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Mendeleev Commun., 2022, **32**, 686–687

Mendeleev Communications

Structure of novel *N*-fluorosilylmethyl-*N*-isopropylureas

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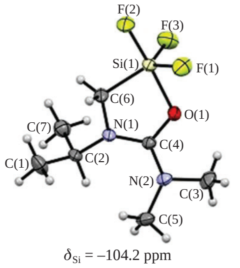
DOI: 10.1016/j.mencom.2022.09.040

Novel *N*-isopropyl-*N'*,*N'*-dimethyl-*N*-(silylmethyl)ureas $Me_2NC(O)N(Pr^i)CH_2SiMe_nX_{3-n}$ (X = OEt, F; *n* = 0–2) were synthesized, and their structure was confirmed by ^1H, ^{13}C and ^{29}Si NMR spectroscopy. According to NMR data, the silicon atom of the fluorosilanes (X = F) is pentacoordinated. The X-ray diffraction analysis of the (trifluorosilyl)methyl-containing urea showed that it exists as (O–Si) chelate with intramolecular dative bond C=O→Si (1.880 Å).



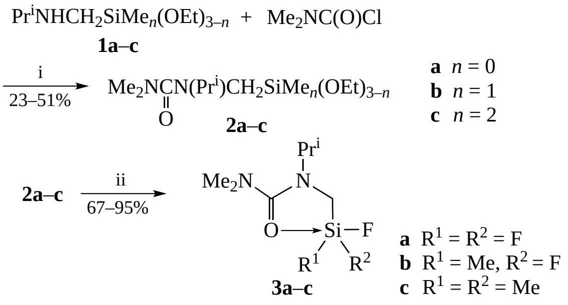
Keywords: organosilicon compounds, fluorosilanes, *N*-isopropyl-*N'*,*N'*-dimethyl-*N*-(silylmethyl)ureas, pentacoordinate silicon, NMR, X-ray diffraction analysis.

The (O–Si) chelate *N*-silylmethylated derivatives of carboxamides and related compounds containing dative bond C=O→Si attract attention because of diversity of their structures, stereodynamic behaviour and enhanced reactivity.[1–6] Compounds containing urea group N–C(O)–N are widely used in organic chemistry and catalysis, they are generally present in natural products and display a broad spectrum of biological activity.[7–10] Especially, there has been an interest in *N*-silylmethylated ureas.[11–24] Ureas are important chelating ligands, however the data on (O–Si) chelate *N*-silylmethylated derivatives with the dative bond C=O→Si are scarce.[11,13,16] The theoretical investigation of the influence of the structure of the silyl group on the formation of neutral intramolecular silicon complexes with multicenter dative bond $X_3Si{\leftarrow}O{\rightarrow}SiX_3$ was conducted by example of *N*,*N'*-bis(silylmethyl)ureas.[16] Recently, we reported on *N*-(silylmethyl)ureas with coordination unit SiC_3OCl[21–23] and showed that hydrolysis of *N*-[chloro(dimethyl)silylmethyl]-*N'*-trimethylsilyl-*N*,*N'*-propyleneurea with air moisture afforded the protonated hypervalent silanol, namely, *N*-[hydroxy(dimethyl)silylmethyl]-*N*,*N'*-propyleneurea hydrochloride.[22,24] The (O–Si) chelate pentacoordinated compounds with coordination units SiC_3OF, SiC_2OF_2 and $SiCOF_3$ are more stable and less susceptible to hydrolysis than the isostructural chlorosilanes, which has been accounted for the higher bond energy E_{Si-F} compared to E_{Si-O} (159 and 126 kcal mol^{-1}, respectively[25]). Such fluorosilanes are used as model compounds in the studies of the influence of the coordination unit structure on the hypervalent interaction C=O→Si in their molecules.[1–6]

Continuing our research of Si-containing ureas,[21–24] we now report on the synthesis and structure of novel *N*-isopropyl-*N'*,*N'*-dimethyl-*N*-(silylmethyl)ureas of (O–Si) chelate fluorosilane chemotype $Me_2NC(O)N(Pr^i)CH_2SiMe_nF_{3-n}$ (*n* = 1–3). Herein *N*-(silylmethyl)isopropylamines **1a–c** were reacted with *N*,*N*-dimethylcarbamoyl chloride giving *N*-isopropyl-*N'*,*N'*-dimethyl-*N*-(silylmethyl)ureas **2a–c** (Scheme 1). Their subsequent treatment with $BF_3{\cdot}Et_2O$ leads to (O–Si) chelate pentacoordinated fluorosilanes **3a–c** (for details, see Online Supplementary Materials).

The structure of the compounds **2a–c** and **3a–c** was confirmed by ^1H, ^{13}C and ^{29}Si NMR, IR spectra and their composition by elemental analysis (see Online Supplementary Materials). The compounds **3a–c** are characterized by an upfield shift of signals in the ^{29}Si NMR spectra and a decrease in the spin–spin coupling constants $^1J(^{29}Si{-}^{19}F)$ compared to the corresponding model silanes $ClCH_2SiMe_nF_{3-n}$ (*n* = 0–2) (Table 1). Note that these spectral characteristics lie in the range of the characteristic values of the (O–Si) chelated *N*-(fluorosilylmethyl)carboxamides with the pentacoordinate silicon atom that confirms the pentacoordination of the silicon atoms of compounds **3a–c**.

The pentacoordination of silicon atom in compound **3a** is confirmed by X-ray diffraction analysis[†] (Figure 1 and Online Supplementary Materials). The length of the intramolecular dative bond C=O→Si in compound **3a** is 1.880 Å that is shorter



Scheme 1 *Reagents and conditions*: i, Et_3N, hexane, reflux, 3 days; ii, $BF_3{\cdot}Et_2O$, hexane, reflux, 3 days.

