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Hypervalent silicon-containing organosilicon derivatives of nitrogen heterocycles

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Abstract. The published data on the methods of synthesis, properties and transformations of organosilicon derivatives of nitrogen heterocycles containing a hypervalent silicon atom are generalised and described systematically. The bibliography includes 173 references.

I. Introduction

Most of the known organosilicon compounds contain a tetracoordinate silicon atom. However, the coordination number of silicon can increase to 5 or 6, especially when the silicon atom is surrounded by electronegative substituents. Intermolecular complexes containing a hexacoordinate silicon atom have been known since the early 19th century when Gay-Lussac and Thenard [1] obtained the addition product of ammonia to tetrafluorosilane, $2\,H_3N\cdot SiF_4$. In the second half of the 20th century, the attention of scientists was attracted by intramolecular complexes of pentacoordinate silicon. Of particular interest among these are silatranes studied in detail by Academician M G Voronkov and his co-workers.[2–16] Studies on silatranes made a valuable contribution to the theoretical, synthetic, medical and applied chemistry. Organosilicon intramolecular complexes are considered in reviews.[17–22] These compounds have an unusual molecular structures, high reactivities and specific biological activities.

During the same period, many researchers were interested in organosilicon derivatives of nitrogen heterocycles,[23–27] which came into use as synthons in organic chemistry for the preparation of biologically active compounds, sorbents, *etc*. It is known that nitrogen-containing rings such as pyrrole, imidazole, pyrazole, pyrimidine, indole, carbazole, *etc*., form the core of alkaloids, natural and synthetic antibiotics and other pharmaceuticals. The introduction of an organosilicon substituent containing a hypervalent silicon atom into nitrogen heterocycle molecules changes considerably their electronic structure and reactivity. The most pronounced changes are observed upon introduction of a silatranyl [inductive constants $\sigma_I = -0.56$,[28] $\sigma^* = -3.49$ (Ref. 29)] and silatranylmethyl [$\sigma_I = -0.36$,[30] $\sigma^* = -2.24$ (Ref. 29)] groups exhibiting strong electron-donating inductive effect and having a high dipole moment. This modification of heterocyclic compounds gives rise to new classes of biologically active products promising for medicine and agriculture.

Hypervalent silicon-containing organosilicon derivatives of nitrogen heterocycles can be classified into three groups.

1. Intermolecular complexes of heterocyclic compounds with tetrahalosilanes and organylhalosilanes, for example, complexes of pyridine, picolines, 2,2′- and 4,4′-bipyridines and 1,10-phenanthroline with tetrafluorosilane and organylfluorosilanes which have been described in detail in a review.[31]

2. Heterocyclic compounds in which the silicon atom becomes hypervalent due to intramolecular coordination with endo- (or exo-)cyclic heteroatom N or O.

3. Heterocyclic compounds in which the hypervalent silicon atom is a part of an exocyclic substituent. The main representatives of this group are silatrane derivatives in which the silicon atom is bound to the heterocycle either directly or through a $(CH_2)_n$, CH_2NR, CH_2S, O or another bridge.

This review deals with organosilicon derivatives of nitrogen heterocycles of the last two groups, except for *N*-(dialkylchlorosilylmethyl)lactams with an O→Si bond and their derivatives, which were studied in detail by Baukov's group (Russia),[25,32] and zwitter-ionic spirocyclic λ^5-*Si*-silicates with an Si–C–N(Het) fragment described by Tacke and coworkers (Germany).[33–35] Some data concerning compounds of the second and third groups obtained by the authors of the present review have been briefly surveyed before.[36–38] The organosilicon compounds considered below that contain simultaneously a nitrogen heterocycle and a hypervalent silicon atom are of substantial theoretical interest for organic chemists. The knowledge of the molecular structure and physical properties of these compounds would extend the existing views on both the stereoelectronic structure of the hypervalent silicon derivatives and the specific influence of organosilicon substituents containing a penta- or hexacoordinate Si atom on the character of the heterocycle and its reactivity. In addition, many of these compounds possess high and specific biological activities and are potential pharmaceutical or agricultural agents.

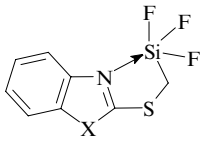
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II. Intramolecular organosilicon complexes of nitrogen heterocycles

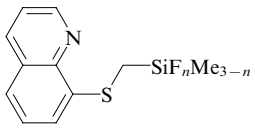
1. Methods of synthesis

The presence of an organosilicon substituent $YSiX_nMe_{3-n}$ (X = Cl, F; n = 1–3; Y is a hydrocarbon or heteroatomic group) in a nitrogen heterocycle may produce, at a certain molecular structure, a pentacoordinate silicon atom through the donor–acceptor interaction with the endocyclic heteroatom, either nitrogen or oxygen. This is observed, for example, in trifluorosilylmethyl derivatives of 2-mercaptobenzoxazole (**1**) or 2-mercaptobenzothiazole (**2**).[39]



1, **2**

X = O (**1**), S (**2**).

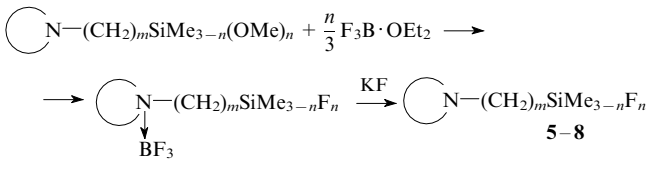


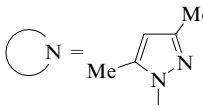
3, **4**

n = 3 (**3**), 2 (**4**).

This type of compounds were synthesised by reactions of *S*-trimethoxysilylmethyl derivatives of heterocycles with boron trifluoride etherate. Trifluoro(8-quinolylthiomethyl)- (**3**) and difluoro(methyl)(8-quinolylthiomethyl)silanes (**4**) were obtained in a similar way.[40] However, UV and IR spectroscopic data did not support the assumption about the presence of intramolecular N→Si donor–acceptor bonds closing six-membered chelate rings in these compounds.

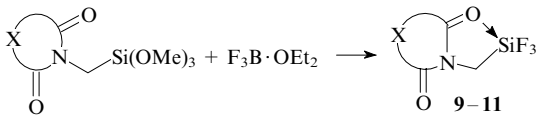
The reaction of *N*-trimethoxysilylalkyl or *N*-dimethoxy(methyl)silylmethyl derivatives of 3,5-dimethylpyrazole and benzimidazole with an excess of boron trifluoride etherate involves not only the replacement of methoxy groups by fluorine atoms but also coordination of nitrogen to the BF_3 molecule to give *B*-trifluoroborazane.[37,38]



N =  (**5**–**7**);  (**8**); n = 3: m = 1 (**5**), 3 (**7**); n = 2, m = 1 (**6**, **8**).

On treatment with potassium fluoride or carbamide, borazanes lose BF_3 being converted into compounds **5**–**8**.

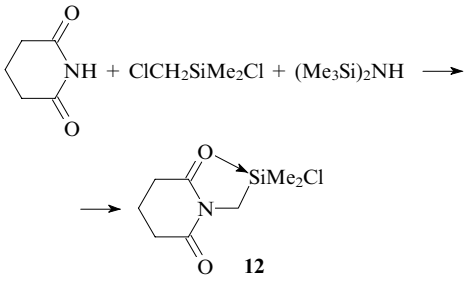
The reaction of *N*-(trimethoxysilylmethyl)imides of dicarboxylic acids, namely, succinic, glutaric and phthalic acids, with boron trifluoride etherate without a solvent at 35–40 °C afforded intramolecular complexes: *N*-(trifluorosilylmethyl)-succinimide (**9**),[41–43] -glutarimide (**10**)[43,44] and -phthalimide (**11**).[45] In these compounds, the silicon atom is pentacoordinated due to the formation of an additional transannular O→Si donor–acceptor bond; the presence of this bond was confirmed by X-ray crystallography and multinuclear NMR and IR spectroscopy.[41,43–45] These compounds refer to the group of so-called dragonoids.[13]



9–**11**

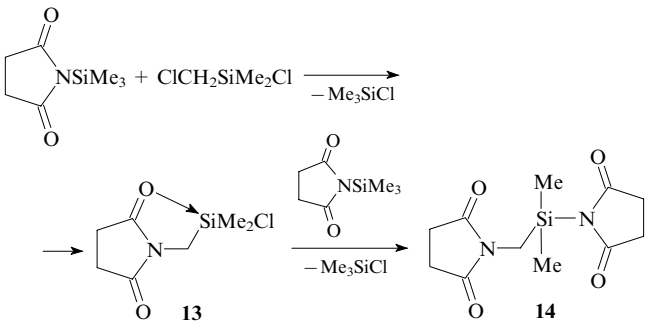
X = $(CH_2)_n$ (n = 2 (**9**), 3 (**10**)), *o*-phenylene (**11**).

N-(Chlorodimethylsilylmethyl)glutarimide (**12**) was prepared by the reaction of *N*-(trimethylsilyl)glutarimide with chloro(chloromethyl)dimethylsilane or by the reaction of unsubstituted glutarimide with a mixture of hexamethyldisilazane and chloro(chloromethyl)dimethylsilane.[46] The presence of a pentacoordinate silicon in compound **12** was demonstrated both in solutions and in crystals



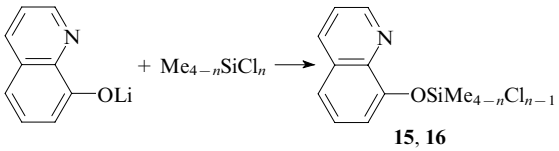
12

In the case of *N*-(trimethylsilyl)succinimide, the formation of the expected *N*-(chlorodimethylsilylmethyl)succinimide (**13**) was accompanied by the formation of organosilicon diimide **14**, resulting from substitution of the imide fragment for chlorine. According to NMR and X-ray diffraction data, the silicon atom in compound **14** is tetracoordinated.



13 **14**

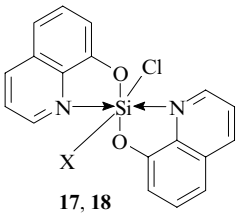
Hensen and Klebe[47] demonstrated that the reaction of *O*-lithio-8-hydroxyquinoline with chloro(methyl)silanes Cl_nSiMe_{4-n} (n = 1, 2) results in substitution of the quinolyloxy group for chlorine to give compounds **15** (n = 1) and **16** (n = 2) with tetracoordinate silicon atoms.



15, **16**

n = 1 (**15**), 2 (**16**).

In an analogous reaction with more chlorinated silanes (n = 3 and 4), two chlorine atoms are replaced, because two molecules of lithiated 8-hydroxyquinoline are involved. In the compounds **17** and **18** thus formed, the silicon atom is linked by N→Si donor–acceptor bonds to both heterocyclic molecules.

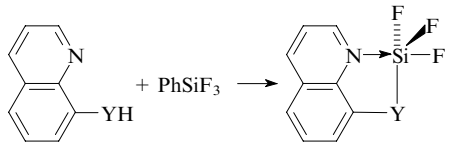


17, **18**

X = Me (**17**), Cl (**18**).

It was found [48] that the silicon coordination polyhedron in (chloro)methyl[bis(8-quinolyloxy)]silane (**17**) is a distorted octahedron.

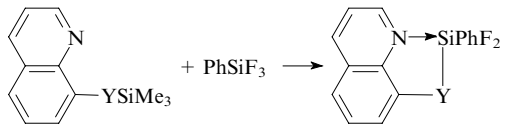
We proposed a new original method for the synthesis of organosilicon intramolecular complexes of quinoline **19** and **20** containing a pentacoordinate silicon atom by protolytic cleavage of the Si–C bond in trifluoro(phenyl)silane under the action of 8-hydroxy- or 8-mercaptoquinoline:[38, 49]



19, **20**

Y = O (**19**), S (**20**).

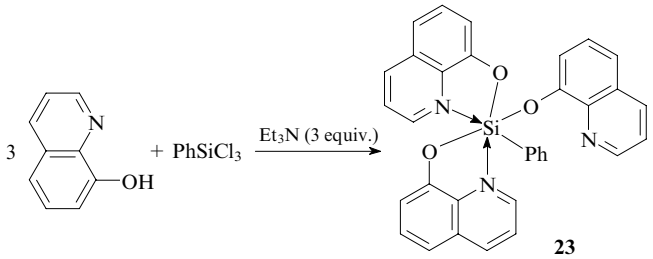
The reaction of trifluoro(phenyl)silane with 8-(trimethylsiloxy)quinoline and its thio analogue occurs as transsilylation with elimination of fluoro(trimethyl)silane to give intramolecular complexes **21** and **22** containing an N → Si donor–acceptor bond.[49]



21, **22**

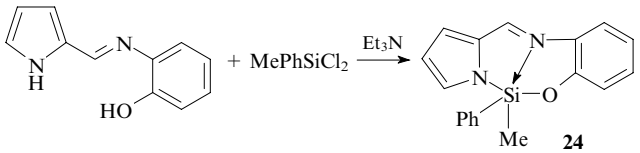
Y = O (**21**), S (**22**).

Trichloro(phenyl)silane can be used to prepare organosilicon derivatives of nitrogen heterocycles. When made to react with 3 equivalents of 8-hydroxyquinoline in the presence of triethylamine as HCl acceptor, this compound produces complex **23** containing a hexacoordinate silicon atom.[50]



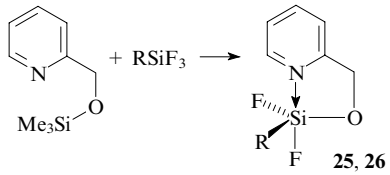
23

The reaction of pyrrole-2-*N*-(*o*-hydroxyphenyl)carbaldimine with dichloro(methyl)phenylsilane results in compound **24**. In this case, the additional coordination of silicon is accomplished through the formation of the donor–acceptor bond with the imine nitrogen.[51]



24

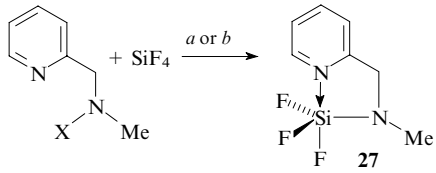
2-(Trimethylsiloxymethyl)pyridine reacts with trifluorophenyl- and tetrafluorosilanes to give compounds **25** and **26**, which also contain intramolecular N→Si coordination bonds.[52]



25, **26**

R = Ph (**25**), F (**26**).

The reaction of lithium methyl(2-pyridylmethyl)amide with SiF_4 in ether gives intramolecular complex **27** with pentacoordinate silicon in 20% yield.[53]

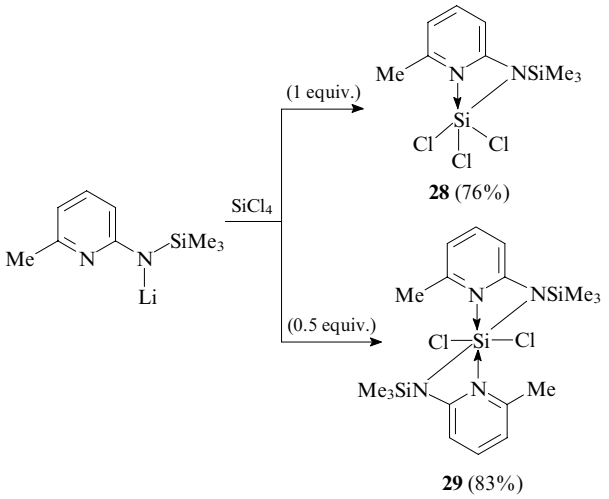


27

(*a*) Et_2O, X = Li; (*b*) CH_2Cl_2, −25 °C, X = Me_3Si.

