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Synthesis and characterisation of trimethylsilyl phosphorohalidates: $Me_3SiOP(O)FX$ (X = Cl, Br) and $(Me_3SiO)_2P_2O_3F_2$

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Abstract

Trimethylsilyl phosphorochloridofluoridate, $Me_3SiOP(O)FCl$, has been prepared by reaction of $POFCl_2$ with hexamethyldisiloxane or by treatment of bis(trimethylsilyl) phosphorofluoridate with phosphorus pentachloride. The compound could be purified by vacuum distillation and has been isolated in 55% yield. The ester $Me_3SiOP(O)FBr$ is formed in an analogous reaction of $POFBr_2$ with $(Me_3Si)_2O$, however its susceptibility to spontaneous decomposition makes its isolation unfeasible. Condensation of $Me_3SiOP(O)FCl$ with $(Me_3SiO)_2P(O)F$ or heating of $POFBr_2$ with excess hexamethyldisiloxane gave bis(trimethylsilyl) diphosphorodifluoridate, $(Me_3SiO)_2P_2O_3F_2$, in 45–53% yield. The existence of both expected diastereoisomers was revealed by ^{19}F and ^{31}P NMR spectroscopy.

Keywords: Trimethylsilyl esters; Phosphorochloridofluoridate; Phosphorobromidofluoridate; Diphosphorodifluoridate; Condensation reactions; Thermal decomposition

1. Introduction

Trimethylsilyl phosphorodihalidates of the general formula $Me_3SiOP(O)X_2$ (X = F, Cl or Br) may be useful precursors of dihalogenophosphate groups. These esters react with electrophilic metal chlorides, either forming donor–acceptor complexes via the terminal oxygen atom of the $Me_3SiOP(O)X_2$ or giving covalent chloride–dihalogenophosphates under the cleavage of Si–O bonds [1–3]. On the other hand, treatment of $Me_3SiOP(O)F_2$ with a nucleophilic halide or pseudohalide anion leads to the corresponding difluorophosphate [4]. In both cases, the formation of volatile trimethylsilyl halides or pseudohalides as the leaving groups facilitates the isolation of pure products.

Except for $Me_3SiOP(O)Br_2$ [3], trimethylsilyl phosphorodihalidates with two identical halogens are generally accessible by the treatment of the phosphoryl fluoride [4,5] or phosphoryl chloride [6] with hexamethyldisiloxane. Both $Me_3SiOP(O)F_2$ and $Me_3SiOP(O)Cl_2$ have also been prepared from $(Me_3Si)_2O$ and $P_2O_3F_4$ [7] and $P_2O_3Cl_4$ [6], respectively, while the silylation of the free acid [4] or its salts [8] with chlorotrimethylsilane remains limited to the synthesis of the former, and the silylation of $MeOP(O)Cl_2$ with bromotrimethylsilane [9] to the preparation of the latter ester.

In our search for suitable precursors of fluorohalogenophosphate groups, we became interested in a study of chemical reactivity of phosphorofluoridohalogenidates $Me_3SiOP(O)FCl$ and $Me_3SiOP(O)FBr$. However, in contrast to the esters mentioned above, no trimethylsilyl phosphorodihalidate with two different halogens was so far reported. Nevertheless, in view of the existence of fairly stable alkyl esters ROP(O)FCl and ROP(O)FBr [10], a sufficient stability of the corresponding trimethylsilyl esters could be expected. Since $POFCl_2$ and $POFBr_2$ are the only readily available derivatives of HOP(O)FCl and HOP(O)FBr, respectively, their reactions with hexamethyldisiloxane were selected for the syntheses of the esters. The course of these reactions has been studied by NMR spectroscopy, and it was soon realised that both esters undergo spontaneous decomposition, which leads to the bis(trimethylsilyl) diphosphorodifluoridate as the main end product. This novel ester could also be isolated and its preparation together with the synthesis of pure $Me_3SiOP(O)FCl$ and a likely pathway of its decomposition is reported here.

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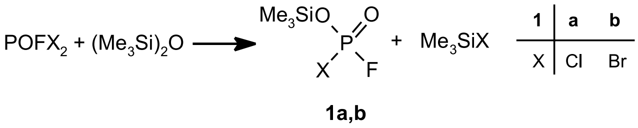
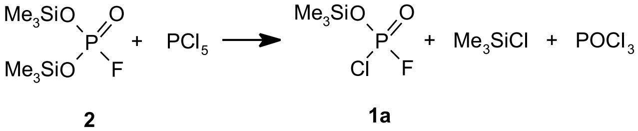


Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Syntheses of trimethylsilyl phosphorochloridofluoridate and phosphorobromidofluoridate

In the synthesis of trimethylsilyl phosphorochloridofluoridate (**1a**), hexamethyldisiloxane reacts with phosphoryl dichloride fluoride (Scheme 1) at ambient temperature very slowly, and in order to determine the time necessary for establishing of equilibrium, the course of the reaction was monitored by ^{31}P NMR spectroscopy. According to the recorded spectra, the equilibrium corresponding to approximately 70% conversion to **1a** was reached after 30 days and even an elevated temperature did not enhance the yield significantly. Moreover, a higher temperature promotes some successive reactions and the formation of undesired by-products. The equilibrium could not be shifted either by pumping off volatile products because the difference between boiling points of Me$_3$SiCl and POFCl$_2$ is only 5 °C and both compounds would distil simultaneously.