Crystals of compound **3a** suitable for single crystal X-ray structural analysis were grown from benzene solution. The X-ray diffraction analysis

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[†] *Crystal data for* **3a**. $C_7H_{15}F_3N_2OSi$, *M* = 228.30, colorless prism (0.20 × 0.20 × 0.40 mm), monoclinic, space group $P2_1/c$, *a* = 5.8697(3), *b* = 23.6229(11) and *c* = 8.1910(4) Å, *β* = 108.35(1)°, *V* = 1078.03(9) Å^3, *Z* = 4, at 293 K, d_{calc} = 1.388 g cm^{-3}, *μ* = 0.232 mm^{-1}, *F*(000) = 468. Total 30692 reflections were collected (3172 independent reflections) and used in the refinement, 150 refined parameters, *S* = 1.015, and final *R* factor was 4.42 (R_{int} = 0.0857).

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Table 1 Chemical (δ ^{29}Si) and coordination $\Delta\delta$ $^{29}\mathrm{Si} = \delta_{\mathrm{Si^V}} - \delta_{\mathrm{Si^{IV}}}$ shifts[3] and the ^1J(^{29}Si–^{19}F) values for compounds **3a–c** and related (O–Si) chelate pentacoordinated fluorosilanes.

Compound	δ_{Si}/ppm	$\Delta\delta_{\mathrm{Si}}$/ppm	$^1J_{\mathrm{SiF}}$/Hz	Reference
$Me_2NC(O)N(Pr^i)CH_2SiF_3$ **3a**	–104.23	32.93	210.5	this work
$MeC(O)N(Me)CH_2SiF_3$	–103.65	32.35	211.4	26
$PhC(O)N(Me)CH_2SiF_3$	–103.58	32.28	212.3	27
$ClCH_2SiF_3$	71.30	–	267.0	
$Me_2NC(O)N(Pr^i)CH_2SiMeF_2$ **3b**	–59.57	50.57	249.4	this work
$MeC(O)N(Me)CH_2SiMeF_2$	–55.84	46.84	255.6	28
$PhC(O)N(Me)CH_2SiMeF_2$	–55.30	46.30	266.1	27
$ClCH_2SiMeF_2$	–9.00	–	300.0	
$Me_2NC(O)N(Pr^i)CH_2SiMe_2F$ **3c**	–18.28	43.08	259.5	this work
$MeC(O)N(Me)CH_2SiMe_2F$	–19.37	44.17	257.2	27
$PhC(O)N(Me)CH_2SiMe_2F$	–17.98	42.78	259.4	27
$ClCH_2SiMe_2F$	24.80	–	287.0	

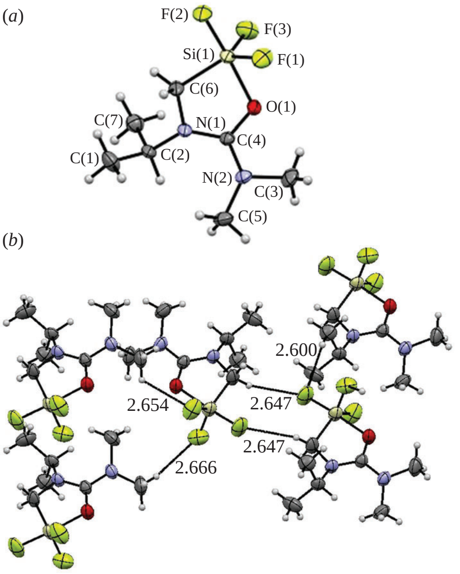

Figure 1 X-ray data for compound **3a**: (*a*) molecular structure (ORTEP, 30% thermal ellipsoids) and (*b*) short contacts F···H–C in the crystal.

than in previously studied *N*-[(trifluorosilyl)methyl]acetanilide and *N*-[(trifluorosilyl)methyl]benzanilide [1.913(4) and 1.915(1) Å, respectively][30] and almost identical to O→Si bond length in *N*-[(trifluorosilyl)methyl]acetamide [1.878(1) Å].[31] The length of the axial bond Si–F$_{ax}$ is 1.633 Å that is 0.05 Å longer than the lengths of the equatorial Si–F$_{eq}$ bonds (average 1.583 Å). The deviation of the silicon atom from the equatorial plane formed by C, F and F atoms is 0.109 Å. The structure of (O–Si) chelate heterocycle of compound **3a** is typical of trifluorosilanes containing pentacoordinate silicon atom.[27,30,31]

The crystal structure of compound **3a** is formed due to short contacts between the fluorine atom and the hydrogen atoms of the methyl groups of neighboring molecules [see Figure 1(*b*)]. The lengths of intermolecular bonds F···H–C range from 2.600 to 2.666 Å.

In summary, a convenient protocol for the synthesis of *N*-[(alkoxysilyl)methyl]ureas from *N*-(silylmethyl)isopropylamines and readily available dimetylcarbamoyl chloride is described. Subsequent treatment of these compounds with boron trifluoride etherate leads to *N*-isopropyl-*N′*,*N′*-dimethyl-*N*-[(fluorosilyl)methyl]ureas which exist as (O–Si) chelates with intramolecular dative bond C=O→Si.

These results were obtained using analytical equipment of the Baikal Center for Collective Use of the SB RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.040.

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Received: 7th April 2022; Com. 22/6862

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was carried out on a Bruker D8 Venture diffractometer with MoKα radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[29] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set.[29]

CCDC 2141508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.