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Synthesis and Structure of Silicon-containing *N*-Methyl- and *N*-Benzoylamides of Diisopropylphosphoric Acid

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Abstract — Diisopropyl *N*-benzoyl-*N*-(trimethylsilyl)phosphoramidate reacts with $ClCH_2SiMe_2Cl$ under mild conditions to form diisopropyl *N*-benzoyl-*N*-[(chlorodimethylsilyl)methyl]phosphoramidate (**III**). Diisopropyl *N*-methyl-*N*-(trimethylsilyl)phosphoramidate with $ClCH_2SiMe_2Cl$ affords an N-transsilylation product which does not rearrange into diisopropyl *N*-[(chlorodimethylsilyl)methyl]-*N*-methylphosphoramidate (**XV**) even under severe conditions (4 h, 130°C). Compound **X**V was prepared by the reaction of diisopropyl phosphorochloridate with *N*-[(methoxydimethylsilyl)methyl]-*N*-methylamine followed by treatment of diisopropyl *N*-[(methoxydimethylsilyl)methyl]-*N*-methylphosphoramidate with boron trichloride. Analysis of experimental and calculated ^{29}Si chemical shifts points to a five-coordinate silicon atom in compound **III** and a four-coordinate silicon atom in compound **XV**. According to B3LYP calculations with due regard to solvent effects, compound **III** is an isomer with a C=O→Si bond. By variation of substituents at silicon, phosphorus, and carbonyl carbon atoms, chelate structures with either C=O→Si or P=O→Si dative bonds can be obtained.
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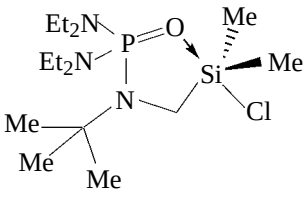
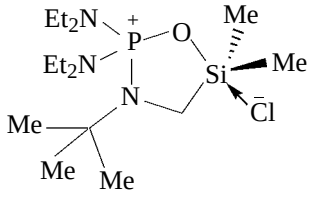
The intensive development of the chemistry of organic derivatives of five-coordinate silicon in the last three decades is due to the key role of trigonal-bipyramidal intermediates in chemical transformations of organoelement compounds [1–9]. The enhanced reactivity of hypervalent organosilicon compounds [10, 11] makes them promising synthons in organic and organometallic synthesis [12–15]. However, certain aspects of the chemistry of five-coordinate silicon are practically unexplored. In particular, this relates to the problem of formation and conditions of existence of coordination bonds of the silicon atom with the phosphoryl group P=O possessing a strong donating ability [16–19]. The existence of intramolecular coordination bonds P=O→M (M = Si, Ge, Sn) was proved in phosphine oxides and esters of phosphoric acids [20–25]. *N*-Silylmethyl derivatives of carboxamides and related compounds with a C_3XSiO (X = Hal, OTf) coordination entity are among the most studied hypervalent silicon compounds [1–5]. Among phosphoramidates such compounds are unknown. The only attempt to synthesize a phosphoramidate with a C_3ClSiO coordination entity by successive reactions of $(Et_2N)_2P(O)NHBu$-*t* with BuLi and $ClCH_2SiMe_2Cl$ led, according to NMR and X-ray diffraction data, to zwitter ionic structure **B** with a Cl→Si coordination bond, rather than to chelate **A**.



