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Donor-Stabilized Five-Coordinate Cationic Chelate Silicon Compounds with Two (O→Si)-Coordinating Ligands

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Abstract—Cationic O→Si-coordinated bis-C,O-chelate silicon complexes $[(LCH_2)_2Si(F)]BF_4$, containing monoanionic $AcN(Me)CH_2$, 2-oxoperhydroazepinomethyl, 2,2-dimethyl-4-oxobenzo[1,3]oxazin-3-ylmethyl, and 4-methyl-2-oxoquinolinomethyl C,O-coordinating ligands were synthesized by the reaction of trimethylsilyl derivatives of amides, lactams, and related compounds with $(ClCH_2)_2SiCl_2$ in a 2:1 ratio. The synthesized complexes were reacted with KF to obtain six-coordinate bis-C,O-chelates $[(LCH_2)_2SiF_2]$ which were then converted into the starting tetrafluoroborates by treatment with $BF_3{\cdot}Et_2O$. First representatives of cationic bis-O,O'-chelate silicon complexes with a 2-hydroxyacid amide fragment $\{XSi[OCH(R)C(O)NMe_2]_2\}Y$ (X = Cl, Me, *t*-Bu, Ph, $BrCH_2$; R = H, Me; Y – Cl^-, $ClHCl^-$, $HgBr_3^-$) were synthesized by the reaction of $XSiCl_3$ with O→$SiMe_3$ derivatives of dimethylamides of (*S*)-lactic and glycolic acids in a 1:2 ratio or by transesterification of $XSi(OMe)_3$ with glycolic acid dimethylamide followed by addition of acetyl bromide (ratio 1:3:1). The structure of the resulting chelates was proved by X-ray diffraction analysis.

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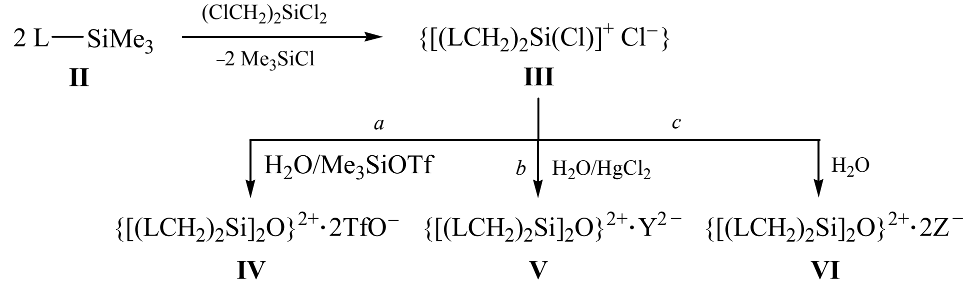
Stability of silylium ions in various media, features of their structure and reactivity, and their possible role as intermediates in certain reactions are a focus of organoelement chemistry [1–3]. A great deal of recent research attention has been given to stabilization of such ions by intraionic coordination. Note that the most part of known donor-stabilized silicon complexes are N→Si-chelates [4, 5]. Such O→Si-coordinated silylium ions we first synthesized in 1993 from lactams L^nH **I** in our study on reactions of their trimethylsilyl derivatives $L^n–SiMe_3$ **II** with $(ClCH_2)_2SiCl_2$, undertaken with the aim to prepare hypercoordinated dichlorosilanes $(L^nCH_2)_2SiCl_2$ **III** (L^nCH_2 is an *n*-membered lactamomethyl ligand) [6]. With pyrrolidin-2-one, after treatment of the corresponding hydrolytically unstable dichloride with trimethylsilyl triflate, we isolated and characterized by X-ray diffraction a dicationic bis-C,O-chelate complex $\{[(L^5CH_2)_2Si]_2O\}^{2+}2TfO^-$ (Scheme 1, route *a*) [6]. Later other analogous binuclear complexes of five-coordinate silicon, containing, according X-ray diffraction analysis, disiloxane dications with monoanionic amidomethyl and related C,O-coordinating ligands like **IV, V**, and **VI** with five-membered rings (Scheme 1) [7, 8], as well as with six-membered rings on the basis of 1,1-dimethyl-2-acylhydrazines were prepared [9]. At the same time, mononuclear analogs of such complexes, except for few examples [9, 10], have been, in fact, scarcely described. Almost no donor-stabilized silylium cations containing monoanionic O,O'-coordinating ligands on the basis of disubstituted amides of 2-hydroxyacids have been reported.

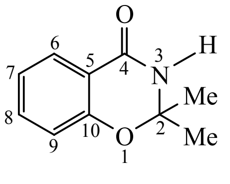
In the present work we report on the synthesis and X-ray diffraction study of mononuclear donor-stabilized O→Si-coordinated five-coordinate silicon complexes—new bis-C,O-chelates of the general formula $[(LCH_2)_2Si(F)]BF_4$, with amidomethyl and related ligands LCH_2, as well as the first representatives of

Scheme 1.

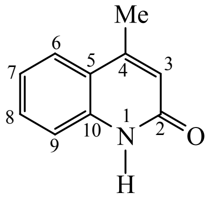


bis-O,O'-chelates $\{XSi[OCH(R)C(O)NMe_2]_2\}Y$ with a 2-hydroxyacid amide residue as a ligand (X = Cl, Me, *t*-Bu, Ph, $BrCH_2$; R = H, Me; Y = a low-nucleophilicity anion, Cl^-, $ClHCl^-$, $HgBr_3^-$, etc.).

Bis-C,O**-chelates.** As precursors of C,O-coordinating ligands LCH_2 for cationic C,O-chelates we used *N*-methylacetamide (**Ia**), perhydroazepin-2-one L^7H (**Ib**), 2,2-dimethylbenzo-1,3-oxazin-4-one (BonH, **Ic**), and 4-methylquinolin-2-one (QonH, **Id**).



BonH, **Ic**

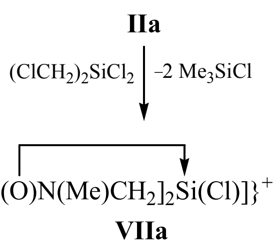


QonH, **Id**

The above-described general strategy of the synthesis of binuclear donor-stabilized bis-C,O-chelate cationic O→Si coordinated silicon complexes involves reaction of bis(chloromethyl)dichlorosilane c amide or lactam derivatives L–$SiMe_3$ **II** in a 1:2 ratio in fairly rigid thermodynamically controlled conditions, followed by conversion of the initially formed hydrolytically unstable dichlorides $(LCH_2)_2SiCl_2$ **III** into more stable final products **IV**–**VI** (Scheme 1) [7, 8]. The structure of most products was confirmed by X-ray diffraction. Note that the reactions shown in Scheme 1 were performed under conditions not excluding access of air maisture, and, therefore, they could be accompanied by hydrolysis of dichlorides **III** and, as a result, formation of binuclear complexes **IV–VI**.

The results of X-ray diffraction analysis of **VIIa** [10], isolated in the reaction of $SiMe_3$ derivative **IIa** with $(ClCH_2)_2SiCl_2$ suggest with a high probability an ionic structure of dichlorides **III**.

It should be stressed that now complex **VIIa** (Fig. 1, Table 1) is the only reliably structurally characterized representative of mononuclear bischelates with of the general formula $[(LCH_2)_2Si(Hlg)]^+Y^-$ having amidomethyl or related C,O-coordinating ligands.



$$\{[MeC(O)N(Me)CH_2]_2Si(Cl)]\}^+\ [ClHCl]^- \quad (1)$$

Complex **VIIa** is formed in the reaction at 0°C in dry CH_2Cl_2 under restricted access of air moisture which, however, is sufficient for partial hydrolysis of dichloride $(ClCH_2)_2SiCl_2$ or/and compound **VIIa**, involving HCl evolution. When the reactants are boiled in air, the reaction produces disiloxane hydroxonium trichloride $\{[AcN(Me)CH_2]_2Si\}_2O^{2+}\ 3Cl^-{\cdot}H_3O^+$ (**VIa**), $2Z^- = 3Cl^-H_3O^+$ (Scheme 1, route *c*) [8]. Further evidence for the structure of the hydrolytically unstable complex **VIIa** is provided by the formation of tetrafluoroborate $\{[AcN(Me)CH_2]_2Si(F)\}^+BF_4^-$ (**VIIIa**) after treatment of the crude product synthesized by reaction (1) with $BF_3{\cdot}Et_2O$.

To synthesize fairly stable mononuclear bis-C,O-chelate cationic silicon complexes we further made use of the conversion of the readily hydrolyzed dichlorosilanes **III** into fluorusilylium ions with bulky $BonCH_2$ and $QonCH_2$ ligands. In view of the fact that these substituents contain a fused benzene ring, we expected formation of readily crystallized, high-melting compounds feasible for X-ray diffraction analysis. Note that the first examples of mononuclear bis-*C,O*-chelates of this type, specifically hexachlorodimercurate $\{[L^6CH_2]_2SiCH_2Cl\}^+\ 0.5Hg_2Cl_6^{2-}$ and tetrafluoroborate $\{[L^7CH_2]_2Si(F)\}^+BF_4^-$ (**VIIIb**), were described in [11, 12], but their full X-ray diffraction data were not reported.

