears as a triplet, which is evidence of a stereodynamic process, resulting in the averaging of two spin-spin coupling constants $^1J(^{29}Si,^{19}F)$. A decrease in the temperature to −50 °C is accompanied by the appearance of a multiplet with two different coupling constants $^1J(^{29}Si,^{19}F)$. The ^{19}F NMR spectrum of complex **181c** exhibits a similar temperature dependence. Thus, an AX system [$^2J(^{19}F,^{19}F)$ 22.3 Hz] is observed at −50 °C instead of the expected nonequivalence of F atoms.

It should be noted that one-dimensional (1D) ^{19}F and ^{29}Si NMR spectroscopic methods proved to be insensitive to stereodynamic processes in the coordination unit of complex **181h**, whereas the spectrum recorded using two-dimensional (2D) ^{19}F NMR pulse sequence (^{19}F EXCY) shows a cross-peak even at room temperature, and this cross-peak disappears as the temperature is lowered to −50 °C.

Neutral hexacoordinate complexes **182–184** with the central $SiO_2N_2S_2$ coordination units were synthesized in ~80% yields from tetracyanatesilane and the corresponding ligands in the presence of Et_3N (4 equiv.) in acetonitrile (Scheme 80).[131] Compounds **182–184** were characterized by X-ray diffraction and CP/MAS NMR spectroscopy at different nuclei (^{13}C, ^{15}N, ^{29}Si). The chemical shifts of the signals in the solution ^{29}Si NMR spectra of compounds **182** and **184** (−157 ppm, $CDCl_3$; −162.1 ppm, CD_2Cl_2, respectively) are close to the isotropic chemical shifts determined by solid-state ^{29}Si CP/MAS NMR spectroscopy. This is indicative of a similar (hexacoordinate) structure of the central unit in the solid and liquid phases.

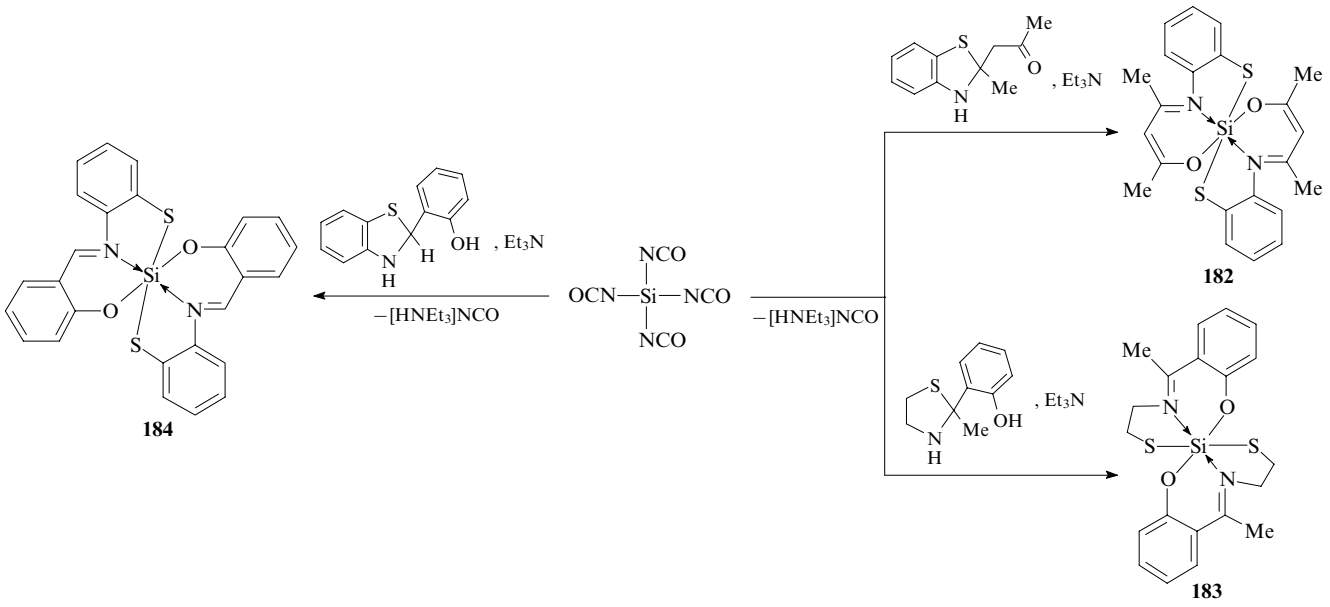
Noteworthy is the difference in the shape of the signal in the ^{29}Si NMR spectra of complexes **184** and **182**. Thus, the signal of the former compound appears as a narrow singlet (−162.1 ppm), whereas the signal of the latter is somewhat broadened and is observed at δ ~ −157 ppm. An increase in the temperature to 80°C in $C_2D_2Cl_4$ does not lead to a substantial change in the shape and the chemical shift of the signal of complex **182** (−156.9 ppm). By contrast, two signals at δ −155.0 and −158.1 ppm appear in the ^{29}Si NMR spectrum as the temperature is lowered to −60 °C (CD_2Cl_2). Two sets of signals are observed also in the low-temperature ^{1}H NMR spectra, which is indicative of the presence of two forms in solution. The structures of these forms were not considered. It should be noted that the low-temperature ^{1}H and ^{29}Si NMR spectra of complex **184**, unlike those of compound **182**, do not exhibit signals of several forms.

The reactions presented in Scheme 80 [or related reactions with $Si(NCS)_4$] in the absence of Et_3N unexpectedly gave quite different products, *viz.*, hexacoordinate complexes **185a**,**b**, **186** and **187a**,**b** with the central SiO_2N_4 unit (Scheme 81).[132] The yields of the products vary in the range of 30%–70%.

