Trifluoromethyl Phosphoranide, erste Phosphoranide mit C_{sp^3}-P Bindungen: Synthese, Eigenschaften und Derivate

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aus
Bila Tserkva (Ukraine)

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- Ph. D. -

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Эту работу я посвящаю Оксане и родителям

Contents

List of abbreviations

Alk .....Alkyl
R_f.....Perfluoroalkyl
Me .....Methyl
Et .....Ethyl
Bz.....Benzyl
Ar .....Aryl
Ph .....Phenyl
Het .....Heteroatom
Hal .....Halogen
L .....Ligand
L_{eq} .....Ligand in equatorial position
L_{ax} .....Ligand in apical position
HFA.....Hexafluoroacetone
TMS .....Tetramethylsilane
TASF.....Tris(dimethylamino)sulfonium trimethyldifluorosiliconate
TAS.....Tris(dimethylamino)sulfonium
TMAF .....Tetramethylammonium Fluoride
TMA .....Tetramethylammonium
DMI 1,3-dimethylimidazolidin-2-one
DFI™.....2,2-difluoro-1,3-dimethylimidazolidine
CDC .....2-chloro-1,3-dimethylimidazolinium Chloride
FDC .....2-fluoro-1.3-dimethylimidazolinium Chloride
TMFC.....Tetramethyl-fluor-formamidium Chloride
TMCC .....Tetramethyl-chloro-formamidium Chloride
DFTMU .....Difluoro-*N,N,N′,N′*-tetramethylmethanediamine
HMPTA .....Hexamethylphosphoric Acid Triamide
DMAP *N*,*N*-dimethyl-4-pyridinamine
TDAE .....Tetrakis(dimethylamino)ethylene
NMP.....*N*-Methylpyrrolidone
THF.....Tetrahydrofurane

MG .....Monoglyme

DG .....Diglyme

TG .....Triglyme

RT .....Room Temperature

LT NMR .....Low Temperature NMR Measurement

NMR.....Nuclear Magnetic Resonance

ppm.....Parts Per Million

δ.....Chemical Shift in ppm

J .....Coupling Constant

br.....Broad

s .....Singlet

d.....Doublet

t.....Triplet

q.....Quartet

quin .....Quintet

sext .....Sextet

sept.....Septet

okt.....Octet

non.....Nonet

dec.....Decet

undec.....Undecet

MS .....Mass Spectrometry

eV .....Electronvolt

FAB.....Fast Atom Bombardment

EI .....Electron Impact

CI .....Chemical Ionisation

FT-ICR.....

HRMS .....High Resolution Mass Spectrometry

M^+ .....Molecular Ion

b.p.....Boiling Point

m.p.....Melting Point

FW .....Formula Weight

Hz ....Hertz

g...............................Gram

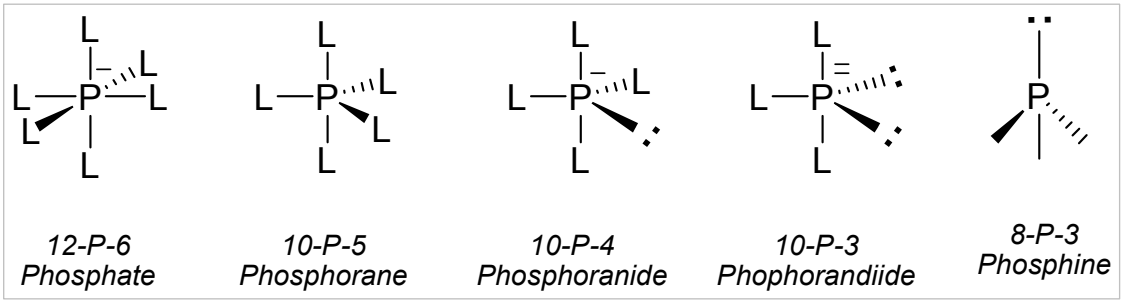
h...............................Hour

D ....Day

A. Introduction

The chemistry of phosphorus is very wide and various. Being very important industrial products and produced on large scale as chemical fertilizers, insecticides, pharmaceutical substances and so forth, phosphorus containing compounds are also indispensable to life as phospholipids, coenzymes, bone tissues and energy source (ATP). Multifaceted chemical properties of this element and its derivatives have been subject of research for many years but until now a lot of discoveries are still possible in this field.

Recently, much attention has been paid to the chemistry of hypervalent phosphorus compounds, having more than four electron pairs in the valence shell, because of their unique structures and reactivity. Classification of such type of compounds, and not only of phosphorus derivatives was elaborated by Martin and co-workers in 1980[1]. This generally useful N-X-L system designates the bonding about any atom (*X*) in a resonance structure in terms of the number of valence shell electrons (*N*) formally associated directly with that atom and the



Scheme 1

number of ligands (*L*) directly bonded to it. Typically, high valence electron counts at phosphorus are accompanied by high coordination numbers (*Scheme 1*). Low valence electron counts at phosphorus are similarly accompanied by low coordination number. Anionic and neutral six-coordinate compounds are derived from pentavalent phosphorus by incorporation of one ligand, however, a few of such systems based on trivalent phosphorus have been identified. In their turn, tetra-coordinate derivatives are closely related with neutral trivalent and, again

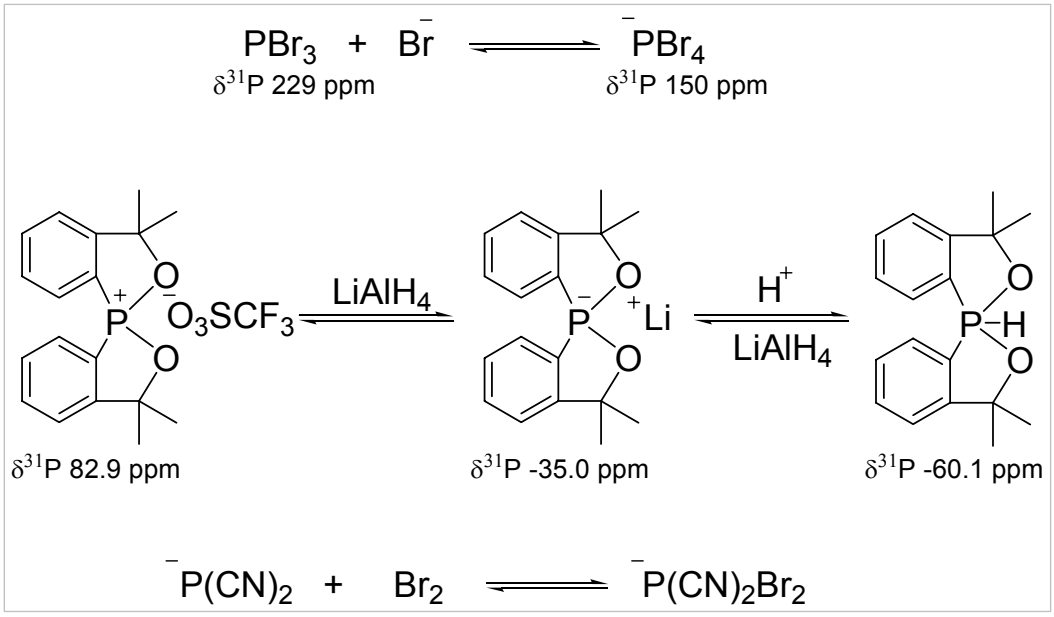
pentavalent phosphorus. Conceptually, 10-P-3 species can be viewed as two electron reduction of the common 8-P-3 center.

As compounds mentioned above are formally hypervalent they have been the subject of interest and debate with regard to the question of d-orbital involvement in the bonding. The status of this concept has been comprehensively reviewed recently[2], especially in the context of binding in phosphorus compounds. Initially, the involvement of d-orbitals arose out of a particular difficulty concerning the existence of hypervalent compounds. To explain the structure of high coordinated atoms the hybridization theory of bonding was proposed by Pauling[3,4]. Later, a simple and fairly easily understood model was developed which explains the bonding in “non-octet” compounds and which does not require the use of d-orbitals. This is the three-center, four-electron bond (electron-rich, 3c-4e bond)[5-7]. Bonding is envisaged as partly ionic that explains why electronegative groups are crucial ligands in hypervalency. Nowadays, this concept has completely replaced the sp^3d^2 model for hexacoordinate[8] and sp^3d model for pentacoordinate hypervalent centers[9].

Pentacoordinate phosphorus inorganic compounds have been known as stable species since the 19th century. Thus, phosphorus pentafluoride was synthesized in 1876, even before discovering of fluorine as chemical element by Moissan in 1886. In 1949, Wittig and co-workers succeeded in the synthesis of pentaphenylphosphorane as the first example of a pentacovalent organophosphorus compound having five carbon ligands[10]. Then in 1955, the synthesis of the first substituted fluorophosphorane[11] and in 1964 the Ramirez reaction affording oxyphosphoranes by oxidative addition of α-diketones with trivalent phosphines[12] were reported. Parallel to phosphoranes, the chemistry of neutral six-coordinate phosphorus centers started to be explored by Holmes[13], Gutmann[14] and Beattie[15]. Their work had served as catalysts for further investigation in the field of hypervalent phosphorus chemistry. Since then numerous papers have been published, the most comprehensive and contemporary reviews should be noted. Such are the comprehensive two-volume work of Holmes on pentavalent pentacoordinate phosphorus chemistry[16] the large review of early works on pentacoordinate phosphorus fluorine chemistry by

Schmutzler[17], NMR studies of the stereochemistry and fluxionality of five- and six-coordinate phosphorus compound[18] and the review of neutral six-coordinate phosphorus[19] by Cavell, the review of hypercoordinate P^{II}, P^{III} and P^{IV} phosphorus derivatives with intramolecular coordination by Chuit[20], the review of low-coordinate hypervalent phosphorus by Arduengo[21] and finally, the review of hypervalent organophosphorus compounds by Kawashima[22].

The chemistry of phosphoranides has been reviewed by Riess[23] and more recently by Dillon[24]. It is also relevant to mention three theoretical studies on phosphoranides of the PX_4^- type[25-27]. Phosphoranides, hypervalent anionic phosphorus species, may be also regarded as the conjugate bases of phosphoranes containing P-H bonds. From *VSEPR* considerations their structure is considered to be a trigonal bipyramide (*ψ-tbp*) with phosphorus in a 10-P-4 arrangement in the *N-X-L* nomenclature. Phosphoranides are of considerable importance as models for reactive intermediates (or transition states) in the nucleophilic substitution at phosphorus(III) centers, and their participation in both inorganic[28] and organic[29,30] reactions had been postulated even before their existence was demonstrated. The most important preparative methods for phosphoranides comprise (*Scheme 2*):



Scheme 2

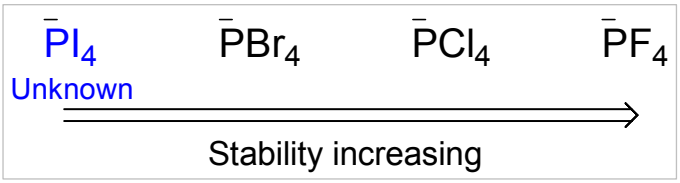
◙ Addition of an anion to a phosphorus (III) precursor[31]

◙ Deprotonation by a suitable base of phosphorane with a P-H bond[32]

◙ Oxidation of an anionic phosphorus(I) species by a halogen, interhalogen or pseudohalogen[33]

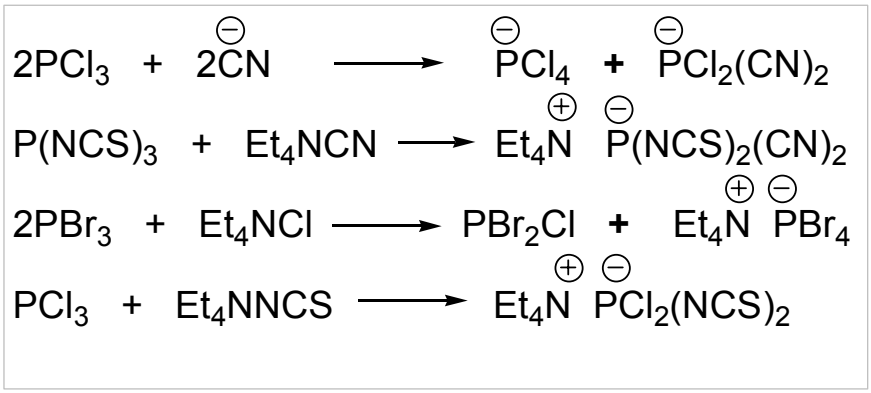
Ligands forming a phosphoranide ion must be effectively electronegative in order to stabilize the negative charge on phosphorus centre. The stability of a phosphoranide ion increases parallel to increasing of P-L bond energy, in other words the ligand must be a weak leaving group.

The first phosphoranide to be isolated was PBr_4^- (as its Pr_4N^+ salt, **1**) by Dillon and Waddington in 1969[31]. The process of hypervalent ion formation was



Scheme 3

showed to be reversible, but cooling led to the product precipitation. Later the same reversible process was observed for PCl_4^- TMA^+ (**2**)[34]. The successive synthesis and characterization of PF_4^- TMA^+ (**3**) by Christe[35] completed the array of $PHal_4^-$ phosphoranides (*Scheme 3*). Contrary to chloro and bromo derivatives, the tetrafluorophosphoranide anion proved to be absolutely stable in

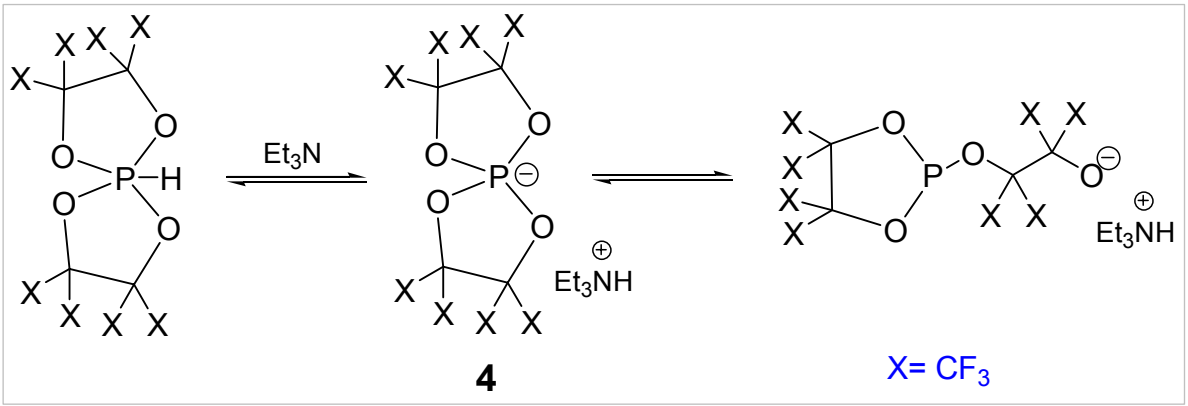


Scheme 4

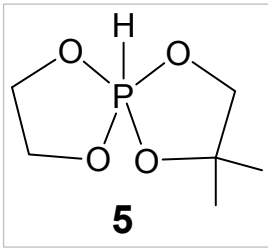
solution at RT as was expected from the relative strength of P-Hal bonds. NMR studies of PF_4^- showed a classical Berry pseudorotation mechanism[36] involving a pyramidal C_{4v} transition state with four equivalent fluorine positions.

Many mixed phosphoranides containing halogens and pseudohalogens were isolated[24] some examples of which are shown in *Scheme 4*.

Clear evidence for a cyclic organophosphoranide anion firstly was obtained by Granoth and Martin in 1978[32]. The first organophosphoranide to be analyzed



Scheme 5

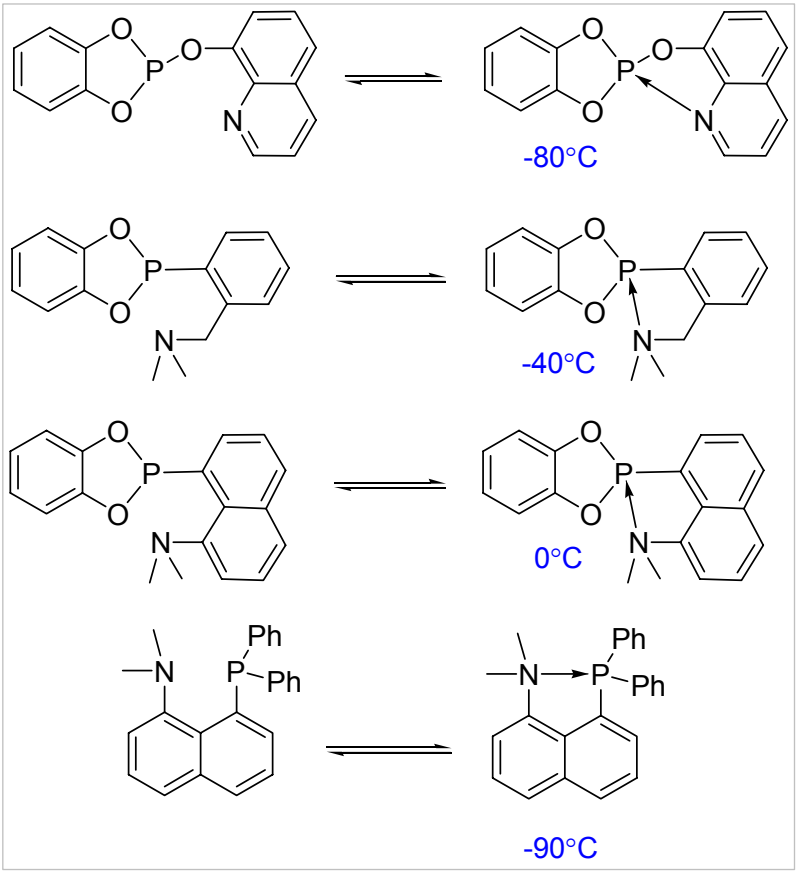


by X-Ray diffraction was **4** by Röschenthaler *et al*.[37] An equilibrium between the phosphoranide ion and the open-chain monocyclic phosphite anion shown within *Scheme 5* is typical for such cyclic compounds strongly depending on the electrophilicity of the phosphorus center. For instance, the anion derived from phosphorane **5** exists exclusively in the phosphite form[38].

A series of dynamic equilibria were described for hypervalent P(III) compounds[39,40] (*Scheme 6*) based on the formation of intramolecular N-P interaction. It is noteworthy that a small ligand geometry change increases the stability of the coordination significantly.

More recent findings have shown that several organophosphoranides, particularly of the type $[RP(CN)_2X]^-$, (R = Me, Et, Ph, C_6F_5, 2-MeC_5H_4, 4-ClC_6H_4 and X= Cl, Br, I, NCS) could be synthesized[41-43]. In the case of the very electronegative C_6F_5 group other types of phosphoranides were prepared by Ali and Dillon[44,45]. These comprise the ions $[P(C_6F_5)X_2Y]^-$ and $[P(C_6F_5)_2XY]^-$ (X,Y = Cl, Br, I, NCS).

Until recently, in most phosphoranides known, the central phosphorus atom was bound mainly to halogen, pseudohalogen, nitrogen or oxygen. Direct P-C bonding was quite rare and predominantly limited to sp^2 carbon. Only isolated cases of P-C_{sp^3} bond presence in a phosphoranide ion were to be found in literature; in addition, the number of such the bonds had never exceeded *one*. It



Scheme 6 *Temperatures are set up at which signals of hypervalent compounds become detectable in the temperature dependent ^{31}P NMR spectra*

is known that the CF_3 group possesses strong electron withdrawing properties, being more electronegative than Br and Cl. Therefore relative high stability of trifluoromethyl phosphoranides was predicted by Dillon[24]. This virgin area was just waiting for its discoverers.

Tetrakis(trifluoromethyl)phosphoranide (as TAS^+ salt, **6**) was synthesized by Kolomeitsev and Röschenthaler in 1995[46]. It was the first phosphoranide having more than one P-C_{sp^3} bond. Due to its extreme instability it was impossible to obtain this salt analytically pure even at low temperature. This problem was overcome by using TMAF as fluoride ion source[47]. Pure compounds (as TMA^+

salts, **7**, **8**) were isolated and analyzed by multinuclear temperature dependent NMR spectroscopy and their reactions with electrophiles (*Scheme 7*). Formation of the new phosphoranide, $[(CF_3)_2PF_2]^-$ (**9**) as decomposition product via difluorocarbene abstraction from $[(CF_3)_3PF]^-$ was reported. Independently, $[(CF_3)_2PF_2]^-$ was generated from the reaction of TMAF with $(CF_3)_2PF$. Attempts to fluorinate $(CF_3)PCl$ using $(Et_2N)_3PF_2$ gave instead of the expected $(CF_3)_2PF$ a new stable hypervalent species, namely $[(CF_3)_2PFCl]^-[FP(NEt_2)_3]^+$ (**10**)[48] which was successfully characterized by X-Ray diffraction analysis (*Figure 1*). Both compounds **7** and **8** were shown to be pyrophorus and extremely reactive towards all common solvents due to the ease of trifluoromethyl anion abstraction. These phenomena were at least partially responsible for all unsuccessful attempts to obtain single crystals of the respective phosphoranides.

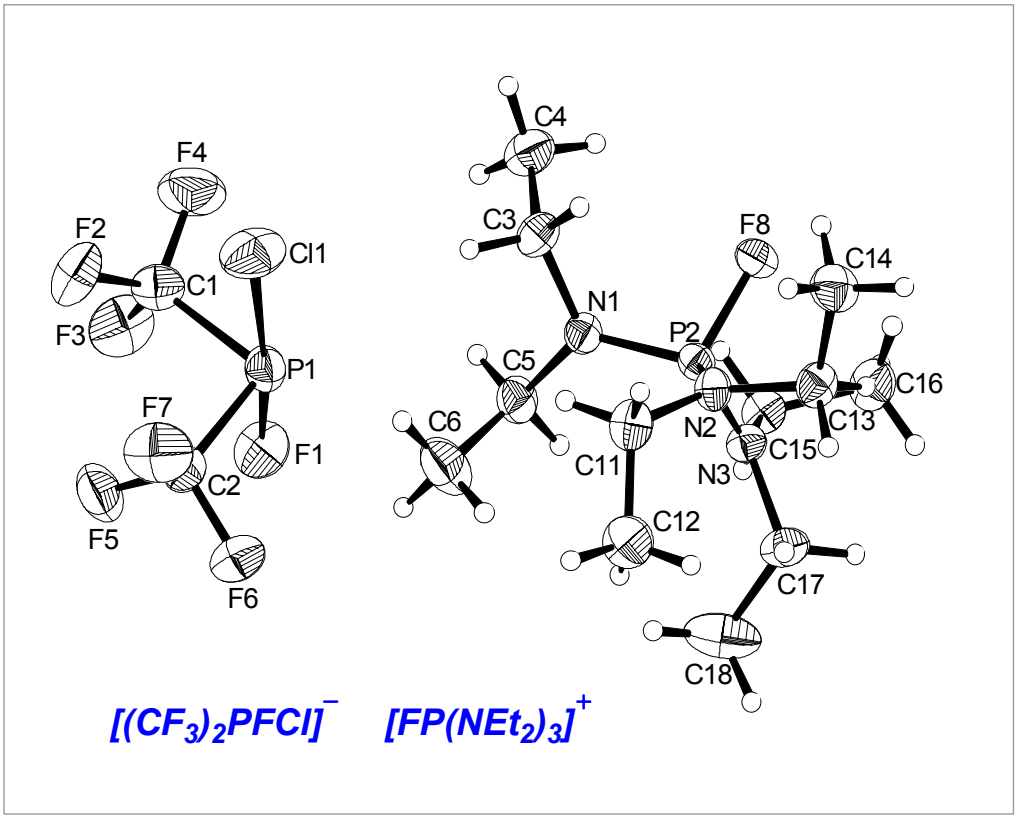
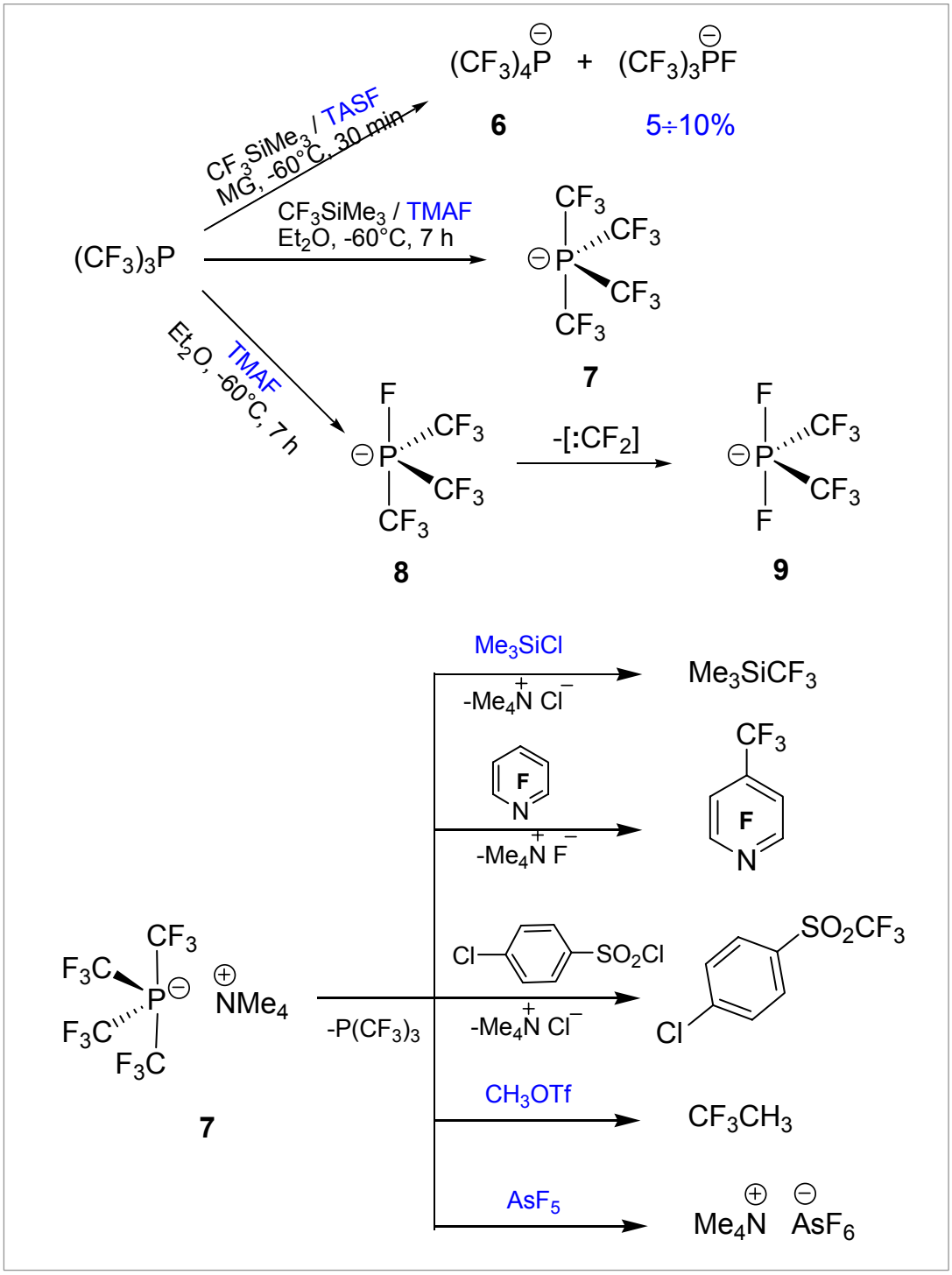


Figure 1


(CF3)4P⊖ + (CF3)3PF⊖
6
5÷10%
CF3SiMe3 / TASF
MG, -60°C, 30 min
CF3SiMe3 / TMAF
Et2O, -60°C, 7 h
(CF3)3P
7
Et2O, -60°C, 7 h
TMAF
-[:CF2]
8
9
Me3SiCl
-Me4N+ Cl−
Me3SiCF3
-Me4N+ F−
-P(CF3)3
-Me4N+ Cl−
CH3OTf
CF3CH3
AsF5
Me4N⊕ AsF6⊖
7

Scheme 7

B. Setting of the aims of research

This work was initiated predominantly due to the lack of X-Ray, ^{13}C NMR and MS data of the title phosphoranides. Besides, synthetic procedures were not optimized and the stability of phosphoranide salts should be also investigated. It was clear that the nature of the counter ion plays an important role, defining the decomposition rate of hypervalent species discussed - first experiments showed noticeably increased stability of TMA salts in comparison to TAS derivatives. However, a certain kind of interaction between cation and anion was not established. The chemical properties of the phosphoranides were investigated superficially and the experiments carried out did not answer all the questions but added new ones and the possibility to synthesize novel compounds was the real challenge to carry out this work.

The aims of research to be conducted were defined as follows:

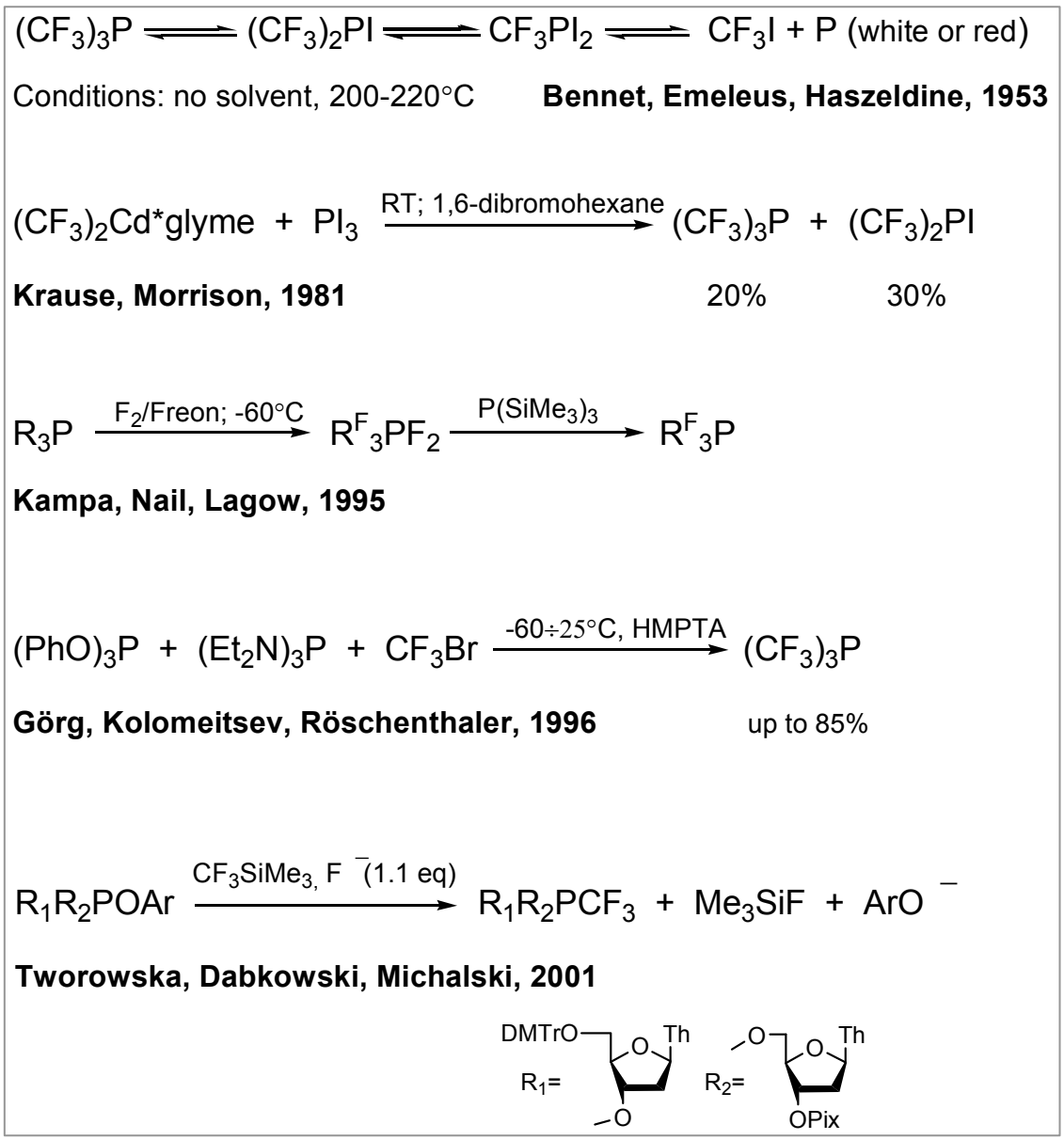
1. Taking into account the difficulties in synthesizing the starting compounds, to develop safer and simpler ways optimizing known and inventing new synthetic methods.
2. Synthesis of stable phosphoranide salts which would allow obtaining single crystals for X-Ray analysis.
3. Studying the stability of the phosphoranide anions dependent on the nature of the counterions as well as the interaction within ionic pairs.
4. Investigation of geometrical stability of phosphoranides in solution and comparison with the fluxional behavior of other penta-coordinate phosphorus compounds.
5. Studying the chemical properties of phosphoranides, defining the routes of their transformations and predicting further direction of investigation with the aim to obtain new hypervalent phosphorus compounds.
6. Collection and systematization of all the data obtained and comparing the trifluoromethylphosphoranides with other phosphoranides described in the literature.

C. Results and discussion

C1. Synthesis of starting compounds; new approaches and properties

C1.1. Trifluoromethylphosphines

The synthesis of most of the phosphoranides discussed here is based on the nucleophilic addition of various anions to the phosphorus(III) precursors. Tris(trifluoromethyl)phosphine (**11**), bis(trifluoro)fluorophosphine (**12**), bis(trifluoro)chlorophosphine (**13**) and difluoro(trifluoromethyl)phosphine (**14**) were such precursors. Therefore, we were interested in simpler, more versatile and reliable synthetic routes superior to those described in the literature. Known methods are not simple and cheap, in most cases toxic or environmentally unfriendly compounds are used. Thus, phosphine **11**, which has been found some use as a ligand in transition metal coordination chemistry[49], can be synthesized from CF_3I and white phosphorus[50], from $Cd(CF_3)_2$ and PI_3[51], by reducing $(CF_3)_3PF_2$ obtained from direct fluorination[52], and from the reaction of the Ruppert system, $CF_3Br/P(NEt_2)_3$ with triphenylphosphite[53] (*Scheme 8*). The first route is limited only to trifluoromethyl- derivatives, attempts to synthesize other tris(perfluoroalkyl)phosphines were unsuccessful[54]. The high cost of CF_3I and harsh reaction conditions are inherent disadvantages of this method. Ligand-exchange process between PI_3 and $Cd(CF_3)_2$ occurs in low yield and is not applicable. The direct phosphine fluorination process with successive difluorophosphorane reduction is very expensive. Among the methods mentioned above, the Ruppert method is most convenient and versatile, but the original synthetic procedure involves the use of carcinogenic HMPTA and $(Et_2N)_3P$ (teratogen and sterilizer) as well as “ozone killer”- bromotrifluoromethane. Later, first steps were undertaken in our laboratory to improve this process- triglyme as solvent was used without significant yield decrease[55]. Due to the high reactivity of $(CF_3)_3P$ towards air and occasional pressure changes inside the reaction

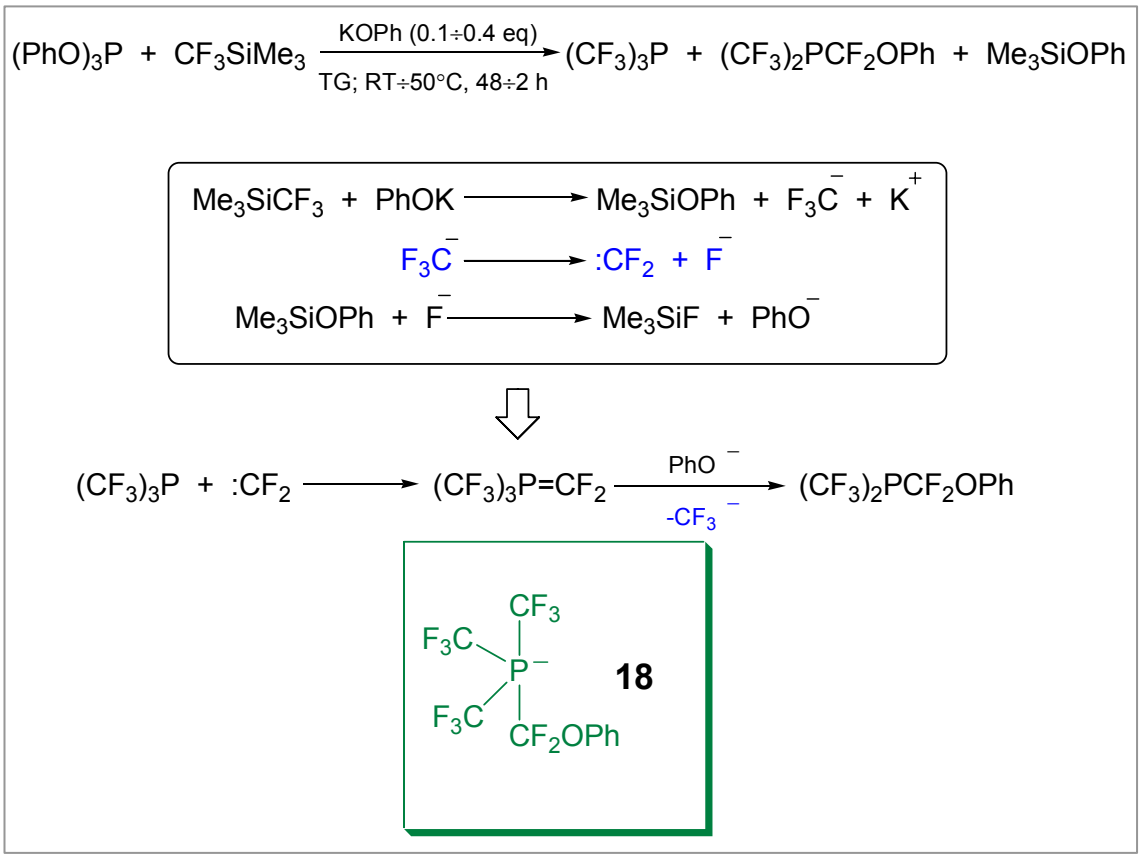


Scheme 8

vessel, carrying out this reaction in usual laboratory glass is quite dangerous and is limited only to small amounts of the starting phosphite. Here we report large scale synthesis made in *monel*-autoclave with 77% yield of $(CF_3)_3P$, absolutely safe and simple.