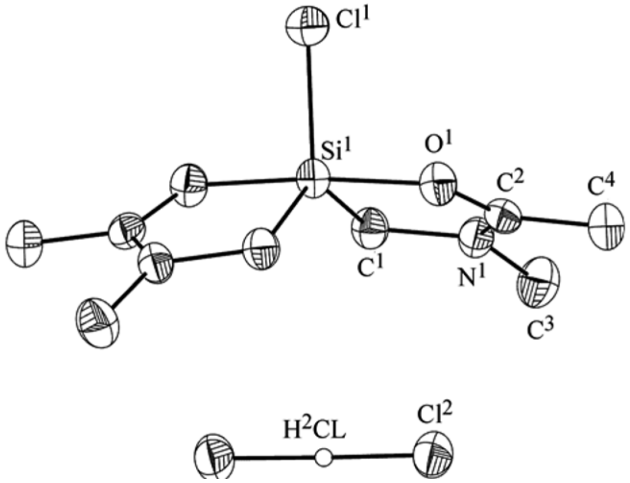
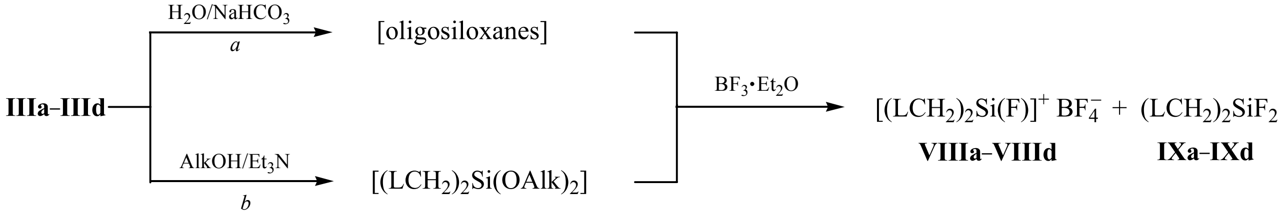


Fig. 1. General view of complex **VIIa** in crystal (H atoms, except for the H atom of the anion, are not shown).

The general synthetic approach to mononuclear bis-*C,O*-chelate silylium ions, developed in the present work, is based on the reaction of $(ClCH_2)_2SiCl_2$ with compounds $AcN(Me)SiMe_3$ (**IIa**), L^7SiMe_3 (**IIb**), $BonSiMe_3$ (**IIc**), and $QonSiMe_3$ (**IId**) in a 1:2 ratio (Scheme 1), followed by hydrolysis of intermediate chlorides **III** in the presence of $NaHCO_3$ to form mixtures of corresponding oligosiloxanes and treatment of the latter in situ with $BF_3{\cdot}Et_2O$ (Scheme 2, route *a*). Alternatively, chlorides **III** were treated with alcohol in the presence of triethylamine and intermediate alkoxysilanes were reacted with $BF_3{\cdot}Et_2O$ (Scheme 2, route *b*). These reactions were performed in a one-pot version, and they generally led to hardly separable mixtures of tetrafluoroborates $[LCH_2]_2Si(F)^+BF_4^-$ **VIIIa–VIIId** and neutral six-coordinate bis-*C,O*-chelate difluorosilanes $(LCH_2)_2SiF_2$ **IXa–IXd**. As an example, we present in Scheme 2 the reaction of *N*-$SiMe_3$-4-methylquinolin-2-one (**IId**) with $Cl_2Si(CH_2Cl)_2$ to give tetrfluoroborate **VIIId** and difluorosilane **IXc** in 44 and 36.5% isolable yields, respectively.

Scheme 2.



Alk = Me, *i*-Pr.

Table 1. Mean bond lengths (Å) and bond angles (deg) in the coordination entity of the silicon atom and five-membered *C,O*-chelate ring of the cations in complexes **VIIa, VIIIa, VIIIc**, and **VIIId**)

Bond, angle	**VIIa**	**VIIIa**	**VIIIc**	**VIIId**
Si–O	1.848(2)	1.826(2)	1.840(2)	1.830(3)
Si–C	1.874(3)	1.861(4)	1.880(3)	1.875(4)
Si–Hlg	2.0740(14)	1.602(3)	1.5911 (16)	1.875(4)
O–C	1.285(3)	1.304(5)	1.287(3)	1.299(4)
N–C	1.296(4)	1.303(6)	1.312(3)	1.338(5)
N–C_{eq}[a]	1.473(4)	1.463(5)	1.467(3)	1.468(5)
OSi^1O	174.62(14)	176.3(2)	176.99(9)	171.69(13)
CSi^1C	128.1(2)	130.3(3)	125.99(12)	134.81(18)

[a] C_{eq} stands for the C atom attached to Si.

It was found that tetrafluoroborates **VIIIa–VIIId** could be synthesized by the reaction of neutral difluorides **IXa–IXd** with $BF_3 \cdot Et_2O$ (Scheme 2, route *a*). In its turn, the reverse reaction, i.e. conversion of tetrafluroborates **VIII** into difluorides **IX**, takes place in the reaction of tetrafluoroborates with anhydrous KF (Scheme 2, route *b*).

Reactions (2) usually form purer and better identified compounds with yields varying from 60 to about 100%. Note that a process analogous to reaction 2*b* was previously observed by Voronkov et al. [13] in the reaction of compounds $F_3Si(CH_2)_3NRR' \cdot BF_3$ with KF, forming trifluorosilanes $F_3Si(CH_2)_3NRR'$ and KBF_4.

$$\underset{\textbf{IXa–IXd}}{(LCH_2)_2SiF_2} \underset{b,\ KF}{\overset{a,\ BF_3\cdot Et_2O}{\rightleftarrows}} \underset{\textbf{VIIIa–VIIId}}{[(LCH_2)_2Si(F)]^+\ BF_4^-}. \qquad (2)$$

Attempted synthesis of the mononuclear bis-*C,O*-chelate $[(QonCH_2)_2Si(F)]Cl$ by the reaction of the previously unknown binuclear complex $\{[(QonCH_2)_2Si]_2O\}^{2+} \cdot 4Cl^- \cdot 2H_3O^+$ (**VId**) {Scheme 1, route *c* ($2Z^- = 3Cl^- \cdot H_3O^+$)} with $BF_3 \cdot Et_2O$ gave a neutral difluride $(QonCH_2)_2SiF_2$ (**IXd**) in 61% yield, rather than the expected ionic complex [reaction (3)].

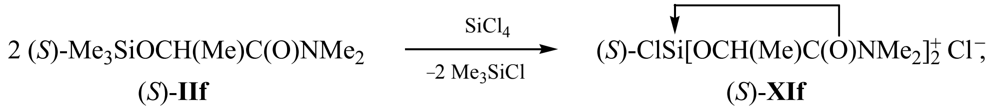
$$\underset{\textbf{VId}}{[(QonCH_2)_2SiOSi(CH_2Qon)_2]^{2+}\ 4Cl^- \cdot 2H_3O^+}$$

$$\xrightarrow{BF_3\cdot Et_2O} \underset{\textbf{IXd}}{(QonCH_2)_2SiF_2}. \qquad (3)$$

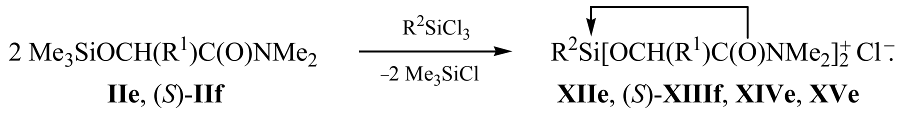
Reaction (3) is the second example of siloxane bond cleavage in a binuclear dicationic bis-C,O-chelate disiloxane complex. The first example of such transformation, which we described previously [8], involved the reaction of ditriflate $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot 2TfO^-$ (**IVc**) with $BF_3 \cdot Et_2O$ to form a mononuclear complex $[(BonCH_2)_2Si(F)]OTf$ (**Xc**). Note that boiling ditriflate **IVc** with $SOCl_2$ in benzene with the aim to prepare the mononuclear complex $[(BonCH_2)_2Si(Cl)]OTf$ resulted in no siloxane bond cleavage; instead, 85% of the starting ditriflate **IVc** was recovered. In its turn, hydrolysis of fluoride triflate **Xc** gives rise to the expected binuclear dicationic disiloxane $\{[(BonCH_2)_2Si(F)]_2O\}^{2+} \cdot 2TfO^-$ rather than the previously obtained difluoride **IXc** [14].

Thus, we prepared mononuclear monocationic bis-*C,O*-chelates $[(LCH_2)_2Si(Hlg)]^+Y^-$ containing a Si–Hlg covalent bond (Hlg = F, Cl).

Bis-*O,O'*-chelates. The first representatives of mononuclear monoanionic cationic bis-*O,O'*-chelates with a 2-hydroxyacid dimethylamide fragment were synthesized by the reaction of $SiCl_4$ [reaction (4)] and organic trichlorosilanes $RSiCl_3$ [reaction (5)] with O–$SiMe_3$ derivatives of glycolic and lactic acid dimethylamides (**IIe** and **IIf**, respectively) in a 1:2 ratio. Note that the reaction of (*S*)-$Me_3SiOCH(Ph)C(O)NMe_2$ with $SiCl_4$ was studied previously, but it gave a neutral monochelate five-coordinate (according to X-ray diffraction data) complex (*S*)-$Cl_3Si[OCH(Ph)C(O)NMe_2]$ [15].



$$\underset{(S)\text{-}\textbf{IIf}}{2\ (S)\text{-}Me_3SiOCH(Me)C(O)NMe_2} \xrightarrow[-2\ Me_3SiCl]{SiCl_4} \underset{(S)\text{-}\textbf{XIf}}{(S)\text{-}ClSi[OCH(Me)C(O)NMe_2]_2^+\ Cl^-}, \qquad (4)$$



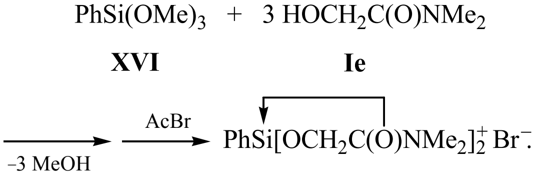
$$\underset{\textbf{IIe},\ (S)\text{-}\textbf{IIf}}{2\ Me_3SiOCH(R^1)C(O)NMe_2} \xrightarrow[-2\ Me_3SiCl]{R^2SiCl_3} \underset{\textbf{XIIe},\ (S)\text{-}\textbf{XIIIf},\ \textbf{XIVe},\ \textbf{XVe}}{R^2Si[OCH(R^1)C(O)NMe_2]_2^+\ Cl^-}. \qquad (5)$$

R^1 = H, R^2 = Me (**XII**); R^1 = R^2 = Me (**XIII**); R^1 = H, R^2 = *t*-Bu (**XIV**), R^1 = H, R^2 = Ph (**XV**).