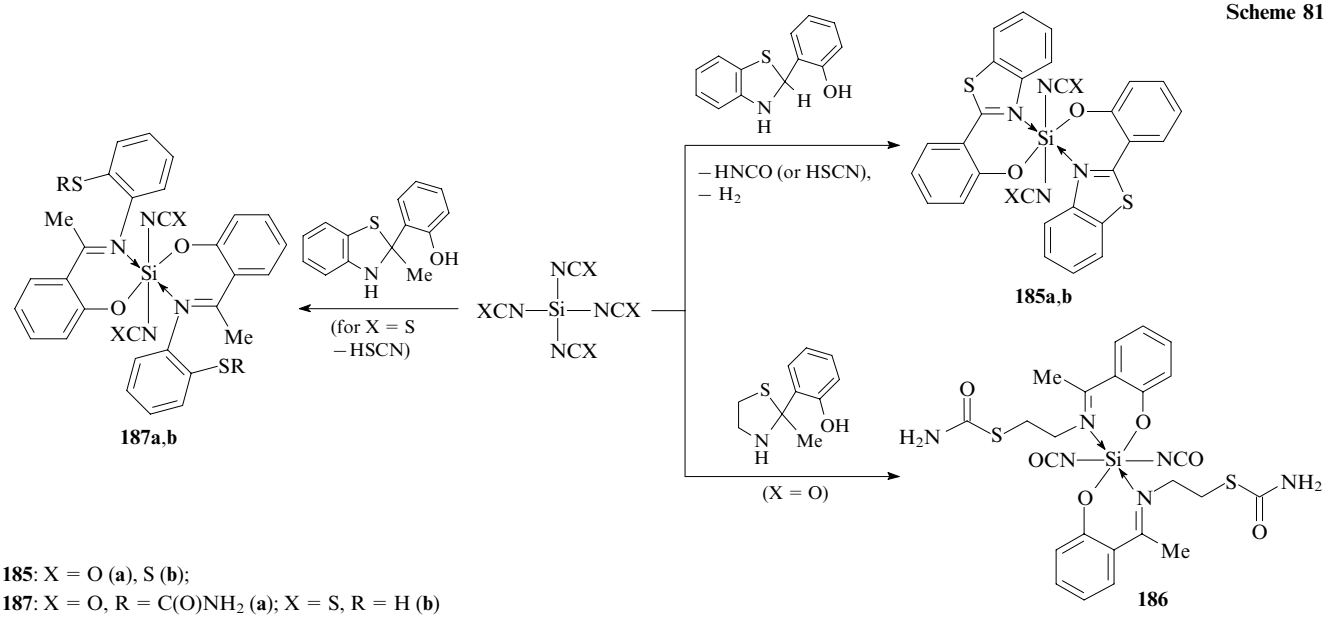
All complexes **185–187** were studied by X-ray diffraction and multinuclear (^{13}C, ^{15}N, ^{29}Si) CP/MAS NMR spectroscopy. The isotropic ^{29}Si NMR chemical shifts of complexes **185–187** have similar values (vary from −202 to −207 ppm) and they are similar to those for the structures containing the SiO_2N_4 unit with two bidentate O,N ligands and two isocyanate and isothiocyanate ligands.[133]

Compounds **188a–c** were synthesized by the reaction of silane **10a** with acetylacetone derivatives **189a–c** (Scheme 82).[134] The synthesis was performed in acetonitrile at 20 °C. Products **188a–c** were obtained in good yields (57%, 89% and 87%, respectively). By contrast, the reaction of silane **10a** with derivatives **189d** gave an adduct of pentacoordinate complex **190** with one acetonitrile molecule

Scheme 80



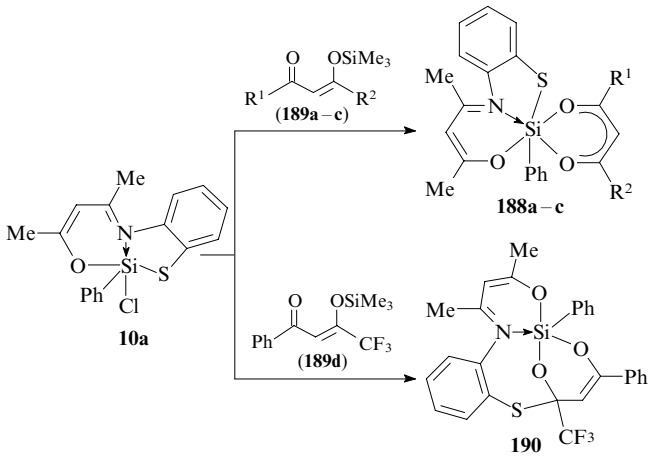
Scheme 81



185: X = O (**a**), S (**b**);
187: X = O, R = C(O)NH$_2$ (**a**); X = S, R = H (**b**)

(δ^{29}Si −124.6 ppm in CD_2Cl_2) (see Scheme 82) instead of the expected hexacoordinate complex.

Scheme 82



188, **189**: R^1 = R^2 = Me (**a**), Ph (**b**); R^1 = Me, R^2 = Ph (**c**)

The chemical shifts of the signals in the ^{29}Si CP/MAS NMR spectra of complexes **188a–c** (−160.6, −159.1 and −157.9 ppm, respectively) attest to their hexacoordinate structures in the solid state. These results correlate well with the data for complexes **182** and **183** (see Scheme 80). The ^{29}Si NMR signals observed at high field in solution (−158.9, −158.3 and −158.7 ppm for compounds **188a–c**, respectively) are indicative of the retention of the hexacoordinate structure of these complexes in the liquid phase.

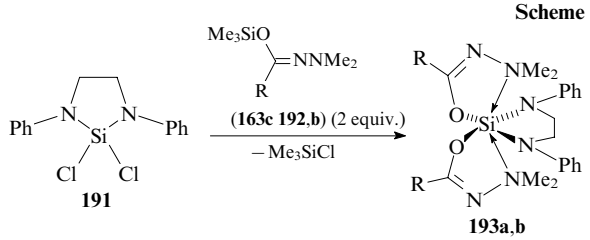
It should be noted that the ^{1}H NMR spectra of complexes **188b** and **190** (CD_2Cl_2, 23 °C) show well-resolved signals, whereas, under the same conditions, the signals of two methyl groups of the O,O-bidentate ligand of complex **188a** are observed as a broadened singlet. An increase in the temperature to 80 °C in $C_2D_2Cl_4$ was accompanied by the transformation of the latter into a narrow singlet, whereas two signals were observed in the spectra as the temperature was lowered to −20 °C. A further decrease in the temperature caused a broadening of all signals in the spectrum, which may be evidence of the existence of more than one isomer under these conditions. At −80 °C the ^{1}H NMR spectrum displayed two sets of signals; however, most of them were substantially broadened. This may be due to an increase in the viscosity of the solvent at very low temperatures.

