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# *N*-Isopropyl-*N′*,*N′*-diphenyl-*N*-(silylmethyl)ureas: synthesis and structure

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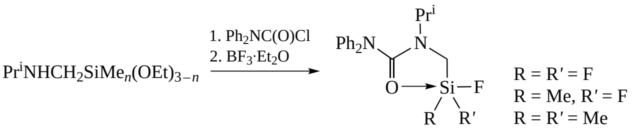
**New *N*-isopropyl-*N′*,*N′*-diphenyl-*N*-(silylmethyl)ureas were obtained, and their structure was explored by $^1$H, $^{13}$C, $^{29}$Si NMR spectroscopy and X-ray analysis. These results have shown that *N*-isopropyl-*N′*,*N′*-diphenyl-*N*-[(fluorosilyl)-methyl]ureas exist as (O–Si) chelates with intramolecular dative bond C=O→Si.**

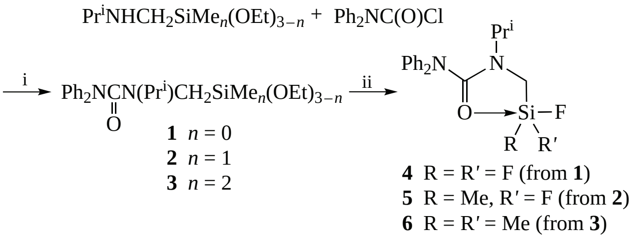


*Keywords*: *N′*,*N′*-diphenyl-*N*-(silylmethyl)ureas, (O–Si) chelates, dative bond, pentacoordinate silicon atom, organosilicon compounds, NMR, X-ray.

Substituted ureas are useful as synthons and catalysts for the synthetic organic chemistry, they are generally present in the nature and display a broad spectrum of biological activity.[1–4] They have found applications as dyes,[5] antioxidants[6] and corrosion inhibitor.[7] The (O–Si) chelate *N*-silylmethylated carboxamides and related compounds with dative bond C=O→Si possess interesting structural features, stereodynamic behaviour and reactivity.[8–13] Ureas have high chelating ability,[14] however (O–Si) chelates of *N*-silylmethylated ureas with the dative bond C=O→Si remain insufficiently studied.[15–25] Recently,[25] we reported on *N*-isopropyl-*N′*,*N′*-dimethyl-*N*-(silylmethyl)ureas.[25] Herein, we prepared novel *N*-isopropyl-*N′*,*N′*-diphenyl-*N*-(silylmethyl)ureas and investigated their structures.

The precursor *N*-isopropyl-*N′*,*N′*-diphenyl-*N*-(silylmethyl)-ureas **1–3** were obtained by reaction of *N*,*N*-diphenylcarbamoyl chloride with appropriate *N*-isopropyl-*N*-silylmethylamines. These reactions were run in benzene in the presence of excess triethylamine as a base (Scheme 1). The subsequent treatment of compounds **1–3** with BF$_3$·Et$_2$O led to the target (O–Si) chelate fluorosilanes **4–6**.

The structure of compounds **1–6** was confirmed by $^1$H, $^{13}$C and $^{29}$Si NMR, IR spectra and elemental analysis. Compounds **4–6** are characterized by an upfield shifts of signals in the $^{29}$Si NMR spectra and a decrease in the spin–spin coupling constant values $^1J(^{29}\text{Si}–^{19}\text{F})$ compared to the corresponding model silanes ClCH$_2$SiMe$_n$F$_{3-n}$ ($n$ = 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.



**1** $n$ = 0
**2** $n$ = 1
**3** $n$ = 2

**4** R = R′ = F (from **1**)
**5** R = Me, R′ = F (from **2**)
**6** R = R′ = Me (from **3**)

**Scheme 1** *Reagents and conditions*: i, Et$_3$N, C$_6$H$_6$, reflux, 2 days; ii, BF$_3$·Et$_2$O, C$_6$H$_6$, reflux, 1 day.

