

New Anions of Pentacoordinate Phosphorus Containing Fluorine and Trifluoromethyl Groups

Natalya V. Pavlenko,^[a] Lesya A. Babadzhanova,^[a] Igor I. Gerus,^[b] Yurii L. Yagupolskii,^{*,[a]} Wieland Tyrra,^[c] and Dieter Naumann^[c]

Dedicated to Professor Karl Otto Christe on the occasion of his 70th birthday

Keywords: Phosphorus / Fluorides / Silanes / Pentacoordinate anions

The unique pseudo-trigonal-bipyramidal $\text{CF}_3\text{PF}_3\text{O}^-$ and $(\text{CF}_3)_2\text{PF}_2\text{O}^-$ anions were obtained and characterised for the first time. They were formed by the reactions of $(\text{PhO})_3\text{P}(\text{O})$, Me_3SiCF_3 and the fluoride ion sources $[\text{Me}_4\text{N}]\text{F}$ and CsF , respectively, in glyme. These anions represent the stable transition states postulated for nucleophilic substitution at a

tetrahedral phosphorus atom. The salt $\text{Cs}[(\text{CF}_3)_2\text{PF}_2\text{O}]$ (**7**) is stable at room temperature for a month, while $[\text{Me}_4\text{N}][\text{CF}_3\text{PF}_3\text{O}]$ (**1**) dismutates into $[\text{Me}_4\text{N}][\text{CF}_3\text{PF}(\text{O})\text{O}]$ (**2**) and $[\text{Me}_4\text{N}][\text{CF}_3\text{PF}_5]$ (**3**) above 0 °C.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The importance of fluorinated compounds is rapidly increasing in many fields of modern agrochemistry, pharmaceutical industry and material sciences.^[1] During the past several decades numerous methods were developed for the direct introduction of fluorinated substituents, in particular trifluoromethyl groups, into different types of molecules. Among a wide variety of reagents for CF_3 group introduction, commercially available trimethyl(trifluoromethyl)silane had become the reagent of choice.^[2] However, only a few phosphorus-containing electrophiles have been used for nucleophilic trifluoromethylation with Me_3SiCF_3 .^[3]

It has been shown that it is possible to convert $\text{P}^{\text{V}}\text{-F}$ compounds into the corresponding $\text{P}^{\text{V}}\text{-CF}_3$ derivatives by reactions of Me_3SiCF_3 in the presence of catalytic amounts of F^- sources.^[3] In order to avoid the use of toxic phosphorous oxofluorides as starting materials and taking into account two examples of successful trifluoromethylation of aryl esters of P^{III} -acids by Me_3SiCF_3 ^[3c] and by Ruppert's method,^[4] we investigated the reactions of triphenylphosphate and Me_3SiCF_3 in the presence of fluoride sources. It should be noted in advance that the results differ from each other depending on the initiator, $[\text{Me}_4\text{N}]\text{F}$ or CsF , and will therefore be described separately.

Results and Discussion

Reactions of $(\text{PhO})_3\text{P}(\text{O})$ with Me_3SiCF_3 and $[\text{Me}_4\text{N}]\text{F}$

The reactions of $(\text{PhO})_3\text{P}(\text{O})$ with Me_3SiCF_3 and $[\text{Me}_4\text{N}]\text{F}$ yielded complex product mixtures. The composition strongly depended on the stoichiometry of the starting materials, the solvent and the temperature. The conditions for obtaining tetramethylammonium trifluoro(trifluoromethyl)phosphoranolate (**1**) as the major phosphorus-containing compound were 4 equiv. $[\text{Me}_4\text{N}]\text{F}$, 1 equiv. Me_3SiCF_3 and 1 equiv. $(\text{PhO})_3\text{P}(\text{O})$, with dme as the solvent and a temperature of –40 °C (Scheme 1).

Salt **1** contains a unique anion that represents the stable transition state usually postulated in the course of nucleophilic substitution at a tetrahedral phosphorus atom.^[5] Compound **1** is stable for a reasonable time, both in solution and in the solid state at temperatures equal to or below 0 °C. It presents one more example of hypervalent compounds whose stability is significantly increased by the introduction of perfluoroalkyl groups.

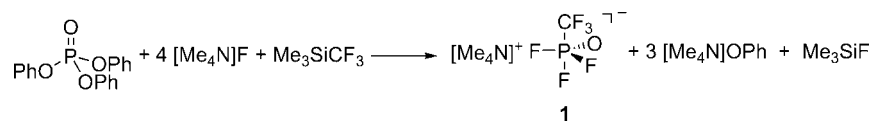
The formation of the trifluoro(trifluoromethyl)phosphoranolate anion and its structure were established by NMR spectroscopic and mass spectrometric data. NMR spectra recorded at 20 °C are of first order and imply that the anion appears to be rigid at this temperature (Figure 1, Table 1).

The anion exhibits two signals in the ^{19}F NMR spectrum for the fluorine atoms attached to the phosphorus centre with an integrative ratio of 1:2. The low-field doublet of triplets ($\delta = -46.9$ ppm) corresponds to the fluorine atom in the axial position ($^1J_{\text{F}_{\text{ax}}-\text{P}} = 812$ Hz, $^2J_{\text{F}_{\text{ax}}-\text{F}_{\text{eq}}} = 82$ Hz),

[a] Institute of Organic Chemistry, National Academy of Sciences of Ukraine,
5 Murmanskaya St., 02094 Kiev 94, Ukraine

[b] Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine,
1 Murmanskaya St., 02094 Kiev 94, Ukraine

[c] Institut für Anorganische Chemie, Universität zu Köln,
Greinstrasse 6, 50939 Köln, Germany



Scheme 1.