In the ^{1}H, ^{13}C and ^{29}Si NMR spectra of compound **188c** at 23 °C, the signals are broadened. An increase in the temperature to 60 °C was accompanied by the improvement of the resolution of the signals. A decrease in the temperature (CD_2Cl_2, −10 °C) resulted in the appearance of two sets of signals with the intensity ratio of 2 : 1. The ^{29}Si NMR spectrum also shows two signals at δ −159.3 and −159.1 ppm. The observed reversibility of the spectral changes is indicative of the dynamic exchange in solution involving two forms with a hexacoordinate silicon atom.

2. Trischelate complexes with a N → Si coordination bond

Neutral trischelate hexacoordinate silicon complexes were synthesized by the transsilylation using two approaches.[135] One approach is based on the reaction of monocyclic dichlorosilane **191** with trimethylsilyl derivatives of hydrazides **163c** and **192** (2 equiv.), resulting in the replacement of two chlorine atoms with the bidentate hydrazine derivative (complexes **193a**,**b**; 97% and 82% yields, respectively) (Scheme 83). The synthesized compounds were characterized by multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR spectroscopy and elemental analysis. According to the XRD data, both compounds have a trichelate hexacoordinate structure in the solid state. It should be noted that the N–Si bond in the hydrazide-containing chelate is substantially longer than the

Scheme 83



R = Ph (**163c**), Me (**192**); **193**: R = Me (**a**), Ph (**b**)

Table 6. Peak widths at half height ($\Delta\nu$), coalescence temperatures (T_c), Gibbs free energies of activation ($\Delta G^{\#}$) and rate constants (k_c) for characteristic groups (NMe/CH_2) of complexes **193a**,**b**.[135]

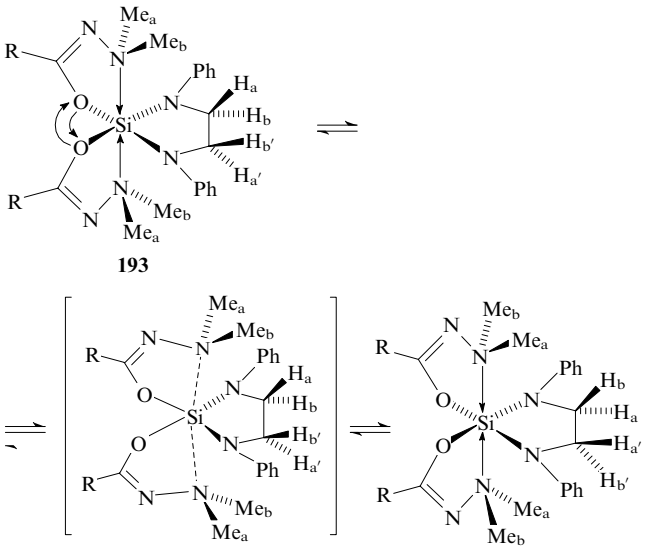
Complex	$\Delta\nu$ /Hz	T_c /K	k_c /s^{-1}	$\Delta G^{\#}$ /kcal mol^{-1}
193a (NMe/CH_2)	54/386	286 ± 2/306 ± 2	121/857	14.0 ± 0.2/13.8 ± 0.2
193b (NMe/CH_2)	26 / 400	292 ± 2/316 ± 2	58/888	14.7 ± 0.2/14.3 ± 0.2

N–Si covalent bond in the diazasilolidine ring (2.05–2.09 and 1.80 Å, respectively). The chemical shifts of the signals of complexes **193** in the ^{29}Si NMR spectra (~ −145 ppm) indicate that they have a hexacoordinate structure in solution as well.[135]

It was found that in solution complexes **193** undergo enantiomerization. Thus, the signals of both pairs of diastereotopic *N*-methyl and geminal CH_2 protons in the ^{1}H NMR spectra are broadened even at room temperature. All broadened signals become narrower with decreasing temperature: the signals of methyl groups are observed as singlets, and the signals of the CH_2 group (AA′BB′ system) appear as a well-resolved multiplet. The Gibbs free energies of activation determined at the coalescence temperature of the signals, the peak widths at half height and the rate constants of the isomerization are given in Table 6.

In the authors' opinion, the inversion of the configuration of the chiral silicon atom, which results in the dynamic exchange of diastereotopic groups observed in the ^{1}H NMR spectra, is caused by the mutual exchange of two hydrazide-containing ligands through a bicapped tetrahedral intermediate or transition state (Scheme 84).

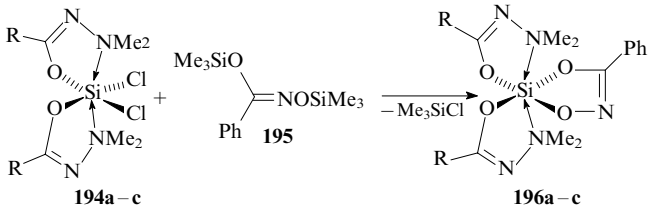
Scheme 84



193

The second approach is based on the transsilylation of silicon-containing bischelates **194a–c** with two monodentate ligands (chlorine atoms) with compound **195** and was used to synthesize neutral hexacoordinate trischelates **196a–c** in 58%, 63% and 72% yields, respectively (Scheme 85).[135] It should be noted that this approach to the synthesis of hexacoordinate silicon compounds [using bis(*O*-trimethylsilyl)pyrocatechol] was described for the first time by Kalikhman *et al.*[115] The synthetic scope of this ligand as the potential reagent was demonstrated by Tacke and co-workers.[136, 137]

Scheme 85



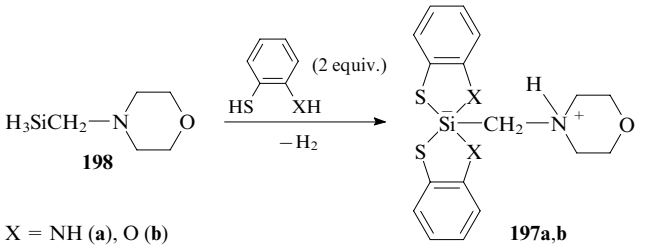
194a–c **195** **196a–c**

R = Me (**a**), Ph (**b**), Bu^t (**c**)

IV. Zwitterionic tetravalent silicon complexes

The synthesis of new zwitterionic λ^5-Si-complexes **197a**,**b** containing SiS_2N_2C and SiS_2O_2C coordination units, respectively, (Scheme 86) was documented.[138] These complexes were synthesized by the reaction of (morpholinomethyl)silane (**198**) with 2-sulfanylaniline or -phenol (2 equiv.) at 20 °C in acetonitrile and THF in 65% and 52% yields, respectively. These complexes were not characterized in solution because of their low solubility and the tendency to undergo decomposition upon dissociation. The complexes were identified by elemental analysis, ^{13}C, ^{15}N and ^{29}Si CP/MAS NMR spectroscopy and X-ray diffraction.