**Table 1** Chemical ($\delta$ $^{29}$Si) and coordination [$\Delta\delta$ $^{29}$Si = $\delta_{\text{Si}^\text{V}}-\delta_{\text{Si}^\text{IV}}$] shifts[10] and the $^1J(^{29}\text{Si}–^{19}\text{F})$ constants for compounds **4–6** and related (O–Si) chelate pentacoordinated fluorosilanes.

| Compound | $\delta_\text{Si}$/ppm | $\Delta\delta_\text{Si}$/ppm | $^1J_\text{SiF}$/Hz | Reference |
|---|---|---|---|---|
| Me$_2$NC(O)N(Pr$^i$)CH$_2$SiF$_3$ | –104.23 | 32.93 | 210.5 | 25 |
| MeC(O)N(Me)CH$_2$SiF$_3$ | –103.65 | 32.35 | 211.4 | 26 |
| Ph$_2$NC(O)N(Pr$^i$)CH$_2$SiF$_3$ (**4**) | –103.79 |  | 211.7 | this work |
| PhC(O)N(Me)CH$_2$SiF$_3$ | –103.58 | 32.28 | 212.3 | 27 |
| ***ClCH$_2$SiF$_3$*** | ***71.30*** |  | ***267.0*** |  |
| Me$_2$NC(O)N(Pr$^i$)CH$_2$SiMeF$_2$ | –59.57 | 50.57 | 249.4 | 25 |
| MeC(O)N(Me)CH$_2$SiMeF$_2$ | –55.84 | 46.84 | 255.6 | 28 |
| Ph$_2$NC(O)N(Pr$^i$)CH$_2$SiMeF$_2$ (**5**) | –53.95 | 44.95 | 259.8 | this work |
| PhC(O)N(Me)CH$_2$SiMeF$_2$ | –55.30 | 46.30 | 266.1 | 27 |
| ***ClCH$_2$SiMeF$_2$*** | ***–9.00*** |  | ***300.0*** |  |
| Me$_2$NC(O)N(Pr$^i$)CH$_2$SiMe$_2$F | –18.28 | 43.08 | 259.5 | 25 |
| MeC(O)N(Me)CH$_2$SiMe$_2$F | –19.37 | 44.17 | 257.2 | 27 |
| Ph$_2$NC(O)N(Pr$^i$)CH$_2$SiMe$_2$F (**6**) | –10.13[a] | 34.93 | –[a] | this work |
| PhC(O)N(Me)CH$_2$SiMe$_2$F | –17.98 | 42.78 | 259.4 | 27 |
| ***ClCH$_2$SiMe$_2$F*** | ***+24.80*** |  | ***287.0*** |  |

[a] Broad signal.

The single crystals of **4–6** were obtained by recrystallization from hexane/chloroform solution, their molecular structures are depicted in Figure 1.[†] Crystal data, data collection and structure

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[†] *Crystal data for* **4**. C$_{17}$H$_{19}$F$_3$N$_2$OSi, $M$ = 352.43, colorless needle (0.30 × 0.05 × 0.05 mm), monoclinic, space group $P2_1/n$, $a$ = 9.112(2), $b$ = 10.210(2) and $c$ = 19.596(4) Å, $V$ = 1791.7(7) Å$^3$, $Z$ = 4, $d_\text{calc}$ = 1.307 g cm$^{-3}$, $\mu$ = 0.166 mm$^{-1}$, $F(000)$ = 736. Total of 32085 reflections were collected (5269 independent reflections) and used in the refinement, which converged to $R_1$ = 0.0597, $wR_2$ = 0.1566; GOOF = 0.982. The data were collected at 293(2) K on a Bruker D8 Venture diffractometer with MoKα radiation ($\lambda$ = 0.71073 Å) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[34] Data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX programs set.[34]