The yields of reactions (4) and (5) were 58–88%. The structures of the products, except for (*S*)-**XIIIf**, were confirmed by X-ray diffraction.

Note that similar reactions of tetrahalogermanes $GeCl_4$ [15] and $GeBr_4$ [16] with disubstituted amides of lactic and mandelic acids gave, irrespective of the reagent ratio, to neutral *O,O'*-monchelates, namely, five-coordinate trihalohermanes $Hlg_3GeOCH(R)C(O)NMe_2$ (by X-ray diffraction data, Hlg = Cl, Br; R = Me, Ph).

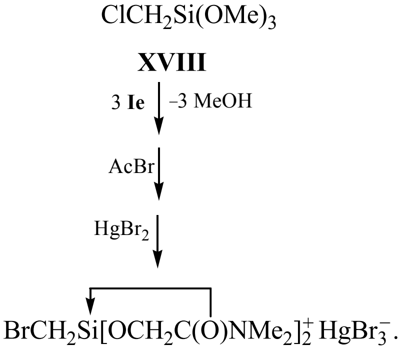
We suggested an alternative approach to cationic bis-O,O'-chelates via the reaction of organyltrialkoxysilanes with disubstituted amides of 2-hydroxyacids followed by treatment of the initially formed transesterification products (in situ) with acyl halides. Thus, a one-pot reaction of trimethoxy(phenyl)silane (**XVI**), amide $HOCH_2C(O)NMe_2$ (**Ie**), and acetyl bromide gave a cationic bis-O,O'-chelate **XVIIe** [reaction (6)].



$$\underset{\textbf{XVI}}{PhSi(OMe)_3} + \underset{\textbf{Ie}}{3\,HOCH_2C(O)NMe_2} \xrightarrow[-3\,MeOH]{} \xrightarrow{AcBr} PhSi[OCH_2C(O)NMe_2]_2^+Br^-. \quad (6)$$

XVIIe

Under the same conditions we reacted (chloromethyl)trimethoxysilane (**XVIII**) with amide **Ie** and acetyl bromide. The resulting oily product was treated with $HgBr_2$ to obtain a crystalline tribromomercurate $BrCH_2Si[OCH_2C(O)NMe_2]_2{}^+HgBr_3{}^-$ (**XIXe**) [reaction (7)]. Its structure was established by X-ray diffraction. Note that here chlorine in the chloromethyl group is replaced by bromine.



$$\underset{\textbf{XVIII}}{ClCH_2Si(OMe)_3} \xrightarrow[-3\,MeOH]{3\,\textbf{Ie}} \xrightarrow{AcBr} \xrightarrow{HgBr_2} BrCH_2Si[OCH_2C(O)NMe_2]_2^+HgBr_3^-. \quad (7)$$

XIXe

The yields of compounds **XVIIe** and **XIXe**, per starting trialkoxysilanes, were 85 and 37%, respecttively. The structure of the C,O- and O,O'-bischelate complexes obtained in the present work was proved by elemental analysis (except for compounds **XIV** and **XIXe**), IR and NMR spectroscopy, and X-ray diffraction analysis [except for **IXb, IXd**, and (*S*)-**XIIIf**].

IR spectroscopy. Evidence for the fact that the bichelate cationic complexes in focus contain a five-coordinate Si atom is provided by a low-frequency shift of the carbonyl absorption band at 1700–1400 cm^{-1} and appearance of an additional absorption band of the amide fragment. In particular, the IR spectra of solutions of cationic bis-C,O-chelates **VIIIa–VIIId** show in this range two absorption bands at 1630–1624 (s) and 1471–1478 cm^{-1} (m), related to associated stretching vibrations ν(C=O) and ν(C=N) of the $N\overset{\cdots}{—}C\overset{\cdots}{—}O$ of the chelate ring. Analogous bands were previously reported for binuclear dicationic bis-C,O-chelate disiloxane complexes **IV–VI** [6–8]. This fact is evidence showing that mononuclear complexes **VIIa–VIId**, like the mentioned binuclear complexes, involve an intraionic coordination bond O→Si.

The solid-phase spectra of bis-O,O'-chelates **XI–XV** contain two associated NCO vibration bands peaking at 1680–1670 (s) and 1470–1480 cm^{-1} (m). These bands are strongly broadened, which is probably explained by the phase state of the samples.

NMR spectroscopy. The ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of cationic bis-C,O-chelates **VIIIa–VIIId** and neutral difluorosilanes **IXa** and **IXd** correspond to the suggested structures. The ^{29}Si NMR signals of complexes **VIIIa–VIIId** are observed at δ_{Si} –55 to –63 ppm, and those of difluorosilanes **IXa** and **IXd** at δ_{Si} –117 to –130 ppm, which points to a five-coordinate state of silicon in ionic complexes **VIIIa–VIIId** and a six-coordinate state of silicon in neutral difluorosilanes **IXa** and **IXd** in the liquid phase [17, 18]. These results are consistent with our previously published data for tetrafluoroborate $\{[L^7CH_2]_2Si(F)\}^+BF_4^-$ (**VIIIb**) (δ_{Si} –57.9 ppm) [12] and diflurosilanes $[BonCH_2]_2SiF_2$ (**IXc**) (δ_{Si} –124.3 ppm) [14] and $[MeC(O)N(CHPhMe)CH_2]_2SiF_2$ (**XX**) (δ_{Si} –129.1 ppm) [19] and are evidence for an intramolecular O→Si coordination in these complexes in the liquid phase.

The signals of monoanionic cationic bis-O,O'-chelates **XI–XV, XVI**, and **XIX** are registered at δ_{Si} –62 to –76 ppm (for chlorosilane **XIf**, δ_{Si} ~ –95 ppm), and, therewith, diastereomers **XIf** and **XIIIf** give by two signals (δ_{Si} –94.1 and –94.6 ppm for **XIf** and –66.9 and –68.0 ppm for **XIIIf**). These data are consistent with the five-coordinate chelate structure of complexes **IX–XIII**.

Note that the signal of a neutral monochelate five-coordinate trichlorosilane $Cl_3SiOCH(Ph)C(O)NMe_2$ is registered at δ_{Si} –93.8 ppm [15].

X-ray diffraction study. The X-ray diffraction studies showed that the silylium cation complexes are almost all mononuclear. The binuclear structure was established only for cationic complex **VId** (Fig. 2) which is structurally quite similar to acetamidomethyl complex **VIa** reported in [8]. The two silicon-containing bischelate fragments in **VId** are turned with respect to each other by 93.5°. The structures of the Si^1 and Si^2 coordination entities are similar to those in the mononuclear complexes under consideration.

Unlike the studied cationic complexes, the Si atom in a neutral bis-C,O-chelate difluorosilane **IXa** is six-

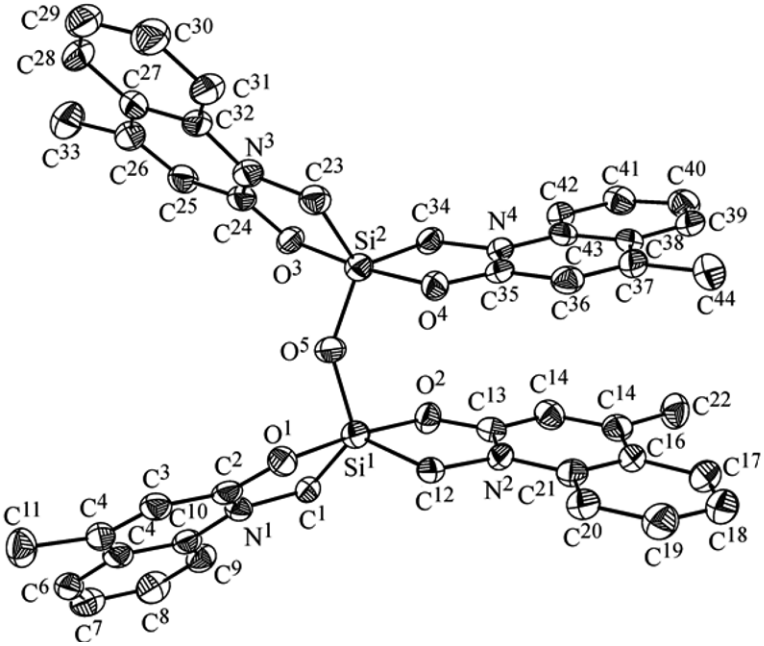


Fig. 2. General view of the dication of binuclear complex **VId** in crystal. Principal bond lengths (Å) and bond angles (deg): Si^1–O^5 1.636(3), Si^1–O^1 1.827(3), Si^1–O^2, 1.858(3), Si^1–C^1, 1.873(4), Si^1–C1^2 1.888(4), Si^2–O^5 1.618(3), Si^2–O^3 1.835(3), Si^2–O^4 1.855(3), Si^2–C^{34} 1.885(4), Si^2–C^{23} 1.886(4), O^1–C^2 1.300(4), O^2–C^{13} 1.295(4), O^3–C^{24} 1.300(5), O^4–C^{35} 1.297(4), N^1–C^2 1.337(5), N^1–C^{10} 1.397(5), N^1–C^1 1.461(5), N^2–C^{13} 1.343(5), N^2–C^{21} 1.404(5), N^2–C^{12} 1.468(5), N^3–C^{24} 1.337(5), N^3–C^{32} 1.384(5), N^3–C^{23} 1.458(5), N^4–C^{35} 1.343(5), N^4–C^{43} 1.400(5), N^4–C^{34} 1.488(4), Si^{2}O^{5}Si^1 144.08(18), O^{1}Si^{1}O^2 174.54(13), O^{3}Si^{2}O^4 173.93(13), C^{34}Si^{2}C^{23} 122.98(18), C^{1}Si^{1}C^{12} 124.76(17).

coordinate and has a distorted octahedral configuration (Fig. 3). The structure of the central coordination entity in complex **IXa** is like that we described previously for bis-C,O-chelate difluorosilanes **IXc** and **XX** [14, 19]. The Si coordination entity is not as symmetric as, for example, in complex **IXc** [14]. Actually, the Si^1–O^1 and Si^1–O^2 bond lengths in complex **IXa** [1.9277(14) and 1.9623(15) Å] more differ from each other than complex **IXc** [14] (1.960 and 1.967 Å). In their turn, the Si–F bond lengths in **IXa** differ from each other by 0.01 Å.