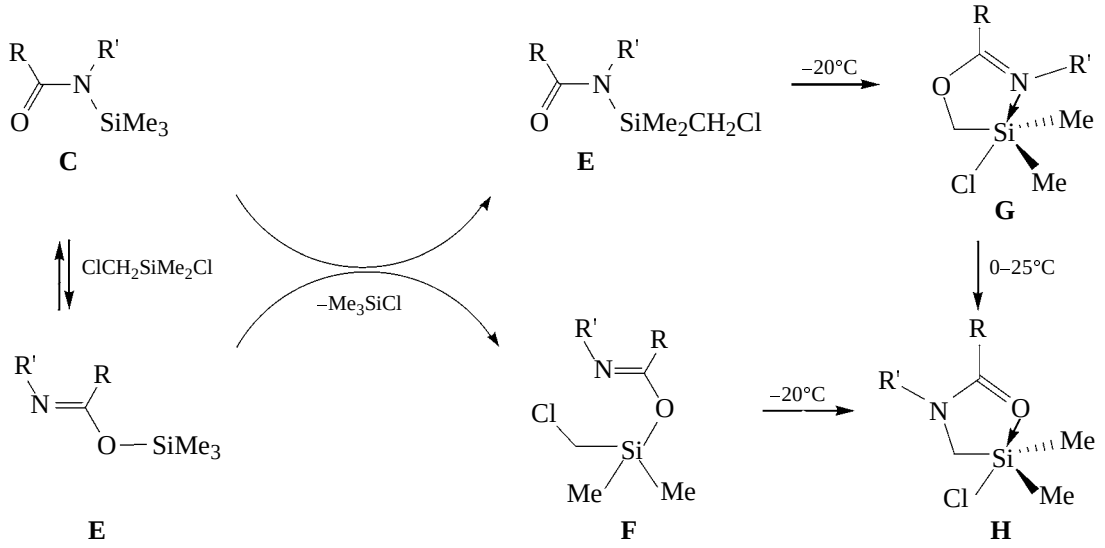
A



B

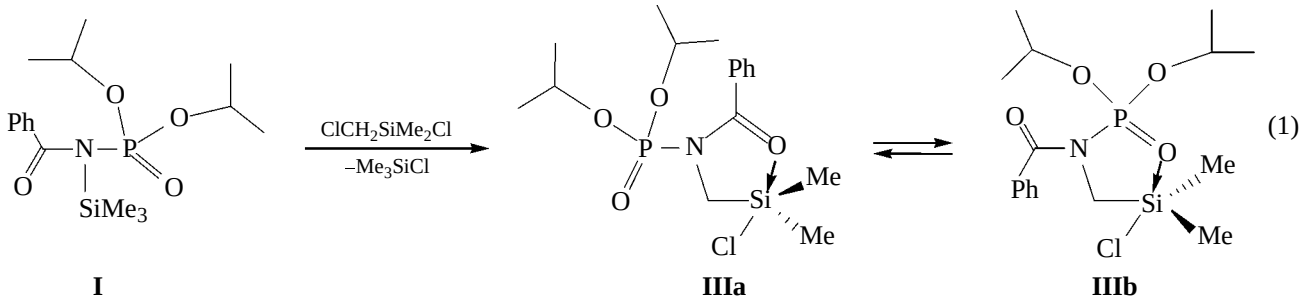
Five-coordinate silicon (O–Si) chelate compounds with a C_3ClSiO coordination entity are commonly synthesized by the reaction of *N*(*O*)-trimethylsilyl derivatives of lactams and carboxamides **C** and **D** with $ClCH_2SiMe_2Cl$. The monitoring of the reaction by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy showed that the first stage that occurs even at low temperatures gives unstable N- and/or O-transsilylation products **E** and **F** [2–5].

N-Silyl derivative **E** then suffers a kinetically controlled intramolecular O-silylmethylation to form imidate **G** with a five-coordinate silicon atom. Imidate **G** and *O*-silyl derivative **F** rearrange into a stable (O→Si) chelate product **H**. It is not inconceivable that (O→Si) chelate compounds of five-coordinate silicon with a P=O→Si intramolecular coordination bond can be synthesized by similar transformations.



The aim of the present work was to assess the structure of the reaction products of *N*-(trimethylsilyl)phosphoramidates with $ClCH_2SiMe_2Cl$ and of transsilylation products and to analyze the possibility of competitive C=O→Si vs. P=O→Si coordination in the presence of both the carbonyl and phosphoryl group in a molecule. The objects for study were diisopropyl *N*-benzoyl-*N*-(trimethylsilyl)phosphoramidate (**I**) and diisopropyl *N*-methyl-*N*-(trimethylsilyl)phosphoramidate (**II**).

The reaction of $PhC(O)N(SiMe_3)P(O)(OPr\text{-}i)_2$ (**I**) with $ClCH_2SiMe_2Cl$ proceeds at room temperature and is complete in one day:



(1)

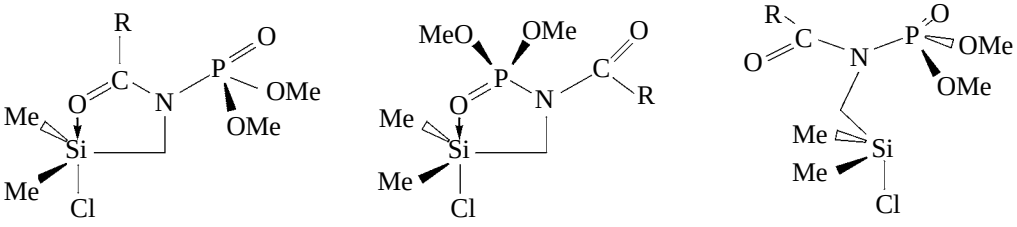
The structure of product **III** was investigated by multinuclear NMR spectroscopy. The ^{29}Si signal (δ_{Si} –16.6 ppm) is shifted upfield with respect to that in a model four-coordinate silicon compound $ClCH_2SiMe_2Cl$ (δ_{Si} = 23.6 ppm), implying that the silicon atom in **III** is five-coordinate. It should be noted that the coordination shift Δ_{Si} in compound **III** is 40.2 ppm. This value is substantially lower than the Δ_{Si} in *N*-[(chlorodimethylsilyl)methyl]-*N*-methylacetamide (61.2 ppm [27]). A similar decrease of the coordination shift due to introduction of the second acetyl group to the amide nitrogen atom was observed in *N*-acetyl-*N*-[(chlorodimethylsilyl)methyl]-acetamide (Δ_{Si} 47.8 ppm [28]). In the ^{13}C NMR spectrum of compound **III**, the signal of the C=O group is shifted downfield by ~2 ppm with respect to that in compound **I** (δ_C 176.40 and 174.34 ppm, respectively). The downfield shift of the C=O signal in the ^{13}C NMR spectra of (O–Si) chelate compounds $XSiMe_2CH_2NRC(O)R'$ with respect to those with a four-coordinate silicon atom, due to a weaker carbon nuclear shielding, is ~2–3 ppm [29]. The P=O signal in the ^{31}P NMR spectrum of compound **III** is also shifted downfield with respect to compound **I** (11.47 and 4.46 ppm, respectively). *N*-Acylphosphoramidates RC(O)NHP(O)XY (R = Alk, Ar; X, Y = OR, R_2N, RNH) are potentially bidentate ligands [30–32] capable of competitively coordinating the car-