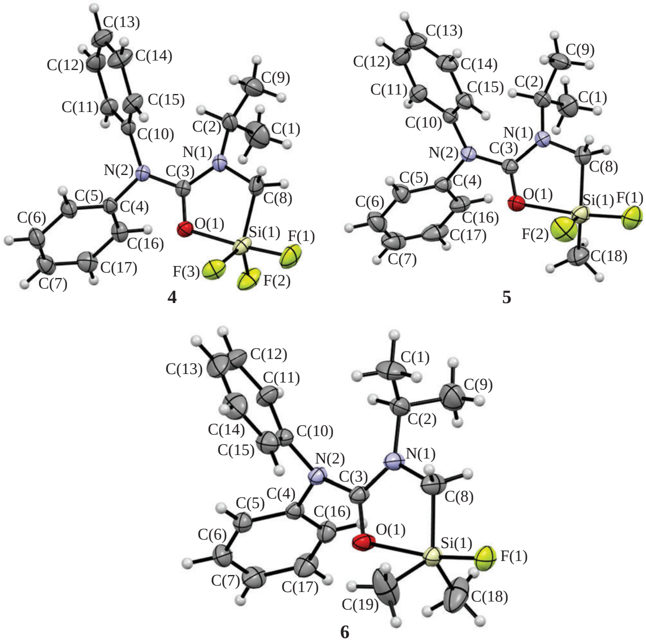

**Figure 1** The molecular structure of compounds **4**–**6** (displacement ellipsoids are drawn at 30% probability level).

refinement details, principal bond distances, bond angles and torsion angles of compounds **4**–**6** are summarized in Online Supplementary Materials.

Molecules of compound **4** crystallize in monoclinic syngony, whereas those of compounds **5** and **6** crystallize in orthorhombic syngony. One molecule is located in the asymmetric unit for all compounds **4**–**6**. The selected geometric parameters of the axial fragment, the sum of equatorial angles ($\sum_{eq.}$), the degree of pentacoordination [$\eta_e$ (%)] of ureas **4**–**6** and related compounds are presented in Table 2. The structure of (O–Si) chelate heterocycles in compounds **4**–**6** is typical for (O–Si) chelate fluorosilanes containing pentacoordinate silicon atom.[25,28–31] The value of the O→Si dative bond length in ureas **4**–**6** increases with a decrease in the number of fluorine atoms at the silicon atom, but at the same time, the degree of pentacoordination [$\eta_e$ (%)] estimated by the Kano–Tamao formula[32] and the value of the sum of equatorial angles ($\sum_{eq.}$) decrease. The deviation of the silicon atom from the equatorial plane is 0.115, 0.187 and 0.235 Å in compounds **4**–**6**, respectively. The length of the axial bond Si–F$_{ax}$ is greater than the lengths of the equatorial Si–F$_{eq}$ bonds in compounds **4** and **5**.

Note that a lower basicity of the carbonyl group in *N*-phenylureas compared to the corresponding *N*-methylureas is indicative of its lower electron-donating ability.[33] The replacement of the dimethyl substituent by the diphenyl one at the nitrogen atom, all else being equal, causes a decrease of the O→Si dative interaction (lengths dative bonds are 1.880 and 1.891 Å for ureas $Me_2NC(O)N(Pr^i)CH_2SiF_3$ and **4**, respectively). Analysis of the structure data of the (O–Si) chelate fluorosilanes (Table 2) allows us to conclude that the nature of the substituents at the heteroatoms of the chelate heterocycle has a significant effect on the degree of O→Si dative binding. The decrease in the degree of pentacoordination of the silicon atom and the increase in the length of the dative bond are determined by the reduction of the electron-donating properties of substituents at nitrogen and carbonyl group.

In the crystal, molecules **4** form dimeric structure by short contacts between the fluorine atom and the hydrogen atoms of the $CH_2$ groups of neighbouring molecules (see Online Supplementary Materials, Figure S1). The lengths of intermolecular F···H–C bonds are 2.571 and 2.707 Å. In addition there are T-stacking between C$_{Ar}$–H hydrogen and π-system of phenyl ring of neighbouring molecules (Figure S2).

