Synthesis, structure and dynamic stereochemistry of (O → Si)-chelate N-(trifluorosilylmethyl)-[N-(S)-(1-phenylethyl)]acetamide and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine: Retention of the O → Si coordination in the adduct with KF and 18-crown-6

Vadim V. Negrebetsky [a,*], Peter G. Taylor [b], Evgeniya P. Kramarova [a],
Aleksander G. Shipov [a], Sergey A. Pogozhikh [c], Yuri E. Ovchinnikov [c],
Alexander A. Korlyukov [d], Allen Bowden [b], Alan R. Bassindale [b], Yuri I. Baukov [a]

[a] *Russian State Medical University, Ostrovityanov St. 1, Moscow 117997, Russia*
[b] *Department of Chemistry, Open University, Walton Hall, Milton Keynes MK7 6AA, UK*
[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Vavilov St. 28, 119991 Moscow, Russia*
[d] *Novosibirsk State Pedagogical University, Vilyuiskaya St. 28, Novosibirsk 630126, Russia*

Abstract

The novel compounds, N-(trifluorosilylmethyl)-[N-(S)-(1-phenylethyl)]-acetamide (**1a**) and 1-(trifluorosilylmethyl)-2-oxoperhydroaze-pine (**1b**) have been prepared from the corresponding NH-compounds using $ClCH_2SiCl_3/Et_3N$ or $ClCH_2SiCl_3/(Me_3Si)_2NH$ followed by methanolysis or hydrolysis of the reaction mixture in the presence of Lewis bases, and then BF_3 etherate. Potassium-(18-crown-6)-(2-oxoperhydroazepinomethyl)tetrafluorosilicate (**2**) was synthesized by reaction of the trifluoride (**1b**) with KF in the presence of 18-crown-6. Using ^{19}F, ^{29}Si NMR and X-ray diffraction techniques it was established that the silicon atom is pentacoordinate in the trifluorides (**1a,b**) and hexacoordinate in the adduct **2**. Thus the internal coordination of the O → Si bond present in the trifluoride (**1b**) is retained in the adduct **2**.

The stereochemical non-rigidity of the trifluorides (**1a,b**) and the N-(trifluorosilylmethyl)-N-methylacetamide (**1c**) was investigated using dynamic ^{19}F NMR spectroscopy. The activation barriers for permutational isomerization are in the range 9.5–10 kcal mol^{-1}. Lower values of $\Delta G^{\#}$ for permutation of trifluorides (**1a–c**) compared to the monofluorides with the coordination core $OSiC_3F$ together with small negative values for the activation entropy implies a non-dissociative mechanism. Quantum-chemical analysis suggests a mechanism involving a turnstile rotation.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Pentacoordination; Hexacoordination; X-ray diffraction study; Stereochemical non-rigidity; Dynamic NMR; Quantum-chemical calculations

1. Introduction

In recent years, the structural properties and reactivity of hypercoordinated compounds, in particular penta- and hexacoordinated chelate compounds of silicon, have been the subject of intensive investigations [1]. Synthetic methodologies have been developed that allow the synthesis of a range of N-silylmethyl derivatives of amides and lactams containing one and occasionally two or three electron-accepting substituents at silicon [2,3]. The distinctive properties of their spatial arrangement and (O → Si)-chelation

---

* Corresponding author. Tel.: +7 495 434 04 65.
E-mail address: negrebetsky@rsmu.ru (V.V. Negrebetsky).

[3c,4], stereochemical non-rigidity about the trigonal-bipyramidal environment of silicon [5] and their reactions such as nucleophilic substitution at silicon [3a,6] have all been investigated.

Damrauer and Danahey [7] and others [1b] have reported that organic fluorosilanes yield stable nonhygroscopic complexes $[K^+ \cdot 18\text{-crown-6}][R_nSiF_{5-n}]^-$ ($n = 1$–3), upon treatment with KF in the presence of crown-ethers. Similarly (N → Si)-chelated trifluorosilanes produce the corresponding anion complexes which retain the (N → Si)-chelate structure, the coordination number of silicon increasing up to 6 [8].
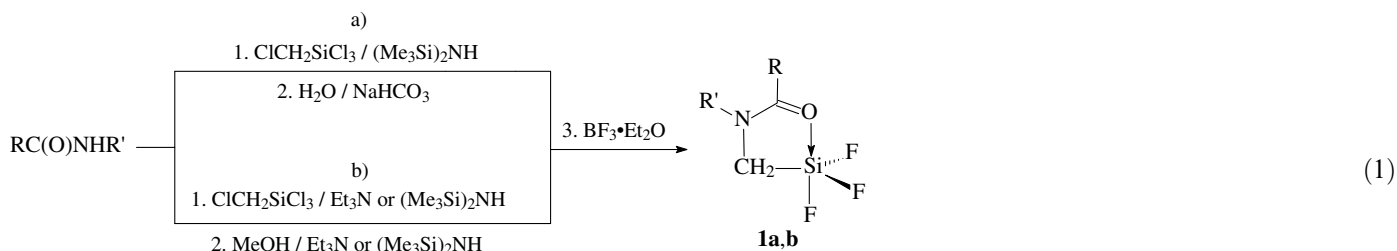
As far as we are aware, there are no literature data concerning the interaction of (O → Si)-chelate trifluorosilanes with KF in the presence of crown-ethers. In the 8-dimethylamino-1-silatranylnaphthalene the N → Si coordination bond is present, although fairly weak [9], whereas in the 1-[1-(2-oxoperhydroazepino)ethyl]silatrane [10] (O → Si)-chelation is absent. Such chelation is absent in the anions of 1,10-phenanthroline (benzoyloxymethyl) tetrafluorosilicate [11a] and ammonium (4-fluorobenzoyloxymethyl) pentafluorosilicate [11b] where the silicon atoms, according to X-ray data, are penta- and hexacoordinated, respectively. At the same time in the case of the tetrafluorosilicate $[K^+ \cdot 18\text{-crown-6}][RSiF_4]^-$ bearing a 2-(phenylazo)phenyl group (R = PhN=NC$_6$H$_4$) the reversible photoswitching of the coordination number of silicon was observed, i.e. six for the (E)-isomer which has N → Si coordination and five for the (Z)-isomer which has no coordination [8b].

This paper describes the synthesis and (O → Si)-chelate structure of the novel compounds N-(trifluorosilylmethyl)-[N-(S)-(1-phenylethyl)]acetamide (**1a**) and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine (**1b**). It describes the expansion of the silicon coordination environment upon reaction of the trifluoride (**1b**) with KF in the presence of 18-crown-6 resulting in adduct (**2**) with retention of (O → Si)-chelation. Based on dynamic ^{19}F NMR inves-

tigations and quantum-chemical calculations, the stereodynamical behavior of the above compounds and the N-(trifluorosilylmethyl)-N-methylacetamide (**1c**) are discussed.

2. Results and discussion

2.1. Synthesis and structure

For the synthesis of the trifluorides (**1a, b**) we used the one-pot procedure developed earlier [12]. Thus, treatment of N-(S)-(1-phenylethyl)acetamide or ε-caprolactam with $(Me_3Si)_2NH/ClCH_2SiCl_3$, followed by hydrolysis of the reaction mixture with NaHCO$_3$ and heating of the organic residue in the presence of BF$_3 \cdot$ Et$_2$O gave the trifluorides (**1a, b**) in yields of 4% and 26%, respectively (Reaction 1a). It was possible to increase the yield of **1b** to 60% by the use of triethylamine as a base and further treatment of the reaction mixture with methanol instead water in the presence of triethylamine. This resulted in the formation of the intermediate 1-(trimethoxysilylmethyl)-2-oxoperhydroazepine [13], whose further reaction with BF$_3 \cdot$ Et$_2$O, in the reaction mixture, gave the final product (**1b**, (Reaction 1b)). A similar approach taken with N-(S)-(1-phenylethyl)acetamide, using hexamethyldisilazane as the base, resulted in the trifluoride (**1a**) in a yield of 55%.

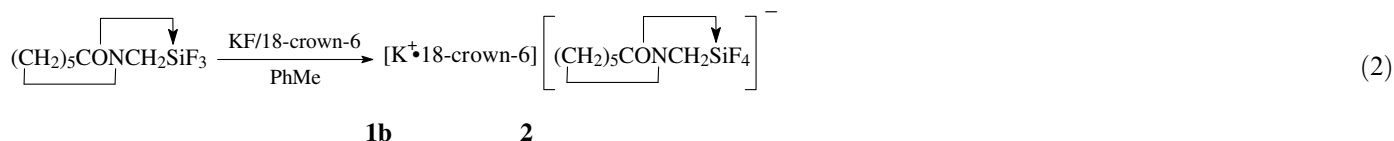$$ \text{(1)} $$

1a, R = Me, R' = CH(Ph)Me; **1b**, R,R' = (CH$_2$)$_5$

ible photoswitching of the coordination number of silicon was observed, i.e. six for the (E)-isomer which has N → Si coordination and five for the (Z)-isomer which has no coordination [8b].

