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Phenylhalosilazanes

S. V. Basenko, L. E. Zelenkov, M. G. Voronkov, and A. I. Albanov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: sv_basenko@irioch.irk.ru

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Abstract—A method of synthesis of phenylhalosilazanes by the reaction of phenyl(fluoro)chlorosilanes $PhSiF_{3-n}Cl_n$ (n = 0–3) with hexamethyldisilazane at room temperature is elaborated. The thermolysis of 1,1,1-trimethyl-3-phenyl-3,3-difluorodisilazane affords cyclic phenylfluorosilazanes $(PhSiFNHSiMe_3)_n$ (n = 3–5). The process may occur via the intermediate formation of phenylfluorosilimine.

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Earlier we have shown that organylfluoro- [1] and organylchlorosilanes [2] split the Si–N bond in hexamethyldisilazane **I** even at room temperature to form the corresponding organylchloro- and fluorodisilazanes.

In continuation of this research we have studied the reaction of phenyl(fluoro)chlorosilanes with compound **I** [3]. Phenyl(difluoro)chlorosilane was found to react with compound **I** (25°C, molar ratio 1:1, 2 h) to form 1,1,1-trimethyl-3-phenyl-3,3-difluorodisilazane in up to 92% yield.

$$PhSiF_2Cl + Me_3SiNHSiMe_3 \rightarrow PhSiF_2NHSiMe_3 + Me_3SiCl.$$

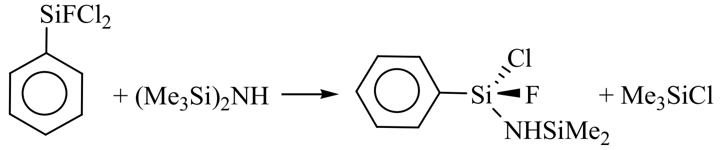
Therefore, only the Si–Cl bond of phenyl(difluoro)chlorosilane enters the reaction.

The increase of the molar content of compound **I** does not change the course of the reaction. The substitution of the fluorine atom of 1,1,1-trimethyl-3-phenyl-3,3-difluorodisilazane by the trimethylsilylamino group proceeds at room temperature very slowly, after 72 h the conversion is only 15%.

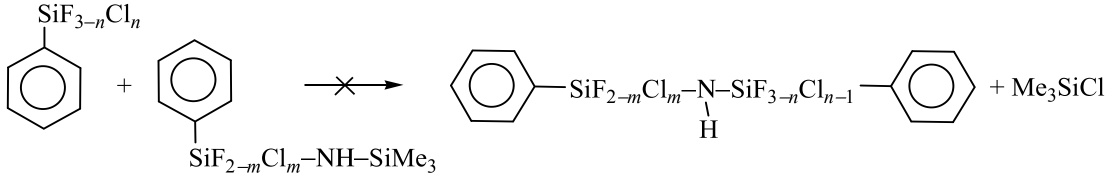
$$PhSiF_2NHSiMe_3 + Me_3SiNHSiMe_3$$
$$\rightarrow PhSiF(NHSiMe_3)_2 + Me_3SiF.$$

The reaction of phenyl(difluoro)chlorosilane with the equimolar mixture of compound **I** and hexamethyldisiloxane **II** (molar ratio 1:1:1, 25°C) proceeds exclusively with the cleavage of the Si–N bond.

In the reaction of phenyl(fluoro)dichlorosilane with compound **I** (molar ratio 1:1, 25°C, 4 h) the 1,1,1-trimethyl-3-phenyl-3-fluoro-3-chlorodisilazane is formed in up to 73% yield.

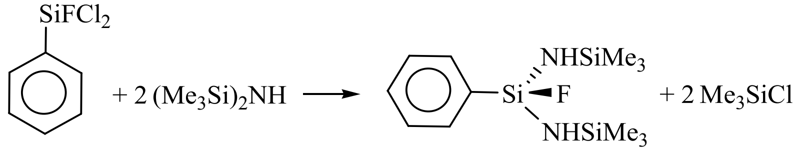


The formed 1-phenyl-1,1-difluoro- and 1-phenyl-1-fluoro-1-chloro-3,3,3-trimethyldisilazanes do not react with the starting phenylfluorochlorosilanes under the studied conditions.