Table 1. Interatomic distances Si–O and Si–Cl (Å), energies (ΔE_c) and Gibbs energies (ΔG_c) of complex formation (kcal mol^{-1}), ^{29}Si chemical shifts (ppm), and silicon five-coordination degrees (η_α, %) for compounds **IV, V**, and **XVII** in the gas phase and in chloroform (PCM approximation)

Compound		B3LYP/6-31G(d)					GIAO B3LYP/6-311++G(2d,p)		δ_{Si} (exp.)	Δ_{Si} (exp.)
		l_{Si-O}	l_{Si-Cl}	η_α [a]	ΔE_k [b]	ΔG_k [b]	δ_{Si}	Δ_{Si} [c]		
IVa	gas	2.295	2.189	61	7.6	8.9	–	–	–	–
	$CHCl_3$	2.146	2.260	74	8.1	9.5	–19.7	52.8	–	–
IVb	gas	2.469	2.174	58	2.5	3.4	–	–	–	–
	$CHCl_3$	2.254	2.246	75	2.7	3.6	–15.7	48.8	–16.6 [e]	40.2 [e]
Va	gas	2.302	2.189	61	0.0	–	–	–	–	–
Vb	gas	2.468	2.173	58	4.5 [d]	–	–	–	–	–
XVIIa	gas	2.912	2.139	37	1.9	1.1	–	–	–	–
	$CHCl_3$	2.841	2.166	43	1.1	0.8	33.0	0.1	27.6 [f]	4.0 [f]

[a] $\eta_\alpha = [(1095 - 1/3\sum_{n=1}^{3} \theta_n)/(109.5 - 90)] \times 100\%$ where θ_n is the bond angle between axial SiCl and equatorial SiC bonds [34]. [b] With respect to open-chain form **c** with a zero-point energy correction; ΔG_c at 298 K and 1 atm. [c] $\Delta_{Si} = \delta_{Si}(ClCH_2SiMe_2Cl) - \delta_{Si}$ (studied compound); $\sigma(TMS)^{calc} = 327.4$. δ_{Si}: ($ClCH_2SiMe_2Cl$) = 33.1 (calc.); 23.6 (exp.). [d] Relative energy of isomers **a** and **b** with respect to the most stable isomer **a**.

bonyl or phosphoryl group. The experimental evidence in hand does not allow us to establish unambiguously whether silicon is coordinated with the C=O or P=O group. Therefore, the structure of structurally similar model compounds **IV** and **V** was studied by the DFT method at the B3LYP/6-31G(d) or B3LYP/6-311++G(2d,p) level [33] with full geometry optimization and identification of bond critical points (bcp). Three minima corresponding to structures **a**, **b**, and **c** were found on the potential energy surface.



a **b** **c**

R = Me (**IV**); R = Ph (**V**).

The calculated δ_{Si} values for **IVa** and **IVb** are substantially shifted upfield with respect to $ClCH_2 \cdot SiMe_2Cl$ and are close to the experimental value for compound **III** (Table 1). This does not allow us to decide between structures **IIIa** and **IIIb** on the basis of ^{29}Si NMR data solely. Judged from the E_c and ΔG_c values (Table 1), both in the gas phase and in a chloroform solution, compound **IV** exists exclusively as isomer **IVa** with a C=O→Si dative bond.

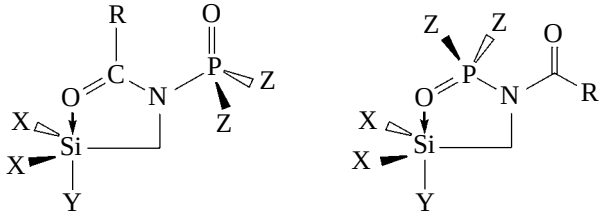
The NBO analysis showed that the strong interaction of the nitrogen lone pair with the antibonding π orbital of the C=O bond [$E(n_N, \pi^*_{CO})$ –70 kcal mol^{-1}], which is substantially, more than by 40 kcal mol^{-1}, stronger than its interaction with orbitals of the PO_3 fragment, makes the carbonyl oxygen a stronger donor compared to the phosphoryl oxygen. The electron density characteristics of the Si–O bond critical points (bcp), found by the AIM analysis of the electron

Table 2. Electron density [$\rho(r)$, e Å^{-3}], Laplacian of electron density [$\nabla^2\rho(r)$, e Å^{-5}], and electron energy density [$E_e(r)$, au Å^{-1}] of the bcp (3, –1) in the Si···O internuclear region of molecules **IV** and **XVII** in chloroform

Comp. no.	$\rho(r)$	$\nabla^2\rho(r)$	$-E_e(r)$
IVa	0.244	1.312	0.070
IVb	0.311	1.630	0.110
XVIIa	0.097	0.854	0.003

distribution ρ in isomers **IVa** and **IVb** (Table 2), suggest, according to the Cremer–Kraka criterion [35], that the SiCNCO and SiCNPO heterorings are closed by highly polar covalent SiO bonds. It should be underlined that the substantial difference of the calculated structural parameters of the $ClSiC_3O$ coordination entity in compound **IV** (especially $l_{Si–O}$ and $l_{Si–Cl}$ in the axial fragment ClSiO) in the isolated state and in solution (Table 1) is typical of hypervalent silicon compounds [36, 37]. Comparison of the calculated geometries and relative energies of molecules **IV** and **V** demonstrates that molecule **IV** is a good structural model for the synthesized compound **III**. This allows us to conclude that not only **IV** but also **III** are structures with a C=O→Si dative bond.