An alternative route to **1a** involves a partial chlorination of bis(trimethylsilyl) phosphorofluoridate (**2**) with PCl$_5$ (Scheme 2), which proceeds at much higher rate than the previous reaction. Upon dissolving PCl$_5$ in phosphorofluoridate **2** at laboratory temperature, the reaction is completed within 30 min and all volatiles can be distilled off under vacuum. In both cases, the distillation of higher-boiling fraction at a reduced pressure on a Vigreux fractionating column yields pure phosphorochloridofluoridate (**1a**).

In the pure state, **1a** is a colourless liquid, fuming strongly in moist air, and it should be handled only under strictly anhydrous conditions. Due to its slow decomposition at room temperature, it is best stored at −20 °C. It was identified by multinuclear NMR (Table 1) and vibrational spectra. A comparison of the observed ^{31}P NMR parameters with those reported for EtOP(O)FCl [11] shows a good agreement especially when the reported change of the chemical shift of phosphorus esters after the replacement of one silyl group by alkyl group [12] is considered.

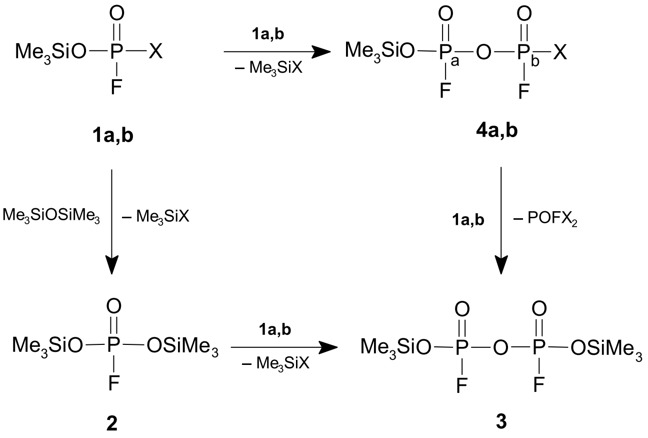
In an attempt to prepare an analogous trimethylsilyl phosphorobromidofluoridate (**1b**), POFBr$_2$ was treated with hexamethyldisiloxane. In contrast to the reaction with POFCl$_2$, this reaction proceeds quite quickly and according to ^{19}F and ^{31}P NMR spectroscopy, the bromidofluoridate **1b**

Table 1
NMR parameters of compounds **1**–**5**.

	Compound	^{1}H NMR δ	^{19}F NMR δ, J (Hz)[b]	^{29}Si NMR δ, J (Hz)	^{31}P NMR δ, J (Hz)
1a	Me$_3$SiOP(O)FCl	0.64 s	−39.0 d 1064 ^1J(PF)	33.2 m 7 ^2J(SiH)	−14.5 d
1b	Me$_3$SiOP(O)FBr		−25.4 d 1115 ^1J(PF)		−30.5 d
2	(Me$_3$SiO)$_2$P(O)F	0.69 s	−72.6 d 928 ^1J(PF)	25.5 m	−25.0 d
3	(Me$_3$SiO)$_2$P$_2$O$_3$F$_2$	0.60 s	−71.0 d[a] 972 ^1J(PF) −2.2 ^3J(P′F) 2.3 $^4J(FF')$	32.6 m	−32.3 d[a] 7.6 ^2J(PP′)
4a	Me$_3$SiOP$_a$(O)F–O–**P**$_b$(O)FCl		−39.4 d 1110 ^1J(PF)		−17.2 dd 13 ^2J(PP)
	Me$_3$SiO**P**$_a$(O)F–O–P$_b$(O)FCl		−70.9 d 991^1J(PF)		−34.3 dd 13 ^2J(PP)
4b	Me$_3$SiOP$_a$(O)F–O–**P**$_b$(O)FBr		−25.8 d 1163 ^1J(PF)		−34.1 dd 18 ^2J(PP)
	Me$_3$SiO**P**$_a$(O)F–O–P$_b$(O)FBr		−70.3 d 992 ^1J(PF)		
5	Me$_3$SiO**P**$_a$(O)F–O–P$_b$(O)F–O–**P**$_a$(O)F(OsiMe$_3$)		−69.7 d 986 ^1J(PF)		−33.4 dm 6.7 ^2J(P$_a$P$_b$) 2.5 ^3J(P$_a$F$_b$)
	Me$_3$SiOP$_a$(O)F–O–**P**$_b$(O)F–O–P$_a$(O)F(OsiMe$_3$)		−70.4 d 1015 ^1J(PF)		−38.3 dm 6.7 ^2J(P$_a$P$_b$) 3.5 ^3J(P$_b$F$_a$)

[a] AA′XX′ spin system.