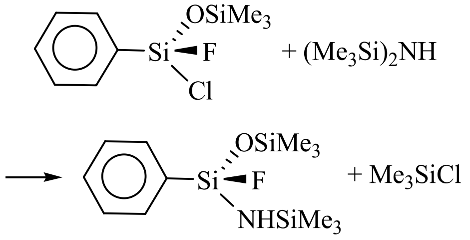


n = 1, 2; m = 0, 1.

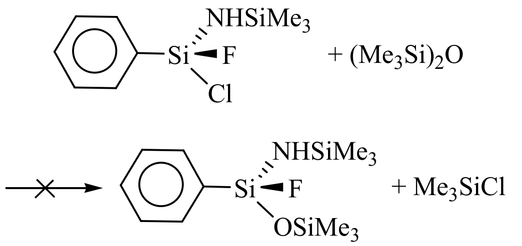
The reaction of phenyl(fluoro)dichlorosilane with compound **I** (molar ratio 1:2, 25°C, 24–36 h) results in the formation of 1,1,1,5,5,5-hexamethyl-3-phenyl-3-fluorotrisilazane in a high yield (79–87%).



The difference in the reactivity of the Si–N and Si–O bonds of compounds **I** and **II**, respectively, allowed obtaining the earlier unknown mixed phenyl(fluoro)-siloxazanes. Thus, the successive reaction of phenyl (fluoro)dichlorosilane with siloxane **II** (molar ratio 1:1, 25°C, 12–24 h) and silazane **I** leads to 1,1,1,5,5,5-hexamethyl-3-phenyl-3-fluorosiloxazane.



Note that the reaction of 1-phenyl-1-fluoro-1-chloro-3,3,3-trimethyldisilazane with hexamethyldisiloxane does not give the above product under the studied conditions.



Our investigations suggest that the ammonium salts which could be formed in small amounts due to the reaction of ammonia dissolved in silazane with hydrogen halides in halosilanes do not possess catalytic activity [4].

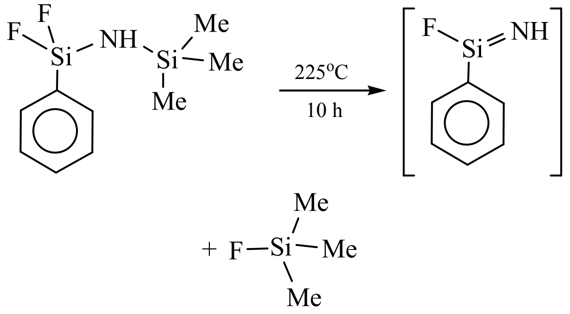
The investigation of the three-component concurrent reactions of the mixtures of phenylhalosilanes $PhSiF_{3-n}Cl_n$ (n = = 0–3) with hexamethyldisilazane (molar ratio of the reagents 1:1:0.9, 25°C) gives the following order of activity of phenylhalosilanes with respect to hexamethyldisilazane: $PhSiF_2Cl > PhSiFCl_2 > PhSiCl_3 > PhSiF_3$.

The ease of the reaction of phenylfluorochlorosilanes (especially of $PhSiF_2Cl$) with hexamethyldisilazane is due to much larger polarizability and less strength of the Si–Cl bond as compared to the Si–F bond, which results in the selective substitution of the chlorine atom in the studied reactions.

The available literature data [5] suggest that these reactions are assisted by the effect of n,σ^*-interaction, which should result in stabilization of the lone electron pair of the fluorine atom, in the shortening of the Si–F bond and the elongation of the Si–Cl bond, favoring the rupture of the latter in the studied reactions.