Scheme 86



198 **197a**,**b**

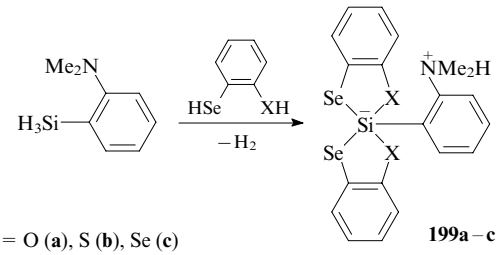
X = NH (**a**), O (**b**)

The pentacoordination of the silicon atom in complexes **197a**,**b** is evidenced by the upfield shifts of the signals in the ^{29}Si CP/MAS NMR spectra (−76.2 and −68.0 ppm, respectively).[138] According to the XRD data, complex **197b** contains the SiS_2O_2C coordination unit having distorted TBP geometry, with the sulfur atoms in the axial positions.

Unlike unstable complexes **197a**,**b**, zwitterionic λ^5-Si-complexes **199** and **200** proved to be stable both in the solid state and in solution (Schemes 87 and 88).[139]

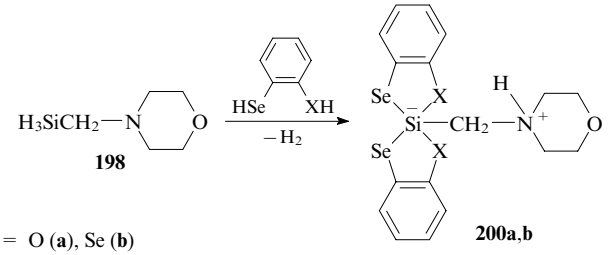
According to the results obtained by multinuclear NMR spectroscopy and X-ray diffraction data, these complexes are pentacoordinate.

Scheme 87



X = O (**a**), S (**b**), Se (**c**) **199a–c**

Scheme 88



X = O (**a**), Se (**b**)

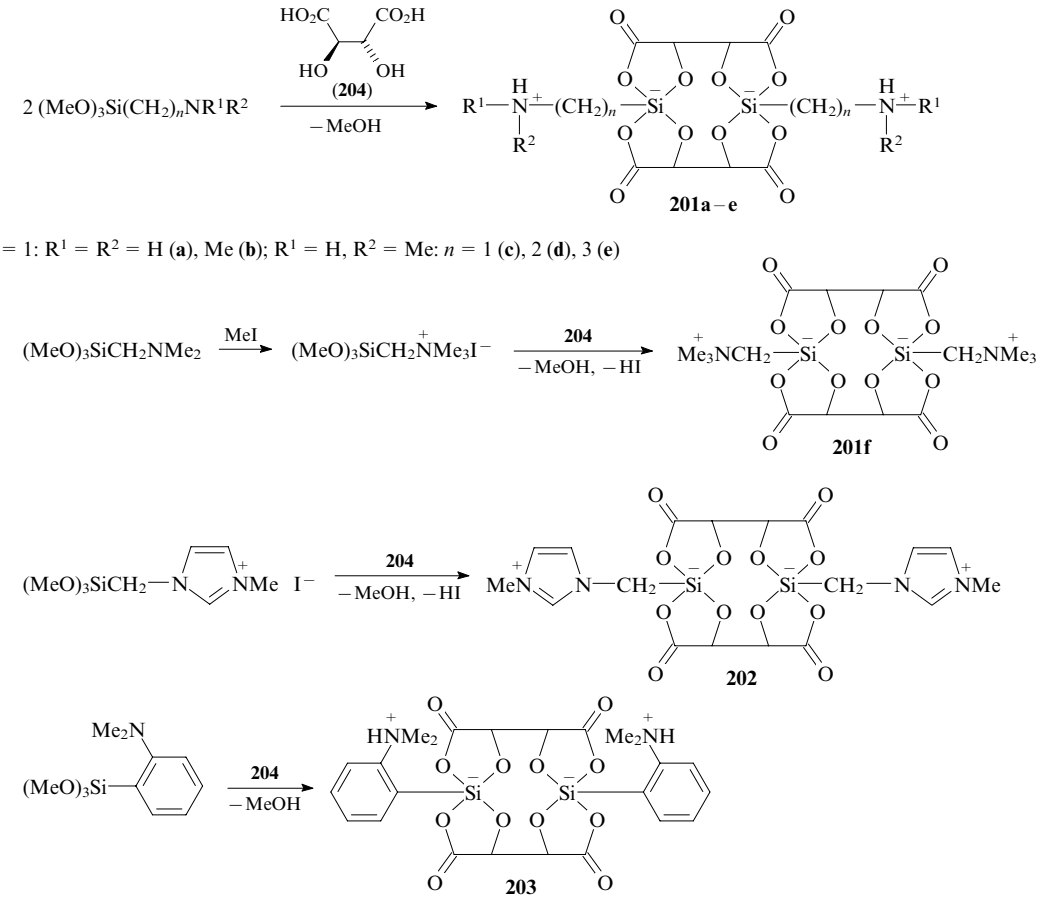
In compounds **199a**,**c** and **200a**,**b**, the coordination unit has a distorted TBP structure, whereas the coordination unit in complex **199b** has distorted square pyramidal geometry. It should be noted that four isomers with the different arrangement of the ligands were found in the crystals of compound **199b**. However, the ^{29}Si CP/MAS NMR spectra show only two broadened signals (−66.6 and −70.7 ppm) with an integrated intensity ratio of 92 : 8. This observation indicates that a stereodynamic process takes place in solution, resulting in the averaging of the signals in the spectrum.