To avoid harmful substances, a new method of phosphine **11** preparation based on using (trifluoromethyl)trimethylsilane **15** (Ruppert reagent) was developed. Silane **15** was first prepared by Ruppert *et al.* in 1984[56] and is commercially available. Recently, Hoge and coworkers have replaced – a CN group at the P(III) center for a CF_3 group using **15**[57], also Michalski and coworkers have reported syntheses of phosphorus(III) compounds containing P-

CF_3 group by nucleophilic trifluoromethylation of the corresponding P-F or P-OAr precursors[58]. One or two CF_3 groups were introduced into molecules but surprisingly, the authors left out tris(trifluoromethyl)phosphine. We have shown that **11** is readily formed in the reaction of triphenylphosphite with Ruppert reagent in ethereal solvents at room temperature in 85% yield (*Scheme 9*). The reaction slowly occurs at ambient temperature and even after 24 h



Scheme 9

triphenylphosphite is still present in the reaction mixture. Raising the temperature up to 50ºC allowed a significant reaction time shortening with a yield decrease to 80%. The reaction was catalyzed by TMAF or KOPh. In the case of using other (perfluoroalkyl)trimethylsilanes, corresponding phosphines would be also available. Precursor compounds can be applied in two ways: excess of the triphenylphosphite or of the silane. Taking excess of phosphite, traces of the intermediate product, $CF_3P(OPh)_2$ (**16**) and traces of CF_3H were observed in the ^{31}P and ^{19}F NMR spectra. No intermediate products but a small amount of CF_3H were observed in the case of silane excess. Phosphine **11** formed was pumped

off from the reaction mixture in high vacuum and purified by simple distillation with a Vigreux column at atmospheric pressure.

Unexpected signals in the NMR spectra of the reaction mixture were observed all the time regardless what reactant was taken in excess. The relative intensities of these signals seemed to be in close correlation to the amount of catalyst used (*Figure 2*). Taking into account relative signal intensities of the two groups of fluorine nuclei in the molecule and the low volatility of the compound, we can suggest the structure of this enigmatic species to be $(CF_3)_2PCF_2OPh$ (**17**). The mechanism of this product formation may include the generation of the very reactive tris(trifluoromethyl)difluorophosphonium ylide followed by rapid reaction with the PhO^- anion present in solution in catalytic amounts to give the

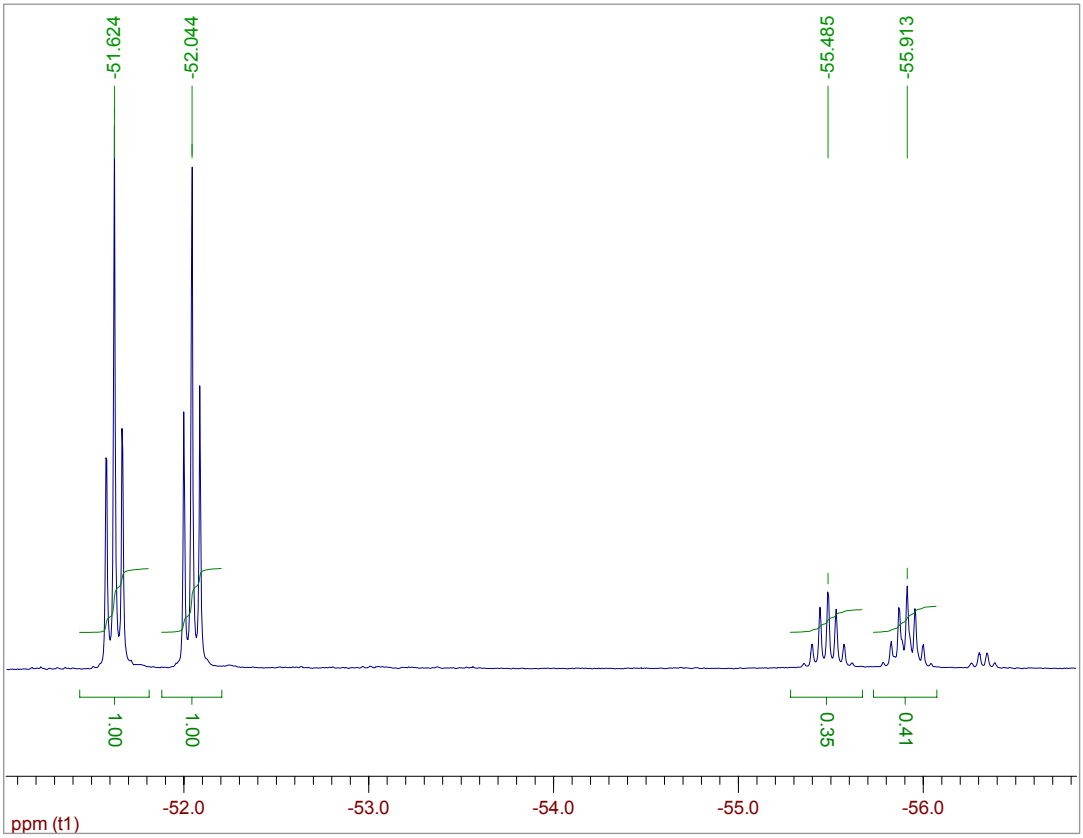
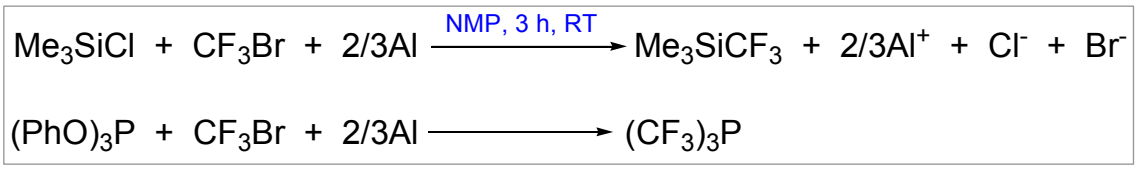


Figure 2 *19F NMR spectrum of reaction mixture with the phosphine **11** and all volatiles pumped off.*

unstable phosphoranide ion **18** (*Scheme 9*).

Relative low toxicity, stability, and the ease of handling allowed Ruppert reagent **15** to be widely adopted in the synthesis of perfluoroalkyl containing compounds. One example of its successful application we just have shown. But general methods for the preparation of perfluoroalkylated organosilicon

compounds are based on perfluoroalkyl anion generation followed by the reaction with electrophilic silylhalides[59], the same synthetic approach as for perfluoroalkylated phosphines. Then, the question appeared - why to generate the trifluoromethyl anion from the Ruppert reagent or to have one additional step, synthesizing this silane, when it was possible to generate CF_3^- directly. That is why we decided to use the cheapest and easiest route to Me_3SiCF_3 – the Grobe method, for synthesizing tris(trifluoromethyl)phosphine.



Scheme 10

In 1995 Grobe and Hegge showed that the reducing power of Al powder suffices to activate CF_3Br [60]. A good yield of silane **15** was achieved in NMP - a strongly coordinating solvent (*Scheme 10*). Our initial attempts to obtain **11** in this way were promising. As expected, no substitution reaction was observed in triglyme even at 100ºC but in NMP or DMI the reaction slowly occurs at room

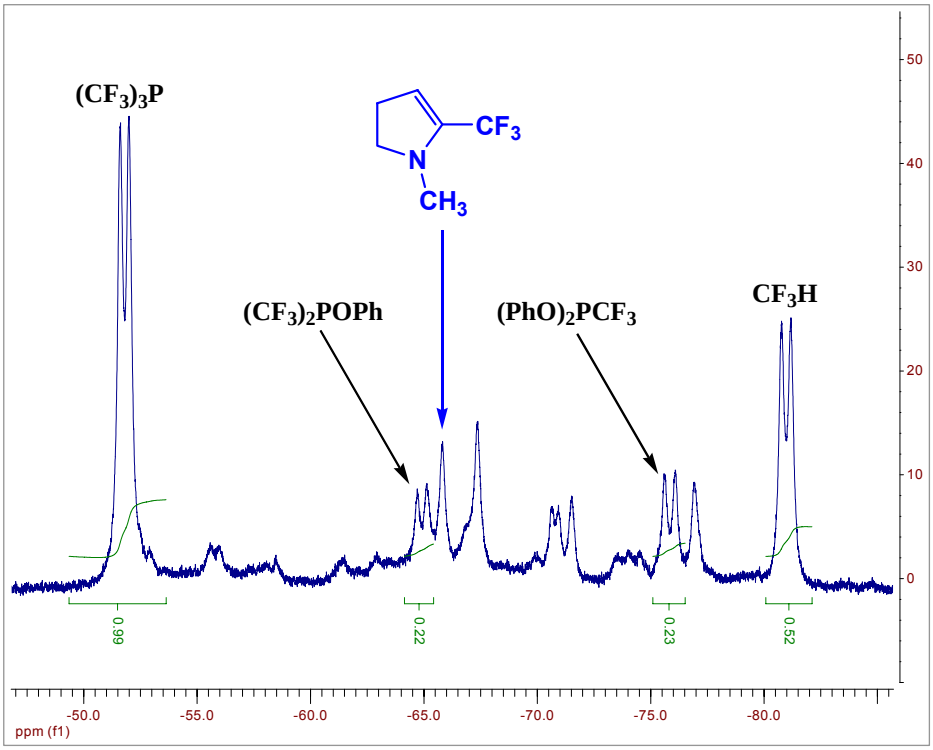


Figure 3 *The main fragment of the spectrum relevant to trifluoromethylphosphines area, enamine **20** is shown in blue colour*

temperature to give small amounts of $(CF_3)_3P$, as well as $(PhO)_2PCF_3$ and $(CF_3)_2POPh$ (**19**). All possible trifluoromethyl substituted phosphines were detected in the reaction mixture when DMF was used as a solvent. This fact is quite surprising since DMF is known as an efficient trifluoromethyl anion trap and thus can serve as a CF_3 transfer reagent[61], furthermore DMF is the common solvent or co-solvent for reactions of electrochemical trifluoromethylation[62]. As was mentioned above, the process of trifluoromethylated phosphines formation being discussed was very slow at ambient temperature (total conversion of the starting triphenylphosphite was 13% after 12 hr and 22.5% after 72 hr at RT; solvent - NMP, estimated by ^{31}P NMR). Raising the temperature accelerated the reaction (total phosphite conversion - 31.8% after 3hr at 60ºC, in NMP, estimated by ^{31}P NMR) and the target phosphine **11** began to dominate in the mixture of trifluoromethylated phosphines. But at elevated temperatures, negative consequences were also observed - the solvent started to react rapidly with trifluoromethyl anion generated during the reaction to give enamine **20** on the mechanism previously described by Bürger *et al* [63] (*Figure 3*). Enamine **20** is thermally unstable and even slight heating of its solution led to significant decomposition. New signals of relatively high intensity appeared in the spectrum of the reaction mixture, while even after long period of time at RT the spectrum contained mainly signals of phosphines **11**, **16**, **19** and of minor amounts of impurities. In the case of DMI as a solvent only weak signals of $(CF_3)_3P$ were observed in the spectrum of the reaction mixture after stirring for 3 hr at 60ºC. Here, signals of mono- and bistrifluoromethylated derivatives were prevalent. Interestingly, that signals of compound **17** were again present in every spectrum and the

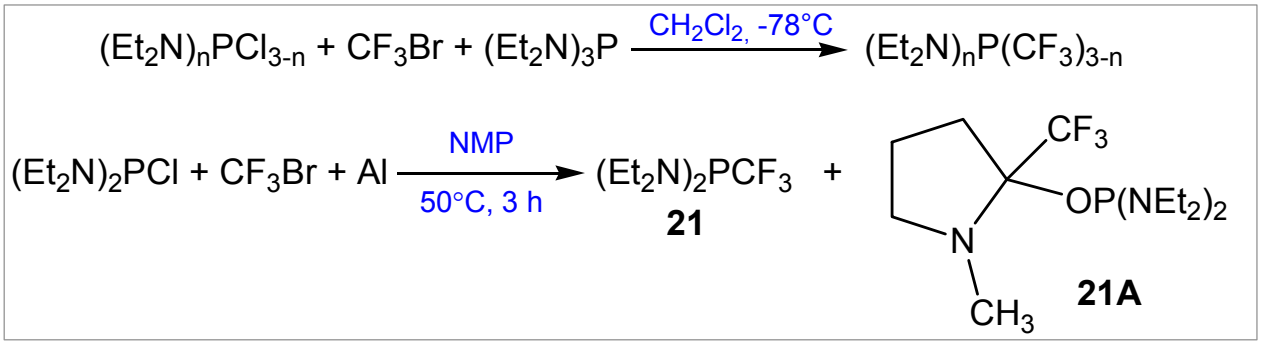
Phosphine	***NMP; 72Hr, RT***	***NMP; 3Hr, 60ºC***	***DMI; 3Hr, 60ºC***
$(CF_3)_3P$ **11** %	6.9	14.3	0.8
$(CF_3)_2POPh$ **19** %	2.5	5.5	1.8
$(PhO)_2PCF_3$ **16** %	10.8	8.2	7.9
$(CF_3)_2PCF_2OPh$ **17** %	2.3	3.8	1.8
$(PhO)_3P$ %	77.5	68.2	87.7
Isolated yield of phosphine **11** %	4	12.7	-

Table 1 *Composition of reaction mixtures by ^{31}P NMR*

maximal concentration of it was obtained in NMP at 60ºC.

In all the solvents, including DMF and of course except TG, the reaction occurred to give huge amounts of friable brown precipitate - Al(III) salts and the reaction mixture gradually turned dark brown with an immediate viscosity rising. The same changes were observed while reproducing the original Grobe reaction. Unfortunately in contrast to this synthesis, the yields of the target phosphine **11** are low (*Table 1*) though in TG at the same temperatures the use of the Ruppert system - $(Et_2N)_3P/CF_3Br$ or the Ruppert reagent allows to obtain **11** at least in 60% yield. Probably, there is an equilibrium between the enamine **20** formation and nucleophilic substitution. In the case of the more reactive Me_3SiCl the last reaction is fast enough to obtain the desired product in good yield; in case of the less reactive (due to the strong P-O bond) triphenylphosphite the equilibrium is shifted to the enamine **20**. The last process is strongly accelerated by the presence of a Lewis acid as was especially pointed out by Bürger *et al*[63]. Triphenylphosphite plays the role of a Lewis acid but not as strong as phosphorus trichloride does, whose reaction proceeds fast with trifluorobromomethane and aluminium and is strongly exothermic to produce a very viscous black material. No phosphorus signal was found in the ^{31}P spectrum. Here, phosphorus is probably included either in the non-soluble inorganic salts or in an organic polymer. Finally, the best results were obtained in the reaction of $(PhO)_3P$ and Al/CF_3Br system in NMP at 60ºC with a 5-fold excess of Al powder. Tris(trifluoromethyl)phosphine was isolated in 27.5% yield.

The syntheses of bis(diethylamino)trifluoromethylphosphine **21** and bis(trifluoromethyl)diethylaminophosphine **22** starting from corresponding chloroderivatives and Ruppert system were reported by Röschenthaler *et al*.

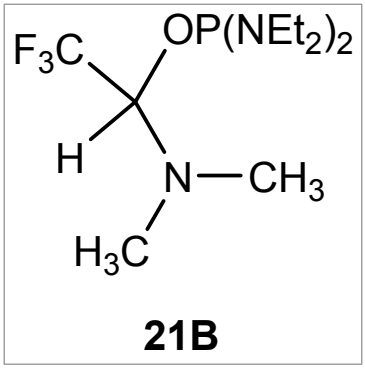


Scheme 11

(*Scheme 11*)[64]. The use of the Al/CF_3Br system let us to obtain phosphine **21** in 31% yield (by NMR). The reaction was carried out in NMP at a temperature range RT ÷ 60ºC, 5-fold aluminium and bromotrifluoromethane excess was taken and the reaction mixture was diluted to overcome the rising viscosity. Due to negligible difference of boiling points the solvent and the product were not separated.

The precursor bis(diethylamino)chlorophosphine is a very reactive compound and strong Lewis acid what can be explained by substituents effect (push-pull mechanism). Therefore not only the target product was formed but also enamine **20** precursor - **21A**. In the ^{31}P NMR spectrum of the reaction mixture signals of phosphine **21**, **21A** and $(Et_2N)_2PF$ were observed in 1 : 0.6 : 0.1 ratio. Compound **21A** (m, δ_P = 54.7; s., δ_F = -65.9) was likely to be the coupling product of the highly reactive P-Cl derivative with the intermediate anionic species formed during the reaction of CF_3^- anion with NMP. It has never been isolated but its structure was assigned from its chemical shifts in the NMR spectra and the nonvolatility. Taking into account the ratio of **21** and **21A** to be 1 : 0.8 in the ^{19}F NMR spectrum, one can state that the nucleophilic substitution reaction only slightly prevails over side reactions and it proved to be impossible to find reaction conditions where side products would not be formed. The presence of $(Et_2N)_2PF$ in the reaction mixture can be explained by substituting of chlorine by fluorine in the starting $(Et_2N)_2PCl$. The decomposing trifluoromethyl anion serves as fluoride anion source in this case.

When DMF was used as a solvent, the target product **21** was obtained in 6% yield (by NMR) and again, the product of the reaction between the anionic intermediate formed from the solvent and starting phosphine (**21B**) was detected (dec, δ_P = 53.8, J_{PH} =14 Hz; d, δ_F = -67.3, J_{FH} = 14.7 Hz). One should note that no enamine could be derived from **21B** according to the mechanism proposed. Close resemblance of chemical shifts in ^{31}P and ^{19}F spectra of compounds **21A** and **21B** implied their structural similarity. Therefore, “non-enamine” form was also accepted for **21A** though for some time a signal

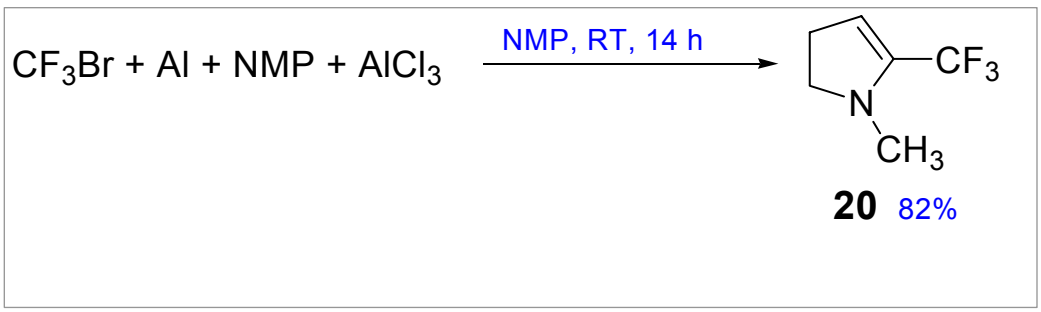


21B

corresponding to one in ^{19}F spectrum was interpreted as the signal of enamine **20**. Unfortunately, not identified decomposition products (δ_P = 15÷0) dominated in the reaction mixture and the conversion of the starting phosphine into products was low. Finally, it turned out that the Al/CF_3Br system could not be applied in the synthesis of trifluoromethylated phosphines. Neither tris(trifluoromethyl)phosphine nor bis(diethylamino)trifluoromethylphosphine were synthesized in good yields.

To avoid difficulties in separating the product from the solvent an attempt to synthesize bis(diethylamino)trifluoromethylphosphine without any solvent was undertaken. Merely heating of the mixture of bis(diethylamino)chlorophosphine and Ruppert reagent with Cl^- anion catalysis at 180ºC during 1.5 h gave phosphine **21** in high yield. Initially, this reaction was carried out without a catalyst and only traces of the target compound with comparable amounts of other not identified compounds were detected indicating that some decomposition processes occurred with at least the same rate as the product formation. Surprisingly, in the presence of catalytic amount of 2-chloro-1,3-dimethylimidazolinium chloride (CDC) pure phosphine was formed without any impurities detectable in ^{31}P and ^{19}F NMR spectra. During the transformation, the content of the reaction vessel gradually turned dark brown but simple distillation yielded colorless clear product. It should be noted that no reaction was detected in TG solution at 60÷80ºC - typical conditions for the synthesis of tris(trifluoromethyl)phosphine.

As expected, bis(trifluoromethyl)diethylaminophosphine **22** was synthesized in 93% yield starting from corresponding chloroderivative and Ruppert reagent



Scheme 12

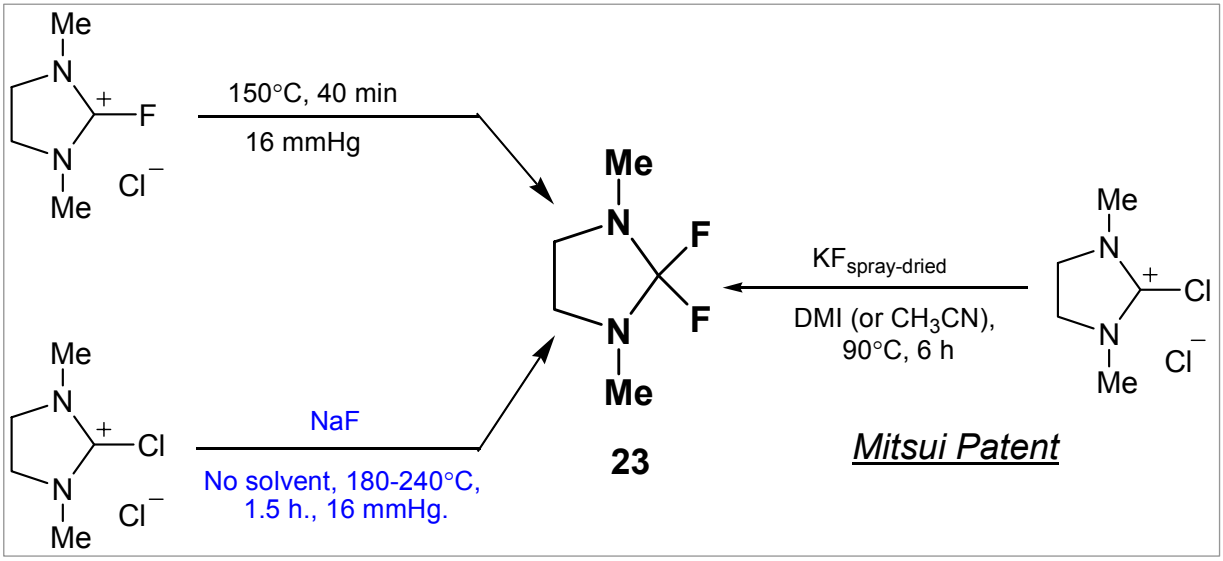
under Cl^- (CDC) anion catalysis while heating at 180ºC during 2 h without a solvent.

According to the Grobe method, enamine **20** was obtained in 82% yield (relative to $AlCl_3$ taken; *Scheme 12*) while Bürger *et al.* reported only 25÷36% yield; as expected no product was detected in the absence of the Lewis acid. Once again the thermal instability of **20** should be noted as well as the mild reaction conditions.

C1.2. A new method to 2,2-difluoro-1,3-dimethylimidazolidine (DFI™), difluoro-N,N,N',N'-tetramethylmethanediamine (DFTMU) and tris-(diethylamino)difluorophosphorane

Different fluoride ion sources were used in the synthesis of trifluoromethyl-phosphoranides discussed in this work to investigate the stability of the hypervalent species dependent on the nature of counterion (chapter C2.1). Surprisingly, not in all the cases the desired compounds were formed.

Unexpected products, perphosphoranides were obtained in reactions between trifluoromethylphosphines and DFI **23** (chapter C4), therefore not only DFI but also CDC (2-chloro-1,3-dimethylimidazolinium chloride) and FDC (2-fluoro-1,3-dimethylimidazolinium chloride, **23B**) were chosen to be applied in this synthesis. During the process of FDC preparation and as a consequence of occasional overheating of the product obtained, small quantities of DFI were revealed in the trap connected to the reaction vessel. Aforethought heating of FDC sample gave DFI in quantitative yield. This fact together with being aware of the comprehensive work on the synthesis of fluorides by metathesis using sodium fluoride[65], led us to the synthesis of DFI in high yield (*Scheme 13*). This fairly simple and inexpensive route to the target compound has numerous

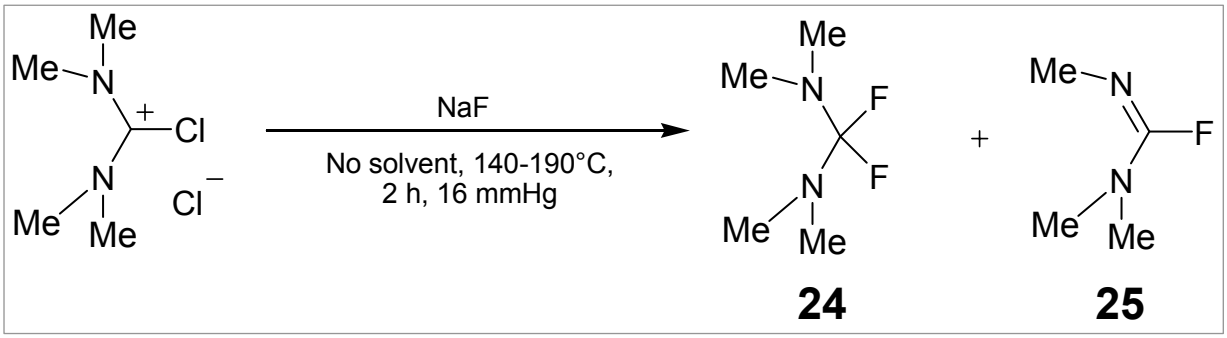


Scheme 13

advantages compared to that patented by Hayashi *et al*. (Mitsui Chemicals, Inc.)[66] and makes DFI widely available in laboratory use. Absence of solvent,

cheapest fluorinating agent and the possibility to get the pure compound directly from the reaction vessel without time consuming distillation are highlights of the process discovered. Though the thermal decomposition of **23** was reported[67] to begin at 150ºC the product was obtained in analytically pure state despite the high temperature of the reaction.

The same approach was applied in the synthesis of DFTMU **24** (*Scheme 14*). While DFI showed sufficient thermal stability to be generated and immediately removed from reaction mixture without decomposition, DFTMU proved to be not stable at high temperatures and at some reaction conditions the target product was obtained in a non-separable mixture with *N*,*N*,*N*'-trimethyl-



Scheme 14

fluoroformamidine **25**. It is not absolutely clear whether compound **25** is a product of decomposition of **24** or the product of alternative interaction of the intermediate *N*,*N*,*N'*,*N'*-tetramethyl-fluoro-formamidium chloride (TMFC) with sodium fluoride. Anyway, formation of MeF was detected by ^{19}F NMR spectroscopy (see experimental part) resembling the thermal decomposition of tetramethylammonium fluoride[68]. While heating the mixture of **24** and **25** in a closed system at 240ºC a rapid formation of dark-brown solid was observed. The ratio of compounds taken did not change significantly the product distribution (by ^{31}P NMR). Presumably, the rates of *N,N,N*'-trimethyl-fluoroformamidine generation and of the reaction of its further decomposition are approximately equal. Pyrolysis of pure TMCC salt under the same conditions (14mmHg, 180ºC) gave at least two compounds: one was a volatile colorless liquid (the main product); the other was a white slightly volatile solid (minor amounts). After staying for 20 min at room temperature the liquid pyrolysis product polymerized spontaneously and with heat elision to give white powder (mp 174°C). Attempts

to dissolve this liquid in common deuterated solvents for NMR analysis failed since it either polymerized immediately to give a nonsoluble polymer ($CDCl_3$, CD_3CN, C_6D_6) or violently and very exothermically reacted with solvents (DMSO-d_6, D_2O). Initially, this compound was thought to be *N,N,N'*-trimethyl-chloroformamidine (**26**). But we found that compound **26** is described as solid hydrochloride[69] (mp 69÷71°C) or as distillable liquid[70] (bp 72÷74°C, 0.05 mmHg) and no polymerization process was mentioned. Probably the substance obtained is **26** in really pure state and its instability could be explained by the highly polar C-Cl bond, therefore high positive charge on the corresponding carbon atom stabilized by dimethylamino groups in one separate molecule. Therefore, having two active reaction centers molecules of the compound discussed should be inclined to polymerization. As described, even the hydrochloride is not very stable and sensitive to heating hence **26** must be unstable and extremely reactive. It is difficult to believe that it could be distilled under the conditions reported. The stability of **25** ought to be higher than of **26**; here the influence of the fluorine atom plays an important role and **25** exists in a mixture with **24** even at elevated temperatures.

Pure product **24** (s, δ_F = -93.7) was obtained after heating of the mixture of starting compounds while gradual temperature rising from 140ºC to 160ºC during 2 hr; starting from 170ºC the signal of **25** appeared (s, δ_F = -62.1) in the ^{19}F spectrum and its relative intensity reached a maximum (approximately 0.35 vs. main product) in the case of the pyrolysis temperature equal to 240ºC. The higher the temperature of the reaction the less is the total yield of the mixture **24** + **25** due to complete decomposition of compounds mentioned. High volatility of the intermediate TMFC should be also noted. This feature together with the thermal instability of DFTMU had determined the conditions of the synthesis. Carrying out the reaction whether at 0.2 mmHg or at 14-19 mmHg, but anyway at temperatures higher than 160ºC, led to a product significantly contaminated by TMFC. Therefore distillation was necessary to get the pure compound.

The yield of DFI as well as of DFTMU depends on the initial charge of precursors and varies from nearly quantitative on a small scale (5–10 g), to 85% on a larger scale (80–100 g).

DFI and DFTMU are fluorinating agents applicable for practical transformations of oxygen-containing functional groups to the corresponding fluorides. Between other deoxofluorinating agents such as Yarovenko[71] and Ishikawa reagent[72], DAST[73], Deoxo-Fluor™[74] these compounds possess an outstanding thermal stability and no specific equipment or technique is required in their synthesis and reactions.

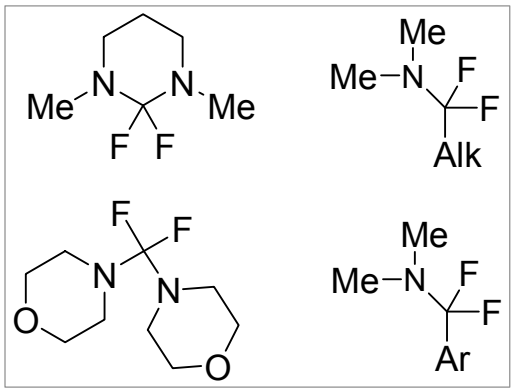
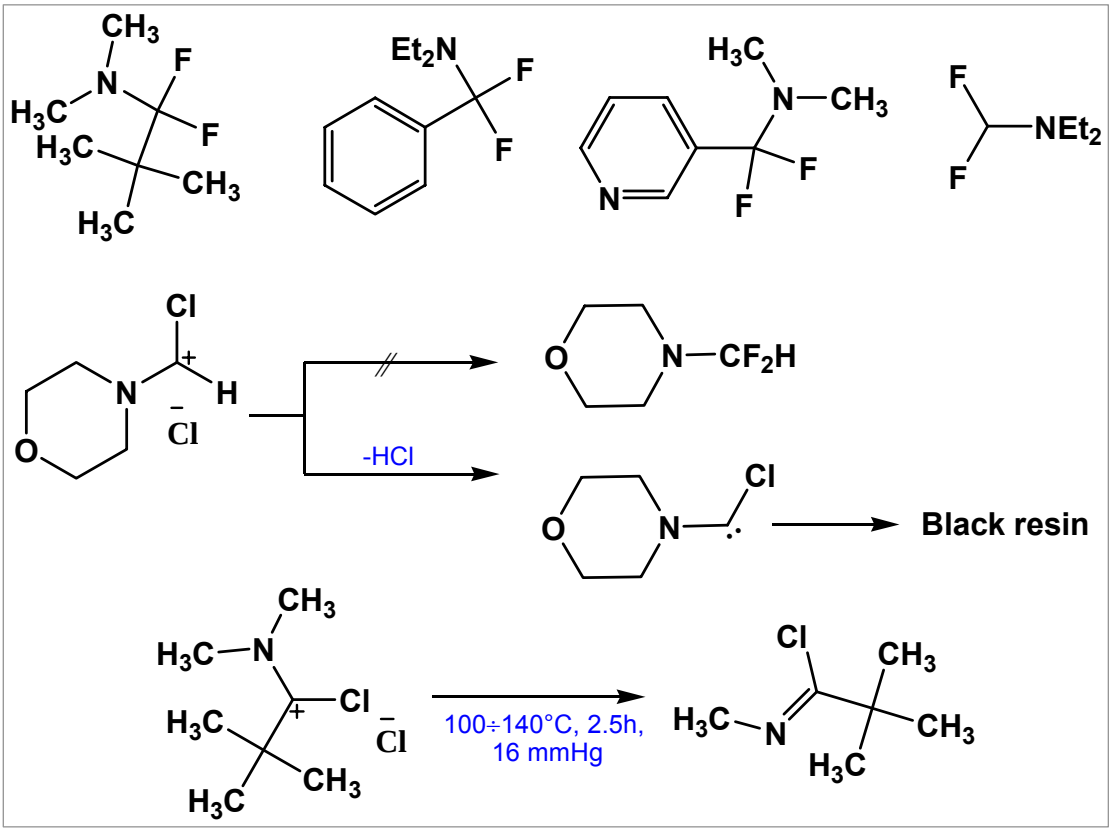


Figure 4

Other N-CF_2 analogues shown in the *Figure 4* are very promising industrial fluorinating agents and are of great commercial interest[75,76]. This spurred us to further investigations. Unfortunately, it proved to be impossible to obtain difluoro-



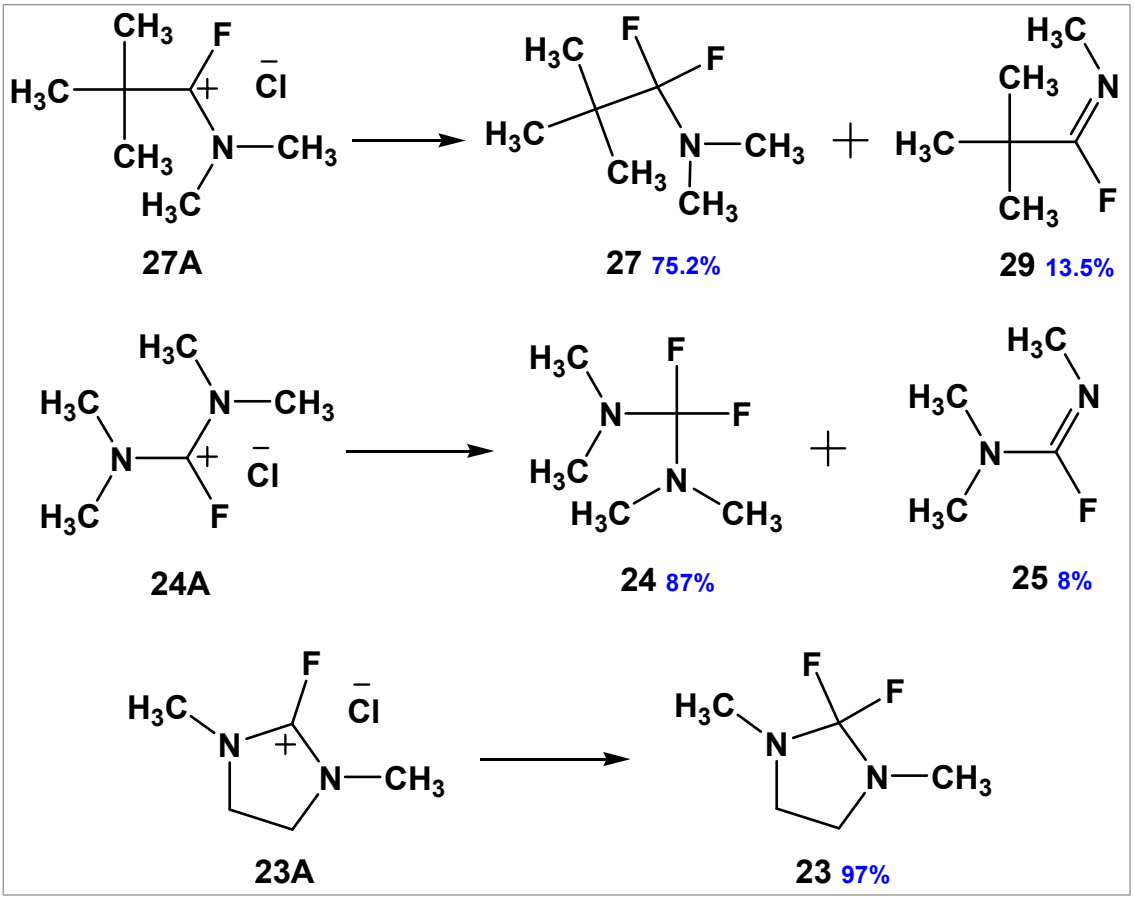
Scheme 15 *List of N-CF_2 reagents not synthesized by pyrolysis of the corresponding dichlorides in the presence of sodium fluoride. Possible ways of decomposition processes are shown*

derivatives shown in *Scheme 15* by the method described above. Probably, high boiling points of some of these compounds, preventing fast product removal from

the high temperature reaction zone and leading to its decomposition, or structural peculiarities of others were the reasons of failure. Thus we can state, that the absence of one dialkylamino group (compared to DFTMU) results in higher positive charge on the central carbon atom and, in its turn, on the peripheral carbon atom attached to nitrogen. This facilitates alkyl halide abstraction and formation of imidoyl halides. Especially, the decomposition of 1,1-dichloro-*N,N*-2,2-tetramethyl-1-propanamine **27B** should be noted as a proof of an analogous decomposition of TMCC, in both cases giving corresponding imidoyl chlorides. As expected, *N*,2,2-trimethylpropanimidoyl chloride **28** is formed quantitatively at lower temperatures, and is a stable liquid with relatively low boiling point (63°C, 50 mmHg). The process of carbene formation shown on *Scheme 15* is obvious since at pyrolysis conditions halide ions (Cl^- or F^-) are very basic and are able to abstract an acidic proton from the carbo cation given as an example, to render the acid as the only reaction product isolated.

