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Mendeleev Commun., 2022, **32**, 798–800

Mendeleev
Communications

N-(Chlorodimethylsilyl)methyl anilides: synthesis and structure

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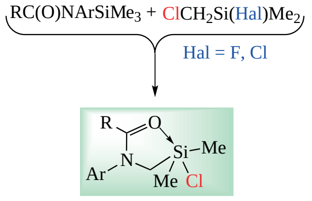
DOI: 10.1016/j.mencom.2022.11.030

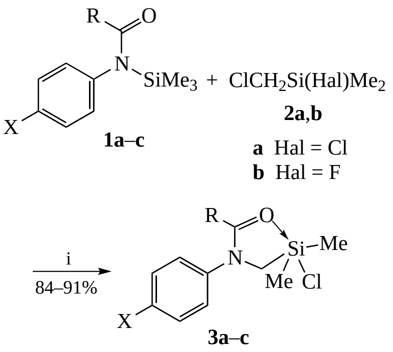
***N*-(Chlorodimethylsilyl)methyl anilides of formula $RC(O)N(C_6H_4X)CH_2SiMe_2Cl$ (R = Me, Ph; X = H, Me, Cl) were obtained by the reaction of *N*-TMS-containing anilides with $ClCH_2Si(Hal)Me_2$ (Hal = F, Cl). The silicon atom in these compounds is pentacoordinate according to the results of NMR and X-ray diffraction analysis.**



Keywords: *N*-(chlorodimethylsilyl)methyl anilides, *N*-TMS anilides, chloromethyl(dimethyl)halogenosilanes, silicon pentacoordinate, NMR, X-ray diffraction analysis, organosilicon compounds.

Pentacoordinate silicon compounds have been extensively studied in recent years.[1–5] They play a key role as intermediates in the biocatalytic transformations and industrially important reactions.[6–11] Intense efforts in the last decade have been undertaken to better understand the synthesis features, structure and reactivity of (O–Si) chelate amides and related compounds.[12–22] Among them amides with the coordination unit $C{=}O\rightarrow SiC_3X$ [X = Hal, TfO or RC(O)O] were the most promising owing to their structural diversity, stereodynamic flexibility and high reactivity, which would facilitate the search for the correlations between the structure and properties of the hypervalent organosilicon compounds. To complement these studies, herein three (O–Si) chelate *N*-[(chlorodimethylsilyl)-methyl] anilides were prepared (Scheme 1) from available reactants **1a–c** and **2a**,**b**. The thus obtained *N*-(chlorodimethylsilyl)methyl-*N*-(4-methylphenyl)acetamide **3a** and *N*-(chlorodimethylsilyl)methyl-*N*-phenylbenzamide **3c** are new while *N*-(chlorodimethylsilyl)methyl-*N*-(4-chlorophenyl)acetamide **2b** was synthesized earlier from *N*-(4-chlorophenyl)acetamide and chloromethyl(dimethyl)chlorosilane in the presence of Et_3N.[23]

Recently we demonstrated that the trans-silylation reaction of *O*-*N*-TMS-*N*-methylacetamide with $ClCH_2SiMe_2F$ led to *N*-(chlorodimethylsilyl)methyl-*N*-methylacetamide as single product.[24] In this work, we have employed the trans-silylation reactions for the synthesis of *N*-(chlorodimethylsilyl)methyl anilides **3a–c** from *N*-TMS anilides **1a–c** and chloro(chloromethyl)dimethylsilane **2a** or chloromethyl(fluoro)dimethylsilane **2b** (see Scheme 1). Fluorosilane **2b** reacted with *N*-TMS anilides **1a–c** essentially slower than chlorosilane **2a**. Note that the nature of halogen atom at the silicon atom in reactants **2a**,**b** had little effect on the yield of final products **3a–c**.



a R = Me, X = Me (10 h with **2a**, 48 h with **2b**)
b R = Me, X = Cl (3 h with **2a**, 24 h with **2b**)
c R = Ph, X = H (48 h with **2a**, 240 h with **2b**)

Scheme 1 *Reagents and conditions*: i, $CHCl_3$, room temperature, 3–240 h.