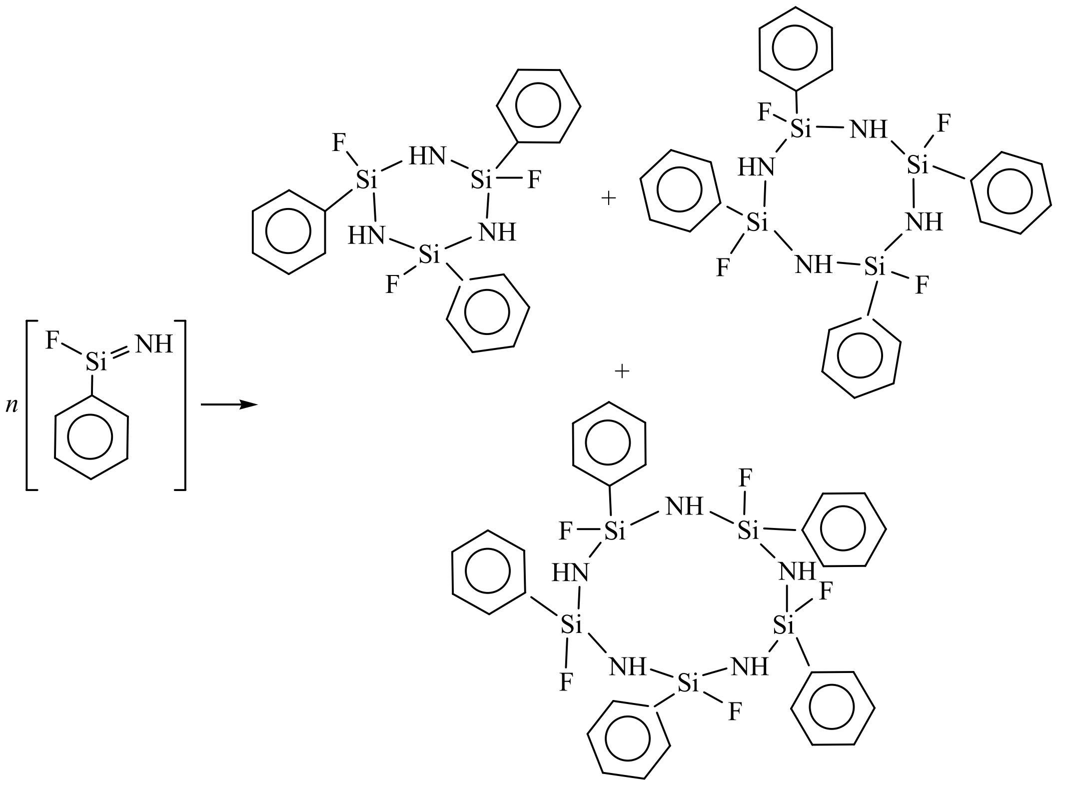
An alternative point of view on the electronic effects in the systems containing the chlorine and fluorine atoms at the same silicon or carbon atom is named "the effect of positive charge" [6]. This effect is also consistent with the data obtained in the present study.

The thermolysis of 1,1,1-trimethyl-3-phenyl-3,3-difluorodisilazane results in the formation of cyclic structures, which were identified by the methods of ^{19}F, ^{29}Si NMR spectroscopy and chromatomass spectrometry. It can be assumed that the thermolysis proceeds with the intermediate formation of phenylfluorosilimine, which undergoes further cyclization.



Phenylfluorocyclosilazanes with 3- and 4-phenylfluorosilazane links are predominantly formed.

The products of insertion of phenylfluorosilimine into the molecules of the starting 1,1,1-trimethyl-3-phenyl-3-fluorosilazane were registered only by the ^{19}F NMR spectroscopy method and are contained as admixtures (see the table). Apparently, the formed linear products of insertion undergo further thermal decomposition with the formation of phenylfluoro-



$n = 3–5.$

silimine, whereas phenylfluorocyclosilazanes may be more stable under the conditions of the reaction.

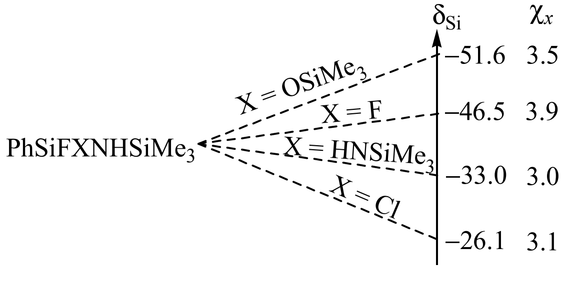
Earlier it was mentioned that the increase in the number of aminogroups in silazanes $Me_{4-n}Si(NR_2)_n$ from 1 to 4 leads to successive shielding of the silicon atom [7].