The transformation of **27B** into **28** while heating without a solvent occurs very slowly at the melting point of the dichloride (101°C). The process becomes much faster at 4-5°C higher and prevents the formation of 1,1-difluoro-*N,N,*2,2-tetramethyl-1-propanamine **27** when the reaction is carried out in the presence of sodium fluoride. The only way to overcome this problem was to take a solvent, providing contacts between the reactants at lower temperature. Thus, the pyrolysis process was modeled in chlorobenzene. We found that the CF_2 derivative was formed very slowly at room temperature, a little bit faster at 50°C and relatively fast at 77°C. The yield of **27** was controlled by evaluating the ratio of its signal and a standard ($PhCF_3$) in the ^{19}F NMR spectra. Maximum yield of 26% was reached after heating the reaction mixture at 77°C during 5 h. Continuing the process gave no yield increase indicating that in solution the reaction of imidoyl chloride formation also prevails over formation of the difluoro derivative. However, when **27** is formed it is stable and no *N*,2,2-trimethylpropanimidoyl fluoride **29** was detected in the spectra.

Taking into account all the facts discussed above, symmetrization of the mixed salt - 1-chloro-1-fluoro-N,N,2,2-tetramethylpropan-1-amine **27A** should be also noted (*Scheme 16*) leading to a mixture of products which consists of **27**, **29**

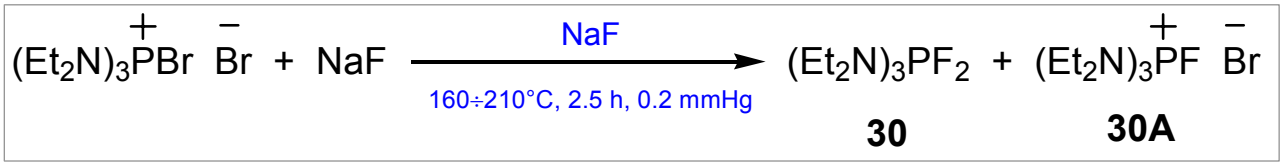


Scheme 16

and **27A**. As expected, in this case the content of **29** in the mixture was higher than of **25** in the case of symmetrization of *N,N,N',N'*-tetramethyl-fluoro-formamidinium chloride. Only traces of a by-product were detected after carrying out the symmetrization of dichloride **23A**. Probably such outstanding thermal stability of DFI could be explained by higher activation energy of the double bond formation (a five-membered ring containing one double bond reveals a somewhat strained cyclic system) compared with that of **25** or **29**.

Starting FCl salts were synthesized by simple mixing of the corresponding dichloro and difluoro derivatives in acetonitrile. The driving force of this process is the formation of a cation stabilized by an alkyl or dialkylamino group, as well as by fluorine. The salts formed are thermodynamically more stable than the precursor CF_2 reagents in which strong repulsion forces exist between lone electron pairs of the nitrogen and electron-rich fluorines.

Tris(diethylamino)difluorophosphorane **30**, a very mild fluorinating agent was also synthesized starting from the corresponding dibromo derivative and sodium fluoride (*Scheme 17*). The high volatility of the intermediate bromofluorophosphorane in vacuum did not let us to obtain the pure compound



Scheme 17

directly form reaction mixture but the potential usefulness of this method was shown. One can state that providing longer contact between NaF heated up to the necessary temperature and the mixture of volatile phosphoranes (for instance in the tubular reactor) would led to a high yield of desired compound. When the reaction was carried out at 16 mmHg or at atmospheric pressure the reaction mixture consisted predominantly of salt **30A** and other unidentified products though phosphorane **30** was also detectable.

The optimal reaction conditions to be found were: 5–fold excess of NaF, slow temperature rising from 160ºC to 210ºC during 2.5 h at 0.2 mmHg. The overall conversion of the precursor reached 84.5% with a ratio **30** : **30A** to be 2 : 1. Tris(diethylamino)difluorophosphorane was isolated in 52% yield.

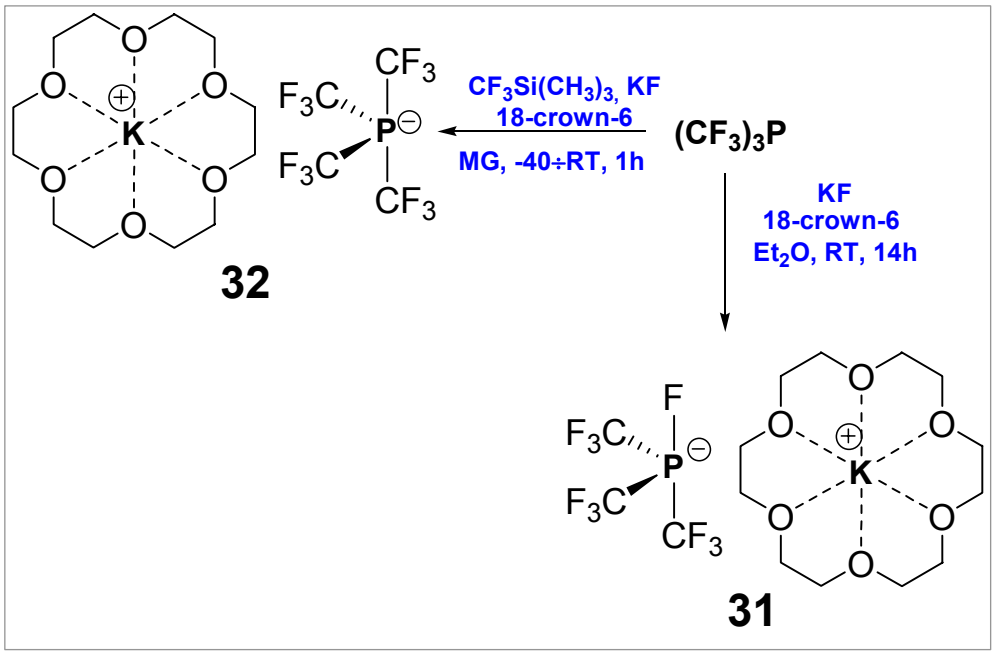
The closest analogy of such metathesis process was found in the literature for trialkyldifluorophosphoranes[77]. Here, the synthesis of phosphoranes of type R_3PF_2 (R= Et, iPr, nBu) in boiling acetonitrile was reported with 20% excess of NaF in up to 85% yield. The reaction occurs for 3 d and there are only two limitations of the method described: the solubility of the starting bromophosphonium bromide in the reaction media and the steric hindrance of the substituents, therefore the synthesis of Me_3PF_2 and tBu$_3$PF$_2$ failed. The only demands to the substrate in our method are a melting point lower than 160ºC and sufficient thermal stability.

C2. Trifluoromethyl phosphoranides

C2.1. Synthesis of trifluoromethyl phosphoranides

An invention of a simple method of tris(trifluoromethyl)phosphine preparation made comprehensive studies of its chemical properties possible. As it was mentioned before, the most significant part of these studies was dedicated to reactions of nucleophilic addition to phosphorus, in other words syntheses of trifluoromethylphosphoranides. Contrary to processes of anionic species formation, the syntheses of trifluoromethylphosphonium salts, in which phosphorus is charged positively, were also elaborated and are now underway. The third direction is the synthesis and characterization of highly reactive (trifluoromethyl)ylides and this part is in our plans for the future.

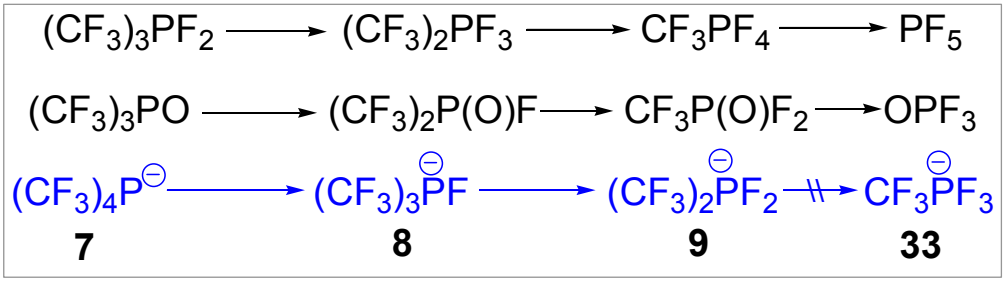
Insufficient thermal stability of the first phosphoranides to be synthesized (TAS and TMA salts) did not allow us to grow crystals suitable for X-Ray analysis and to thoroughly investigate their chemical reactivity. This feature of the phosphoranide ions was noticed to be strongly influenced by the nature of the counterion. Successful preparation and characterization of bis(trifluoromethyl)phosphanide salts of outstanding stability by Hoge and coworkers[78] stimulated us to use the same cation, (K^+)*18-crown-6 etherate, for our purpose. The new tris(trifluoromethyl)fluorophosphoranide (**31**) and tetrakis(trifluoromethyl)phosphoranide (**32**) salts were synthesized (*Scheme 18*). Replacement of TMA cation by (K^+)*18-crown-6 system led nearly to the same stability increase as while replacing of the TAS cation by TMA. Thus, the TAS salt of tetrakis(trifluoromethyl)phosphoranide slowly decomposes even at -60ºC in ether, i.e. in the solid phase, TMA phosphoranide starts to decompose in MG solution at -45÷-40ºC as pure compound and at 10°C when equimolar amounts of phosphine **11** are added while the solution of phosphoranide **32** can be warmed up to RT without significant decomposition (*Figure 7*). Being stabilized by equimolar amount of phosphine **11**, phosphoranide **32** decomposes at least two times slower than **7** and after 24 hrs at RT 74% of the compound dissolved



Scheme 18

are still present intact in solution. Comparative temperature dependent NMR investigations of phosphoranides **7**, **8**, **32**, **31** were done (*Figure 5-7,9*) and some interesting details were found which we would try to explain on the basis of the NMR data and chemical properties of phosphoranides obtained (*see chapter C2.3*).

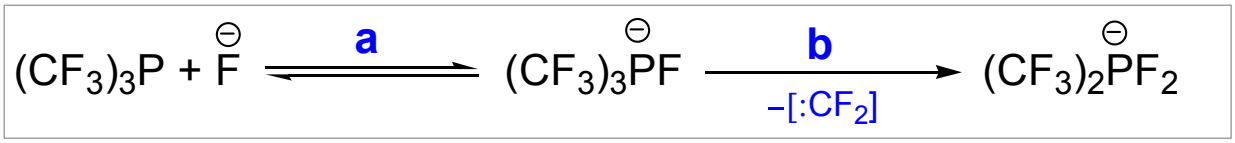
As it was said above, phosphoranides as well as (trifluoromethyl)-fluorophosphoranes[79] and (trifluoromethyl)phosphine oxides[80], undergo formal CF_2 elision under mild conditions (*Scheme 19*). However, bis(trifluoromethyl)phosphoranide **9** seems to be thermodynamically stable and monotrifluorophosphoranide **33** has never been detected as decomposition product. Rate and temperature of these processes depend on the nature of ions, temperature and concentration of phosphoranide salt in solution. The term "formal" is used since initially, loss of trifluoromethyl anion occurs followed by its



Scheme 19

decomposition to give difluorocarbene and fluoride ion which reacts in its turn with phosphine **11** to give the corresponding decomposition product. The easy cleavage of the P-C bond can be explained by the theory of hypervalent bond which is supposed to be partly ionic, three centered, filled with four electrons (3c-4e) and significantly elongated as compared with a usual bond. This fact is also supported by the high efficiency of phosphoranides **7**, **32** as trifluoromethylating agents (*see chapter C2.3*).

In the case of phosphoranides **8** and **31** there are two possible ways of decomposition (*Scheme 20.1*): detachment of fluoride or of the trifluoromethyl anion from phosphorus. The first path is reversible and does not lead to phosphoranide **9**. The existence of anion **8** (TMA salt) in equilibrium with starting phosphine **11** and a fluoride ion was supported by NMR experiments. It was noticed that the ^{31}P spectrum of the phosphoranide revealed a slightly broadened decet ($\Delta\nu_{½}$ = 7.3 Hz, δ = -58.7, -38°C) as well as the ^{19}F spectrum consisted of a broad singlet (1F, $\Delta\nu_{½}$ = 188 Hz, δ = -16.5, -38°C) and a broad doublet (9F, $\Delta\nu_{½}$= 188 Hz, δ = -58.2, -38°C) in *acetonitrile* in all the range of temperatures feasible. The lack of fine structure indicates that the $(CF_3)_3PF^-$ ion undergoes relatively



Scheme 20.1

fast *intermolecular* exchange under these conditions. However, when excess of TMAF was added to the sample, the intermolecular exchange process slowed down and the ^{31}P NMR spectrum at RT revealed a doublet of quartets of septets at δ = -54.87.

Only very slow (on NMR time scale) intermolecular exchange occurs in solution of the phosphoranide **8** in MG. In this case the NMR spectra under normal conditions reveal a clear distinction between axial and equatorial CF_3 groups with all signals being somewhat broadened due to *intramolecular* ligand exchange process. It is very important to note, that when even small amounts of TMAF are present in the solution (the impurity resulting from incomplete reaction during phosphoranide **8** formation), the intramolecular exchange was slowed

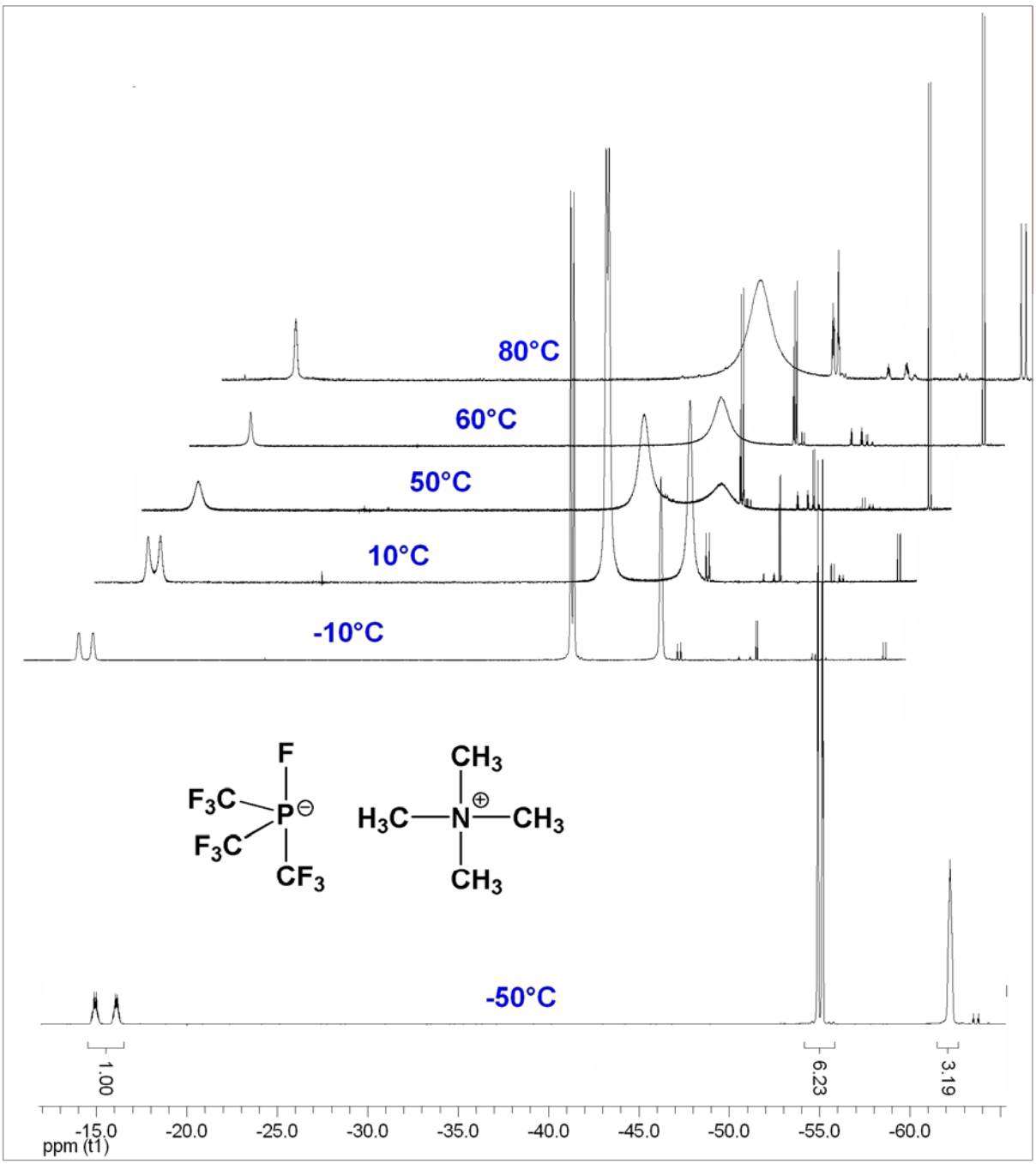
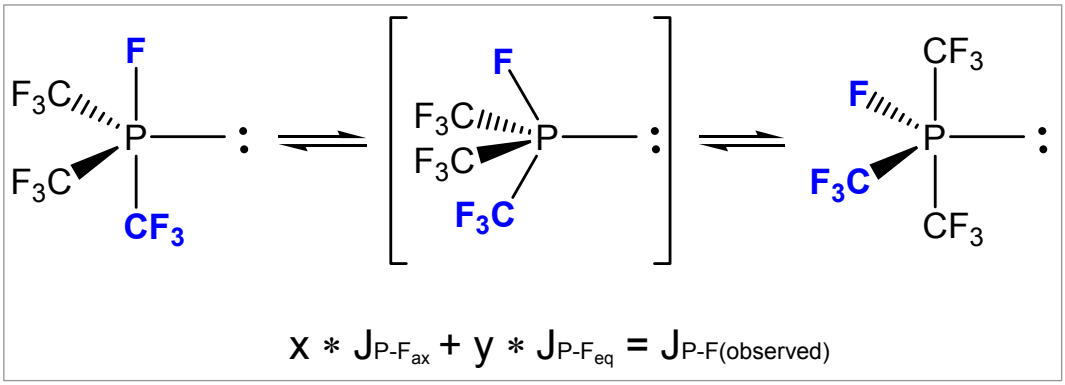


Figure 5 *Temperature dependent ^{19}F NMR spectrum of phosphoranide salt **8**. Conditions: Bruker AMX360, monoglyme, 20 min time interval between measurements.*

down and the ^{31}P NMR spectrum revealed resolved signal at δ = -54.87 already at RT. The same result could be also obtained by gradual cooling the sample (without addition of TMAF, MG); complete splitting of the signal due to "freezing" of intramolecular transformations happened at -60ºC and further cooling the sample gave no signal transformation (*Figure 5*). The numeric value of the direct P-F coupling constant also varies with the temperature change. It monotonously increases with the temperature decrease from approximately 367 Hz at 30ºC to 399.8 Hz at -60ºC and represents an averaged value depending on the relative

contents of two possible forms showed on *Scheme 20.2.* Taking into account that at 30ºC, i.e. “on the edge” between intermolecular and intramolecular processes, X should be nearly equal to Y we can roughly evaluate $J_{P\text{-}F_{eq(30ºC)}}$ and suppose it to be equal to 336 Hz.



Scheme 20.2

In early experiments it was suggested that possible traces of HF or H_2O present in the solution were the cause of the signals broadening. To disprove this supposition the super strong base, $TMG_3P{=}N\textit{t}Bu$[81] (TMG = tetramethylguanidine) was added to samples of **8** and **31**. No changes in spectra were detected and the signal of the phosphazene (^{31}P: δ = -22.6) stayed to be a singlet, indicating that solutions did not contain any acidic impurities.

The behavior of (K^+)*18-crown-6 salt of $(CF_3)_3PF^-$ (**31**) phosphoranide differs markedly from the TMA salt. No distinction between axial and equatorial CF_3 groups was observed either in the ^{19}F or ^{31}P NMR spectra at any temperature (-90ºC, lowest feasible temperature) in MG. It is very surprising since we expected that fluorine at a hypervalent phosphorus center in **31** would be less mobile due to lower Lewis acidity of (K^+)*18-crown-6 cation and fine structure was supposed to be observed at higher temperature than in the case of TMA salt. It is clearly seen within *Figure 7* where signals at δ = -19.7 (s, 1F) and at δ = -57.8 (d, 9F) correspond to compound **31**. The last signal reveals a broad doublet ($^1J_{PF}$ = 67.8 Hz, $\Delta\nu_{½}$= 32.7 Hz; MG, RT). The shape and disposition of the signals are indicative of a fast intermolecular interchange process occurring in the MG solution. It seems to be rather unusual to suppose the existence of such interchange in low-polar media but spectra of **31** in MG coincide with those of **8** or **31** in acetonitrile; moreover, while gradual raising the temperature spectra of **8**

in MG also tends to transform into the spectra measured in acetonitrile (*Figure 5*) indicating that at temperatures > 60°C a ligand averaging process is gradually substituted by intermolecular fluoride ion exchange process. It is not absolutely evident from ^{19}F spectra shown in *Figure 5* but a clear transformation of the completely resolved signal at -60°C into a broad decet at 80°C with intermediate formation of a broad multiplet at 50÷60°C according to a free ligand exchange, can be observed in the set of ^{31}P spectra. To evaluate the relative influence of both counterion discussed, TMA^+ and (K^+)18-crown-6, on tris(trifluoromethyl) fluorophosphoranide ion, a portion of TMAF was added to a MG solution of **31** and conversely, a portion of KF/18-crown-6 to a MG solution of **8**. In the last case no transformation of the NMR spectra was observed, but addition of an extra amount of TMAF to **31** changed all the spectra dramatically. Both, intermolecular and intramolecular exchange processes were significantly slowed down and partially resolved signals, absolutely the same as at -60°C for compound **8**, were revealed at normal conditions.

Summarizing all these observation, one can draw some important conclusions. *First*, polar solvents like acetonitrile favor intermolecular fluoride ion exchange; lowering the temperature does not afford to observe fine structure in NMR spectra. Of course, at room temperature solutions of phosphoranide **8** or **31** in acetonitrile quickly become yellow as a result of the reaction of fluoride ion with the solvent. *S*olvation effects are extremely important. Probably poor solvation of the TMA cation leads to the existence of **8** in MG as tight ionic pair in which pseudorotation is significantly slowed down (see also the second clause) but in acetonitrile both the ions are already sufficiently solvated and are separated from each other. High affinity of (K^+)*18-crown-6 cation to MG could be the reason of better ion solvation in phosphoranide salt **31** and rapid intermolecular exchange occurs in this solvent even at -90°C while for the salt **8** (MG solution) such process takes place only at elevated temperatures. *Second*, the unique difference in the spectra of TMA^+ and (K^+)*crown phosphoranide salts could be explained from another point of view - probably there is some interaction between the TMA cation and phosphorus which favors P-F bond formation, slows down the pseudorotation process and makes fine structure of the signals of $^{ax}CF_3$

and $^{eq}CF_3$ groups visible even at RT. As it will be shown below, despite strong electron withdrawing effects of substituents, phosphorus could be relatively easy oxidized (*chapters C2.3, C3*); therefore there is no reason to disregard the possibility of weak P-N interaction and this supposition can explain why addition of TMAF to MG or acetonitrile solutions of **8** or **31** led to complete or partial suppression both of intermolecular F^- ion exchange and permutation processes.

The synthesis and properties of hypervalent bismuth derivatives, compounds related to the title phosphoranides are described in the literature[82]. It was reported that the ^{19}F spectrum of tris(trifluoromethyl)fluorobismutate ($[Et_2N]_3PF^+$, TAS^+, TMA^+ salts) revealed a broad singlet at δ = -39.84 (-58ºC, THF-d_8, 9F) shifted to higher field compared to the parent molecule $Bi(CF_3)_3$ δ = -33.40, and a singlet for fluoride δ = -106.33. Authors explained this spectrum by fast exchange of axial and equatorial substituents. But these data could be also explained by the existence of the $(CF_3)_3BiF^-$ anion in an equilibrium with a F^- ion and $(CF_3)_3Bi$ in solution even at low temperatures. Since Bi is bigger than P, the Bi-F bond is weaker and longer than the P-F bond this equilibrium may be shifted towards dissociated ions much stronger than that for $(CF_3)_3PF^-$.

In general, the rate of tris(trifluoromethyl)fluorophosphoranide anion decomposition depends on which side the equilibrium **a** is shifted to and on the relative rate of process **b** (*Scheme 20.1*). It is clear that the salt **31** should be more stable than salt **8** (only MG solutions of pure compounds are meant due to fast decomposition occurring in acetonitrile or benzonitrile) since route **b** is statistically less probable due to weak P-F bonding. Decomposition of **8** in MG at RT occurs within two weeks completely (*Figure 6*). After two weeks staying at RT the solution of **31** consisted of 85% starting phosphoranide and even after 7 weeks traces of one were still present in the reaction mixture. The previously reported scheme of this process proved to be somewhat inaccurate (*see introduction*). Significant amounts of by-products were formed and their signals were observed in the spectra. Initially, it was supposed two signals at δ =-150 and δ = -2 to belong to one compound of the phosphinoperphosphoranide type, but the ^{31}P

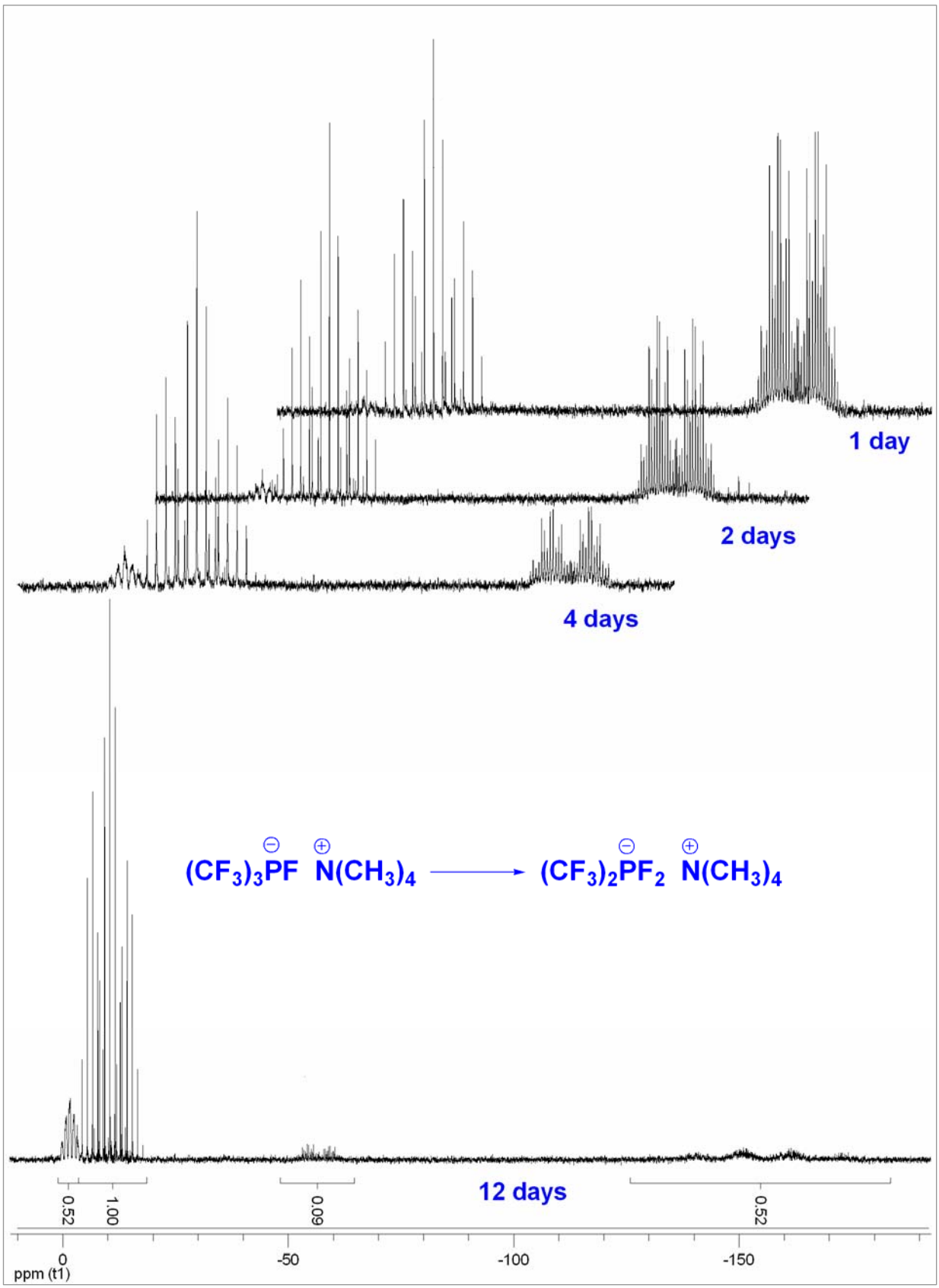


Figure 6 *Decomposition of phosphoranide salt **8** at room temperature in monoglyme*

spectrum of the solid obtained after exposition of phosphoranide salt **8** at RT during 12 d without addition of a solvent showed a ratio of phosphoranides **8**/**9** to

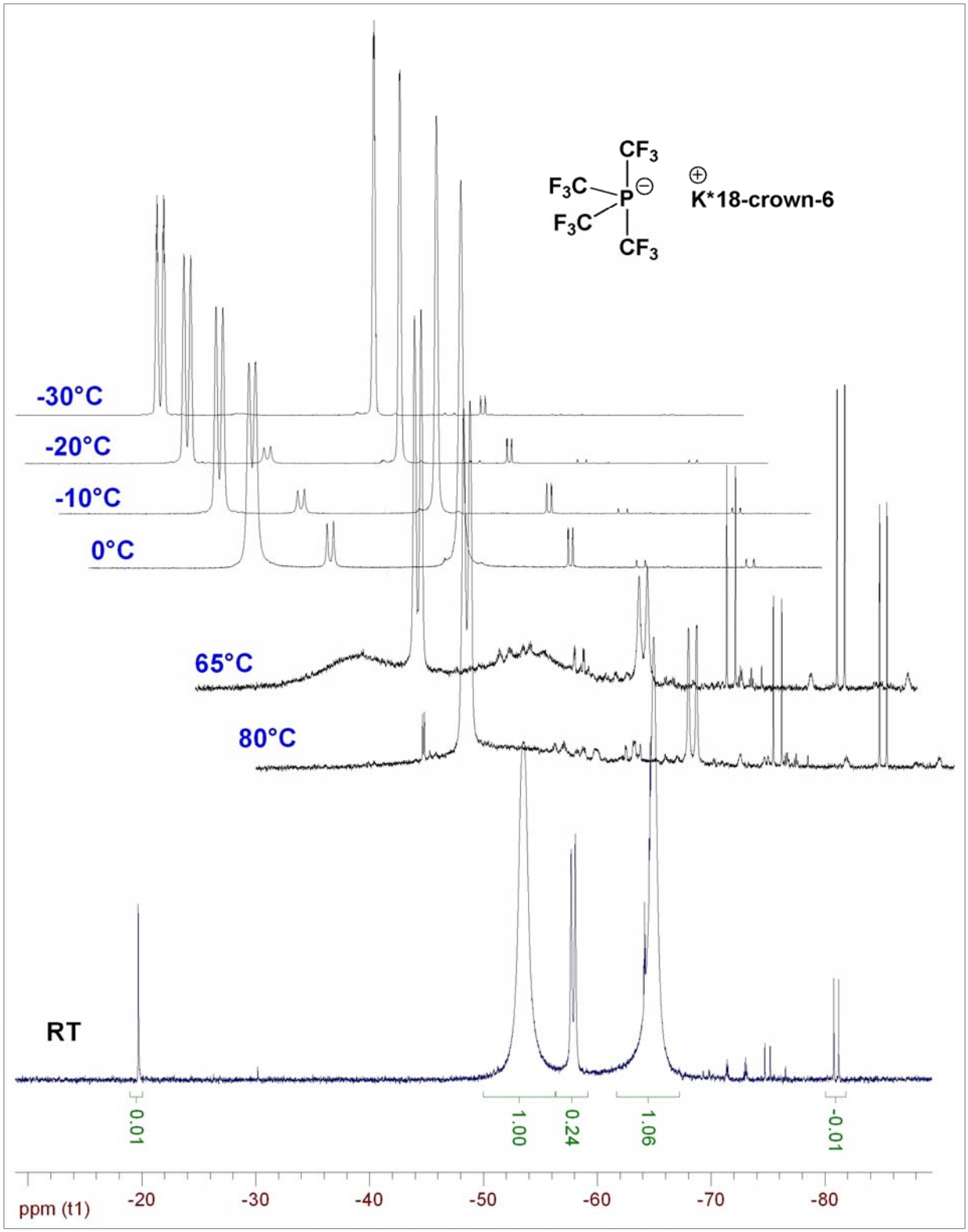
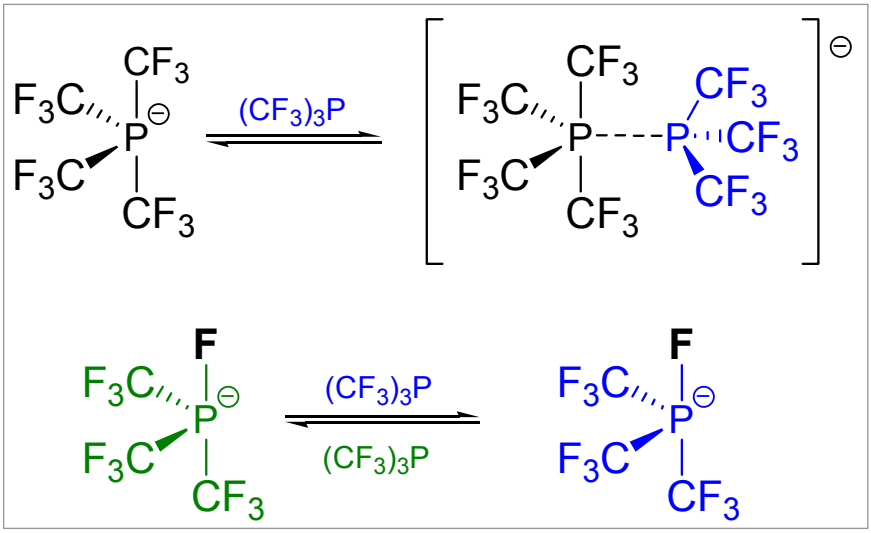


Figure 7 *Temperature dependent ^{19}F NMR spectrum of phosphoranide salt **32**. Conditions: Bruker DPX200, monoglyme, 20 min time interval between measurements*

be equal to 1.89/1, a multiplet at δ = -150 with an intensity of 1.26 relative to compound **9** and only a faint hint of a multiplet at δ = -2. Due to the complex structure of the ^{19}F NMR spectra it was impossible to bring all the visible signals in correlation with the signals in ^{31}P spectra and propose structures for this by-

products, though phosphoranide **9** was successfully described. It is also should be noted that compound **9** could not be synthesized in pure state starting from bis(trifluoromethyl)phosphine and TMAF or KF/18-crown-6 system. This reaction is complicated by the process of phosphinoperphosphoranide **55** formation (*Chapter C3*) and usually mixtures consisting of **9** and **55** were obtained. Taking a large excess of a fluoride ion source the yield of the desired phosphoranide can be significantly improved but not higher than 60% in the mixture with **55**.

