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Si-Containing Amides of Phosphoric Acid

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Summary. The first representative of the *N*-silylmethylamides of phosphoric acid $O{=}P[NMe(CH_2SiMe_n(OEt)_{3-n}]_3$ have been synthesized by interaction of $MeNHCH_2SiMe_n(OEt)_{3-n}$ ($n = 2$, 3) with $POCl_3$. The interaction of the *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(ethoxydimethylsilyl)methyl]triamide phosphoric acid with $BF_3 \cdot Et_2O$ or BCl_3 results in the formation of the *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(fluorodimethyl-silyl)methyl]triamide phosphoric acid or *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(chlorodimethylsilyl)methyl]triamide phosphoric acid. NMR data show on the tetracoordinate state of silicon in these products.

Keywords. *N*-Silylmethylamides; Phosphoric acid.

Introduction

The investigation of the synthesis, reactivity, and structure of amides of phosphoric acid is significant in organophosphorus chemistry. These compounds have attracted attention in early studies [1] and they have been studied more extensively in many laboratories [2]. Substantially this interest is caused by their use as bidentate P,N-ligands in metallocomplex catalysis [3]. The hexamethyltriamidophosphate, $(Me_2N)_3P{=}O$, is best known among such compounds. It is used both as a reagent [4] and solvent [1]. The development of synthetic methods for polyheteroatomic structures containing several reactive centers holds promises for the progress of modern organoelement chemistry. So, the chemistry of compounds containing simultaneously P and Si groups has developed intensively in the last decades [5]. The compounds X-CH_2-M with heteroatoms $X = O$, S, or N in geminal position relative to a group 14 element ($M = Si$, Ge, Sn) often show unusual reactivity and exhibit unexpected spectroscopic properties in comparison with the carbon analogs XCH_2CY_3 [6]. We observed recently that the nitrogen in α-silylmethylamines $R_2NCH_2SiX_3$ has a surprisingly high reactivity [7]. The intramolecular electronic interactions in the fragment X-CH_2-Si determine it, however their nature is still a

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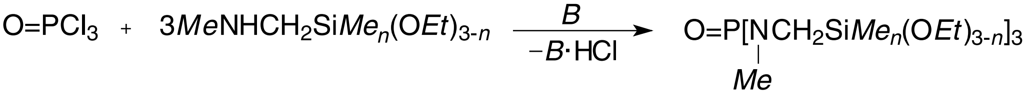
subject of discussion [8]. We have continued our investigation of the reactivity of α-silylmethylamines and we have studied their interaction with the phosphorus oxychloride. We speculate that the introduction of the organosilicon substituent in the α-position to the nitrogen atom in the amides of the phosphoric acid can result to the production of interesting multifunctional compounds with unique reactivity.

Results and Discussion

The reaction of amines $RR'NH$ with a P(O)–Cl bond is a classical method for the synthesis of amides of phosphoric acid [9]. However, phosphorus halogenides give rise to cleavage of the Si–O–C bond [10] and the reaction of the amines $R\mathrm{NHCH_2Si}Me_n(\mathrm{O}Alk)_{3\text{-}n}$ with $\mathrm{P(O)Cl_3}$ can be complicated by side processes. Despite this, we have synthesized the first representatives of the N-silylmethylamides of phosphoric acid, $\mathrm{O{=}P[N}Me\mathrm{(CH_2Si}Me_n\mathrm{(O}Et)_{3\text{-}n}]_3$ (Scheme 1).

Compounds **1** and **2** were synthesized by phosphorylation of the amines by phosphoric acid chloroanhydrides in the presence of hydrogen chloride acceptors. These reactions were conducted in anhydrous Et_2O or *THF* in the temperature interval from −8 to +10°C. An excess of triethylamine or pyridine was necessary for trapping hydrogen chloride. Table 1 summarizes the yields of **1** and **2** obtained by changing the base, solvent, and temperature. The yield of compound **1** does not depend on a solvent, temperature, and base. The yield of compound **2** depends considerably on temperature. The cleavage of the Si–O–C bond runs sluggishly at low temperature. Therefore it is necessary to monitor the temperature carefully.