The effect of the nature of the substituents on the structure of the complexes was discussed in relation to investigation of the possible stabilization of hypercoordinate silicon compounds.[140] Compounds **201a** – **f**, **202** and **203** were synthesized by the reactions of the corresponding trimethoxy(aminoalkyl)silanes with (*R*,*R*)-tartaric acid (**204**, H_2tartr) (in a ratio of 1 : 1) at room temperature (Scheme 89). The target products were isolated in rather high yields (> 70%). It was found that all these compounds undergo hydrolysis even at room temperature accompanied by the Si—O bond cleavage to form the starting (*R*,*R*)-tartaric acid.

More recently, Theis *et al.*[141] synthesized zwitterionic complex **201g** starting from (*R*,*R*)-tartaric acid and choline (Scheme 90). Unexpectedly, compound **201g** rather easily underwent hydrolysis even at room temperature to form dianionic disilicate **205** stable in an aqueous solution (> 10 days).

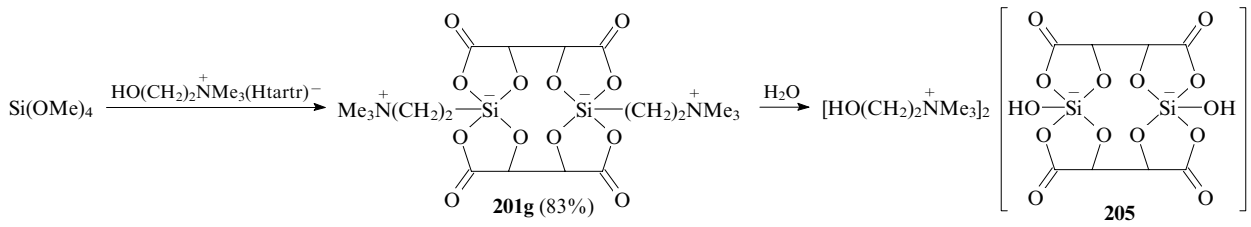
The reactions of trichloro[2-(dialkylphosphino)imidazol-1-yl]silanes **206a**,**b** with aceto- and propionitriles produced binuclear pentacoordinate silicon complexes **207a** – **d** with two bridging dianionic N,N ligands

Scheme 89



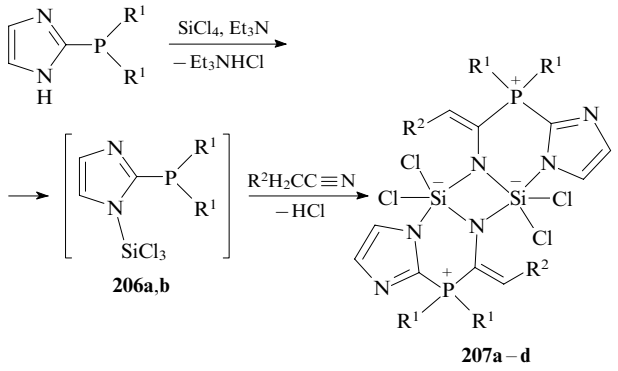
n = 1: $R^1 = R^2$ = H (**a**), Me (**b**); R^1 = H, R^2 = Me: *n* = 1 (**c**), 2 (**d**), 3 (**e**)

Scheme 90



(Scheme 91) in yields from 27% (**207d**) to 55% (**207a**).[142] The complexes were characterized by elemental analysis. Their structures were established by X-ray diffraction and CP/MAS NMR spectroscopy at different nuclei (^{13}C, ^{15}N, ^{29}Si, ^{31}P). According to the XRD data, the coordination units of complexes **207** have a distorted TBP structure, in which the Si atoms formally bear a negative charge, whereas the tetracoordinate phosphorus atoms are positively charged. The ^{29}Si CP/MAS NMR spectra of the complexes show signals in the range from −120 to −125 ppm.[142]

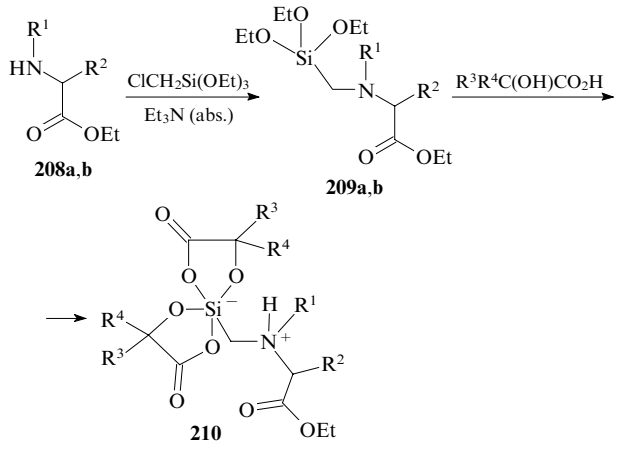
Scheme 91



206: R^1 = Et (**a**), Pr^i (**b**);
207: R^2 = H: R^1 = Et (**a**), Pr^i (**b**); R^2 = Me: R^1 = Et (**c**), Pr^i (**d**)

The inclusion of biologically active natural α-amino and α-hydroxy acids in zwitterionic complexes in the future may lead to the design of drugs having high efficiency and a broad spectrum of biological activities. For this purpose, amino acid esters **208a**,**b** were subjected to silylmethylation with chloromethyltriethoxysilane in the presence of an equimolar amount of Et_3N to prepare *N*-triethoxysilylmethyl derivatives **209a**,**b** in yields >50% (Scheme 92).[73, 143]

Scheme 92



208, **209**: $R^1-R^2 = (CH_2)_3$ (**a**); R^1 = Me, R^2 = H (**b**);
R^3 = R^4 = H, Me, Ph; R^3 = H, R^4 = Ph

With the aim of developing approaches to the synthesis of new pentacoordinate silicon compounds based on α-hydroxy acids widespread in nature, the reactions of compounds **209a**,**b** with the following α-hydroxy acids were studied: glycolic, dimethylglycolic, mandelic and diphenylglycolic.

Pentacoordinate zwitterionic complexes **210** were synthesized in yields >75%. The pentacoordination of the silicon atom in these compounds in solution is evidenced by the chemical shifts of the signals in the ^{29}Si NMR spectra (from −91.1 to −103.5 ppm).