The existence of compound **III** in form **IIIa** is slightly unexpected, since there is experimental evidence for a stronger donating ability of the phosphoryl group compared to the carbonyl group [18, 19]. For example, the enthalpies of formation of the complexes $(MeO)_3P{=}O{\cdot}SbCl_5$ and $(MeO)_2C{=}O{\cdot}SbCl_5$ in 1,2-dichloroethane, measured by calorimetry, are 23.0 and 15.2 kcal mol^{-1}, respectively [18]. Apparently, the donating abilities of the carbonyl and phosphoryl groups in *N*-acylphosphoramidates are determined not only by the difference in their polarities [EO(P) < EO(C)] and inductive effects of substituents at the carbon and phosphorus atoms, but also by stereoelectronic interactions of the n,σ^* and n,π^* type in the C(O)–N–P(O) fragment. Experimental study of competitive C=O→Si vs. P=O→Si coordination in silylated *N*-acylphosphoramidates is an interesting independent problem going beyond the scope of the present study. In this paper we performed a theoretical investigation of the effect of the valence surroundings of the silicon and phosphorus atoms and of the carbonyl group on the degree of the C=O→Si (isomer **a**) and P=O→Si (isomer **b**) coordination bonding in model *N*-silylmethylated *N*-acylphosphoramidates $RC(O)N(CH_2SiX_2Y)P(O)XY$ **VI**–**XIII**. Table 3 lists the O→Si coordination bond lengths and coordination degrees (see notes to Table 1). Thermodynamic parameters for the equilibria between the C=O→Si and P=O→Si coordination isomers of compounds **VI**–**XIII** are given in Table 4.



VI: R = Me, X = Me, Y = F, Z = OMe; **VII**: R = Me, X = F, Y = Cl, Z = OMe; **VIII**: R = Me, X = F, Y = F, Z = OMe; **IX**: R = Me, X = F, Y = Cl, Z = NMe_2; **X**: R = Me, X = F, Y = F, Z = NMe_2; **XI**: R = Me, X = Me, Y = Cl, Z = Me; **XII**: R = CF_3, X = F, Y = F, Z = NMe_2; **XIII**: R = CCl_3, X = F, Y = Cl, Z = NMe_2.

The O→Si interatomic distances, coordination degrees, and thermodynamic parameters show that, as the acceptor properties of the silicon atom enhance in the order $FMe_2Si < ClMe_2Si < F_3Si < ClF_2Si$ at the same surroundings at the phosphorus atom (Z = OMe) and carbonyl carbon (R = Me), isomers **IVa**, **VIa**, **VIIa**, and **VIIIa** with C=O→Si coordination are more stable than isomers **IVb**, **VIb**, **VIIb**, and **VIIIb** with P=O→Si coordination. As the basicity of the P=O group increases with decreasing electronegativity of

Table 3. Si–O interatomic distances ($l_{Si–O}$, Å) and silicon five-coordination degrees (η_α, %) in the gas phase in isomers **a** and **b** of compounds **VI**–**XIII**, calculated at the B3LYP/6-31G(d) (**VIII, X**–**XII**) and B3LYP/6-311G(d,p) (**VI, VII, IX, XIII**) levels

Izomer	Parameter	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**	**XIII**
a	$l_{Si–O}$	2.459	2.096	2.083	2.009	2.034	2.202	2.338	2.107
	η_α	50	61	62	69	66	67	64	57
b	$l_{Si–O}$	3.064	2.005	2.051	1.917	1.963	2.333	1.984	1.930
	η_α	27	74	70	83	78	67	75	81