The trifluoride (**1c**; R = R' = Me) has been synthesized previously by reaction of the triethoxyderivative MeC(O)-N(Me)CH$_2$Si(OEt)$_3$ with BF$_3$ etherate in a yield of 61% [14]. In the work described here, this compound was obtained in a yield of 92% using the trimethoxy derivative MeC(O)N(Me)CH$_2$Si(OMe)$_3$ [13].
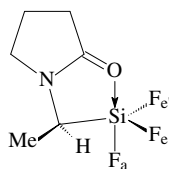
Complex **2** was obtained by treating the trifluoride (**1b**) with potassium fluoride in the presence of 18-crown-6 (Reaction 2). The X-ray diffraction data (see below) and elemental analysis suggest the complex was isolated in the form of a monosolvate with toluene, **2** · PhMe.

$$(CH_2)_5CONCH_2SiF_3 \xrightarrow[\text{PhMe}]{\text{KF/18-crown-6}} [K^+ \bullet 18\text{-crown-6}] \left[(CH_2)_5CONCH_2SiF_4 \right]^- \qquad (2)$$
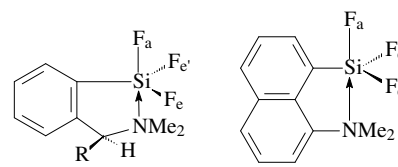
$$\mathbf{1b} \qquad\qquad \mathbf{2}$$

The presence of O → Si internal coordination in the polyfluorides (**1a, b** and **2**), as in the trifluoride (**1c**) described earlier [14], was confirmed by the presence of a peak in their IR spectra in the range 1620–1500 cm^{-1}, characteristic of strong-coupled valence vibrations from the amide fragments N═C═O, as well as by the absence of absorption bands corresponding to vibrations of the non-chelate amide groups [4c]. X-ray data support such a structure.

The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of the compounds (**1a–c** and **2**) at different temperatures also supports the suggested structures (see Table 1 and Section 4). Prominent upfield shifts in the ^{29}Si NMR spectra (-102 to -104 ppm) provides evidence for pentacoordination of the silicon atom in the trifluorides (**1a–c**). Additionally, the down field shifts of the respective signals in the ^{19}F NMR spectra (~-132 ppm) relative to the model compound ClCH$_2$SiF$_3$ (δ_{Si} -71.3 ppm, δ_F -144.0 ppm) containing a tetracoordinated Si atom [15] suggest a pentacoordinated structure.

It should be mentioned that in the trifluorides (**1a–c**) the O → Si coordination bond is not only stronger than the O → Si internal coordination bond in N-(trifluorosilylmethyl)succinimide (**3**) (δ_{Si} -75.7 ppm [15a]) and N-(trifluorosilylmethyl)phthalimide (**4**) (δ_{Si} -72 ppm [15b]), but also stronger than the internal coordination bond in [α-(N-pyrrolidino-2)-ethyl]trifluorosilane (**5**) (δ_{Si} -91.7 ppm [16]).

This observation is in agreement with the general tendency for the strengthening of the O → Si internal coordination bond in the order of imide derivatives to pentalactams and then the corresponding derivatives of acyclic amides and hexa- and heptalactams [4c,5,15a,17].

The above trend is also observed in the somewhat lower down field shifts of δ_F in the trifluorides (**1a–c**) in comparison with the position of this signal in the ^{19}F NMR spectra of the trifluorosilylmethyl derivatives of imides (-133.5 and -134.6 ppm for trifluorides (**3**) and (**4**), respectively [15a]), that indicates the formation of more rigid O → Si coordination bond in trifluorides (**1a–c**). A decrease in the temperature by 40 °C is accompanied by a slight down field shift (~1–1.5 ppm) in the ^{19}F NMR spectra of the compounds **1a–c** (Table 1). This fact may be indicative of strengthening of the O → Si bonding at low temperatures.

The expansion of the coordination environment of the silicon atom of the tetrafluoride (**2**) compared to the trifluoride (**1b**) can be seen by the upfield shift (71 ppm) of the ^{29}Si NMR peak relative to the trifluoride (**1b**). A similar shift in the ^{29}Si NMR spectra (57–60 ppm) was observed, upon formation of the 18-crown-6 potassium salts of hexacoordinated tetrafluorosilicates from (N → Si) chelate pentacoordinated trifluorosilanes (**6–8**) [8a].

5

6 (R = H), **7** (R = Me)   **8**

Table 1
The values of chemical shifts of signals in the ^{19}F, ^{29}Si ($^1J_{SiF}$, Hz) NMR spectra of compounds **1, 2** in a 1:1 equivalent mixture of CDCl$_3$ and CD$_2$Cl$_2$

Compound	δ ^{19}F (^{29}Si, $^1J_{SiF}$, Hz), ppm					
	20 °C	0 °C	−20 °C	−40 °C	−60 °C	−80 °C
1a	s, −132.12 (quartet, −101.8, $^1J_{SiF}$ 213.2)	s, −131.90	s, −131.56	s, −132.77	s, −137.59	s, −117.28, s, −137.88
1b	s, −132.11 (quartet, −103.8, $^1J_{SiF}$ 204.7)	s, −131.86	s, −131.59	s, −131.98	s, −137.11	s, −118.14, s, −137.26
1 c	s, −132.43 (quartet, −102.5, $^1J_{SiF}$ 211.4)	s, −132.19	s, −131.92	s, −131.87	s, −120.27, s, −136.27	s, −116.55, s, −137.82
2	s, −121.91 (quintet, −174.8, $^1J_{SiF}$ 176.2)					

In the ^{19}F NMR spectrum of the tetrafluoride (**2**), at room temperature the fluorine peaks occur as a singlet indicating fast (on the NMR timescale) positional exchange of the fluorine atoms. Decreasing the temperature leads to broadening of the signals and at temperatures lower than −90 °C an extremely broad signal ($\Delta v_{1/2} \sim 350$ Hz) is observed in the range −85 to −106 ppm.

2.2. X-ray structural studies

As expected, the silicon atom in molecules **1a** and **1b** is characterized by a distorted trigonal-bipyramidal (TBP) configuration (Fig. 1).

The chemical bonding in the axial fragment, O–Si–F, in **1a** and **1b** is usually considered to be a hypervalent (three-centered four electrons) bond (HVB). Axial Si–O and Si–F bonds which constitute the HVB are elongated in comparison to the standard values by about 0.25 and 0.04 Å, respectively (Table 2) [1f]. In both **1a** and **1b** the HVB are almost linear, the O(1)Si(1)F(1) angles being 177.31(6), and 177.8(2) (Table 3). The lengths of the equatorial Si–F and Si–C bonds are typical for organosilicon compounds [1f].

The Si–O coordination bond in **1a** and **1b** can be considered as a "weak" component of the HVB and is usually highly sensitive to modifications of the ligand as well as changes in the equatorial environment of the silicon atom. In **1a** and **1b** the lengths of the Si–O bonds suggest an insignificant influence of the 7-membered lactam ring on the

Table 2
Important bond lengths in compounds **1a**–**c** and **2**

Bond	d (Å)			
	1a	**1b**	**1c** [14a]	**2**
Si(1)–F(1)	1.636(1)	1.661(6)	1.635(1)	1.676(1)
Si(1)–F(2)	1.593(1)	1.586(5)	1.594(1)	1.671(1)
Si(1)–F(3)	1.595(1)	1.589(5)	1.587(1)	1.702(1)
Si(1)–F(4)				1.684(1)
Si(1)–O(1)	1.902(1)	1.898(6)	1.879(1)	1.925(1)
Si(1)–C(1)	1.876(2)	1.870(8)	1.871(2)*	1.934(2)
K(1)–F(1)				2.720(1)
K(1)–F(2)				2.758(1)
K(1)–F(3)				2.821(1)

According to initial numbering system, atom C(1) is denoted as C(3).

Table 3
Important bond angles in compounds **1a**–**c** and **2**

Angle	ω (grad)			
	1a	**1b**	**1c*** [14a]	**2**
O(1)–Si(1)–F(1)	177.31(6)	177.8(2)	177.4(1)	178.69(5)
O(1)–Si(1)–F(2)	86.97(6)	87.5(2)	87.0(1)	87.83(5)
O(1)–Si(1)–F(3)	86.88(7)	87.0(2)	88.0(1)	87.68(5)
O(1)–Si(1)–F(4)				87.44(5)
O(1)–Si(1)–C(1)	83.97(7)	84.1(2)	84.1(1)	84.16(5)
C(1)–Si(1)–F(1)	93.34(7)	93.7(2)	93.5(1)	95.14(6)
C(1)–Si(1)–F(2)	122.24(8)	123.0(3)	124.4(1)	171.96(6)
C(1)–Si(1)–F(3)	122.76(8)	124.0(3)	123.4(1)	91.09(6)
C(1)–Si(1)–F(4)				90.96(6)
F(1)–Si(1)–F(2)	94.42(7)	94.2(2)	93.5(1)	92.86(5)
F(1)–Si(1)–F(3)	94.66(7)	93.7(2)	94.2(1)	91.23(5)
F(2)–Si(1)–F(3)	113.47(7)	111.6(2)	110.9(1)	87.83(5)
F(2)–Si(1)–F(4)				89.43(5)
F(3)–Si(1)–F(4)				174.49(5)

According to initial numbering system, atom C(1) is denoted as C(3).

electronic structure of the HVB. The differences in the Si–O bond lengths between **1a** and **1b** can be explained by the electron-acceptor effect of the phenyl group. A similar situation is observed in the case of MeC(O)N(Me)CH$_2$SiMe$_2$Cl (**9**) and MeC(O)N(CHMePh)CH$_2$SiMe$_2$Cl (**10**) [18], where the Si–O bonds are 1.945(2) and 1.975(2) Å respectively.