The structure of the coordination entity of the Si atom in all the mononuclear complexes, both C,O-chelate (Fig. 4, Table 1) and O,O-chelate (Figs. 5–8, Table 2) is a distorted trigonal bipyramid. The silylium cation in these complexes has *C*2 symmetry, the axial Si–O$_{ax}$ bond lengths vary no more than 0.02 Å on average.

The most essential deviations from an ideal *C*2 symmetry are observed for structure **XIVe**, where the axial both lengths differ from each other by more than 0.03 Å [1.8326(17) and 1.8680(17) Å] because of the presence of a bulky *tert*-butyl substituent at the silicon atom. The deviation of Si from the equatorial plane in the mononuclear complexes is no more than 0.04 Å. The axial Si–O bonds are longer by 0.18–0.22 Å compared to the standard value (1.64 Å) [20]. The shortest Si–O$_{ax}$ bonds are observed in complex **VIIIa**, where the Si atom is bonded to fluorine, and the longest Si–O$_{ax}$ bonds are characteristic of structures **XIIe** and **XVe**, where this atom is bonded to a less electronegative atom. Therewith, the range of variation of Si–O$_{ax}$ bond lengths is fairly narrow. These bond lengths can also be affected by cation–anion contacts, hydrogen bonds, and other weak interatomic interactions in the crystal.

The equatorial bonds Si–O$_{eq}$ in the mononuclear cationic complexes are only slightly longer that the standard value; and the equatorial Si–C, Si–F, and Si–Cl bond lengths are close to standard values [20].

In certain structures the interactomic distances between the C^l and Si atoms are close to the sum of the van der Waals radii of these elements (3.68 Å) [21]. Thus, the Si^1···C^{6S} distance in **XVe** is 3.727(2) Å, and the C^{6S}Si^{1}C^{01} angle is 159.43(9)°. This finding can be interpreted as evidence for additional weak Si···Cl

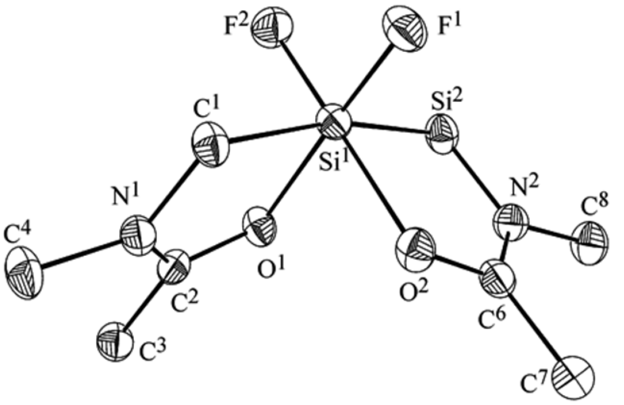


Fig. 3. General view of difluoride **IXa** in crystal (H atoms are not shown). Principal bond lengths (Å) and bond angles (deg): $Si^1–F^1$ 1.6693(12), $Si^1–F^2$ 1.6722(13), 1.9277(14), $Si^1–O^2$ 1.9623(15), $Si^1–C^1$ 1.914(2), $Si^1–C^5$ 1.920(2), $O^1–C^2$ 1.287(2), $O^2–C^6$ 1.285(2), $F^1Si^1O^1$ 174.23(6), $F^2Si^1O^2$ 174.34(6), $F^1Si^1F^2$ 94.53(7), $C^1Si^1C^5$ 167.56(10).

coordination with a solvate chloroform molecule. Furthermore, the Si atom in structure **VIIIc** forms a shortened contact with the F^2 atom of the BF_4^- anion [3.345(4) Å], and the $F^2Si^1F^1$ angle is 161.6(1)° (the sum of the van der Waals radii of Si and F is 3.33 Å [21]). Apparently, the additional coordination in the studied cationic complexes is an unfavorable process. Instead of forming such bonds, the F, Cl, and Br atoms of the counterions are involved in interaction with the antibonding orbital of the O–C–C and N–C=O fragments of the five-membered chelate ring. This is evidenced in structures **VIIa, VIIIa**, (*S*)-**XIf**, **XIIe, XVe**, and **XIXe** by short interatomic distances Hlg···C (Hlg = F, Cl, Br) equal to 3.1–3.4 Å. In structure **VIIIc**, analogous interaction with the O^2 atom of a neighboring molecule is observed [$C^2···O^2$ distance 3.217(5) Å].

Structures **XVe** (Fig. 8) and **XVIIe** contain the same anion but different counterions (Cl^- and Br^-). In structure **XVIIe** the Si atom is disposed on a second-order crystallographic axis, whereas in structure **XVe** it occupies a general position.

The principal bond lengths and angles in the central coordination entities of our synthesized cationic C,O- and O,O'-bischelate complexes are listed in Tables 1 and 2. Their structures are shown in Figs. 1 and 4–8.

Structural analysis of spirocyclic cations is performed in the framework of the Holmes's approach which describes the coordination polyhedron as a point on the potential energy surface of a hypothetical polytopic rearrangement (method of dihedral angles [22]). During this rearrangement the coordination polyhedron of the Si atom changes from an ideal trigonal bipyramid to an ideal square pyramid. The rearrangement coordinate is the sum of dihedral angles formed by the normals to the edge-shared facets of the Si coordination polyhedron. This sum is usually related to those of ideal trigonal bipyramid (%TBP) and square pyramid (%SP), and the resulting relative deviations are plotted against each other. Considering a series of complexes with similar coordination polyhedrons one can describe a part of the pseudorotation trajectory. The %TBP and %SP values are listed in Table 3, and the plot of %SP against %TBP is presented in Fig. 9.

All the complexes studied show linear dependences of %SP on %TBP, and the deviation (Δ) is no larger than 1.18%. Thus, the variation of the %SP and %TBP values is described in terms of Berry pseudorotation (BPR). The deviation of the Si polyhedron from ideal bipyramidal geometry is 12–37%. Consequently, the

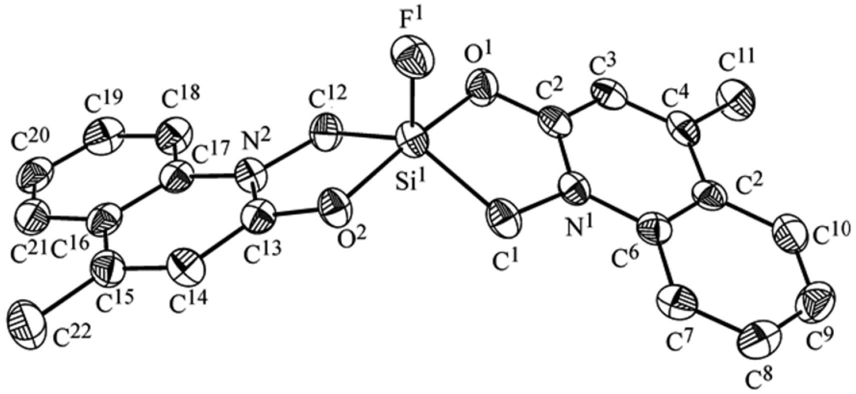


Fig. 4. General view of the cation in structure **VIIId**, with atoms represented as 50% probability thermal ellipsoids (H atoms are not shown).

Table 2. Mean bond lengths (Å) and bond angles (deg) in the coordination entity of the silicon atom and five-membered O,O-chelate ring of the cations in complexes **XIf, XIIe, XIVe, XVe, XVIIe**, and **XIXe**

Bond, angle	(*S*)-**XIf**·Py·HCl	**XIIe**	**XIVe**	**XVe**	**XVIIe**	**XIXe**
$Si^1–O_{ax}{}^a$	1.800(2)	1.8472(2)	1.8503(17)	1.847 (5)	1.839(2)	1.842 (6)
$Si^1–O_{eq}{}^a$	1.655(2)	1.6663(8)	1.6675(17)	1.665 (4)	1.657(2)	1.666 (6)
$Si^1–X$	2.0775(10)	1.8515(11)	1.888 (3)	1.860 (7)	1.874(4)	1.864 (8)
$C–O_{ax}{}^a$	1.294(4)	1.2803(12)	1.274(3)	1.280 (7)	1.277(3)	1.281 (9)
$C–O_{eq}{}^a$	1.427(4)	1.4104(12)	1.407 (3)	1.417 (7)	1.412(3)	1.411 (9)
C–C	1.498 (5)	1.5065(14)	1.512 (3)	1.490 (9)	1.500(4)	1.508 (10)
$O_{eq}Si^1O_{eq}{}^a$	130.11 (12)	122.99 (4)	120.28 (9)	127.9 (2)	123.43(16)	125.7 (3)
$O_{ax}Si^1O_{ax}{}^a$	174.34 (11)	171.11 (4)	168.61 (9)	169.0 (2)	172.08(14)	169.7 (3)

[a] O_{eq} and O_{ax} stand for the axial and equatorial O atoms attached to Si.

studied series of complexes describes the initial BPR stage. Therewith, the C,O-chelate complexes are closer to an ideal trigonal bipyramid than the O,O-chelates. It should be noted that different BPR coordinates are observed not only for similar cations in different crystals (**XVe** and **XVIIe**), but also for independent cations in the same structure (**XVIIe**_1 and **XVIIe**_2), **VIIIa**_1 and **VIIIa**_2). This difference was earlier

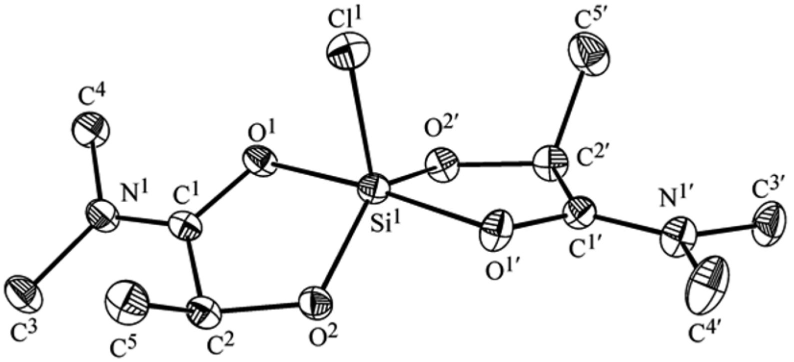


Fig. 5. General view of the cation in structure (*S*)-**XIf**·Py·HCl, with atoms represented as 50% probability thermal ellipsoids (H atoms are not shown).