[b] To ensure a consistence with the most literature data, ^1J(PF) are given as positive, though their absolute sign is always negative [38].



Scheme 3.

is formed as the main product. However, parallel to its formation, two successive reactions also occur. In the first, **1b** reacts readily with excess hexamethyldisiloxane under substitution of the remaining bromine to give **2**. The subsequent condensation of **2** with **1b** then furnishes the symmetric bis(trimethylsilyl) diphosphorodifluoridate (**3**) with loss of bromotrimethylsilane (Scheme 3).

Although the thermal instability of bromidofluoridate **1b** prevents its isolation in a pure state, the doublet at -30.5 ppm can be assigned to **1b** without any doubt because of considerable changes of signal intensity in the ^{31}P NMR spectrum during the formation and decomposition of **1b**. Also a large coupling constant $^1J(\mathrm{PF}) = 1115$ Hz is characteristic for compounds containing a PFBr moiety and corresponds well to the values observed for HOP(O)FBr [13] and POF_2Br [14,15].

2.2. Thermal decomposition of trimethylsilyl phosphorochloridofluoridate

While the phosphorobromidofluoridate **1b** is unstable even at -20 °C and could not be isolated from the reaction mixture, the esters **1a** and **3** are stable indefinitely at this temperature when stored in the absence of moisture. However, in contrast to **3**, chloridofluoridate **1a** starts to decompose slowly at room temperature. According to ^{31}P NMR measurements, about 13% of **1a** decomposed within 1 month at 20 °C.

Slight decomposition of **1a** has already been observed during its synthesis by the long-term reaction of $POFCl_2$ with hexamethyldisiloxane at ambient temperature. In addition to the main signals of **1a** and the unreacted $POFCl_2$, two weak multiplets appeared in the ^{31}P NMR spectrum, providing evidence of the growing concentration of by-products, which were formed in the successive reactions. A doublet at -32.0 ppm ($^1J(\mathrm{PF}) = 966$ Hz) is assigned to **3** and two doublets ($^1J(\mathrm{P_aF}) = 991$ Hz and $^1J(\mathrm{P_bF}) = 1111$ Hz) of doublets ($^2J(\mathrm{P_aP_b}) = 13$ Hz) at -34.2 and -17.5 ppm, respectively (peaks C and G in Fig. 1), were assigned to a transient intermediate, the trimethylsilyl ester of 2-chloro-1,2-difluorodiphosphoric acid (**4a**) (Scheme 3). Both esters were found also amongst the other products formed by thermal degradation of **1a** at elevated temperatures.

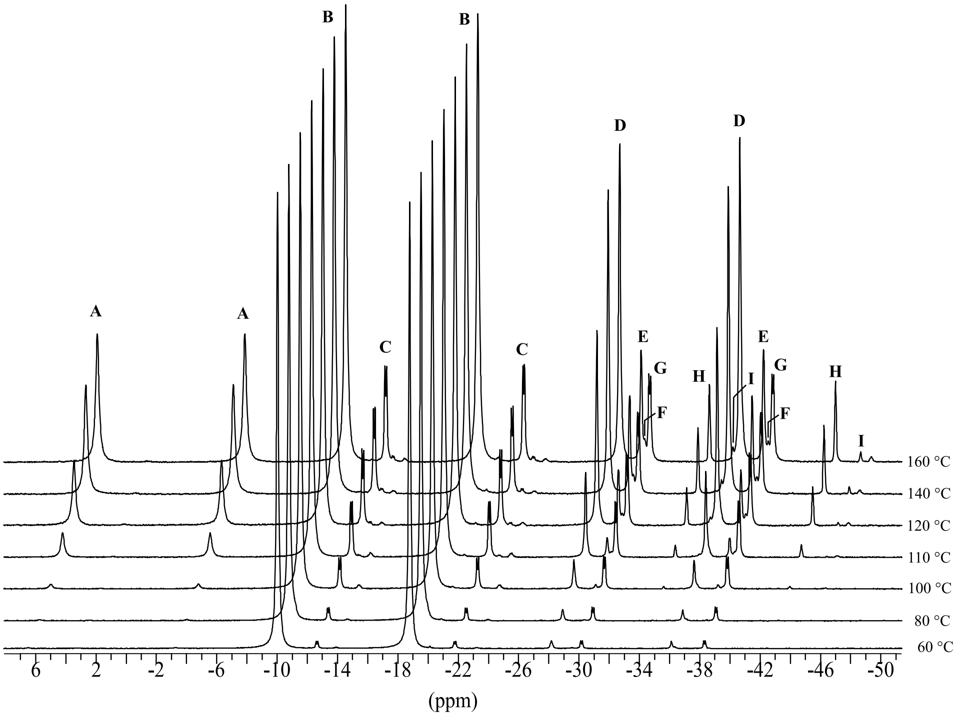


Fig. 1. Thermal decomposition of $Me_3SiOP(O)FCl$ at different temperatures monitored by ^{31}P NMR spectra. The NMR tube with a sample of neat **1a** was sealed off and tempered 1 h at every given temperature. For assignment of signals see Table 2.