Parameters of ^{19}F, ^{29}Si NMR spectra of phenyl(fluoro)-chlorodisilazanes (CCl_4, 20%)

Compound	δ_{Si}, ppm		δ_F, ppm	J_{SiF}, Hz
	PhSi≡	$SiMe_3$		
$PhSiF_2NHSiMe_3$	–46.5	6.2	–134.57	262.5
$PhSiFClNHSiMe_3$	–26.1	–6.9	–122.26	289.9
$PhSiF(NHSiMe_3)_2$	–33.0	4.3	–131.44	257.9
$PhSiFOSiMe_3(NHSiMe_3)$	–51.6	4.5/11.1 ($OSiMe_3$)	–130.53	254.4
$PhSiCl_2NHSiMe_3$	–11.5	7.3	–	–
$(PhSiFNH)_3$	–35.7	–	–126.28	272.4
$(PhSiFNH)_4$	–35.6	–	–125.45	273.8
$(PhSiFNH)_5$	–35.0	–	–125.23	269.2

Number of amino groups	$n = 1$	$n = 2$	$n = 3$	$n = 4$
δ_{Si}	5.9	–1.7	–17.2	–28.6
$\Delta\delta_{Si}$	0	7.6	23	35

However, the replacement of the fluorine atom in 1,1,1-trimethyl-3-phenyl-3,3-difluorodisilazane with the second trimethylsilylamino group results in deshielding of the silicon atom by 14 ppm, with the chlorine atom, by 20 ppm, whereas its replacement with trimethylsiloxy group, on the contrary, leads to the shielding of the silicon atom by 5 ppm. The correlation relationship δ_{Si}–χ_x can be represented as follows.



Oppositely directed variation in the ^{29}Si chemical shifts in $Me_{4-n}Si(NR_2)_n$ and $PhSiF_{4-n}(NHSiMe_3)_n$ with variation in the number of the Si–N bonds can be explained as follows: ^{29}Si chemical shifts in these series of compounds lie on the branch of the $\delta \sim f(\chi_x)$ relationship, where the increase in the electronegativity of the substituents leads to the shielding of the silicon atom [8]. Whereas the increased number of amino-groups in amino(methyl)silanes increases the $\Sigma\chi_x$, for compounds $PhSiF_{4-n}(NHSiMe_3)_n$ it has the opposite effect. The replacement of the fluorine atom in $PhSiF_2\cdot(NHSiMe_3)$ by chlorine also decreases the sum of electronegativities at the silicon atom $\Sigma\chi_x$ and, hence, causes deshielding of ^{29}Si.

The increase of the silicon shielding upon the replacement of the fluorine atoms in these molecules by trimethylsiloxy group is anomalous since the latter is less electronegative as compared to fluorine atom. However, a larger shielding of the silicon atom by the trimethylsiloxy group has already been mentioned in the literature [7].

It was noted [9] that the decrease in the size of the ring of dimethylcyclosilazanes results in deshielding of the silicon atom by 3–5 ppm. In the case of phenylfluorocyclosilazanes the ring size has practically no effect on the chemical shifts of silicon, fluorine, and the coupling constants (J_{SiF}).

EXPERIMENTAL

^{1}H, ^{19}F and ^{29}Si spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100.13 (^{13}C), 376.47 (^{19}F), 79.49 (^{29}Si) MHz in CCl_4 (for ^{1}H $CDCl_3$ was added), internal reference tetramethylsilane (^{1}H, ^{13}C, ^{29}Si), and CCl_3F (^{19}F).

Mass spectra were taken on a Shimadzu GCMS-QP5050A chromatomass spectrometer, injector temperature 200–250°C, carrier gas helium, temperature of detector 250°C, quadruple mass analyzer, electron ionization with the ionization voltage 70 eV.

Mixed phenyl(fluoro)chlorosilanes $PhF_{3-n}Cl_n$ (n = 1–2) were prepared by disproportionation of $PhSiF_3$ with $PhSiCl_3$ [10].