Note that compound **27** is also formed on treatment of 2-[methyl(trimethylsilyl)aminomethyl]pyridine with tetrafluorosilane in dichloromethane at −25 °C (yield 62%).[53]

Lithium trimethylsilyl(6-methylpyridin-2-yl)amide reacts with tetrachlorosilane in ether giving rise to intramolecular complexes **28** or **29**, depending on the reactant molar ratio (1 : 1 or 2 : 1), in good yields.[54]

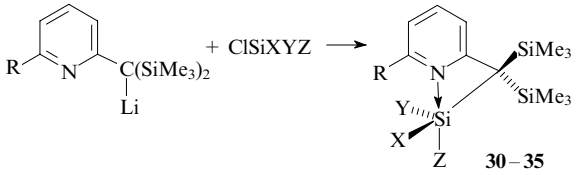


28 (76%)

29 (83%)

Compound **28** contains pentacoordinate silicon, while dimer **29** contains a hexacoordinate silicon atom. Dimer **29** is stable on heating to 100 °C, whereas compound **28** decomposes even at 50 °C.

It was found [55, 56] that reactions of chloromethylsilanes $Me_{4-n}SiCl_n$ (n = 2, 3) or $HSiCl_3$ with 2-[lithiobis(trimethylsilyl)]methylpyridine or its 6-methyl derivative afford compounds **30**–**35**. These intramolecular complexes contain a pentacoordinate silicon atom incorporated in a four-membered (!) coordination ring through the N→Si bond.

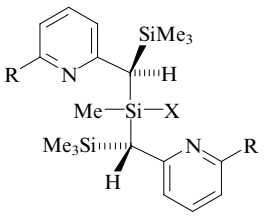


30–**35**

X = H, Y = Z = Cl: R = H (**30**), Me (**31**); X = Me, Y = Z = Cl: R = H (**32**), Me (**33**); X = Y = Me, Z = Cl: R = H (**34**), Me (**35**).

It is noteworthy that no N→Si coordination bond was found in related compounds **36** (X = Y = Z = Me, R = H) and **37** (X = Y = Z = R = Me) obtained from chlorotrimethylsilane.

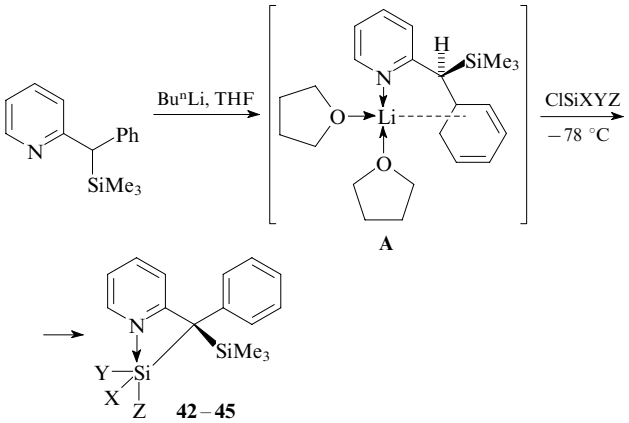
However, when analogous lithio derivatives of picoline and lutidine containing one trimethylsilyl group are made to react with trichloro(methyl)- or dichloro(dimethyl)-silane, crystalline racemates with tetracoordinate silicon, compounds **38–41,** are formed.[56]



38–41

X = Cl: R = H (**38**), Me (**39**); X = Me: R = H (**40**), Me (**41**).

The metallation of 2-[(trimethylsilyl)phenyl]methylpyridine with n-butyllithium in tetrahydrofuran gives a red-coloured solution of complex **A**. Its subsequent reaction with $SiX_{4-n}Cl_n$ (X = H, n = 3; X = Me, n = 1–3) in THF at −78 °C leads to compounds **42–45** containing pentacoordinate silicon; the THF solutions of these products are dark-red.[56]

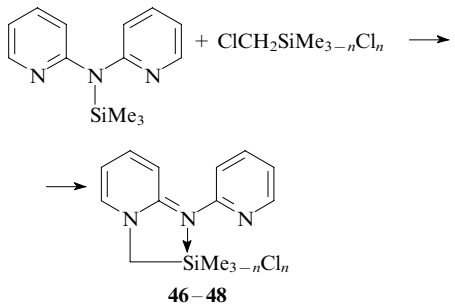


A

42–45

X = H, Y = Z = Cl (**42**); X = Me, Y = Z = Cl (**43**);
X = Y = Me, Z = Cl (**44**); X = Y = Z = Me (**45**).

Intramolecular organosilicon complexes **46–48** were synthesised by the reaction of bis(2-pyridyl)(trimethylsilyl)amine with chloro(halomethyl)methylsilanes $XCH_2SiMe_{3-n}Cl_n$ (X = Cl, Br; n = 1–3).[57] For X = Cl, the reaction proceeds as shown below

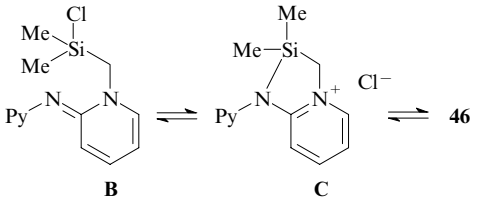


46–48

n = 1 (**46**), 2 (**47**), 3 (**48**).

Evidently, the reaction starts with quaternisation and isomerisation of the pyridine fragment accompanied by elimination of chlorotrimethylsilane. Formally, the $SiMe_3$ group is substituted by CH_2SiMe_2Cl (*i.e.*, the reaction occurs as transsilylation [25]) (Scheme 1).

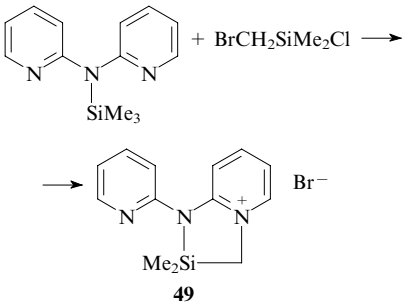
Scheme 1



B **C**

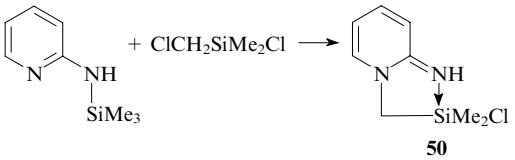
The compound **B** thus formed isomerises to give pyridinium salt **C**. The silicon atom in intermediates **B** and **C** is tetracoordinated. However, in product **46** containing an N→Si donor–acceptor bond, the silicon atom is pentacoordinated.

As opposed to this mechanism, for X = Br, the pyridinium nitrogen atom becomes the reaction site; therefore, the reaction yields stable pyridinium bromide **49**.[57]



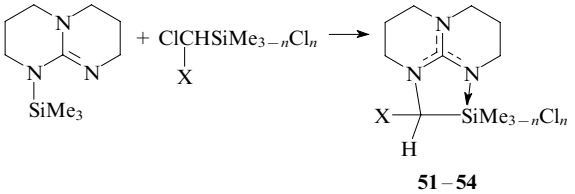
49

Compound **50** was prepared in a similar way from *N*-trimethylsilyl-2-pyridylamine and chloro(chloromethyl)dimethylsilane.[27]



50

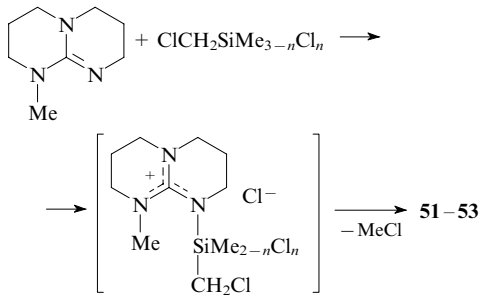
The reactions of chloro(chloromethyl)methylsilanes, trichloro(1-chloroethyl)silane and trichloro(chloromethyl)silane with 1-trimethylsilyl-2*H*-1,3,4,6,7,8-hexahydropyrimido[1,2-*a*]-pyrimidine have been studied.[58] These reactions give crystalline intramolecular complexes **51–54** containing a pentacoordinate silicon atom in nearly quantitative yields (88%–94%).



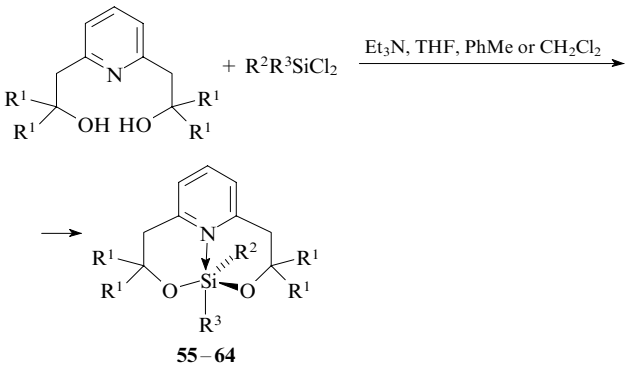
51–54

X = H: n = 1 (**51**), 2 (**52**), 3 (**53**); X = Me, n = 3 (**54**).

Compounds **51–53** were also obtained (yields 86%–92%) from 1-methyl-2*H*-1,3,4,6,7,8-hexahydropyrimido[1,2-*a*]pyrimidine and appropriate chloro(chloromethyl)silanes.[58]

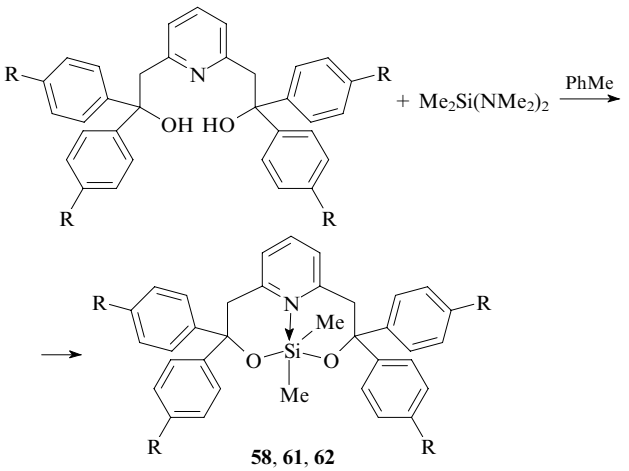


The reactions of substituted 2,6-bis(2-hydroxyethyl)pyridines with dimethyl-, diphenyl- and methylphenyl-dichlorosilanes and with bis(dimethylamino)dimethylsilane yield compounds **55**–**64**:[59–63]



55–**64**

R^1 = Ph: R^2 = R^3 = Me (**55**), Ph (**56**); R^2 = Me, R^3 = Ph (**57**);
R^1 = C_6H_4F-4: R^2 = R^3 = Me (**58**), Ph (**59**); R^2 = Me, R^3 = Ph (**60**);
R^1 = C_6H_4Br-4, R^2 = R^3 = Me (**61**);
R^1 = $C_6H_4Bu^t$-4, R^2 = R^3 = Me (**62**);
R^1_2COH is 2-hydroxyadamantan-2-yl: R^2 = R^3 = Me (**63**), Ph (**64**).

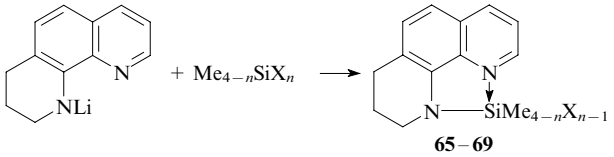


58, **61**, **62**

R = F (**58**), Br (**61**), Bu^t (**62**).

Compound **63** was the first example of a 1,3-dioxa-7-aza-2-silacyclodecane system incorporating a heterocycle (pyridine) and containing a weak transannular N→Si coordination bond (length 2.727 Å).[59] The structure of this compound was confirmed by ^{29}Si NMR spectroscopy [the silicon chemical shift $\delta(^{29}Si)$ was −41.9]. The silicon atom geometry in molecule **63** is much closer to tetrahedral than to trigonal-bipyramidal (see Section II.2.a). The silicon atom in compound **55** also has a geometry intermediate between a tetrahedron and a trigonal bipyramid.[60]

The reaction of *N*-lithio-1,2,3,4-tetrahydro-1,10-phenanthroline with halo(methyl)silanes $Me_{4-n}SiX_n$ (X = F, Cl; n = 1–4) follows the route shown below:[47,64]



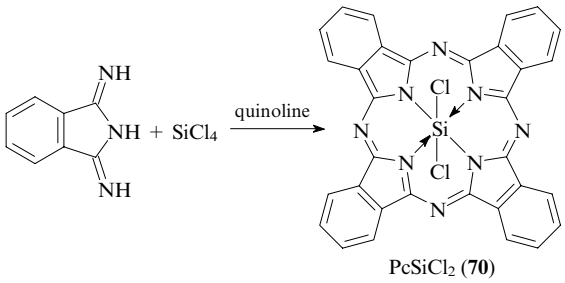
65–**69**

X = Cl: n = 1 (**65**), 2 (**66**), 3 (**67**); n = 4: X = F (**68**), Cl (**69**).

According to X-ray diffraction data,[64–68] and ^{15}N, ^{29}Si (Ref. 69) and ^{19}F (Ref. 70) NMR spectroscopy, the silicon atom in compounds **66**–**69** is pentacoordinated due to the formation of the intramolecular N→Si coordination bond. The same is true for the isostructural compound containing an SiF_2Cl group.[67] Meanwhile, intramolecular N→Si interaction in 1-trimethylsilyl-1,2,3,4-tetrahydro-1,10-phenanthroline (**65**) is absent or very weak.[67]

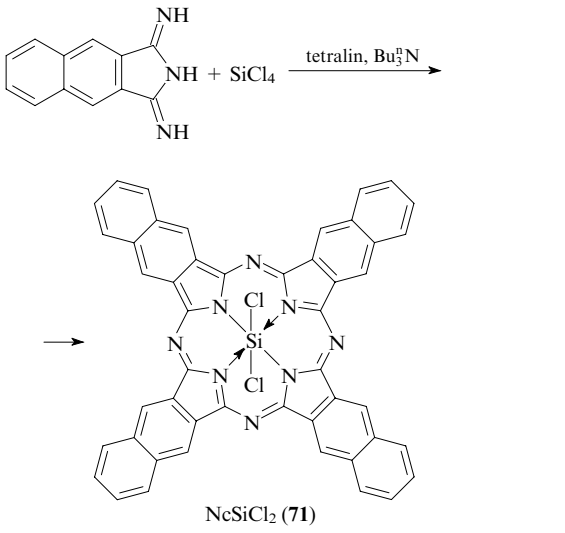
Organosilicon intramolecular complex derivatives of phthalocyanine (Pc), naphthalocyanine (Nc), porphyrin, *etc.* containing a hexacoordinate central silicon atom attracted attention of researchers back in the beginning of the second half of the 20th century.[71,72] These compounds can be regarded as siliconium(VI) derivatives. Over the period from 1960 to 1965, a dozen of publications were devoted to these compounds, the studies by Joyner *et al.*[73,74] being pioneering. In this review we dwell only on the compounds studied over the last two decades.