Table 2
Decomposition products of **1a**

Compound	Signal multiplicity	Legend for Fig. 1
$POFCl_2$	d	A
$Me_3SiOP(O)FCl$ (**1a**)	d	B
$Me_3SiOP(O)F–O–\mathbf{P}(O)FCl$ (**4a**)	dd	C
$(Me_3SiO)_2P_2O_3F_2$ (**3**)	d[a]	D
$Me_3SiO\mathbf{P}(O)F–O–P(O)F–O–\mathbf{P}(O)F(OSiMe_3)$ (**5**)	dd	E
$Me_3SiO\mathbf{P}(O)F–[O–P(O)F]_n–O–\mathbf{P}(O)F(OSiMe_3)$	d	F
$Me_3SiO\mathbf{P}(O)F–O–P(O)FCl$ (**4a**)	dd	G
$Me_3SiOP(O)F–O–\mathbf{P}(O)F–O–P(O)F(OSiMe_3)$ (**5**)	dtt	H
$Me_3SiOP(O)F–[O–\mathbf{P}(O)F]_n–O–P(O)F(OSiMe_3)$	d	I

[a] $AA'XX'$ spin system.

^{31}P NMR monitoring of **1a** decomposition in the 60–160 °C temperature range revealed gradually increasing intensities of several first-order multiplet patterns (Fig. 1) belonging to at least four newly formed species. Their assignments are given in Table 2. The most likely reaction course involving all observed compounds is shown in Scheme 3. In the first step, an autocondensation of **1a** occurs with the release of Me_3SiCl and **4a** is formed. This unsymmetrical ester then undergoes an unexpected Cl/Me_3SiO exchange reaction with **1a** that affords $POFCl_2$ and diphosphorodifluoridate **3**.

In the reaction of $POFBr_2$ with hexamethyldisiloxane, the **4b**, a bromine analogue of **4a**, is formed also, but only a doublet ($^1J(PF) = 1163$ Hz) of doublets ($^2J(P_aP_b) = 18$ Hz) due to P_b atom at −34.1 ppm was observed because the signal of P_a is probably overlapped with the strong and broad doublet of **3**. Therefore, it can be assumed that the two possible pathways of decomposition shown in Scheme 3 may be applied to both fluorohalogenidates **1a** and **1b**. However, it appears that in the presence of hexamethyldisiloxane the increased reactivity of **1b** towards $(Me_3Si)_2O$ promotes the formation of **3** via the intermediate **2**.

2.3. *Synthesis of bis(trimethylsilyl) diphosphorodifluoridate*

The trimethylsilyl ester **3** was prepared by two methods. In the first route, $POFBr_2$ was heated at 100 °C with hexamethyldisiloxane in an approximately 1:2.5 molar ratio. The excess of $(Me_3Si)_2O$ used enhances the formation of **2**, the necessary intermediate for the production of diphosphorodifluoridate **3**. In an alternative route, pure esters **1a** and **2** were condensed at room temperature under elimination of Me_3SiCl. However, this reaction proceeds much more slowly, and it needs approximately 2–3 months to reach equilibrium. All volatiles were pumped off then and the diphosphorodifluoridate **3** was separated from high-boiling components by a vacuum distillation. Interestingly, the condensation of $EtOP(O)FCl$ with $(EtO)_2P(O)F$ was used for the synthesis of $(EtO)_2P_2O_3F_2$ but it proceeds only at much higher temperatures (140 °C) with a yield under 30% [16].

The pure ester **3** is a colourless liquid, which in contrast to **1a**, does not fume on the air, but hydrolyses quickly in contact with moisture. The compound was unambiguously identified by its multinuclear NMR spectra (Table 1). In the ^{31}P NMR spectrum, the FP–O–PF moiety displays only partly resolved $AA'XX'$ pattern that allows the direct extraction of only $|^1J(PF) + {}^3J(P'F)| = 970$ Hz. However, a band shape analysis and simulation of spectrum gave coupling constants that compare well with those of the $[P_2O_5F_2]^{2-}$ ion (Table 3). The NMR parameters of $[P_2O_5F_2]^{2-}$ were re-determined in the present study because the literature data [18,19] showed considerable differences in the magnitudes of $^2J(PP')$ (2.5 and 17.1 Hz). The established value 13.6 Hz is commensurable with magnitudes of both $^2J(PP)$ constants (12.1 and 14.5 Hz) reported for the anion $[FPO_2OPO_2OPO_3]^{4-}$ [20].