The replacement of the substituent on the amide carbon atom by one with a pronounced electron-withdrawing effect (such as Ph and CF$_3$) leads to a noticeable elongation of the Si–O bond length. For example, in the organosilicon trifluorides PhC(O)N(Me)CH$_2$SiF$_3$ (**1d**) [14c] and CF$_3$C(O)N(Me)CH$_2$SiF$_3$ (**1e**) [14b] the Si–O bonds are elongated by up to 1.915 and 1.943 Å. Similar changes have also been revealed with the pentacoordinated dimethyl(lactamomethyl)siliconchorides [19].

Analysis of the silicon atom deviation from the plane of the equatorial atoms (Δ_{Si}) suggests that the Si–O coordination bonds in **1a**–**c** have almost the same strength (Δ_{Si} are 0.121, 0.113 and 0.110 Å, respectively) (Table 4).

On the other hand, the Si–O bonds in **1d** and **1e** are weakened in comparison with those in **1a**–**1c** (Δ_{Si} 0.135 and 0.141 Å).
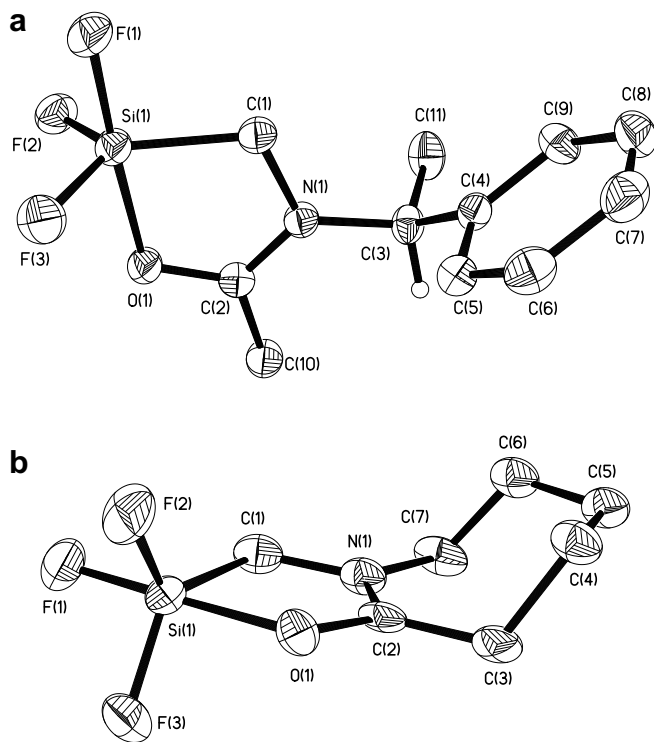

Fig. 1. Molecular structure of **1a** and **1b**. Atoms are represented by thermal ellipsoids with 50% probability. Hydrogen atoms are omitted for clarity, except for the H atom at C(3) in the structure **1a**.

Table 4
Selected geometrical parameters and parameters describing the deviation of the silicon atom coordination polyhedron from an ideal TBP in **1a, b** and related compounds

Compound	d(O–Si) (Å)	d(Si–X) (Å)	OSiX (°)	Σ_{eq} (°)[c]	ΔSi (Å)[a]	$\Delta\Omega$ (°)[b]	η_{eq} (%)[c]	η_{ax} (%)[c]	η_Ω (%)[c]
1a	1.902	1.636	177.3	358.5	0.121	43	95	79	76
1b	1.898	1.661	177.2	358.6	0.113	41	95	80	77
1c	1.879	1.635	177.4	358.7	0.110	38	96	81	79
1d	1.915	1.619	175.8	358.1	0.135	49	94	76	73
1e	1.942	1.620	177.2	357.9	0.141	50	93	75	72
3	2.096	1.607	177.6	356.0	0.190	69	87	66	62
4	2.654	1.576	177.3	344.4	0.380	130	50	31	28
9	1.944	2.309	170.8	359.7	0.057	19	99	91	89
10	1.975	2.306	170.8	359.8	0.050	10	99	92	94
11	1.950	2.315	171.7	359.7	0.055	15	99	91	91
12	1.865	2.213	175.3	359.4	0.087	24	98	87	86
13	2.149	1.668	172.7	356.8	0.200	62	90	69	65
14	2.187	1.668	172.1	355.5	0.229	72	86	64	60
15	1.954	2.307	171.2	359.8	0.058	19	99	91	89
16	1.852	2.207	174.9	359.7	0.057	19	99	91	89

[a] Deviation of the central atom from the equatorial plane toward the halide atom.

[b] Ω is a solid angle formed by three equatorial bonds of the central Si atom, $\Delta\Omega = 2\pi - \Omega$ (0° for ideal TBP and 180° for ideal tetrahedron).

[c] Pentacoordination character of atom Si; $\eta_{ax} = \frac{109.5 - \frac{1}{3}\sum_{n=1}^{3}\theta_n}{109.5 - 90} \times 100\%$, $\eta_{eq} = 100\% - \frac{120 - \left(\frac{1}{3}\sum_{n=1}^{3}\theta_n\right)}{120 - 109.5}$ (where θ_n are the bond angles between the axial and equatorial bonds at the Si atom, and ϕ_n are those between the equatorial bonds) [20a] and $\eta_\Omega = (1 - \Delta\Omega/\pi) \cdot 100\%$ [20b].

The conclusions that have been made on the basis of the analysis of the axial Si–F and Si–O bond lengths in **1a–e** in the previous sections of this paper can also be made from a consideration of the Tamao parameters η_{eq} and η_{ax} [20a] as well as the η_Ω parameter which we have previously proposed [20b] (see Table 4).

The extent of trigonal bipyramid formation η_Ω from tetrahedron (% TH→TBP) calculated on the basis of an integral parameter $\Delta\Omega$ allows one to clearly demonstrate the distortion of the coordination polyhedron of the silicon atom. In the case of complexes **1**, **3**, **4**, **9**, **10**, L[7]CH$_2$SiMe$_2$Cl (**11**) [4d], L[7]CH$_2$SiCl$_3$ (**12**) [4d], MeC(O)N(CHMePh)CH$_2$SiMe$_2$F (**13**) [18a], MeC(O)N-(CH$_2$SiMe$_2$F)$_2$ (**14**) [18b], L[6]CH$_2$SiMe$_2$Cl (**15**) and L[6]CH$_2$SiCl$_3$ (**16**), the values of η_Ω vary in the range 28–94% (L = 6 or 7-membered lactam ring). It can be seen from Table 4 that η_Ω decreased along with an increase of interatomic Si···O distance.

The anionic tetrafluoride complex **2** contains a hexacoordinated silicon atom with two HVBs(1)–Si(1)–F(1) and F(3)–Si(1)–F(4) (Fig. 2).

The Si–O and Si–F bonds in **2** are slightly elongated compared to **1b**. In **2** the differences between the Si–F bonds are less than in the case of **1a** and **1b**. A similar distribution of Si–F bonds lengths was observed in [MeC(O)-N(CHMePh)CH$_2$]$_2$SiF$_2$ (**17**) and in the 18-crown-6 potassium salt of [8-(dimethylamino)naphthyl]tetrafluorosilicate (**18**) containing a hexacoordinated silicon atom [8a,21]. These structural trends can be explained by two effects. The first effect is related to the increase in the coordination number of the silicon atom and the second effect arises from weak intermolecular contacts of the F(1), F(2) and F(3) atoms with the counterion. The K$^+$···F$^-$ interatomic distances (2.72–2.82 Å, Table 2) are typical for salts with a potassium cation and anions containing fluoride atoms (such as SiF$_6^{2-}$) [22]. The maximal deviation of F(2)–
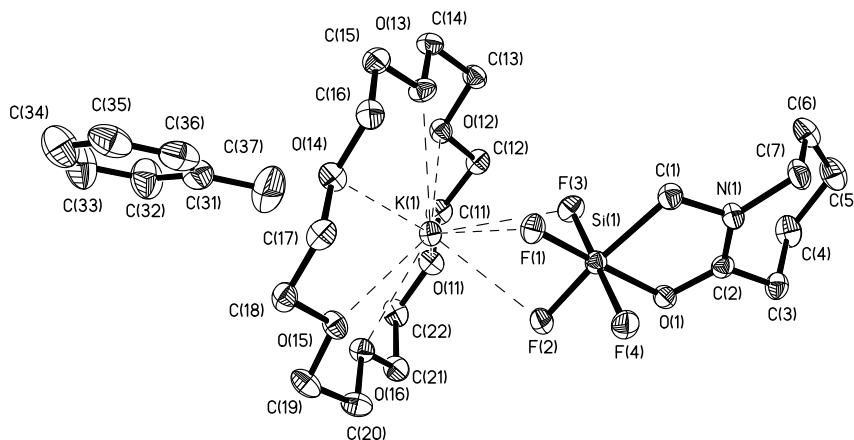

Fig. 2. Molecular structure of **2**. Atoms are represented by thermal ellipsoids with 50% probability. Hydrogen atoms are omitted for clarity.

Si(1)–C(1) from the ideal value (180°) is 8°, similar to that in **18** (10°).