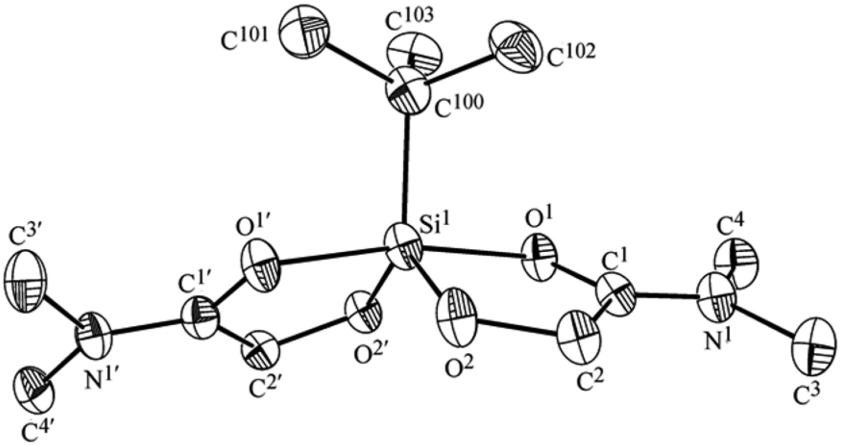


Fig. 6. General view of the cation in structure **XIVe**, with atoms represented as 50% probability thermal ellipsoids (H atoms are not shown).

Table 3. Deviations of %TBP and %SP for certain synthesized compounds

Polyhedron[a]	%TBP	%SP	Δ, %
VIc_1	15.63	14.57	1.06
VIc_2	12.22	12.22	0
VIIa	20.36	20.36	0
VIIIa_1	17.58	17.58	0
VIIIa_2	27.01	27.01	0
VIIIb	13.67	13.67	0
VIIIc	36.69	36.69	0
XIf	24.99	24.99	0
XIIe	16.99	16.99	0
XIVe	16.75	15.56	1.18
XVe	28.95	28.95	0
XVIIe_1	21.79	21.51	0.28
XVIIe_2	15.68	15.68	0
XIXe	23.76	23.76	0

[a] Notations 1 or 2 relate to different (like in binuclear complex **VIc**) or crystallographically independent Si atoms.

noted by Bassindale et al. [23] in a cationic C,O-chelate complex with four independent anions.

EXPERIMENTAL

The IR spectra of 5% solutions were registered on a Specord IR-75 instrument in KBr or CaF_2 cells. The solid-phase spectra were measured on a Bruker Tensor 27 FTIR spectrophotomer with an attenuated total reflectance module. The ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of CD_2Cl_2, $CDCl_3$, DMSO-d_6 solutions were obtained on a Varian XL-400 spectrometer (400.1, 100.6, 396, and 79.5 MHz, respectively). The ^1H, ^{13}C, and ^{29}Si NMR spectra were measured against internal Me_4Si, and the ^{19}F spectra, against external $BF_3{\cdot}Et_2O$.

Commercial trichloro(methyl)silane, *tert*-butyltrichlorosilane, trichloro(phenylsilane), and tetrachlorosilane were used. Trimethoxy(phenyl)silane (**XV**) was distilled before use.

N,N-Dimethylhydroxyacetamide (**Ie**) [24], *N*-methyl-*N*-(trimethylsilyl)acetamide (**IIa**) [25], 2,2-dimethyl-3-(trimethylsilyl)benzo[1,3]oxazin-4-one (**IIc**) [26], 4-methyl-1-(trimethylsilyl)quinolin-2(1*H*)-one (**IId**) [27], *N,N*-dimethylamides of *O*-(trimethylsilyl)glycolic (**IIe**) [28], racemic *O*-(trimethylsilyl)lactic (**IIf**) [15], *O*-(trimethylsilyl)-(*S*)-lactic [(*S*)-**IIf**] [28] acids, as well as dichlorobis(chloromethyl)silane [29] and (chloromethyl)trimethoxysilane (**XVIII**) [30] were prepared by known procedures.

Synthesis of hydrogen dichloride $\{[MeC(O)N(Me){\cdot}CH_2]_2Si(Cl)\}^+HCl_2^-$ (**VIIa**) [10], tetrafluoroborate $[(L^7CH_2)_2Si(F)]BF_4$ (**VIIIb**) [12], and difluoride $(BonCH_2)_2SiF_2$ (**IXc**) [14] was described earlier.

The principal crystal data and results of refinement for 12 complexes studied by X-ray diffraction are listed in Tables 4 and 5. The structures were solved by the direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms. Positions of alkyl and phenyl hydrogens were calculated using geometric considerations

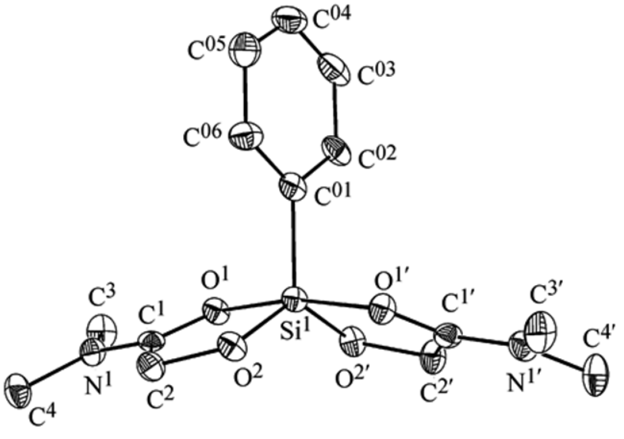


Fig. 7. General view of the cation in structure **XVf**, with atoms represented as 50% probability thermal ellipsoids (H atoms are not shown).

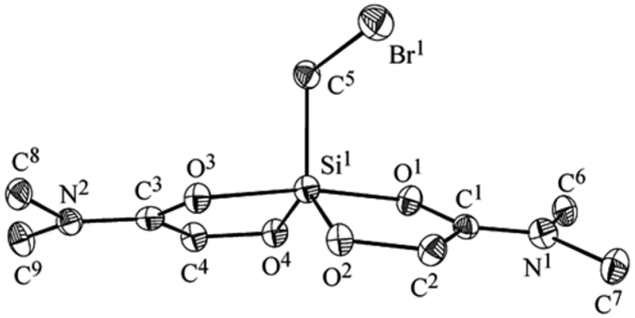


Fig. 8. General view of the cation in structure **XIXe**, with atoms represented as 50% probability thermal ellipsoids (H atoms are not shown).

and refined riding on their attached carbon atoms [U_{eq}(H) = 1.2U_{eq}(C)]. The H atoms in the anions HCl_2^-, cations H_3O^+, water molecules **VId**, as well as pyridinuim fragment in (*S*)-**XIf** were revealed by difference Fourier synthesis, and their thermal parameters were refined as above [U_{eq}(H) = 1.5U_{eq}(O)]. All calculations were performed using SHELXTL-97 V.5.10 [31].

Bis[(*N*-methylacetamidomethyl]fluorosilylium tetrafluoroborate (VIIIa). *a.* To a solution of 5.8 g of *N*-$SiMe_3$-*N*-methylacetamide **IIa** in 10 ml of CH_2Cl_2 at 0°C we added dropwise 4.2 g of $(ClCH_2)_2SiCl_2$, the mixture was left to stand overnight at room temperature and then vacuum-evaporated. Chloroform, 15 ml, and a solution of 4.2 g of $NaHCO_3$ in 40 ml of water were added to the residue. After a day the organic layer was dried with calcinated K_2CO_3, the solvent was evaporated, the residue was treated with 3.0 g of $BF_3·Et_2O$ and heated until ether no longer distilled. The residue was boiled in 15 ml of a (1:1) benzene–acetonitrile mixture, cooled, filtered, and the filtrate was vacuum-evaporated. The oil that remained was dissolved in 3 ml of ethanol, 10 ml of ether was then added, and the crystals were filtered off to obtain 0.6 g (10%) of tetrafluoroborate **VIIIa**, mp 168–170°C (benzene–acetonitrile, 5:1). Found, %: C 30.93; H 5.28; N 8.87. $C_8H_{16}N_2BF_5O_2Si$. Calculated, %: C 31.38; H 5.27; N 9.15.

b. To a solution of 5.8 g of amide **IIa** in 10 ml of dry CH_2Cl_2 at 0°C we added dropwise with stirring 4.2 g of $(ClCH_2)_2SiCl_2$, and the mixture was left to stand for 24 h at room temperature. Compound **IIIa** precipitated and filtered off (4.9 g, 90%), dissolved in 15 ml of absolute methanol, 4 g of triethylamine was added dropwise to a stirred solution, and the resulting mixture was boiled for 2 h. After a day it was filtered off, the filtrate was vacuum-evaporated, and the residue was treated with 3 ml CH_2Cl_2 and 3.0 g $BF_3·Et_2O$ and heated for 20 min until solvents no longer distilled. The residue was boiled for 5 min in 30 ml of a 2:1 benzene–acetonitrile mixture, the solution was filtered, and the filtrate was evaporated. The oil that remained was boiled in 15 ml of the above solvent mixture, the solution was cooled to room temperature and filtered, and the solvent was vacuum-evaporated. The residue was triturated with 20 ml of ether and 5 drops of acetonitrile to obtain 2.4 g (39%) of tetrafluoroborate **VIIIa**, mp 163–166°C (ethanol). IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1620, 1490 (NCO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.11 s (6H, CH_3), 2.24 br.s (4H, CH_2), 3.23 s (6H, CH_3N). ^{13}C NMR spectrum ($CDCl_3$), $δ_C$, ppm: 16.13 [$CH_3C(O)$], 37.28 d (NCH_2, $^2J_{CF}$ 10.8 Hz), 37.49 (NCH_3), 176.17 (C=O). ^{19}F NMR spectrum ($CDCl_3$), $δ_F$, ppm: –111.7 (SiF), –153.0 (BF_4). ^{29}Si NMR spectrum ($CDCl_3$), $δ_{Si}$, ppm: –59.7 d ($^1J_{SiF}$ 244.9 Hz). Single crystals of tetrafluoroborate **VIIIa** for X-ray diffraction analysis were obtained by crystallization from ethanol.