$$\mathrm{O{=}PCl_3} + 3Me\mathrm{NHCH_2Si}Me_n\mathrm{(O}Et)_{3\text{-}n} \xrightarrow[-B\cdot\mathrm{HCl}]{B} \mathrm{O{=}P[}\underset{\displaystyle Me}{\mathrm{N}}\mathrm{CH_2Si}Me_n\mathrm{(O}Et)_{3\text{-}n}]_3$$

$n = 3$ (**1**)

$n = 2$ (**2**)

Scheme 1

Table 1. Influence of base, solvent, and temperature on the yield of **1** and **2**

n	Base	Solvent	T/°C	Yield/%
3	Et_3N	Et_2O	−8	75.5
3	Et_3N	Et_2O	0	77.0
3	Et_3N	Et_2O	10	76.4
3	Et_3N	*THF*	0	78.2
3	C_5H_5N	Et_2O	0	75.8
2	Et_3N	Et_2O	0	57.0
2	Et_3N	Et_2O	−8	65.6
2	Et_3N	Et_2O	10	39.8
2	C_5H_5N	Et_2O	0	51.4
2	C_5H_5N	Et_2O	−8	52.7
2	Et_3N	*THF*	0	56.5

Table 2. ^1H, ^{29}Si, ^{31}P NMR data for **1–4** ($CDCl_3$, $T = 25°C$)

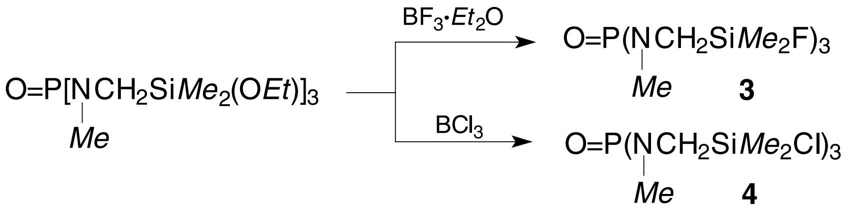
No.	δ_H					δ_{Si}	δ_P
	*Me*Si	CH_3(O*Et*)	NCH_2Si	N*Me*	CH_2(O*Et*)		
1	0.16 s		2.90, 2.85 (12dd)	2.75 (d, $^3J_{PH} = 13.64$ Hz)		0.82 ($^3J_{SiP} = 11.98$ Hz)	34.72
2	0.21 (s)	1.19 (t, $J = 6.96$ Hz)	2.71, 2.55 (2dd, $^2J_{AB} = 15.45$ Hz, $^3J_{PH} = 9.13$, 8.87 Hz)	2.75 (d, $^3J_{PH} = 13.7$ Hz)	3.70 (q)	13.78 ($^3J_{SiP} = 13.6$ Hz)	34.82
3	0.37 (d, $^3J_{FH} = 6.9$ Hz)		2.80 (m)	2.85 (d, $^3J_{PH} = 14.1$)		30.0 ($^1J_{SiF} = 285.7$ Hz, $^3J_{SiP} = 12.6$ Hz, 29.8 (−55°C)	35.0
4	0.56 (s)		2.92, 2.79 (2dd, $^2J_{AB} = 15.68$ Hz, $^3J_{PH} = 9.72$, 12.2 Hz)	2.78 (d, $^3J_{PH} = 13.4$ Hz)		25.42 ($^3J_{SiP} = 10.7$ Hz) 25.40 (−55°C)	33.29

Table 3. ^{13}C NMR data for **1–4** ($CDCl_3$, $T = 25°C$)

No.	*Me*Si	CH_3(*Et*)	NCH_2Si	N*Me*	CH_2O
1	−1.37		40.07	36.8 ($^2J_{CP} = 3.06$ Hz)	
2	−2.38 ($^4J_{CP} = 6.52$ Hz)	18.25	38.87 ($^2J_{CP} = 2.3$ Hz)	36.53 ($^2J_{CP} = 2.30$ Hz)	58.27
3	−1.90 ($^4J_{CP} = 10.35$, $^2J_{CF} = 13.42$ Hz)		39.80 ($^2J_{CF} = 15.72$ Hz)	36.66 ($^2J_{CP} = 3.83$ Hz)	
4	1.9 ($^4J_{CP} = 12.0$ Hz)		41.83	37.18 ($^2J_{CP} = 1.92$ Hz)	

1 and **2** are high-boiling, oleaginous liquids with a weak odour. Their structure was confirmed by multinuclear NMR spectroscopy (Tables 2 and 3). The assignment of signals in the ^1H NMR spectra was based on their chemical shifts, multiplicity, and integral intensity.