2.3. Dynamic ^{19}F NMR

The presence in the trifluorosilanes (**1a**–**c**) of three fluorine atoms, which are able to occupy stereochemically different positions (two equatorial and one axial), gives the possibility of positional exchange in their coordination set (permutational isomerization) involving participation of three monodentate ligands. This exchange can be investigated by the use of a DNMR technique. An impurity-catalyzed intermolecular exchange of fluoride ion in these compounds can also take place [23].

The ^{19}F NMR spectra of the trifluorides (**1a**) and (**1b**) containing additional chiral elements, over the temperature range from −85 to −95 °C (equimolar mixture of CDCl$_3$ and CD$_2$Cl$_2$), display the axial fluorine signal as a multiplet ($\delta(^{19}F) \sim −116$ to −118 ppm), and the signal corresponding to the two equatorial fluorine atoms occurs as two doublets with similar chemical shifts in the range ∼−148 to −150 ppm. The coupling constant $^2J_{F'e–Fe} \sim 17$ Hz is approximately half the value of $^2J_{Fa–Fe}$ (∼35 Hz). The assignment of the down field shift to the axial fluorine and the upfield shift to the two equatorial fluorine atoms was carried out on the basis of their integral intensity as well as considering the ^{19}F NMR spectroscopic data obtained earlier for chelates bearing a trifluorosilyl group – the derivatives of 2-pyrrolidone (**5**) [16], N,N-dimethylbenzylamine (**6,7**) and 8-dimethylaminonaphthalene (**8**) [24].

Nonequivalence of the axial and equatorial fluorine atoms at low temperatures has been observed earlier for different derivatives of pentacoordinated silicon with three bound fluorine atoms that also possess an additional asymmetric carbon atom in its structure (see Refs. [16,24,25]). Complex **1c** has no additional centres of symmetry, such that the signals of the two equatorial fluorine atoms, in contrast to trifluorides (**1a**) and (**1b**), under the same conditions gave a much broader singlet with a doubled integral intensity at temperatures close to −110 °C.

A temperature increase is accompanied by a broadening and coalescence of signals corresponding to the equatorial fluorine atoms. As a result two signals were observed in the ^{19}F NMR spectrum in the temperature range −70 to −75 °C, and the strongest upfield shift signal (−135 to −140 ppm.) has an integral intensity of twice that of the signal with the lower upfield shift.

At higher temperatures (from −70 °C to room temperature) one broadened singlet is observed in the ^{19}F NMR spectrum as a result of coalescence of the signals corresponding to the axial and equatorial fluorine atoms. A temperature decrease restores the spectral picture. The observed temperature-dependent change of the signal patterns corresponds to the permutation of the ligands in the coordination set of the compounds studied.

Activation parameters calculated using ^{19}F DNMR on the basis of a full line shape analysis of the one axial and two equatorial fluorine atoms (integral intensities ratio is 1:2) as well as by two equatorial fluorine atoms (integral intensities ratio is 1:1) are presented in Table 5.

The determined values of the activation barriers are all within experimental error. The calculated $\Delta G^{\#}$ values are close to the values estimated for the 2-pyrrolidone (**5**) derivative (∼9.5 kcal mol^{-1}) [16].

The diastereotopic doubling of the signals corresponding to the equatorial fluorine atoms in the trifluoride (**1a**) is a result of the chiral carbon atom. The diastereotopic nature of the equatorial fluorine atoms in **1b**, in analogy with the diastereotopic nature of the equatorial methyl groups in N-(dimethylgermylmethyl)- and N-(dimethylstannylmethyl)hexahydro-2-azepinones [26], is caused by a slowing on the NMR timescale at low temperatures of the process of inversion in the 7-membered lactam ring. In the ^1H NMR spectrum of **1b** the signal superposition of the lactam ring and the protons of the methylene group (NCH$_2$) is observed at low temperatures complicating the use of this group for the calculation of $\Delta G^{\#}$.

2.4. Quantum-chemical calculations

In order to estimate the energetic characteristics of the stereodynamic processes for **1a**–**1c** and study the mechanisms of these processes we have carried out quantum-chemical investigations of the potential energy surface (PES) applying the theory of functional density (hybrid functional PBE1PBE) and a basis set 6-311+G(d).

For the calculations we applied the parameters of geometry optimization that were more precise than the default (corresponding to the instruction for the GAUSSIAN 98W software [27] – Opt = VTight and Int(Grid = Ultrafine)).

Table 5
The activation parameters of permutational isomerisation in trifluorides **1a**–**c** (CD$_2$Cl$_2$ + CDCl$_3$)

Compounds	$\Delta G^{\#}_{298}$ (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal mol^{-1} K^{-1})	$\Delta G^{\#}_c$ (kcal mol^{-1})	T_c (°C)
1a	9.7 ± 0.2	12.1 ± 0.1	−7 ± 2.3	9.7 ± 0.2	−78
	9.5 ± 0.2*				−83
1b	9.3 ± 0.2	11.1 ± 0.1	−6 ± 1.2	9.4 ± 0.2	−76
	9.2 ± 0.2*				−86
1c	9.8 ± 0.2	10.2 ± 0.2	−4 ± 1.3	9.2 ± 0.2	−75

* Found from the coalescence temperature of the signals due to the equatorial fluorine atoms.

Information about the PES of monochelate complexes with trigonal-bipyramidal (TBP) configurations of the silicon atom is poor and restricted to descriptions of acyclic silyl anions of the type $X_3SiH_2^-$ (X = F, Cl, Br) [28]. Two transition states have been found for such anions, one with a square-pyramidal (SP) configuration and the other with a TBP configuration [28]. The latter is characterized by a much lower potential energy barrier and imaginary frequency in comparison with the SP-configured transition state. For example, the values for the permutational barrier for the TBP and SP transition states of $H_2SiF_3^-$ are 7.6 and 11.1 kcal mol^{-1}, and the imaginary frequency values are -105.1 cm^{-1} and -227.6 cm^{-1}, respectively [28].

2.4.1. Permutational isomerization

Our quantum chemical studies of the potential energy surface have shown that in 1a–c isomerisation can occur through a transition state A with a TBP configuration of the silicon atom (Fig. 3). The absence of a transition state with an SP configuration can be explained by the steric hindrance due to the cyclic O,C ligands.

The geometries of the lowest stationary points are close to the experimental crystal structures of 1a–c. The main differences are observed in the Si–O bond lengths which are elongated by ca. 0.13 Å (Table 6) in comparison with the experimental values. Such differences are typical for monochelated complexes with a pentacoordinate silicon atom [29].
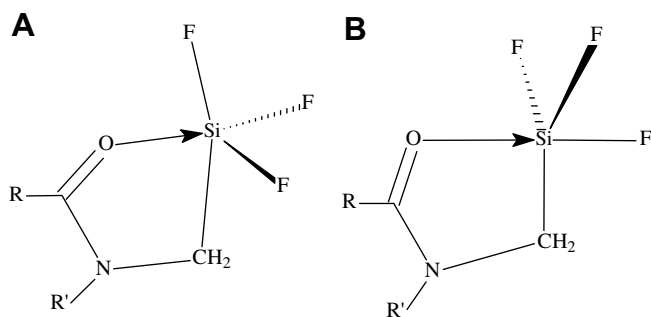
The carbon atom of a 5-membered ring where the silicon takes a TBP transient configuration occupies an axial position, whereas the oxygen atom takes an equatorial position. Imaginary frequency values are equal to 64.7, -62.3, and 67.0 cm^{-1} that is close to the reported data; and the vibration mode corresponds to migration of the C(1) atom from an axial to an equatorial position. The length of the Si–C bond in A is larger than in B by 0.06 Å (Tables 6 and 7). In the transition state the Si–O bond is shorter by 0.12 Å than in B, which corresponds to the energy minimum (Tables 6 and 7).

Another essential difference is the distribution of lengths among the Si–F bonds. Configuration (b) has all the Si–F bonds aligned, whereas in configuration (a) the axial bond is longer than the equatorial bonds by 0.03 Å (Tables 6 and 7). The transition states in 1a, 1b, and 1c have an energy level higher than structure A by 10.65, 10.21, and 10.82 kcal mol^{-1}, respectively, in the structure A. The average $\Delta H_{170\,K}$ is -10.4 kcal mol^{-1}, which is close to the experimental data obtained by use of the DNMR method.

2.4.2. Inversion of 7 membered cycle

As well as permutational isomerization, the inversion of the 7-membered ring is also possible in 1b. We have demonstrated that isomer E in a "boat" conformation (Fig. 4) leads to an energy increase by 3.20 kcal mol^{-1} compared to structure C with the 7-membered ring in a "chair" conformation. The latter conformation was found in crystals of the trifluoride (1b) and also in the (O → Si)-chelate N-(trichlorsilylmethyl)-2-oxoperhydroazepinone [30].

Diastereomers, which are conformationally stable at low temperatures and have a 7-membered lactam ring and a chiral pentacoordinated silicon atom in the molecule, have been analysed by X-ray crystallography for the dichloride $L^7CH_2SiMeCl_2$ that has one chlorine atom in an axial position and a methyl group and the second chlorine atom in two distinct equatorial positions relative to the 7-membered ring existing in a "chair" conformation [30].

Inversion proceeds via a transition state (F, Fig. 4) in which the 7-membered ring takes a conformation close to a "half-chair" conformation; the fold goes through C(3) and C(7) atoms. The calculated barrier for this process corresponds to 10.2 kcal mol^{-1} (the imaginary frequency value of the vibration of the corresponding inversion is equal to

Fig. 3. The structures corresponding to isomers of isolated molecules 1a–c and to transition states during ligand exchange.