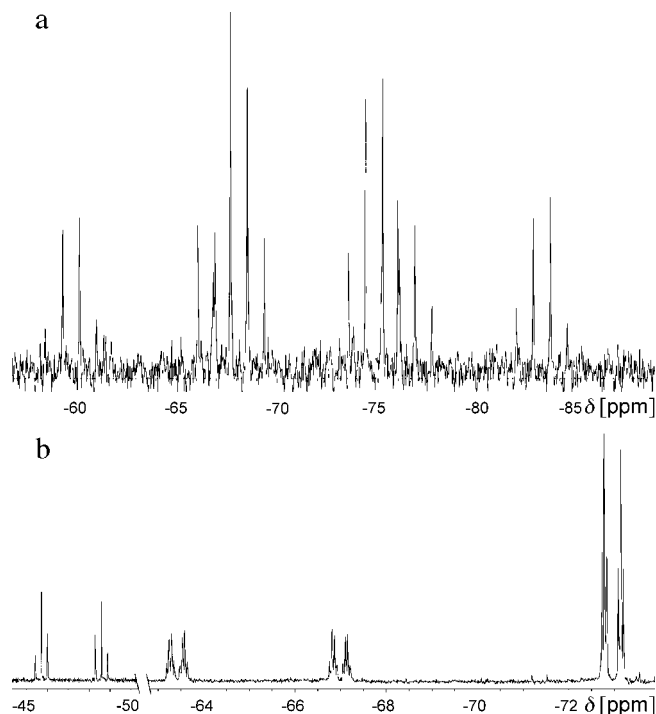


Figure 1. NMR spectra of $[\text{Me}_4\text{N}][\text{CF}_3\text{PF}_3\text{O}]$ (**1**) recorded in CD_3CN : (a) ^{31}P spectrum (121.42 MHz) and (b) ^{19}F spectrum (282.41 MHz).

and the doublet of doublets of quartets ($\delta = -65.2$ ppm) is assigned to two equatorial fluorine atoms ($^1J_{\text{F}_{\text{eq}}-\text{P}} = 1010$ Hz, $^2J_{\text{F}_{\text{eq}}-\text{F}_{\text{ax}}} = 82$ Hz, $^3J_{\text{F}_{\text{eq}}-\text{CF}_3} = 15$ Hz). The signal of the CF_3 group is found at $\delta = -73.0$ ppm and appears as a doublet of triplets ($^2J_{\text{CF}_3-\text{P}} = 100$ Hz, $^3J_{\text{CF}_3-\text{F}_{\text{eq}}} = 15$ Hz). The chemical shift ($\delta < -70$ ppm) of the CF_3 group suggests axial position in comparison with NMR spectroscopic data of related compounds.^[7] The triplet of doublets of quartets ($\delta = -71.3$ ppm) in the ^{31}P NMR spectrum falls into the shift range of pentacoordinate phosphorus^[7,8] and proves additionally that the anion contains two different types of fluorine atoms and one CF_3 group. Thus the anion of salt **1** has the structure of a trigonal bipyramid with one fluorine atom and the trifluoromethyl group in axial positions and two fluorine atoms and the oxygen atom in the equatorial plane. The ^1H NMR spectrum shows only the signal of the tetramethylammonium cation at $\delta = 2.95$ ppm.

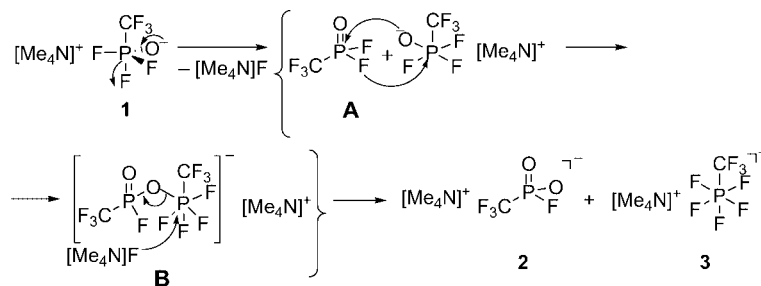
Salt **1** undergoes slow dismutation at temperatures above 0°C , forming stable tetracoordinate and hexacoordinate (compounds **2** and **3**, respectively) phosphorus species (Scheme 2). Therefore, NMR spectra could be run at ambient temperature.

Dismutation of salt **1** presumably proceeds with initial formation of the (trifluoromethyl)phosphonyl difluoride (**A**) by fluoride elimination; **A** reacts with the anion **1** to form the second intermediate, the dimeric anion **B**. The

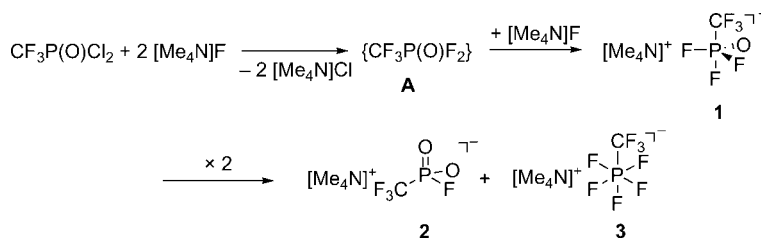
Table 1. Compilation of ^{19}F and ^{31}P NMR spectroscopic data of all synthesised compounds.