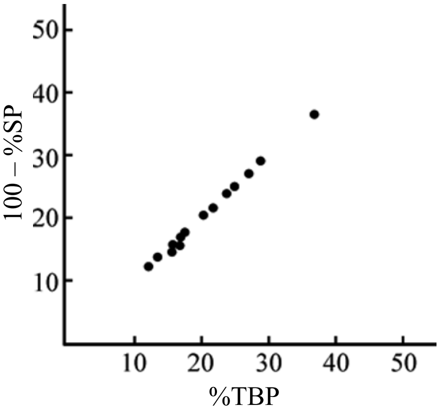


Fig. 9. Dependence between % SP and %TBP.

Bis[(*N*-methylacetamido)methyl]difluorosilane (IXa). To a solution of 0.75 g of tetrafluroborate **VIIIa** in 5 ml of acetonitrile we added 0.29 g of anhydrous KF. The reaction mixture was boiled for 4 h, the undissolved residue was filtered off, and the filtrate was vacuum-evaporated to obtain 0.42 g (72%) of difluride **IXa**, mp 208–211°C (benzene–acetonitrile, 12:1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1620, 1510 (NCO). ^1H NMR spectrum ($CDCl_3$) δ, ppm: 2.09 s (6H, CH_3), 2.26 br.s (4H, CH_2), 3.13 s (6H, CH_3N). ^{13}C NMR spectrum ($CDCl_3$), $δ_C$, ppm: 16.79 [CH_3C (O)], 37.83 (NCH_3), 44.01 t (NCH_2, $^2J_{CF}$ 51.5 Hz), 172.24 (C=O). ^{19}F NMR spectrum ($CDCl_3$): $δ_F$ –111.75 ppm. ^{29}Si NMR spectrum ($CDCl_3$) $δ_{Si}$, ppm: –129.72 t ($^1J_{SiF}$ 260.9 Hz). Found, %: C 40.31; H 6.75; N 11.77. $C_8H_{16}N_2F_2O_2Si$. Calculated, %: C 40.32; H 6.77; N 11.75. Single crystals of difluoride **IXa** for X-ray diffraction analysis were obtained by crystallization from benzene.

Bis(2-oxoperhydroazepinomethyl)fluorosilylium tetrafluoroborate (VIIIb). To a suspension of 0.2 g of difluorosilane **IXb** in 2 ml of benzene we added to 0.11 g of $BF_3·Et_2O$. The reaction mixture was boiled for 3 h, evaporated in a vacuum, and the residue was crystallized by trituration with 5 ml of ether to obtain 0.2 g (82%) of tetrafluoroborate **VIIIb**, mp 214–217°C

Table 4. Principal crystal data for structures **VId, VIIa, VIIIa, VIIIc**, (*S*)-**XIf**, and **XIIe**

Parameter	(*S*)-**XIf**	**XIIe**	**VId**	**VIIa**	**VIIIa**	**VIIIc**
Brutto formula	$C_{15}H_{26}Cl_3N_3O_4Si$	$C_9H_{20}Cl_2N_2O_4Si$	$C_{48}H_{55}Cl_{10}N_5O_9Si_2$	$C_8H_{17}Cl_3N_2O_2Si$	$C_8H_{16}BF_5N_2O_2Si$	$C_{22}H_{24}BF_5N_2O_4Si$
Molecular weight	446.83	319.26	1256.65	307.68	306.13	514.33
T, K	100	100	120	120	120	120
Space group	$P6_3$	$P2_1/c$	P-1	$P4_{31}$	$Ibca$	$P2_1/n$
Z	6	4	2	4	16	4
a, Å	18.1132(13)	14.1786(6)	11.414(3)	6.9558(11)	13.164(4)	12.177(2)
b, Å	18.1132(13)	9.8291(4)	15.254(4)	6.9558(11)	20.419(6)	10.296(2)
c, Å	11.3261(14)	11.1100(5)	18.523(5)	29.219(7)	20.770(7)	19.190(4)
α, deg	90.00	90.00	83.262(6)	90.00	90.00	90.00
β, deg	90.00	102.0680(10)	76.308(6)	90.00	90.00	106.54(3)
γ, deg	120.00	90.00	68.309(6)	90.00	90.00	90.00
V, Å^3	3218.1(5)	1514.09(11)	2909.9(12)	1413.7(4)	5583(3)	2306.4(8)
d_{calc}, g cm^{-3}	1.383	1.401	1.434	1.446	1.457	1.481
μ, cm^{-1}	5.07	5.15	5.76	7.22	2.24	1.75
F(000)	1404	672	1296	640	2528	1064
2θ$_{max}$, deg	61	66	52	60	60	56
Reflections measured	25777	20377	25436	9069	10441	5381
Unique reflections	6353	5804	11315	2003	3906	5127
Reflections with $I > 2\sigma(I)$	4391	4757	6148	1414	1550	3350
Number of refined parameters	242	172	675	108	203	412
R_1	0.0550	0.0321	0.0584	0.0501	0.0994	0.0558
wR_2	0.1149	0.0875	0.1216	0.1025	0.2863	0.1282
GOOF	1.014	1.026	1.002	0.971	0.889	1.043
Residual electron density, e Å^{-3} (d_{min}/d_{max})	0.484/–0.436	0.526/–0.339	0.456/–0.460	0.608/–0.311	1.258/–0.613	0.438/–0.358

(benzene–acetonitrile, 4:1) (mp 217–220°C [12]). IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1620, 1510 (NCO).

Bis(2-oxoperhydroazepinomethyl)difluorosilane (IXb). *a*. A suspension of 3 g of crude dichlorosilane **IIIb** [12], 1.8 g of isopropanol, 3 g of triethylamine, and 15 ml of benzene was boiled for 2 h. After a day the residue was filtered off, the filtrate was evaporated in a vacuum, the residue was dissolved in 3 ml of benzene, treated with 1.22 g of $BF_3·Et_2O$, heated until complete removal of ether and benzene, and boiled with 15 ml of benzene. The hot solution was filtered

Table 5. Principal crystal data for structures **VIIId, IXa, XIVe, XVe, XVIIe, XIXe**

Parameter	**VIIId**	**IXa**	**XIVe**	**XVe**	**XVIIe**	**XIXe**
Brutto formula	$C_{24}H_{23}BF_5N_3O_2Si$	$C_8H_{16}F_2N_2O_2Si$	$C_{24}H_{51}Cl_3N_4O_8Si_2$	$C_{16}H_{23}Cl_7N_2O_4Si$	$C_{14}H_{21}BrN_2O_4Si$	$C_9H_{18}Br_4HgN_2O_4Si$
Molecular weight	519.35	238.32	686.22	583.60	389.33	766.57
T, K	120	120	120	100	100	100
Space group	$P2_12_12_1$	$P2_1/c$	$C2/m$	Cc	$Pnna$	P-1
Z	4	4	4	4	8	2
a, Å	8.0145(16)	6.7230(15)	18.047(2)	15.6892(15)	13.7295(7)	7.5843(7)
b, Å	12.943(3)	12.637(2)	27.767(3)	14.3073(13)	21.0502(10)	10.9284(10)
c, Å	23.074(5)	12.931(3)	7.2012(8)	11.3660(10)	12.0109(6)	12.2002(11)
α, deg	90.00	90.00	90.00	90.00	90.00	110.690(2)
β, deg	90.00	91.601(5)	94.497(2)	92.126(2)	90.00	100.237(2)
γ, deg	90.00	90.00	90.00	90.00	90.00	94.038(2)
V, Å^3	2393.6(8)	1098.2(4)	3597.5(7)	2549.6(4)	3471.3(3)	921.13(15)
d_{calc}, g cm^{-3}	1.441	1.441	1.267	1.520	1.490	2.764
μ, cm^{-1}	1.65	2.26	3.67	8.51	24.55	171.08
F(000)	1072	504	1464	1192	1600	704
2θ$_{max}$, deg	54	56	60	52	61	58
Reflections measured	2782	7782	20932	3841	34540	21815
Unique reflections	2782	2621	5305	3888	5309	4899
Reflections with $I > 2\sigma(I)$	1821	1852	2764	3464	3207	3956
Number of refined parameters	325	200	197	276	239	194
R_1	0.0487	0.0639	0.0470	0.0563	0.0466	0.0424
wR_2	0.1008	0.1645	0.1012	0.1591	0.1262	0.1170
GOOF	1.039	1.008	0.987	1.053	1.004	1.056
Residual electron density, e Å^{-3} (d_{min}/d_{max})	0.312/–0.199	1.560/–0.298	0.647/–0.388	0.755/–0.367	1.043/–0.569	2.911/–2.413

off, the solvent was evaporated, and the residue was crystallized by trituration with 5 ml of ether to obtain 0.3 g (11%) of difluoride **IXb**, mp 157–160°C (benzene–acetonitrile, 4:1).

b. To 0.3 g of a solution of tetrafluoroborate **VIIIb** in 2 ml of acetonitrile we added 0.09 g of anhydrous KF. The reaction mixture was boiled for 11 h, the solveтe was removed in a vacuum, the residue was dissolved in 10 ml of ether, and the solution was filtered. The filtrate was evaporated in a vacuum, the residue was crystallized by trituration with 3 ml of ether, and the crystals were filtered off to obtain 0.18 g (71%) of difluoride **IXb**, mp 162–164°C (benzene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1620, 1510. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.49–1.98 m (12H, $H^{4–6}$), 2.40 br.s (4H, H^3), 2.56 br.s (4H, NCH_2), 3.53 br.s (4H, H^7). Found, %: C 40.31; H 6.75; N 11.77. $C_8H_{16}N_2F_2O_2Si$. Calculated, %: C 40.32; H 6.77; N 11.75. The spectral characteristics of difluoride **IXb** obtained by methods *a* and *b* were coincident.