Table 6
Geometrical parameters of the nuclear configurations A and B for compounds 1a and 1c

Bond lengths and angles	1a		1c	
	A	B	A	B
Si–O	1.874	1.995	1.877	1.999
Si–C	1.950	1.890	1.953	1.892
Si–F$_{ax}$	1.636	1.642	1.634	1.642
Si–F$_{eq1}$	1.633	1.613	1.633	1.612
Si–F$_{eq2}$	1.634	1.613	1.633	1.612
C(2)–O(1)	1.274	1.251	1.273	1.251
OSiF	166.0	175.9	165.9	175.6
COSi	116.2	113.5	116.4	113.6

Table 7
Geometrical parameters of the atomic configuration C–F for compound 1b

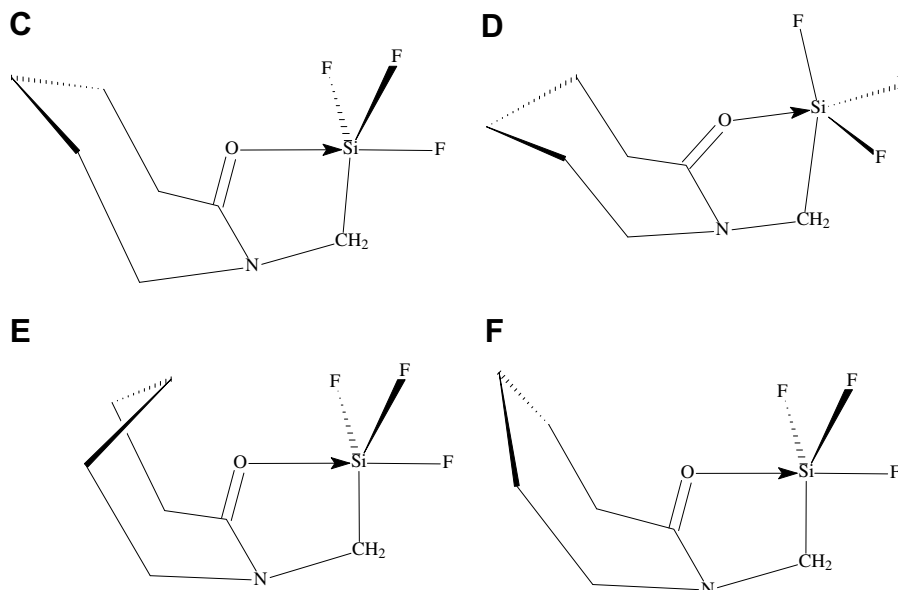| Bond lengths and angles	C	D	E	F
Si–O	1.989	1.871	1.999	2.000
Si–C	1.893	1.953	1.895	1.896
Si–F$_{ax}$	1.644	1.635	1.643	1.643
Si–F$_{eq1}$	1.613	1.633	1.614	1.614
Si–F$_{eq2}$	1.614	1.635	1.612	1.612
C(2)–O(1)	1.253	1.275	1.251	1.251
OSiF	175.7	166.4	176.0	176.0
COSi	113.4	116.2	112.9	112.6

Fig. 4. The structures corresponding to isomers of isolated molecule **1b** and transition states in processes of ligand exchange and inversion.

-246.5 cm^{-1}). In configurations **E** and **F** the geometry of the 5-membered ring changes little and, apparently, the atoms in the 5-membered chelate and 7-membered ring may have nearly independent motion. This allowed us to conclude that inversion of 7-membered cycle and permutational isomerization of the silicon atom in **1b** take place simultaneously and independently from one another.

2.5. The mechanism of permutational isomerization

Table 8 gives the theoretical values for the chemical shifts for the axial and equatorial fluorine atoms in the ^{19}F NMR spectra of structures **C**–**F** (Fig. 4) belonging to the complex **1b**. The values were obtained using the GAUSSIAN 98W software (PBE1PBE/6-311+G(d), GIAO) [27].

The data suggests the equatorial fluorine atoms in structures **C**, **E** and **F**, which differ from each other only by the conformation of the 7-membered cycle, show more prominent upfield shifts compared to the signal of the axial fluorine. This observation is supported by the trend in the experimentally determined ^{19}F NMR spectra (Table 1). Nevertheless, the theoretical data has larger chemical shifts compared to the experimental data. We believe that this arises from specific intermolecular interactions in solution that are common for many pentacoordinated silicone fluorides (for example see [23]). Thus, in general the geometries of the trifluorides investigated in solution are close to the

geometries determined by X-ray diffraction on the crystalline state of matter.

Based on quantum-chemical analysis data two possible mechanisms can be proposed to describe the processes leading to the equivalence of the fluorine atoms in the ^{19}F NMR spectra of the trifluorosilanes **1a**–**c**, i.e. regular ($\mathbf{B} \leftrightarrows \mathbf{A} \leftrightarrows \mathbf{B}'$) and non-regular mechanisms where the latter includes an "open" intermediate (**G**) (Scheme 1).

For mono- and trifluorosilanes (**1a**–**c**) the lower values for the barrier (9–11 kcal mol^{-1}, Table 5) compared to the barrier for exchange of the methyl groups in monofluorosilanes (>24 kcal mol^{-1} [31]) suggests different mechanisms for the stereodynamic transformations. In the sequence from monofluoride MeC(O)N(CHMePh)CH$_2$Si-Me$_2$F (**13**) to trifluorides (**1a**–**c**) shortening of the O–Si bond length from $\sim$2.15 [18a] to 1.88–1.90 Å is observed (Table 2). In the case of the trifluorides (**1a**–**c**) a non-regular mechanism involving an "open" intermediate (**g**) should lead to an increase in $\Delta G^{\#}$ compared to the monofluoride (**13**) ($\Delta G^{\#}$ is greater than 24 kcal mol^{-1} [31]), for which a non-regular mechanism of permutation involving cleavage of the O $\rightarrow$ Si internal coordination bond is suggested; but such an assumption contradicts the experimental data.

In the case of the monochelated pentacoordinated trifluorosilanes (**6**–**8**) with an N $\rightarrow$ Si internal coordination bond, for which the pseudorotation mechanism (relative to the mechanism presented in Scheme 1) will also be considered, similar values for the activation barrier are determined, i.e. 11.7, 12, and 13.1 kcal mol^{-1}, respectively [24]. As in the case of the monochelate trifluoro- and monofluorosilanes with O $\rightarrow$ Si coordination (see above) the energy barrier of the methylphenylfluorosilyl analog of the trifluoride (**8**) is increased (to 23 kcal mol^{-1}). The authors believe [24] that in the latter case the process involves a cleavage of the coordination bond.

Table 8
The theoretical values of ^{19}F NMR for structures **C**–**F**

δ^{19}F (ppm)	C	D	E	F
F(1)	−142.38	−146.37	−141.99	−142.18
F(2)	−157.46	−122.31	−155.28	−156.06
F(3)	−157.21	−124.31	−157.41	−157.12
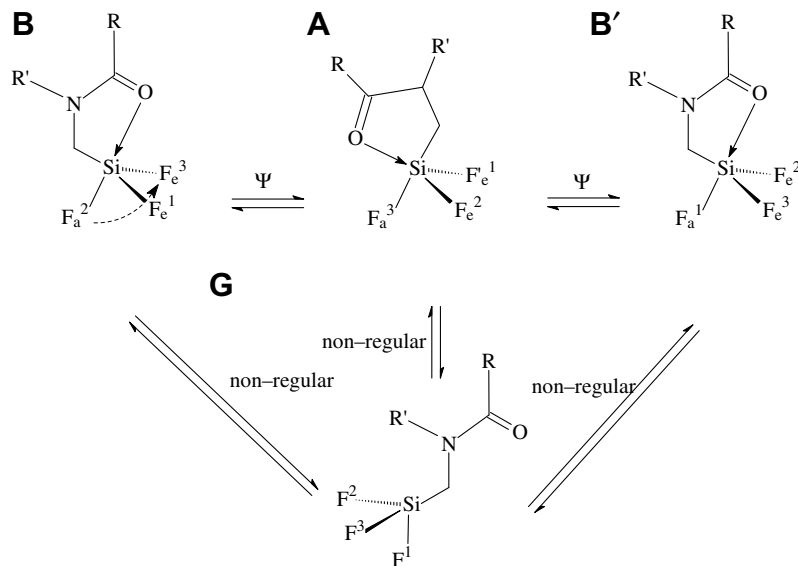
Scheme 1.

The lowest value for the barrier for pseudorotation in diorganotrifluorosilyl anions $R_2SiF_3^-$ has been found in anion complexes having a silicon atom incorporated into a 5-membered silacarbocycle, for example **17a** [32] and **17b** [25c].

$M^+ = [K•18\text{-}crown\text{-}6]^+$
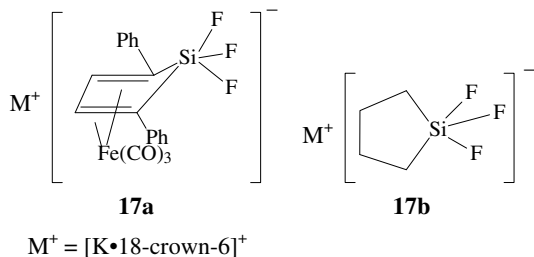
The process of pseudorotation is so fast for these compounds that only an averaged signal for the axial and equatorial fluorine atoms can be observed in the ^{19}F NMR spectra even at very low temperatures ($-105\ °C$). The estimation of the activation barrier by applying the Eyring equation for anion **17a** gave a value of less than $6\ kcal\ mol^{-1}$.