A key method for the synthesis of phthalocyanino- or naphthalocyanino-λ^6-siliconium dichlorides is the reaction of silicon tetrachloride with 1,3-diiminoisoindoline.[75]



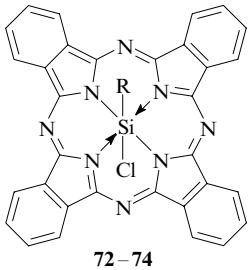
$PcSiCl_2$ (**70**)

or 1,3-diiminobenzoisoindoline.[76]



$NcSiCl_2$ (**71**)

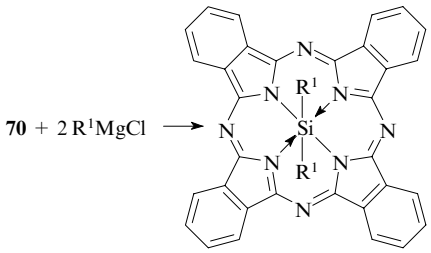
Organosilicon phthalocyanines have received much more attention than phthalocyanino-λ^6-siliconium dichlorides. Chloroorganylsilyl phthalocyanine derivatives **72**–**74** were obtained by the reaction of chloroorganylsilanes with 1,3-diiminoisoindoline (yields up to 80%).[77, 78]



72–**74**

R = Me (**72**), Ph (**73**), n-C_8H_{17} (**74**).

Phthalocyanino-λ^6-siliconium chlorides can also serve as the starting compounds for the synthesis of organosilicon phthalocyanines. For example, symmetric phthalocyanino-λ^6-siliconium derivatives **75**–**84** were prepared from dichloride **70** by the reaction with Grignard reagents.[78, 79]

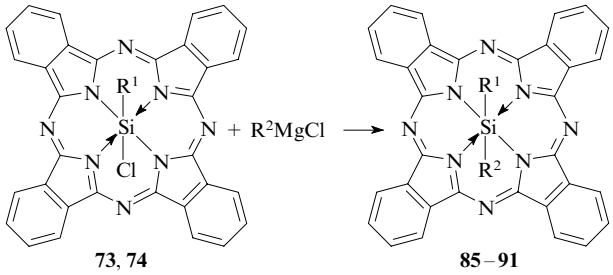


75–**84**

R^1 = Me (**75**), $R^2C_6H_4$ [R^2 = H (**76**), 4-Me (**77**), 4-MeO (**78**), 3-CF_3 (**79**)], n-C_8H_{17} (**80**), $R^3C\equiv C$ [R^3 = H (**81**), Me (**82**), Bu^t (**83**), Ph (**84**)].

Similarly, chlorine-containing precursors $PcSiR^1Cl$ were converted into unsymmetrical organosilicon phthalocyanine derivatives **85**–**91**.[78]

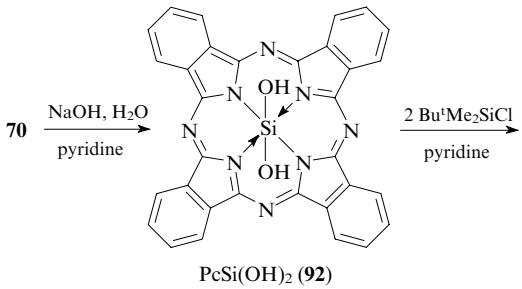
Dichloride $PcSiCl_2$ (**70**) is hydrolysed on treatment with an aqueous solution of pyridine or NaOH to give silanediol



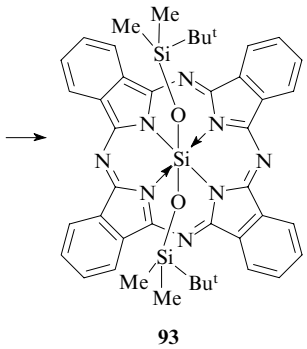
73, **74** **85**–**91**

R^1 = Ph: R^2 = $R^3C_6H_4$ [R^3 = 4-Me (**85**), 4-MeO (**86**), 3-CF_3 (**87**)],
R^1 = n-C_8H_{17}: R^2 = $R^4C_6H_4$ [R^4 = H (**88**), 4-Me (**89**), 4-MeO (**90**), 3-CF_3 (**91**)].

$PcSi(OH)_2$ (**92**).[80] The reaction of this product with *tert*-butyl(chloro)dimethylsilane results in siloxy derivative **93**.



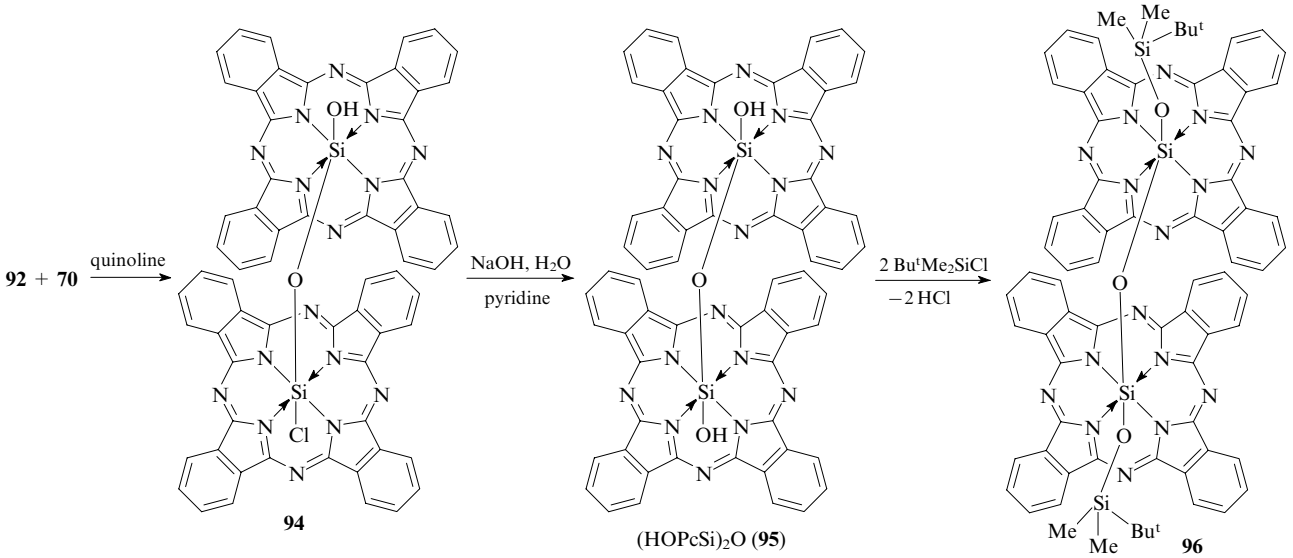
$PcSi(OH)_2$ (**92**)



93

The reaction of phthalocyanine **92** with an excess of $PcSiCl_2$ (**70**) followed by hydrolysis of product **94** (Scheme 2)

Scheme 2

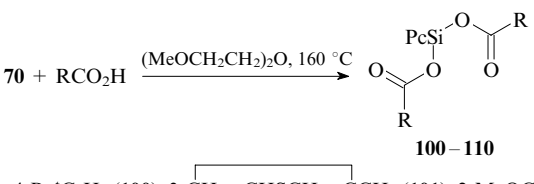


94 $(HOPcSi)_2O$ (**95**) **96**

affords $[HOPcSi]_2O$ (**95**), which reacts with Bu^tMe_2SiCl in dry pyridine giving rise to compound **96**.[80]

The reaction of chlorotrihexylsilane with $PcSi(OH)_2$ (**92**) in the presence of tributylamine in dry γ-picoline furnished phthalocyanine $PcSi[OSi(n\text{-}C_6H_{13})_3]_2$ (**97**). An analogous transformation has also been described for naphthalocyanino-λ⁶-siliconium derivative. For example, treatment of dichloride **71** with concentrated H_2SO_4 yields diol $NcSi(OH)_2$ (**98**), which reacts with $(n\text{-}C_6H_{13})_3SiCl$ to be converted into bis(trihexylsiloxynaphthalocyanino)-λ⁶-siliconium $NcSi[OSi.(n\text{-}C_6H_{13})_3]_2$ (**99**).[76]

Organosilicon phthalocyanino-λ⁶-siliconium derivatives **100**–**110** were formed upon reaction of dichloride **70** with appropriate carboxylic acids.[81]



100–**110**

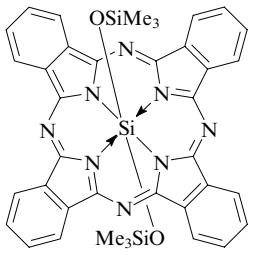
R = 4-$Bu^tC_6H_4$ (**100**), 3-CH=CHSCH=CCH$_2$ (**101**), 2-$MeOC_6H_4CH_2$ (**102**), 3-$MeOC_6H_4CH_2$ (**103**), 4-$MeOC_6H_4CH_2$ (**104**), 2,5-$(MeO)_2C_6H_3CH_2$ (**105**), 3,4-$(MeO)_2C_6H_3$ (**106**), 3,4-$(MeO)_2C_6H_3CH_2$ (**107**), 3,4,5-$(MeO)_3C_6H_2CH_2$ (**108**), 3,4-$(MeO)_2C_6H_3(CH_2)_2$ (**109**), 3,4-$(MeO)_2C_6H_3(CH_2)_3$ (**110**).

At R = 4-$Bu^tC_6H_4$, compound **100** with a rigid orthogonal arrangement of the aroyloxy groups is produced. Bis(3-thienylcarboxylate) **101** is conformationally more flexible. The change in the nature of the aromatic substituent in phthalocyanino-λ⁶-siliconium induces a change in its spectroscopic properties, which are related to the energies of excited states, while elongation of the aliphatic chain causes changes in the luminescence time and the quantum yield.[81]

Dichlorosilylphthalocyanine (**70**) reacts with 4-hydroxy-4′-nitroazobenzene in the presence of sodium hydride to give organosilicon bis(azobenzo)phthalocyanine **111** with a hexacoordinate central silicon atom. Compound **111** is the first example of azobenzo conjugated phthalocyanino-λ⁶-siliconium (Scheme 3).[82] The electrochemical properties of this compound indicate that it is promising for the use in devices such as photoelectric relays.

The synthesis of *Si*-disubstituted phthalocyanino-λ⁶-siliconium derivatives containing two 1,3-bis(dimethylamino)isopropoxy groups (compound **112**) [83] or one (**113**) or two (**114**) 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose fragments at the central silicon atom was reported.[84] Organosilicon phthalocyanine derivatives, especially unsymmetrical ones, proved to be highly efficient carcinostatics with respect to human carcinoma cells HepG2 and were captured by the mouse macrophage J774. The photodynamic activity of these compounds is due to their absorption by cancer cells and efficient generation of singlet oxygen.

The reaction of $PcSi(OH)_2$ (**92**) with *N*,*O*-bis(trimethylsilyl)acetamide in the presence of pyridine gives $PcSi(OSiMe_3)_2$ (**115**).[85] Similarly, compounds $Me_3SiO(PcSiO)_nSiMe_3$ (n = 2–5) were prepared from $HO(PcSiO)_nH$.



115

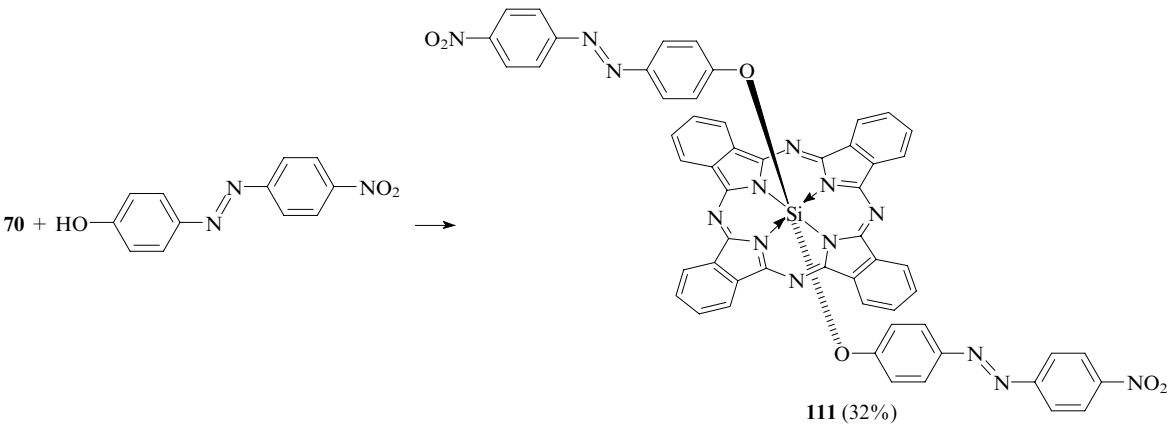
More than 100 papers published during the last 30 years were devoted to the methods of preparation, structure, and properties (chemical, physical, optical and electronic) of organosilicon phthalocyanine polymers and the scope of their applications in advanced fields of engineering and medicine.[86–94]

Axially disubstituted phthalocyanino-λ⁶-siliconium derivatives with ester groups at the silicon atoms and with phenyl, terphenyl, thienyl, pyrenyl [95,96] and fullerrene [97] substituents have been synthesised. Electrochemical, absorption and film-forming characteristics of these compounds and dependence of properties on the nature of substituents at the hexacoordinate silicon atom were studied.