The interaction of the *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(ethoxydimethylsilyl)methyl]-triamide phosphoric acid (**2**) with $BF_3 \cdot Et_2O$ or BCl_3 results in the formation of the *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(fluorodimethylsilyl)methyl]triamide phosphoric acid (**3**) or *N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris[(chlorodimethylsilyl)methyl]triamide phosphoric acid **4** (Scheme 2).



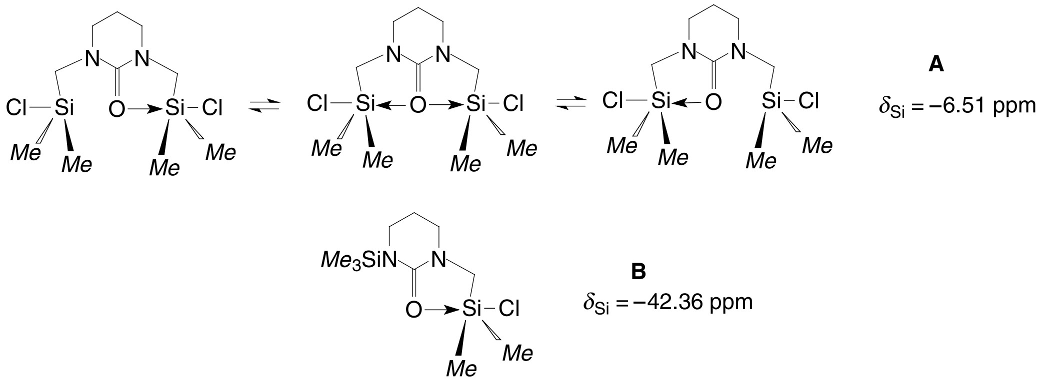
Scheme 2

These compounds are viscous, slightly yellowish, opalescent liquids, which do not crystallize even after long storage. They decompose upon vacuum distillation.

The structure of the synthesized compounds was investigated by multinuclear NMR spectroscopy (Tables 2 and 3). We assumed that compounds **3** and **4** exist in the form of chelates (type A) with an intramolecular coordination bond P=O→Si. Earlier we reported that the *N*-methyl-*N*-[(alkoxymethylsilyl)methyl]amides of carboxylic acids, $RC(O)NMeCH_2SiMe_n(OEt)_{3\text{-}n}$, react easily with $BF_3 \cdot Et_2O$ with the formation of *N*-methyl-*N*-[(fluoromethylsilyl)methyl]amides of carboxylic acids, $RC(O)NMeCH_2SiMe_nF_{3\text{-}n}$ [11]. The latter exist in the form of O,Si-chelates with an intramolecular O→Si coordination bond. Among the compounds of hypervalent silicon *N*-[(halogendimethylsilyl)methyl]amides of carboxylic acids have been most studied. Their structure has been investigated by various spectroscopic methods and the factors determining the degree of the coordination interaction C=O→Si are established [12]. The most important criterion for the existence of the interaction C=O→Si in these compounds is the high field shift of ^{29}Si in comparison with compounds of tetracoordinate silicon XCH_2SiMe_2Y [13]. The chemical shifts observed in the ^{29}Si NMR spectra are 30.0 ppm for **3** ($^1J_{SiF} = 285.7$ Hz) and 25.42 ppm for **4**, which is typical of compounds of tetracoordinate silicon. The ^{29}Si chemical shift in **3** and **4** is observed at low field in comparison with $ClCH_2SiMe_2F$ ($\delta_{Si} = 24.8$ ppm, $J_{SiF} = 287$ Hz) and $ClCH_2SiMe_2Cl$ ($\delta_{Si} = 23.7$ ppm) and the value of J_{SiF} varies insignificantly. All these data show the absence of an intramolecular coordination bond P=O→Si in **3** and **4**. We note that the δ_{Si} value in the compounds **3** and **4** does not vary when the temperature is decreased (Table 2).