The ^{29}Si NMR spectra of compounds **3a–c** show singlets at –34.3, –31.6 and –32.3 ppm, respectively, which lie in the range typical for (O–Si) chelate compounds with the coordination unit $C{=}O\rightarrow SiC_3Cl$[1,4,23] (see Online Supplementary Materials, Table S1) that confirms the pentacoordinate state of silicon atom in them.

Single crystals of anilides **3a**,**b** were obtained by recrystallization from benzene solution while single crystals of anilide **3c** were prepared from the melt, and their X-ray diffraction analysis was carried out (Figure 1).[†] The crystal data, data collection and structure refinement details are summarized

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[†] *Crystal data for* **3a**. $C_{12}H_{18}ClNOSi$, $M = 255.81$, colourless prism (0.25 × 0.40 × 0.40), monoclinic, space group $C2/c$, $a = 17.3707(11)$, $b = 10.0019(6)$ and $c = 16.2210(9)$ Å, $\beta = 99.797(2)°$, $V = 2777.1(3)$ Å^3, $Z = 8$, at 293 K, $d_{calc} = 1.224$ g cm^{-3}, $\mu = 0.343$ mm^{-1}, $F(000) = 1088$. Total 45061 reflections were collected (4133 independent reflections) and used in the refinement, 150 refined parameters, $S = 1.021$, and final R factor was 4.85 ($R_{int} = 0.1158$).

Crystal data for **3b**. $C_{11}H_{13}Cl_2NOSi$, $M = 274.21$, colourless prism (0.45 × 0.50 × 0.50), monoclinic, space group $C2/c$, $a = 17.4552(8)$, $b = 9.8986(5)$ and $c = 16.0718(8)$ Å, $\beta = 99.984(2)°$, $V = 2734.9(2)$ Å^3, $Z = 8$, at 293 K, $d_{calc} = 1.332$ g cm^{-3}, $\mu = 0.542$ mm^{-1}, $F(000) = 1136$. Total 25787 reflections were collected (3843 independent reflections) and used in the refinement, 168 refined parameters, $S = 1.032$, and final R factor was 4.94 ($R_{int} = 0.1031$).

Crystal data for **3c**. $C_{16}H_{18}ClNOSi$, $M = 303.85$, colourless prism (0.29 × 0.32 × 0.34), tetragonal, space group $P4_1$, $a = 10.5266(4)$, $b = 10.5266(4)$ and $c = 13.9411(7)$ Å, $\beta = 90°$, $V = 1544.80(14)$ Å^3, $Z = 4$, at 100 K, $d_{calc} = 1.381$ g cm^{-3}, $\mu = 0.185$ mm^{-1}, $F(000) = 640$. Total 45285 reflections were collected (4363 independent reflections) and used in the refinement, 183 refined parameters, $S = 1.058$, and final R factor was 2.57 ($R_{int} = 0.0289$).

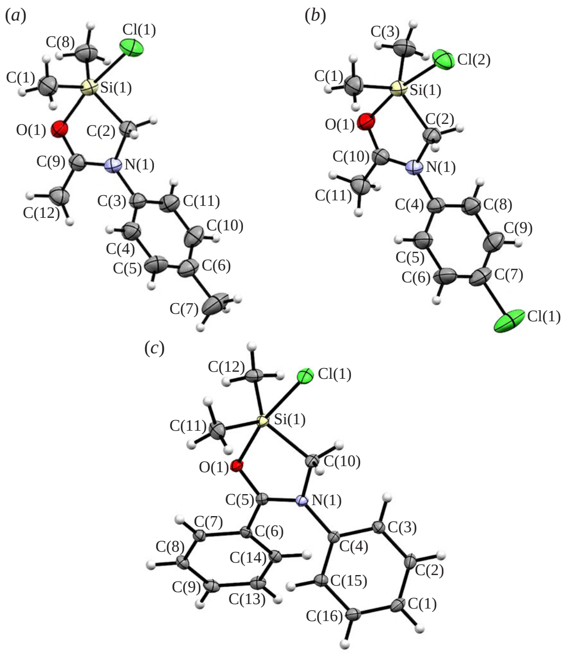


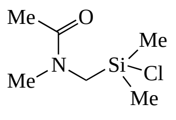
Figure 1 Molecular structures of compounds (*a*) **3a**, (*b*) **3b** (ORTEP, 20% thermal ellipsoids) and (*c*) **3c** (ORTEP, 50% thermal ellipsoids).

in Table S1, and the principal bond distances, bond angles and torsion angles are presented in Table S2 (see Online Supplementary Materials).