Contrary to tris(trifluoromethyl)fluorophosphoranides, tetrakis(trifluoromethyl)phosphoranides **7**, **32** show nearly identical behavior in solution except their thermal stability. The difference in energy barriers to pseudorotation between these compounds is not so significant like in the case of compounds **8** and **31**. The spectra of **32** at 0ºC still represent an intermediate state between the full distinction of axial and equatorial environments observed below -50ºC and the fast exchange which is approached upon warming to 80°C (*Figure 7*). In the case of TMA salt **7** complete resolution of signal was achieved at -45°C indicating that weak coordination of the cation to the lone pair the phosphoranide ion may exist. The striking demonstration of stability increase occurring with cation replacement is the detection of the salt **32** in solution at 80°C while TMA salt **7** has never been detected at temperatures higher than 10°C. Here, the



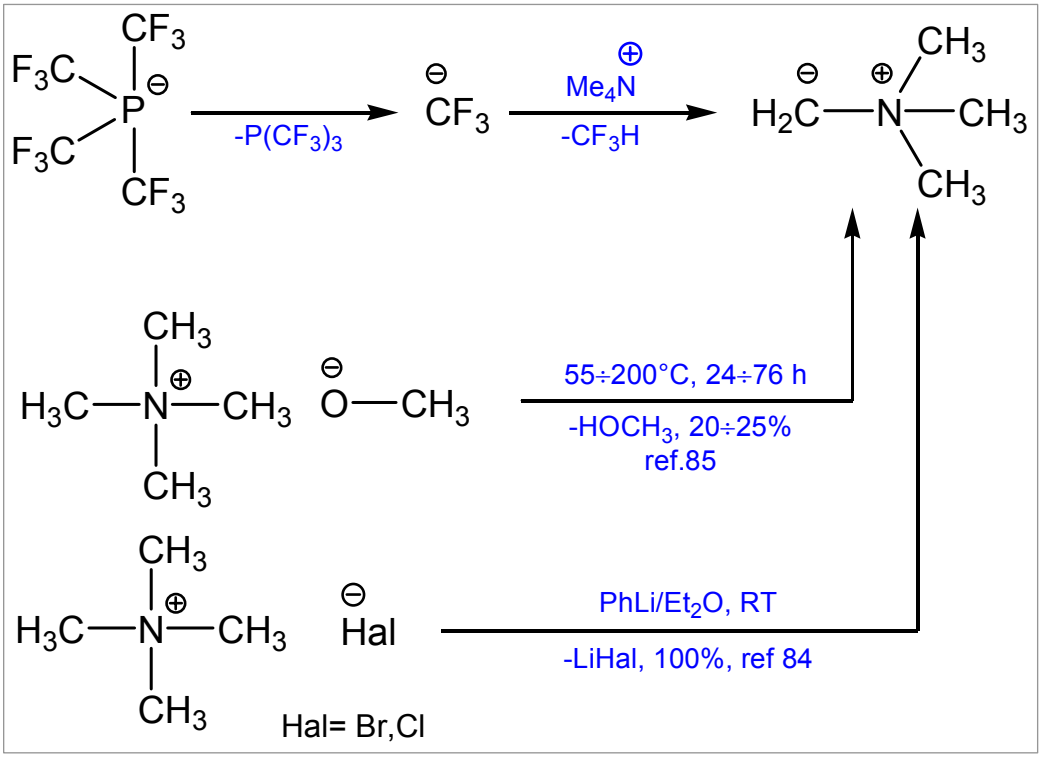
Scheme 21

Lewis acidity (more correctly - affinity to fluoride ion) of the counterion must play a decisive role in the effect observed.

We also found that the stability of tetrakis(trifluoromethyl)phosphoranide in solution could be significantly improved by addition of equimolar amounts of phosphine **11**. This stabilization is surely caused by the coordination of the phosphine to the phosphoranide lone pair what reduces electron density on the central phosphorus and consequently in hypervalent bond rendering this bond stronger. Here we should shortly return to compounds **8**, **31** and note different mechanisms of their stabilization by phosphine **11**. While tetrakis-(trifluoromethyl)phosphoranide is stabilized by P-P coordination, tris-(trifluoromethyl)fluorophosphoranide may be stabilized by $^{ax}F\cdots P(CF_3)_3$ interaction (*Scheme 21*). The first type of stabilization leads to a higher pseudorotation barrier and therefore to signals' splitting in the NMR spectra at higher temperatures; the second type leads to the drift of fluoride between phosphine molecules i.e. to broadening of signals which has already been discussed above. For the sample of phosphoranide **32** with phosphine **11** added, the fine structure in the ^{19}F NMR spectrum was observed already at -30ºC, proving our assertion. We should assume P-P coordination otherwise in the case of intermolecular CF_3 exchange broad signals could be expected. Finally, independently on the possible stabilization mechanism, addition of phosphine **11** to the phosphoranide was that trick which allowed us to get stable at RT solutions of phosphoranides **8**, **31** (for several month) and **32** (for several hours).

Replacement of the TMA cation by (K^+)*18-crown-6 etherate led to a stability increase not only in solution but also in the solid state. It is very important to mention that tetra(trifluoromethyl)phosphoranide salt **8** may decompose with violent gas elision (explosively) during isolation while solid salt **32** is relatively stable and only slowly decomposes at RT at the rate of 2.6% per 24 h. It was noticed that the stability of **8** significantly decreased with full removal of the solvent but when traces of one are still present it was possible to handle this compound. This process closely resembles that of the decomposition of $(CF_3)_2Cd$ which is also very unstable when stabilizing amounts of base or solvent are removed[83]. Both phosphoranide salts being metastable, differ so strong from

each other and it seems to be impossible to explain this discrepancy only by difference in the rates of CF_3 group loss from the hypervalent anion due to



Scheme 22

different Lewis acidity of the cation or different geometrical environment in the crystal. To understand this phenomenon we should also take into account the stability of possible decomposition products. Thus, formation of tetramethylammonium ylide[84,85] (**34**), very reactive species unstable when isolated as solid powder[86], could be supposed starting from tetramethylammonium and the trifluoromethyl ions (*Scheme 22*) evolved. The ylide mentioned was shown to be an effective carbene donor[87]. Further reaction

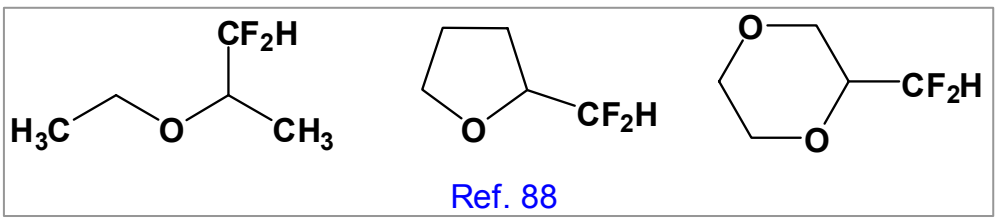


Figure 8

of carbene or difluorocarbene being formed from the decomposing trifluoromethyl anion, polymerization should occur rather exothermic in that way leading to complete phosphoranide ion destruction. Anyway, significant amounts of

phosphine **11** should be observed in the NMR spectra but it is not the case: signals in the ^{31}P spectrum are very weak and surprisingly, only traces of **11** can be detected and the signal of PF_3 dominates here. Signals of CF_3H, Me_3N, CF_2CF_2, PF_3 (mixture of gases obtained after decomposition) and TMA+ ion (solid residue) were clearly seen in the ^{1}H and ^{19}F spectra. A solid black polymer poorly soluble in common (deuterated) solvents was also obtained. This indicates that decomposition occurs more completely and the solid must contain the rest of the substance. The detection of CF_3H and Me_3N in the reaction mixture let us suppose a decomposition route including formation of tetramethylammonium ylide as an intermediate compound. On the contrary, in solution CF_2 carbene trends to react with the solvent to give CF_2H derivatives as was previously reported by Hu and coworkers[88] (*Figure 8*). Typical signals at -80.7 ppm with $^{2}J_{FH}$ = 79.3 Hz were detected in ^{19}F NMR spectra of phosphoranides **7**, **8,** as well as of **31** and **32** having no possibility to form ylide **34**. Following *ref. 88*, it is easy to explain why phosphoranides **7** and **8** were synthesized in low yield in THF, since it was shown that using this solvent or 1,4-dioxane, maximum extent of CF_2H by-product was obtained[88].

Here, after discussing the stability and dynamic NMR aspects for trifluoromethylphosphoranides, the concept of “intramolecular transformations” used above, should be defined more exactly. The mechanism by which the intramolecular ligand exchange process occurs is most likely the classical Berry pseudorotation mechanism involving a pyramidal transition state (*Scheme 20.2*). It should be noted that NMR spectroscopy alone could not distinguish between this and other mechanism that result in the same permutation of CF_3 groups[89], to answer the question definitively extensive computations of all transitional states should be carried out. Other mechanisms have been favored for compounds such as ClF_3[90], SiH_4F^-[91] or PH_4F[92]; competitive with Berry pseudorotation turnstile rotation[93] cannot be also strictly excluded. A wide array of hypervalent compounds isoelectronic to phosphoranides such as SF_4[94], PF_4^-[35], set of trifluoromethylphosphoranes[95], pentacoordinate silicon compounds[96] were shown to undergo intramolecular exchange on Berry pseudorotation mechanism.

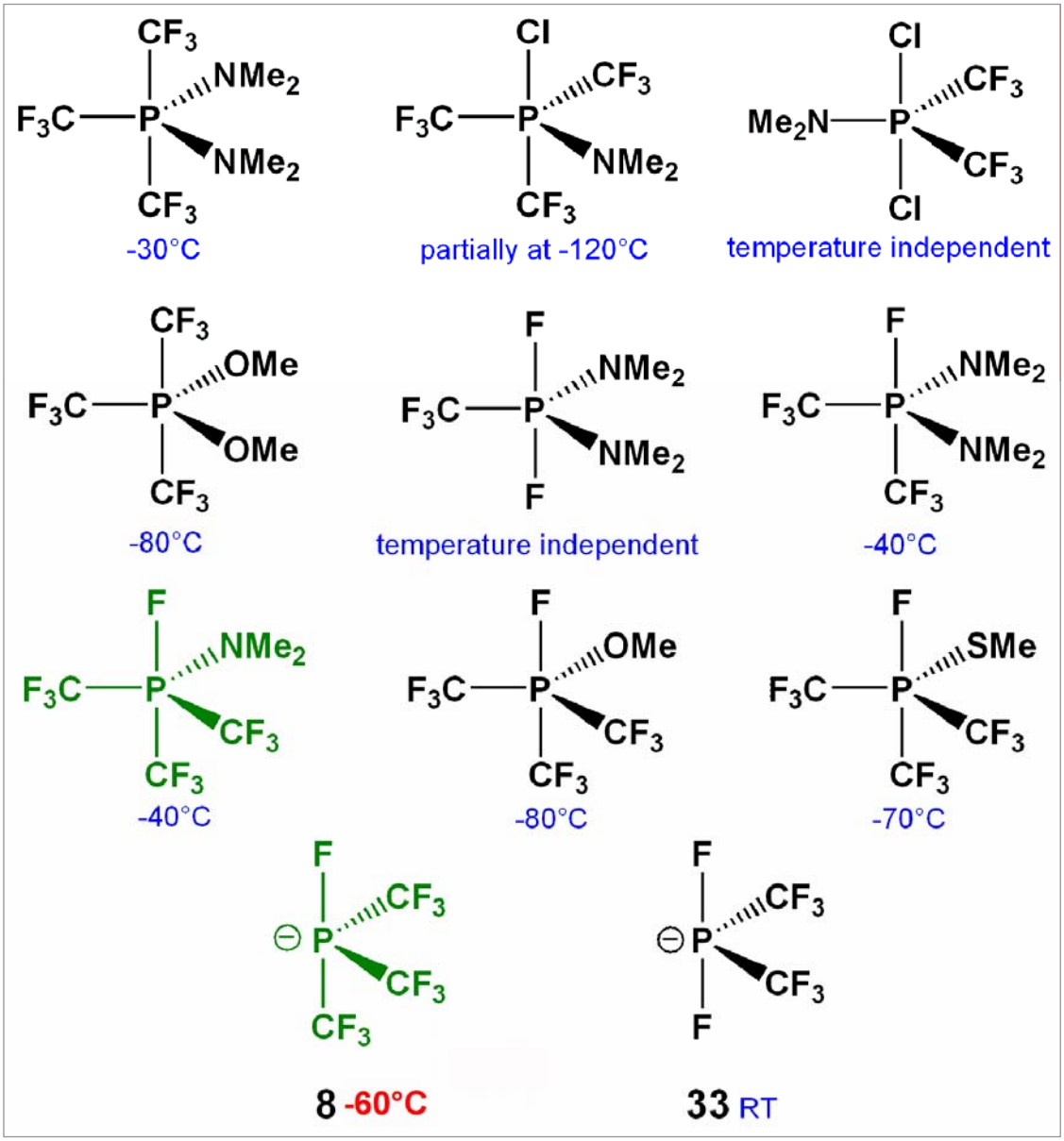


Figure 9

It was revealed that the barriers to positional interchange processes which render CF_3 and F environments indistinguishable are not regular in phosphoranides. Temperatures of signals' complete resolution in the ^{19}F NMR spectra of trifluoromethylphosphoranes according *to ref. 95* are shown on *Figures 9, 10*. In authors' description: "the relative barriers are understandable if a Berry permutationally equivalent mechanism is responsible since this mechanism requires one $N(CH_3)_2$ [also OCH_3 or SCH_3] group to occupy an axial position which is likely a highly unfavorable configuration"[95a]. Mono- or dihalo substituted compounds can undergo a pseudorotation rearrangement in which halogens (also Cl, despite its lower electronegativity than CF_3[97]) remain

preferentially in apical position and other ligands occupy the rest of the sites. In general, substituents follow the “electronegativity rule” formulated by Muetterties and coworkers[98]. Comparative analysis of the barriers to pseudorotation for a set of compounds shown in *Figure 9* allows to conclude that the most important influencing factor is the relationship of substituents’ electronegativity, next the volume of substituents defining sterical hindrances (repulsion between basal ligands) in the pyramidal transition state.

It is clear that the lone electron pair of phosphoranide ions formally having the lowest electronegativity (pseudo-substituent) should strictly avoid the apical position. Therefore, its presence in the phosphoranide molecules makes only one pathway of ligands’ spatial interchange shown in *Scheme 20.2* possible and the barriers to a pseudorotatory process must be relatively low since the difference in electronegativity of substituents is not high and consequently, the equilibrium between two isomers should be defined presumably by sterical interaction of the ligands.

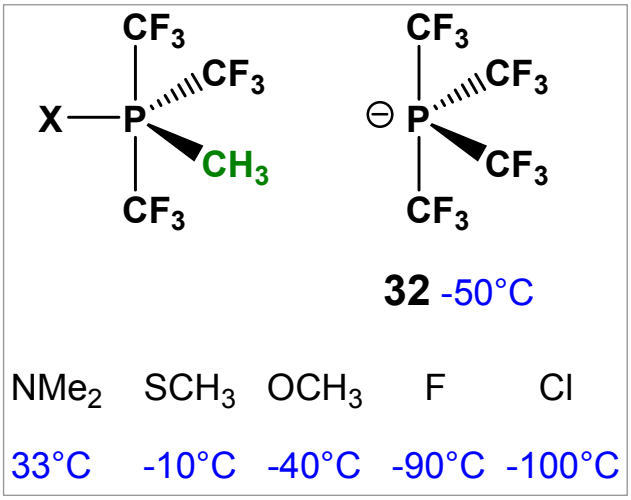


Figure 10

So, we can explain why the energy barrier to pseudorotation should be low for tris(trifluoromethyl) fluorophosphoranide. However, analyzing the array of $(CF_3)_3PF$**X** phosphoranes and concerning the features of X (X = -NMe_2, -OMe, -SMe; *Figure 10*) it is difficult to understand why the barrier is so low.

The resolution of the ^{19}F spectrum of phosphoranide **32** at -50°C also does not seem to be in line with the regularity found for trifluoromethylphosphoranes. If it was possible to suppose the existence of an tris(trifluoromethyl) methylphosphoranide ion we would predict very roughly the temperature of pseudorotation “freezing” to be higher or equal to 33°C (*Figure 10*). Of course, the substitution of the methyl group by a trifluoromethyl group should lead to enormous reducing of the energy barrier. A good example of such a substitution

effect could be presented by a pair of phosphoranes: $(CF_3)_3P(NMe_2)_2$ and $(CF_3)_3P(NMe_2)Cl$ (*Figure 9*). Thus, we could expect *full* resolution of signals in the ^{19}F spectrum of **32** to be observed at least at -80°C. Probably, the introduction of the fourth CF_3 group in the molecule increases steric hindrance in the transition state in that way slowing down pseudorotation and providing the higher barrier for the tetrakis(trifluoromethyl)phosphoranide in comparison with tris(trifluoromethyl)fluorophosphoranide.

As it was mentioned before, addition of phosphine **11** or TMAF to solutions of corresponding phosphoranides led to a permutation barrier increasing. It is easily understood if one considers the mechanism of Berry pseudorotation including drawing together the axial ligands i.e. shortening of hypervalent bond. In this case the higher volume has the equatorial ligand the higher the repulsion forces between one and axial groups are.

The temperature independence of NMR spectra of **9** suggests that either any positional averaging process is fast and prevents the detection of different CF_3 environments or the ground-state of the molecule is trigonal bipyramidal with two axial F at all temperatures.

The magnitudes of $^2J_{PF(ax)}$, $^2J_{PF(eq)}$ and J_{PF} are smaller by its numerical values than the corresponding values in $(CF_3)_3PF_2$[99], $(CF_3)_2PF_3$[100], $(CF_3)_3(CH_3)POMe$[95c] and $(CF_3)_3P(NMe_2)_2$[95a] in which CF_3 groups occupy equatorial or both equatorial and axial position (*Table 2*). The difference in values of the coupling constants for axial and equatorial CF_3 allows precise

Compound	J_{PF}	$^2J_{PF(ax)}$	$^2J_{PF(eq)}$	$^4J_{FF(ax-eq)}$	$^4J_{FF(eq-eq)}$
$(CF_3)_4P^-$ -50°C		2.5	68.9	8.5	
$(CF_3)_3PF^-$ -50°C	384.8	28.5	85.3	9.6	10.9
$(CF_3)_2PF_2^-$ 25°C	309.6		93.6	13.3	
$(CF_3)_3PF_2$ 25°C	992.0		166.2		
$(CF_3)_2PF_3$ 25°C	964.5		167.0		
$(CF_3)_3(CH_3)POMe$ -50°C		62.0	108.5		
$(CF_3)_3P(NMe_2)_2$ -40°C		50.8	107.0		

Table 2

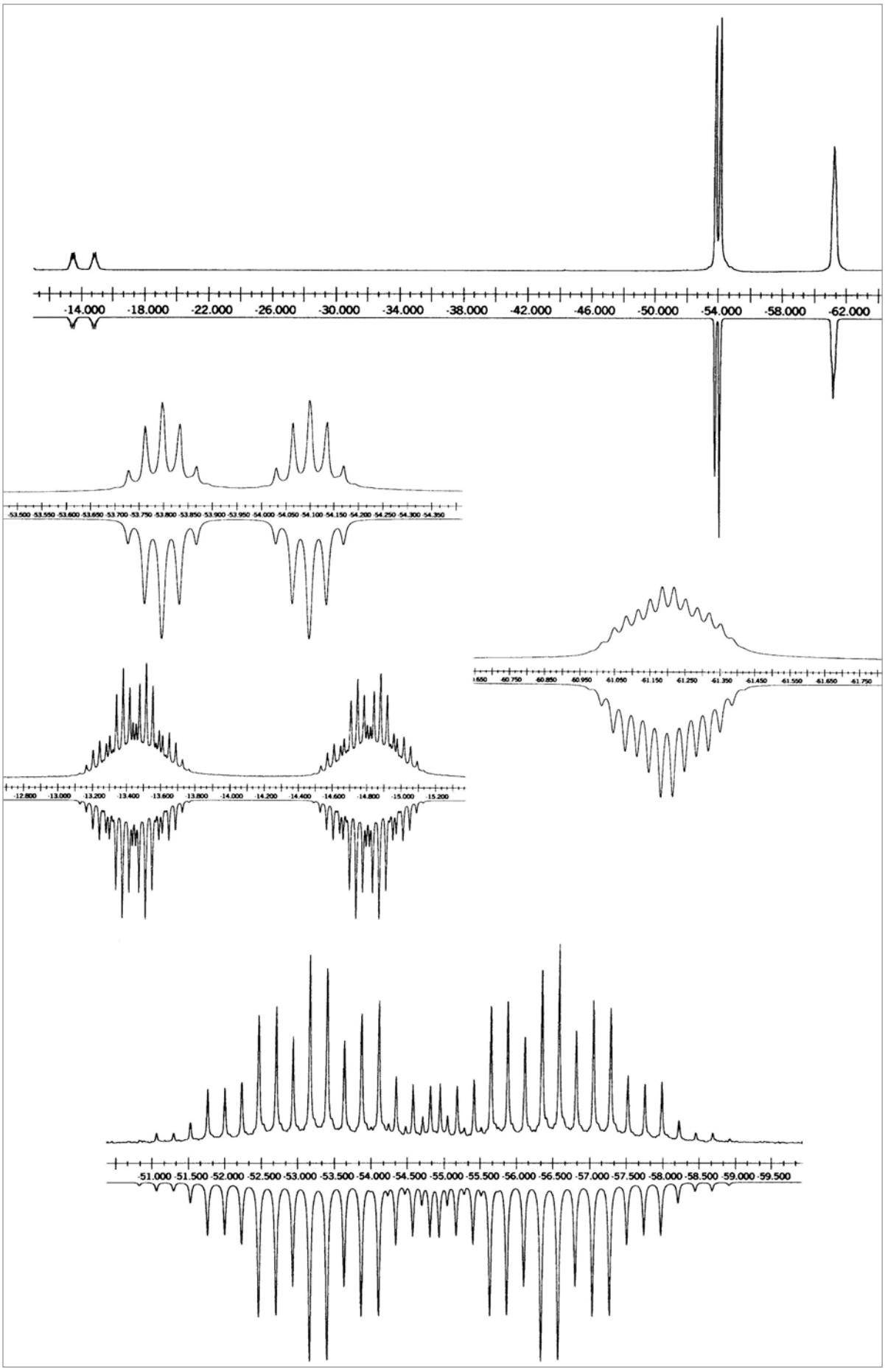


Figure 11 *Experimental (upper line) and calculated [low-rate, 223K] spectra (lower line) of compound* **8**

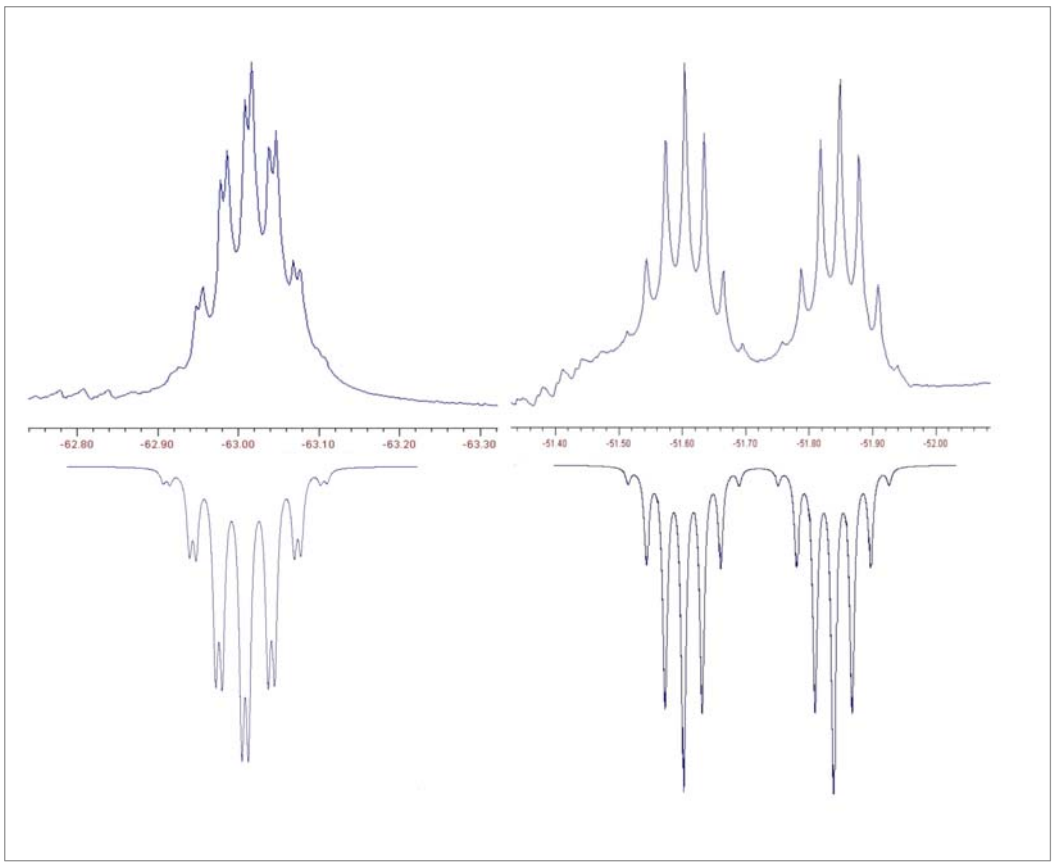
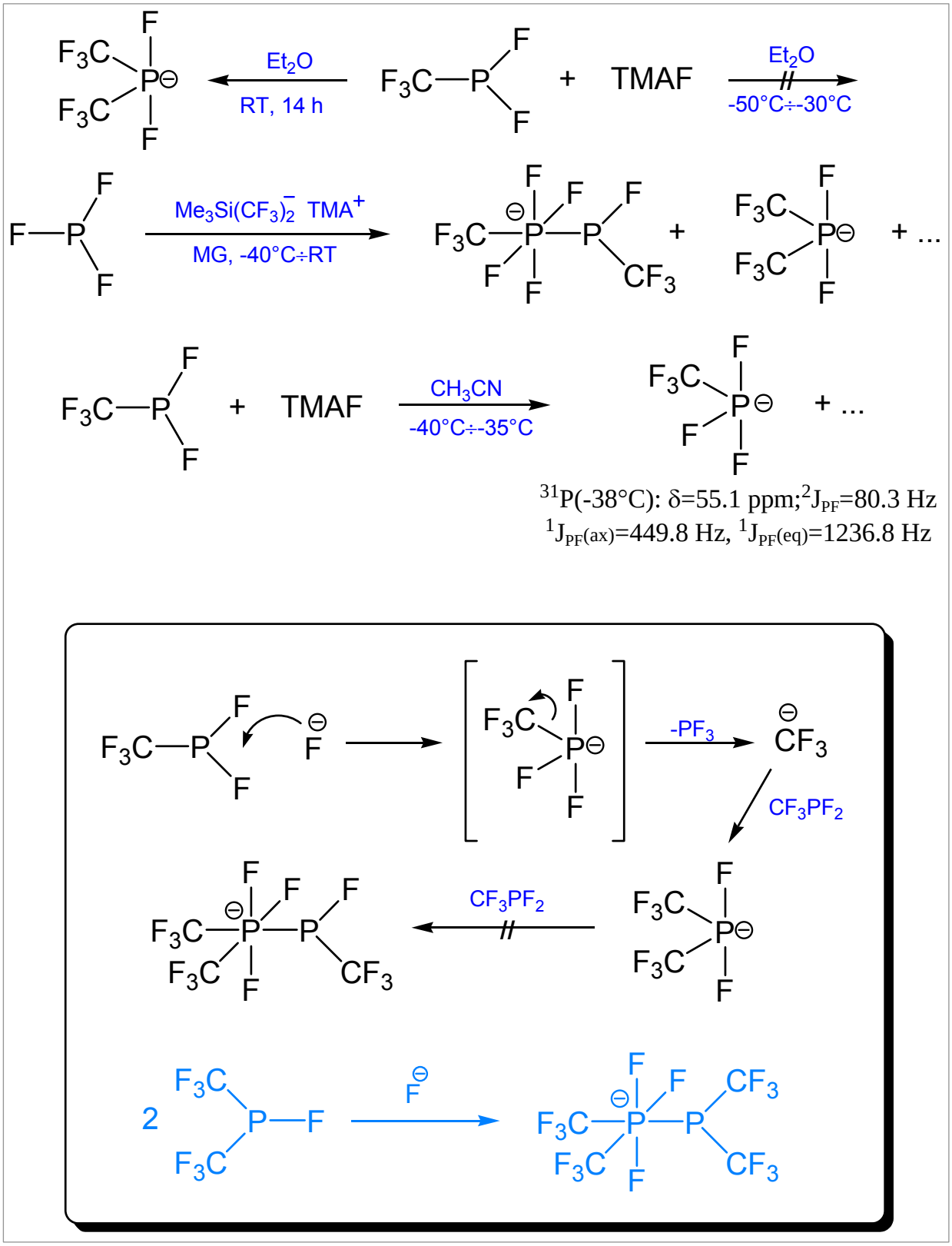


Figure 12. *Experimental (upper line) and calculated spectra (lower line) of compound **32** [223K]*

distinguishing these groups. It is clearly seen that except the direct PF coupling constant, the magnitude of PF and FF coupling constants in phosphoranides becomes higher with decreasing the number of CF_3 groups attached to phosphorus. Parallely, signals of *equatorial* CF_3 groups consistently shift into strong field: from -51.7 ppm for **7**/**32** towards -54.0 ppm for **8**/**31** and -63.75 ppm for **9**. In the opposite direction *axial* CF_3 groups are shifting: -63.0 ppm (**7**/**32**), -61.2 ppm (**8**/**31**). One of the most unexpected phenomena is the inequivalence of equatorial CF_3 groups in tris(trifluoromethyl)fluorophosphoranide ion giving rise to a high-order spin system. Experimental ^{31}P and ^{19}P spectra compared with calculated[101] ones are presented in *Figures 11 and 12*.

Though, tetrakis(trifluoromethyl)-, tris(trifluoromethyl)fluoro- and bis(trifluoro methyl)difluorophosphoranides have been discussed in detail, nothing definite has still been said about (trifluoromethyl)trifluorophosphoranide **33**, which we have not managed to synthesize and characterize so far. Numerous attempts and strategies failed (*Scheme 23*). We may only suppose a



Scheme 23

(trifluoromethyl)trifluorophosphoranide salt formation as an intermediate product but its signals have never been detected in the respective spectra. Only a low temperature experiment made in acetonitrile showed a very suspicious signal of

weak intensity which may correspond to phosphoranide mentioned. The reaction of (trifluoromethyl)difluorophosphine with TMAF carried out in conditions typical for the preparation of other phosphoranides (ether, low temperatures, process' duration 5-8 h) resulted in quantitative isolation of the starting phosphine and TMAF. Unexpectedly, stirring the reaction mixture overnight at RT allowed the isolation of the TMA salt of bis(trifluoromethyl)difluorophosphoranide (**9**) and trifluorophosphine. Symmetrization is surely to be realized through intermolecular ligand exchange leading to the thermodynamically most stable products. Probably, the process' driving force is the low affinity of PF_3 to the CF_3 anion. In general, the Lewis acidity of PF_3 is quite low and for a quite long time PF_3 was even thought not to possess Lewis acidity at all[102]. Only relatively recently this point of view was changed[103] and the hypervalent PF_4^- anion was thoroughly characterized[35]. Taking into account the inability of isolation of **9** in pure state just by the reaction of TMAF and $(CF_3)_3PF$ in ether, it is difficult to explain why no by-products are formed in the reaction of TMAF and CF_3PF_2 in the same solvent. Two possible speculations are possible in this case: some stabilizing effect of PF_3 (probably due to coordination on phosphoranide lone pair) or bad solubility of **9** in the solvent together with the lower Lewis basicity of intermediate $[(CF_3)PF_3]^-$ compared to that of $[(CF_3)_2PF_2]^-$. This question has been not answered yet. However, when MG was taken as solvent only phosphinoperphosphoranides were formed (*Scheme 23*) and no trace of the desired phosphoranide was detected. It is also worth noting that carrying out the reaction discussed in a Et_2O/CH_3CN (1/1) mixture, signals corresponding to PF_4^-, $[(CF_3)FP\text{-}P(CF_3)F_4]^-$ and $[(CF_3)PF_5]^-$ ions were detected in the spectra. As it was mentioned before, the reaction media polarity increase led to stability decrease of the hypervalent phosphorus species formed. Therefore, more complex mixtures were usually obtained.

Interestingly, products of analogous symmetrization reactions were isolated while mixing PCl_3, PBr_3 or $P(CN)_3$ with CN^-, NCS^-, NCO^- ion sources[24]. In some cases PX_3Y^- salts together with symmetrized products were either only detected or isolated and characterized.

C2.2. Trifluoromethylphosphoranides: ab-initio calculations, X-Ray structures, FT-ICR investigations

Due to the problem of growing single crystals suitable for X-Ray analysis, which we'd had for a long time, ab-initio calculations of electronic and geometrical parameters[104] as well as selected gas-phase acidities[105] were performed before receiving experimental data. Results of these calculations are presented in *Tables 3-6* and in *Figure 13.*

As one can see, the hypervalent nature of the phosphoranide ions becomes apparent not only with relatively high *natural charge* (parameter, describing ionic constituent of chemical bond[106]) of the axial substituents and the elongation of the L_{ax}-P bonds. Unexpectedly high *Wiberg index* (characterizing covalent bond order[107]) for L_{eq}-P bonds may imply electron enriched bond also participating in negative charge delocalization (see below). Thus, the term "hypervalent" may concern the whole phosphoranide ion though using this term we should mainly keep in mind a 3c-4e bond between axial substituents and phosphorus atom.