	Species (solvent)	^{31}P	^{19}F				Coupling constants [Hz]			
		δ [ppm]	δ [ppm]	Integral			$^1J_{\text{P}-\text{F}}$	$^2J_{\text{P}-\text{CF}_3}$	$^2J_{\text{F}-\text{F}}$	$^3J_{\text{F}-\text{CF}_3}$
1	$\text{CF}_3\text{PF}_3\text{O}^-$ (CD_3CN)	-71.3 (tdq)	-46.9 (dt)	1	F_{ax}	812				
			-65.2 (ddq)	2	F_{eq}	1010			82	
			-73.0 (dt)	3	CF_3		100			15
7	$(\text{CF}_3)_2\text{PF}_2\text{O}^-$ (CD_3CN)	-64.9 (tsept)	-75.0 (dsept)	1 (2)	F_{eq}	1080				
			-74.3 (dt)	3 (6)	CF_3		113			16
			-39.0 (dd)	1	F_{ax}	790				
14	$\text{CF}_3\text{PF}_2(\text{OPh})\text{O}^-$ (dme)	-76.2 (ddq)	-68.9 (ddq)	1	F_{eq}	1004			74	
			-72.5 (dd)	3	CF_3		86			14
			-74.3 (dq)	1	F	985				
12	$\text{CF}_3\text{P}(\text{O})(\text{F})\text{O}^-$ (CD_3CN)	-8.9 (dq)	-74.3 (dq)	3	CF_3		107			8
			-72.4 (dq)	1	F	1020				
			-73.3 (dd)	3	CF_3		120			12
2	$\text{CF}_3\text{P}(\text{O})(\text{F})\text{O}^-$ (D_2O)	-6.7 (dq)	-72.9 (dm)	1	F_{ax}	720			42	2.5
			-73.9 (dm)	4	F_{eq}	819				13
			-69.5 (dqintd)	3	CF_3		140			
3, 13	$\text{CF}_3\text{PF}_5^{-[\text{a},\text{b}]}$ (D_2O)	-147.5 (quintdq)								
8	$(\text{CF}_3)_2\text{P}(\text{O})(\text{OH})_2^{[\text{c},\text{d}]}$ (CD_3CN)	-5.8 (dsept)	-73.3 (d)				96			
10	$([\text{D}_6]\text{dmsO})$	-6.0 (q)	-71.8 (d)				92			
			-3.8 (q)				107			
4	F_4PO^- ($[\text{D}_6]\text{dmsO}$)	-75.1 (quint)	-54.2 (d)			827				
5	$\text{F}_2\text{P}(\text{O})\text{O}^-$ ($[\text{D}_6]\text{dmsO}$)	-14.1 (t)	-76.2 (d)			954				

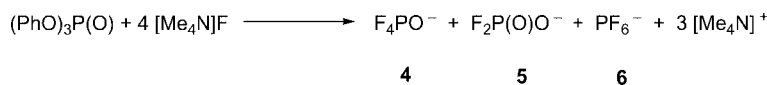
[a] The spectrum is of higher order ($\text{A}_3\text{B}_4\text{CX}$ spin system). [b] $^{13}\text{C}\{^{19}\text{F}\}$ NMR (D_2O): $\delta = 126.2$ (d, $^1J_{\text{P}-\text{C}} = 422$ Hz) ppm. [c] Cf. ref.^[6] [d] $^{13}\text{C}\{^{19}\text{F}\}$ NMR (D_2O): $\delta = 122.3$ (d, $^1J_{\text{P}-\text{C}} = 248$ Hz) ppm.



Scheme 2.



Scheme 3.



Scheme 4.

fluoride anion liberated in the first reaction step then attacks the hexacoordinate phosphorus atom of intermediate **B** to give salts **2** and **3** as the final reaction products. Both salts were separated by fractional crystallisation and characterised by NMR spectroscopic methods and elemental analyses.

It is explicitly noteworthy that the result of the reaction between $(\text{PhO})_3\text{P}(\text{O})$, Me_3SiCF_3 and $[\text{Me}_4\text{N}]\text{F}$ provides a new method to obtain two important perfluoroalkyl-containing phosphorus anions, that is, fluoro(trifluoromethyl)phosphonate (in salt **2**) and hard-to-prepare λ^6 -pentafluoro(trifluoromethyl)phosphate (in salt **3**).^[9] The doubtless advantages of this method are the good availability of the starting materials, the mild reaction conditions and the high yields of the target products.

An equimolar mixture of salts **2** and **3** was also obtained by fluorination of (trifluoromethyl)phosphonyl dichloride with $[\text{Me}_4\text{N}]\text{F}$ (Scheme 3).

However, in this case we were unable to isolate salt **1**. It was only detected in the NMR spectra of the mixture together with salts **2** and **3**. This may be explained by the initial formation of (trifluoromethyl)phosphonyl difluoride (**A**) which adds $[\text{Me}_4\text{N}]\text{F}$ to form salt **1**. Similarly the dismutation process starts as outlined earlier, analogous to the elusive tetrafluorophosphate dismutation presented by Christe et al.^[8] The latter anion was obtained by F^- addition to $\text{P}(\text{O})\text{F}_3$, and its composition was elucidated by NMR experiments performed at -140°C . In one of our experiments, triphenylphosphate was treated with 4 equiv. $[\text{Me}_4\text{N}]\text{F}$ in dme at -40°C . All phosphorus-containing products were insoluble in dme at this temperature as well

as at 20°C . The ^{19}F - and ^{31}P NMR spectra analysis ($[\text{D}_6]$ -dmsol, room temperature) showed that the reaction mixture contained tetrafluorophosphoranolate (**4**) as the major product and its dismutation products **5** and **6** as minor ones (Scheme 4).