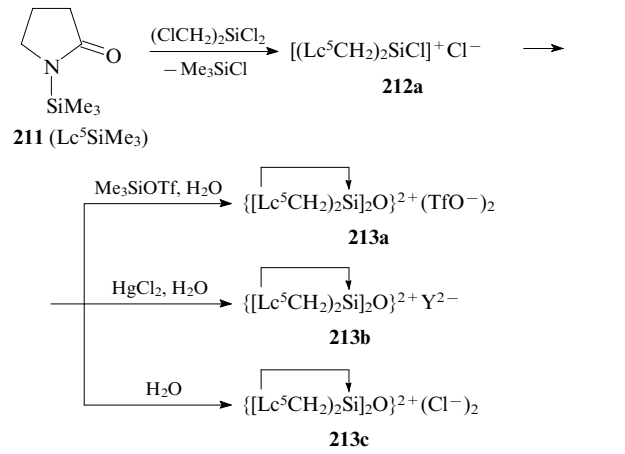
V. Cationic tetravalent silicon complexes

Stability of silylium ions under different conditions, the structural features of these ions, the reactivity and possible role as intermediates in some reactions are in the centre of attention in the modern chemistry of heteroorganic compounds.[144–146] The stabilization of these ions through intramolecular coordination has been extensively studied. It should be noted that most of the known cationic donor-stabilized silicon complexes belong to compounds with an intramolecular N → Si coordination bond.[1, 147]

1. Pentacoordinate silicon complexes with a O → Si coordination bond

First positive results on the synthesis of silylium ions with O → Si coordination based on lactams Lc^nH were obtained in the studies of the reactions of their *N*-TMS derivatives Lc^nSiMe_3 with $(ClCH_2)_2SiCl_2$, which were performed with the goal of synthesizing hypercoordinate dichlorosilanes $(Lc^nCH_2)_2SiCl_2$.[148] The reaction of pyrrolidin-2-one derivative **211** with $(ClCH_2)_2SiCl_2$ afforded hydrolytically unstable dichloride **212a**. After the treatment of the latter with trimethylsilyl triflate, the dicationic bis-C,O-chelate complex, *viz*., ditriflate $\{[(Lc^5CH_2)_2Si]_2O\}^{2+}(TfO^-)_2$ (**213a**) (Scheme 93), was isolated and characterized by X-ray diffraction.

Scheme 93

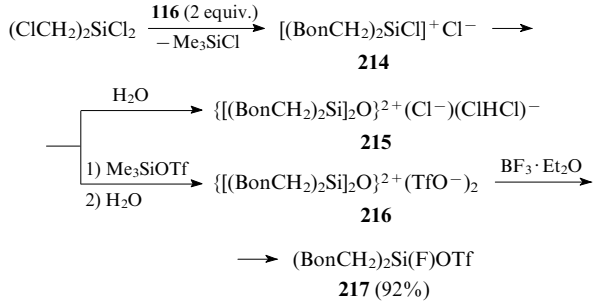


Y = Hg_2Cl_6, $HgCl_4$

Other binuclear pentacoordinate silicon complexes (for example, **213b**,**c**) containing disiloxane dications (XRD data) were also synthesized (see Scheme 93). Related compounds with monoanionic amidomethyl ligands and C,O-coordinating ligands were prepared starting from 1-acyl-2,2-dimethylhydrazines.[85, 149, 150]

The developed route to bischelate silicon complexes with the $BonCH_2$ ligand is based on the reaction of bis(chloromethyl)dichlorosilane $(ClCH_2)_2SiCl_2$ with TMS derivative **116** (see Scheme 51) in a ratio of 1 : 2. The primary reaction product, bischelate dichloride $[(BonCH_2)_2SiCl]^+Cl^-$ (**214**), is easily subjected to hydrolysis to form compound **215** (Scheme 94).[82]

Scheme 94

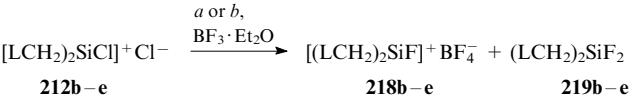


Another approach to the synthesis of bischelate silicon complexes with the $BonCH_2$ ligand employs the reaction of dichloride **214** with trimethylsilyl triflate followed by the addition of water to the reaction mixture. This method was used to prepare the cationic disiloxane complex $\{[(BonCH_2)_2Si]_2O\}^{2+}(TfO^-)_2$ (**216**) (see Scheme 94). The disiloxane moiety Si–O–Si is then cleaved with boron trifluoride diethyl etherate to give fluoride triflate **217** in high yield. This was the first representative of bis-C,O-chelate Si complexes with different monodentate ligands, in which the coordination of the silicon atom can be described as 5 + 1 (the triflate ligand is located at a larger distance from the Si atom).[82]

The ^1H, ^{13}C and ^{29}Si NMR spectra of bischelate mononuclear complexes **214** and **217** show one set of signals, whereas the spectra of binuclear complex **216** exhibit two sets of signals. The signals of silicon atoms are observed in the range from −56.5 to −58.3 ppm for the mononuclear complexes and from −64.5 to −65.0 ppm for the binuclear complex, which is indicative of the pentacoordination of the silicon atom in both cases. It should be noted that the mononuclear analogues of the compounds under consideration, except for a few examples,[150, 151] are virtually unknown. Data on donor-stabilized silylium cations containing monoanionic O,O′-coordinating ligands based on disubstituted 2-hydroxy acid amides were also lacking. Hence, of particular interest are the data on the synthesis and the results of X-ray diffraction study for mononuclear donor-stabilized cationic pentacoordinate silicon complexes with O → Si coordination, *viz.*, new bis-C,O-chelates of the general formula $[(LCH_2)_2Si(F)]BF_4$ with amidomethyl and related ligands LCH_2, as well as for the first representatives of bis-O,O′-chelates $\{XSi[OCH(R)C(O)NMe_2]_2\}^+Y^-$ containing the 2-hydroxy acid amide group as the ligand (X = Cl, Me, Bu^t, Ph, CH_2Br; R = H, Me; $Y^- = Cl^-$, $ClHCl^-$, $HgBr_3^-$, *etc.*).[152]

The reaction of TMS derivatives of amides, lactams and related compounds with $(ClCH_2)_2SiCl_2$ in a ratio of 2 : 1 (see Scheme 93) followed by the hydrolysis or alcoholysis of chlorides **212b–e** and the treatment of intermediates with BF_3 etherate without isolation (Scheme 95, conditions *a*) afforded complexes **218b–e** and **219b–e**.[152] The reactions were accomplished in a one-pot fashion; in most cases, these reactions produced difficult-to-separate mixtures of tetrafluoroborates $[(LCH_2)_2SiF]^+BF_4^-$ (**218b–e**) and neutral hexacoordinate bis-C,O-chelate difluorosilanes $(LCH_2)_2SiF_2$ (**219b–e**).