Close interrelationships of different electronic parameters for each group of substituents were established which allowed us to make some important conclusions on reciprocal influence of equatorial and axial ligands in phosphoranides. First, it was noted that Wiberg indexes of F_{ax}-P bonds [$W(PF_{ax})$] constantly decrease with axial fluorine [$q(F_{ax})$] natural charge decrease and with increasing the number of CF_3 groups attached to phosphorus. Reverse trends were revealed for equatorial fluorines. Shortly, introduction of CF_3 groups in the molecule made the F_{ax}-P bond weaker, longer and less polar. Second, we realized that the higher the degree of fluorine substitution by trifluoromethyl groups, the higher $W(PCF_{eq})$ and lower $W(PCF_{ax})$ and parallel to this, $q(C_{eq}F_3)$ and $q(C_{ax})$ get smaller, $q(C_{ax}F_3)$ together with $q(C_{eq})$ rose. In other words, starting with compound **33** and finishing with compound **7** the CF_{3eq}-P bond becomes stronger and shorter; the CF_{3ax}-P bond becomes weaker and slightly longer. Third, the phosphorus lone pair s-character and phosphorus natural charge decreased in the range of phosphoranides **3**>**33**>**9**>**8**≈**7**, showing the expected dependence on the substituent electronegativity.

Compound % **s** (LP)	q($\mathbf{F}_{ax}$)	q($\mathbf{F}_{eq}$)	q($\mathbf{C}F_{ax}$)	q($\mathbf{C}F_{eq}$)	q($C_{ax}\mathbf{F}_3$)	q($C_{eq}\mathbf{F}_3$)	q(P)	W(PF_{ax})	W(PF_{eq})	W(PCF_{ax})	W(PCF_{eq})
PF_4^- (**3**) 69.4	-0.759	-0.647	-	-	-	-	1.864	0.418	0.539	-	-
$[P(CF_3)F_3]^-$ (**33**) 67.5	-0.745 -0.742	-0.659	-	0.866	-	-0.443	1.588	0.408 0.420	0.547	-	0.752
$[P(CF_3)_2F_2]^-$ (**9**) 64.2	-0.733	-	-	0.903	-	-0.390	1.246	0.402	-	-	0.796
$[P(CF_3)_3F]^-$ (**8**) 58.9	-0.737	-	0.831	0.927	-0.520	-0.348	0.954	0.353	-	0.667	0.812
$[P(CF_3)_4]^-$ (**7**) 59.3	-	-	0.829 0.829	0.937 0.941	-0.534 -0.534	-0.321 -0.316	0.705	-	-	0.579 0.579	0.817 0.801

Table 3 *Calculated Natural Charges (q), Wiberg Indexes (W) and Phosphorus Lone Pair s-Characters in Compounds $[P(CF_3)_nF_{4-n}]^-$. (RHF/6-31+G** optimized structures)*

Compound	P-F_{ax}	P-F_{eq}	P-C_{ax}	P-C_{eq}	‹F_{ax}P**X**^{a} ‹**F_{ax}PCF_{3ax}** (**F_{ax}**)	‹F_{eq}P**X**^{a} ‹**F_{eq}PF_{eq}**	‹C_{ax}P**X**^{a} ‹**CF_{3ax}PC** **F_{3ax}**(**F_{ax}**)	‹C_{eq}P**X**^{a} ‹**CF_{3eq}PC** **F_{3eq}**	θ	Symmetry	Energy, a.u.
PF_4^- (**3**)	1.746 **1.740**	1.609 **1.60**	-	-	84.2 **168.3**	50.1 **99.9**	-	-	90.0	C_{2v}	-738.634651
$[P(CF_3)F_3]^-$ (**33**)	1.749 1.736	1.614	-	1.914	81.1 85.1	54.1	-	46.1	91.3	C_1	-975.3544
$[P(CF_3)_2F_2]^-$ (**9**)	1.748	-	-	1.907	82.8	-	-	51.3	86.7	C_2	-1212.081209
$[P(CF_3)_3F]^-$ (**8**)	1.782 **1.787**	-	2.007 **1.974**	1.910 **1.886** **1.890**	75.6	-	92.4 **170.47**	54.4 **104.00**	90.0	C_{2v}	-1448.792359
$[P(CF_3)_4]^-$ (**7**)	-	-	2.074 2.074 **2.060** **2.038**	1.902 1.921 **1.910** **1.889**	-	-	87.6 87.6 **175.18**	67.6 39.0 **104.79**	90.0	C_s	-1685.496815

Table 4 *Calculated and **Determined** Bond Length (Å), Interatomic Bond Angles (°), Molecular Symmetries in Compounds $[P(CF_3)_nF_{4-n}]^-$. (RHF/6-31+G** optimized structures).* [a] ***X*** *is located on the cross section of two planes [X_{ax}-P-Y_{ax}, M_{eq}-P-N_{eq}] with the angle θ in between.*

Good agreement of calculated geometric parameters with the determined ones being an incontestable proof of correctly made mathematical optimizations, let us to trust the data set in *Table 3, 4*.

As one can see, stepwise introduction of trifluoromethyl groups in phosphoranide molecule does not lead to monotonous change in Wiberg indexes of axial and equatorial bonds. Especially significant alteration of parameter mentioned was observed in the following cases:

- Insertion of second CF_3 group (**33**→**9**) resulted in very significant increase of $W(PCF_{eq})$, the difference was Δ_w= 0.044, but nearly did not influence $W(PF_{ax})$, Δ_w= 0.006. The lowest value of $W(PCF_{eq})$ for ion **33** might characterize low stability of this compound and should be considered while discussing the mechanism of **9** formation shown in *Scheme 23*. Further gradual substitution of fluorine atoms was accompanied by decreasing Δ_w values (0.016 and 0.005 correspondingly).
- Maximal change in $W(PF_{ax})$, Δ_w= -0.049, was attained while entering the third CF_3 group into phosphoranide (**9**→**8**). We speculated *vide infra* on the nature of the P-F_{ax} bond in the tris(trifluoromethyl)fluorophosphoranide ion. Theoretical investigation showed that indeed this bond was the weakest and longest P-F_{ax} bond in the range of trifluoromethylphosphoranides. While axial fluorine was significantly distant from the core phosphorus, the CF_{3ax}-P bond was characterized by relatively high value of $W(PCF_{ax})$.
- Substitution of the last fluorine atom (**8**→**7**) led to an enormous drop in $W(PCF_{ax})$, Δ_w= -0.088, indicating that spatial averaging of axial CF_3 groups occurred.

The negative charge of phosphoranide ions is localized on the electronegative ligands and of course, axial ligands are charged more negatively. The positive charge is localized on carbon atoms and the central phosphorus. It is interesting to note that the higher the substitution level, the less positively phosphorus is charged. It can be explained by not only lower electronegativity of CF_3 groups compared to that of F, but also by the charge sequence rule[108] (F^{-}-C^{+}-P^{-}-C^{+}-F^{-}) resulting in partial distribution of the positive charge on carbon atoms. Therefore phosphorus is significantly less charged than it could be

expected. This trend seems to be common and in such a way the induced stability of phosphine **11** to hydrolysis ought to be explained, too. Starting from the relative electronegativity of fluorine and the trifluoromethyl group, it may seem that the negative charge of F_{ax} in **33** should be at least the same as in **3**, and in **9** it should be even higher than in **33**, because of formal increase of the negative charge that a single F_{ax} has to accept. In reality, we can observe quite different trends of charge modification - it constantly reduces. To clarify the nature of the effect mentioned, repulsion forces between the lone electron pair and the electron rich equatorial fluorine atoms should be taken into account here. As the proof of the assertion we can note that in phosphoranide ions **9** and **8** containing no F_{eq} atoms, the negative charge of F_{ax} remains nearly constant.

As it was mentioned before, the phosphorus lone pair s-character decreased in parallel to the q(P) drop. Since a higher s-orbital character in the atomic orbital refers to increased electronegativity of the corresponding orbital and therefore higher acidity of the conjugated acid, we can suppose highest acidity for HPF_4 (**34**). Calculations of gas-phase acidities (ΔG_{acid}, kcal/mol; DFT B3LYP on 6-311+G** level of theory) for HPF_4 and $HP(CF_3)_4$, two compounds confining the array of acids conjugated with the title trifluoromethylphosphoranides, were performed. Calculated data and acidities of other known compounds[109] are set in *Table 5*. Surprisingly, HPF_4 proved to have the lowest acidity equal to acidity of H_2SO_4 and high acidity for $HP(CF_3)_4$ comparable with that of $HN(SO_2F)_2$ in the

Compound	ΔG_{acid}	Compound	ΔG_{acid}
HPF_2	355.2	$HP(CF_3)_2$	319.4
H_2SO_4	301.2 **302.2**	HBr	**318.3**
HPF_4	298.5	**$HP(CF_3)_4$**	283.7
FSO_3H	290.6 **299.8**	$HN(SO_2F)_2$	282.4
HPF_6	276.6	$HP(CF_3)_6$	not known

Table 5 *Calculated (DFT B3LYP 6-311+G** level) and **tentatively found** gas phase acidities (ΔG_{acid} values given in kcal/mol)*

gas phase was found. Acidity values for other H-phosphoranes are surely to lie within the range defined by the two phosphoranes calculated.

On the basis of data from *Tables 3-5* this phenomenon seems to be inexplicable. The reason of such intriguing acidity is to be found while analyzing geometrical parameters of H-phosphoranes **34**, **35** (*Table 6*). One can notice that both F_{ax}-P and F_{eq}-P bond lengths are distinctly shorter in **34** when compared with corresponding ones in phosphoranide **3**. The bond's shortening leads to more cramped vicinity of substituents and therefore to raising repulsion forces between electron pair of P-H bond and fluorine atoms resulting in polarization of this bond and imparting partial negative charge (δ-) to the proton. Moreover, high electron density in p-orbitals of fluorines can to some extent compensate the strong inductive attraction what is especially important on short distances. Opposite to the P-H bond in phosphorane **34** which we may suggest to be relatively electron rich, the P-H bond in phosphorane **35** ought to be electron poor and consequently weak due to the strong electron withdrawing effect of CF_3 groups. Hence, phosphorane **35** should be the strongest Brønsted acid in the array of trifluoromethylphosphoranes. Here a pair of two compounds, CF_3H (strong base with $pK_a \approx 33$)[84] and $(CF_3)_3CH$ (acid, ΔG_{acid} = 326.6 kcal/mol)[109b], could be mentioned for comparison.

Compound	H-P	F_{ax}-P	F_{eq}-P	P-$CF_{3\ ax}$	P-$CF_{3\ eq}$
HPF_4 (34)	**1.392(3)**	1.740 **1.629(2)**	1.60 **1.574(2)**	-	-
$HP(CF_3)_4$ (35)	**1.421(3)**	-	-	2.060(8) 2.038(6) **2.000(2)**	1.910(15) 1.881(7) **1.967(9)** **1.958(1)**

Table 6. *Bond lengths of phosphoranides **3**[35] and **7** compared with **calculated** (DFT B3LYP 6-311+G** level) bond lengths (Å) of phosphoranes **34**, **35**.*

It is interesting to note that the calculated equatorial bonds are longer in phosphorane **35** when compared to equatorial bonds in the corresponding phosphoranide (*Table 6*). The angle between these substituents is also larger in **35** (117.54° vs. 104.42° in **7**) indicating that steric hindrance in the molecule lowers.

Phosphoranide ions are unstable – hypervalent bonds can be easily cleaved and this feature defines the chemical and physicochemical properties of the compounds discussed (*Chapter C3*). Phosphoranes **34** and **35** do not exist; all attempts to synthesize them will surely result in HF and CF_3H formation: However, it is possible to predict the existence of the relatively stable phosphorane $(CF_3)_5P$ with somewhat shortened axial bonds and the angle between the equatorial substituents equal to 120°. Phosphoranes bearing substituents comparable by volume, $(CF_3)_3P(NEt_2)_2$ and $(CF_3)_3P(OMe_2)_2$, have been already mentioned in *Chapter C1*. It is more difficult to evaluate the possibility of a $HP(CF_3)_6$ synthesis, a compound possessing very high acidity and therefore of great scientific and commercial interest as a source of the low coordinating hexakis(trifluoromethyl)phosphate anion[109c]. This derivative should possess four P-CF_3 bonds lying in-plane at an angle of 90°. The known cone angle for CF_3 group is calculated[110] to be 97°. In phosphoranides and phosphoranes where axial and equatorial bonds are of different length, the angle between the substituents could be lower than the cone angle but in $HP(CF_3)_6$ equatorial substituents are located strictly opposite each other and repulsion could be strong. We suggest the hexakis(trifluoromethyl)phosphate anion having four equivalent CF_{3eq} groups to be steric hindered and therefore relatively unstable. The compound may exist at RT and, like trifluoromethylphosphoranes quickly decompose while heating to give fluoro(trifluoromethyl)phosphate ions.

The crystal structures of phosphoranides **31** and **32** are shown in *Figures 13-16.* Both phosphoranide ions exhibit the expected distorted trigonal-bipyramidal coordination of phosphorus with all P-C bonds' being different. Axial bonds (P-C or P-F) are longer than corresponding bonds in PF_3[111] and $P(CF_3)_3$[112] {*1.570(1)Å and 193.017Å correspondingly*}. The angles between two equatorial CF_3 groups are smaller than the CF_3-P-CF_3 angle in phosphine **11** (99.6°) and nearly equal in both the phosphoranides {105.05(1)°÷104.06(2)°} thus, depending on only the substituents' charge and volume.

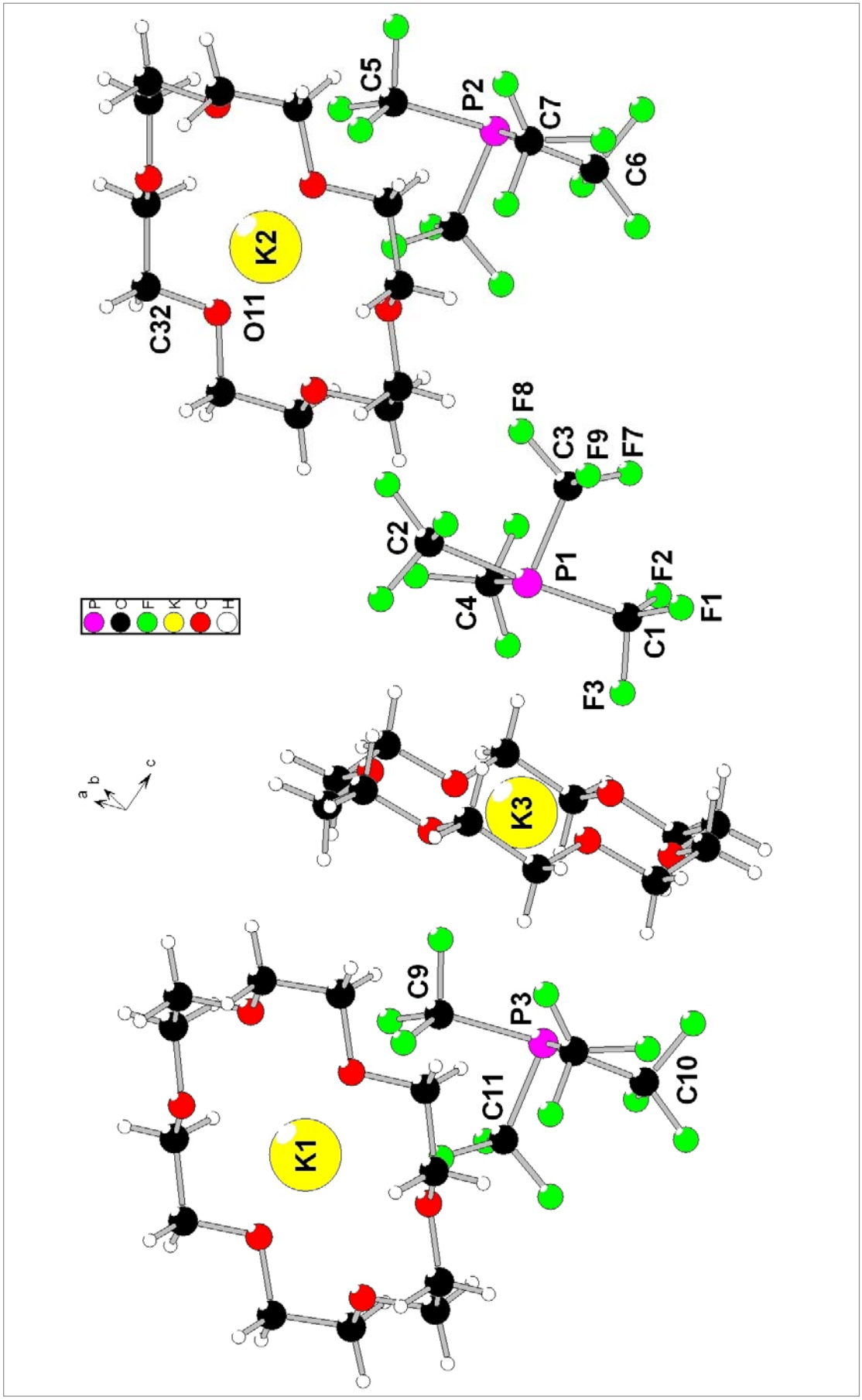


Figure 13 *Molecular structure of phosphoranide* ***32***

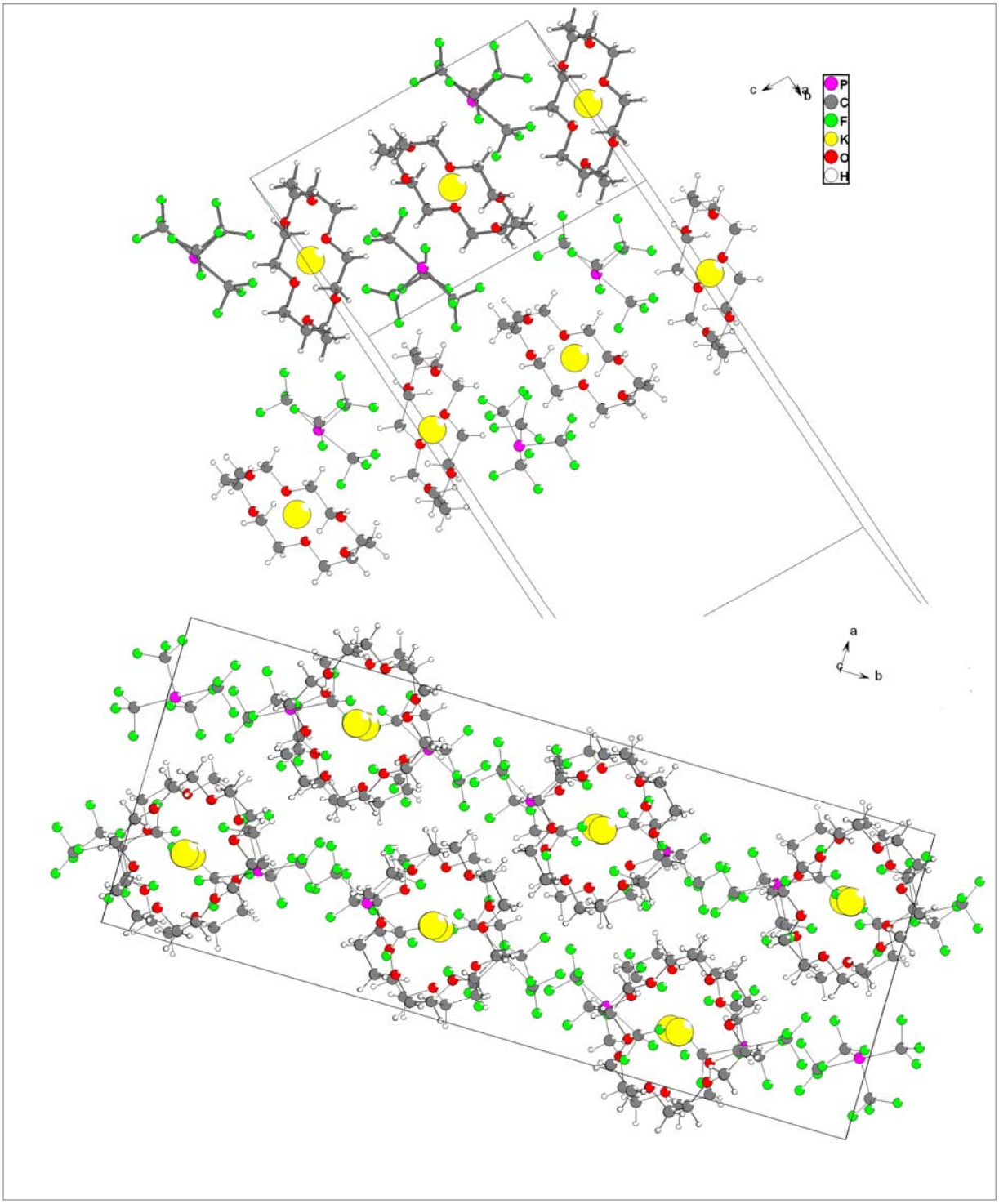


Figure 14 *Partially filled unit cell of **32** (upper picture). Unit cell packing of **32** in the a, b plane (lower picture).*

The comparison with the $(CF_3)_2P^-$ anion structure {P-C bond: 184.0(1)Å, C-P-C angle: 96.9(5)°}[78b] reveals that in the oxidative addition of two CF_3 groups the CPC angle opens by approximately 9° with noticeable P-C bonds' lengthening (13÷22 pm. for axial bonds and 4÷6 pm. for equatorial bonds). The L_{ax}-P-L_{ax} angle in compound **31** {170.47(1)° vs. 174.74(1)°÷176.02(1)° in **32**} is

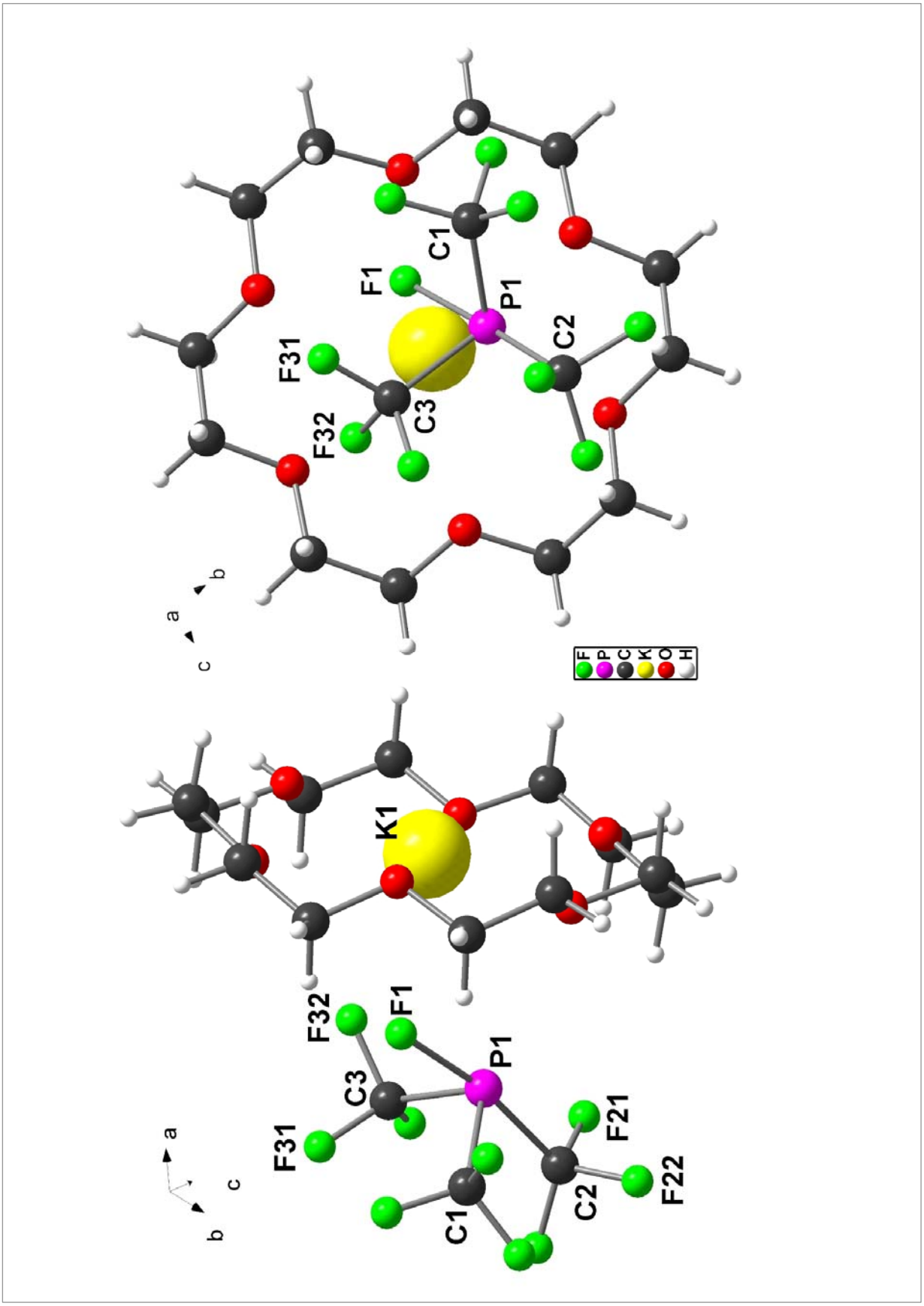
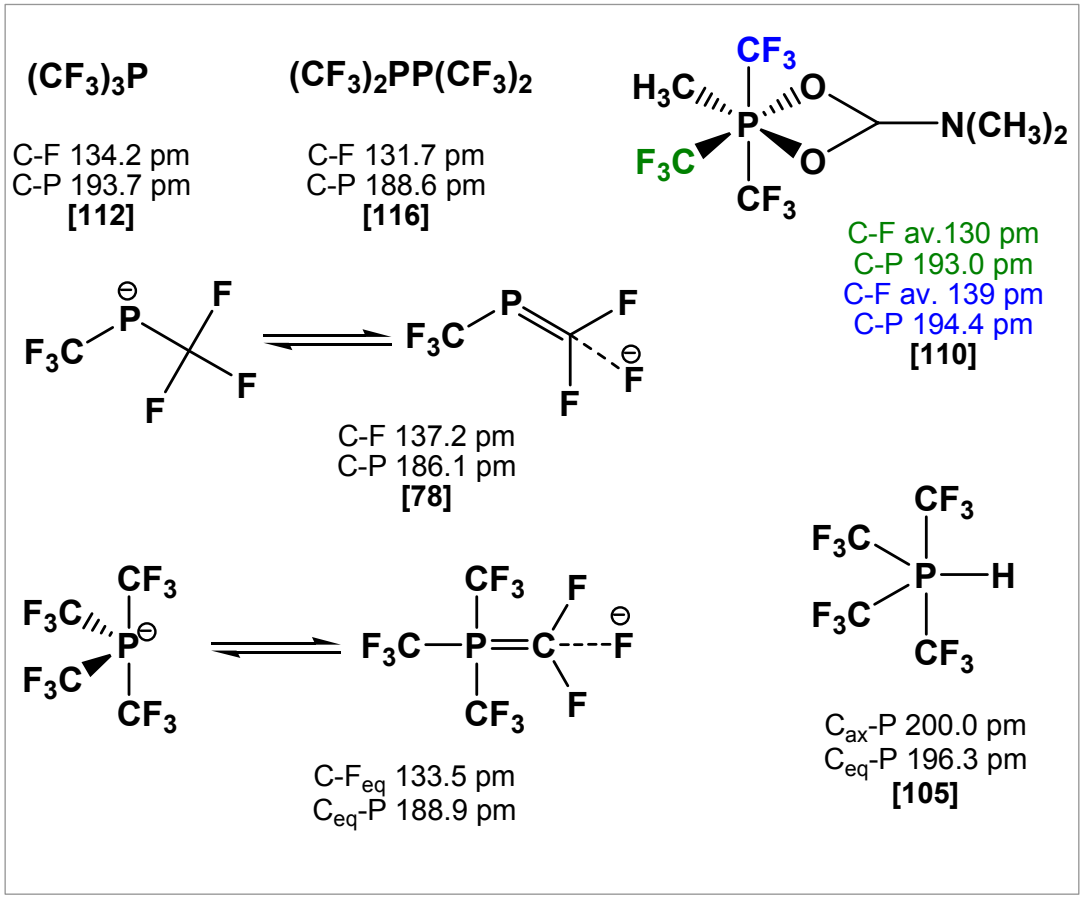


Figure 15 *Molecular structure of phosphoranide **31***

relatively small indicating that repulsion between the phosphorus lone electron pair and F_{ax} is stronger due to the shorter C-F bond and higher charge concentration on F_{ax} as compared with the CF_{3ax} group in **32** and **31**. It is necessary to note that the angle decreasing occurs mainly owing to deviation of the C-F constituent from perpendicular to CF_{3eq}-P-CF_{3eq} plane position since the CF_{3eq}-P-CF_{3ax} angles are approximately equal in both the phosphoranides {90.79(1)° and 89.94(1)° for **31** and on average, 90.7° and 87.5° in **32**}.

Equatorial P-CF_3 bonds in phosphoranides should be discussed separately. As we have already mentioned, they are noticeably shorter, or at least have the same length, than P-C bonds in $(CF_3)_3P$ as well as in $CH_3(CF_3)_3P[O_2CNMe_2]$[110],



Scheme 24

$(CF_3)_4PH$ (*Table 6*) and $(CF_3)_2P$-P$(CF_3)_2$[113] derivatives. The shortening is also accompanied by slight elongation of C-F distances in CF_3 groups which can be attributed to negative hyperconjugation or formulation of additional resonance structures. The effect of hyperconjugation is also established for

bis(trifluoromethyl)phosphanide[78] and trifluoromethoxide[114] anions being suitable examples and the basis for our assumptions (*Scheme 24*).

The axial 3c-4e bond is asymmetric in $F(CF_3)_3P^-$ (the salt **31**) the longest in the array of trifluoromethylphosphoranides P-F_{ax} component {P-F_{ax}= 1.787(14)Å, P-CF_{3ax}= 1.974(17)Å} but the P-CF_{eq} distances are equal. Common confrontation of bond lengths and angles for this derivative allows concluding that the lone pair lies almost in plane with the CF_{3eq} groups. Surprisingly, the hypervalent C-P-C bond in **32** is also asymmetric and P-CF_{3eq} bonds differ significantly {2.060Å and 2.038Å for P-CF_{3ax} components, 1.908Å and 1.880Å for P-CF_{3eq} bonds on average} despite the chemical equivalence of the substituents. In this compound the lone electron pair may be lying out of the CF_{3eq}-P-CF_{3eq} plane towards the more distant CF_{3ax} group and also out of the CF_{3eq}-P-CF_{3eq} plane towards the more distant CF_{3eq} group. An important feature of the molecular structures of the compounds discussed (and of other phosphoranides though exceptions are also known, for instance Br_4P^-[115] and Cl_4P^-[116]) is the bending of the axial groups towards the equatorial ones. This is consistent with large steric requirements of the phosphorus lone electron pair. However, when it is replaced by any not too bulky functional group or hydrogen atom, axial substituents might rearrange against the equatorial ones like in the six-coordinate carbamato complex $CH_3(CF_3)_3P[O_2CNMe_2]$[110] with an angle mentioned being equal to 186.9(4)° or in calculated phosphoranes **34**, **35** (181.72° and 189.16° correspondingly).

The packing in the unit cell in a, b plane for salt **32** is shown in *Figure 14*. The unit cell is formed by zigzag ordered chains {‹P3-P1-P3 = 94.64(1)°} which uniformly fill the cell volume in two rows. Within the cell each chain consists of two potassium centers symmetrically surrounded by the crown ether and two phosphoranide anions with slightly different geometrical parameters. In general, there are three geometrically non equivalent anions (*Figure 13*) distributed with unintelligible system (for example, the sequence of P-indexes in one selected row: P3-P1, P1-P3, P2-P2, P3-). Probably, the discrepancy of geometrical parameters of anions arises from the unique crystal structure.

The packing in the unit cell in a, c plane for salt **31** is shown in *Figure 16*. It is very simple in comparison with that of salt **32** and each cell consists of only two

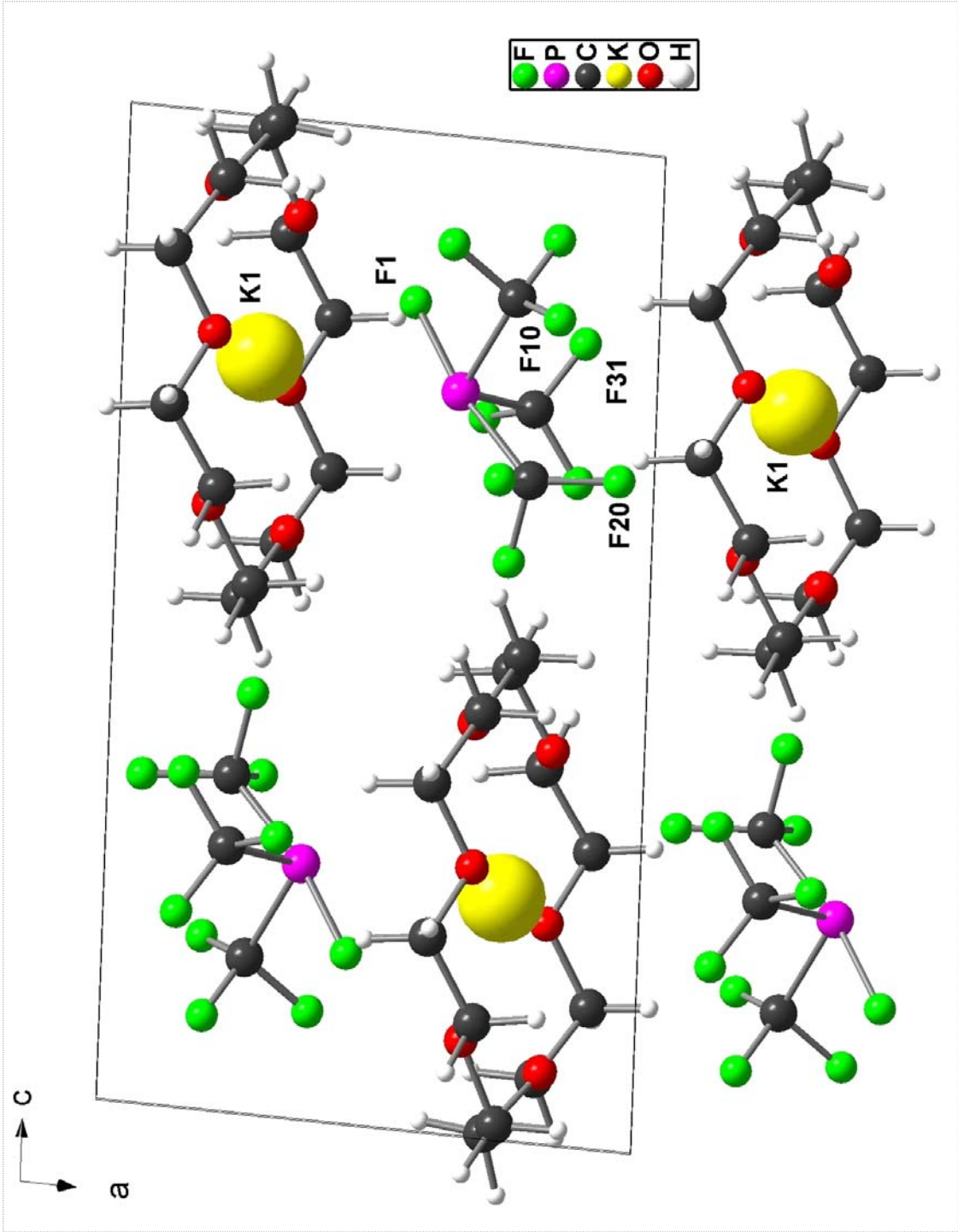


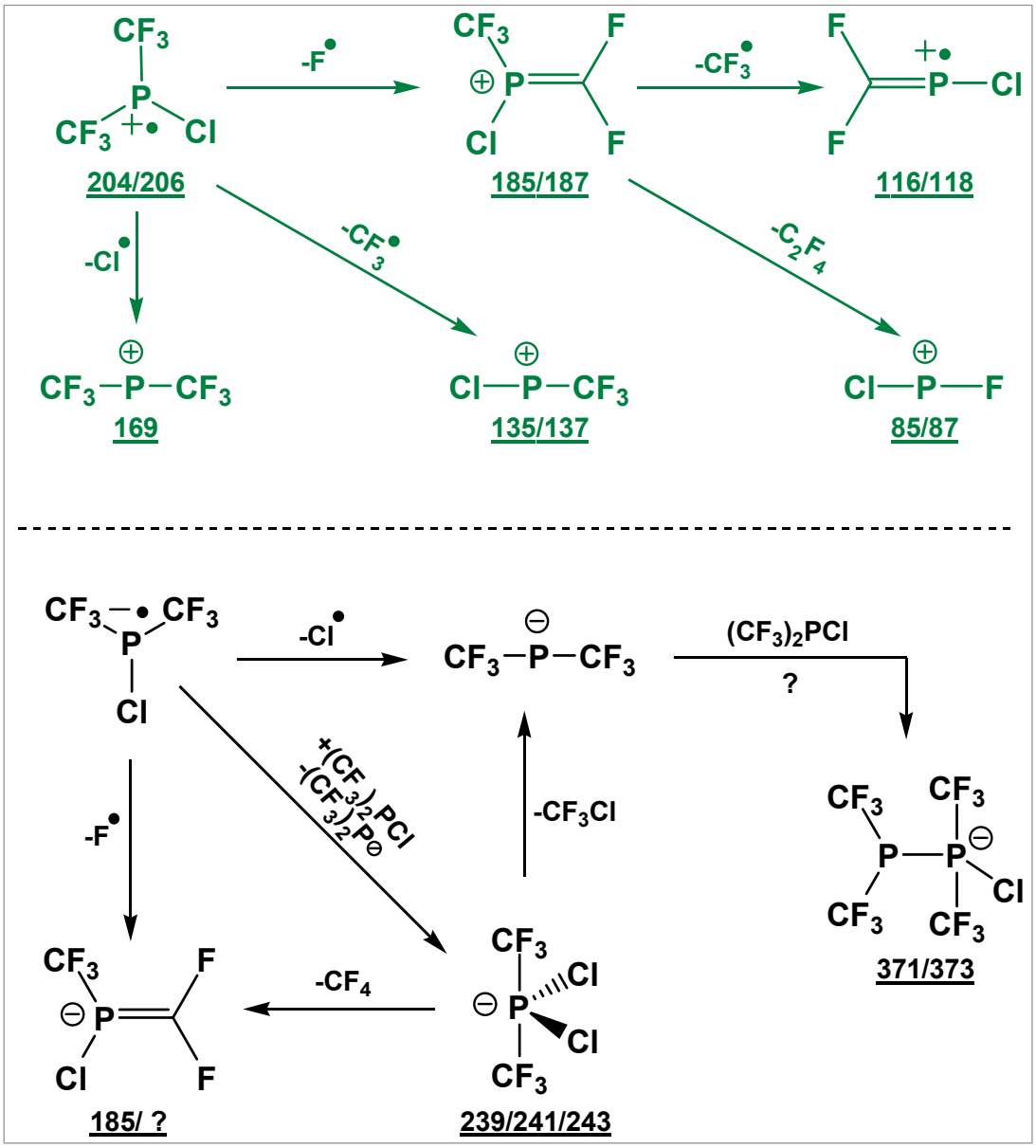
Figure 16

ionic pairs. Generally speaking, in both the molecular structures discussed anions and cations are placed to provide maximal number and shortest distance for F-K contacts (F as single substituent and as part of CF_3 group). The long P-K distance varying in the range of 4.454(3)Å÷5.436(7)Å for **32** and 3.649(9)Å for **31** implies the packing of well isolated ions.

