Letters to the Editor

Intermolecular coordination interactions in *N*-(fluorodimethylsilylmethyl)carboxamides

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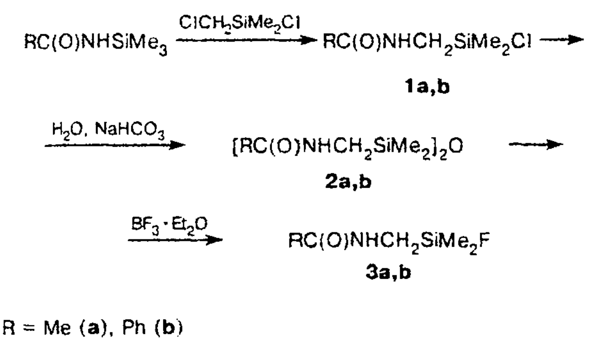
Most of the presently known *N*-silylmethyl derivatives of amides and related compounds containing at least one fairly electronegative substituent at the silicon atom are characterized by an O—Si chelate structure with an intramolecular O→Si coordination bond.[1,2] Much less is known about intermolecular homoassociates with the participation of these compounds.[2]

Previously,[3] we have described *N*-(chlorodimethylsilylmethyl)acetamide (**1a**), which is the first representative of monosubstituted amides of the general formula $RC(O)NHCH_2SiMe_2X$. Coordination interactions in these compounds can occur not only through the oxygen atom of the amide group but also through the hydrogen atom of the NH group and can, in principle, lead to intermolecular hydrogen bonding that affects intramolecular coordination bonds. The data of ^1H and ^{29}Si NMR and IR spectroscopy provided evidence for the existence of intramolecular O→Si coordination bonds only in concentrated solutions of chloride **1a**. The structure of the latter in the crystalline state has not been studied due to problems associated with the preparation of crystals suitable for X-ray diffraction study.

In the present work, previously unknown monosubstituted *N*-(fluorodimethylsilylmethyl)amides **3a,b** were synthesized from chlorides **1a,b** (prepared from the corresponding *N*-trimethylsilylamides by transsilylation)* through intermediate disiloxanes **2a,b** (Scheme 1). The reasonable data of elemental analysis were obtained for all isolated compounds except for chloride **1a**. The crystal structures of fluorides **3a,b** were established by X-ray diffraction analysis and confirmed by the data of

Scheme 1



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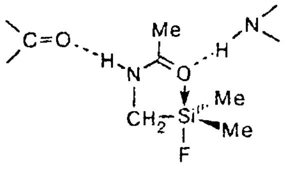
*The multistage scheme of these transsilylation reactions was discussed in detail in the review.[1]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1820—1822, September, 1999.

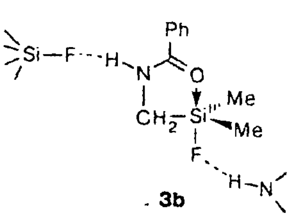
1066-5285/99/4809-1796 $22.00 © 1999 Kluwer Academic/Plenum Publishers

^{1}H, ^{19}F, and ^{29}Si NMR spectroscopy for solutions in $CDCl_3$ (a Varian XL-400 instrument operating at 400.1, 100.6, and 79.5 MHz, respectively, 20 °C).

According to the X-ray diffraction data, the coordination environment about the Si atoms in these compounds is a trigonal bipyramid (the coordination number is 5) with the central atom deviating from the equatorial plane toward the fluorine atom. In the crystal of fluoride **3a**, the molecules are linked *via* intermolecular (N)H...O interactions (the O...N distance is 2.93 Å; the sum of the van der Waals radii[4] of the O and N atoms is 3.07 Å). In the crystal of monofluoride **3b**, another type of intermolecular hydrogen bonding is observed, *viz.*, (N)H...F (the N...F distance is 2.83 Å; the sum of the van der Waals radii[4] of the F and N atoms is 3.03 Å). In all cases, the N—H—X angles (X = O or F) are close to 180° and the N—H bond lengths vary in the range of 0.78—0.88 Å. In the crystals, the molecules are linked in chains along one of the crystallographic axes through hydrogen bonds.



3a



3b

The O...Si distance (2.37 Å) in fluoride **3a**, containing the additionally coordinated O atom, is among the longest distances known for hypervalent fluorosilanes with the intramolecular O→Si coordination bond.[2] To the contrary, the corresponding distance in compound **3b**, containing the additionally coordinated F atom, is somewhat smaller (2.115 Å) than that, for example, in the analogous fluoride $MeC(O)N(CHPhMe)CH_2SiMe_2F$ (**4**) (2.15 Å), in which an intermolecular interaction is definitely absent.[5]