Bis[(2,2-dimethyl-4-oxo-4*H*-benzo[1,3]oxazin-3-yl)methyl]fluorosilylium tetrafluoroborate (VIIIc). To a solution of 0.45 g of diflurosilane **IXc** [14] in a mixture of 4 ml of toluene and 2 ml of acetonitrile we added dropwise 0.14 g of $BF_3·Et_2O$. The mixture was boiled for 8 h, cooled, the crystal that formed were filtered off, and vacuum-dried to obtain 0.48 g (93%) of tetrafluoroborate **VIIIc**, mp 241–245°C (benzene–acetonitrile, 5:1). IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1630, 1520 (NCO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 s and 1.83 s [12H, $C(CH_3)_2$], 2.95, 3.49 d.t (4H, NCH_2, $^2J_{HH}$ 16.7, $^2J_{HH}$ 5.2 Hz), 7.81 d (1H, H^9, $^3J_{HH}$ 7.9 Hz), 7.63 t (1H, H^8, $^3J_{HH}$ 7.9 Hz), 7.18 t (1H, H^7, $^3J_{HH}$ 7.9 Hz), 7.04 d (1H, H^6, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.39 d (NCH_2, $^2J_{CF}$ 12.3 Hz), 22.82, 25.3 [$(CH_3)_2$], 92.91, 110.73, 123.25, 128.62 (C^2, C^5, C^7, C^6), 117.97, 138.33, 155.97 (C^9, C^8, C^{10}), 166.15 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –112.08 (Si–F), –151.51 (BF_4). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: –56.1 t ($^1J_{SiF}$ 252.4 Hz). Found, %: C 51.64; H 4.95; N 5.12. $C_{22}H_{24}BF_5N_2O_4Si$. Calculated, %: C 51.37; H 4.70; N 5.44. Single crystals of tetrafluoroborate **VIIIc** for X-ray diffraction study were obtained by crystallization from a 5:1 benzene–acetonitrile mixture.

Bis[(2,2-dimethyl-4-oxo-4*H*-benzo[1,3]oxazin-3-yl)methyl]difluorosilane (IXc). *a*. Synthesized similarly to difluorosilane **IXb** from 0.6 g of crude dichlorosilane **IIIc** [14], 1.8 g of isopropanol, 3 g of triethylamine, and 1.1 g of $BF_3·Et_2O$. Yield 0.56 g (100%), mp 247–248°C (benzene) (mp 247–250°C [14]).

b. To a solution of 0.48 g of tetrafluoroborate **VIIIc** in 2 ml of acetonitrile we added dropwise 0.11 g of anhydrous KF, the mixture was boiled for 8 h, after which 6 ml of benzene was added, and boiling was continued for an additional 15 min. The undissolved residue was filtered off, and the transparent filtrate was vacuum-evaporated to obtain 0.39 g (94%) of difluoride **IXc**, mp 243–250°C (mp 247–250°C [14]).

c. To a solution of 0.45 g of fluoride triflate $[(BonCH_2)_2Si(F)]OTf$ [8] in 5 ml of chloroform we added with stirring 0.013 g of water and 0.07 g of triethylamina. After a day 3 ml of water was added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with 4 ml of chloroform. The combined organic layers were dried over calcinated K_2CO_3, and the solvent was vacuum-evaporated to obtain 0.15 g (92%) of difluoride **IXc**, mp 245–247°C (benzene) (mp 247–250°C [14]). The spectral characteristics of compound **IXc** synthesized by methods *a–c* and isolated in a yield of 45% from the reaction by Scheme 2, route *a* [14], were concident.

Bis[4-methyl-2-oxo-1*H*-quinolin-1-yl)methyl]-fluorosilylium tetrafluoroborate (VIIId). A mixture of 0.05 g of difluoride **IXd**, 0.03 g of $BF_3·Et_2O$, and 2 ml of toluene was boiled for 18 h and vacuum-evaporated. The residue was dissolved with 3 ml of ether, and the filtrate was filtered to obtain 0.03 g (51.5%) of tetrafluoroborate **VIIId**, mp 257–260°C (toluene). IR spectrum (CH_3CN), ν, cm^{-1}: 1630, 1520 (NCO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 s (6H, CH_3), 3.28 br.s (4H, NCH_2), 6.72 s (2H, CH=), 7.81 d (1H, H^9, $^3J_{HH}$ 7.9 Hz), 7.41 t (1H, H^8, $^3J_{HH}$ 7.9 Hz), 7.71 t (1H, H^7, $^3J_{HH}$ 7.9 Hz), 7.82 d (1H, H^6, $^3J_{HH}$ 7.9 Hz). Found, %: C 55.10; H 4.18; N 6.01. $C_{22}H_{20}BF_5N_2O_2Si$. Calculated, %: C 55.25; H 4.21; N 5.86. Single crystals of tetrafluoroborate **VIIId** for X-ray diffraction analysis were obtained by crystallization from toluene.

1,1,3,3-Tetrakis[(4-methyl-2-oxo-1*H*-quinolin-1-yl)methyl]-1,3-disiloxanedihydroxonium tetrachloride (VId). To a solution 8.05 g of *N*-$SiMe_3$-4-methylquinolin-2(1*H*)-one (**IId**) [27] in 25 ml of dry chloroform, colled with ice water, we added dropwise 3.43 g bis(chloromethyl)dichlorosilane. Chloroform, 15 ml, was added to the precipitate that formed in a few minutes, and the mixture was stirred for 3 h. After a day the precipitate was filtered off, washed with ether, and recrystallized from 300 ml of a 1:2:3 toluene–acetonitrile–chloroform mixture to obtain 8 g (69%) of compound **VId** as disolvate **VId**$·CHCl_3·CH_3CN$, mp 253–255°C. The structure of the disolvate was established by elemental analysis and X-ray diffraction. ^1H NMR spectrum (CD_3CN), δ, ppm: 2.58 s (12H, CH_3), 3.04 m (8H, NCH_2), 6.96 m (4H, CH=), 7.8–7.92, 8.08–8.3, 8.34–8.44 m (16H, 4Ar). Found, %: C 50.88; H 4.25; N 6.71. $C_{47}H_{50}Cl_7N_5O_7Si_2$. Calculated, %: C 51.26; H 4.58; N 6.36.

Bis[(4-methyl-2-oxo-1*H*-quinolin-1-yl)methyl]-difluorosilane (IXd). To a suspension of 0.55 g of disolvate **VId**$·CHCl_3·CH_3CN$ in 2 ml of chloroform we added 0.14 g of $BF_3·Et_2O$, and the mixture was boiled 1 h. After a day the reaction mixture was diluted with 3 ml of chloroform and brought to boiling. The undissolved precipitate was separated (0.3 g), the chloroform solution was evaporated, and the residue was recrystallized from a 1:1 chloroform–ethanol mixture to obtain 0.25 g (61%) of difluoride **IXd**, decomp. point 350°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1635, 1540, 1510 (NCO, Ar). ^1H NMR spectrum (CD_3CN), δ, ppm: 2.79 s (6H, CH_3), 3.82 m (4H, NCH_2), 7.19 s (2H, CH=), 7.82 d (2H, H^9, $^3J_{HH}$ 7.9 Hz), 7.42 t (2H, H^8, $^3J_{HH}$ 7.9 Hz), 7.72 t (2H, H^7, $^3J_{HH}$ 7.9 Hz), 7.83 d (2H, H^6, $^3J_{HH}$ 7.9 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: –131.2 t ($^1J_{SiF}$ 258.4 Hz). Found, %: C 64.68; H 5.20; N 6.57. $C_{22}H_{20}F_2N_2O_2Si$. Calculated, %: C 64.37; H 4.91; N 6.82.

Reaction of 4-methyl-1-(trimethylsilyl)quinolin-2(1*H*)-one (IId) with bis(chloromethyl)dichlorosilane. To a solution of 4.6 g of compound **IId** in 40 ml of $CHCl_3$ was added dropwise 2.0 g of $(ClCH_2)_2 \cdot SiCl_2$. The solution was stirred for 2 h, after which 60 ml of $CHCl_3$ and, in small portions, a solution of 8.4 g of $NaHCO_3$ in 100 ml of water were added. After a day the layers were separated, the aqueous layer was washed with $CHCl_3$ (2×25 ml), the chloroform extracts were dried with calcinated K_2CO_3, and the solvent was vacuum-evaporated. The residue was transferred into a distillation flask, and 6 ml of CH_2Cl_2 and 3 g of $BF_3{\cdot}Et_2O$ were added. Self-heating was observed, which was accompanied by distillation of a mixture of CH_2Cl_2 and ether (7 ml). The residue that crystallized was boiled with 50 ml of $CHCl_3$ and vacuum-evaporated. The residue was recrystallized from 40 ml of acetonitrile to obtain 2.1 g (44%) of tetrafluoroborate **VIIId**, mp 258–260°C (CH_3CN). The structure was established by X-ray diffraction. The oil that remained after vacuum evaporation of the mother liquor was triturated with 15 ml of ether, and the crystals that formed were separated to obtain 1.5 g (36.5%) of difluoride **IXd**, mp 298–300°C (ethanol–acetonitrile, 4:1). The spectral characteristics of tetrafluoroborate **VIIIc** and difluoride **IXd**, isolated in this experiment and synthesized as described above were coincident.