Shortly turning back, we should mention that *ab-initio* calculated and tentatively found (*X-Ray analysis*) geometrical parameters slightly differ. The

reason for this discrepancy is that calculations were performed for TMA^+ salts but experimentally found for (K^+)*18-crown-6 salts.

As it will be shown later, trifluoromethylphosphoranides **31**, **32** and **9** decompose while heating to give starting phosphines and corresponding products. It is also well known that even phosphoranes being more stable compared to phosphoranides, do not show a parent ion in mass spectra[95,117]. Therefore, we expected to obtain the mass spectra of the phosphoranides

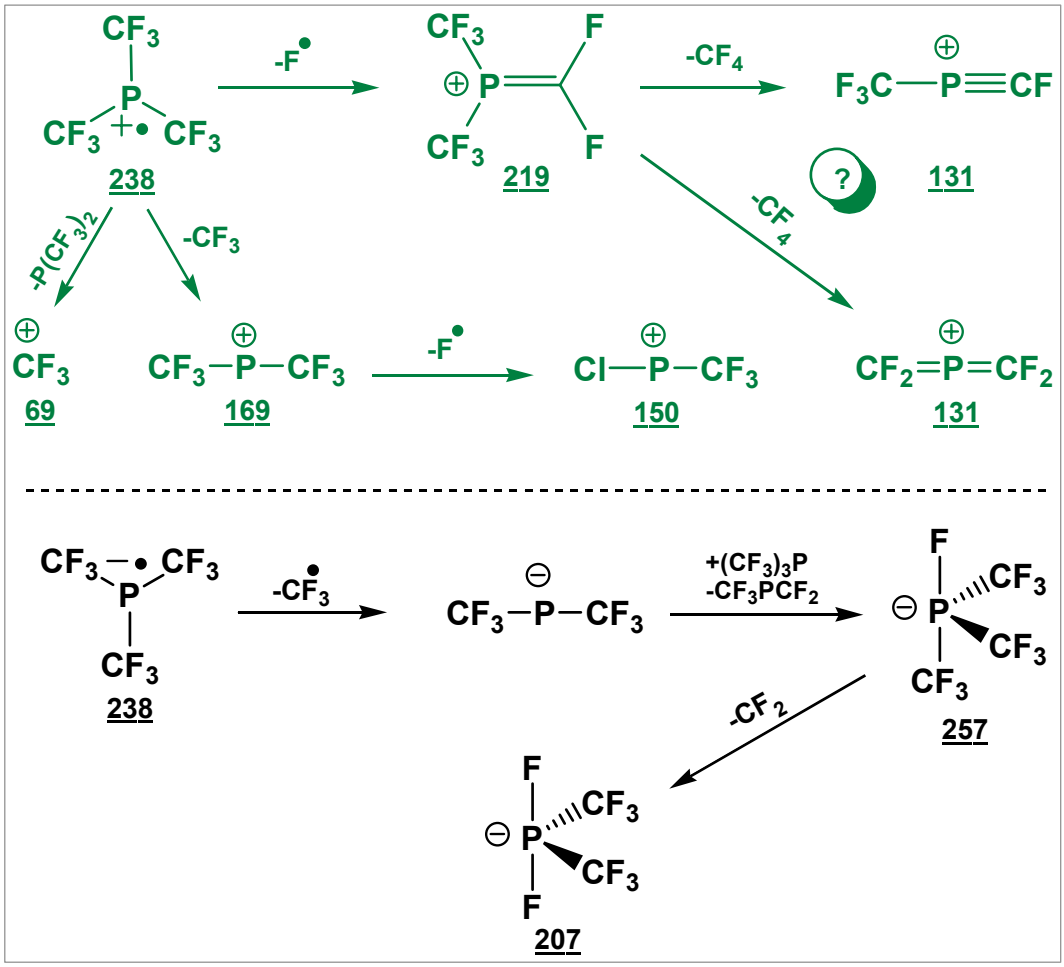


Scheme 25 *Fragmentation routes of the $(CF_3)_2PCl$ cation-radical in **positive** and **negative** modes (only reactions leading to stable fragments are listed, m/z values are given in nominal masses).*

resembling those of precursor phosphines. Relatively stable salts **32** and **8** were taken as the objects of investigation. Unfortunately, instead of expected and explainable signals in the mass spectra we obtained a set of signals of very high m/z (up to 659 m/z; no peaks were detected below m/z 200.8) in the negative mode and intense peak for the cation in the positive mode.

It was decided to carry out the FT-ICR investigations on $(CF_3)_3P$ and $(CF_3)_2PCl$ phosphines, as the precursor for the above discussed condensed phase chemistry. It should be studied, besides a possible formation of phosphonium cations, if the phosphoranide in question can be generated in the gas phase.

In the positive mode both $(CF_3)_2PCl$ and $(CF_3)_3P$ phosphines showed a loss of neutral fragments resulting in the formation of phosphonium ions as the most stable products. $(CF_3)_2PCl$ in both modes preferably yielded the m/z 185/187 ion which contains a PC double bond, $[CF_3P(Cl)=CF_2]^+$ and $[CF_3P(Cl)=CF_2]^-$. Two



Scheme 26 *Fragmentation routes of the $(CF_3)_3P$ cation-radical in **positive** and **negative** modes (only reactions leading to stable fragments are listed, m/z values are given in nominal masses).*

possible structures of the m/z 131 fragment of $(CF_3)_3P$ can be conceived, namely $[CF_3P=CF]^+$ or $[CF_2=P=CF_2]^+$. In solution these compounds show a different behavior e.g. phosphaalkynes for which a number of addition and cycloaddition reactions are reported[118]. For the anion, the loss of Cl is more prominent than in the positive mode, possibly due to the –I effect of the two CF_3 groups; the Cl adduct seems to be an intermediate m/z 187 could not be resolved. In addition there are a number of peaks at m/z values higher than the molecular ion that could not yet be correlated with any reasonable structure. Rearrangement reactions of fragments obviously are less important compared to $(CF_3)_3P$. Both compounds in the negative mode show halide transfer reactions to neutral molecules, yielding the phosphoranides $[(CF_3)_2PCl_2]^-$ and $[(CF_3)_3PF]^-$. The $(CF_3)_3P$ anion, under normal conditions only yields the M-CF_3 (m/z 169) fragment, which has to be accelerated during the reaction delay to obtain a larger number of collision with neutrals in order to produce the M+ F^- adduct. $(CF_3)_2PCl$ also reacts by forming a P-P bond resulting in the formation of a diphosphane anion, $[(CF_3)_2P\text{-}P(CF_3)_2Cl]^-$.

C2.3. Chemical properties of trifluoromethylfluorophosphoranide salts.

All the trifluoromethyl phosphoranides discussed are thermally unstable and very reactive species. Their chemical and structural properties are clearly defined by theirs hypervalent nature namely by significant elongation of axial 3c-4e bond as well as by a low (lowest in the array of hypervalent P-compounds) coordination number of the phosphorus centre.

Outward appearance and melting points.

The phosphoranide salts could be isolated from reaction mixtures as white (usually $[K^+]$*18-crown-6 etherates) either slightly yellow or cream-colored (TMA salts) powders sensitive to moisture and atmospheric oxygen spontaneously igniting probably due to elision of starting phosphines. Pure samples showed sufficient stability in vacuum however drying powders at reduced temperatures (0 ÷ -30ºC) allowed to obtain analytically pure compounds whereas powders dried at room temperature contained traces of fluorine containing impurities.

The phosphoranides do not have sharp melting points and for all the compounds decomposition precedes liquefying. The exact dependence of the decomposition temperature on the number of trifluoromethyl groups at phosphorus was found and the higher that number the lower the decomposition temperature. The nature of the cation was of large importance for the stability of phosphoranides not only in solution as it was discussed above, but also in the solid state. The unique instability of TMA salt **8** initially presumed to be the exception concerning only the tetrakis(trifluoromethyl) derivative turned out to be a rule for all the TMA salts. As one can see from *Table 7*, the TMA salts start to decompose and then to melt at lower temperature than the corresponding $[K^+]$*18-crown-6 etherates. Pyrolysis carried out in evacuated but closed tubes (under static vacuum), showed the same dependence giving mixtures consisting of PF_3, $(CF_3)_3P$, CF_3H and Me_3N. It should be noted that decomposition occurs before melting. Black solid usually remained in tubes which could be warmed up till red heat without significant loss of mass and is not soluble in most used

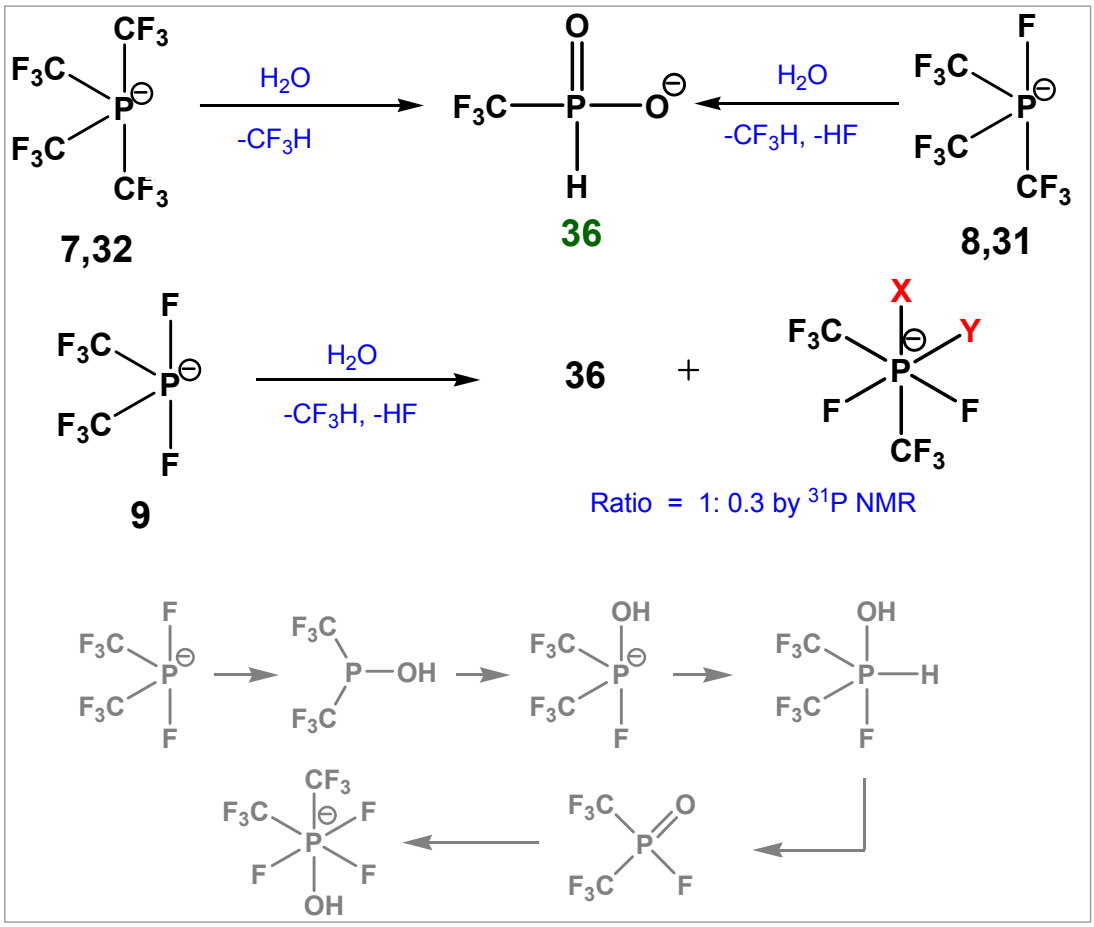
deuterated solvents. It was carbon - the black solid which had always formed during burning phosphine **11** in air but rather unexpected in this case since it was known[50] that the phosphine could be synthesized by direct reaction between white phosphorus and CF_3I at 220ºC therefore the temperature of pyrolysis was not sufficient to cause complete decomposition of **11**. Pyrolysis of $[K^+]$*18-crown-6 etherates under the same conditions led to formation of predominantly phosphine **11** and only negligible amounts of PF_3 and CF_3H. The possible route of the decomposition has been already discussed (*vide supra*, *Scheme 22*) and data obtained while investigating the stability of other phosphoranides seem to be in line with the mechanism supposed.

Temperature ºC / Phosphoranide	Decomposition	Melting point	Pyrolysis	Main products of pyrolysis
$(CF_3)_4P\ NMe_4$ **7**	60	93 (with gas evolution)	RT÷53 (spontaneously, explosion)	PF_3, CF_3H, Me_3N
$(CF_3)_3PF\ NMe_4$ **8**	108	127-129 (with gas evolution)	104 (explosion)	PF_3, $(CF_3)_3P$, CF_3H, Me_3N
$(CF_3)_2PF_2\ NMe_4$ **9**	82	172 (gas evolution at 184)	84÷90 (spontaneously, explosion)	PF_3, CF_3H, Me_3N
$(CF_3)_4P$ $[K^+]$*18-crown-6 **32**	110	140-144 (with gas evolution)	138-142	$(CF_3)_3P$
$(CF_3)_3PF$ $[K^+]$*18-crown-6 **31**	138 (becomes slightly yellow)	147 (gas evolution and rapid darkening at 157)	160	$(CF_3)_3P$

Table 7

Hydrolysis.

Fast hydrolysis of the phosphoranides occurs in wet monoglyme (MG/H_2O = 15/1) to give $CF_3P(H)(O)O^-\ Q^+$ salt (**36**) as the only (for compounds **7**,**8**,**32**,**31**) or main (for derivative **9**, *Scheme 26*) product. Salts **8** and **31** hydrolyze somewhat slower than salts **7** and **32**. It is clear that here occurs basic hydrolysis since fluoride ion, a rather strong base is present in solution. Formation of the salt **36** supports this because of the high stability of $(CF_3)_3P$ to hydrolysis in acidic or neutral media revealed. In the case of tetrakis(trifluoromethyl)phosphoranide

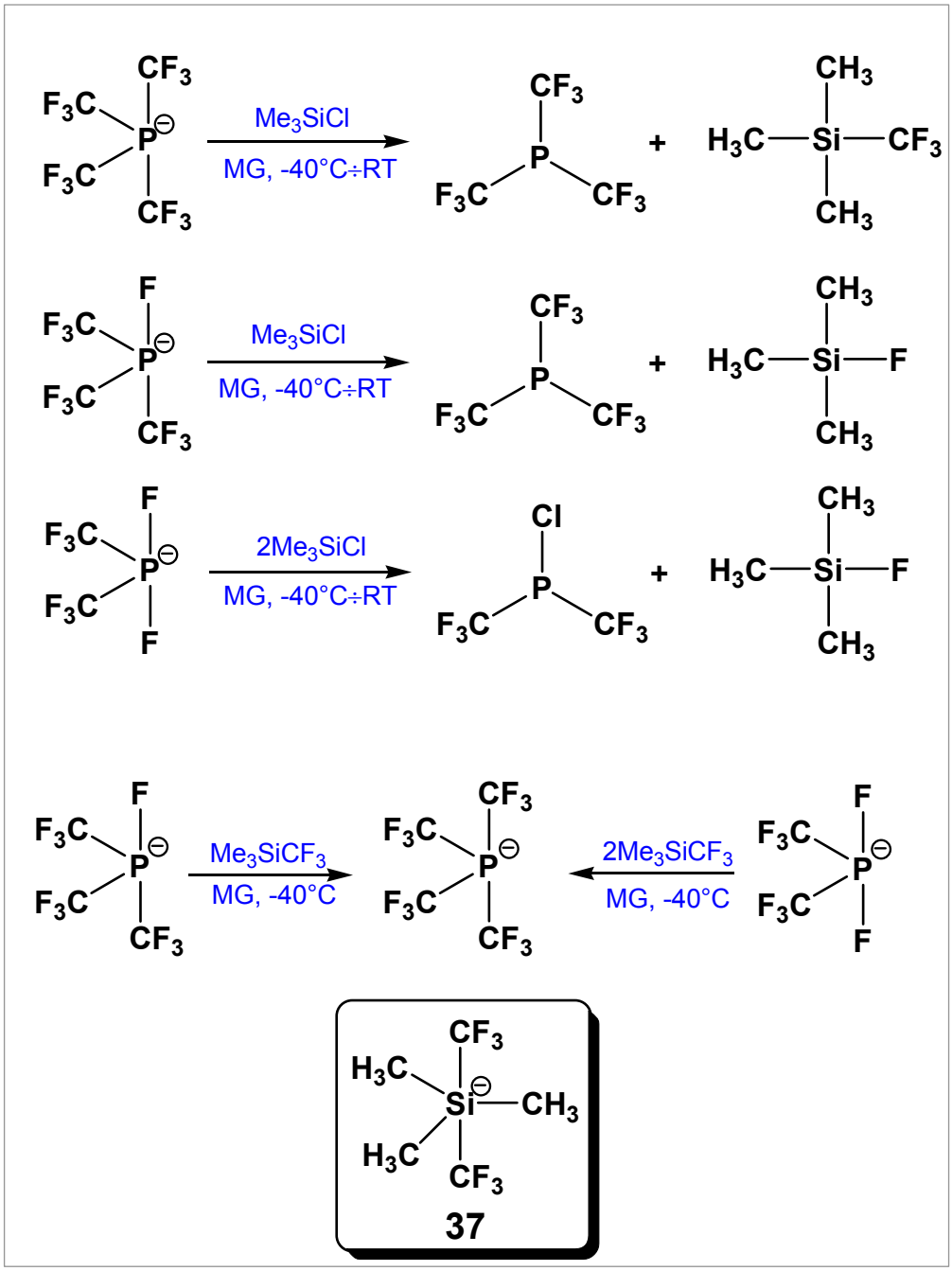


Scheme 26

salts the fluoride ion is surely a product of the trifluoromethyl anion decomposition and the intensity of signals corresponding to CF_3H in ^{19}F NMR spectra of all the phosphoranides are always lower than expected. Further transformation of salt **36** occurred very slowly but addition of several drops of aqueous NaOH to the samples resulted in fast and complete hydrolysis to give $P(OH)_3$ and CF_3H quantitatively. Unexpectedly, signals of a new six-coordinate phosphorus compound were observed in the spectra after hydrolysis of salt **9**. Despite the relative simplicity of ^{31}P and ^{19}F NMR spectra it proved to be very difficult to correlate all signals and to suppose a structure for this compound. We can only state that the compound is six-coordinate and possess two nonequivalent trifluoromethyl groups as well as two types of fluorine atoms (or probably the mixture of two isomers; one of the most likely candidates is $[(CF_3)_2P(OH)F_3]^-$ ion). The nature of other substituents and mechanism of this species' formation are still hazy. Unfortunately, small quantity of the substance did not allow us to characterize it completely.

Reactivity.

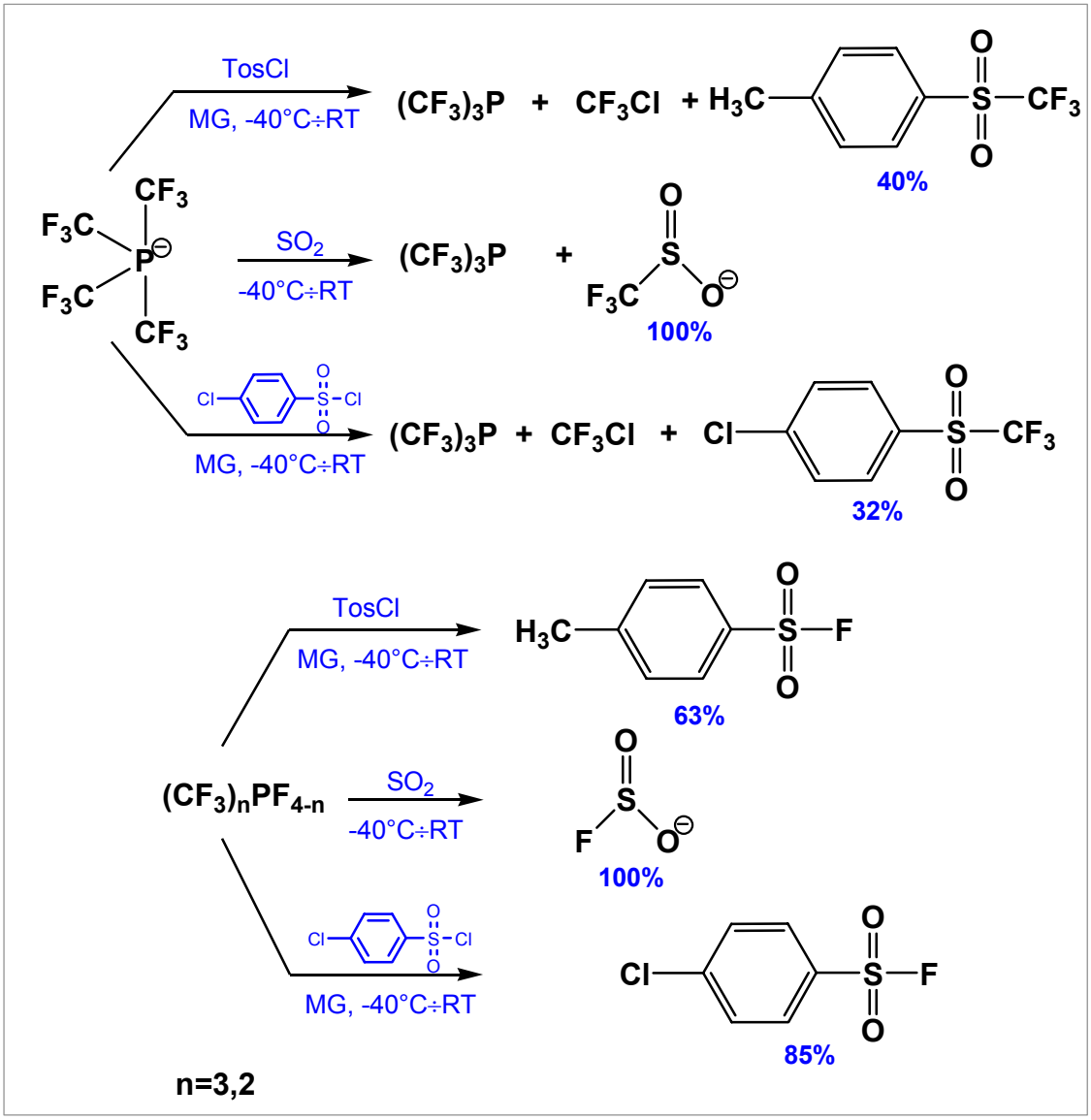
Most of the reactions described in the literature concern cyclic organophosphoranides or mixed-valence compounds and comparatively few have been reported for halogeno or pseudohalogeno derivatives. In their turn, the reactions reported predominantly demonstrate the nucleophilic properties of phosphoranides, their oxidation and action as ligands in metal complexes[24]. However, trifluoromethylphosphoranides are inclined to lose an apical ligand which reacts successively with an electrophile. Nucleophilic substitution is limited



Scheme 27

for phosphoranides to a few examples only. Like nonfluorinated analogs trifluoromethylphosphoranides can be relatively easily oxidized.

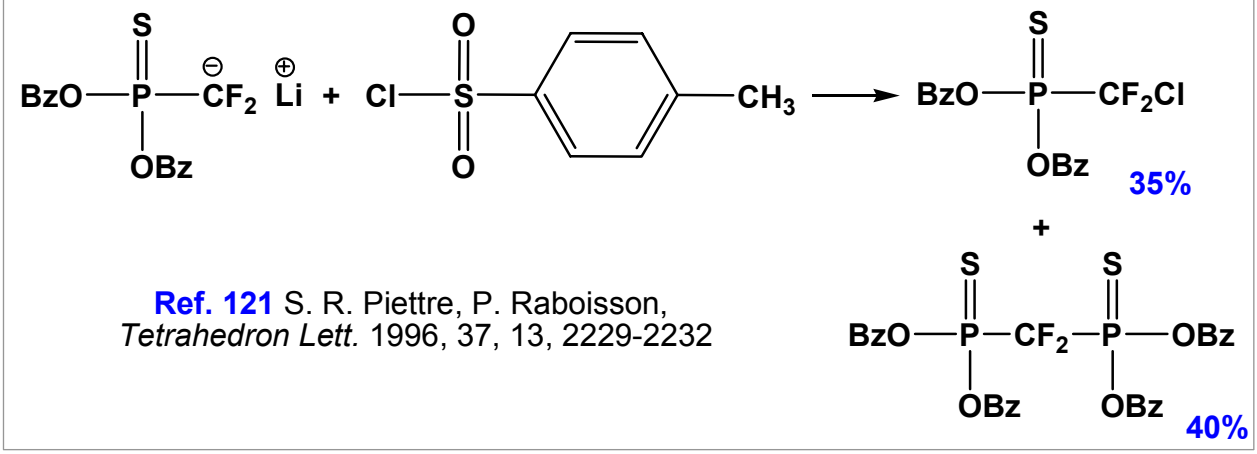
As it has been already mentioned, tetrakis(trifluoromethyl)phosphoranide salts **7**, **32** usually act as trifluoromethylating agents and parallel to this, tris(trifluoromethyl)fluoro- and bis(trifluoromethyl)difluorophosphoranide salts **8**, **9**, **31** act as fluorinating agents. Thus, in reaction of these hypervalent species with Me_3SiCl the corresponding silicon derivatives were obtained. The reactions occur quantitatively and fast while warming up to RT (*Scheme 27*). Rather unexpected was the detection of $(CF_3)_2PCl$ in the case of taking the starting silane in excess. We were able to observe mixed F-Cl phosphoranide formation which can also be a fluoride ion donor and force the formation of Me_3SiF. When



Scheme 28 *Reactions of the phosphoranides with S-electrophiles. Only fluorine containing products and by-products are shown*

the reagents were taken in a 1:1 ratio (salt **9** : Me_3SiCl) this phosphoranide $[(CF_3)_2PFCl]^-$ TMA^+ (**10B**)] was isolated quantitatively. Here insufficient Lewis acidity of phosphine **11** to give $[(CF_3)_3PCl]^-$ ion should be noted.

Especially important for us was the information about the reactivity of the phosphoranides towards Ruppert reagent. Having obtained an explosive compound while synthesizing the salt **7**, we thought that the reason of such behaviour could be the formation of the highly unstable hypervalent ion **37** first obtained and described by Kolomeitsev and coworkers[119]. However, no reaction was detected between the salt **7** and the reagent up to RT but only a weak stabilizing effect of Me_3SiCF_3 resulting in longer lifetime of the phosphoranide in solution. As expected the salts **8** and **9** quantitatively produce the completely characterized hypervalent anion **7** in the reaction discussed.

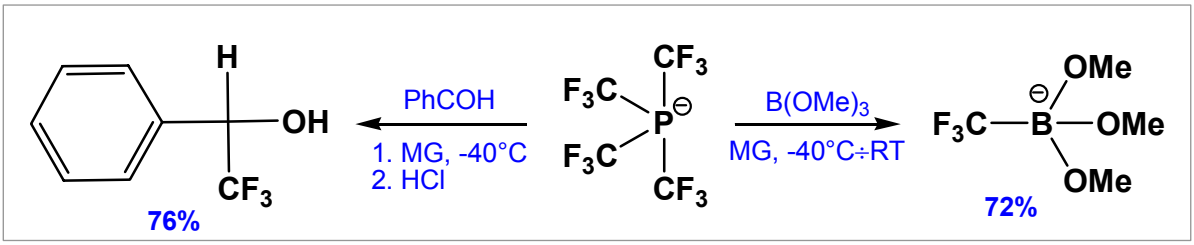


Ref. 121 S. R. Piettre, P. Raboisson, *Tetrahedron Lett.* 1996, 37, 13, 2229-2232

Scheme 29

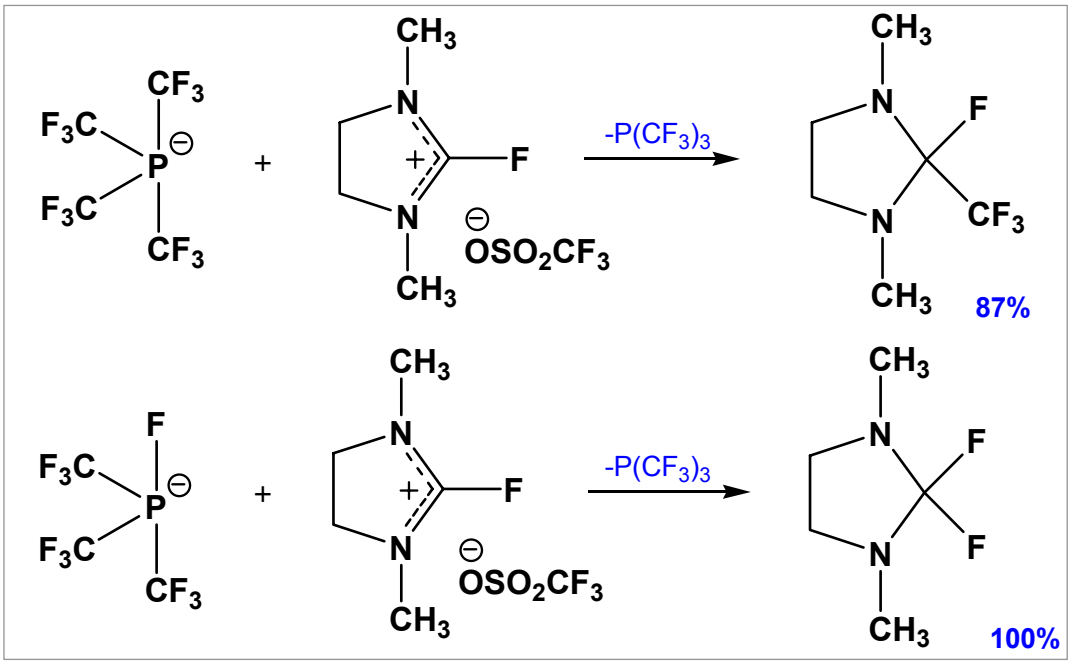
Reactions of the title phosphoranides with sulfur dioxide and tosyl chloride or 4-chlorobenzene-1-sulfonyl chloride led to the formation of a set of expected and unexpected products (*Scheme 28*). Reactions of the first two reagents with the salts **7**, **32** are complicated by the nucleophilic substitution of the aryl group in sulfonyl chlorides by the trifluoromethyl anion leading to CF_3Cl (δ = -29.7, lit.[120]: -33) and corresponding sulfinate ion. The chemical interaction occurs nearly quantitatively to give CF_3Cl while rapid warming up from -60ºC to RT but in the case of warming up during several hours trifluoromethylsulfonyl derivatives were obtained in low yield together with not yet identified fluorinated phosphorus compounds. As one can note the more electrophilic 4-chlorobenzene-1-sulfonyl

chloride exhibits a more pronounced tendency to halogenophilic reactions in comparison to tosyl chloride. We found that such a process had been already described in the literature (*Scheme 29*) and in the case reported no target compound but only side products were obtained. The sulfonyl chlorides also react with fluoride ion donors - the salts **8**, **31** and **9** to give sulfonyl fluorides and not identified six-coordinate phosphorus compounds in all the cases. For tosyl chloride the yield of the product is lower probably due to the acidic character of the methyl protons which could be abstracted by fluoride to give higher contents of by-products. Two moles of sulfonyl chloride per one mole of the salt **9** were taken and again formation of $(CF_3)_2PCl$ was detected. Reactions of trifluoromethyl phosphoranides with sulfur dioxide proceed smoothly and quantitatively with SO_2 serving both as a reagent and as a solvent. A clear 1:3 ratio of signals was observed in the ^{19}F NMR spectra of the reaction mixture obtained after condensing SO_2 to the salt **7** or **32**. As expected, no signals in the ^{19}F NMR spectra were observed in liquid SO_2 except those which correspond to phosphine **11** in the case of using the salts **8**, **31** or **9** as substrates. This happens due to very rapid intermolecular fluoride ion interchange[122]. Careful removing all the volatiles from the reaction mixtures gave a light brown or creamy solid which after dissolving in acetonitrile revealed a singlet at 103 ppm (lit.[122]: 103.3 ppm). Contrary to $(CF_3)_3P$, signals in the NMR spectra corresponding to $(CF_3)_2PF$ were distorted in liquid SO_2 therefore we even supposed the formation of a new product. However, proper chemical shifts were revealed after carrying out the reaction in monoglyme though excess of SO_2 was also taken. An analogous problem also was met in the case of measuring the spectra of the phosphorane $(CF_3)_3PF_2$ in SO_2 probably caused by solvation effects (*vide infra*).



Scheme 30

Tetrakis(trifluoromethyl)phosphoranides also react with boronic acid esters and aldehydes to give trifluoromethylated products in high yields. Examples of these reactions are shown on the *Scheme 30*. Trifluoromethane is the main by-product revealed.