These results were unexpected. The P=O group has high donor properties [14] which explains the very good solvating ability of the $O{=}P(NMe_2)_3$ [1]. The amides of phosphoric acid are widely used as ligands in the synthesis of coordination compounds of main group elements (Al, Sn, Pb) [15]. The formation of a complex between a *Lewis* acid and the phosphoryl group of the diethyl crotylphosphonate provides the stereoselective course of the *Mukayami-Michael* reaction [16]. The phosphoryl group is capable of forming intramolecular coordination bonds P=O→*M*, where *M* is an element of group 4 (Si, Ge, Sn). For example, the interaction of the *in situ* generated $LiCH_2NMeP(O)(NMe_2)_2$ with $H\text{-}GeR_3$ results in the production of a compound with an intramolecular coordination bond P=O→Ge [17]. The existence of the intramolecular coordination interaction P=O→*M* (*M* = Si, Ge, Sn) has been proved in phosphinoxides and ethers of phosphoric acid [18]. The authors [19] expected, that the reaction of the *N*,*N*,*N′*,*N′*-tetraethyl-*N″*-*tert*-butyltriamide of phosphoric acid with *Bu*Li and the subsequent interaction with $ClCH_2SiMe_2Cl$ resulted in the formation of an O,Si-chelated cycle with the intramolecular coordination bond P=O→Si. However, the product of this reaction is 2-phospha-4-silaoxazolidine, with formation of a coordination bond Cl→Si. At present the number of compounds with an intramolecular coordination bond P=O→Si is extremely small.

The nature of the substituents *R* and *R′* of *R*C(O)N*R′*− amide group in the series of O,Si-chelated amides of carboxylic acids significantly influences the degree of the intramolecular C=O→Si coordination bond [20]. So, the introduction of a second *N*-acetyl group in *N*-(chlorodimethylsilyl)methyl-*N*-acetylacetamide ($\delta_{Si} = -24.2$ ppm [20a]) results in a significant weakening of the intramolecular



A

$\delta_{Si} = -6.51$ ppm

B

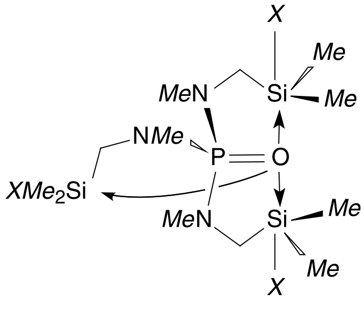
$\delta_{Si} = -42.36$ ppm

Fig. 1. Competitive interaction of two Si-containing groups with one donor center in compound **A** and only one such interaction in **B**

coordination interaction as compared with *N*-(chlorodimethylsilyl)methyl-*N*-methylacetamide ($\delta_{Si} = -37.6$ ppm [20b, 20c]). Apparently, it is caused by a possibility of competitive interaction of the one silyl group with two C=O donor groups. We determined that a more significant weakening of the intramolecular coordination interaction C=O→Si in the *N*,*N′*-bis[(chlorodimethylsilyl)methyl]tetrahydro-2-pyrimidinone (**A**) is observed as compared to the *N*-trimethylsilyl-*N′*-[(chlorodimethylsilyl)methyl]tetrahydro-2-pyrimidinone (**B**) [21] (Fig. 1).