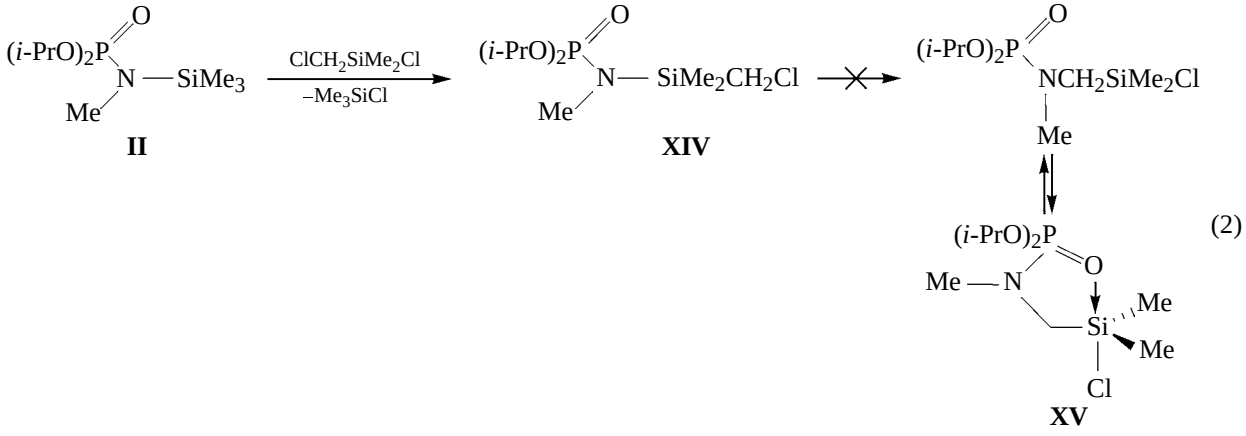
the first atom in substituent Z at phosphorus (O > N > C), the isomer with P=O→Si coordination (molecules **IX**, **X**, and **XI**) is stabilized. Replacement of Me by CF_3 or CCl_3 decreases the basicity of the carbonyl group and provides existence of molecules **XII** and **XIII** exclusively in the P=O→Si chelate form. Structures **XIIb** and **XIIIb** are characterized by a high degree of silicon five-coordination η_α (75% and 81%, respectively) and short O···Si contacts (1.984 Å and 1.930 Å, respectively).

On an example of molecule **IV** (Table 1), within the framework of the PCM model, we obtained evidence for a strong solvent effect on the geometry of the $ClSiC_3O$ coordination entity. However, the energy gap between isomers **a** and **b** only slightly depends on the medium. Therefore, not resorting to time-consuming solvation calculations, we still have grounds to suggest that the conclusion that the equilibrium **a** $\rightleftarrows$ **b** in compounds **VI**–**XII** depends on the nature of substituents R, X, Y, and Z, drawn for isolated molecules, is valid for polar media. Finally, the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) calculations for molecule **X** showed that expansion of the basis set leads to only minor changes in the geometry of the silicon polyhedron (maximum difference in the O→Si distances ~0.02 Å) and the ΔE value (~0.8 kcal mol^{-1}).

Diisopropyl *N*-benzoyl-*N*-(trimethylsilyl)phosphoramidate (**I**) reacts with $ClCH_2SiMe_2Cl$ in the same way as *N*-trimethylsilylated carboxamides, that is, the P(O)(OPr-*i*)$_2$ group acts only as a substituent in the amide fragment. In view of the theoretically demonstrated possibility of formation of P=O→Si-coordinated *N*-silylmethylated phosphoramidates, the question arises: How $ClCH_2SiMe_2Cl$ will react with *N*-silylated phosphoramidates in the absence of the carbonyl group? It turned out that diisopropyl *N*-methyl-*N*-(trimethylsilyl)phosphoramidate (**II**) readily reacts with $ClCH_2SiMe_2Cl$ at room temperature with quantitative liberation of Me_3SiCl:

Table 4. Thermodynamic parameters (kcal mol^{-1}) for the equilibria between the C=O→Si and P=O→Si chelates of compounds **IV**–**XIII**, calculated at the B3LYP/6-31G(d) (**IV, X**–**XII**) and B3LYP/6-311G(d,p) (**VI**–**X, XIII**) levels

Equilibrium	ΔE	ΔH^0	ΔG^0
IVa $\rightleftarrows$ **IVb**	5.13	5.13	5.48
VIa $\rightleftarrows$ **VIb**	4.02	4.04	4.20
VIIa $\rightleftarrows$ **VIIb**	3.60	3.56	4.12
VIIIa $\rightleftarrows$ **VIIIb**	4.94	4.90	5.78
IXa $\rightleftarrows$ **IXb**	–0.63	–0.57	–0.55
Xa $\rightleftarrows$ **Xb**	–0.12	0.07	–0.46
XIa $\rightleftarrows$ **XIb**	–1.20	–1.12	–0.93
XIIa $\rightleftarrows$ **XIIb**	–5.23	–5.21	–5.45
XIIIa $\rightleftarrows$ **XIIIb**	–10.05	–9.99	–10.51

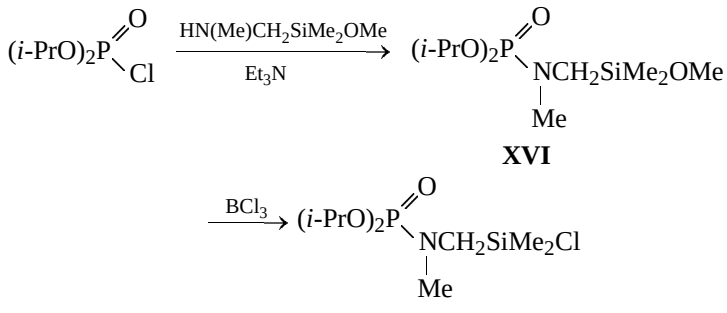


II **XIV** **XV** (2)

However, the compound isolated by vacuum distillation, according to ^1H, ^{13}C, and ^{29}Si NMR spectral data, was N-transsilylation product **XIV**. Unlike its carbonyl analogs **E**, the latter does not rearrange to (O–Si) chelate form **XV** even upon heating to 130°C during 4 h. Apparently, the stability of N-transsilylation product **XIV** is due to the nature of the phosphoramide group N–P=O. The phosphoryl group P=O group determines the properties of O=PXYZ compounds, and its structure was studied in [38–43]. The