Phthalocyanino-λ⁶-siliconium oligomers $R_3SiO(SiPcO)_n.SiR_3$ (n = 2–4) comprising two, three or four monomers cross-linked by siloxane bridges have also been described. The spatial and electronic structures of these compounds were investigated by NMR and UV/Vis absorption spectroscopy and by other physical, kinetic and computational methods.[98–103]

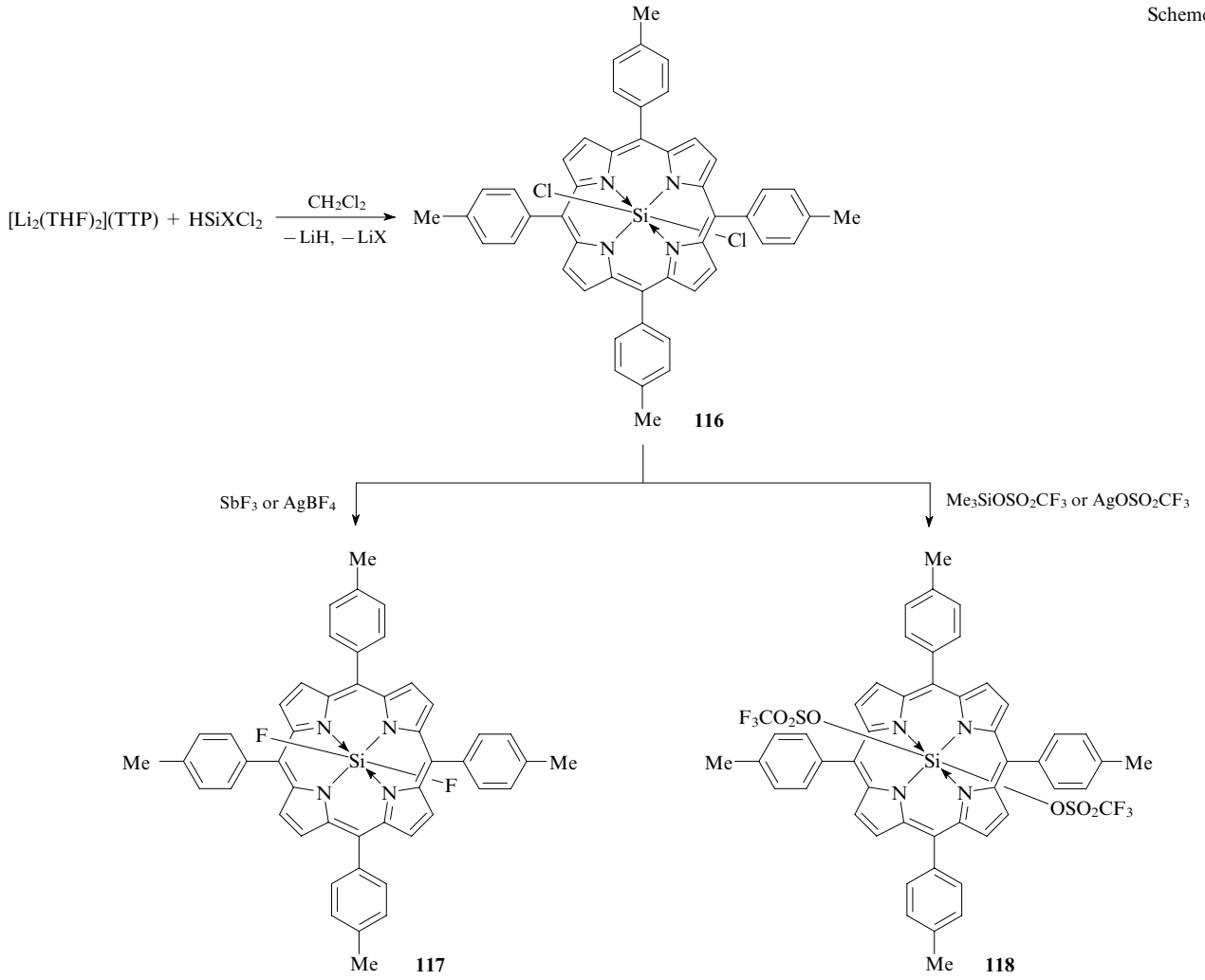
As a conclusion of this Section, consider examples of silicon-containing derivatives of tetra(*p*-tolyl)porphyrin (TTP). The reduction of $Si(TTP)Cl_2$ (see Ref. 104) with the Na/Hg–THF system afforded tetratolylporphyrino-λ⁶-siliconium $Si(TTP)(THF)_2$.[105] The reaction of the lithium derivative of TTP with trichlorosilane in dichloromethane at −78 °C gave compound **116**.[104] The reactions of compound **116** with SbF_3 (or $AgBF_4$) and with $Me_3SiOSO_2CF_3$ (or $AgOSO_2CF_3$) in CH_2Cl_2 gave difluoride **117** and ditriflate **118** in quantitative yields (Scheme 4).

Scheme 3



111 (32%)

Scheme 4



X = H, Cl.

2. Studies of the molecular structure

a. X-Ray diffraction method

The pentacoordinate silicon atom present in organosilicon intramolecular complex derivatives of nitrogen heterocycles containing an endocyclic N → Si coordination bond exists in a trigonal-bipyramidal environment. The lengths of the bonds between silicon and two apical ligands for some of these molecules are presented in Table 1.

The N→Si dative bond and the Si−X bond (X = F, Cl, O, N) usually occupy axial positions. If two or three electronegative atoms are attached to silicon, then the apical position is occupied by the atom with a higher apical activity (the ability to occupy this site and ensure *trans*-coordination of the ligands), which decreases in the sequence Cl, OCOR > F ≈ SR > OR, NR_2 > Ar > Alk > H.[108, 109] The position of an atom or an atomic group in this sequence is correlated with their electronegativity and the polarisability of their bonds with silicon.

The displacement of the silicon atom (ΔSi) from the central plane formed by three equatorial ligands toward the axial vertex *Z* (see Table 1) varies from 0.01 to 0.380 Å.

The compounds of pentacoordinate silicon contain most often a five-membered chelate ring. Compounds with four-membered (**28**,[54] **30**–**35**,[55, 56] **42**–**44**[56]) and six-membered (**55**–**64**)[59–63] coordination rings are also known.

The variations of the N→Si and Si−Z interatomic distances are antiparallel. In molecules **46**, **50**, **51** and **66**, shortening of the Si−Cl bond in the N→Si−Cl axial fragment from 3.908 to 2.269 Å is accompanied by elongation of the Si−N bond from 1.766 to 2.028 Å. This is in good agreement with the

Table 1. Bond lengths N→Si and Si−Z in the N→Si(X)(Y)−Z fragment of intramolecular silicon heterocyclic complexes.

Compound	X	Y	Z	N→Si /Å	Si−Z /Å	ΔSi /Å	Ref.
1	F	F	F	1.967	1.624		106
2	F	F	F	1.988	1.632		106
9	F	F	F	2.096 [a]	1.607	0.290	41
10	F	F	F	1.977 [a, b]	1.619	0.160	107
				1.992		0.180	
11	F	F	F	2.654 [a]	1.576	0.380	45
12	Me	Me	Cl	2.171	2.210	0.190	46
27	F	F	F	1.974	1.621		53
28	Cl	Cl	Cl	1.975	2.107		54
30	H	Cl	Cl	2.066	2.167		55
31	H	Cl	Cl	2.072	2.163		56
46	Me	Me	Cl	1.898	2.598	0.167	57
48	Cl	Cl	Cl	1.901	2.238	0.010	57
50	Me	Me	Cl	1.766	3.908		27
				1.777	4.111		
51	Me	Me	Cl	1.852	2.679	0.166	58
66	Me	Me	Cl	2.028	2.269		68
67	Me	Cl	Cl	2.027	2.207		68
68	F	F	F	1.969	1.621	0.195	64
69	Cl	Cl	Cl	1.984	2.150		65, 66, 68

[a] The O→Si bond length is given; [b] bond lengths for two conformers, namely, with an envelope (α) and planar (β) geometries of the six-membered heterocycle are given.

hypervalence theory proposed by Musher[110] and developed later by Pestunovich, Sidorkin, and Voronkov.[14,15,111] According to this concept, the axial atoms are bound to the silicon p_z-orbital by a system of three-centre four-electron ($3c-4e$) molecular orbitals.

The equatorial substituents interact with the axial fragment, thus shortening the N → Si bond and lengthening the Si—Cl bond.[14] This effect is not very pronounced but evidently significant. However, in molecules **66**, **67** and **69** differing in the number of equatorial chlorine atoms (1, 2 and 3, respectively), the N→Si bond length and the axial Si—Cl bond length decrease as the number of chlorine atoms increases (see Table 1).[68] The equatorial bonds in an ideal trigonal bipyramid (TBP) with the silicon atom in the equatorial plane ($\Delta Si = 0$) are orthogonal to the three-centre MOs. Shortening of the bonds is apparently caused by the electron-withdrawing effect of silicon, which makes the silicon atom approach the axial substituents.

In molecule **51**, the silicon atom is located at the centre of a disordered TBP the axial positions of which are occupied by the heterocycle nitrogen atom and the chlorine atom (the N—Si—Cl angle is 167.9°).[58] The length of the very short N→Si bond (1.852 Å) is close to a covalent bond length (1.796 Å), while the length of the very long Si—Cl bond (2.679 Å) attests to a substantial polarisation.

The two interatomic distances N—Si in 2-[methyl(trifluorosilyl)aminomethyl]pyridine (**27**)[53] are non-equivalent, the N → Si coordination bond being much longer than the covalent bond. In the TBP of molecule **27**, the pyridine nitrogen atom and the fluorine atom are in the axial positions (the NSiF angle is 178.0°). The $Si-F_{ax}$ bond (1.621 Å) is longer than $Si-F_{eq}$ (1.603 Å).

Attention is attracted by the considerable difference between the O→Si bond lengths in the *N*-(trifluorosilylmethyl)succinimide (**9**) and -glutarimide (**10**) molecules and that in the *N*-(trifluorosilylmethyl)phthalimide (**11**) molecule, indicating much stronger bonds in the case of compounds **9** and **10** than in compound **11**.[41,43–45,107] This is due to the fact that the five-membered pyrroline-2,5-dione ring in the molecule of organosilicon phthalimide derivative **11** is aromatic, as it has a closed six-π-electron shell. Therefore, the nucleophilicity of the carbonyl oxygen atoms in compound **11** is lower than that in non-aromatic molecules **9** and **10**.

The C=O bond incorporated in the five-membered coordination ring of molecules **9**–**11** (see Table 1) is 0.04, 0.038 and 0.02 Å longer than the exocyclic C=O bond (1.202, 1.202 and 1.210 Å, respectively) in which the oxygen atom is not coordinated.[43] Due to the donor–acceptor bonding of the O and Si atoms in molecules **9**–**11**, the lengths of the two endocyclic N—C bonds in the heterocycle are different. The N—C bond in compounds **9**–**11** incorporated in the coordination ring (1.323, 1.357 and 1.367 Å, respectively) is much shorter than the N—C bond at the second carbonyl group (1.400, 1.409 and 1.393 Å, respectively). These data suggest a higher degree of p,π-conjugation of nitrogen with the carbonyl group incorporated in the coordination heterocycle in molecules **9**–**11**.

The surrounding of the silicon atom in the 2-diphenyl(methyldichlorosilyl)methylpyridine molecule is nearly tetrahedral, whereas in the 2-[dichlorobis(trimethylsilyl)silylmethyl]-pyridine molecule (**30**), the silicon atom of the dichlorosilyl group is located at the centre of the TBP, the N→Si bond length being 2.066 Å.[55]

According to X-ray diffraction[64–66] and neutron diffraction[64] data, the lengths of the N→Si coordination bonds in 1-trifluoro- and 1-trichlorosilyl-1,2,3,4-tetrahydro-1,10-phenanthroline (**68**) and (**69**) (see Table 1) are much longer than the length of the Si—N valence bond (1.732 and 1.737 Å, respectively). The replacement of one or two chlorine atoms in molecule **69** by methyl group(s) results in a slight increase in the N→Si distance (see Table 1).[68] However, when all three Cl atoms are replaced by methyl groups (trimethylsilyl phenanthroline derivative **65**), the N→Si donor–acceptor bond is substantially elongated (2.689 Å). The environment of the silicon atom in molecule **65** can be defined as a highly disordered tetrahedron, unlike that in analogous molecules **68** and **69** where the silicon atom is located at the center of a TBP.[67]

The structures of 2-(trifluorosilylmethyl)thiobenzoxazole (**1**) and -benzothiazole (**2**) resemble each other in many respects. The silicon atom polyhedron is a TBP in both molecules and the lengths of the N→Si donor–acceptor bonds are equal to 1.967 and 1.988 Å, respectively. The $Si-F_{ax}$ bonds in compounds **1** and **2** (1.624 and 1.632 Å, respectively) are longer than the equatorial $Si-F_{eq}$ bonds (1.594 and 1.589 Å, respectively).[106]

In molecule **28**, the silicon atom is pentacoordinated and has a distorted trigonal-bipyramidal geometry.[54] The axial positions of the bipyramid are occupied by the N(Py) and Cl atoms (the NSiCl angle is 167.9°). The equatorial $N_{eq}-Si$ valence bond (1.753 Å) is much shorter than the $N_{ax}-Si$ bond (1.975 Å), which attests to the presence of N(Py)→Si dative interaction.

In the molecule of compound **56**, the axial N → Si—C angle is 170°, which implies a distorted TBP.[61] The equatorial Si—C bond is 0.1 Å shorter than chemically the same axial bond (Table 2), which is a typical feature of this geometry. The N → Si bond in **56** is somewhat longer than those in compounds **55** and **63** (by 0.087 and 0.063 Å, respectively) (see Table 2), which is attributable to a higher positive charge of the silicon atom in the $SiPh_2$ group compared with $SiMe_2$.[59–61]

In the molecule of compound **61**, which is a bromophenyl analogue of compound **56**, the pentacoordinate silicon atom is at the vertex of a square pyramid. This type of geometry is seldom encountered in hypervalent silicon compounds.[62] The N→Si interatomic distance in molecule **61** (1.950 Å, see Table 2) is shorter than this diastance in any of the studied silatranes (see Section III.2).[15]

Unlike compound **56**, the silicon polyhedron in molecules **58** and **60** is a distorted TBP in which the apical positions are occupied by the nitrogen atom and the phenyl group.[63] The N→Si interatomic distance (see Table 2) is rather long but it is still markedly shorter than the sum of the van der Waals radii of these elements (3.65 Å). Structural studies of compound **58** have shown[59,60] that the N→Si distance is somewhat shorter than those found in compounds **55** and **63**.

The silicon atom in molecule **17** has a distorted octahedral geometry. The two bidentate ligands in chloro(methyl)bis-(8-quinolyloxy)silane (**17**) are nearly mutually orthogonal and occur in the *cis*-positions, hence, the silicon atom becomes a chiral centre.[48] The Si—O bonds form an angle of 168.7° and the NSiN angle is close to right angle (85.3°). The N→Si coordination bonds (see Table 2) are much longer than the N—Si covalent bond, *i.e.*, they are the same as in many compounds of penta- and hexacoordinate silicon.

The disordered structure of $Si(TTP)(THF)_2$ has been studied by X-ray diffraction.[104] Four nitrogen atoms and one silicon atom are coplanar, the Si atom being situated in a slightly distorted octahedral environment, while the *meso*-carbon atoms are located above or below the SiN_4 plane. The oxygen atoms of tetrahydrofuran are in axial positions and are bound to silicon by a dative bond.