In the trifluoride (**17a**) the silicon atom has a distorted TBP configuration with an equatorial bond angle F_{eq}–Si–F_{eq} ($108.8°$) – slightly less than in the trifluorides **1a**–**c** (~111.0–$113.5°$) and much less than the value of $120°$ characteristic for an ideal TBP structure. The difference between the bond lengths of the F_{ax}–Si bond and the average distance for F_{eq}–Si is less than that in compound **17a** (1.668 and $1.626\ Å$) compared to the trifluorides (**1a**–**c**) (Table 2) [32].

3. Conclusion

Thus, we have shown that the lower $\Delta G^{\#}$ values for permutation in the trifluorides of pentacoordinated silicon species compared to the values established for derivatives with a coordination set $OSiC_3F$ correspond to non-dissociative processes.

In general non-dissociative permutational isomerization can proceed via a Berry mechanism of pseudorotation [33] (a) or turnstile mechanism [34] (b) (Scheme 2).

However, the quantum-chemical analysis, suggests the absence of a SP configuration of the transition state making it possible to rule out the Berry mechanism of pseudorotation. At the same time formation of the structure **b** proceeds in one step and thus, taking into account the low activation barriers (Table 5), a turnstile mechanism for this process seems to be the more reasonable.

4. Experimental

IR spectra of compounds (solutions in $CHCl_3$ and CCl_4) were recorded using a Specord IR-75 instrument. The ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectra of the compounds studied in $CDCl_3$ and equimolar mixture of $CDCl_3$ and CD_2Cl_2 were recorded on a Varian VXR-400 and Jeol JNM-EX400 instruments (400.1, 100.6, 396 and $79.5\ MH_2$, respectively). ^1H, ^{13}C and ^{29}Si chemical shifts were measured using tetramethylsilane as the internal reference. Chemical shifts of ^{19}F were measured using external reference $CFCl_3$. The solvents were dried over molecular sieves 4A (Cambridge Isotope Laboratories Inc., CAS [865-49-6]). The abundance of deuterium is 99%.

Temperature calibrations were performed using the distance between non-equivalent protons of methanol (-90 to $+30\ °C$) and ethylene glycol ($+30$ to $+85\ °C$) [35]. Activation parameters of the stereodynamic processes were calculated using DNMR-SIM software [36] and modified Eyring equation [37]. The number of temperature points was from 10 to 15. The correlation coefficient varied from 0.997 to 0.999.

a

ÒBP   SP

b

Scheme 2.
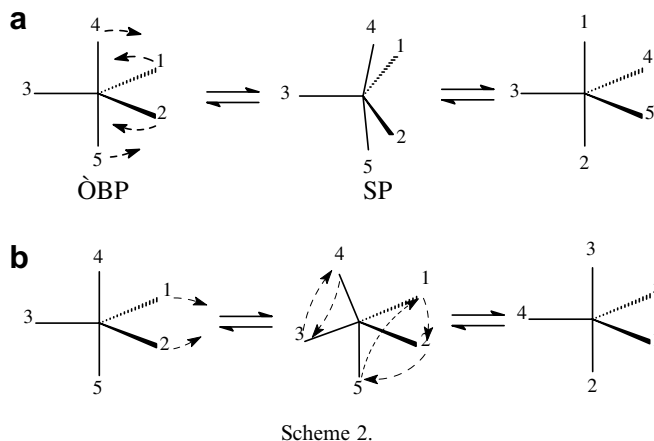
X-ray diffraction measurements for **1a**,**b** and **2** were carried out with a Bruker SMART CCD and Siemens P3 diffractometers. Structures are solved by direct method and refined in anisotropic approximation against F^2 for all non-hydrogen atoms. Hydrogen atoms are calculated geometrically and refined in isotropic approximation with constrained thermal displacement parameters $U_{eq}(H) = 1.5\ U(C)$ for methyl groups and $U_{eq}(H) = 1.2\ U(C)$ for others. Experimental dataset for crystal **1c** was corrected using profile fitting procedure implemented in PROFIT software [38]. Absolute structure of compounds **1a**,**b** was determined by Flack parameter [39]. All calculations were carried out using the SHELXTL 5.1 program package [40]. Details of crystallographic data and experimental condition are presented in Table 9.

4.1. N-(S)-(1-phenylethyl)-N-(trifluorosilylmethyl) acetamide (1a)

(a) Chloromethyltrimethylsilane (9.2 g, 0.05 mol) was added dropwise to the solution of N-(S)-(1-phenylethyl)acetamide (8.1 g, 0.05 mol) and hexamethyldisilazane (3.5 g, 0.022 mol) in benzene (80 ml). The mixture was refluxed for 3 h and cooled down to room temperature. Then the solution of methanol (25 g, 0.8 mol) in hexamethyldisilazane (48 g, 0.3 mol) was added dropwise. Next day the precipitate was filtered out, the solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (5 ml) and $BF_3 \cdot Et_2O$ (7.1 g, 0.05 mol) was added. The mixture was refluxed for 30 min, then the volatiles were distilled off and the residue was extracted with hot benzene (3 × 70 ml). Combined extracts were cooled down to room temperature to produce crystals of **1a**. Yield 7.0 g (55%). M.p. 178–179 °C (octane-toluene, 1:2), $[\alpha]_D^{20} - 29.6$ (c, CH_3CN, 29 mg mL^{-1}). Anal. Calc. for $C_{11}H_{14}NOSiF_3$: C, 50.56; H, 5.40; N, 5.36. Found: C, 50.59; H, 5.41; N, 5.37%. IR spectrum (CHCl$_3$, v, cm^{-1}): 1580, 1510 (NCO). ^{1}H NMR spectra (δ, ppm, CDCl$_3$): 1.59 (d, 3H, *CCH$_3$, $^3J_{HH}$ 6.9 Hz), 2.31 (m, 3H, CH$_3$CO), 2.13, 2.45 (dd, 2H, NCH$_2$, $^2J_{HH}$ 17.1 Hz), 5.08 (qu, 1H, *CCH, $^3J_{HH}$ 6.9 Hz), 7.13–7.37 (m,

5H, C$_6$H$_5$). ^{13}C NMR spectra (δ, ppm, CDCl$_3$): 56.72 (CH), 17.21 (CH$_3$C(O)), 17.45 (CH$_3$CH), 25.40 (qu, NCH$_2$, $^2J_{CF}$ 27 Hz), 173.98 (C=O), 137.29 (C^{ipso}), 129.36 (C^{ortho}), 128.40 (C^{para}), 126.62 (C^{meta}).

(b) Chloromethyltrimethylsilane (18.4 g, 0.1 mol) was added dropwise to the solution of N-(S)-(1-phenylethyl)acetamide (16.3 g, 0.1 mol) and hexamethyldisilazane (6.44 g, 0.04 mol) in benzene (80 ml). The mixture was refluxed for 2 h and cooled down to room temperature. Next day the solution of NaHCO$_3$ (25 g) in water (100 ml) was added. The organic layer was collected, the aqueous solution was extracted with chloroform (3 × 50 ml). The combined organic extracts were dried over K$_2$CO$_3$, then the volatiles were removed in vacuo, the residue was treated with $BF_3 \cdot Et_2O$ (14.2 g, 0.1 mol). The volatiles were distilled off, the remaining oil was re-crystallised from the mixture of octane and benzene (4:1, 300 ml) to produce crystalline **1a**. Yield 1 g (4%). M.p. 172–174 °C (hexane–benzene, 2:3). IR spectrum (CHCl$_3$, v, cm^{-1}): 1580, 1510 (NCO).