**Table 2** The selected geometric parameters of ureas and related compounds.

| Compound | *l*/Å | | | | O–Si–F/deg | $\sum_{eq.}$ | $\eta_e$ (%) | Reference |
|---|---|---|---|---|---|---|---|---|
| | O→Si | Si–F$_{ax.}$ | Si–F$_{eq.}$ | Si–F$_{eq.}$ | | | | |
| $Ph_2NC(O)N(Pr^i)CH_2SiF_3$ (**4**) | 1.891(1) | 1.634(1) | 1.593(1) | 1.585(1) | 174.2(1) | 358.6 | 95 | this work |
| $Ph_2NC(O)N(Pr^i)CH_2SiMeF_2$ (**5**) | 2.050(2) | 1.638(2) | 1.594(2) | | 173.4(1) | 358.1 | 89 | this work |
| $Ph_2NC(O)N(Pr^i)CH_2SiMe_2F$ (**6**) | 2.219(1) | 1.656(1) | | | 171.9(2) | 355.2 | 85 | this work |
| $Me_2NC(O)N(Pr^i)CH_2SiF_3$ | 1.880(1) | 1.633(1) | 1.585(1) | 1.581(1) | 176.3(5) | 358.7 | 93 | 25 |
| $MeC(O)NMeCH_2SiF_3$ | 1.878(1) | 1.635(1) | 1.587(2) | 1.594(1) | 177.4(4) | 358.7 | 96 | 29 |
| $MeC(O)NPhCH_2SiF_3$ | 1.893(2) | 1.637(2) | 1.580(2) | 1.584(2) | 177.2(1) | 358.8 | 96 | 30 |
| $PhC(O)NMeCH_2SiF_3$ | 1.913(4) | 1.620(4) | 1.601(5) | 1.585(5) | 175.6(2) | 358.1 | 94 | 31 |
| $PhC(O)NPhCH_2SiF_3$ | 1.915(1) | 1.629(1) | 1.596(1) | 1.590(1) | 176.4(1) | 358.1 | 94 | 30 |
| $MeC(O)NMeCH_2SiMeF_2$ | 1.969(1) | 1.686(1) | 1.619(1) | | 171.7(1) | 358.1 | 94 | 28 |
| $PhC(O)NPhCH_2SiMeF_2$ | 2.000(1) | 1.661(1) | 1.615(1) | | 172.5(1) | 357.8 | 93 | 28 |
| $PhOC(O)NPhCH_2SiMeF_2$ | 2.176(1) | 1.632(2) | 1.601(1) | | 172.4(1) | 354.8 | 84 | 28 |

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*Crystal data for* **5**. $C_{18}H_{22}F_2N_2OSi$, $M = 348.46$, colorless prism ($0.40\times0.35\times0.22$ mm), orthorhombic, space group $P2_12_12_1$, $a = 8.483(1)$, $b = 10.195(1)$ and $c = 21.258(1)$ Å, $V = 1838.5(1)$ Å$^3$, $Z = 4$, $d_{calc} = 1.259$ g cm$^{-3}$, $\mu = 0.153$ mm$^{-1}$, $F(000) = 736$. Total of 18454 reflections were collected (3371 independent reflections) and used in the refinement, which converged to $R_1 = 0.0319$, $wR_2 = 0.0933$; GOOF = 1.004.

*Crystal data for* **6**. $C_{19}H_{25}FN_2OSi$, $M = 344.50$, colorless plate ($0.7\times0.34\times0.06$ mm), orthorhombic, space group *Pbca*, $a = 7.865(1)$, $b = 19.928(2)$ and $c = 25.227(2)$ Å, $V = 3954.1(6)$ Å$^3$, $Z = 8$, $d_{calc} = 1.157$ g cm$^{-3}$, $\mu = 0.135$ mm$^{-1}$, $F(000) = 1472$. Total of 47389 reflections were collected (3629 independent reflections) and used in the refinement, which converged to $R_1 = 0.0422$, $wR_2 = 0.1277$; GOOF = 1.004.

The X-ray diffraction experiments for **5** and **6** were carried out at 296(2) K on a Bruker KAPPA APEX II diffractometer (graphite-monochromated MoKα radiation). Reflection intensities were corrected for absorption by SADABS-2016 program.[35] The structure of compounds was solved by direct methods using the SHELXT-2014 program[36] and refined by anisotropic (isotropic for all H atoms) full-matrix least-squares method against $F^2$ of all reflections by SHELXL-2018.[36] The positions of the hydrogen atoms were calculated geometrically and refined in riding model.

CCDC 2223501 (**4**), 2222921 (**5**) and 2222920 (**6**) contain 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.

In summary, a convenient synthesis of *N*-isopropyl-*N'*,*N'*-diphenyl-*N*-[(fluorosilyl)methyl]ureas has been described. These compounds exist as (O–Si) chelates with intramolecular dative bond C=O→Si. Analysis of the structure data of the (O–Si) chelate fluorosilanes demonstrates that the degree of O→Si dative binding is determined by the nature of the substituents at nitrogen atom and carbonyl group.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.019.

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