The silicon atom in the molecule $(TTP)Si(OSO_2CF_3)_2$ (**118**) has a slightly distorted octahedral geometry with triflate groups in the *trans*-position. In this molecule, the porphyrin rings have a corrugated geometry favourable for the incorporation of a small silicon atom. The O—Si—O angle (178°) is nearly linear. The average Si—N distance in molecule **118** is shorter than in molecules **17**[48] or **115**[85] (by 0.145 and 0.050 Å,

Table 2. Bond lengths N→Si and Si−X (or Si−Y) in the N→Si−X fragment of intramolecular complex silicon heterocycles. (Y)

Compound	X	Y	N→Si, /Å	Si−X or Si−Y /Å	Ref.
17	Cl	Me	2.014	1.94 (C)	48
			2.016	2.199 (Cl)	
23	Ph	OC_9H_6N	2.034		50
			1.966	1.754	
55	Me	Me	2.703	1.859	60
				1.852	
56	Ph	Ph	2.790	1.970	61
				1.871	
58	Me	Me	2.665	1.862	63
				1.856	
60	Ph	Me	2.570	1.886	63
				1.867	
61	Me	Me	1.950	1.896	62
				1.868	
63	Me	Me	2.727	1.871	59
				1.854	
100	$O_2CC_6H_4Bu^t$-4	$O_2CC_6H_4$ Bu^t-4	1.914	1.754	81
			1.909		
101	$CH_2O_2C.$	$CH_2O_2C.$	1.906	1.762	81
	$.C_4H_3S$-3	$.C_4H_3S$-3	1.912		
109	$(CH_2)_2O_2C.$	$(CH_2)_2O_2C.$	1.904	1.756	81
	$.C_6H_3(OMe)_2$	$.C_6H_3(OMe)_2$	1.913		
			1.924		
115	$OSiMe_3$	$OSiMe_3$	1.922	1.678	85
			1.918	1.680	
			1.915		
			1.873		
118	OSO_2CF_3	OSO_2CF_3	1.848	1.842	105
			1.887	1.821	
			1.874		

respectively). The molecule $[Bu^tMe_2SiO(Pc)Si]_2O$ (**96**) represents a dimer with PcSi units linked by an oxygen atom.[80] In the molecule $PcSi(OSiMe_3)_2$ (**115**), the central silicon atom is located in a distorted octahedral environment. Two symmetrically independent Si(Pc)−O−Si(Me) bond angles are 157.8 and 156.6°.[85]

b. ^{29}Si NMR spectroscopy

In the ^{29}Si NMR spectra of hypervalent silicon compounds, typical upfield shifts of the ^{29}Si signals compared to those of tetracoordinate silicon are observed. The chemical shifts in the ^{29}Si NMR spectra of heterocyclic derivatives of pentacoordinate silicon are summarised in Table 3.

According to ^{29}Si NMR data, the N→Si coordination interaction in Si(V) or Si(VI) organosilicon compound considered here is either missing or very weak if the coordination-induced change in the chemical shift ($\Delta\delta$) defined as

$$\Delta\delta = \delta[^{29}\text{Si(V or VI)}] - \delta[^{29}\text{Si(VI)}]$$

is close to zero.

Yet another feature of the ^{29}Si NMR spectra of heterocyclic derivatives of hypervalent silicon is the clear-cut temperature dependence of the $\delta(^{29}\text{Si})$ value. As temperature decreases, the ^{29}Si signal shifts upfield, indicating an increase in the strength of the N→Si coordination bond. The low-temperature change in $\delta(^{29}\text{Si})$ may be caused by two processes taking place on decreasing the temperature:

(1) shift of the equilibrium between the tetra- and pentacoordinate states of silicon toward the latter;

(2) shortening of the N → Si coordination bond in the coordination polyhedron of hypervalent silicon.[112–114]

Nevertheless, in some cases, the ^{29}Si chemical shift changes in the opposite direction upon decrease in the temperature. For example, in the ^{29}Si NMR spectrum of compound **46**, the chemical shift is −6.2 ppm at 100 °C and −18.4 ppm at −80 °C.[57] This is due to the equilibrium interconversion of compounds **B** and **C** (see Scheme 1), which decreases the silicon coordination number to 4 *via* the stable iminium chloride **C**.

Attention is attracted by the fact that the pentacoordinate state of Si in *N*-trifluorosilylmethylsuccinimide (**9**), -glutarimide (**10**) and -phthalimide (**11**) in solutions is much less pronounced than in most dragonoids studied by ^{29}Si NMR.[41–45] The presence of intramolecular O→Si coordination bond in organosilicon derivatives of cyclic imides **9**–**11** is indicated by lower shielding constants of ^{19}F nuclei [$\delta(^{19}\text{F})$ = −133.5 (for compound **9**), −134.19 (**10**), −134.6 (**11**)] and the $^1J(^{29}\text{Si}-^{19}\text{F})$ spin-spin coupling constants [248.8 (for compound **9**), 224.5 (**10**) and 256.3 Hz (**11**)] compared to those for tetracoordinate (chloromethyl)trifluorosilane [$\delta(^{19}\text{F})$ = −143.99, $^1J(^{29}\text{Si}-^{19}\text{F})$ = 267 Hz]. In the ^{29}Si NMR spectra, the silicon signal [−75.7 (**9**), −94.2 (**10**), −72.0 ppm (**11**)] is shifted upfield relative to that for (chloro-

Table 3. Chemical shifts (δ) in the ^{29}Si NMR spectra of heterocyclic derivatives with pentacoordinate silicon Het−SiXYZ.

Compound	X	Y	Z	$\delta(^{29}\text{Si})$	Ref.
9	F	F	F	−75.7	41, 43
10	F	F	F	−94.2	43, 44
11	F	F	F	−72.0	45
12	Me	Me	Cl	6.1	46
16	Cl	Me	Me	−21.0	47
22	F	F	Ph	−79.8	49
23	Ph	OC_9H_6N	OC_9H_6N	−149.8	50
30	H	Cl	Cl	−18.0	55, 56
31	H	Cl	Cl	−30.90	56
32	Me	Cl	Cl	−64.82	56
33	Me	Cl	Cl	−33.06	56
34	Me	Me	Cl	−14.72	56
35	Me	Me	Cl	−11.18	56
42	H	Cl	Cl	−27.03	56
43	Me	Cl	Cl	5.32	56
44	Me	Me	Cl	15.59	56
46	Me	Me	Cl	6.4	57
51	Me	Me	Cl	17.1	58
52	Me	Cl	Cl	−19.3	58
53	Cl	Cl	Cl	−81.9	58
54	Cl	Cl	Cl	−77.6	58
55	–	Me	Me	−32.4	60
56	–	Ph	Ph	−63.8	61
57	–	Ph	Me	−49.4	62
58	–	Me	Me	−31.7	63
59	–	Ph	Ph	−60.9	63
60	–	Ph	Me	−48.9	63
61	–	Me	Me	−56.5	62
62	–	Me	Me	−58.0	62
63	–	Me	Me	−41.6	59
64	–	Ph	Ph	−72.6	62
65	Me	Me	Me	−1.5	69
66	Cl	Me	Me	−53.6	69
67	Cl	Cl	Me	−75.9	69
68	F	F	F	−125.2	69
70	–	Cl	Cl	−217	71

methyl)trifluorosilane ($\delta = -71.3$) containing a tetracoordinate silicon atom. This difference, which is most pronounced in low-temperature spectra, allows one to detect the enhanced shielding of ^{29}Si nuclei typical of trigonal-bipyramidal silicon derivatives. However, even at -100 °C, the NMR spectra of compound **11** attest to equivalence of the ^{13}C nuclei of both carbonyl groups [$\delta(^{13}C) = -168.4$] and the axial and equatorial fluorine atoms. Altogether, this suggests substantial weakening of the O→Si coordination bond in the organosilicon phthalimide derivative **11** in low-polarity media and fast (on the NMR time scale) transcoordination of silicon from one oxygen atom to another (pendulum effect).[45] A similar pendulum effect was found in the molecules of *N*-trifluorosilylmethylsuccinimide (**9**), -glutarimide (**10**) and *N*-(dimethylchlorosilylmethyl)glutarimide (**12**).[41,43,44,46] The substantial difference $\Delta\delta$ (relative to $ClCH_2SiF_3$) for compound **10** (-23 ppm) compared to that for compound **9** (-4 ppm) attests to stronger O→Si interaction in the former.

According to ^{29}Si NMR spectra, compound **30** contains two magnetically non-equivalent trimethylsilyl groups at ambient temperature, which is in line with the sterically more rigid structure in the crystal.[55] This confirms the assumption that the nitrogen atom in a distorted TBP of molecule **30** is apically bonded to the silicon atom by an intramolecular coordination bond, which closes a four-membered ring. The carbon atom of the 2-substituent in the pyridine ring bears two $SiMe_3$ groups located in the *cis*- and *trans*-positions with respect to the equatorial H and Cl atoms, respectively.[55] Unlike this compound, derivative **31** exhibits temperature-dependent ^{29}Si NMR chemical shifts. The lowest-frequency signal of the central silicon atom is observed at -70 °C. An increase in intensities of the two resonance signals due to the $SiMe_3$ groups[55] attests to fast equilibrium between tetra- and pentacoordinate states of the silicon atom at this temperature.

The ^{29}Si chemical shifts of the central silicon atom in compounds **30**–**35** (see Table 3) with two trimethylsilyl groups at the exocyclic carbon atom are negative.[56] Meanwhile, in the NMR spectra of isostructural derivatives **42**–**44** in which one $SiMe_3$ group has been replaced by phenyl group, the ^{29}Si chemical shifts may be either negative or positive. In the former case, they correspond to a pentacoordinate silicon atom and in the latter case, to a tetracoordinate silicon atom.[56] The negative ^{29}Si chemical shifts in the spectra of compound **42** indicate that silicon is pentacoordinate. However, in molecules **43** and **44**, it is apparently tetracoordinate. Thus, NMR data imply that the Si atom passes from the tetracoordinate into the pentacoordinate state. The coordination environment of the central silicon atom depends on the chemical nature and the bulk of the substituents attached. In organosilicon pyridine derivatives **42**–**44**, silicon is most often pentacoordinate; however, an increase in the bulk of substituents at the central silicon atom results in its tetracoordination.[56]

The presence of a highly basic ligand at the silicon atom in molecules **51** and **52** changes considerably its coordination with respect to that in compounds **46** and **47** containing weakly basic ligands.[58] Compounds **51**–**54** contain pentacoordinate silicon in the crystalline state (compounds **53** and **54**, also in solution). In the crystal structure of molecule **51**, the TBP coordination of silicon is highly distorted towards tetrahedral with ionisation of the Si–Cl bond (2.679 Å) as compared with compound **46.** The ratio of structures containing tetra- or pentacoordinate silicon atom in compounds **51**–**54** in solutions depends on temperature and the solvent nature. An increase in temperature shifts the equilibrium to the pentacoordinate structure and *vise versa* (the entropy effect). The effect of the solvent nature on the ratio of penta- to tetracoordinate Si atoms (Si–Cl bond ionsation) correlates with the electron-withdrawing properties of the Si-substituents.[58]

The NMR spectra of organosilicon 1,2,3,4-tetrahydro-1,10-phenanthroline derivatives **65**–**68** with methyl groups at the central Si atom being replaced by halogen atoms (see Table 3) also show transition from the tetra- to pentacoordinate state of silicon.[69]

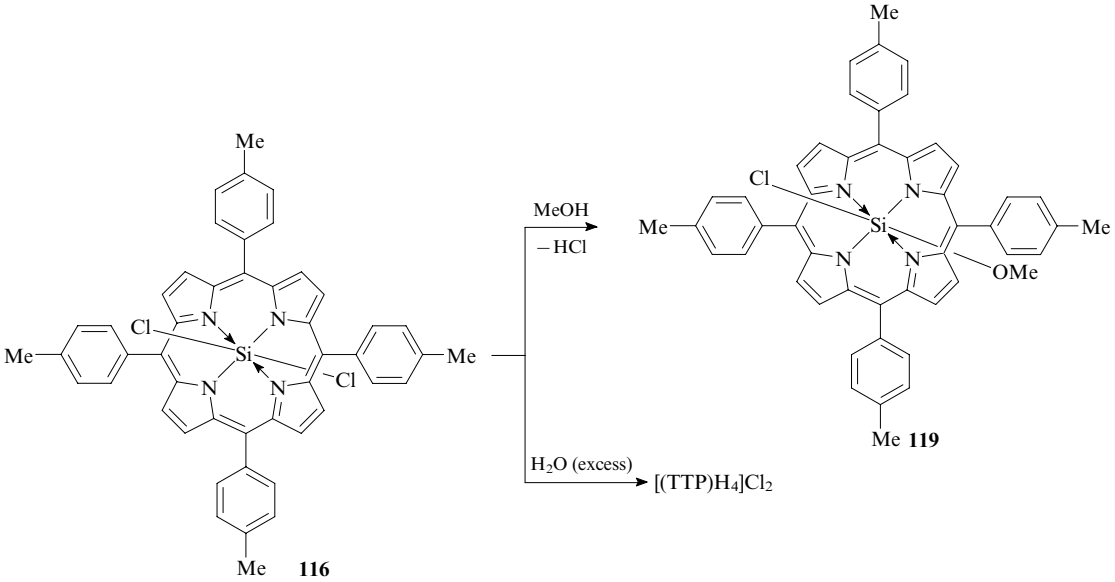
The $\delta(^{29}Si)$ value (-217) in the ^{29}Si NMR spectrum of organosilicon tetrakis(4-tolyl)porphyrin derivative (**116**) is indicative of a hexacoordinate state of silicon.[104] The absence of a low-field signal in the ^1H NMR spectrum and the J_{Si-H} value in the ^{29}Si NMR spectrum of compound **116** correspond to a *trans*-$SiCl_2$ group.

A study of the photophysical and voltammetric properties of organosilicon phthalocyanines containing $OSi(n\text{-}C_6H_{13})_3$ and $OSiBu^s_2(n\text{-}C_{18}H_{37})$ groups has shown[76] that they possess the maximum first oxidation potentials due to the highest steric hindrance in their molecules. Meanwhile, the first reduction potential depends little on the spatial structure.

3. Chemical properties

Strange as it may seem, the chemical properties of organosilicon intramolecular complexes of nitrogen heterocycles received relatively little interest from researchers, who paid attention mainly to their synthesis and molecular and stereoelectronic structures. The works devoted to the reactivity of

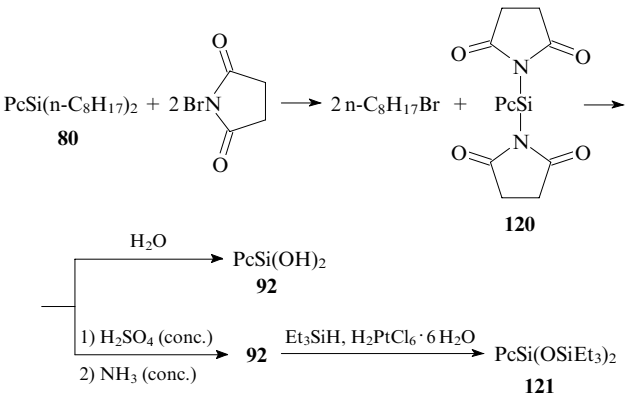
Scheme 5



these compounds were focussed on Si—C and Si—X bond cleavage in organosilicon porphyrin and phthalocyanine complexes (hydrolysis, alcoholysis and halogenolysis).

Organosilicon porphyrin complex **116** containing a central $SiCl_2$ group reacts with protic solvents.[104] When this compound is treated with methanol, only one chlorine atom is replaced by a methoxy group to give (TTP)Si(OMe)Cl (**119**) (Scheme 5). Hydrolysis of compound **116** results in the loss of the central silicon atom.