4.2. 1-(Trifluorosilylmethyl)-2-oxoperhydroazepine (1b)

(a) The mixture of 2-oxoperhydroazepine (11.3 g, 0.1 mol), hexamethyldisilazane (6.4 g, 0.04 mol), chloromethyltrichlorosilane (18.4 g, 0.1 mol) and benzene

Table 9
Crystallographic parameters for compounds **1a**, **b** and **2**

Parameter	1a	1b	2
Molecular formula	C$_{11}$H$_{14}$F$_3$NOSi	C$_7$H$_{12}$F$_3$NOSi	C$_{26}$H$_{44}$F$_4$KNO$_7$Si
Formula weight	261.32	211.27	625.81
Diffractometer	BRUKER SMART CCD		SIEMENS P3
Temperature (K)	120(2)	120(2)	153(2)
a (Å)	10.081(2)	8.291(4)	9.009(3)
b (Å)	10.645(2)	5.943(3)	14.787(6)
c (Å)	11.185(2)	9.990(4)	23.429(7)
α (°)	90	90	90
β (°)	90	110.632(8)	95.36(3)
γ (°)	90	90	90
V (Å^3)	1200.3(3)	460.7(4)	3107(2)
d_{calc} (g cm^{-3})	1.446	1.523	1.338
Space group, Z	$P2_12_12_1$, 4	Pn, 2	$P2_1/n$, 4
$2\theta_{max}$ (°)	60	52	52
$F(000)$	544	220	1328
Data collection	$\omega/2\theta$	$\omega/2\theta$	$\theta/2\theta$
Reflections collected	6581	2384	6496
Number of independent reflections (R_{int})	3338 (0.021)	1565 (0.047)	6094 (0.015)
Number of reflections with $I > 2\sigma(I)$	2800	863	5221
Parameters	156	118	361
Linear absorption (cm^{-1})	2.17	2.62	2.75
$R_1\ [I > 2\sigma(I)]$	0.037	0.050	0.031
wR_2 (all reflections)	0.095	0.108	0.077

(60 ml) was refluxed for 1 h. The mixture was cooled with ice and the solution of $NaHCO_3$ (35 g) in water (200 ml) was added dropwise. After 1 h the organic layer was collected, the aqueous solution was extracted with chloroform (3 × 20 ml). Organic extracts were combined, the volatiles were removed *in vacuo* and the residue was treated with $BF_3 \cdot Et_2O$ (9.9 g, 0.07 mol). The volatiles were distilled off, the remaining oil was extracted with benzene (40 ml). The extract was distilled to produce 5.5 g (26%) of **1b**. B.p. 222–224 °C (10 mm Hg), m.p. 107–109 °C (benzene–hexane, 1:1). Anal. Calc. for $C_7H_{12}F_3NOSi$: C, 39.79; H, 5.72; N, 6.63. Found: C, 39.93; H, 5.92; N, 6.43%. IR spectrum ($CHCl_3$, v, cm^{-1}): 1580, 1500 (NCO). ^1H NMR spectra (δ, ppm, $CDCl_3$): 1.72 (m, 2H, H(4)); 1.70 (m, 2H, H(5)); 1.81 (m, 2H, H(6)); 3.56 (m, 2H, H(3)); 2.73 (s, 2 H, NCH_2); 3.56 (m, 2H, H(7)). ^{13}C NMR spectra (δ, ppm, $CDCl_3$): 34.62 (C(3)); 29.31 (C(4)); 26.03 (C(5)); 22.04 (C(6)); 50.81 (C(7)); 34.69 (NCH_2); 179.26 (C=O).

(b) The solution of chloromethyltrichlorosilane (23 g, 0.12 mol) in benzene (20 ml) was added dropwise to the solution of 2-oxoperhydroazepine (11.3 g, 0.1 mol) and triethylamine (12.2 g, 0.12 mol) in benzene (60 ml). The mixture was refluxed for 30 min, then cooled with ice and the solution of methanol (11.6 g, 0.36 mol) and triethylamine (36.5 g, 0.36 mol) in benzene (20 ml) was added. Next day the precipitate was filtered out and the volatiles were removed *in vacuo*. The residue was treated with $BF_3 \cdot Et_2O$ (14.2 g, 0.1 mol) and the volatiles were again removed *in vacuo*. The remaining oil was distilled to produce 12.7 g (60%) of **1b**. B.p. 182–190 °C (1 mm Hg), m.p. 107–108 °C (benzene–hexane, 1:1).

4.3. N-(trifluorosilylmethyl)-N-methylacetamide (1c)

$BF_3 \cdot Et_2O$ (2.84 g, 0.02 mol) was added dropwise to the solution of N-(trimethoxysilylmethyl)-N-methylacetamide [13] in hexane (10 ml). The solution was refluxed for 30 min. Next day the volatiles were removed *in vacuo* and the remaining oil was extracted with benzene (20 ml). The solvent from the extract was distilled off, the residue was washed with hexane (10 ml) to produce crystalline **1c**. Yield 2.4 g (92%). M.p. 69–71 °C (benzene–hexane, 1:5). Lit. [14a]: b.p. 120 °C (1 mm Hg), m.p. 70–72 °C. ^1H NMR spectra (δ, ppm, $CDCl_3$): 2.25 (br. s., 3H, CMe), 3.18 (s, 3H, NMe), 2. 61 (br. s, 2 H, NCH_2). ^{13}C NMR spectra (δ, ppm, $CDCl_3$): 16.46 (*Me*C), 37.36 (qu, NCH_2, $^2J_{CF}$ 26.3 Hz), 36.94 (s, NMe), 174.50 (C=O).

4.4. Potassium 18-crown-6-(2-oxoperhydroazepinomethyl) tetrafluorosilicate, monosolvate with toluene (2 · PhMe)

The mixture of 1-(trifluorosilylmethyl)-2-oxoperhydroazepine (1.05 g, 0.005 mol), 18-crown-6 (1.32 g, 0.005 mol), KF (0.29 g, 0.005 mol) and benzene (10 ml) was refluxed until all KF was dissolved. The mixture was cooled down to room temperature to produce crystalline **2 · PhMe**. Yield 2.2 g (70%), decomp. >350 °C. IR spectrum ($CHCl_3$, v, cm^{-1}): 1617, 1510 (NCO). Anal. Calc. for $C_{26}H_{44}KF_4NO_7Si$: C, 49.90; H, 7.08; N, 2.23. Found: C, 50.14; H, 7.05; N, 2.26%. ^1H NMR spectra (δ, ppm, $CDCl_3$): 1.72 (m, 2H, H(4)); 1.76 (m, 2H, H(5)); 1.82 (m, 2H, H(6)); 2.80 (m, 2H, H(3)); 3.19 (s, 2H, NCH_2); 3.45 (m, 2H, H(7)). ^{13}C NMR spectra (δ, ppm, $CDCl_3$): 32.27 (C(3)); 22.24 (C(4)); 26.02 (C(5)); 29.74 (C(6)); 52.31 (C(7)); 46.50 (NCH_2); 176.21 (C=O).

Acknowledgements

References

[1] (a) S.N. Tandura, M.G. Voronkov, N.V. Alekseev, Top. Curr. Chem. 131 (1986) 99;
(b) C. Chuit, R.J.P. Corriu, C. Reyé, J.C. Young, Chem. Rev. 93 (1993) 1371;
(c) A.R. Bassindale, P.G. Taylor, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, 1989, p. 839;
(d) R.R. Holmes, Chem. Rev. 96 (1996) 927;
(e) E. Lukevics, O.A. Pudova, Chem. Heterocyclic Comp. 32 (1996) 1381;
(f) D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, 1998, p. 1339;
(g) C. Chuit, R.J.P. Corriu, C. Reyé, in: Kin-ya Akiba (Ed.), The Chemistry of Hypervalent Compounds, Wiley-VCH, Weinheim, 1999, p. 81;
(h) M. Kira, L.C. Zhang, in: Kin-ya Akiba (Ed.), The Chemistry of Hypervalent Compounds, Wiley-VCH, Weinheim, 1999, p. 147;
(i) R. Tacke, M. Pülm, B. Wagner, Adv. Organomet. Chem. 44 (1999) 221;
(j) M.A. Brook, Silicon in Organic, Organometallic and Polymer Chemistry, Wiley, New York, 2000, pp. 97;
(k) D. Kost, I. Kalikhman, Adv. Organomet. Chem. 50 (2004) 1.
[2] (a) R.W. Hillard, C.M. Ryan, C.H. Yoder, J. Organomet. Chem. 153 (1978) 369;
(b) C.H. Yoder, C.M. Ryan, G.F. Martin, P.S. Ho, J. Organomet. Chem. 190 (1980) 1;
(c) C.H. Yoder, W.D. Smith, B.L. Buckwalter, C.D. Shaeffer, Ir.K.J. Sullivan, M.F. Lehman, J. Organomet. Chem. 492 (1995) 129.
[3] (a) Yu.I. Baukov, E.P. Kramarova, A.G. Shipov, G.I. Oleneva, O.B. Artamkina, A.I. Albanov, M.G. Voronkov, V.A. Pestunovich, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 70 (1989) 127;
(b) I.D. Kalikhman, A.I. Albanov, O.B. Bannikova, L.I. Belousova, M.G. Voronkov, V.A. Pestunovich, A.G. Shipov, E.P. Kramarova, Yu.I. Baukov, J. Organomet. Chem. 361 (1989) 147;
(c) A.G. Shipov, E.P. Kramarova, O.B. Artamkina, Yu.E. Ovchinnikov, Yu.I. Baukov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 67 (1997) 1680.
[4] (a) K.D. Onan, A.T. McPhail, C.H. Yoder, R.W. Hillyard, J. Chem. Soc. Chem. Commun. 5 (1978) 209;
(b) A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, G.I. Oleneva, E.P. Kramarova, A.G. Shipov, Yu.I. Baukov, J. Chem. Soc., Chem. Commun. 11 (1988) 683;
(c) M.G. Voronkov, V.A. Pestunovich, Yu.I. Baukov, Metalloorg. Khim. (Organomet. Chem., USSR) 4 (1991) 1210;

(d) Yu.T. Struchkov, Yu.E. Ovchinnikov, A.G. Shipov, Yu.I. Baukov, Russ. Chem. Bull. 44 (1995) 1705.

[5] Vad.V. Negrebetsky, Yu.I. Baukov, Russ. Chem. Bull. 46 (1997) 1807.