The ^{19}F NMR spectrum of **3** consists of two doublets at −70.9 and −71.1 ppm, both with the same intensities and exactly the same separation (970 Hz) of lines as in the ^{31}P NMR spectrum. All lines are broadened ($w_{1/2} = 30$ Hz) and the expected fine structure of an $AA'XX'$ spectrum is not resolved. This apparent first-order pattern remains unchanged also at low temperatures down to −80 °C, while the difference in chemical shifts of both doublets has only slightly decreased. Since recording the spectrum at a higher field (500 MHz spectrometer) did also not change its pattern, the two observed doublets can be assigned to two diastereoisomers of **3**.

The $(Me_3SiO)_2P_2O_3F_2$ molecule has two stereogenic centres and carries the same substituents at each phosphorus atom. Accordingly, there are three stereoisomers for **3**, from which two form a pair of enantiomers, which are diastereoisomeric with respect to the achiral *meso* stereoisomer. Each of the two diastereoisomers may exhibit a distinct $AA'XX'$ spectrum with slightly different chemical shifts and coupling constants. In the ^{19}F NMR spectrum chemical shifts of this particular pair of diastereoisomers are different, while the $^1J(PF)$ are incidentally identical and the magnitudes of all remaining coupling constants are too small to allow the observation of their differences by a routine measurement.

Table 3
^{31}P NMR parameters for the $AA'XX'$ spectra of $(Me_3SiO)_2P_2O_3F_2$ and $(Me_3NH)_2 \cdot P_2O_5F_2$

Compound	δ_P	$^1J(PF)$ (Hz)	$^2J(PP')$ (Hz)	$^3J(P'F)$ (Hz)[a]	$^4J(FF')$ (Hz)	Solvent
$(Me_3SiO)_2P_2O_3F_2$ (**3**)	−32.3	972	7.6	−2.2	2.3	CH_2Cl_2
$(Me_3NH)_2\ P_2O_5F_2$ [17]	−15.7	919	13.6	−2.1	1.7	CH_3CN

[a] The sign of $^3J(P'F)$ is positive, if $^1J(P'F)$ is taken as negative.

Since only one multiplet for **3** is observed in the ^{31}P NMR spectrum, either both diastereoisomers have accidentally the same chemical shift or there exists an exchange process permitting a fast alteration of ligand configurations at each stereogenic centre on the NMR timescale. Although the lack of ^{29}Si satellites in ^{31}P NMR spectrum suggests that such an exchange process in **3** may exist, this alternative can be rejected because the consequences of such exchange should be observed also in the ^{19}F NMR spectrum. The absence of these satellites as well as the missing splitting of ^{1}H decoupled ^{29}Si NMR signal may be caused by a very small ^{2}J(POSi) coupling constant. Actually, the values of only 5–6 Hz have been reported for $Me_3Al{\cdot}OP(OSiMe_3)_3$ and related compounds [21]. Nevertheless, in a ^{31}P spectrum recorded at −40 °C, the resonances of **3** are split into doublets, which are separated by only 10 Hz at 202 MHz. This separation obviously corresponds to the difference between chemical shifts of particular diastereoisomers and increases to 16 Hz at −80 °C.

Therefore, it may be presumed that the appearance of spectra and their changes at variable temperature experiments are strongly influenced by conformational processes since there are two Si–O and four P–O single bonds in **3**, and as rotation proceeds around them a series of more or less stable conformations arise. As follows from their vibrational spectra (cf. 2.5), **1a** and the other trimethylsilyl phosphorodihalogenidates occur as two rotational isomers, and for **3** the existence of rotamers is also probable.

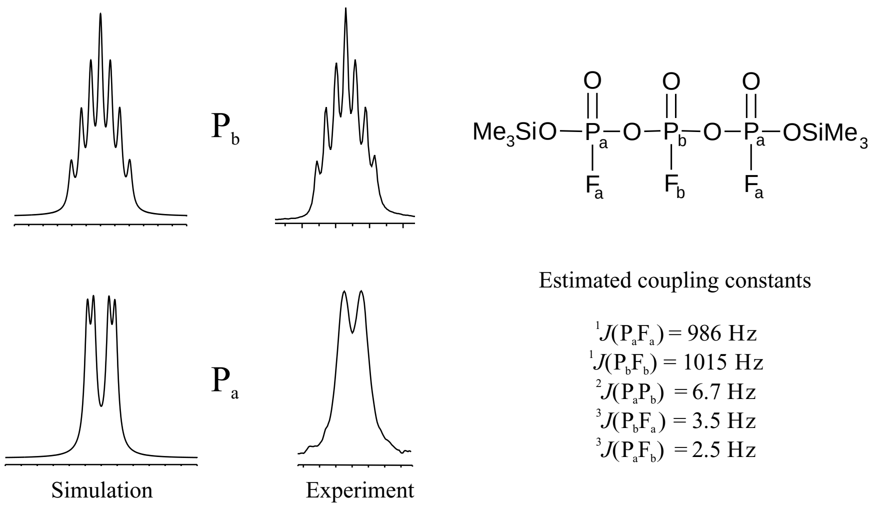
2.4. Formation of bis(trimethylsilyl) polyphosphoropolyfluoridates