When phthalocyanino-λ^6-siliconium **80** containing two octyl groups reacts with an excess of *N*-bromosuccinimide in benzene (20 °C), the colour of the reaction mixture gradually changes from dark green to deep blue-violet.[78] According to GLC, the reaction is complete in 2 h giving rise to 1-bromooctane (yield 60%). As a result, both Si—C bonds are cleaved. After being washed with water, methanol, and diethyl ether, the blue-violet precipitate proved to be dihydroxy derivative $PcSi(OH)_2$ (**92**). Treatment of intermediate **120** with conc. H_2SO_4, NH_4OH and then Et_3SiH in the presence of $H_2PtCl_6 \cdot 6H_2O$ resulted the phthalocyanine $PcSi(OSiEt_3)_2$ (**121**). This product results evidently from the reaction of Et_3SiH with diol **92**.



The Si—C bonds in phthalocyanino-λ^6-siliconium derivatives **76**–**80** are cleaved by halogens or iodine monochloride even at room temperature.[78] The Si—C(Octyl) bond in compound **80** cleaves more readily under the action of bromine than under the action of chlorine or iodine. The reactivities of the Si—Ar bonds in organosilicon phthalocyanine complexes **76**–**80** depend on the nature of the aromatic substituent, decreasing in the sequence 4-$MeOC_6H_4$ > 4-MeC_6H_4 > Ph ≫ 3-$CF_3C_6H_4$.

The cleavage of Si—C(Alk) and Si—C(Ar) bonds with iodine chloride occurs in different ways. In the former case, a mixture of chloroalkane and iodoalkane is formed, while in the latter case, aryl iodide is produced.[78] The Si—C(Alk) bond in phthalocyanino-λ^6-siliconium derivatives cleaves with greater difficulty than the Si—C(Ar) bond. Halogen induced cleavage of the Si—C(Alk) bond affords alkyl radicals, whereas the Si—C(Ar) bond is cleaved according to the common electrophilic substitution mechanism.

The Si—C bonds in organosilicon Pc complexes **76**–**80** are cleaved in reactions with $CuCl_2$ or $CuBr_2$ (THF, 50 °C) to form the Si—X bond (X = Cl, Br).[78]

$$PcSiR_2 + 4\,CuX_2 \longrightarrow PcSiX_2$$

76–**80**

X = Cl, Br.

Organosilicon phthalocyanine complexes **78** and **80** do not react with peroxybenzoic acid.[78] This fact was attributed to high stability of these complexes with hexacoordinate silicon atom caused by the macrocycle rigidity.

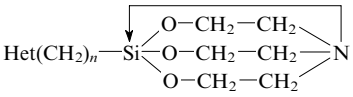
Particular attention is devoted to silicon phthalocyanine polysiloxanes.[100,115–117] These polymers are regarded as precursors of conducting polymers. The possibility of the radiation-induced synthesis,[100] the ability to form liquid crystals,[116] dark electrical conductivity, electrochemical properties and conduction of microwave radiation were studied in detail for these compounds.

Studies on the chemical properties of hexacoordinate silicon compounds provide valuable information on the mechanisms of Si—C and Si—X bond cleavage and formation. This knowledge helps determining the routes of similar reactions also for Si(VI)-organic complexes with simpler structure.

III. Silatranyl derivatives of nitrogen-containing heterocycles

1. Methods of synthesis

The first representatives of silatranyl derivatives of nitrogen heterocycles, 1-(heterylalkyl)silatranes with the general formula



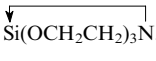
(n = 0–3)

were synthesised in the 1970s.[118–124] Since 1993, we have carried out systematic investigations into these compounds.[36–40]

1-(Heterylalkyl)silatranes are synthesised most often by transetherification of (heterylalkyl)trialkoxysilanes on treatment with tris(2-hydroxyethyl)amine (TEA):[5,8,10,13,15]

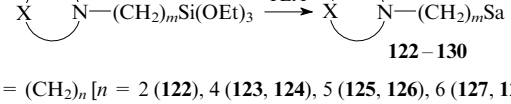
$$HetYSi(OR)_3 + (HOCH_2CH_2)_3N \longrightarrow HetYSi(OCH_2CH_2)_3N,$$

where Het is the heterocyclic fragment, Y is a hydrocarbon bridge $(CH_2)_n$ (n = 0–3) or a heteratom (S, O, N) connecting the heterocycle to the silicon atom of the silatranyl group (Sa)



The reaction is carried out in the presence of a basic catalyst (AlkONa, KOH, *etc.*) or without a catalyst, usually with distillation of ethanol.

This method was employed to carry out the first syntheses of 1-[(*N*-azacycloalkyl)alkyl]silatranes **122**–**130** (yields 70%–79%) in which the Si atom and the heterocycle N atom are linked through one, two or three methylene units. The reactions were carried out in chloroform, benzene or *o*-xylene [118–121] without a catalyst.



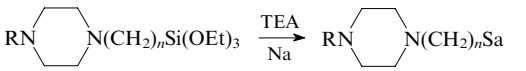
122–**130**

X = $(CH_2)_n$ [n = 2 (**122**), 4 (**123**, **124**), 5 (**125**, **126**), 6 (**127**, **128**)], $(CH_2)_2O(CH_2)_2$ (**129**, **130**); m = 1 (**123**, **125**, **127**, **129**), 2 (**122**), 3 (**124**, **126**, **128**, **130**).

Note that (pyrrolidinomethyl)- (**123**) and (piperidinomethyl)silatranes (**125**) with m = 1 have higher melting points than the homologues with m = 3 (compounds **124** and **126**, respectively). [120] However, low-melting (perhydroazepinoalkyl)silatranes (**127**, **128**) do not follow this regularity.

1-(Piperazinoalkyl)silatranes and their N'-derivatives (**131**–**135**) were synthesised by the reaction of the corres-

ponding (piperazinoalkyl)triethoxysilanes with tris(2-hydroxyethyl)amine in boiling xylene in the presence of a catalytic amount of metallic sodium.[122]

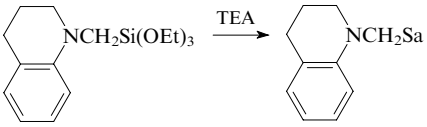


131–**135** (75%–90%)

n = 1: R = H (**131**), Me (**132**); n = 3: R = H (**133**), Me (**134**), Ph (**135**).

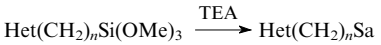
The same route was used to convert N,N'-bis[3-(triethoxysilyl)propyl]piperazine into 1,4-bis(3-silatranylpropyl)piperazine (**136**) (yield 40%).[122]

Heating tetrahydroquinoline with (chloromethyl)triethoxysilane in xylene followed by transetherification of the resulting *N*-(triethoxysilylmethyl)tetrahydroquinoline with tris(2-hydroxyethyl)amine affords 1-(tetrahydroquinolinomethyl)silatranes (**137**) in a moderate yield.[123, 124]

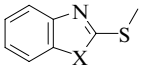
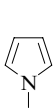
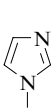
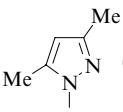
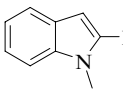
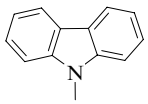
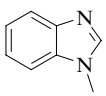
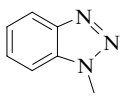
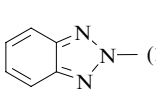
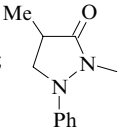
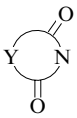


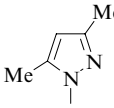
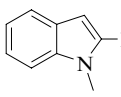
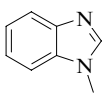
137 (16%)

Transetherification of the corresponding (8-quinolylthiomethyl)-, (2-heterylthiomethyl)- and (*N*-heterylalkyl)trimethoxysilanes with tris(2-hydroxyethyl)amine carried out without a solvent or a catalyst resulted in 1-(8-quinolylthiomethyl)- (**138**), 1-(2-heterylthiomethyl)- (**139**–**141**) and 1-(*N*-heterylalkyl)silatranes (**142**–**158**) (yields 73%–92%) (Refs 37, 39, 40 and 125).

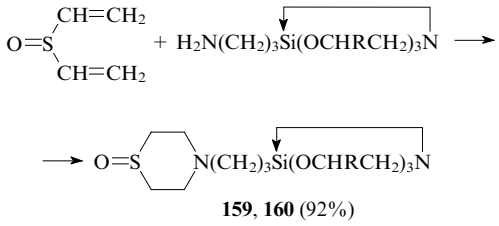


138–**158**

n = 1: Het =  (**138**);  (X = NH (**139**), O (**140**), S (**141**));  (**142**);  (**143**);  (**144**);  (**145**);  [R = H (**146**), Me (**147**)];  (**148**);  (**149**);  (**150**);  (**151**);  (**152**);  [Y = $(CH_2)_2$ (**153**), $(CH_2)_3$ (**154**), *o*-phenylene (**155**)];

n = 3:  (**156**);  (**157**);  (**158**).

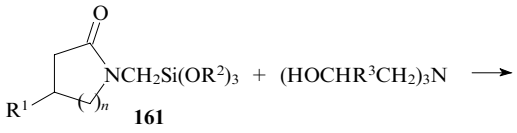
The reaction of 4-(3-triethoxysilylpropyl)thiomorpholine 1-oxide with tris(2-hydroxyethyl)amine in the presence of a catalytic amount of a saturated methanolic sodium methoxide gives 4-[3-(1-silatranyl)propyl]thiomorpholine 1-oxide (**159**) in 40% yield.[126] 1-(3-Aminopropyl)silatrane or its 3,7,10-trimethyl derivative reacts with divinyl sulfoxide in ethanol at 45–65 °C to give *N*-[3-(1-silatranyl)propyl] derivatives of thiomorpholine 1-oxide **159**, **160**.[127]



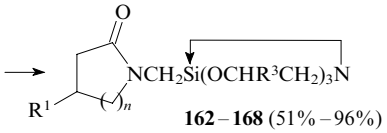
159, **160** (92%)

R = H (**159**), Me (**160**).

N-(Trialkoxysilylmethyl)lactams **161** react with tris(2-hydroxyethyl)- or tris(2-hydroxypropyl)amines in boiling xylene in the presence of KOH giving rise to *N*-(silatranylmethyl)lactams **162**–**168**.[128]



161

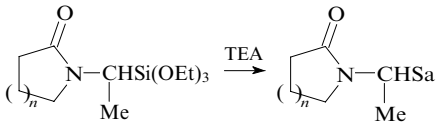


162–**168** (51%–96%)

R^1 = R^3 = H: n = 1 (**162**), 2 (**163**), 3 (**164**);
R^1 = H, R^3 = Me: n = 1 (**165**), 2 (**166**), 3 (**167**);
R^1 = Ph, R^3 = H, n = 1 (**168**); R^2 = Me, Et.

These silatranyllactams have also been prepared by a one-pot procedure involving the reaction of *N*-(trimethylsilyl)-lactams with (chloromethyl)trimethoxysilane and tris-(2-hydroxyethyl)amine without intermediate isolation of *N*-(trimethoxysilyl)methyl derivatives (yields 30%–63%).[128]

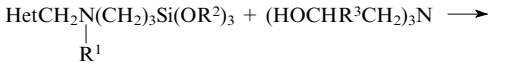
Transetherification of *N*-(triethoxysilylethyl)lactams with tris(2-hydroxyethyl)amine in boiling xylene without a catalyst afforded, 1-[1-(2-oxoperhydroazepino)ethyl]- (**169**) and 1-[1-(2-oxopyrrolidino)ethyl]silatranes (**170**).[129, 130]

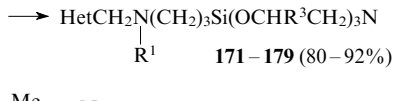


169, **170**

n = 1 (**169**), 3 (**170**).

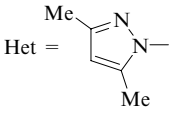
Transetherification of *N*-(trialkoxysilylpropylamino)-methyl derivatives of imidazole, 3,5-dimethylpyrazole, 5-methyl-3-phenylpyrazole and benzotriazole with tris-(2-hydroxyethyl)amine or tris(2-hydroxypropyl)amine furnished silatrane derivatives **171**–**179**.[131]

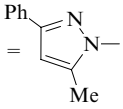




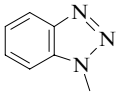
$\longrightarrow$ $HetCH_2N(CH_2)_3Si(OCHR^3CH_2)_3N$ (with R^1)

171 – 179 (80 – 92%)

Het =  : R^1 = CH_2Het, R^3 = H (**171**), Me (**172**);

R^1 = Ph, R^3 = H (**173**); R^3 = H: Het = , R^1 = CH_2Het (**174**),

Ph (**175**); Het = , R^1 = CH_2Het (**176**), Ph (**177**);

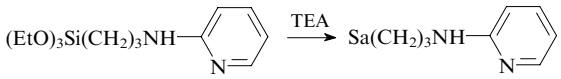
Het = , R^1 = CH_2Het (**178**), Ph (**179**); R^2 = Me, Et.

Another synthetic route to compounds **171**, **173 – 179** is based on anhydrocondensation of the corresponding 1-(3-aminopropyl)silatranes with 1-hydroxymethylated 3,5-dimethylpyrazole, 5-methyl-3-phenylpyrazole, imidazole or benzotriazole in dichloroethane at room temperature.[132]

$Sa(CH_2)_3NHR + HOCH_2Het \longrightarrow HetCH_2N(R)(CH_2)_3Sa$

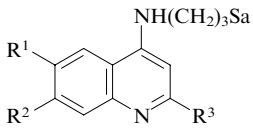
171, **173 – 179**

The condensation of (3-aminopropyl)triethoxysilane with 2-aminopyridine yielded 2-[3-(triethoxysilyl)propyl]aminopyridine, which was then converted into 2-[3-(1-silatranyl)propyl]aminopyridine (**180**) by transetherification.[133]



180 (98%)

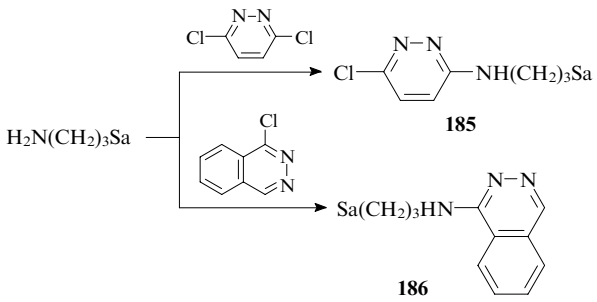
1-(Quinolylaminoalkyl)silatranes **181 – 184** were synthesised by two routes: transetherification of 4-[3-(triethoxysilyl)-propyl]aminoquinolines on treatment with tris(2-hydroxyethyl)amine or by heating of 4-chloroquinoline with 1-(3-aminopropyl)silatrane in diglyme (yields 51% – 65%).[124]



181 – 184

R^1 = R^2 = R^3 = H (**181**); R^2 = R^3 = H, R^1 = Me (**182**);
R^1 = R^3 = H, R^2 = Cl (**183**); R^1 = H, R^2 = Cl, R^3 = Me (**184**).