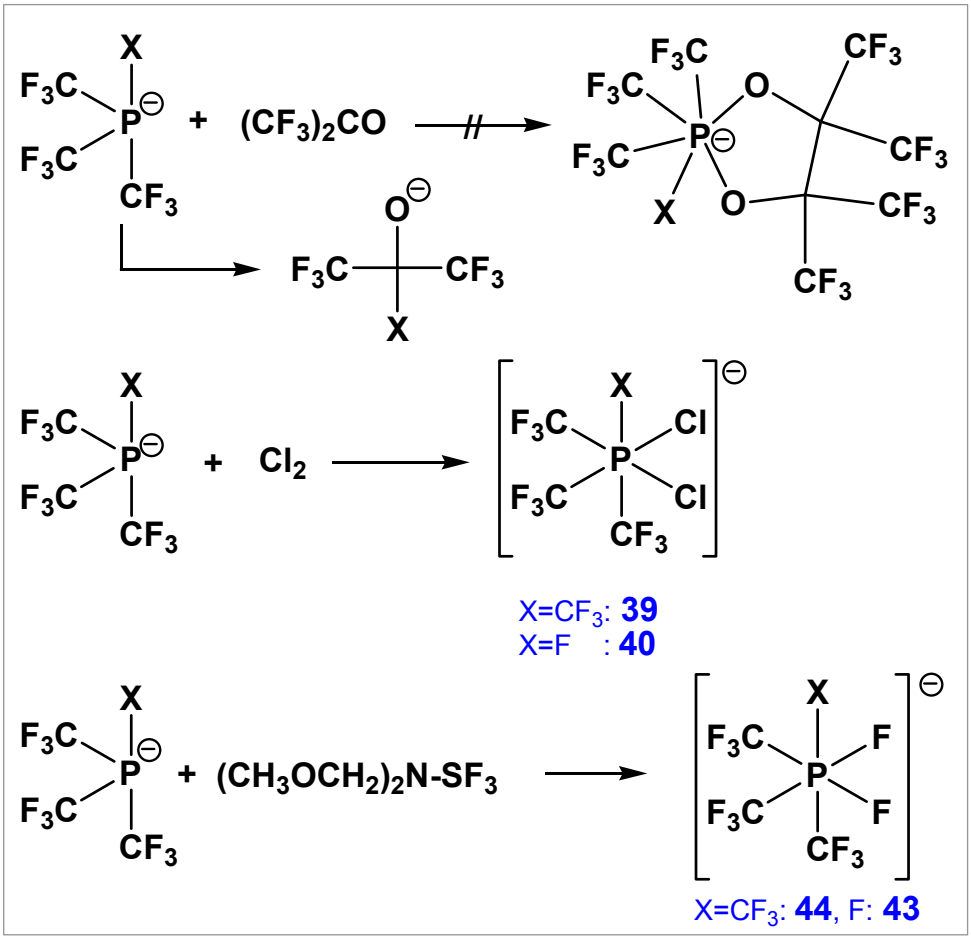
Scheme 31

Since no reaction was detected between $(CF_3)_3P$ and DFI leading to formation of perphosphoranide (see the *Chapter C5*) it was interesting for us to investigate the reactivity of the phosphoranides towards this fluorinating agent. No reaction but only decomposition products of phosphoranides and DFI itself were identified in the direct reaction in monoglyme. Fluorine atoms are covalently (covalent constituent of the bond prevails over ionic one) bound to carbon in DFI and even in polar media it exists as very tight ionic pair revealing a broad singlet in NMR spectra. Hence the result obtained was expected. However, its triflic salt was quickly trifluoromethylated[123] or even fluorinated by phosphoranides **32** and **31** (*Scheme 31*). The 2-fluoro-1,3-dimethylimidazolidinium cation proved to be a stronger fluoride ion acceptor than phosphine **11** and this fact may help to understand why perphosphoranide **38** had not been obtained, as well as, the moderate fluorinating power of DFI.

Attempts to oxidize the trifluoromethylphosphoranide ions by HFA failed. Instead of a six-coordinate compound a stable product of a trifluoromethyl group

or fluoride ion addition to HFA was isolated. But we managed to oxidize the phosphoranides using elemental chlorine or bis(2-methoxyethyl)aminosulfur trifluoride (Deoxo-Fluor™; *Scheme 31*). In all the cases the reaction occurs at low temperature in high yields. $[(CF_3)_4PCl_2]^-$ TMA^+ **39** was isolated as an individual compound; however, $[(CF_3)_3PCl_2F]^-$ TMA^+ **40** was obtained as a mixture of at least three isomers. As it will be shown later, the whole array of trifluoromethylphosphate ions obtained exhibit high thermal stability and usually only one intensive peak for each compound corresponding to the molecular ion can be observed in the MS spectra, what allowed us to unambiguously prove the molecular composition of this species. Despite the complexity of NMR spectra of the salt **40** it's MS spectrum was quite simple and ease to interprete.

Chlorination of the compounds mentioned should be carried out carefully with a stochiometric amount of chlorine. Excess of the oxidizer causes formation

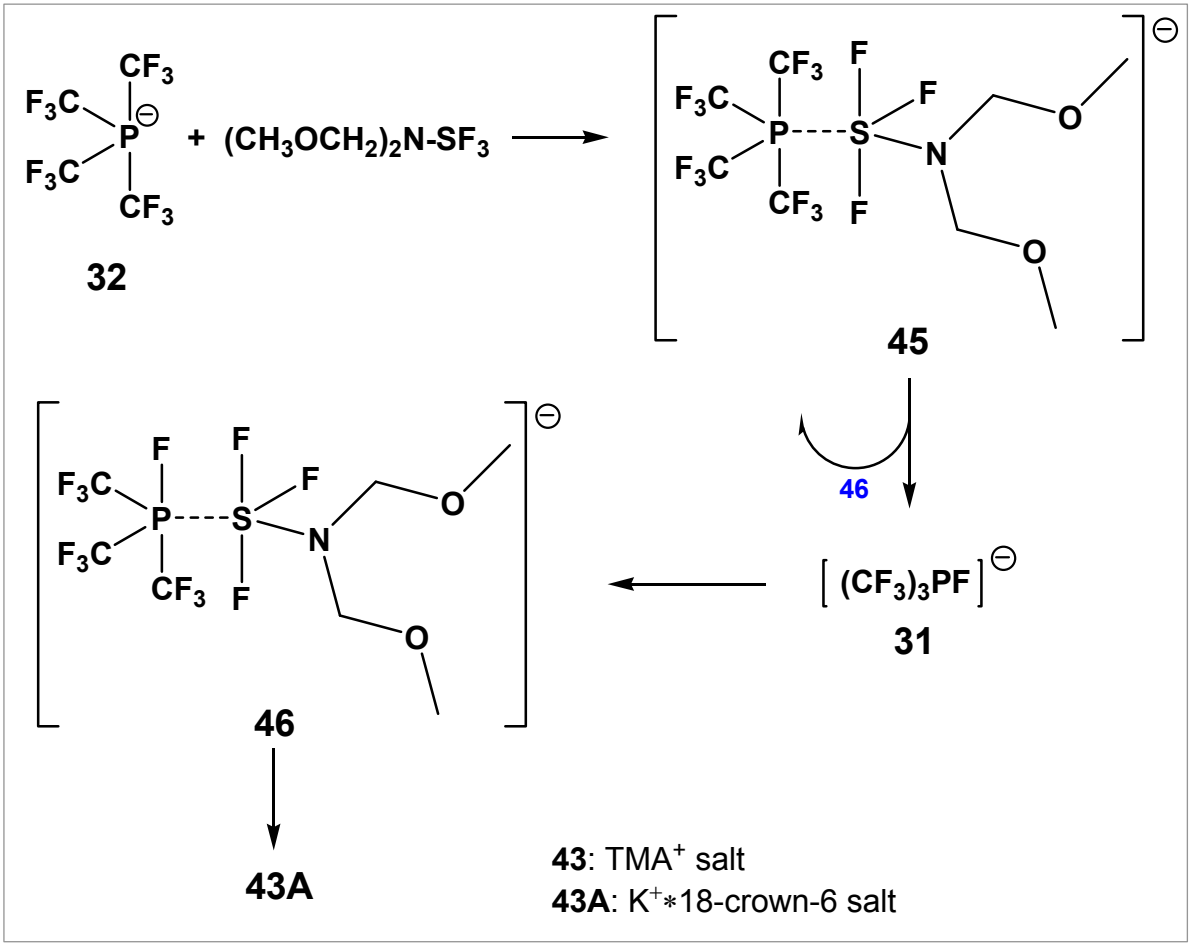


Scheme 32

of a mixture consisting of different phosphate salts poorly soluble in frequently used organic solvents. However, even in the case of exact dosage of chlorine and low reaction temperature small amounts of by-products are also formed and identified by NMR spectroscopy and MS spectrometry. The salt **39** has always comprised 7÷10 of phosphate $[(CF_3)_3PCl_3]^-$ TMA^+ (**41**) and the salt **40** comprised approx. 5÷15% of phosphate $[(CF_3)_3PF_2Cl]^-$ TMA^+ (**42**) which could be considered to be a disproportionation product.

Oxidation by Deoxo-Fluor™ requires excess of reagent and surprisingly, starting from both the phosphoranides **7** and **8** the same product – $[(CF_3)_3PF_3]^-$ TMA^+ (**43**) was obtained. Taking the oxidizer in equimolar amount to the phosphoranide salt led to formation of a solid complex stable even while short-term heating to 60ºC. Addition of an extramolar portion of Deoxo-Fluor™ led to rapid dissolution of the precipitate and formation of the final phosphate salt.

Only 21% (79% - salt **43A**) of expected $[(CF_3)_4PF_2]^-$ $[K^+]$*18-crown-6 salt (**44**) were isolated after slow warming the mixture consisting of



Scheme 33

tetrakis(trifluoromethylphosphoranide and Deoxo-Fluor™ from -50ºC till RT overnight. During this process, bis(methoxymethyl)aminosulfur trifluoride is seemingly trifluoromethylated by the phosphoranide with following fluoride elision. As intermediate, a CTC complex (**45)** is formed which decompose in time to give $[(CF_3)_3PF]^-$ and $(CH_3OCH_2N)_2S(CF_3)F_2$ (**46**) not isolated but detected by ^{19}F NMR spectrometry (3.82 ppm (q.), -67.4 ppm (t.), J = 18.1 Hz – good correlation with that described in literature[124] for $CF_3SF_2(CH_3)_2$: -1.8 ppm (br. s.), -63.9 ppm (t.), J = 12.4 Hz). In its turn, tris(trifluoromethyl)fluorophosphoranide formed is slowly oxidized by excess of Deoxo-Fluor™ to give the final product (*Scheme 33*). On this stage formation of CTC may be also postulated (derivative **46**).

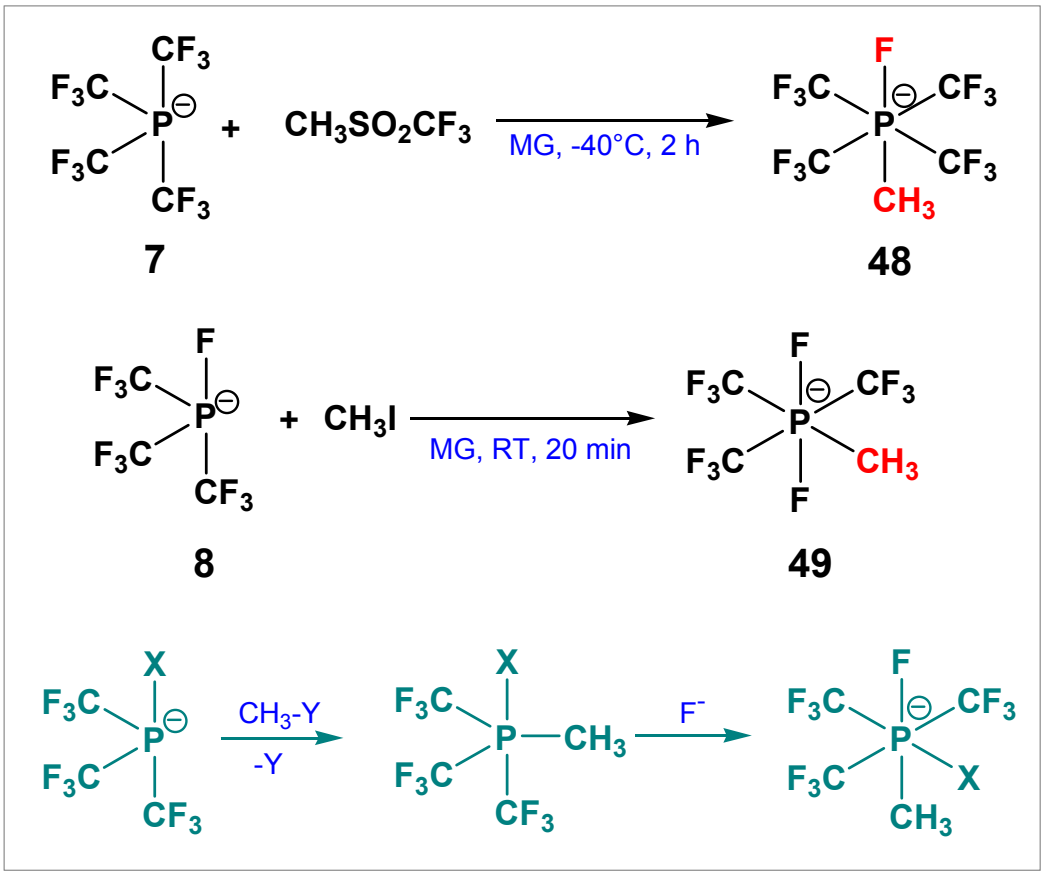
Summarizing these data we can assume that tris(trifluoromethyl)fluoro-phosphoranides are readily oxidized by bis(methoxymethyl)aminosulfur trifluoride while tetrakis(trifluoromethyl)phosphoranides tend to replace one trifluoromethyl group by fluorine under the influence of the reagent mentioned and the real oxidation process occurs to a much smaller extent than it could be expected. Despite the low yield of **44**, this phosphate salt was fully characterized by multinuclear NMR. A previous method of its generation[125] described by Chan and Willis did not allow to obtain acceptable results. They only stated the fact of this species' formation starting from the comparative analysis of a set of IR spectra measured for an array of trifluoromethylphosphate salts.

Successive oxidation of the phosphoranides stimulated us to investigate the possibility of lone electron pair alkylation. It is known[126] that phosphine **11** can be alkylated by using very strong alkylating agent[127] – $MeOSO^+$ AsF_6^-. Phosphoranide molecules are negatively charged therefore it was supposed that their alkylation should occur easier. The only question stayed opened – what would be alkylated: the phosphoranide itself or its detaching ligand?

It was reported previously that derivative **7** reacted with methyl triflate to give only 1,1,1-trifluoroethane **47** (*Scheme 7*). Taking this into account we attempted to alkylate the phosphoranide salt with methyl iodide - a not too strong alkylating agent. The philosophy of this attempt was to lower the possible steric hindrances in the transitional state and to detect highly coordinate derivatives. The reaction

started at approximately 0ºC but its rate became noticeable only at RT and again, presumably compound **47** was formed in equimolar ratio to phosphine **11**. However, additional signals of relatively high intensity were observed in the spectra. The analysis of the ^{31}P NMR spectrum (after 100000 scans; 36 h at RT) showed the presence of five- and six-coordinate phosphorus species in the reaction mixture and at least two compounds of each coordination number. The intensities of signals corresponding to phosphine **11** and the sum of other compounds are comparable (1:{0.16+0.52}).

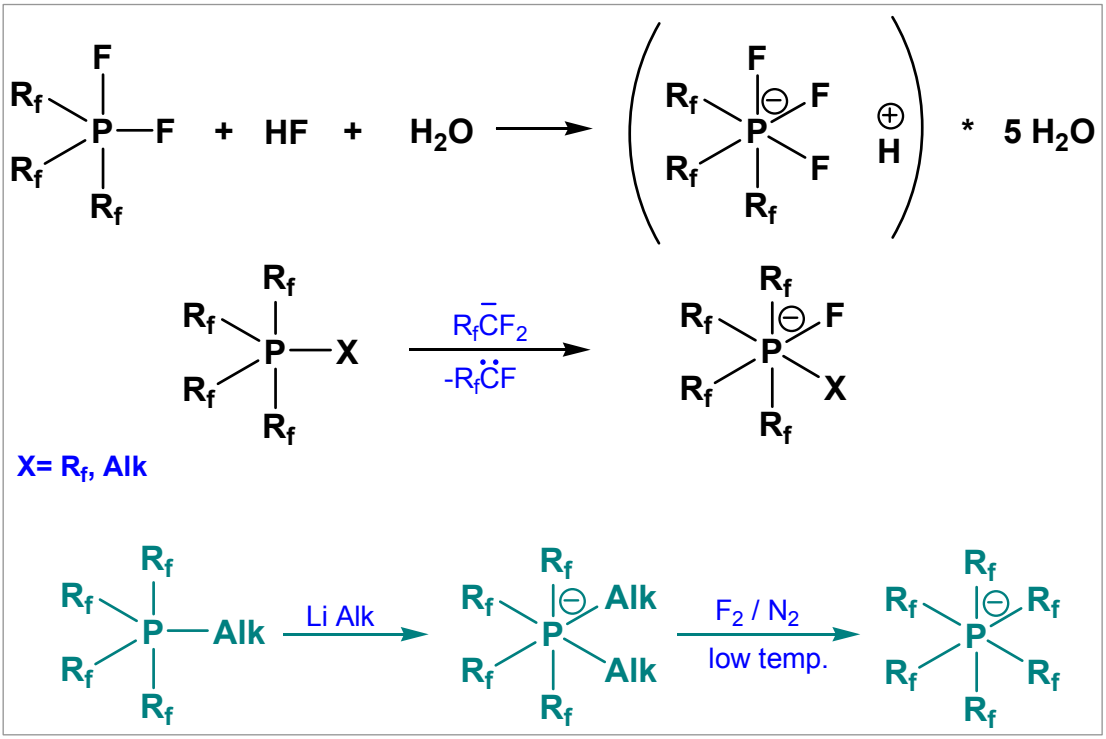
Since it was difficult to make a definite conclusion about the nature of the reaction products in this case due to complexity of the spectral data we decided to turn back to methyl triflate and reinvestigate this process thoroughly. We hoped that higher reactivity of the reagent would allow carrying out the reaction at lower temperature in order to prevent the possible thermal decomposition of intermediates and products generated. The increased reactivity of the methylating agent had played a decisive role and analytically pure



Scheme 34

$[(CF_3)_4P(CH_3)F]^-$ TMA^+ (**48**) was isolated in 52% yield. 1,1,1-trifluoroethane – the only byproduct of the reaction, was detected by NMR. The reaction conditions were not optimized and probably higher yield might be accessible but nevertheless, this result was in striking contrast with that presented in *Scheme 7*. It should be noted that raising the reaction temperature had negative consequences – the mixture turned black while slow warming up to RT overnight albeit the salt **48** could be identified by NMR spectrometry. Phosphoranide **8** was also successfully methylated and surprisingly, methylation occurred fast and quantitatively at RT by using methyl iodide to give corresponding $[(CF_3)_3P(CH_3)F_2]^-$ TMA^+ phosphate (**49**, *Scheme 34*).

The formation of phosphate ions but not trifluoromethylmethylphosphoranes was prognosed. Knowing that phosphoranides often act as X-ligand donor (X = CF_3, F), we could predict it's abstraction from the phosphoranide molecule by the very electrophilic phosphorane formed intermediately. Thus, two molecules of phosphoranide produce one molecule of phosphate and one molecule of phosphine **11**. High steric hindrance makes the second stage of the process very sensitive towards the bulkiness of the entering ligand. Four sterically demanding

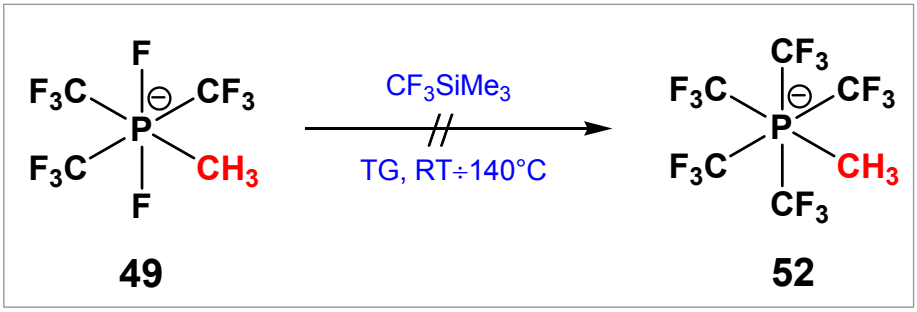


Scheme 35

CF_3 groups and one methyl group occupy so much space that the trifluoromethyl anion is not able to add to phosphorus at -40ºC hence higher temperatures are necessary in this case to overcome this energy barrier. However, this demand is in conflict with thermal stability of the trifluoromethyl anion. Decomposition of the CF_3^- ion occurs instead of its incorporation into the phosphorane molecule even at low temperature and anion **48** was formed but not the desired $[(CF_3)_5P(CH_3)]^-$ TMA^+ phosphate **50**.

Formation of **48** can be also explained from another point of view. It is known[128] that the fluoride ion affinity of tris(perfluoroalkyl)difluorophosphoranes is so high that in aqueous HF the hydrolysis of phosphoranes is suppressed and the corresponding tris(perfluoroalkyl)trifluorophosphoric acids are formed in nearly quantitative yield (*Scheme 35*). This fact could be used to explain immediate decomposition of the trifluoromethyl anion in our case and probably direct synthesis of hexakis(perfluoroalkyl) phosphates will be always complicated by analogous side reaction so then indirect ways should be found.

Phosphate **49** was isolated from the reaction mixture as *trans*- isomer but in MG solution it transforms into the *cis*- isomer within three days completely. The transformation process could be significantly accelerated by addition of some polar solvent like acetonitrile or just water indicating that the process is dissociative and occurs via the free phosphorane and a fluoride ion. Hydrolysis also occurs but its rate is approximately 10-15 times slower than the recombination process which dominates due to the reason discussed above. The only hydrolysis product isolated is the salt $[CF_3(CH_3)P(O)O]^-$ TMA^+ (**51**) and some TMAF. Introduction of an electron donating methyl group into the molecule partially reduce the positive charge on phosphorus and makes the dissociation of



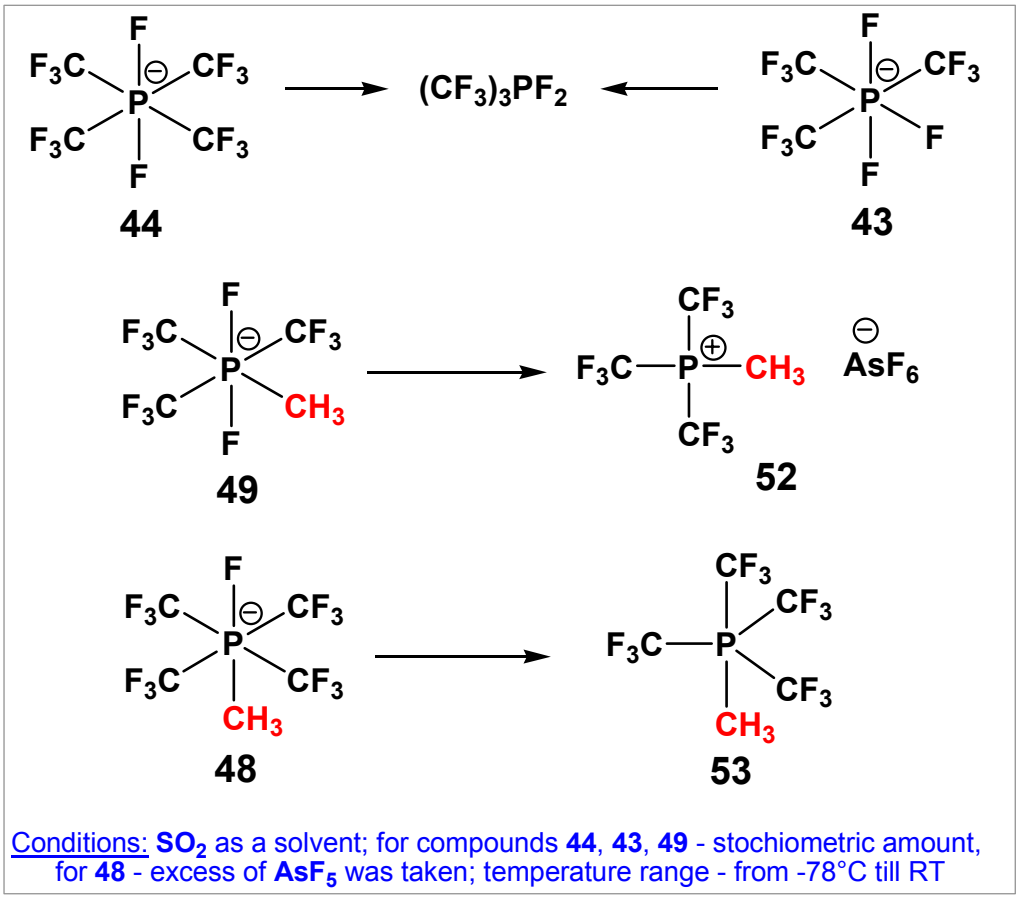
49 **52**

Scheme 36

49 into ions possible. This also lead to hydrolysis quenching on the stage of salt **51** formation since it is known[129] that the stability of three- and five-coordinate trifluoromethylphosphorus compounds towards hydrolysis strongly depends on the electronic effects of substituents. An attempt to use the feature of the salt **49** to dissociate into ions, for substitution of fluorine atoms for trifluoromethyl group (*Scheme 36*) failed.

Contrary to the salt **49**, the salts **43**, **44**, **48** are hydrolytically stable, the salt **39** very slowly hydrolyses to give $(CF_3)_3PO$ but does not rearrange into *cis*- form in time. In derivative **48** the fluorine is *trans* relative to the methyl group, compound **44** exist in the *cis*-form, phosphate **43** is reported[128] to be formed as a mixture of *meridianal* and *facial* isomers which are fluxionally stable.

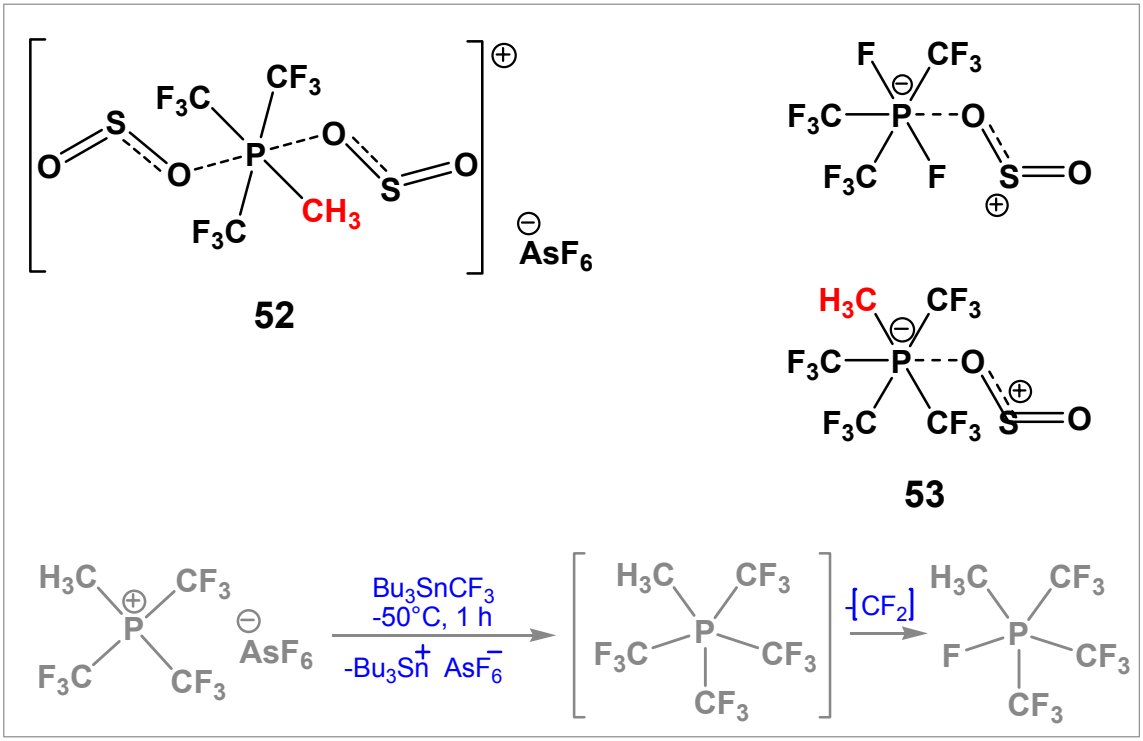
Using[127] strong Lewis acid and fluoride ion acceptor – arsen pentafluoride we successfully abstracted fluorine atoms from the whole array of phosphate ions synthesized (*Scheme 37*). Unexpected formation of tris(trifluoro-methyl)difluorophosphorane was detected in the first example. Local excess of



Scheme 37

AsF_5 (at the moment of mixing the reagents) might lead to formation of very unstable cation or the unstable tetrakis(trifluoromethyl)methylphosphorane. We cannot explain what really happens, yet however, allied phosphorane **53** was synthesized quantitatively. Being stable in solution this derivative is very important for us as a precursor to the previously discussed $(CF_3)_5P$ and gives us hope for a successful synthesis. Warming the NMR sample of **53** to 40ºC for a short time does not lead to decomposition of the substance, though several years ago Dieckbreder[126] did not manage even to detect this phosphorane in the reaction of the salt **52** with Bu_3SnCF_3 (*Scheme 38*). Trace signals of phosphorane **54** were observed in the spectra only after exposition of the sample (**53** in liquid SO_2) for 3 weeks at RT.

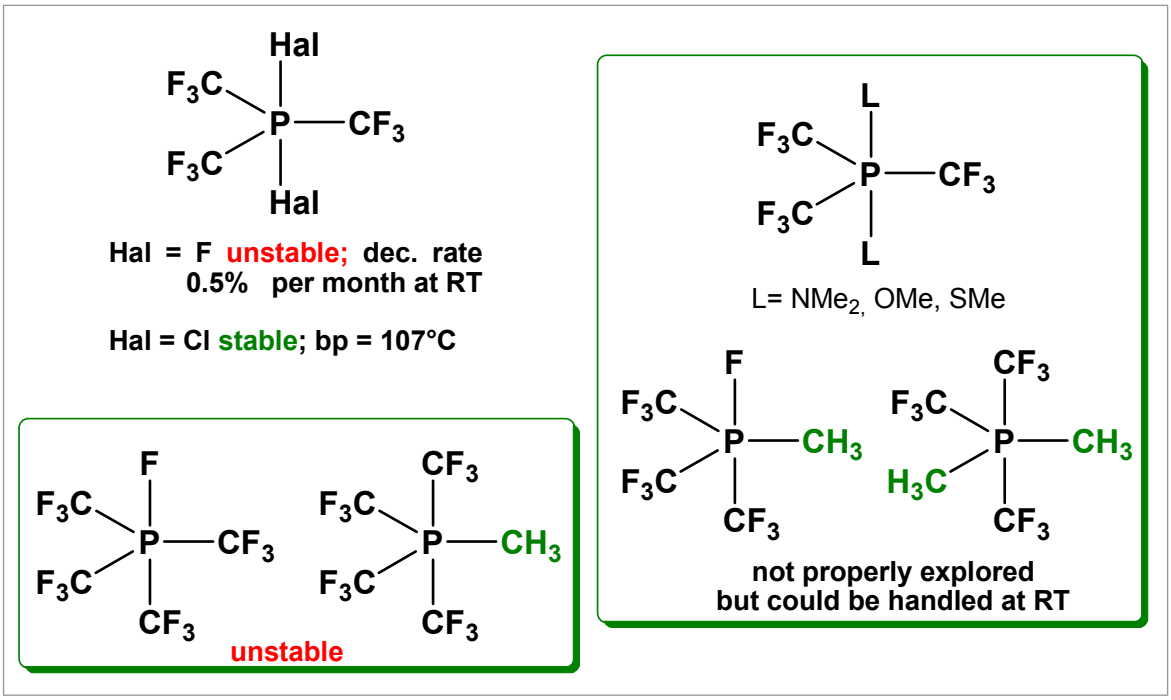
Phosphonium salt **52** was generated without isolation of intermediate $(CF_3)_3(CH_3)PF$ phosphorane. Despite extreme instability reported[126] for this compound we got samples absolutely stable for more than one week what allowed us to carry ^{13}C NMR measurements. Such the stabilization effect may be referred to the solvent influence and was observed not only in the case of the phosphonium salt discussed but also for $(CF_3)_4PCH_3$ and $(CF_3)_3PF_2$ phosphoranes. Strong distortion of the ^{19}F NMR spectra was observed for the compounds though the drift of signals in ^{31}P and ^{1}H NMR spectra was negligible.



Scheme 38

Addition of fluoride to the samples led to the formation of starting compounds – $[(CF_3)_3PMeF_2]^-$, $[(CF_3)_3PF_2]^-$ and $[(CF_3)_4PMeF]^-$ TMA^+. Possible interaction of the solvent and the very electrophilic substrates is presented in *Scheme 38*.

The role of the solvent in the stabilization of very electrophilic trifluoromethyl phosphorus derivatives is extremely important. This was supported by simple recondensing the sample of **53** in SO_2 into another NMR tube with a Teflon™ stop-cock. During recondensation, the complex of the substrate and the solvent decomposed for a moment and then recombined immediately on the walls of the second tube. This short time existence in an unsolvated state gave significant rise to the content of phosphorane **54** in the mixture proving Dieckbreder's observations. Why phosphorane **53** is so unstable after all? This question has not been answered, yet. Analyzing the literature data one can notice that introduction of fluorine into the phosphorane molecule leads to decreased thermal stability while substitution of this atom by chlorine (*bromo- and iodo-phosphoranes possess relatively low stability due to weak P-Hal bond*) or by electrondonor functional group increase the stability of these species (*Scheme 39*). Therefore it would be possible to suppose that the positive charge of the phosphorus but not the steric interaction of the ligands, defines the stability.



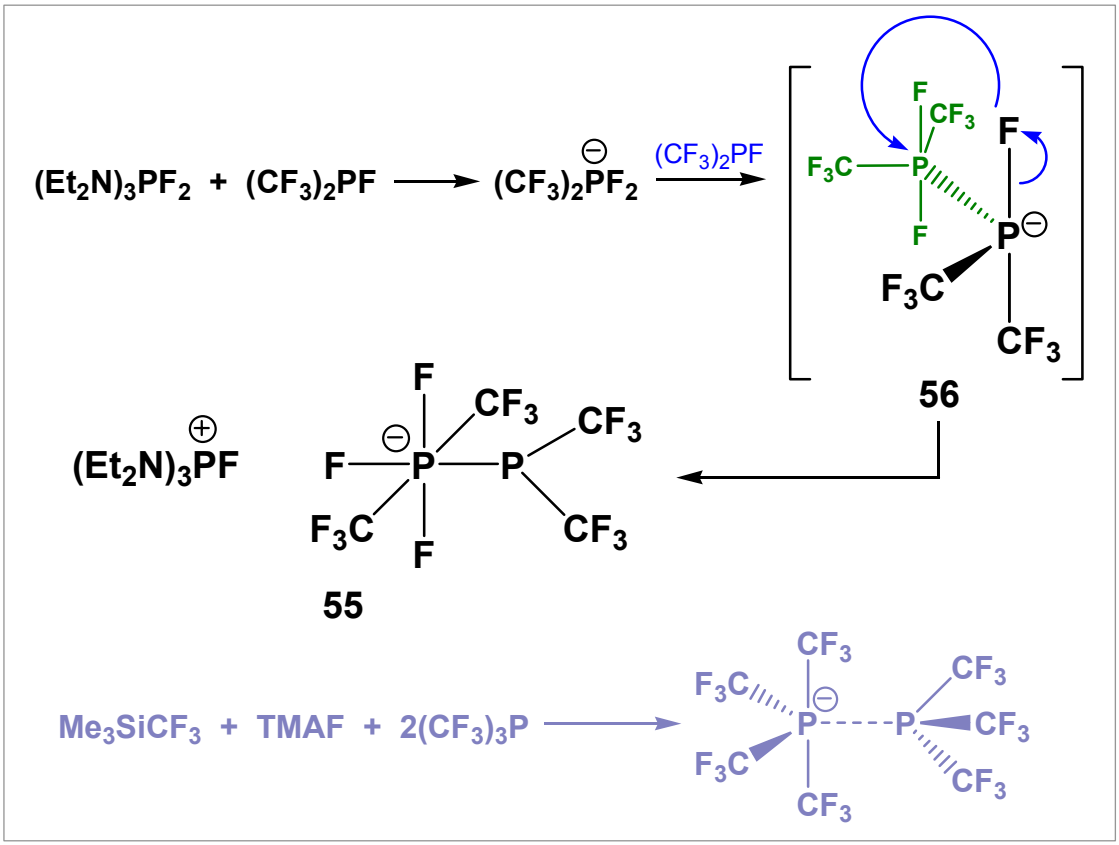
Scheme 39 *Thermal stability of trifluoromethyl phosphoranes*

However, this point of view implies sufficient stability for tetrakis(trifluoromethyl)-phosphoranes. Low stability of **54** is especially inexplicable taking into account the presence of methyl group partially compensating the electron withdrawing effect of other substituents and comparing these compounds with phosphoranides **7**, **32**. At the same time introduction of the second methyl group into the molecule makes the compound stable at RT. A too high positive charge of phosphorus may be compensated as a consequence of solvent coordination. Formation of stable solvates (*Scheme 38*) may serve as additional argument in favor of our supposition about the crucial role of electronic effects in the properties of the trifluoromethyl phosphoranes discussed.