Bis[1-(dimethylcarbamoyl)ethoxy]chlorosilylium chloride [(*S*)-XIf]. To a solution of 5.0 g of $SiCl_4$ in 10 ml of hexane we added dropwise a solution of 5.7 g of *N,N*-dimethylamide of *O*-$SiMe_3$-(*S*)-lactic acid in 10 ml of hexane. The precipitate that formed was filtered off, washed with hexane (2×10 ml), and vacuum-dried to obtain 4.0 g (81%) of chloride (*S*)-**XIf**, mp 145–146°C (MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1679 s, 1630 s, 1454 m, 1253 m, 1125 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.54 d (6H, $C\underline{H}_3CH$, $^3J_{HH}$ 6.8 Hz), 3.32 s and 3.37 s [12H, $(CH_3)_2N$], 5.23 q (2H, CH, $^3J_{HH}$ 6.8 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 19.96 ($\underline{C}H_3CH$), 39.23, 39.45 [$(CH_3)_2N$], 69.39 (CH), 177.81 (C=O). ^{29}Si NMR spectrum (CD_3CN), δ_{Si}, ppm: –94.07, –94.59. Found, %: C 36.61; H 5.88; Si 8.16. $C_{10}H_{20}Cl_2N_2O_4Si$. Calculated, %: C 36.26; H 6.09; Si 8.48. Single crystals of compound (*S*)-**XIf**·Py·HCl for X-ray diffraction analysis were obtain by passing ether vapors through a solution of chloride (*S*)-**XIf** in a 10:1 MeCN–pyridine mixture in air.

Bis[(dimethylcarbamoyl)methoxy]methylsilylium chloride (XIIe·HCl). To a solution of 4.2 g of *N,N*-dimethylamide of *O*-$SiMe_3$-glycolic acid in 10 ml of hexane we added dropwise a solution of 1.8 g of trichloro(methyl)silane in 10 ml of hexane. The precipitate that formed was filtered off, washed with hexane (2×15 ml), and vacuum-dried to obtain 3.0 g (88%) of chloride **XIIe**·HCl, mp 235–236°C (MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1638 s, 1508 w, 1408 m, 1271 m, 1085 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.12 s (3H, $SiCH_3$), 3.12 s [12H, $(CH_3)_2N$], 4.64 br.s (4H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –1.26 ($SiCH_3$), 37.55, 37.70 [$(CH_3)_2N$], 62.28 (CH_2), 175.17 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –62.17 ppm. Found, %: C 37.90; H 6.67; Si 9.45. $C_9H_{19}ClN_2O_4Si$. Calculated, %: C 38.22; H 6.77; Si 9.93. Single crystals of chloride **XIIe**·HCl for X-ray diffraction analysis were obtained by passing hexane vapors through a solution of compound **XIIe** in MeCN in air.

Bis[1-(dimethylcarbamoyl)ethoxy]methylsilylium chloride [(*S*)-XIIIf]. To a solution of 3.8 g of dimethylamide (*S*)-**IIf** in 15 ml of hexane we added dropwise a solution of 3.0 g of trichloro(methyl)silane in 5 ml of hexane. The precipitate that formed was filtered off, washed with hexane (2×15 ml), and vacuum-dried to obtain 3.0 g (97%) of chloride (*S*)-**XIIIf,** mp 216–217°C (MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1636 s, 1456 w, 1408 w, 1273 m, 1113 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.29 s (3H, $SiCH_3$), 1.46 d (6H, $C\underline{H}_3CH$, $^3J_{HH}$ 6.2 Hz), 3.24 s and 3.29 s [12H, $(CH_3)_2N$], 4.95 q (2H, CH, $^3J_{HH}$ 6.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.43 ($SiCH_3$), 19.98 ($\underline{C}H_3CH$), 38.52, 38.96 [$(CH_3)_2N$], 68.42 (CH), 178.40 (C=O). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: –68.00, –66.94. Found, %: C 42.23; H 7.37; Si 8.78. $C_{11}H_{23}ClN_2O_4Si$. Calculated, %: C 42.50; H 7.46; Si 9.04.

Bis[(dimethylcarbamoyl)methoxy]-*tert*-butylsilylium chloride (XIVe). To a solution of 4.4 g of dimethylamide **IIe** in 10 ml of hexane we added dropwise 2.4 g of *tert*-butyltrichlorosilane in 5 ml of hexane. The precipitate that formed was filtered off, washed with hexane (2×20 ml), and vacuum-dried to obtain 3.6 g (87%) of chloride **XIVe**, mp 222–223°C (MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1638 s, 1507 w, 1416 m, 1268 m, 1085 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 s [9H, $C(CH_3)_3$], 3.28 s [12H, $(CH_3)_2N$], 4.6–4.9 m (4H, $2CH_2$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.31 (SiC), 28.24 [$C(\underline{C}H_3)_3$], 37.98, 38.01 [$(CH_3)_2N$], 62.94 (CH_2), 175.75 (C=O). ^{29}Si NMR spectrum (CD_3CN): δ_{Si} –61.88 ppm. Found, %: C 44.28; H 7.70; Si 8.32. $C_{12}H_{25}ClN_2O_4Si$. Calculated, %: C 44.36; H 7.76; Si 8.64. Single crystals of compound **XIVe**·0.5HCl for X-ray diffraction analysis were obtained by passing ether vapors through a solution of **XIVe** in MeCN in air.

Bis[(dimethylcarbamoyl)methoxy]phenylsilylium chloride (XVe). To a solution of 4.2 g of dimethylamide **IIe** in 15 ml of hexane we added dropwise a solution of 2.5 g trichloro(phenyl)silane in 5 ml of hexane. The precipitate that formed was filtered off, washed with hexane (2×15 ml), and vacuum-dried to obtain 3.1 g (75%) of chloride **XVe**, decomp. point 103–104°C (MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1637 s, 1432 w, 1263 m, 1134 m, 1086 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.24 s and 3.27 s [12H, $(CH_3)_2N$], 4.7–5.0 m (4H, CH_2), 7.2–7.4 m (3H, C_6H_5), 7.5–7.6 m (2H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 37.80, 37.94 [$(CH_3)_2N$], 62.46 (CH_2), 127.71, 129.94, 133.51, 133.76 (C_6H_5), 175.17 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –77.24 ppm. Found, %: C 48.50; H 6.02; Si 7.86. $C_{14}H_{21}ClN_2O_4Si$. Calculated, %: C 48.76; H 6.14; Si 8.14. Single crystals of solvate **XVe**·$2CDCl_3$ for X-ray diffraction analysis were obtained by slowly evaporating the solvent from a solution of compound **XVe** in $CDCl_3$.

Bis[(dimethylcarbamoyl)methoxy]phenylsilylium bromide (XVIIe). A mixture of 0.99 g of trimethoxy(phenyl)silane **XV**, 1.55 g of dimethylamide **Ie**, 15 ml of *o*-xylene, and a crystal of *p*-toluenesulfonic acid was heated for 3 h at 120–130°C until methanol no longer released, after which 0.61 g of a solution of acetyl bromide in 5 ml of *o*-xylene was added dropwise at 0°C. The precipitate that formed within 3 h was filtered off and washed with 5 ml of hexane to obtain 1.65 g (85%) of bromide **XVIIe**, mp >350°C (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1685 s and 1480 m (NCO), 1109 s (SiO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.25 d (12H, $N(CH_3)_2$), 4.75 and 4.99 d.d (4H, OCH_2 *J* 15.3 Hz), 7.32 d (2H, ^2H, ^6H *J* 7.9 Hz), 7.36 br.s (^4H, Ar), 7.59 d (2H, ^3H, ^5H, *J* 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.15 [$N(CH_3)_2$] 62.83 (OCH_2), 127.84 (C^2, C^6), 130.05 (C^1), 133.70 (C^4), 133.87 (C^3, C^5), 175.42 (C=O). NMR spectrum ^{29}Si ($CDCl_3$): δ_{Si} –77.2 ppm. Found, %: C 43.04; H 5.59; N 6.97. $C_{14}H_{21}BrN_2O_4Si$. Calculated, %: C 43.19; H 5.44; N 7.20. Single crystals of compound **XVIIe** for X-ray diffraction analysis were obtained by crystallization from methylene chloride.

Bis[(dimethylcarbamoyl)methoxy](bromomethyl)silylium tribromomercurate (XIXe). A mixture of 0.55 g of (chloromethyl)trimethoxysilane **XVIII**, 1.03 g of dimethylamide **Ie**, 15 ml of *o*-xylene, and a crystal of *p*-toluenesulfonic acid was heated for 3 h at 120–130°C until methanol no longer released, after which a solution of 0.4 g of acetyl bromide in 5 ml of *o*-xylene was added dropwise at 0°C. The solvent was evaporated in a vacuum, the oil that remained was dissolved in 5 ml of CH_3CN, and 1.15 g of $HgBr_2$ was added to the solution. Crystals formed within a day and were filtered off to obtain 0.94 g (37%) of tribromomercurate **XIXe**, mp 200–203°C (CH_3CN). IR spectrum, ν, cm^{-1}: 1676 s и 1478 m (NCO), 1110 s (SiO). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.84 d (4H, OCH_2, *J* 4.9 Hz) 3.91 s [12H, N $(CH_3)_2$], 4.05 s (2H, $BrCH_2$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 35.2 ($BrCH_2$), 39.5 [$N(CH_3)_2$], 59.92 (OCH_2), 171.62 (C=O). NMR spectrum ^{29}Si (DMSO-d_6): δ_{Si} –59.5 ppm. Single crystals of tribromomercurate **XIXe** for X-ray diffraction analysis were obtained by crystallization from acetonitrile.

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