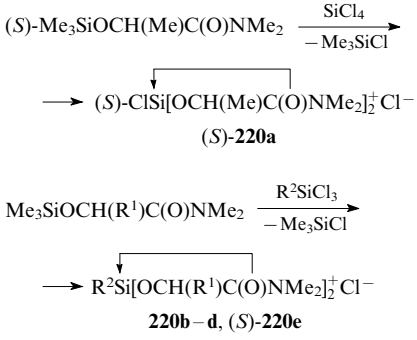
Scheme 95



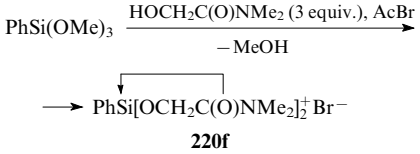
(*a*) $NaHCO_3$, H_2O, through intermediate oligosiloxanes;
(*b*) AlkOH, Et_3N, through $(LCH_2)_2Si(OAlk)_2$;
Alk = Me, Pr^i; L = AcN(Me) (**b**), Lc[7] (**c**), Bon (**d**), Qon (**e**);
QonH is 4-methylquinolin-2-one

First representatives of cationic bis-O,O′-chelate silicon complexes **220a–e** containing the 2-hydroxy acid amide group $\{XSi[OCH(R)C(O)NMe_2]_2\}^+Y^-$ (X = Cl, Me, Bu^t, Ph, CH_2Br; R = H, Me; $Y^- = Cl^-$, $ClHCl^-$, $HgBr_3^-$) were synthesized by the reactions of tetrachloro- and trichlorosilanes with *O*-trimethylsilyl derivatives of (*S*)-lactic and glycolic acid dimethylamides (in a ratio of 1 : 2) (Scheme 96). Related compound **220f** was prepared by the transesterification of $PhSi(OMe)_3$ with glycolic acid dimethylamide followed by the addition of acetyl bromide (the reactant ratio was 1 : 3 : 1). The yields of the final products were from 60% to 90%.

Scheme 96



R^1 = H: R^2 = Me (**b**), Bu^t (**c**), Ph (**d**); $R^1 = R^2$ = Me (**e**)

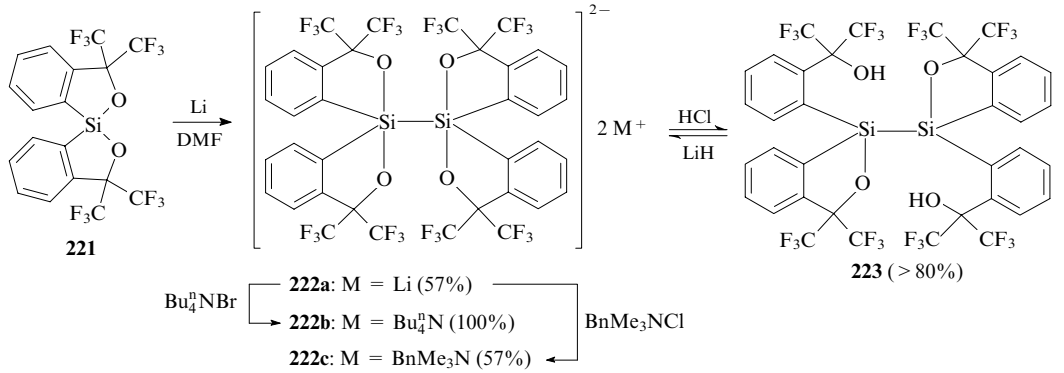


According to the XRD data, bis-C,O- and bis-O,O′-chelate complexes contain silylium ions stabilized by two O → Si coordination bonds. The silicon atoms have the coordination number 5 and adopt a distorted TBP configuration open towards the anion; the axial positions are occupied by O atoms and the equatorial plane is formed by two C atoms and one halogen atom in C,O-chelates or two O atoms and one C (or Cl) atom in O,O′-chelates, respectively.

The synthesis of stable dianionic complexes with two pentacoordinate silicon atoms and a Si–Si bond (Scheme 97) was described by Kano *et al.*[153] Thus, the treatment of silane **221** containing two bidentate ligands with lithium in dimethoxyethane (DME) at −78 °C followed by heating of the reaction mixture to room temperature gave disilyllithium **222a**.

The reaction of complex **222a** with tetrabutylammonium bromide and benzyltrimethylammonium chloride in an acetone–water mixture results in the exchange of cations to form ammonium salts **222b,c**, respectively. The protonation of compounds **222** with a hydrochloric acid solution in diethyl ether gave complex **223** in high yield; in the latter compound, both silicon atoms are tetracoordinate (see Scheme 97).

Scheme 97



The complexes were identified by elemental analysis, multinuclear (^{1}H, ^{7}Li, ^{13}C, ^{19}F and ^{29}Si) NMR spectroscopy and X-ray diffraction; molecular orbitals in these compounds were characterized by UV spectroscopy and quantum chemical calculations.[153]

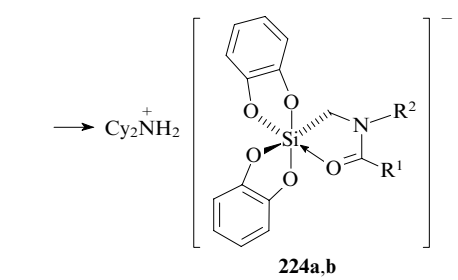
The pentacoordination of the silicon atom in complexes **222** is evidenced by the upfield shift of the signal in the ^{29}Si NMR spectrum (−59.3 ppm), whereas the ^{29}Si NMR spectra of tetracoordinate compounds **221** and **223** show signals at δ 3.2 and −14.4 ppm, respectively. According to the XRD data, compound **222c** contains two $SiSiO_2C_2$ coordination units with distorted TBP geometry, the oxygen atoms being in axial positions.