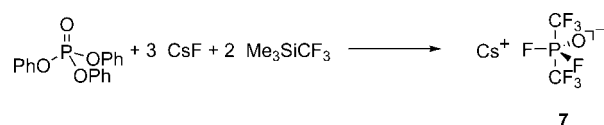
NMR investigations of 1:1 mixtures of $(\text{PhO})_3\text{P}(\text{O})$ and $[\text{Me}_4\text{N}]\text{F}$ at -70°C gave no evidence for the key ion $[(\text{PhO})_3\text{-PFO}]^-$ but allowed the detection of $(\text{PhO})_2\text{P}(\text{O})\text{F}$ $\{\delta_{\text{F}}$ (dme/ $[\text{D}_8]$ thf, v/v = 50:50, -40°C) = -78.7 ppm, $^1J_{\text{F-P}}$ = 996 Hz; δ_{P} (dme/ $[\text{D}_8]$ thf, v/v = 50:50, -40°C) = -17.0 ppm, $^1J_{\text{F-P}}$ = 996 Hz^[10] and its consecutive products **5**, $[(\text{PhO})_2\text{P}(\text{O})\text{O}]^-$ and $[\text{PhOPF}(\text{O})\text{O}]^-$.^[11,12]

The characteristic NMR spectroscopic data for the compounds **4**, **5** (Table 1) and **6** are in full agreement with the data given by Christe et al.^[8] The main advantage of the $[\text{F}_4\text{PO}]^-$ anion synthesis starting from triphenylphosphate is the relative stability of this anion in the solid state as well as in dmsol solution at 20°C . This result supports the suggestion that the presence of excess $\text{P}(\text{O})\text{F}_3$ used in the known procedure significantly accelerates the dismutation process.^[8]

Reactions of $(\text{PhO})_3\text{P}(\text{O})$ with Me_3SiCF_3 and CsF

To our great surprise we were unable to obtain the Cs analogue of salt **1** under the same reaction conditions using CsF instead of $[\text{Me}_4\text{N}]\text{F}$. The product of this reaction was the pentacoordinate phosphorus anion difluorobis(trifluoromethyl)phosphoranolate, $[(\text{CF}_3)_2\text{PF}_2\text{O}]^-$, while reasonable

amounts of the starting material triphenylphosphate remained unchanged. Variation of the stoichiometry to 3 equiv. CsF, 2 equiv. Me₃SiCF₃ and 1 equiv. (PhO)₃P(O) led to a nearly pure solution of cesium difluorobis(trifluoromethyl)phosphoranolate (**7**) (Scheme 5).



Scheme 5.

By comparison to the known structure^[13] and NMR spectroscopic data^[7] of the closely related (CF₃)₂PF₃ and the easily interpretable ¹⁹F- and ³¹P NMR spectra of salt **7** on a first order basis (Figure 2, Table 1), we propose both CF₃ groups reside in axial positions, while the two fluorine atoms and the oxygen atom are located in the equatorial plane of a trigonal bipyramid.

The triplet of septets in the range of pentacoordinate phosphorus ($\delta = -64.9$ ppm) in the ³¹P NMR spectrum gives evidence that anion **7** contains two magnetically equivalent fluorine atoms and two equivalent CF₃ groups. The ¹⁹F NMR spectrum exhibits the signal of two fluorine atoms bonded to the phosphorus atom as a doublet of septets centred at $\delta = -75.0$ ppm. Correspondingly, the signals of the trifluoromethyl groups are split into doublets of triplets centred at $\delta = -74.3$ ppm with ²*J*_{CF₃-P} = 113 Hz and ³*J*_{CF₃-F_{eq}} = 16 Hz. The high-field shifts of both signals, compared with values found for compounds with opposite arrangement of the CF₃ groups and the fluorine atoms,^[7] as well as the value of ¹*J*_{F-P} = 1080 Hz, indicate that the fluorine atoms are located in the equatorial plane of the trigonal bipyramid.

Salt **7** is stable in dme or CH₃CN solutions, as well as in the solid state for months at 20 °C, but it is extremely sensitive to moisture. Also, storing the solid especially in glassware causes decomposition into bis(trifluoromethyl)phosphinic (**8**)^[6,14] and (trifluoromethyl)phosphonic (**10**)^[6,15] acids (Scheme 6).

The degradation of **7** can be explained on the assumption of the intermediate formation of bis(trifluoromethyl)phosphinyl fluoride (**C**) which is hydrolysed either by replacement of the fluorine atom or the trifluoromethyl group by hydroxy groups. In the latter case, NMR spectroscopic evidence was found for fluoro(trifluoromethyl)phosphonic acid (**9**) [δ_{F} (CD₃CN) = -71.8 ppm (d, ¹*J*_{F-P} = 980 Hz), -72.7 ppm (d, ²*J*_{F-P} = 102 Hz); δ_{P} (CD₃CN) = -8.8 ppm (dq, ¹*J*_{F-P} = 980 Hz, ²*J*_{F-P} = 102 Hz)] which is rapidly hydrolysed to acid **10**.