Each synthesis of **3** is invariably accompanied by the formation of a compound which ^{31}P NMR spectrum consists of a doublet ($^{19}F = 986$ Hz) of doublets (5 Hz) at −33.4 ppm (peaks E in Fig. 1) and a doublet ($^{1}J(PF) = 1015$ Hz) of apparent septets (3.5 Hz) at −38.3 ppm (peaks H in Fig. 1) with a 2:1 relative intensity of signals. However, the relative line intensities within the latter multiplet do not comply with those expected for a septet. Therefore the observed pattern is considered to be a triplet of triplets with a coupling constant having accidentally the twofold magnitude of the other coupling constant involved. Considering the relevant chemical relations, this set of multiplets is assigned to the bis(trimethylsilyl) ester of 1,2,3-trifluorotriphosphoric acid (**5**) and to our knowledge, it is its first reported derivative. Both multiplets could be analysed as a first-order spectrum and the obtained NMR parameters are given in Table 1. The observed and simulated signal patterns in the ^{31}P NMR spectrum are compared in Fig. 2. The unresolved splitting of the P_a signal by $^{3}J(P_aP_b)$ may presumably be accounted for by conformational changes of **5**, which also make difficult to give a spectral proof of the three predicted diastereoisomers.

The ester **5** is probably formed by the condensation of **1a**,**b** with **3**, although in reaction systems where **2** occurs, its condensation with **4a**,**b** can also be considered (Scheme 4). Eventually, two very weak doublets at −34.0 ppm ($^{1}J(PF) = 995$ Hz) (peaks F in Fig. 1) and −39.9 ppm ($^{1}J(PF) = 1028$ Hz) (peaks I in Fig. 1) can probably be assigned to the $Me_3SiOP(O)F$– and –[OP(O)F]– groups, respectively. Thus, simultaneous formation of small amounts of $Me_3SiOP(O)F[OP(O)F]_2OPF(O)OSiMe_3$ or other bis(trimethylsilyl) polyphosphoropolyfluoridates with even longer chains through successive condensation reactions appears to be very likely.

2.5. Vibrational spectra of trimethylsilyl phosphorochloridofluoridate and bis(trimethylsilyl) diphosphorodifluoridate

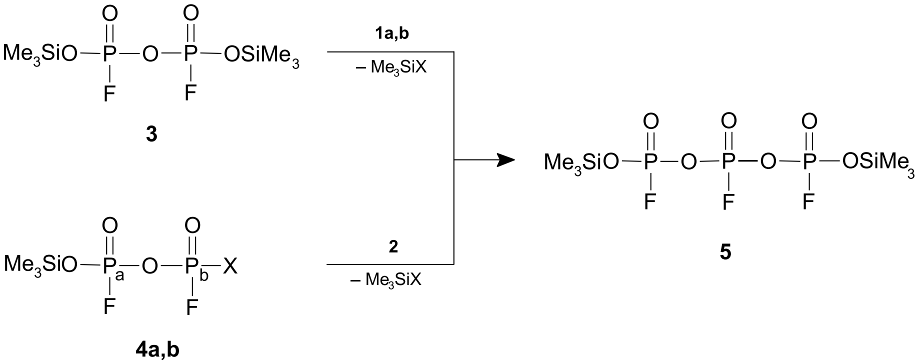
Selected infrared and Raman frequencies of **1a** and **3** are given and some of them are tentatively assigned in the



Estimated coupling constants

$^{1}J(P_aF_a) = 986$ Hz
$^{1}J(P_bF_b) = 1015$ Hz
$^{2}J(P_aP_b) = 6.7$ Hz
$^{3}J(P_bF_a) = 3.5$ Hz
$^{3}J(P_aF_b) = 2.5$ Hz

Fig. 2. Comparison of simulated and observed ^{31}P NMR spectrum of **5**. Only one half of corresponding doublets is depicted.



Scheme 4.

Sections 4.2 and 4.4, respectively. The bands of $\delta_{as}CH_3$, ν_sCH_3 and $\nu_{as}CH_3$ fundamentals occurring in the region 1350–3000 cm^{-1} were omitted for brevity.

The molecule of **1a** is asymmetric, while the highest possible symmetry of **3** is C_2 for both enantiomers and C_s for the *meso* diastereoisomer. Thus, regardless of their symmetry, all 48 fundamental vibrations of **1a** as well as 99 fundamentals of **3** should be active in either the IR or Raman spectrum. However, a higher local symmetry C_{3v} of the Me_3Si groups and the accidental degeneration of some pairwise occurring in-phase (ν) and out-of-phase (ν') modes in **3** reduce the number of actually observed fundamentals considerably. Nevertheless, the fundamental vibrations of the Me_3SiO group can be identified by comparison with vibrational assignments of other trimethylsilyl compounds [22].