P=O group, like C=O, is strongly polarized $P^{\delta+}$–$O^{\delta-}$ and possesses a strong electron-acceptor effect. However, the difference in the hybridizations of the C=O carbon (sp^2, planar) and P=O phosphorus (sp^3, tetrahedral) is responsible for the different electronic effects of substituents on these groups. Thermodynamic stability of the P=O bond is characteristic of the phosphorus chemistry and is a driving force of a large number of reactions. Thus, the silylotropic equilibrium >P(O)NR($SiMe_3$) $\rightleftarrows$ >P(=NR)O$SiMe_3$ in N-silylated phosphoramidates is substantially if not completely shifted to the left due to the higher stability of the >N–P=O triad as compared to the >N=P–O– triad [44, 45]. By the same reason, phosphorimidates rearrange to the corresponding phosphoramidates [46–50]. Alkylation and silylation reactions are uncharacteristic of the phosphoryl group, but they still proceed under certain conditions. Thus, trialkyloxonium tetrafluoroborates alkylate hexamethylphosphoric triamide to afford salts $[ROP(NMe_2)_3]^+BF_4^-$ (R = Me, Et) [51]. The strong electron-donor power of the triamidophosphazo group much enhance the basicity of the phosphoryl group, so that O=P[N=$P(NMe_2)_3]_3$ is already alkylated with methyl iodide to form a stable methoxyphosphonium salt $MeOP^+\cdot[N=P(NMe_2)_3]_3I^-$ [52]. It is interesting to mention that the phosphatrane $O=P(NMeCH_2CH_2)_3N$ reacts with chlorosilanes ClSiZ (Z = $MeCl_2$, Cl_3) to give salts $[ZSiOP^+(NMeCH_2CH_2)_3N]Cl^-$ [51]. Apparently, by varying the valence surroundings of the phosphorus and/or silicon atoms we can find conditions for further transformation of N-transsilylation products into compounds with a P=O→Si coordination bond.

The afore-mentioned absence of data on compounds containing a P=O→$SiMe_2$Hal coordination fragment, as well as the resistance of N-transsilylation product **XIV** to rearrangement prompted us to synthesize compound **XV** by an alternative procedure, using the following transformations:

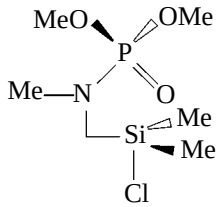


XVI

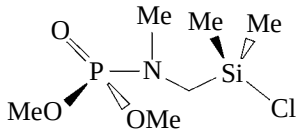
XV

The reaction of diisopropyl phosphorochloridate with α-silylmethylamine $MeNHCH_2SiMe_2OMe$ proceeds at room temperature in the presence of a 4-fold excess of triethylamine. The large excess of Et_3N is necessary to avoid consumption of the organosilicon amine for binding the liberated HCl. Treatment of the resulting diisopropyl *N*-[(methoxydimethylsilyl)methyl]-*N*-methylphosphoramidate (**XVI**) with boron trichloride in diethyl ether at –10°C gives rise to the target compound **XV**. The ^{29}Si NMR signal (δ_{Si} 27.6 ppm) of **XV** is slightly shifted downfield with respect to $ClCH_2SiMe_2Cl$ (δ_{Si} 23.6 ppm), which is indicative of a four-coordinate silicon atom. Further evidence for the absence of noticeable P=O→Si coordination in compound **XV** was obtained from a theoretical analysis of its close model analog **XVII** in the chelate (**XVIIa**) and open-chain (**XVIIb**) forms (Tables 1 and 2).

It turned out that the Si bond angles in **XVIIa** noticeable (by 4–11°) differ from those in open-chain form **XVIIb**. The possible reason for the deformation of the silicon polyhedron toward trigonal bipyramid is Si···O attractive interaction. Actually, the Si···O distance is ~0.5 Å shorter than the sum of the van der Waals radii of the Si and O atoms (~3.4 Å), and the AIM analysis revealed bcp (3, –1) in the Si···O internuclear region of molecule **XVII**.



XVIIa



XVIIb

Judged from its properties ρ, $\nabla^2\rho$, and E_e (Table 2), the Si···O interaction is weak and has no covalent component [37]. This is readily evidenced by fairly low complex formation energy ΔE_c and five-coordination degree η_α (Table 1), typical of pseudochelate structures stabilized by electrostatic interactions between Si and O. Judging from the ΔG_c values, compound **XVII** in chloroform exists as a mixture of pseudochelate (~63%) and unchelated conformers. The experimental δ_{Si} chemical shifts for **XV** and calculated for the mixture of conformers **XVIIa** and **XVIIb** are in a good agreement.