In order to obtain the Cs analogue of salt **1**, we performed the reaction of (trifluoromethyl)phosphonyl dichloride with CsF (Scheme 7).

The instability of **11** prevented its detection in NMR spectra of the reaction mixture. Only an equimolar mixture of the dismutation products, fluoro(trifluoromethyl)phosphonate **12** and λ⁶-pentafluoro(trifluoromethyl)phosphate **13** was obtained. The salts were separated by fractional crystallisation, and both compounds were characterised. It is noteworthy that salts with the anion CF₃PF₅⁻ were reported at the end of the 1960s,^[9] but the NMR spectroscopic characterisation had remained insufficient until now. The ¹⁹F- and ³¹P NMR spectroscopic data for salt **13** are shown in Figure 3 (cf. Table 1).

The ¹⁹F NMR spectrum of the Cs salt **13** is of higher order; the calculated spectrum^[16] for an A₃B₄CX spin system matched well with the measured spectrum. While the

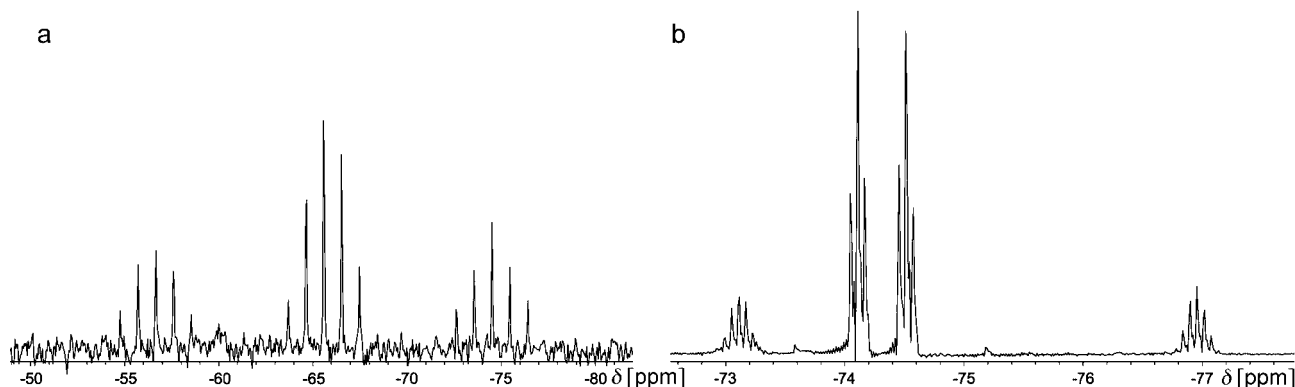
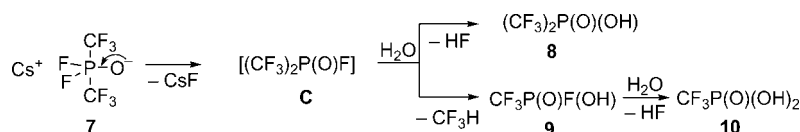
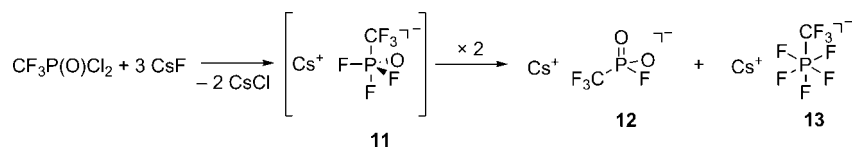


Figure 2. NMR spectra of Cs[(CF₃)₂PF₂O] (**7**) recorded in CD₃CN at 20 °C: (a) ³¹P spectrum (121.42 MHz) and (b) ¹⁹F spectrum (282.41 MHz).



Scheme 6.



Scheme 7.

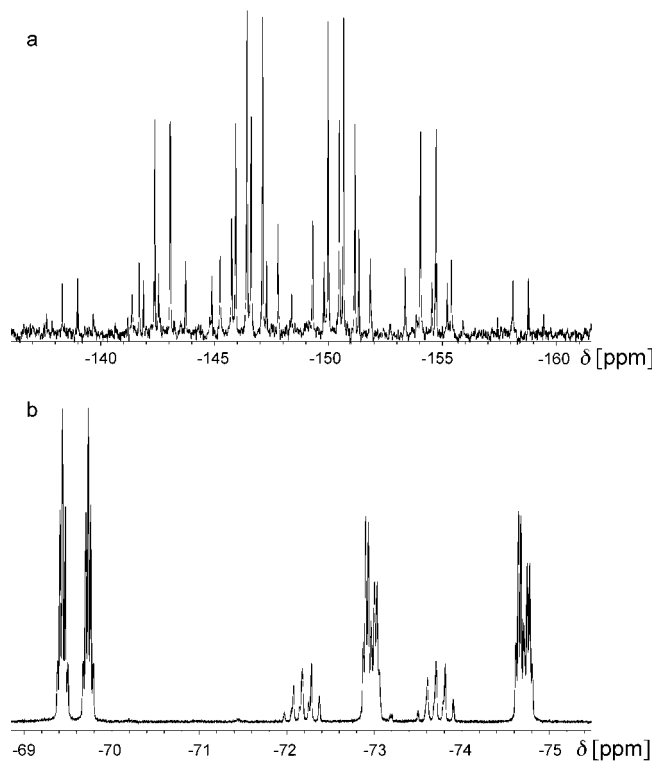


Figure 3. NMR spectra of $\text{Cs}[\text{CF}_3\text{PF}_5]$ (**13**) recorded in D_2O at 20°C : (a) ^{31}P spectrum (202.45 MHz) and (b) ^{19}F spectrum (470.54 MHz).