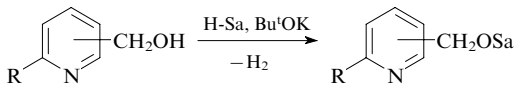
When [3-(*N*-heterylamino)propyl]triethoxysilanes are heated with tris(2-hydroxyethyl)amine in benzene or xylene, 1-{3-[(6-chloropyridazin-3-yl)amino]propyl}- (**185**) and 1-{3-[(phthalazin-1-yl)amino]propyl}silatranes (**186**) are formed.[121] Low yields of the products (20% – 30%) were attributed to the fact that the triethoxy derivatives were not isolated from the reaction mixture. No increase in the yields of compounds **185** and **186** was achieved by preparing them by the reaction of 1-(3-aminopropyl)silatrane with 3,6-dichloropyridazine or 1-chlorophthalazine in the presence of K_2CO_3:



185

186

Silatranes **187 – 191** containing pyridyloxy or pyridylmethoxy group can be prepared by two methods.[134, 135] Dehydrocondensation of isomeric pyridylmethanols with 1-hydrosilatrane in xylene at 130 °C in the presence of 5 mol % Bu^tOK yielded 1-(pyridylmethoxy)silatranes **187 – 190** (yields 44% – 56%). (Note that NaOH, KOH or NaOEt do not catalyse this reaction.)



187 – 190

R = H: 2-pyridyl (**187**), 3-pyridyl (**188**), 4-pyridyl (**189**);
R = Me, 2-pyridyl (**190**).

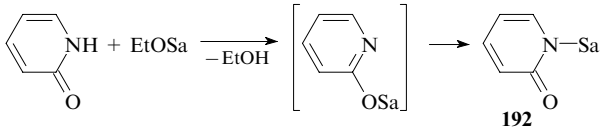
A more efficient method for the synthesis of 1-(6-methylpyridin-2-ylmethoxy)- (**190**) and 1-(3-pyridyloxy)silatranes (**191**) is based on the reaction of hydroxy(methyl)pyridines with tetraethoxysilane and tris(2-hydroxyethyl)amine in xylene in the presence of 3.5 mol % KOH with distillation of ethanol.[135]

$Het{-}OH + Si(OEt)_4 + (HOCH_2CH_2)_3N \xrightarrow{KOH} HetOSa$

190, **191**

Het is 6-methylpyridin-2-ylmethyl (**190**), 3-pyridyl (**191**).

Transetherification of 1-ethoxysilatrane under the action of 2-hydroxypyridine follows an unusual route resulting in 1-silatranyl-2-pyridone (**192**).[136] This compound is the first silatrane that contains an axial N→Si – N fragment and the mechanism of its formation is the first example of a silatranotropic rearrangement.

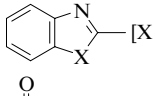


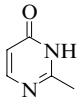
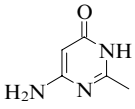
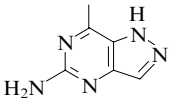
192

The reactions of sodium hetarenethiolates with 1-(chloromethyl)silatrane in DMF furnished (4-hydroxypyrimidin-2-yl)thiomethyl- (**193**), (6-amino-4-hydroxypyrimidin-2-yl)thiomethyl- (**194**), (2-aminopurin-6-yl)thiomethylsilatranes (**195**) and 2-(1-silatranylmethylthio)benzimidazole (**139**), -benzoxazole (**140**) and -benzothiazole (**141**) in 60% – 85% yields.[137]

$Het{-}SNa + ClCH_2Sa \longrightarrow Het{-}SCH_2Sa + NaCl$

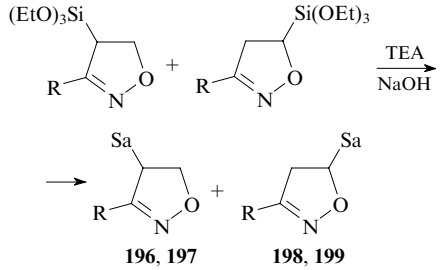
139 – 141, **193 – 195**

Het =  [X = NH (**139**), O (**140**), S (**141**)];

 (**193**);  (**194**);  (**195**).

As regards the reactivity toward 1-(chloromethyl)silatrane, sodium hetarenethiolates occupy an intermediate position between EtSNa and Et_2NCS_2Na.

Refluxing of a mixture of 3-substituted 4(5)-(triethoxysilyl)-2-isoxazolines with tris(2-hydroxyethyl)amine in toluene in the presence of NaOH as the catalyst results in silatranes **196**–**199** in yields of ~70%.[138, 139] Compounds **196** and **197** can be isolated by recrystallisation from chloroform.



196, **197** **198**, **199**

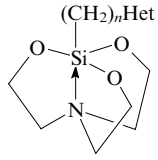
R = Me (**196**, **198**), Ph (**197**, **199**).

2. Studies of the molecular and electronic structures

a. X-Ray diffraction method

The molecular structures of silatranyl derivatives of nitrogen heterocycles in which the Het and Sa groups are linked either by a $(CH_2)_n$ bridge (n = 1, 3) or directly have been comprehensively studied by X-ray diffraction.[11, 12, 15, 18, 22]

Data from numerous X-ray diffraction studies of these compounds indicate that the silatrane cage has a distorted trigonal-bipyramidal structure with a nearly equatorial arrangement of three oxygen atoms and with axial N and C atoms of the $(CH_2)_n$Het substituent at silicon.



The N→Si—C angle amounts to 174–179°, *i.e.*, it is close to the straight angle in an ideal TBP (180°). The O—Si—O and O—Si—C bond angles are in the ranges of 119.0–119.2 and 95.0–95.8°, respectively. The shift (ΔSi) of the silicon atom from the equatorial plane through three oxygen atoms towards the $(CH_2)_n$Het substituent is 0.11–0.18 Å. The average length of the Si—O equatorial bond (1.66–1.67 Å) is greater than in organyltrialkoxysilanes containing a tetrahedral silicon atom [for example, in the $MeSi(OMe)_3$ molecule, this is 1.63 Å].[140] In the crystalline state, the length of the dative N→Si bond in silatranes is usually in the range of 1.965–2.24 Å, which is much shorter than the sum of the van der Waals radii of the silicon and nitrogen atoms (3.65 Å).

The N→Si interatomic distances in silatranes $Het(CH_2)_nSa$ fall into a rather narrow range (2.09–2.15 Å), being a linear function of the inductive constant σ^* of the substituent Het.[29] The same range covers the N→Si bond length in the molecules HetSa, which is 2.12 Å. The Si—C bond length in these molecules (1.89–1.94 Å) is much greater than in compounds of tetracoordinate silicon or in silatranes containing a saturated or unsaturated substituent comprising two carbon atoms at the silicon atom (1.77–1.78 Å).[141] Since the lengths of the transannular N→Si bond and the Si—C bond in the molecules $Het(CH_2)_nSa$ do not differ much, one should admit that irrespective of the nature, the substituent Het affects the structure of the axial N→Si—C fragment in the same way.

Selected geometric parameters of silatranyl derivatives of nitrogen heterocycles are summarised in Table 4.

The length of the transannular N→Si bond in the *N*-(1-silatranylalkyl)pyrazole molecules $Het(CH_2)_nSa$ for $n = 1$ (compound **144**) is 0.036 Å shorter than that for $n = 3$ (**156**). Conversely, the Si—C bond is 0.026 Å longer for $n = 1$ (compound **144**) than for $n = 3$ (**156**). This is caused by the decrease in the inductive effect of the substituent Het on the Sa group following an increase in the number of methylene groups separating them.[146]

In the 8-(1-silatranylmethylthio)quinoline molecule (**138**), the S—CH_2 bond occurs in a nearly ideal crossed position with respect to the silatrane fragment, the SCSiO torsion angle being 179° (Ref. 40). In addition, the *trans*-configuration of the SiCSC bridge is nearly ideal (the torsion angle is 178°). The bridge is approximately in the same plane as the quinoline ring (the CSCC angle is 3°).

In 1-(2-benzothiazolylthiomethyl)silatrane (**141**),[142] the bond lengths of the silatranyl group, except for the Si—C bond length, are similar to the standard values for the XCH_2Sa molecule.[153] As in other silatranes of this type, the exocyclic Si—C bond is elongated (1.912 Å).[141] The geometric parameters of the trigonal-bipyramidal coordination of Si are similar to those established for molecule **138**.[40] The orientation of the planar benzothiazolylthiomethyl substituent in compound **141** is crossed with respect to the Si—O bonds and also resembles that observed in molecule **138**. The full difference Fourier synthesis shows a clear-cut 0.25 e $Å^{-3}$-high electron density peak in the line of the transannular N→Si bond at a 0.65 Å distance from the N atom. In the crystals of 1-halosilatranes

Table 4. Geometric parameters of the $Het(CH_2R)_nSa$ molecules (n = 0, 1, 3).

Compound	Bond length /Å			Bond angle /deg			ΔSi/ Å	Ref.
	N→Si	Si—C	Si—O	C—Si—N	C—Si—O	O—Si—O		
138	2.111	1.893	1.667	175.0	95.8	119.0	0.169	40
141	2.100	1.912	1.663	176.7	95.2	119.2	–	142
142	2.089	1.902	1.665	177.9	95.4	119.1	0.16	143, 144
143	2.088	1.898	1.664	176.1	95.6	119.2	0.15	145
144	2.118	1.913	1.663	178.0	–	–	–	146
145	2.095	1.906	1.661	177.4	95.2	119.2	0.15	147
146	2.11	1.910	1.657	176.8	95.2	119.2	0.11–0.12	144, 148
148	2.097	1.897	1.664	177.8	95.4	119.1	0.16	144, 149
149	2.088	1.909	1.667	177.2	95.2	119.2	–	150
151	2.089	1.908	1.658	176.2	95.0	119.2	0.14	151, 152
156	2.154	1.887	1.664	179.7	–	–	–	146
170	2.122	1.909	1.665	177.3	–	–	0.176	129
196	2.119	1.920	1.644	177.5	–	119.0	0.170	139
197	2.118	1.897	1.657	176.1	–	119.0	0.168	139

XSa (X = F, Cl), this delocalised electron density peak, which reflects the strength of the N→Si donor-acceptor interaction, is located at approximately the same distance from the nitrogen atom.[154]

It is worthy of note that all carbon–carbon bonds in the pyrrole ring of the *N*-(1-silatranylmethyl)pyrrole molecule (**142**) [especially the C(3)–C(4) bond] are equalised and are shorter than those in unsubstituted pyrrole or *N*-methylpyrrole and in the *N*-(1-silatranylmethyl)indole (**146**) or -carbazole (**148**).[143, 144, 148, 149] The N–C bond lengths (1.37 Å) are nearly the same as those in pyrrole or *N*-methylpyrrole. The difference between the C(3)–C(4) and C(2)=C(3), C(4)=C(5) bonds in molecule **142** and in pyrrole or *N*-methylpyrrole can be regarded as a measure of electron density delocalisation in the pyrrole ring. The equalisation of all bonds in the pyrrole ring of *N*-(1-silatranylmethyl)pyrrole (**142**) is also indicated by equal bond angles in the pyrrole ring (∼108°). These data imply that the pyrrole ring in molecule **142** is more aromatic than in pyrrole or *N*-methylpyrrole, which prompts a comparison of compound **142** with the cyclopentadiene rather than 1-aza-cyclopentadiene anion. This is also confirmed by quantum-chemical calculations.[155]

On going from *N*-(1-silatranylmethyl)pyrrole (**142**) to *N*-(1-silatranylmethyl)indole (**146**) and -carbazole (**148**), equalisation of the bond lengths in the pyrrole heterocycle disappears, indicating a lower aromaticity of the pyrrole fragment in these molecules. Conversely, the average length of the bonds between the benzene-ring carbon atoms in compounds **146** and **148** [1.390 (α), 1.386 (β) and 1.390, 1.393 Å, respectively]† is smaller than in benzene. This means that the attachment of an *N*-silatranylmethyl group to the indole and carbazole nitrogen atom increases the aromaticity of the benzene rings.[148, 149]

b. Miscellaneous physicochemical methods

The presence of an intramolecular N→Si bond in *N*-(1-silatranylalkyl)azacycloalkanes **123**–**128** is also supported by ^{1}H NMR spectra.[120] Specifically, the proton chemical shifts of the $SiCH_2$ group in compounds with $m = 1$ (**123**, **125**, **127**) and $m = 3$ (**124**, **126**, **128**) are lower than those in the initial trialkoxysilyl derivatives. The difference between the chemical shifts of the NCH_2- and CH_2O-group protons in derivatives **123**–**128** almost does not depend on the size of the heterocycle, being nearly constant and equal, on average, to 0.97 ppm. This implies transfer of the electronic effect of the substituent $(CH_2)_nN$ to the whole silatranyl group, *i.e.*, the electronic states of both Si and N atoms are changed. Relying on the change in the chemical shift differences $\Delta\delta(SiCH_2)$ and $\Delta\delta(NCH_2)$ in the spectra of $(CH_2)_nNCH_2Si(OCH_2CH_2)_3N$ (**123**, **125**, **127**) and $(CH_2)_nNCH_2Si(OR)_3$, the extent of the $(p-d)\sigma$ interaction in the N→Si–C fragment increases with an increase in the negative inductive effect of the $(CH_2)_nNCH_2$ group.

The change in the NMR chemical shifts of the exocyclic NCH_2 protons of the heterocyclic $(CH_2)_nN$ fragments of silatrane derivatives **123**, **125** and **127** confirms that the basicity of the endocyclic nitrogen atom increases with *n* in the following sequence: 5 < 4 < 6. The basicity of the heterocycle nitrogen atom increases on going from $(CH_2)_nNCH_2Si(OR)_3$ to $(CH_2)_nNCH_2Si(OCH_2CH_2)_3N$.[120]

The ^{1}H NMR chemical shifts of solutions of 1-[(*N*-azacycloalkyl)methyl]silatranes $(CH_2)_nNCH_2Sa$ ($n = 4-6$) (**123**, **125**, **127**) depend on the nature of the solvent.[120] On going from CCl_4 to $DCCl_3$, hydrogen bonds of the $ODCCl_3$ and $NDCCl_3$ types are formed, the latter being stronger. This is confirmed by the frequency shifts $\Delta\nu(C-D\cdots N)$ and $\Delta\nu(C-D\cdots O)$ of $DCCl_3$ in the IR spectra of solutions of compounds **123**, **125** and **127** (∼70 and 10 cm^{-1}, respectively). The assumption about hydrogen bonding between chloroform and silatrane molecules in which the oxygen atoms act as donor centres is consistent with the increase in the dipole moments of alkyl-, alkoxy- and aryloxy-silatranes in chloroform[156] compared with those in ethyl acetate or benzene. 1-[(*N*-Azacycloalkyl)-methyl]silatranes **123**, **125** and **127** form strong hydrogen bonds with proton donors through the heterocycle nitrogen atom. Meanwhile, no hydrogen bond exists between the deuteriochloroform D atom and silatrane nitrogen since the electron pair of nitrogen is involved in the transannular interaction with silicon and is hence inaccessible.