The unexpected, at first glance (σ-acceptor properties of the RC=O and Me groups are compared), substantial increase of the five-coordination degree η_α and decrease of l_{Si-O} in molecule **IVb** compared to **XVIIa** (Table 1) highlights a strong influence of stereoelectronic effects in the N–P=O fragment on the coordinative ability of the phosphoryl group [41, 53]. The results of the NBO analysis show that replacement of the methyl group by acetyl in molecule **XVIIa**, provided the geometry remains unchanged, is followed by a drastic enhancement of (n_N, $\sigma^*_{P=O}$) conjugation, from 0.7 to 8.5 kcal mol^{-1}, and by the corresponding enhancement of the donating ability of the phosphoryl oxygen, measured by the NBO energy of its lone pair oriented to the silicon atom, from –0.94 to –0.87 au. Therefore, one should expect strengthening of the P=O→Si dative bond in going to equibrium structure **IVb**, which is the case.

EXPERIMENTAL

Quantum-chemical calculations were performed using the Gaussian 03 program suite [37]. Positive eigenvalues of the Hessian matrix were used as evidence showing that structures belong to minima on the potential energy surface. The AIM (atoms in molecules) analysis of the MP2(full)/6-311++G(2d,p) electron distribution was performed using the MORPHY 1.0 program [54, 55]. The NBO analysis was performed with HF/6-31G(d) wave functions.

The NMR spectra of 20% solutions in $CDCl_3$ were taken on a Bruker DPX-400 spectrometer at 400, 100, 80, and 160 MHz (^{1}H, ^{13}C, ^{29}Si, and ^{31}P, respectively) against internal TMS or cyclohexane. The solvents were purified according to [56]. All syntheses were carried out under dry argon.

Diisopropyl *N*-benzoyl-*N*-(trimethylsilyl)phosphoramidate (I). Diisopropyl *N*-benzoylphosphoramidate, 2.85 g (0.01 mol), prepared as described in [57], was mixed with 2.34 g (0.01 mol) of $(Me_3Si)_3N$, and the mixture was kept for 60 h at room temperature. Vacuum distillation gave 3.2 g (89.6%) of the product, bp 150–152°C (1.5 mm Hg), n_D^{20} 1.4806. ^{1}H NMR spectrum, δ, ppm: 0.35 s (9H, Me_3Si), 1.33 d (6H, Me_2C), 4.85 heptet (1H, CH), 7.39 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 0.12 (Me_3Si), 23.64 (Me_2C), 73.32 (CH), 127.61, 129.42, 129.45, 130.69 (Ph). ^{29}Si NMR spectrum, δ_{Si}, ppm: 24.9 d ($^2J_{PSi}$ 7.3 Hz). ^{31}P NMR spectrum, δ_P, ppm: 4.46. Found, %: C 53.83; H 8.21; N 4.17. $C_{16}H_{28}NO_4PSi$. Calculated, %: C 53.76; H 7.90; N 3.92.

Diisopropyl *N*-benzoyl-*N*-[(chlorodimethylsilyl)methyl]phosphoramidate (III). Diisopropyl *N*-benzoyl-*N*-(trimethylsilyl)phosphoramidate, 1.8 g (0.005 mol), was mixed with 0.71 g (0.005 mol) of $ClCH_2SiMe_2Cl$, and the mixture was kept for 24 h at room temperature. Chlorotrimethylsilane was removed under a vacuum, and the residue was dried under a vacuum at room temperature for 3 h. ^{1}H NMR spectrum, δ, ppm: 0.68 s (6H, Me_2Si), 1.29 d (6H, Me_2C, *J* 6.8 Hz), 3.20 d (2H, NCH_2Si, ^3J 2.7 Hz), 4.64 heptet (1H, CH, ^3J 6.8 Hz), 7.29 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 5.61 (SiMe), 23.50 and 23.45 (Me_2C), 74.04 d (CH, $^2J_{CP}$ 6.0 Hz), 40.36 (CH_2Si); 176.30 d (C=O, $^2J_{CP}$ 12.1 Hz) 127.19; 127.34; 128.88; 132.18 (Ph). ^{29}Si NMR spectrum, δ_{Si}, ppm: –16.6 d ($^2J_{SiP}$ 12.2 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.65. Found, %: C 48.76; H 6.83; N 3.66. $C_{16}H_{27}ClNO_4PSi$. Calculated, %: C 49.04; H 6.94; N 3.57.

Diisopropyl *N*-methyl-*N*-(trimethylsilyl)phosphoramidate (II). Diisopropyl phosphorochloridate, 2.0 g (0.01 mol), prepared as described in [58], was dissolved in 50 ml of dry ether, cooled to –5°C, and 3 g (0.1 mol) of methylamine in 30 ml of anhydrous ether was added dropwise. The temperature was then raised to ambient, and the mixture was kept for 36 h. The precipitate formed was filtered off, washed with dry ether (2 × 10 ml), and the ether and excess methylamine were removed under a vacuum. The residue (yellowish oil) was mixed with 2.34 g (0.01 mol) of $(Me_3Si)_3N$, and the mixture was kept at room temperature for 48 h. Vacuum distillation gave 1.63 g (61%) of the product, bp 112–115°C (6 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.24 s (9H, $SiMe_3$), 1.29 d (6H, Me_2C, *J* 6.2 Hz), 2.56 d (3H, NMe, *J* 12.9 Hz), 4.50 heptet (1H, OCH, *J* 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 0.24 (SiMe), 23.61 and 23.55 (Me_2C, *J* 4.2 Hz), 30.69 (NMe), 69.57 d (CHO, ^2J 5.1 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: 12.0 d ($^2J_{SiP}$ 7.8 Hz). ^{31}P NMR spectrum, δ_P, ppm: 9.62. Found, %: C 45.18; H 9.94; N 5.20. $C_{10}H_{26}NO_3PSi$. Calculated, %: C 44.92; H 9.80; N 5.24.