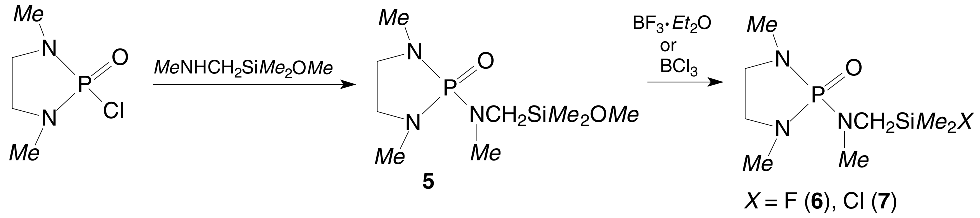
The value of the ^{29}Si chemical shift does not change significantly when the temperature decreases down to −90°C. Probably, a competitive interaction of two Si-containing groups with one donor center exists in **A**, what is known as ⟪flip-flop rearrangement⟫ [22]. We assumed that the low field ^{29}Si shift in compounds **3** and **4** may be associated with fast "flip-flop" rearrangement owing to the competitive interaction of already three silyl groups of the *N*,*N′*,*N″*-trimethyl-*N*,*N′*,*N″*-tris[(halodimethylsilyl)methyl]triamidophosphate to one donor center – the phosphoryl group (**C**) (Fig. 2).

We then synthesized amides **5**–**7** of phosphoric acid containing only one silyl group (Scheme 3).



C

Fig. 2. Competitive interaction of three Si-containing groups with one donor center in compound **C**



Scheme 3

Table 4. ^{1}H, ^{13}C, ^{29}Si, ^{31}P NMR data for **5–7** ($CDCl_3$, $T = 25°C$)

No.		*Me*Si	NCH$_2$Si	*Me*N(CH$_2$–)	N*Me*	*Me*O	CH$_2$–CH$_2$	δ_{Si}	δ_P
5	^{1}H	0.30 (s)	2.28, 2.57 (dd)	2.73 (m)	2.55 (d, $^{3}J_{PH} =$ 9.53 Hz)	3.46 (s)	3.08, 3.16 (m)	6.48 ($^{3}J_{SiP} =$ 13.13 Hz)	29.68
	^{13}C	0.27 ($^{4}J_{CP} =$ 5.52 Hz)	34.03 ($^{2}J_{CP} =$ 4.91 Hz)	31.68	31.62 ($^{2}J_{CP} =$ 5.52 Hz)	51.32	47.81		
6	^{1}H	0.36 (d, $^{3}J_{FH} = 7.5$)	2.32 (m)	2.75 (m)	2.65 (Д, $^{3}J_{PH} =$ 9.86)		3.04, 3.25 (m)	29.47 ($^{1}J_{SiF} =$ 285.26 Hz, $^{3}J_{SiP} = 8.06$ Hz)	30.27
	^{13}C	−1.85 ($^{2}J_{CF} =$ 13.98 Hz)	39.81	31.52	36.12		44.55		
7	^{1}H	0.43	2.68 (m)	2.83 (m)	2.59		3.08, 3.21 (m)	26.43 ($^{3}\mathrm{J}_{SiP} =$ 11.1 Hz)	31.12
	^{13}C	−0.35	37.2	32.36	36.21		45.47		

The "flip-flop" rearrangement does not take place in compounds **6** and **7**. However, values of the ^{29}Si and ^{31}P chemical shift for compounds **6** and **7** almost coincide with the chemical shift for compounds **3** and **4** (Tables 2 and 4). These results show, that the "flip-flop" rearrangement is not the reason for the low field shift of the ^{29}Si resonance in compounds **3** and **4**. The value of $\bar{\nu}_{P=O}$ decreases about 20–70 cm^{-1} upon formation of coordination bonds of type $P{=}O{\rightarrow}A$ [23]. However, this value changes very little in compounds **1–7**.

Conclusion

We synthesized a series of Si containing amides of phosphoric acid. We expected, that the silicon atom in these compounds will be pentacoordinated owing to the intramolecular P=O→Si coordination. However, the spectral data obtained show that the silicon atom is tetracoordinate in all synthesized compounds. Apparently, the reason is due to the different properties of P=O and C=O groups as *Lewis* bases. Probably, the application of hard or soft donors concept [24] will allow to explain the absence of P=O→Si interaction in compounds **3**, **4**, **6**, and **7**. It is necessary to note also, that the *Lewis* acidity is slightly increased with increasing of the number of fluorine atoms at silicon [25]. May be replacement of SiMe_2F by

SiF_3 in Si containing amides of phosphoric acid will provide the intramolecular coordination interaction P=O→Si.