signals for the fluorine atoms directly bonded to phosphorus appear as doublets of complex multiplets ($\delta_{\text{F}_{\text{ax}}} = -72.9 \text{ ppm}$, $\delta_{\text{F}_{\text{eq}}} = -73.9 \text{ ppm}$), the signal of the CF_3 group ($\delta = -69.5 \text{ ppm}$) can be interpreted as a “first order” doublet ($^2J_{\text{CF}_3-\text{P}} = 140 \text{ Hz}$) of quintets ($^3J_{\text{CF}_3-\text{F}_{\text{eq}}} = 13 \text{ Hz}$) of doublets ($^3J_{\text{CF}_3-\text{F}_{\text{ax}}} = 2.5 \text{ Hz}$). The doublet of quintets of quartets in the ^{31}P NMR spectrum unambiguously confirms the predicted octahedral structure of the anion.

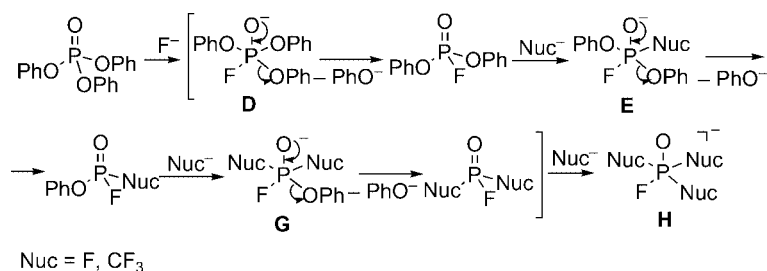
Conclusions

Some general conclusions can be made thus far. Tetracoordinate triphenylphosphate is converted into the highly fluorinated pentacoordinate phosphorus derivatives **1** or **7** in the reaction with Me_3SiCF_3 and sources of fluoride. We assume that the nucleophilic substitution at the tetrahedral phosphorus atom follows the addition-elimination process^[5] and, as far as F^- is in excess relative to the second nucleophile “ CF_3^- ”, the first step of the reaction is the addition of F^- to the $\text{P}=\text{O}$ bond of triphenylphosphate to give intermediate **D** (Scheme 8) followed by spontaneous PhO^- elimination to give $(\text{PhO})_2\text{P}(\text{O})\text{F}$.^[10] The ease of adding fluoride to tris(pentafluoroethyl)phosphane oxide^[17] and phosphoryl trifluoride^[8] further supports this assumption. Upon the substitution of the next PhO group, the highly reactive “ CF_3^- ” nucleophile can compete with the fluoride anion, as is shown in the proposed reaction mechanism (Scheme 8).

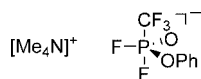
One of the facts that supports this scheme is that the intermediate of type **G** (mixed with salt **1**) was observed in the NMR spectra of the reaction mixture with the reagent ratio $(\text{PhO})_3\text{P}(\text{O})/\text{Me}_3\text{SiCF}_3/[\text{Me}_4\text{N}]\text{F} = 1:2:1$. This intermediate is tetramethylammonium phenyl difluoro(trifluoromethyl)phosphonate (**14**) (Figure 4).

The NMR spectroscopic data (Table 1) allow us to propose the mentioned structure of this unstable anion.

We have characterised three compounds among the possible final structures of type **H**, namely the tetramethylammonium salt of the tetrafluorophosphoranolate ion (**4**), salt **1** with one trifluoromethyl group and salt **7** with two trifluoromethyl groups attached to the phosphorus atom. The stability of anions of type **H** increases significantly in the series $\text{POF}_4^- < \text{CF}_3\text{POF}_3^- < (\text{CF}_3)_2\text{POF}_2^-$, but their solubility in organic solvents changes in the reverse order. The solvent plays a key role in the investigated reactions; *dme* is the best choice allowing selective reactions, whereas mix-



Scheme 8.



14

Figure 4. Tetramethylammonium phenyl difluoro(trifluoromethyl)phosphonate (**14**).

tures are formed in thf, and no reaction is observed in ether or propionitrile. The distinct difference in the results depending on whether $[\text{Me}_4\text{N}]\text{F}$ or CsF is used as a fluoride source is probably a result of their different solubility in dme. The less soluble CsF provides a lower concentration of fluoride in solution, and consequently the possibility of the substrate reacting with the competitive nucleophile “ CF_3^- ” is favoured. The result is the formation of salt **7** containing two trifluoromethyl groups. It is noteworthy that we have never observed an anion with three CF_3 groups bonded to the phosphorus atom even when using a high excess of trimethyl(trifluoromethyl)silane relative to the fluoride source.