Apparently, the intermolecular interactions observed in the crystals of fluorides **3a,b** are also retained to a large extent in solutions. The ^{1}H NMR spectrum of fluoride **3a** has a signal of the $SiMe_2$ group as a doublet with the spin-spin coupling constant $^3J_{HF}$ = 7.5 Hz. At room temperature, the signal of the $SiMe_2$ group of compound **3b**, unlike that of **3a**, is observed as a broadened singlet that evolves into a doublet ($^3J_{HF}$ = 7.9 Hz) at 0 °C. In the ^{19}F NMR spectrum of a solution of fluoride **3b** at the concentration of ~0.05 mol L^{-1}, the signal is broadened ($\Delta\nu \approx 6$ Hz) and is observed at δ −119.0. The increase in the concentration of compound **3b** to ~1 mol L^{-1} leads to an upfield shift of this signal by ~6 ppm ($\Delta\nu \approx 10$ Hz). In the ^{29}Si NMR spectrum, the signal of fluoride **3b** is also observed as a broadened singlet ($\Delta\nu \approx 60$ Hz). The observed broadening of the signals in the ^{19}F and ^{29}Si NMR spectra and the absence of spin-spin coupling with the fluorine atom are indicative of weakening of the Si—F bond in molecule **3b**.

It was demonstrated by the cryoscopic method (benzene) that fluorides **3a,b** exist as monomers in dilute solutions but occur in part as associates at higher concentrations (*C*): for **3a**, M_{exp} = 200.1 and 162.8 g mol^{-1} at *C* = 0.26 and 0.13 mol kg^{-1}, respectively (M_{calc} for the monomer is 149.2 g mol^{-1}); for **3b**, M_{exp} = 260.0 and 213.7 g mol^{-1} at *C* = 0.28 and 0.14 mol kg^{-1}, respectively (M_{calc} for the monomer is 211.3 g mol^{-1}).

Chloride 1a. The yield was 67%, b.p. 164—167 °C (10 Torr) (*cf.* Ref. 3). **Chloride 1b**. The yield was 88%, m.p. 92—95 °C (from benzene). IR (Specord IR-75, KBr cells, dioxane), ν/cm^{-1}: 1618, 1640 (NCO). ^{29}Si NMR (acetone-d$_6$), δ: −26.5 (br.s). Found (%): C, 52.35; H, 6.45; N, 5.94. $C_{10}H_{14}ClNOSi$. Calculated (%): C, 52.73; H, 6.20; N, 6.15. **Disiloxane 2a**. The yield was 84%, b.p. 228—230 °C (7 Torr), n_D^{20} 1.4680. IR ($CHCl_3$), ν/cm^{-1}: 1520, 1640 (NCO). ^{29}Si NMR, δ: 4.5 (s). Found (%): C, 43.18; H, 8.84; N, 9.85. $C_{10}H_{24}N_2O_3Si_2$. Calculated (%): C, 43.44; H, 8.75; N, 10.13. **Disiloxane 2b**. The yield was 75%, b.p. 119—121 °C (from benzene). IR ($CHCl_3$), ν/cm^{-1}: 1640 (NCO). ^{29}Si NMR, δ: 4.7 (s). Found (%): C, 60.12; H, 6.94; N, 7.00. $C_{20}H_{28}N_2O_3Si_2$. Calculated (%): C, 59.96; H, 7.04; N, 6.99. **Fluoride 3a**. The yield was 69%, b.p. 121—123 °C (10 Torr), n_D^{20} 1.4345 (immediately after fractionating), solidified upon storage, m.p. 38—39 °C. IR ($CHCl_3$), ν/cm^{-1}: 1510, 1655 (NCO). ^{19}F NMR (55 °C), δ: −116.1 (s). ^{29}Si NMR, δ: 7.8 (d, $^1J_{SiF}$ = 266.8 Hz). Found (%): C, 39.83; H, 7.99; N, 8.90. $C_5H_{12}FNOSi$. Calculated (%): C, 40.24; H, 8.11; N, 9.39. **Fluoride 3b**. The yield was 63%, m.p. 62—65 °C (from a 1 : 4 benzene—hexane mixture). IR ($CHCl_3$), ν/cm^{-1}: 1540, 1635 (NCO). ^{29}Si NMR, δ: −1.3 (br.s). Found (%): C, 56.66; H, 6.50; N, 6.60. $C_{10}H_{14}FNOSi$. Calculated (%): C, 56.84; H, 6.68; N, 6.63.

Hence, a slight change in the structure of monosubstituted amides $RC(O)NHCH_2SiMe_2F$ leads to a change in the type of intermolecular bonding. In the future, we plan to reveal the factors governing the character of intra- and intermolecular coordination interactions in hypervalent silicon, germanium, and tin compounds.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-33783 and 98-03-32999) and INTAS-RFBR (Grant 95-0070).

References

1. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metalloorg. Khim.*, 1991, **4**, 1210 [*Organomet. Chem. USSR*, 1991, **4**, 593 (Engl. Transl.)].
2. D. Kost and I. Kalikhman, *The Chemistry of Organic Silicon Compounds*, Eds. Z. Rappoport and Y. Apeloig, J. Wiley and Sons, Chichester, 1998, 1339.
3. Yu. I. Baukov, A. G. Shipov, Vad. V. Negrebetsky, E. P. Kramarova, and O. A. Zamyshlyaeva, *Zh. Obshch. Khim.*, 1995, **65**, 2064 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
4. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
5. Yu. I. Baukov, Yu. E. Ovchinnikov, A. G. Shipov, E. P. Kramarova, Vad. V. Negrebetsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 399.

Received April 9, 1999