Reaction of phenylfluorochlorosilanes with silazanes. $PhSiF_2NHSiMe_3$. An ampule was charged with 10 ml (0.067 mol) of dry $PhSiF_2Cl$ under dry argon, degassed five times in a vacuum, 14 ml (0.067 mol) of the similarly degassed $(Me_3Si)_2NH$ was added, and the ampule was sealed. The mixture was kept for 2–4 h. On opening the ampule the content was transferred to the distillation flask pre-filled with argon and pre-heated, and the mixture was distilled. Yield 13.9–14.2 g (90–92%), n_D^{20} 1.4510, bp 55–58°C (2 mm Hg). ^{19}F NMR spectrum, δ_F: –134.57 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –46.5 t (PhSi≡), 6.2 ($SiMe_3$, J_{SiF} 262.5 Hz). Mass spectrum, m/z, %: 231(1) $[M]^+$, 216 (100) $[M - Me]^+$, 200(6) $[M - Me - MeH]^+$, 188(4) $[M - C_3H_7]^+$, 143(5), 135(27) $[PhSiMe_2]^+$, 132(3), 91 (4), 77(6) $[Ph]^+$, 73(12) $[SiMe_3]^+$.

$PhSiFCl(NHSiMe_3)$. Yield 73%, bp 71–71.5°C (2 mm Hg). ^{19}F NMR spectrum, δ_F: –122.26 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –26.1 d (PhSi≡), 6.9 ($SiMe_3$, J_{SiF} 289.9 Hz).

$PhSiF(NHSiMe_3)_2$. Yield 87%, bp 106–108°C (2 mm Hg). ^{19}F NMR spectrum, δ_F: –131.44 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –33.0 d (PhSi≡), 4.3 ($SiMe_3$, J_{SiF} 257.9 Hz). Mass spectrum, m/z, %: 300(1) $[M]^+$, 285(41) $[M - Me]^+$, 269(3) $[M - Me - MeH]^+$, 257(13) $[M - C_3H_7]^+$, 253(9), 175(14), 135(100) $[PhSiMe_2]^+$, 77(6) $[Ph]^+$, 73(30) $[SiMe_3]^+$.

$PhSiFOSiMe_3(NHSiMe_3)$. Yield 84%. ^{19}F NMR spectrum, δ_F: –130.53 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –51.6 d (PhSi≡), 4.5 ($NHSiMe_3$), 11.1 ($OSiMe_3$, J_{SiF} 254.4 Hz) Mass spectrum, m/z %: 301(5) $[M]^+$, 217 (95) $[M - Me]^+$, 270(5) $[M - Me - MeH]^+$, 254(5), 208 (10); 194(35); 176(4), 162(2), 136(28), 135(100) $[PhSiMe_2]^+$, 132(19), 121(6), 107(6), 91(9), 77(12) $[Ph]^+$, 74 (13), 73(33) $[SiMe_3]^+$.

The obtained compounds are very sensitive to heating and air moisture.

Thermolysis of $PhSiF_2NHSiMe_3$. The calcined ampule was charged with 1.16 g (5 mmol) of $PhSiF_2\cdot NHSiMe_3$ in a nitrogen atmosphere, sealed, and maintained at 225°C for 8 h. After opening and removal of solvent the residue was analyzed. On attempt to distillate in a vacuum (1 mm Hg) the mixture polymerizes.

$(PhSiFNHSiMe_3)_3$. ^{19}F NMR spectrum, δ_F: –126.28 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –35.7 d (J_{SiF} 272.4 Hz). Mass spectrum, m/z %: 417(48) $[M]^+$, 399(2), 340(100) $[M - Ph]^+$, 323(44), 321(7), 303(11), 262(29), 260(4), 242(6), 219(5), 199(8), 197(7), 169 (16), 166(7), 161(7), 77(17) $[Ph]^+$.

$(PhSiFNHSiMe_3)_4$. ^{19}F NMR spectrum, δ_F: –125.45 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –35.6 d (J_{SiF} 273.8 Hz).

$(PhSiFNHSiMe_3)_5$. ^{19}F NMR spectrum, δ_F: –125.23 ppm. ^{29}Si NMR spectrum, δ_{Si}, ppm: –35.0 d (J_{SiF} 269.2 Hz).

$(PhSiFNHSiMe_3)_n$ (n = 4–5) could not be detected mass-spectrometrically because of technical limitations of the detector.

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