Experimental Section

General: All reactions were carried out under argon, using Schlenk type glassware with rigorous exclusion of traces of moisture and air. The solvents were purified by standard methods and were condensed in vacuo prior to use. Me_3SiCF_3 was purchased from ABCR. $[\text{Me}_4\text{N}]\text{F}$ ^[18] and $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$ ^[19] were synthesised according to literature procedures. $[\text{Me}_4\text{N}]\text{F}$ and CsF were carefully dried in vacuo directly before use. Room temp. ^1H -, ^{19}F -, ^{31}P - and ^{13}C NMR spectra were recorded with either a Varian VXR-300 or a Bruker Avance II 300 spectrometer and in one case (salt **13**) with a Bruker Avance DRX 500 spectrometer. Low-temperature NMR experiments were performed with a Bruker AC 200 spectrometer. Chemical shifts are given in ppm relative to Me_4Si as internal and CCl_3F and 85% H_3PO_4 as external standards. The NMR spectroscopic data are compiled in Table 1. Negative ESI mass spectra were recorded with a Finnigan MAT 900 apparatus with a flow rate of 2 $\mu\text{L}/\text{min}$. Intensities are referenced to the most intense peak of a group.

Tetramethylammonium Trifluoro(trifluoromethyl)phosphoranolate (1): To a solution of triphenylphosphate (0.60 g, 1.84 mmol) and trimethyl(trifluoromethyl)silane (0.32 g, 2.25 mmol) in dimethoxyethane (dme) (10 mL) at -40°C was added $[\text{Me}_4\text{N}]\text{F}$ (0.69 g, 7.42 mmol) in small portions over a period of 15 min, and the resulting mixture was stirred for 2 h at this temperature and was then warmed slowly (≈ 4 h) to 0°C . Stirring was continued at this temperature for 30 min, and the white precipitate was immediately filtered. The solvent was removed in vacuo, and the residue was suspended in diethyl ether (≈ 5 mL) at 0°C , filtered and dried in vacuo at this temperature to give salt **1**. Yield: 0.38 g (82%). ^1H NMR (CD_3CN): $\delta = 2.95$ (s, NCH_3) ppm. Negative ESI-MS (MeCN): m/z (%) = 151 (20) $[\text{CF}_3(\text{F})\text{P}(\text{O})\text{O}]^-$, 173 (100) $[\text{CF}_3\text{PF}_3\text{O}]^-$, 223 (68) $[(\text{CF}_3)_2\text{PF}_2\text{O}]^-$, 225 (45) $[\text{CF}_3\text{P}(\text{O})(\text{OPh})\text{O}]^-$. *Note:* Care has to be taken that the operations are performed as quickly as possible to avoid decomposition.

The Dismutation Reaction of Compound 1: The solution of **1** (0.38 g, 1.54 mmol) in MeCN (10 mL) was kept at room temp. until

^{31}P NMR spectra showed complete disappearance of a multiplet at $\delta = -71$ ppm (≈ 8 h). The solvent was removed in vacuo, and the residue was extracted with hot dme (3×10 mL). The solvent was reduced to about 10 mL. After storage of the resultant solution at -17°C overnight, colourless crystals unsuitable for XRD measurements of **2** were obtained. Yield: 0.13 g (78%). M.p. 110 – 113°C (dec.). ^1H NMR (D_2O): $\delta = 2.93$ (s, NCH_3) ppm. $\text{C}_5\text{H}_{12}\text{F}_4\text{NO}_2\text{P}$ (225.15): calcd. C 26.67, H 5.37, N 6.22; found C 26.35, H 5.72, N 6.13. The residue after extraction was recrystallised from MeCN to give salt **3**. Yield: 0.18 g (86%). M.p. 263 – 266°C (dec.). ^1H NMR (D_2O): $\delta = 2.89$ (s, NCH_3) ppm. $\text{C}_5\text{H}_{12}\text{F}_8\text{NP}$ (269.15): calcd. C 22.31, H 4.49, N 5.20; found C 22.15, H 4.53, N 5.13.

Fluorination of (Trifluoromethyl)phosphonyl Dichloride with Tetramethylammonium Fluoride: To a solution of $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$ (0.50 g, 2.67 mmol) in dme (10 mL) at -40°C was added $[\text{Me}_4\text{N}]\text{F}$ (0.77 g, 8.27 mmol) in small portions over a period of 15 min. The resulting mixture was stirred for 2 h at this temperature and was then warmed slowly (≈ 4 h) to 0°C . Stirring was continued at this temperature for 30 min, and the precipitate was filtered off. ^{19}F - and ^{31}P NMR spectra of the resultant filtrate showed the presence of compounds **1**, **2** and **3** in a ratio of approximately 2:4:3. The solution was kept at room temp. overnight to complete the dismutation of compound **1**. The solvent was removed in vacuo. The reaction mixture was worked up in the same manner as described earlier. After purification, compounds **2** and **3** were obtained in yields of 72% (0.22 g) and 53% (0.19 g), respectively. Some part of the less soluble salt **3** precipitated together with $[\text{Me}_4\text{N}]\text{Cl}$. Extraction of the primary precipitate with hot MeCN yielded more compound **3** (0.10 g) giving a total yield of compound **3** of 0.29 g (81%).

Cesium Difluorobis(trifluoromethyl)phosphoranolate (7): To a solution of triphenylphosphate (0.60 g, 1.84 mmol) and trimethyl(trifluoromethyl)silane (0.55 g, 3.87 mmol) in dme (10 mL) at -40°C was added CsF (0.84 g, 5.53 mmol) in small portions over a period of 15 min. The resulting mixture was stirred for 2 h at this temperature and was then warmed slowly to room temp. Stirring was continued overnight, the precipitated solid was filtered off, and the solvent was removed in vacuo. The residue was washed with benzene (3×5 mL), filtered and dried in vacuo to give salt **7**. Yield: 0.31 g (48%). M.p. 73 – 75°C (dec.). Because of the extreme moisture sensitivity of compound **7**, we were unable to obtain satisfactory elemental analytical data. Negative ESI-MS (MeCN): m/z (%) = 223 (100) $[(\text{CF}_3)_2\text{PF}_2\text{O}]^-$.