Experimental

NMR spectra of 20% solutions of the compounds in $CDCl_3$ were recorded on a Bruker 400 MHz spectrometer with use of cyclohexane as inner standard. The solvents we purified using standard procedures [26]. MeNHCH$_2$SiMe_n(OAlk)$_{3-n}$ ($n = 2$, 3) have been synthesized using the method described in Ref. [27]. $P(O)Cl_3$ is commercially available from "Acros". Results of elemental analysis agreed favourably with calculated values.

*General Procedure for the Synthesis of **1** and **2***

A solution of 0.003 mol $MeNHCH_2SiMe_3$ or $MeNHCH_2SiMe_2(OEt)$ in 25 cm^3 dry Et_2O was added to 0.0033 mol Et_3N. The mixture was cooled to 0 ± 2°C and 0.001 mol $P(O)Cl_3$ in 10 cm^3 dry Et_2O were added slowly with stirring. The reaction mixture was stirred for 1 h at this temperature. Then the temperature of the solutions was increased up to rt and was stirred for 12 h. The precipitate of triethylamine hydrochloride was filtered off, washed with Et_2O (2×10 cm^3), and the ether was added to the filtrate. The ether was evaporated and the residue was distilled in vacuum.

1 ($C_{15}H_{42}N_3OPSi_3$): Yield 77%; bp = 136–138°C/2 mm Hg; IR: $\bar{\nu}$ = 1260 (P=O) cm^{-1}.

2 ($C_{18}H_{48}N_3O_4PSi_3$): Yield 57%; bp = 168–170°C/2 mm Hg; IR: $\bar{\nu}$ = 1265 (P=O) cm^{-1}, 1105(Si–O–C) cm^{-1}.

N,N′,N″-Trimethyl-N,N′,N″-tris[(fluorodimethylsilyl)methyl]triamide of phosphoric acid (**3**, $C_{12}H_{33}F_3N_3OPSi_3$)

$BF_3 \cdot Et_2O$ (0.0002 mol) was added slowly to 0.0006 mol **2** in 5 cm^3 dry Et_2O. The reaction mixture was stirred for 2 h at ambient temperature. The solvent was evaporated and the residue was dried vacuum. The yield of **3** is practically quantitative. IR: $\bar{\nu}$ = 1268 (P=O) cm^{-1}.

N,N′,N″-Trimethyl-N,N′,N″-tris[(chlorodimethylsilyl)methyl]triamide of phosphoric acid (**4**, $C_{12}H_{33}Cl_3N_3OPSi_3$)

A solution of 0.0006 mol **2** in 5 cm^3 dry pentane was cooled to 5°C and 0.00066 mol BCl_3 in 5 cm^3 dry pentane were added slowly. The reaction mixture was stirred for 1 h at this temperature and then for 2 h at ambient temperature. The solvent was evaporated and the residue was dried in vacuum. The yield of **4** is practically quantitative. IR: $\bar{\nu}$ = 1266 (P=O) cm^{-1}.

*Synthesis of **5*** ($C_8H_{21}ClN_3OPSi$)

To a solution of 0.025 mol $(CH_2NMe)_2POCl$ in 20 cm^3 anhydrous diethyl ether, cooled to 0°C, was slowly added with stirring a solution of 0.05 mol $MeNHCH_2SiMe_2OMe$ in 10 cm^3 of the same solvent. The mixture was stirred for 5 h at this temperature and 18 h at room temperature. The precipitated amine hydrochloride was separated by filtration. The filtrate was evaporated in vacuum and the residue was distilled in vacuum. Bp = 112–114°C/3 mm Hg; IR: $\bar{\nu}$ = 1275 (P=O), 1110 (Si–O–C) cm^{-1}.

Compounds **6** and **7** have been synthesized similarly to **3** and **4**. These compounds are viscous, slightly yellowish, opalescent liquids, which do not crystallize even after 2 weeks storage.

6 ($C_8H_{21}FN_3OPSi$): IR: $\bar{\nu}$ = 1272 (P=O) cm^{-1}.

7 ($C_8H_{21}ClN_3OPSi$): IR: $\bar{\nu}$ = 1275 (P=O) cm^{-1}.

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