Diisopropyl *N*-[(chloromethyl)dimethylsilyl]-*N*-methylphosphoramidate (XIV). Diisopropyl *N*-me-

thyl-*N*-(trimethylsilyl)phosphoramidate, 1.34 g (5 mmol), was mixed with 0.71 g (5 mmol) of $ClCH_2 \cdot SiMe2Cl$, and the mixture was kept for 24 h at room temperature. Vacuum distillation gave 1.04 g (69%) of the product, bp 125–126°C (1.5 mm Hg), n_D^{20} 1.4288. ^{1}H NMR spectrum, δ, ppm: 0.35 s (6H, $SiMe_2$), 1.29 d (6H, Me_2C, *J* 6.2 Hz), 2.59 d (3H, NMe, *J* 12.5 Hz), 3.02 s (2H, CH_2Cl), 4.53 heptet (1H, OCH, *J* 6.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: –2.88 (SiMe), 23.50 (Me_2C), 30.61 (CH_2Cl), 31.01 (NMe), 70.05 (OCH). ^{29}Si NMR spectrum, δ_{Si}, ppm: 8.50 d (J_{SiP} 8.3 Hz). ^{31}P NMR spectrum, δ_P, ppm: 8.87. Found, %: C 40.07; H 8.51; N 4.75. $C_{10}H_{25} \cdot ClNO_3PSi$. Calculated, %: C 39.79; H 8.35; N 4.64.

Diisopropyl *N*-[(methoxydimethylsilyl)methyl]-*N*-methylphosphoramidate (XVI). Triethylamine, 4.1 g (0.04 mol), and 1.33 g (0.01 mol) of $MeNHCH_2 \cdot SiMe_2OMe$ prepared as described in [59] were mixed in 100 ml of anhydrous ether. The mixture was cooled to 10°C, and a solution of 2.0 g (0.01 mol) of diisopropyl phosphorochloridate in 50 ml of anhydrous ether was added dropwise. The temperature was raised to ambient, and the mixture was kept for 48 h. The precipitate formed was filtered off, washed with dry ether (2 × 20 ml), the ether removed on a rotary evaporator, and the residue was distilled under a vacuum to obtain 2.15 g (72.4%) of the product, bp 111–111.5°C (4 mm Hg), n_D^{20} 1.4315. ^{1}H NMR spectrum, δ, ppm: 0.19 s (6H, $SiMe_2$), 1.29 d (6H, Me_2C, *J* 6.2 Hz), 2.57 d (2H, NCH_2Si, *J* 7.9 Hz), 2.66 d (3H, NMe, *J* 10.6 Hz); 3.46 s (3H, OMe), 4.52 heptet (OCH). ^{13}C NMR spectrum, δ_C, ppm: –2.86 (SiMe), 23.62 (Me_2C), 36.22 d (NCH_2Si, *J* 2.7 Hz), 38.56 (NMe), 50.20 (OMe), 70.12 d (OCH, ^2J 5.8 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: 16.6 (J_{SiP} 10.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 10.25. Found, %: C 44.23; H 9.37; N 4.53. $C_{11}H_{28}NO_4PSi$. Calculated, %: C 44.42; H 9.49; N 4.71.

Diisopropyl *N*-[(chlorodimethylsilyl)methyl]-*N*-methylphosphoramidate (XV). A solution of 38 mg (0.33 mmol) of BCl_3 in 15 ml of anhydrous ether was added dropwise to a solution of 0.3 g (1 mmol) of diisopropyl *N*-[(methoxydimethylsilyl)methyl]-*N*-methylphosphoramidate (**XVI**) in 15 ml of anhydrous ether cooled to 0°C. The reaction mixture was kept for 2 h, and the temperature was raised to ambient and kept for another 3 h. The ether was remover, and the residue was dried for 2 h at room temperature under a vacuum to obtain a viscous oil decomposing upon heating. ^{1}H NMR spectrum, δ, ppm: 0.56 s (6H, $SiMe_2$), 1.46 d (6H, Me_2C, *J* 5.5 Hz), 2.76 d. d (1H, NCH_2Si, *A* part of an *AB* quartet, $^2J_{AB}$ 15.0 Hz, ^3J 7.5 Hz), 2.93 d.d. (1H, NCH_2Si, *B* part of an *AB* quartet, ^3J 9.9 Hz), 2.86 d (3H, NMe, *J* 11.6 Hz), 4.98 hept (OCH). ^{13}C NMR spectrum, δ_C, ppm: 1.37 (SiMe), 23.22 (Me_2C), 36.22 d (NCH_2Si, *J* 5.8 Hz), 41.44 (NMe); 78.50 d (OCH, *J* 8.0 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: 27.6 (J_{SiP} 8.8 Hz). ^{31}P NMR spectrum, δ_P, ppm: –0.41. Found, %: C 39.96; H 8.49; N 4.73. $C_{10}H_{25}ClNO_3PSi$. Calculated, %: C 39.79; H 8.35; N 4.64.

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