2. Complexes of hexacoordinate silicon with N → Si and O → Si coordination bonds

Literature data on hexacoordinate complexes with N → Si and O → Si bonds are scarce. For instance, dicyclohexylammonium salts **224a**,**b** were synthesized in 94% and 100% yields, respectively, by the transesterification of the corresponding trimethoxysilanes with pyrocatechol in the presence of dicyclohexylamine (Cy_2NH) (Scheme 98).[154]

According to the XRD data, the resulting salts are anionic silicon complexes, in which the silicon atoms are hexacoordinated by two dianionic O,O′-chelating ligands and one monoanionic C,O-chelating ligands. In the latter case, the chelation occurs through intramolecular O → Si coordination. It should be noted that the tris(disulfato)silicate ion $[Si(S_2O_7)_3]^{2-}$ with three chelating disulfate groups have a similar structure (XRD data). The latter complex was synthesized by the reaction of $SiCl_4$ with oleum in the presence of Na_2SO_4 or Cs_2SO_4.[155]

Scheme 98

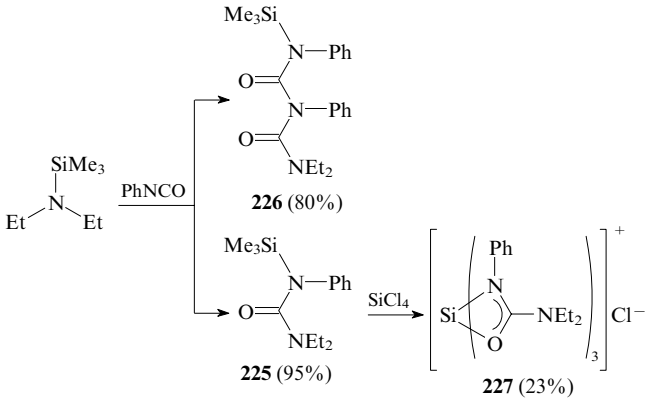


224a,**b**

$R^1 = R^2 = Me$ (**a**), $R^1 - R^2 = (CH_2)_5$ (**b**)

It was found that phenyl isocyanate reacts with *N*-(trimethylsilyl)diethylamine in a ratio of 1 : 1 to form *N*′-silylated *N*,*N*-diethyl-*N*′-phenylurea **225**, whereas compound **226** was obtained in the presence of an excess of phenyl isocyanate (Scheme 99).[156]

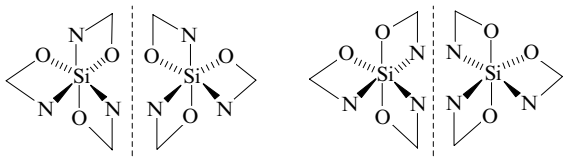
Scheme 99



Compound **226** is of interest as a new potential ligand; however, the main attention was paid[156] to the chelating properties of ligand **225** by studying its reaction with $SiCl_4$ (see Scheme 99). This reaction affords cationic trischelate complex **227** existing as two diastereomers: C_3-symmetric *fac*-**227** and asymmetric *mer*-**227** (pairs of enantiomers are shown).

The signals of diastereomers **227** were detected only by solid-state ^{29}Si CP/MAS NMR spectroscopy. Thus, an intense signal at δ −169.5 ppm and a signal with a lower intensity at δ −164.1 ppm were observed. The solution ^{29}Si NMR spectrum shows only one averaged signal at δ −165.9 ppm, which is, in our opinion, indicative of a fast (on the NMR time scale) stereodynamic process in solution, resulting in the averaging of the signals in the solution ^{29}Si NMR spectrum.

Structures 227



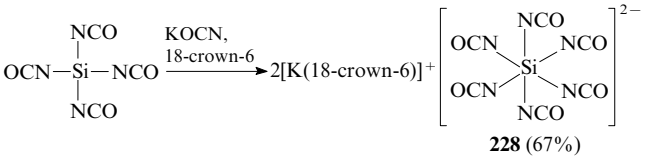
fac-**227** *mer*-**227**

N O = $PhNC(O)NEt_2$

λ^6-Si-Silicate $[K(18\text{-crown-6})]_2[Si(NCO)_6]$ (**228**), which is the first representative of hexa(isocyanato)silicates, was synthesized by the reaction of $Si(NCO)_4$ with KOCN in the presence of 18-crown-6 (Scheme 100).[157] The isotropic chemical shift of the ^{29}Si NMR signal in the solid state

(−248.7 ppm) attests to the hexacoordinate structure of complex **228**. The signal of the $[Si(NCS)_6]^{2-}$ dianion in the related complex has a similar value of $\delta^{29}Si$ (−253), which is evidence of the similar electronic structures of these two complexes.

Scheme 100



228 (67%)

* * *

The synthesis of atranes as organosilicon compounds containing a silicon atom in the unusual coordination state was mentioned for the first time in the 1960s. Research teams headed by Professor Frye (UK) and Academician M G Voronkov (Russia) made a great contribution to the emergence and development of this field of chemistry of heteroorganic compounds. Afterwards, studies of hypercoordinate compounds of Group 14 elements have gained attention throughout the world. Fundamental research performed in laboratories headed by Professors Kost (Israel), Bassindale (UK), Auner (Germany), Corriu (France), Baukov (Russia) and many others are well known and commonly recognized. Even the first results showed that hypercoordinate silicon compounds are not only of purely scientific interest but also hold promise as active ingredients of certain drugs.

The data on the synthesis, structures, reactivity and stereochemical non-rigidity of hypercoordinate silicon compounds published in a rather narrow time interval (2007 – 2012), which are analyzed in the present review, include more than 150 references to both Russian and foreign researchers. Therefore, such studies are still of great interest.

At the present time, researchers focus their efforts on the development of new low-cost methods for the synthesis of hypercoordinate silicon compounds, the determination of their structural features both in the solid state and in solution and investigations of the reactivity and potential biological activity. Studies aimed at determining the influence of solvation effects on the structure of the coordination unit of such complexes also hold promise. It can be expected that the scope of the practical application of the classes of compounds considered in the present review will be substantially extended and supplemented by new classes in the nearest future.

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