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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

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Abstract

The novel compounds, *N*-(trifluorosilylmethyl)-[*N*-(*S*)-(1-phenylethyl)]-acetamide (**1a**) and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine (**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.

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

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[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].

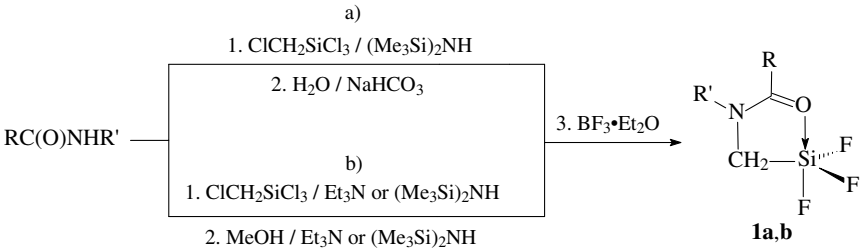
As far as we are aware, there are no literature data concerning the interaction of (O → Si)-chelate trifluorosilanes with KF in the presence of crown-ethers. In the 8-dimethylamino-1-silatranylnaphthalene the N → Si coordination bond is present, although fairly weak [9], whereas in the 1-[1-(2-oxoperhydroazepino)ethyl]silatrane [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 ($R = PhN{=}NC_6H_4$) 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 investigations 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 $BF_3 \cdot Et_2O$ 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 $BF_3 \cdot Et_2O$, 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%.



1a,**b** (1)

1a, R = Me, R' = CH(Ph)Me; **1b**, R,R' = $(CH_2)_5$

The trifluoride (**1c**; R = R′ = Me) has been synthesized previously by reaction of the triethoxyderivative $MeC(O)N(Me)CH_2Si(OEt)_3$ 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 $MeC(O)N(Me)CH_2Si(OMe)_3$ [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.