The remaining 27 fundamental vibrations of **3** belong to the skeleton F(SiO)(O)P–O–P(O)(OSi)F and may be classified into in-phase and out-of-phase vibrations of both –P(O)(OSi)F terminal groups and the skeletal modes of the P–O–P bridge. In vibrational spectra of structurally related $P_2O_5F_2^{2-}$ [23] and $S_2O_5F_2$ [24], where the assignment is supported by a normal-coordinate analysis, the difference between the stretching modes ν and ν' varies from 4 to 31 cm^{-1}. Consequently, the bands occurring in both IR and Raman spectra at 894 and 924 cm^{-1} can be assigned to νPF and ν'PF, respectively. For the same reason, the frequencies at 1336 cm^{-1} (Raman) and 1343 cm^{-1} (IR) were assigned to the stretching modes νPO and ν'PO.

Although the splitting of these fundamentals may be attributed to two diastereoisomers of **3**, only negligible variations of their chemical shifts in ^{19}F and ^{31}P NMR spectra suggest that any greater difference in their vibrational frequencies is not likely. But on the other hand, it has been shown that several fundamental vibrations appear as doublets in the spectra of $CH_3OP(S)Cl_2$ and $CD_3OP(S)Cl_2$ [25,26] due to the existence of rotational isomers. Similarly, the small splitting (5–9 cm^{-1}) of νPO in IR and Raman spectra of several trimethylsilyl phosphorodihalogenidates [2,3,5] can also be attributed to the occurrence of at least two conformers. Considering the structural similarity between these esters and **3**, it appears to be likely that the splitting of some fundamentals in vibrational spectra of **3** may be caused by the same factor.

The stretching modes of the P–O–P bridge were assigned by a comparison with the known frequencies of ν_sPOP and ν_{as}POP in vibrational spectra of similar compounds [22,27,28]. Interestingly, the established frequencies 750 and 1030 cm^{-1} for the ν_sPOP and ν_{as}POP, respectively, are comparable with those reported for $(MeO)_2P_2O_3F_2$ and $P_2O_3Cl_2F_2$ [28], although in **3** an extensive coupling with stretching vibrations of both Si–O–P bridges should be assumed. The assignment of –OP(O)FCl skeletal stretching modes of **1a** was established by comparison with structurally related phosphorus compounds [2,29,30]. As discussed above, splitting of the νPO (5 cm^{-1}) and νSi–OP (10 cm^{-1}) stretching vibrations can obviously be attributed to the existence of two conformers, which result from the rotation around the P–O bond.

3. Conclusions

Convenient routes for the synthesis of trimethylsilyl phosphorochloridofluoridate (**1a**) and diphosphorodifluoridate (**3**) have been developed. The NMR studies of reaction courses and unambiguous identification of the intermediate **4** and by-product **5** enabled us to suggest the most likely pathways of involved reactions. It was shown that during the formation as well as the thermal decomposition of trimethylsilyl phosphorofluoridohalogenidates, condensation reactions with corresponding halogenotrimethylsilane as leaving group are predominant. Although the formation of the Si^{IV}–F bond (581 kJ mol^{-1}) in comparison with the P^V–F bond (460 kJ mol^{-1}) [31] is energetically more favourable, an elimination of Me_3SiF was not observed. Both esters may be valuable synthetic intermediates to various derivatives of fluorophosphoric acids. In contrast to the analogous alkyl esters, a greater reactivity of their trialkylsilyl counterparts can be presumed and the risk of accidental formation of highly toxic dialkyl phosphorofluoridates is precluded.

4. Experimental

4.1. General experimental procedures

All manipulations were carried out under strict exclusion of moisture using standard grease-free Pyrex glass vacuum line and Schlenk techniques. All solvents and hexamethyldisiloxane were purified and dried according to literature methods [32]. Phosphoryl dichloride fluoride was prepared by the treatment of fluorophosphoric acid with PCl_5 according to Roesky [33] and then fractionated on a column. Phosphoryl dibromide fluoride was synthesised by a partial fluorination of phosphoryl tribromide with SbF_3 [34] and separated from the other products of fluorination by fractional distillation on a column. Bis(trimethylsilyl) phosphorofluoridate was obtained by silylation of silver fluorophosphate with trimethylchlorosilane [35]. Since the original synthesis was modified, a brief description of synthetic procedure is provided in Section 4.3.

The NMR spectra were recorded on a Bruker DPX300 spectrometer (^{1}H NMR 300 MHz, ^{19}F NMR 282 MHz and ^{31}P NMR 121 MHz) and on a Bruker DRX500 (^{29}Si NMR 98 MHz, ^{31}P NMR 202 MHz) with external D_2O lock. Chemical shifts were referenced to Me_4Si for ^{1}H and ^{29}Si NMR, $CFCl_3$ for ^{19}F NMR and 85% H_3PO_4 for ^{31}P NMR as external standards with negative shifts being upfield from the reference signal. Raman spectra were recorded on a Bruker Equinox IFS 55/S apparatus connected with Raman adapter FRA 106/S and using Nd:YAG-Laser ($\lambda = 1064$ nm). Infrared spectra were measured as liquid films between AgCl windows on a Bruker IFS 28 FT IR spectrometer. Refractive index was determined on a KRÜSS AR2 refractometer. Gravimetric chemical analysis was carried out for phosphorus, fluorine and chlorine. The fluoride was determined as PbBrF after steam destillation [36], phosphorus as quinolinium phosphomolybdate [37], and chloride as AgCl. Reported boiling points are uncorrected.