Fluorination of (Trifluoromethyl)phosphonyl Dichloride with Cesium Fluoride: To a solution of $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$ (0.40 g, 2.14 mmol) in dme (10 mL) at -40°C was added CsF (0.99 g, 6.52 mmol) in small portions over a period of 15 min. The mixture was stirred for 2 h at this temperature and was then warmed to room temp. Stirring was continued overnight, the solvent was removed in vacuo, and the residue was extracted with hot MeCN (50 mL). After storing the solution at -17°C , the precipitate was filtered off and recrystallised from a 10:1 (v/v) dioxane/water mixture to yield the pure salt **13** as colourless crystals unsuitable for XRD measurements. Yield: 0.31 g (87%). CCsF_8P (327.89): calcd. C 3.66, P 9.45; found C 3.57, P 9.52. ^{19}F - and ^{31}P NMR spectra of the resultant filtrate showed the presence of salt **12** (Table 1) as the major product ($>70\%$). This compound was not fully characterised because of its high sensitivity to moisture.

Acknowledgments

Generous financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged (436 UKR 113/

26). We are indebted to Dr. Mathias Schäfer (Institut für Organische Chemie, Universität zu Köln) for recording the ESI mass spectra.

- [1] a) R. Filler, Y. Kobayashi, L. M. Yagupolskii (Eds.), *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*, Elsevier, Amsterdam, **1993**; b) R. E. Banks, B. E. Smart, J. C. Tatlow (Eds.), *Organofluorine Chemistry – Principles and Commercial Applications*, Plenum Press, New York, **1994**.
- [2] a) G. K. S. Prakash, A. K. Yudin, *Chem. Rev.* **1997**, 97, 756–786; b) G. G. Furin, *Russ. J. Org. Chem.* **1997**, 33, 1209–1242; c) R. P. Singh, J. M. Shreeve, *Tetrahedron* **2000**, 56, 7613–7632; d) E. Abele, E. Lukevics, *Main Group Met. Chem.* **2001**, 24, 315–350.
- [3] a) F. M. Semchenko, O. G. Eremin, B. I. Martynov, *Zh. Obshch. Khim.* **1992**, 62, 473–474; b) R. P. Singh, A. Vij, R. L. Kirchmeier, J. M. Shreeve, *Inorg. Chem.* **2000**, 39, 375–377; c) I. Tworowska, W. Dabkowski, J. Michalski, *Angew. Chem. Int. Ed.* **2001**, 40, 2898–2900.
- [4] A. A. Kolomeitsev, M. Görg, U. Dieckbreder, E. Lork, G. V. Röschenthaler, *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, 109–110, 597–600.
- [5] a) K. C. Kumara Swamy, S. S. Krishnamurthy, *Inorg. Chem.* **1986**, 25, 920–928; b) R. J. P. Corriu, J.-P. Dutheil, G. F. Lanneau, *J. Am. Chem. Soc.* **1984**, 106, 1060–1065.
- [6] T. Mahmood, J. M. Shreeve, *Inorg. Chem.* **1986**, 25, 3128–3131.
- [7] R. Eujen, R. Haiges, *Z. Naturforsch., Teil B* **1998**, 53, 1455–1460.
- [8] K. O. Christe, D. A. Dixon, G. I. Schrobilgen, W. W. Wilson, *J. Am. Chem. Soc.* **1997**, 119, 3918–3928.
- [9] a) S. S. Chan, C. J. Willis, *Can. J. Chem.* **1968**, 46, 1237–1248; b) J. Jander, D. Börner, U. Engelhardt, *Justus Liebigs Ann. Chem.* **1969**, 726, 19–24.
- [10] W. Dabkowski, J. Michalski, *J. Chem. Soc., Chem. Commun.* **1987**, 755–756.
- [11] C. A. Bunton, H. J. Foroudian, N. D. Gilitt, C. R. Whiddon, *Can. J. Chem.* **1998**, 76, 946–954.
- [12] G. S. Reddy, R. Schmutzler, *Z. Naturforsch., Teil B* **1970**, 25, 1199–1214.
- [13] H. Oberhammer, J. Grobe, D. Le Van, *Inorg. Chem.* **1982**, 21, 275–281.
- [14] a) H. J. Emeleus, R. N. Haszeldine, R. C. Paul, *J. Chem. Soc.* **1955**, 563–574; b) A. A. Pinkerton, R. G. Cavell, *Inorg. Chem.* **1971**, 10, 2720–2723.
- [15] F. W. Bennet, H. J. Emeleus, R. N. Haszeldine, *J. Chem. Soc.* **1954**, 3598–3603.
- [16] P. H. M. Budzelaar, *gNMR Version 4.1*, Cherwell Scientific, Oxford, UK, **1998**.
- [17] N. V. Pavlenko, L. M. Yagupolskii, *Zh. Obshch. Khim.* **1989**, 59, 528–534.
- [18] A. A. Kolomeitsev, F. U. Seifert, G. V. Röschenthaler, *J. Fluorine Chem.* **1995**, 71, 47–49.
- [19] J. E. Griffiths, *Spectrochim. Acta* **1968**, 24 A, 303–305.

Received: October 16, 2006

Published Online: March 1, 2007