[6] (a) A.G. Shipov, E.P. Kramarova, O.B. Artamkina, Yu.I. Baukov, Metalloorg. Khim. (Organomet. Chem., USSR) 4 (1991) 1101;
(b) O.B. Artamkina, E.P. Kramarova, A.G. Shipov, Yu.I. Baukov, A.A. Macharashvili, Yu.E. Ovchinnikov, Yu.T. Struchkov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 63 (1993) 2289;
(c) O.B. Artamkina, E.P. Kramarova, A.G. Shipov, Yu.I. Baukov, A.A. Macharashvili, Yu.E. Ovchinnikov, Yu.T. Struchkov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 64 (1994) 263;
(d) A.G. Shipov, E.P. Kramarova, O.B. Artamkina, G.I. Oleneva, N.A. Nepomniashaja, Yu.I. Baukov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 64 (1995) 272.

[7] R. Damrauer, S.E. Danahey, Organometallics 5 (1986) 1490.

[8] (a) C. Breliere, F. Carre, R.J.P. Corriu, W.E. Douglas, M. Poirier, G. Royo, M. Wong Chi Man, Organometallics 11 (1992) 1586;
(b) N. Kano, F. Komatsu, T. Kawashima, J. Am. Chem. Soc. 123 (2001) 10778.

[9] F. Carre, C. Cerveau, C. Chuit, R.J.P. Corriu, N.K. Nayyar, C. Reye, Organometallics 9 (1990) 1989.

[10] V.E. Shklover, Yu.E. Ovchinnikov, Yu.T. Struchkov, V.M. Kopilov, T.G. Koviazina, M.G. Voronkov, Dokl. Chem. USSR 284 (1985) 131.

[11] (a) V.E. Shklover, Yu.T. Struchkov, L.I. Gubanova, M.G. Voronkov, Zh. Struct. Khim. (J. Struct. Chem., USSR) 28 (1987) 118;
(b) A.O. Mozhshukhin, V.E. Shklover, M.Yu. Antipin, Yu.T. Struchkov, L.I. Gubanova, M.G. Voronkov, Metalloorg. Khim. (Organomet. Chem., USSR) 4 (1991) 1188.

[12] E.P. Kramarova, A.G. Shipov, Vad.V. Negrebetsky, Yu.I. Baukov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 67 (1997) 1403.

[13] A.G. Shipov, E.P. Kramarova, O.B. Artamkina, Yu.I. Baukov, Zh. Obsch. Khim. (J. Gen. Chem., USSR) 637 (1993) 1434.

[14] (a) M.G. Voronkov, V.P. Barishok, N.F. Lazareva, G.A. Kuznezova, E.I. Brodskaya, V.V. Beliaeva, A.I. Albanov, L.S. Romanenko, Metalloorg. Khim. (Organomet. Chem., USSR) 5 (1992) 1323;
(b) Yu.E. Ovchinnikov, A.O. Mozhkhukhin, M.Yu. Antipin, Yu.T. Struchkov, V.P. Barishok, N.F. Lazareva, M.G. Voronkov, Zh. Struct. Khim. (J. Struct. Chem., USSR) 34 (1993) 66;
(c) M.G. Voronkov, E.A. Zelbst, V.S. Fundamentskii, A.A. Kashaev, L.I. Gubanova, Russ. Proc. Nat. Acad. Sci. USSR 305 (1989) 1124.

[15] (a) M.G. Voronkov, E.A. Zelbst, Yu.V. Katkevich, A.A. Kashaev, V.S. Fundamentskii, Yu.I. Bolgova, O.M. Trofimova, N.F. Chernov, A.I. Albanov, Yu.I. Baukov, V.A. Pestunovich, Dokl. Chem. USSR 402 (2005) 77;
(b) M.G. Voronkov, E.A. Zelbst, A.A. Kashaev, Yu.V. Katkevich, V.S. Fundamentskii, Yu.I. Bolgova, O.M. Trofimova, A.I. Albanov, N.F. Chernov, V.A. Pestunovich, Dokl. Chem. USSR 393 (2003) 493.

[16] V.A. Pestunovich, M.F. Larin, A.I. Albanov, L.I. Gubanova, M.G. Voronkov, Izv.Akad. Nauk, Ser. Khim. (Russ. Chem. Bull.) 8 (1983) 1331.

[17] S.A. Pogozhikh, Yu.E. Ovchinnikov, E.P. Kramarova, Vad.V. Negrebetsky, A.G. Shipov, A.I. Albanov, M.G. Voronkov, V.A. Pestunovich, Yu.I. Baukov, Russ. J. Gen. Chem. 74 (2004) 1617.

[18] (a) Yu.I. Baukov, Yu.E. Ovchinnikov, A.G. Shipov, E.P. Kramarova, Vad.V. Negrebetsky, Yu.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 399;
(b) A.G. Shipov, E.P. Kramarova, E.A. Mamaeva, O.A. Zamyshlyaeva, Vad.V. Negrebetsky, Yu.E. Ovchinnikov, S.A. Pogozhikh, A.R. Bassindale, P.G. Taylor, Yu.I. Baukov, J. Organomet. Chem. 620 (2001) 139.

[19] (a) A.A. Macharashvili, Yu.I. Baukov, E.P. Kramarova, G.I. Oleneva, V.A. Pestunovich, Yu.T. Struchkov, V.E. Shklover, Russ. J. Struct. Chem. 28 (1987) 114;

(b) A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, V.A. Pestunovich, Yu.I. Baukov, E.P. Kramarova, G.I. Oleneva, Russ. J. Struct. Chem. 29 (1988) 121.

[20] (a) K. Tamao, T. Hayashi, Y. Ito, M. Shiro, Organometallics 11 (1992) 2099;
(b) S.Yu. Bylikin, A.G. Shipov, Vad.V. Negrebetsky, Yu.I. Baukov, Yu.E. Ovchinnikov, S.A. Pogozhikh, S.V. Pestunovich, L.I. Belousova, E.F. Belogolova, V.F. Sidorkin, M.G. Voronkov, V.A. Pestunovich, I. Kalikhman, D. Kost, J. Organomet. Chem. 691 (2006) 779.

[21] E.P. Kramarova, S.A. Pogozhikh, A.G. Shipov, Vad.V. Negrebetsky, T.P. Nikolaeva, S.Yu. Bylikin, Yu.E. Ovchinnikov, Yu.I. Baukov, Russ. Chem. Bull. 53 (2004) 262.

[22] Cambridge Structural Database, Release, 2004.

[23] (a) R.K. Marat, A.F. Janzen, Can. J. Chem. 55 (1977) 1167;
(b) R.K. Marat, A.F. Janzen, Can. J. Chem. 55 (1977) 3845.

[24] F. Carre, R.J.P. Corriu, A. Kpoton, M. Poirier, G. Royo, J.C. Young, C. Belin, J. Organomet. Chem. 470 (1994) 43.

[25] (a) F. Klanberg, E.L. Muetterties, Inorg. Chem. 7 (1968) 155;
(b) C. Breliere, F. Carre, R.J.P. Corriu, A. de Saxce, M. Poirier, G. Royo, J. Organomet. Chem. 205 (1981) C1;
(c) S.E. Johnson, J.S. Payne, R.O. Day, J.M. Holmes, R.R. Holmes, Inorg. Chem. 28 (1989) 3190.

[26] Vad.V. Negrebetsky, Yu.I. Baukov, Izv. Akad. Nauk Ser., Khim. (Russ. Chem. Bull.) 11 (1998) 2379.

[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.9. Gaussian Inc., Pittsburgh PA, 1998.

[28] T. Windus, M.S. Gordon, L.P. Davis, L.W. Burggraf, J. Am. Chem. Soc. 116 (1994) 3568.

[29] A.A. Korlyukov, K.A. Lyssenko, M.Yu. Antipin, Russ. Chem. Bull. 51 (2002) 1423.

[30] Yu.T. Struchkov, Yu.E. Ovchinnikov, A.G. Shipov, Yu.I. Baukov, Izv. Akad., Nauk Ser. Khim. (Russ. Chem. Bull.) 9 (1995) 1774.

[31] Vad.V. Negrebetsky, P.G. Taylor, E.P. Kramarova, S.Yu. Bylikin, I.Yu. Belavin, A.G. Shipov, A.R. Bassindale, Yu.I. Baukov, J. Organometal. Chem. 691 (2006) 3976;
Vad.V. Negrebetsky, Thesis for the degree of Doctor of Chemical Sciences, Moscow, 2006.

[32] F.H. Carre, R.J.P. Corriu, C. Guerin, B.J.L. Henner, W.W.C. Wong Chi, J. Organomet. Chem. 347 (1988) C1.

[33] R.S. Berry, J. Chem. Phys. 32 (1960) 933.

[34] I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, P. Gillespie, Angew. Chem. 82 (1970) 741;
I. Ugi, I. Marquarding, H. Klusacek, P. Gillespie, Acc. Chem. Res. 4 (1971) 288.

[35] A.L. van Geet, Anal. Chem. 42 (1970) 679.

[36] G. Haegele, R. Fuhler, Th. Lenzen, Comp. Chem. 19 (1995) 277.

[37] G. Binsch, in: L.M. Jackman, F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, vol. 45, Academic Press, New York, 1975.

[38] V.E. Strelzov, V.E. Zavodnik, Crystallographia (Sov. Phys. Crystallog.) 34 (1989) 1369.

[39] H.D. Flack, D. Schwarzenbach, Acta Cryst. A44 (1988) 499.

[40] G.M. Sheldrick SHELXTL-97, vol. 5.10, Bruker AXS Inc., Madison, WI, USA, 1997.