The ^{1}H NMR spectra of *N*-(1-silatranylmethyl)lactams contain, apart from the proton signals of the lactam rings and the $Si(OCH_2CH_2)_3N$ group, singlets for the NCH_2Si methylene protons at $\delta = 2.39-2.98$.[128]

In the ^{1}H NMR spectra of unsubstituted (**187**–**189**) and 6-methyl-substituted (**190**) pyridylmethoxysilatranes, the proton signals for the exocyclic CH_2 group are shifted downfield with respect to these signals in the spectra of initial pyridylmethanols. This is due to interaction of the oxygen atom with silicon of the silatranyl group.[134]

In the ^{15}N NMR spectra of *N*-(1-silatranylmethyl) derivatives of imidazole (**143**), 3,5-dimethylpyrazole (**144**), 1,2,4-triazole (**145**), 2-methylindole (**147**), benzimidazole (**149**) and phthalimide (**155**), the CH_2Sa group has little effect on the chemical shifts of the heterocycle nitrogen with respect to the corresponding *N*-methylazoles.[157] Enhancement of the electron-withdrawing effect of the heterocycle (depending on the number, positions and type of bonding of endocyclic nitrogen atoms) increases the shielding of the ^{29}Si nucleus and deshielding of the ^{15}N nucleus in the silatrane cage. These dependences of $\delta(^{15}N)$ and $\delta(^{29}Si)$ are typical of *Si*-substituted silatranes XCH_2Sa.[15]

A comparison of the ^{1}H, ^{13}C and ^{15}N NMR spectra of 1- and 2-substituted (trimethoxysilylmethyl)benzotriazole and 1- (**150**) and 2-(1-silatranylmethyl)benzotriazole (**151**) indicates that the nature of the organosilicon substituent affects only slightly the electron density of the nitrogen atoms, but the nitrogen electron density markedly depends on the substituent position (1 or 2). The difference between the ^{15}N chemical shifts of 1- (**150**) and 2-isomers (**151**) is more than 100 ppm.[152, 158]

IR spectroscopy is often used to confirm the structures of silatranyl derivatives of nitrogen heterocycles. The silatrane cage is responsible for the following absorption bands in the IR spectra of compounds $Het(CH_2)_nSa$ (ν): 340–390 (N→Si bond), 730–790 cm^{-1} (CH_2 rocking vibrations), 2870–3000 cm^{-1} (CH_2 stretching vibrations), 1020–1250 cm^{-1} (NC_3 asymmetric stretching vibrations), 750–820, 1040–1180 and 1270–1280 cm^{-1} (Si–O–C skeletal vibrations with predominance of the C–O and Si–C vibrations).[159] The absorption of Si–C vibrations is typical of most silatranes. These are shifted to lower frequencies relative to the corresponding signals observed for tetracoordinate silicon compounds. The bathochromic shift is indicative of a higher positive charge on the silicon atom and polarisation of the Si–C bond. The skeletal vibrations ν(C–C) produce bands at 1020, 940, 1050 cm^{-1}. The two last-mentioned bands are usually doublets.

The mutual influence of the organosilicon substituent and heterocyclic fragment on the exocyclic sulfur atom in 1-silatranylmethylthio derivatives of quinoline **138**, benzoxazole **140** and benzothiazole **141** containing an SCH_2-Sa group in heterocycle positions 8, 2 and 2, respectively, was studied by UV and IR spectroscopy.[160] In the IR spectra of these com-

† The unit cell of the *N*-(1-silatranylmethyl)indole (**146**) single crystal contains 4 pairs of crystallographically independent molecules of α- and β-modifications; in the case of *N*-(1-silatranylmethyl)carbazole (**148**), the average bond length for each benzene ring of the carbazole ring is given.

pounds, the absorption bands of the silatrane cage do not depend on the nature of the heterocycle. The UV spectra of compounds **138**, **140** and **141** exhibit a considerable bathochromic shift of the bands corresponding to the heterocycle (quinoline, benzoxazole and benzothiazole) with respect to the absorption spectra of their analogues in which the substituent contains a tetracoordinate silicon atom. This shift is due to high positive inductive effect of the silatranylmethyl group with a pentacoordinate silicon atom.

1- (**150**) and 2-(1-Silatranylmethyl)benzotriazoles (**151**) differ in both the number and intensity of UV bands.[152, 161] The UV spectra of a solution of **150** (benzenoid structure) in MeCN show two absorption peaks at 270–290 and 250–270 nm. Their positions are the same as the positions of peaks in the spectra of unsubstituted and 1-methyl-substituted benzotriazoles. The UV spectrum of a solution of compound **151** (quinonoid structure) contains only one peak at 270–285 nm, like the UV spectra of unsubstituted and 2-methyl and 2-sodium derivatives of benzotriazole.[152, 161] The benzenoid and quinonoid structures of benzotriazoles **150**, **151** are also manifested in their IR spectra. The spectra of 1-substituted benzotriazole **150** display bands for ring vibrations at 665–670, 1565–1590, 1614–1616 cm^{-1}, while in the case of 2-substituted benzotriazole **151**, these bands occur at 620–630, 1567–1569 cm^{-1}. The IR absorption frequencies of the substituent $CH_2Si(OCH_2CH_2)_3N$ in compounds **150**, **151** almost do not depend on its position (1 or 2).

In the IR spectra of compounds $O{=}S(CH_2CH_2)_2N.(CH_2)_3Si(OCHRCH_2)_3N$ (R = H, Me) (**159** and **160**), the strong bands at 830 and 1035–1130 cm^{-1} refer to the Si–O–C groups. This range (1040–1060 cm^{-1}) contains also strong bands for S=O. The medium bands at 489 cm^{-1} are due to the S=O bending vibrations. The bands at 570–580 cm^{-1} represent the bending vibrations of the silatrane cage.[127]

In the IR spectra of *N*-(1-silatranylmethyl)lactams (**162**–**167**),[128] the carbonyl absorption is shifted to longer wavelengths by 20–40 cm^{-1} relative to that in the spectra of the *N*-(trialkoxysilyl)- and *N*-(trimethylsilyl)methyl derivatives. This effect is enhanced if the silatranyl group bears three methyl groups in positions 3, 7 and 10. For example, in the spectra of compounds **165**–**167**, ν(C=O) is recorded at 1610 cm^{-1}, which is 25–80 cm^{-1} higher than that for unsubstituted analogues. The lack, in the IR spectra of *N*-(1-silatranylmethyl)lactams, of a band at 1500–1520 cm^{-1}, typical of *Si*-substituted *N*-(dimethylsilylmethyl)lactams with intramolecular O→Si coordination confirms the absence of this coordination bond.

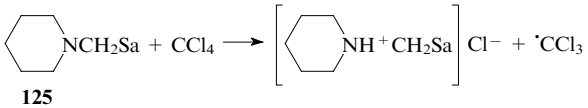
High dipole moments (μ) of silatranes (5–7 D) indicate that the charge transfer from nitrogen to silicon equals 0.1–0.3 e.[5, 8] In line with this, the dipole moments of $(CH_2)_nN(CH_2)_mSi.(OCH_2CH_2)_3N$ (n = 4–6; m = 1, 3) (**123**–**128**) are in the range of μ = 5.0–5.6 D.[120] These values are 3.2–3.4 D higher than the dipole moments of the respective (*N*-azacycloalkyl)triethoxysilanes $(CH_2)_nN(CH_2)_mSi(OEt)_3$ (n = 4–6; m = 1, 3).

The dipole moments of *N*-(1-silatranylmethyl) derivatives of pyrrole (**142**), indole (**146**), 2-methylindole (**147**) and carbazole (**148**) depend on the structure of the heterocyclic substituent.[144] The dipole moments of the silatranylmethyl derivatives increase in the sequence **148** < **146** < **147** < **142**, which is not the case for *N*-(trimethoxysilylmethyl) derivatives of pyrrole, indole and 2-methylindole, the parent heterocycles (pyrrole, indole, carbazole), 2-methylindole or their *N*-methyl derivatives. This effect is due most likely to specific features of the electronic interaction of the Het and Sa fragments in compounds **142**, **146**–**148**. The role of their specific spatial structure in solution cannot be ruled out either.

3. Chemical properties

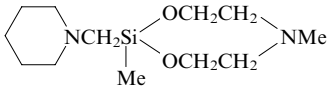
Specific reactivities of 1-(*N*-heterylmethyl)silatranes $Het(CH_2)_nSa$ with polarised Si–C bond are of particular interest.

Indeed, the reaction of 1-(piperidinomethyl)silatrane (**125**) with CCl_4 in benzene gives the corresponding hydrochloride even under daylight [(18–20) 10^3 lux].[162] The hydrogen atom is readily split off from the methylene group attached to silicon to give hydrogen chloride, which adds to another molecule **125**. The subsequent behaviour of the $Cl_3C^{\bullet}$ radicals and the dehydrogenated initial silatrane as well as the composition and structure of the resulting polymeric products or the exact mechanism of this reaction are still obscure. The induction period of this photochemical process is 0.2 h.



125

The induction period of a similar reaction with 5-methyl-(*N*-piperidinomethyl)-1-methylquasisilatrane (**200**)

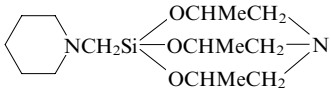


200

is 96 h at the same luminous intensity. The photochemical reaction of CCl_4 with $(CH_2)_5NCH_2Si(OEt)_3$ or Et_3N at the luminous intensity of $(18–20) \times 10^3$ lux starts only after 120 or 144 h, respectively.

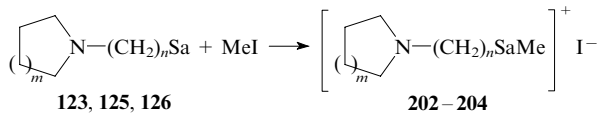
The basicity of nitrogen in 1-(*N*-heterylmethyl)silatranes $Het(CH_2)_nSa$ is much higher than in $R_2NCH_2Si(OEt)_3$ or in aliphatic amines. This is a result of strong electron-releasing effect of the CH_2Sa [29, 30] group and n,σ-hyperconjugation in the NCH_2Si fragment.[162–167]

In molecules such as $NCH_2Si(OR)_3$, the n,σ-interaction decreasing the nitrogen basicity exists in parallel with the electron-releasing effect of the $CH_2Si(OR)_3$ group.[168–170] The enhanced basicity of nitrogen in the NCH_2Sa fragment is also indicated by the ionisation potential (7.46 eV) of the nitrogen lone pair in 1-piperidinomethyl-3,7,10-trimethylsilatrane (**201**),



201

which is much lower than that in *N*-methylpiperidine (8.30 eV).[162, 168] The ionisation potentials of the molecules $(CH_2)_5NCH_2Si(OEt)_3$ and $(CH_2)_5NCH_2SiMe(OCH_2CH_2)_2.NMe$ (**200**) are also increased (7.95 and 8.15 eV, respectively). This is confirmed by equilibrium constants of the phenol complexes with $(CH_2)_5NCH_2Si(OCHMeCH_2)_3N$ (1100 litre mol^{-1}), $(CH_2)_5NCH_2Si(OEt)_3$ (110 litre mol^{-1}), $(CH_2)_5NCH_2SiMe(OCH_2CH_2)_2NMe$ (**200**) (150 litre mol^{-1}) and Et_3N (52 litre mol^{-1}).[162, 171] Note that the basicity of the N atom in methylbis(1-silatranylmethyl)amine is even higher. (Pyrrolidinomethyl)- (**123**) and (piperidinoalkyl)silatranes (**125**, **126**) react with methyl iodide in ethanol or toluene to give methiodides **202**–**204** with melting points above 200 °C.[118]

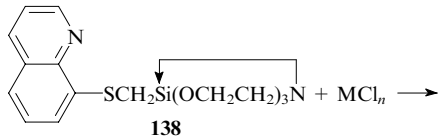


123, **125**, **126** **202** – **204**

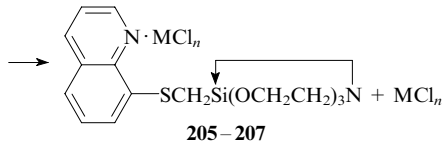
$m = 1, n = 1$ (**123**, **202**);
$m = 2: n = 1$ (**125**, **203**), 3 (**126**, **204**).

(Silatranylalkyl)tetrahydro-1,4-thiazine 1-oxides react with MeI in a similar way to give quaternary ammonium salts.[126]

The reaction of 1-(8-quinolylthiomethyl)silatrane (**138**) with copper(II), zinc(II) and tin(IV) chlorides in chloroform affords 1 : 1 complexes **205** – **207**.[172, 173]



138

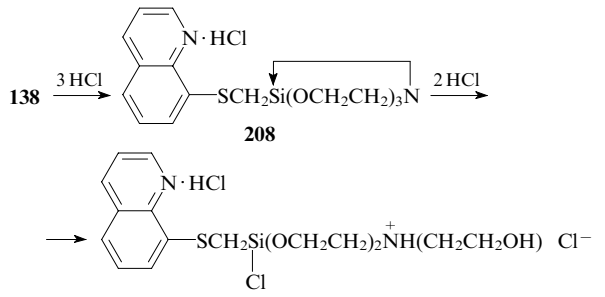


205 – **207**

MCl_n = $CuCl_2$ (**205**), $ZnCl_2$ (**206**), $SnCl_4$ (**207**).

The complex of silatrane **138** with $SnCl_4$ (**207**) contains a strong N→Sn donor – acceptor bond. The complex with $ZnCl_2$ (**206**) has a chelate structure (the zinc atom forms a donor – acceptor bond with nitrogen and sulfur atoms). The reaction product of compound **138** with $CuCl_2$, *viz*., complex **205**, exists in solutions as two species: a complex with the N→Cu bond and a chelate in which Cu is coordinated to N and S atoms.

1-(8-Quinolylthiomethyl)silatrane (**138**) reacts with an equimolar amount of HCl in ether giving 1 : 1 hydrochloride **208**. When an excess of hydrogen chloride is used, one endocyclic Si – O bond is cleaved in the Sa fragment.[172, 173]



Note that in the silatrane derivatives of nitrogen heterocycles $Het(CH_2)_nSa$, the negatively charged oxygen atoms of the silatrane fragment are more prone to form hydrogen bonds than the heterocycle nitrogen atom. In the crystal hydrate of *N*-[1-(1-silatranyl)ethyl]pyrrolidone (**169**), water molecule is connected by O···HO hydrogen bonds to the oxygen atom of the silatranyl group.[130] Unfortunately, the formation of hydrogen bonds by silatrane nitrogen heterocycles has been scarcely studied.

* * *

Silatranes as compounds possessing a cage structure and containing a trace substance, silicon, exert a physiological action on all living organisms, existing at different stages of evolution (from microbes to humans).[16] The biological action of silatranyl nitrogen heterocycles is due to both the presence of a heterocyclic system and the presence of hypervalent silicon atom in appropriate environment. Unfortunately, the biological activity of 1-(*N*-heterylalkyl)silatranes has not been adequately studied as yet. However, we are confident that in the near future valuable pharmaceutical agents or protection means for agricultural plants will be found among this class of compounds.

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