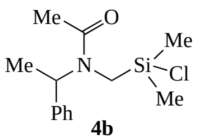
The selected bond lengths and angles for compounds **3a–c** and non-anilide related compounds **4a**,**b** are given in Table 1. The silicon atoms in the molecules **3a–c** have a distorted trigonal bipyramidal environment with three carbon atoms in the equatorial positions and chlorine and oxygen atoms in axial positions. The lengths of the C=O→Si dative bonds in compounds **3a**,**b** almost coincide [2.010(1) and 2.011(1) Å, respectively] and they are considerably longer (Δ ~ 0.035 Å) than the length of the C=O→Si dative bond in compound **3c** [1.976(1) Å]. It is quite possible that such significant difference is associated with the distinction of the thermal conditions: the X-ray diffraction analysis of compounds **3a**,**b** have been carried out at 293 K whereas crystal **3c** was analyzed at 100 K. Recently, we showed that the increase in temperature leads to elongation of the dative bond C=O→Si.[26] The lengths of the Si–Cl bonds are 2.273(1), 2.278(1) and 2.299(1) Å in compounds **3a–c**, respectively. The values of the Cl–Si–O angles differ from the unfolded angle (180°) by almost 10° [170.7(1), 170.1(1) and 169.4(1)° in anilides **3a–c**, respectively]. The pentacoordinate character of the silicon atom in these compounds was determined using the formula proposed by Tamao [η_{ax} (%)][27] and Kano[28] [η_{e} (%)] (see Table 1). The five-membered chelate heterocycles in anilides **3a–c** are almost planar and the deviation of the Si atom from the cycle plane is 0.078, 0.044 and 0.050 Å in them, respectively. The geometrical parameters of anilides **3a–c** are typical for the (O–Si) chelate compounds with the coordination unit C=O→SiC$_3$Cl (see Table 1).[1,15,16,29] The crystal structures of anilides **3a–c** are formed due to short contacts Cl(1)···H(8) (2.874 Å), O(1)···H(15) (2.598 Å) (anilide **3a**), Cl(2)···H(3) (2.803 Å), H(1)···C(10) (2.886 Å) (anilide **3b**) and Cl(1)···H(2) (2.884 Å), O(1)···H(17) (2.521 Å) (anilide **3c**) (see Online Supplementary Materials).

Table 1 The selected bond lengths and angles for compounds **3a**–**c** and related compounds **4a**,**b**.

Compound	l/Å		O–Si–Cl/deg	$\Sigma_{\mathrm{eq.}}$	η_{e} (%)	η_{ax} (%)	Reference
	O→Si	Si–Cl					
3a	2.010(1)	2.2735(7)	170.71	359.15	97.4	84.2	this work
3b	2.011(1)	2.2784(7)	170.08	359.23	97.5	85.0	this work
3c	1.976(1)	2.299(1)	169.42	359.58	98.7	88.7	this work
4a	1.945(2)	2.307(1)	170.69	359.76	99.0	90.4	15
4b	1.974(3)	1.893(3)	170.79	359.81	99.4	92.4	25



4a



4b

In summary, *N*-(chlorodimethylsilyl)methyl anilides were obtained by the reaction of *N*-TMS anilides with chloromethyl(dimethyl)halogenosilanes. The ^{29}Si NMR spectra and X-ray data of these compounds prove that they exist as (O–Si) chelate with 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.2022.11.030.

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The X-ray diffraction analysis was carried out on a Bruker D8 Venture diffractometer with MoKα radiation ($\lambda = 0.71073$) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[30] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set.[30]

CCDC 2156048 (**3a**), 2156049 (**3b**) and 1845007 (**3c**) 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.

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Received: 29th April 2022; Com. 22/6888