*4.2. Trimethylsilyl phosphorochloridofluoridate (**1a**)*

(a) Hexamethyldisiloxane (12.14 g, 74.8 mmol) was added to $POFCl_2$ (10.47 g, 76.5 mmol) and the mixture was stored for 30 days at an ambient temperature. All volatile products were then pumped off under vacuum at 0 °C and the ester obtained was purified by vacuum distillation on a Vigreux fractionating column (b.p. 53–54 °C, 20 Torr). The reaction yielded 7.75 g (55%) of **1a**.

(b) Bis(trimethylsilyl) phosphorofluoridate (**2**) (4.85 g, 19.8 mmol) was added to phosphorus pentachloride (4.12 g, 19.8 mmol). After all PCl_5 dissolved, the volatile products were pumped off and the ester was purified by distillation on a column (see above). Yield: 2.06 g (55%). For NMR parameters see Table 1.

IR: ν (cm^{-1}) 1329 vs (νPO), 1262 s, 1097 sh + 1078 vs (νSi–OP), 892 m (νPF), 857 vs, 766 m, 704 sh, 672 m (νSiO–P), 612 s, 581 m,b (νPCl), 539 sh (δPO_2), 457 w, 417 sh.

Raman: ν (cm^{-1}) 1324 w (νPO), 1268 vw, 1090 sh + 1079 vw (νSi–OP), 894 vw (νPF), 860 vw, 765 vw, 703 vw, 669 w (νSiO–P), 614 m–w, 574 w,b (νPCl), 539 w (δPO_2), 484 vw, 457 vw, 417 m–w, 377 sh, 357 vw, 282 vw, 247 w, 212 sh, 186 m–w.

Refractive index $n_D^{20} = 1.3885$. Anal. calcd. for $C_3H_9ClFO_2PSi$: Cl, 18.6; F, 10.0; P, 16.3. Found: Cl, 18.4; F, 10.4; P, 16.2.

*4.3. Bis(trimethylsilyl) phosphorofluoridate (**2**)*

Trimethylchlorosilane (14.76 g, 0.136 mol) was added to Ag_2PO_3F (32.00 g, 0.102 mol) in a thick-walled screw-cap reaction tube fitted with a glass–Teflon valve and the mixture was shaken with a glass ball for 10 h at an ambient temperature. Excess trimethylchlorosilane was distilled off in static vacuum at 10 °C and the subsequent distillation under dynamic vacuum afforded 12.95 g (78%) of ester **2**. For NMR parameters see Table 1.

*4.4. Bis(trimethylsilyl) diphosphorodifluoridate (**3**)*

(a) The mixture of $POFBr_2$ (3.50 g, 15.5 mmol) and hexamethyldisiloxane (5.95 g, 36.5 mmol) was heated in a closed vessel for 4 h to 100 °C. After cooling the reaction mixture to a room temperature, all volatile products were pumped off, and further portion of hexamethyldisiloxane (4.85 g, 29.9 mmol) was added. The mixture was heated for additional 4 h and the volatiles were pumped off again. The obtained ester **3** was purified by a slow vacuum distillation on a short path distillation apparatus (0.1 Torr, bath temperature 60 °C) with a yield of 1.35 g (53%).

(b) Ester **1a** (1.58 g, 8.3 mmol) was added to phosphorofluoridate **2** (1.88 g, 7.7 mmol) and the mixture was stored in dark at an ambient temperature. After 3 months all volatile products were pumped off and the resulted diphosphorodifluoridate **3** was purified by a vacuum distillation (see above). Yield: 1.23 g (45%). For NMR parameters see Table 1.

IR: ν (cm^{-1}) 1343 vs (νPO + ν'PO), 1262 s, 1111 sh + 1098 s (νSi–OP), 1030 vs (ν_{as}POP), 924 w (ν'PF), 894 s (νPF), 855 vs, 767 m, 750 sh (ν_sPOP), 706 vw, 665 w,b (νSiO–P), 612 w, 500 m.

Raman: ν (cm^{-1}) 1336 w (νPO+ ν'PO), 1269 vw, 1261 sh, 1109 vw,b (νSi–OP), 1030 vw,b (ν_{as}POP), 924 vw (ν'PF), 894 vw (νPF), 858 vw, 765 vw, 750 vw (ν_sPOP), 704 vw, 648 vw (νSiO–P), 613 m, 604 sh, 591 sh, 497 vw, 411 vw, 353 vw, 301 sh, 287 vw, 249 w, 192 m–w, 170 sh.

Refractive index $n_D^{20}20 = 1.3709$. Anal. calcd. for $C_6H_{18}F_2O_5P_2Si_2$: F, 11.6; P, 19.0. Found: F, 11.2; P, 18.8.

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