All the six-coordinate compounds discussed above possess high melting points. Their thermal stability is so high that in MS spectra (except salt **39**) only one intensive peak of molecular ion is present and other few peaks have the relative intensity <5%. Nevertheless, most frequently detached fragment has a mass of 50 Da and corresponds to CF_2 carbene, fragment with m= 70 Da (CF_3H) was observed rarely.

C3. Phosphinoperphosphoranides: new hypervalent phosphorus species.

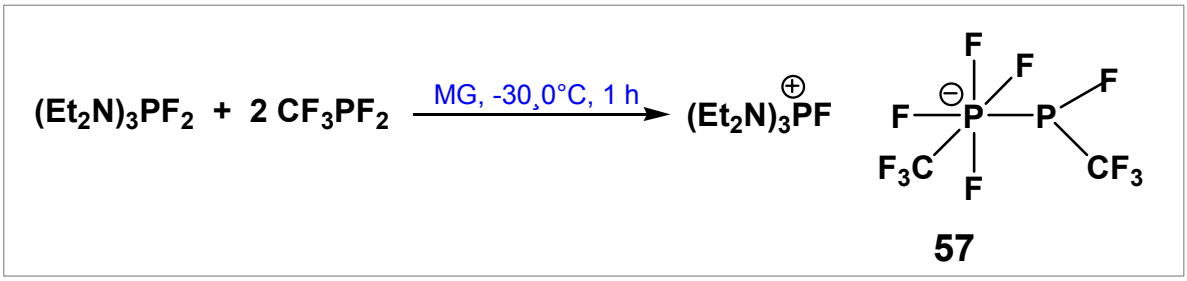
While discussing the stability of tetrakis(trifluoromethyl) phosphoranide we pointed out that addition of phosphine **11** to these derivatives led to it's coordination to the phosphorus lone electron pair resulting in significantly increased stability of the hypervalent species in solutions. In the case mentioned, only weak interaction was assumed and no formation of new compounds was observed. Having met the problem in obtaining phosphoranide **9** in the pure state (*Figure 7 and the related text*) and taking into account successive synthesis of salt **10** ($[(Et_2N)_3P]^+$ $[(CF_3)_2PFCl]^-$), an attempt to prepare the target compound starting from phosphorane **30** was undertaken. Surprisingly, no phosphoranide but a new mixed-valence diphosphorus derivative ($\lambda^3\sigma^3P$-$\lambda^5\sigma^6P$ *system,* **55**) was isolated (*Scheme 40*). Formation of a phosphinoperphosphoranide is surely to occur via intermediate generation of $\lambda^3\sigma^4P$-$\lambda^5\sigma^5P$ derivative **56** immediately rearranging into the final product. Compound **56** have been never observed in



Scheme 40

NMR spectra at any temperature probably due to very high rearrangement rate but the presence of P-P bond in the final product implies the structure proposed for **56**. The striking discrepancy between reactions of phosphoranide **7** or **32** and perphosphoranide **55** formation may be explained by steric interactions of ligands as well as different electrophilicity of starting phosphines. Is it difficult to make a definite conclusion about dominating one or the other factor in this case just as in the case of trifluoromethyl phosphoranes (*Scheme 39*). Here, these factors seem to have parallel influence since the substitution of the trifluoromethyl group by fluorine in the precursor phosphine leads to an increase of the positive charge on phosphorus (as an example see *Tables 3,4*) and decrease of the overall volume of the phosphine as a ligand. Anyway, the synthesis of perphosphoranides can be regarded as an additional proof of the coordination of phosphine **11** to the electron pair of phosphoranide **32**, previously supposed.

After accidental isolation of **55** formation of perphosphoranide **57** was prognosed and this compound did form from the reaction of CF_3PF_2 and $(Et_2N)_3PF_2$ quantitatively (*Scheme 41*).



57

Scheme 41

However, no phosphinoperphosphoranides were obtained starting from PF_3 and $(CF_3)_2PCl$. This allows us to suppose that both features of starting compounds – Lewis basicity of the lone electron pair of phosphoranide depending on its s-character (*Table 3*) and Lewis acidity of phosphine should be considered to explain the results obtained. As one can see, the percentage of s-orbital in LEP is highest for $[PF_4]^-$ and this anion should be not reactive towards any phosphine to be used; in its turn, relatively low positive charge on phosphorus in $(CF_3)_2PCl$ is not sufficient to react with trifluoromethylfluorophosphoranide. The question if the pairs of reagents shown in *Figure 17* may give the corresponding perphosphoranides remains open.

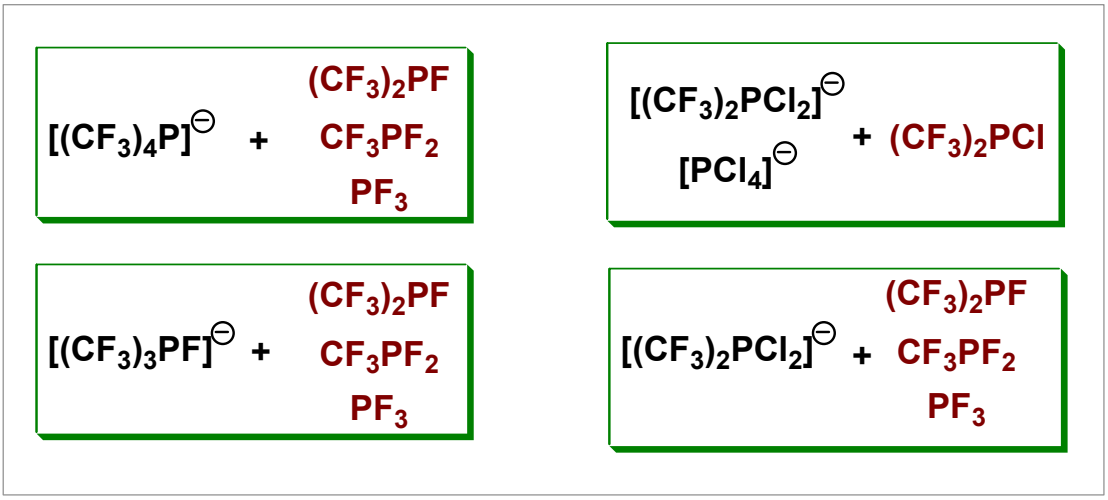


Figure 17

Phosphinoperphosphoranides **55** and **57** comprise a new type of phosphorus compounds. On-line information retrieval gave very limited number of references concerning mixed-valence diphosphorus derivatives. Some examples found are shown on *Figure 18*. As one can note, no compounds possessing both six-coordinate and three-coordinate centers have been known until now.

The phosphinoperphosphoranides prepared were characterized by multinuclear NMR spectrometry and MS spectroscopy. Numerous attempts to grow single crystal for X-Ray failed. Instead of the compounds discussed, decomposition product (*wide infra*) precipitated being much less soluble in a solvent. An attempt to increase stability by changing a counterion (from $[(Et_2N)_3PF]^+$ to TMA^+ and $[(K^+)$*18-crown-6)] did not led to success. It was revealed that only in the case of using TMAF as fluoride ion source, traces of

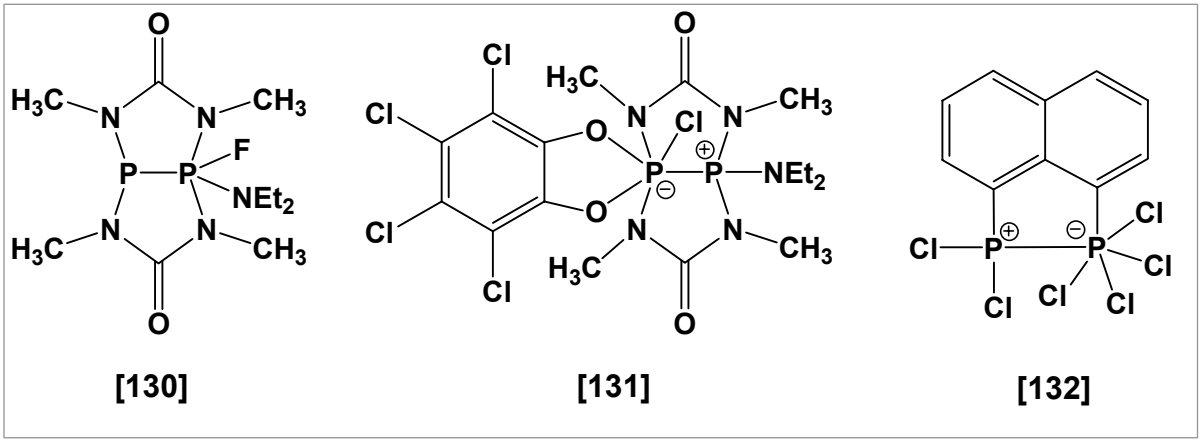


Figure 18

intermediate $[(CF_3)_2PF_2]^-$ ion were detected in the NMR spectra.

The ^{31}P NMR spectra of **55** and **57** show two multiplets corresponding to P(III) and P(VI) moieties as well as doublet of 13-line multiplets due to $(Et_2N)_3PF^+$ (*Figure 19*). All the signals are of sophisticated multiplicity and only selected coupling constants were found. For instance, the magnitude of $^1J_{PP}$ for **55** could be supposed to be in the range of 7÷20 Hz since very broad and complex signals did not allowe us to define it precisely. In contrary, $^1J_{PP}$ for **57** was successfully determined; its value was equal to 9.78 Hz being in good correlation with that assumed for **55**. Values of $^1J_{PP}$ seem to be relatively small probably indicating a weak bonding and therefore low thermal stability of P-P bond in phosphinoperphosphoranides. Though we have not managed to find exhaustive NMR data for the compounds shown in *Figure 18*, coupling constants' values for the derivatives shown in *Figure 19* may help to suppose the "normal" $^1J_{PP}$ values for phosphinoperphosphoranides lying in the range of 100÷200 Hz. Direct P-F coupling constants at six-coordinate centers ($^1J_{FP(VI)}$) proved to be unexpectedly large (966÷1069 Hz) and were comparable with $^1J_{FP}$ of starting phosphines {$(CF_3)_2PF$: 1014 Hz, CF_3PF_2: 1250 Hz} and noticeably larger than those in phosphates and phosphoranes[95, 128] (384÷992 Hz, see also *Table 2*) while $^1J_{FP(III)}$ was observed to be rather small (875.37 Hz) in **57**. At the same time, magnitudes of $^2J_{PF(CF_3)}$ are relatively low (60-68 Hz) in the case of both P(III) and P(VI) centers in comparison with corresponding constants in phosphines {$(CF_3)_2PF$: 87 Hz, CF_3PF_2: 83 Hz}, phosphates[128] (86÷90 Hz), phosphoranes

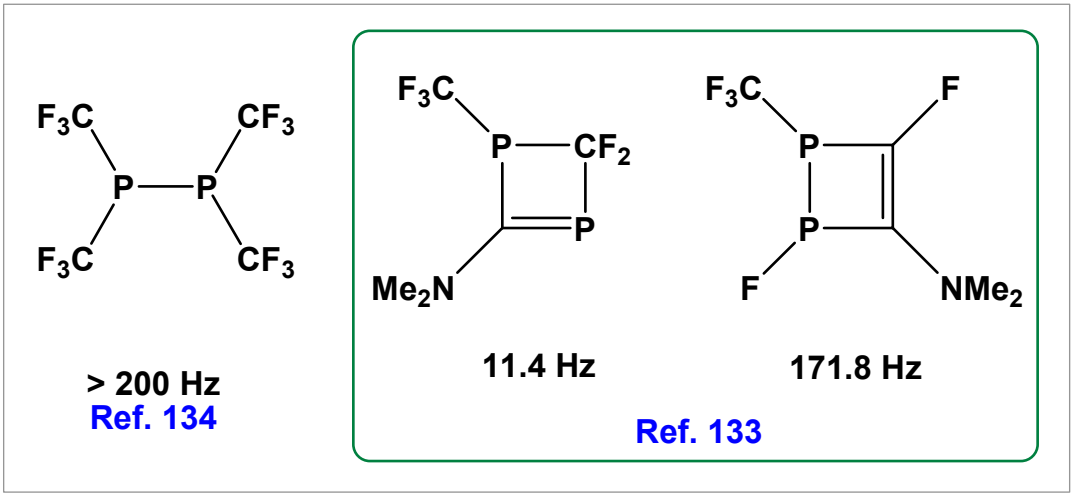


Figure 19

and even phosphoranides (equatorial bonds, *see Table 2*) approximating by values to $^{2}J_{PF(CF_3)}$ for axial CF_3 groups in hypervalent phosphorus species. More intriguing are the chemical shifts in the ^{31}P NMR spectra. Whereas six-coordinate fragments show nearly the same chemical shift value (**55**: -149.3 ppm; **57**: -138.6 ppm), multiplets corresponding to P(III) moieties are shifted irregularly and in the case of phosphinoperphosphoranide **55** the $(CF_3)_2P$ component can be found at δ_P = 20 (starting phosphine δ_P = 123.3, $\Delta_{\delta P}$ = 103), but in the case of derivative **57** CF_3PF component shifts downfield to δ_P = 185.3 (starting phosphine δ_P = 159.8, $\Delta_{\delta P}$ = -25.5). ^{19}F spectra of the compounds discussed are much more informative and could be interpreted relatively easy. Of course, the spectrum of **55** is more complex when compared with that of **57** due to the presence of one more CF_3 group in the molecule. Nevertheless, different CF_3 groups and sets of F atoms are well distinguishable and can be analyzed. It is interesting to note that a single F at the P(III) center in compound **57** reveals a resonance at -234.96 ppm, quite close to the signal of the F atom in $(CF_3)_2PF$ (δ_P = -217.3).

As it was previously noted, phosphinoperphosphoranides are not stable compounds and decompose both in solution and in the solid state. Even after exposition of the samples at -40ºC in the refrigerator for two months traces of decomposition product were detected. It is worth noting that **55** is much more stable than **57** and only for the latter decomposition occurs completely to give $[CF_3PF_5]^-$ $[(Et_2N)_3PF]^+$ (**57A**). Salt $[(CF_3)_2PF_4]^-$ $[(Et_2N)_3PF]^+$ (**55A**) was also successfully identified by NMR spectroscopy. It could be obtained in high yield only after heating the starting phosphoranide at 80ºC during 1 h however, only mixtures of the compounds were observed after 4÷8 month exposition at room temperature. In *Figure 20,* the ^{31}P spectra of **57A** and **55A** (spectrum of the mixture of the compound is given to make a vivid comparison of the signals) are shown as expansion pictures. No noticeable influence of the nature of the counterion on the stability of perphosphoranides was found though, it would be possible to suppose that coordination of a cation at the P(III) moiety should influence the strength of P-P bond. Studying the chemical and physical properties of perphosphoranides is underway now.

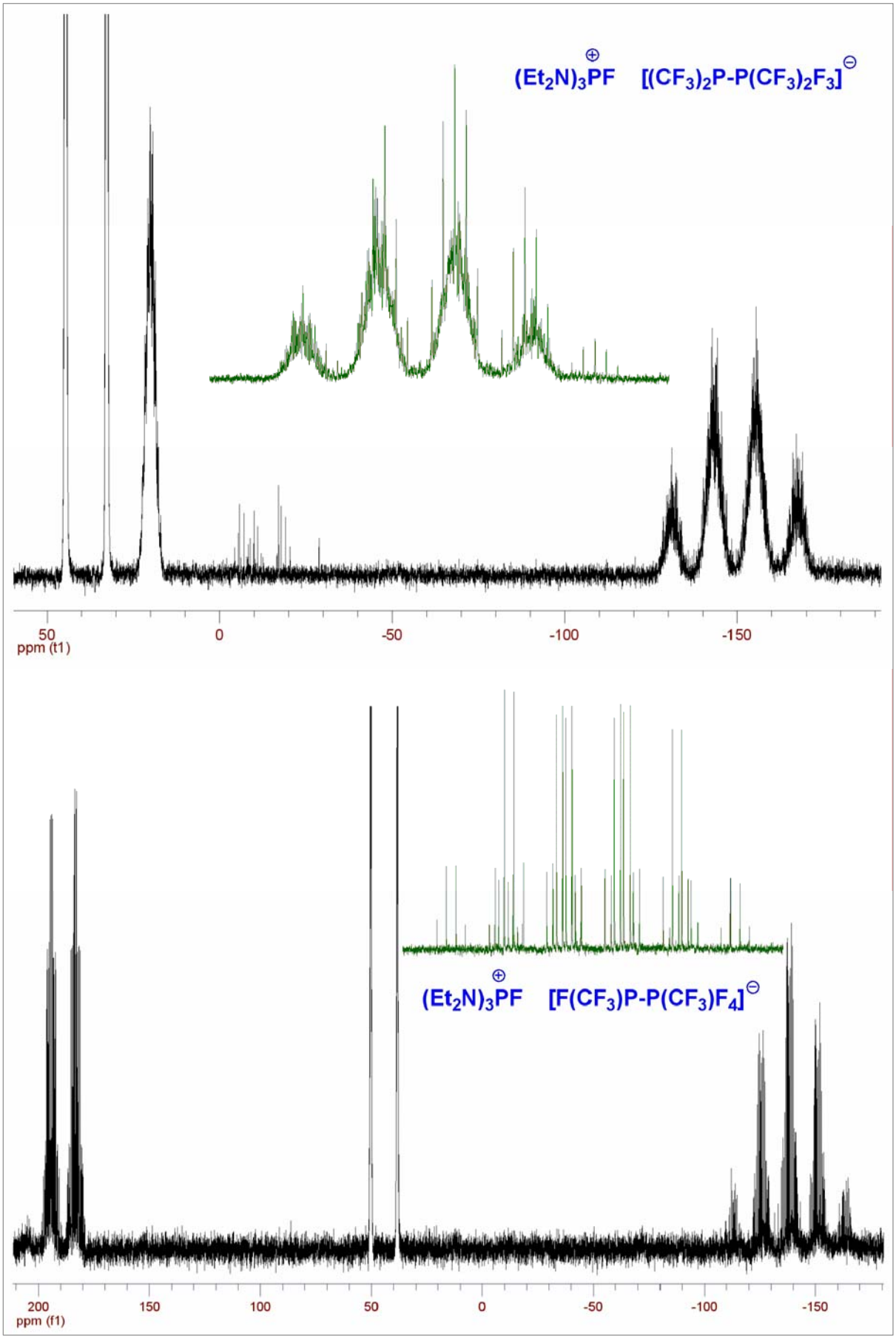
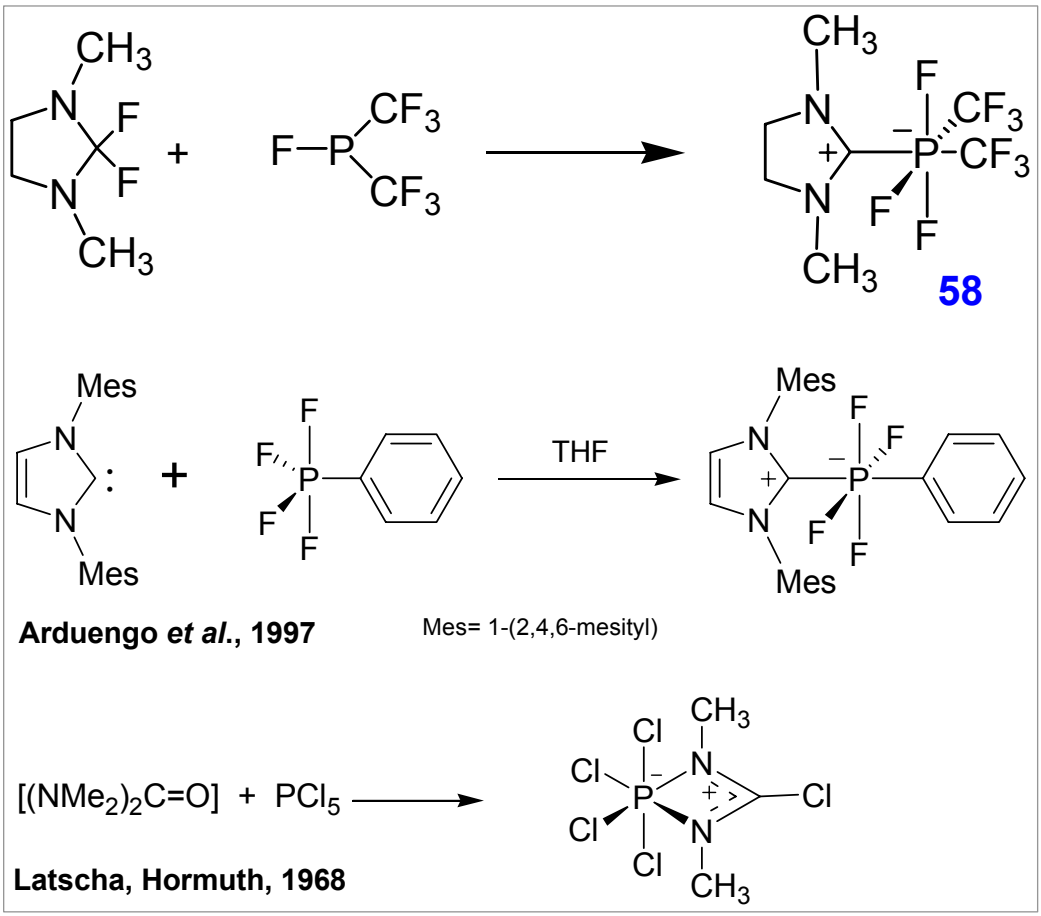

(Et2N)3PF [(CF3)2P-P(CF3)2F3]
50
ppm (t1)
0
-50
-100
-150
(Et2N)3PF [F(CF3)P-P(CF3)F4]
200
ppm (f1)
150
100
50
0
-50
-100
-150

Figure 20

C4. Synthesis of perphosphoranides.

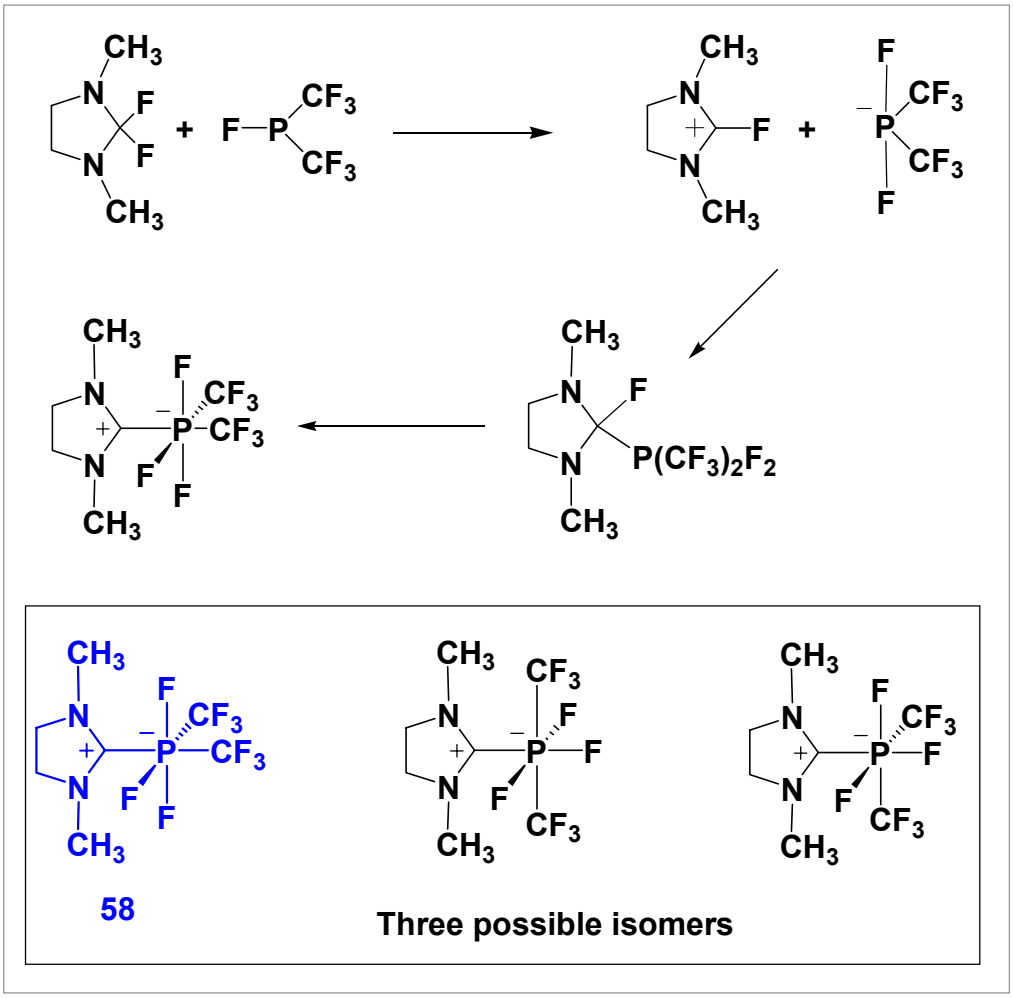
C4.1. Accidental isolation of Bistrifluoromethyl-N,N,N',N'-tetramethyl-difluoroperphosphoranide.

As was mentioned above, the reaction of phosphines $(CF_3)_2PCl$ and $(CF_3)_2PF$ with $(Et_2N)_3PF_2$ or KF led to the corresponding phosphoranide formation, however much more unexpected was the product of the reaction between $(CF_3)_2PF$ and DFI. Instead of the desired phosphoranide, perphosphoranide **58** was obtained in quantitative yield. The compound could be considered as a coupling product between 1,3-dimethylimidazolidin-2-ylidene and bis(trifluoromethyl)trifluorophosphorane similar to that described by



Scheme 42

Arduengo[135]. Structurally **58** closely resembles a six-coordinate phosphorus compound synthesized by Latscha and Hormuth[136] (**58A**) with one important detail – the four membered ring is inverted relative to phosphorus and is attached to it by carbon atom (*Scheme 42*). The chemistry of compounds of type **58A** was extensively elaborated by Kal'chenko *et al.*[137-139]. It was shown that in this case compounds in which chlorine atoms are partially or completely substituted by other electrophilic substituents (F, CF_3, CCl_3, Ar) can exist either as five-coordinate phosphorus derivatives or six-coordinate ones. The rearrangement to the five-coordinate phosphorus isomer was favored by higher temperatures, a decrease in the polarity of the solvent, a rise in electronegativity of the substituents attached to carbon being a part of the chelate ring and an increase in the size of the alkyl group at nitrogen.



Scheme 43

Since the mechanism proposed for the formation of product **58** includes pentacoordinate phosphorus (*Scheme 43*) it is also possible to suppose that the nature of substituents at phosphorus determines the relative stabilities of intermediate five-coordinate and target six-coordinate derivatives and, probably, in the case of taking phosphine bearing one or two alkyl substituents it would be possible to obtain the corresponding phosphorane. Carrying out the reaction discussed, neither the phosphoranide ion nor the related phosphorane were detected in the spectra of the reaction mixture even at -60ºC indicating that all transformation processes are very fast on the NMR time scale. We did not expect that the 2-fluoro-1,3-dimethylimidazolinium cation would be such a strong Lewis acid and even traces of the phosphoranide salt would not be detectable at low temperature. This feature of 2-fluoro-1,3-dimethylimidazolinium being strictly opposite to that of tris(diethylamino)bromophosphonium, is likely to be responsible for the relatively strong fluorinating properties of DFI while tris(diethylamino)difluorophosphorane is a very mild fluorinating agent. Fast rearrangement of the intermediate phosphorane into the six-coordinate derivative **58** can be explained by the ease of fluoride ion abstraction from the organic

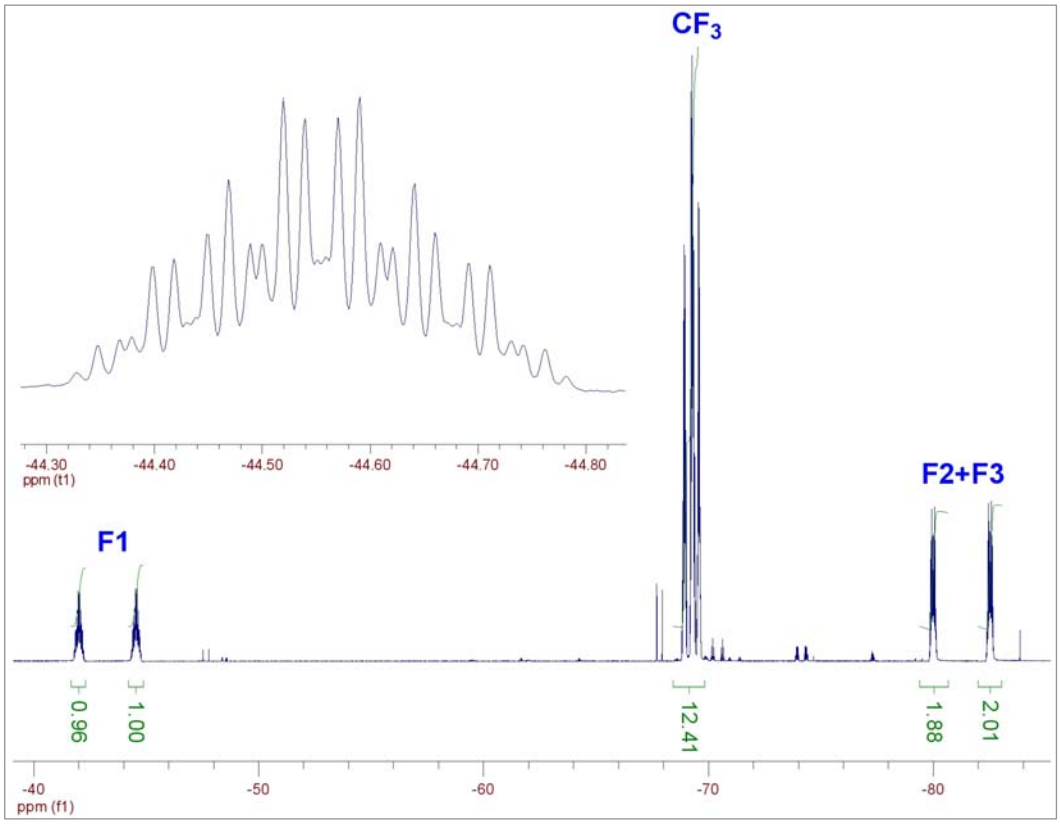


Figure 21

moiety of the phosphorane and by the very high electrophilicity of the phosphorus center.

The NMR spectra of perphosphoranide **58** are quite complex. The general view of the ^{19}F spectrum and one of its fragments are shown in *Figure 21*. All substituents at phosphorus are not equivalent except two apical fluorine atoms forming a hypervalent bond. Due to the partially ionic nature of the hypervalent bond these fluorine atoms labeled as **F2** and **F3** are in the strongest field (d, d, sep, δ_F= -81.2, J_{PF} = 858.1, $^2J_{FF}$ = 41.3, $^3J_{FF}$ = 11.4 Hz) the other single fluorine, **F1** is the in weakest field (d, t, q, q, δ_F = -43.2, J_{PF} = 859.7, $^2J_{FF}$ = 41.3, $^3J_{FF(1)}$ = 17.2, $^3J_{FF(2)}$ = 6.8 Hz). It is noteworthy that **F2** and **F3** do not experience the difference between two trifluoromethyl groups or, probably, this discrepancy is too small and responsible only for a slight broadening of the signals. Contrary to this fact, **F1** has two coupling constants which differ more than two times by magnitude. Most difficult is the analysis of signals according to **CF_3** groups. This portion of the ^{19}F spectrum consists presumably of two overlapping doublets of doublets of triplets of quartets ($\delta_{F(1)}$ = -69.12, $^2J_{PF}$ = 126.5; $\delta_{F(2)}$ = -69.4, $^2J_{PF}$ = 108.4 Hz) though this was not proved unambiguously. The coupling constants between the CF_3 groups and F1, F2+F3, P atoms were observed but we did not manage to extract the CF_3-CF_3 coupling constant. Despite the ^{31}P spectrum seemed to be complex at the first glance, it was successfully resolved to be a quartet of quartets of quartets. It is interesting that only a quartet splitting of phosphorus atom was found (δ_P = -157, J_{PF} = 859.5 Hz) as if all the fluorine atoms were equal. The strong upfield shift of **58** with respect to $(CF_3)_2PF$ (δ_P = 122.7) is clearly consistent with the six-coordinate phosphorus center. A smaller average one-bond P-F spin-coupling is observed for **58** compared with that starting phosphine (J_{PF} = 1014.7 Hz) which suggests a significant decrease in the s-orbital character of the P-F bonds for the perphosphoranide.

On the basis of the analyzed spectra and knowing that perphosphoranide **58** has two equivalent, one single fluorines and two non equivalent trifluoromethyl groups, one of the three possible isomers was suggested for this compound (*Scheme 43*). Later, crystals of **58** suitable for X-ray crystallographic studies were obtained from monoglyme. The X-ray crystal structure of **58** is shown in

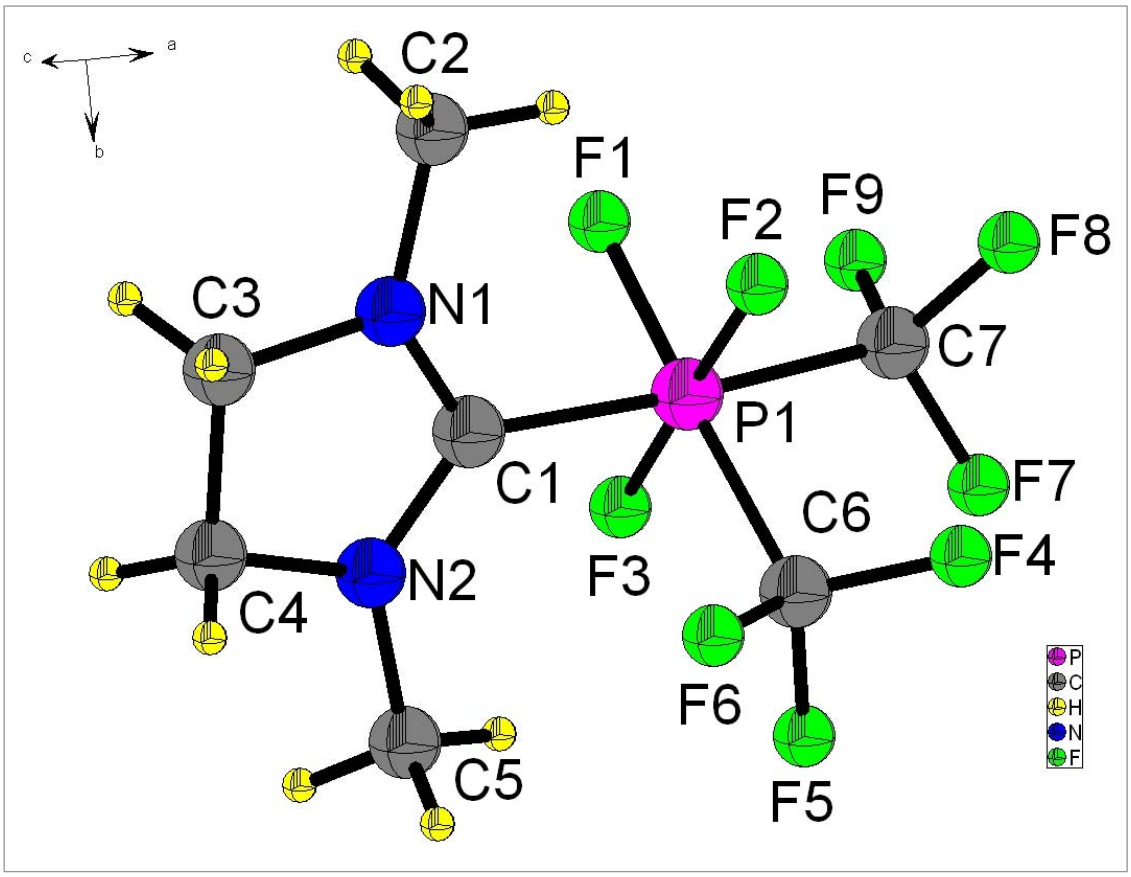


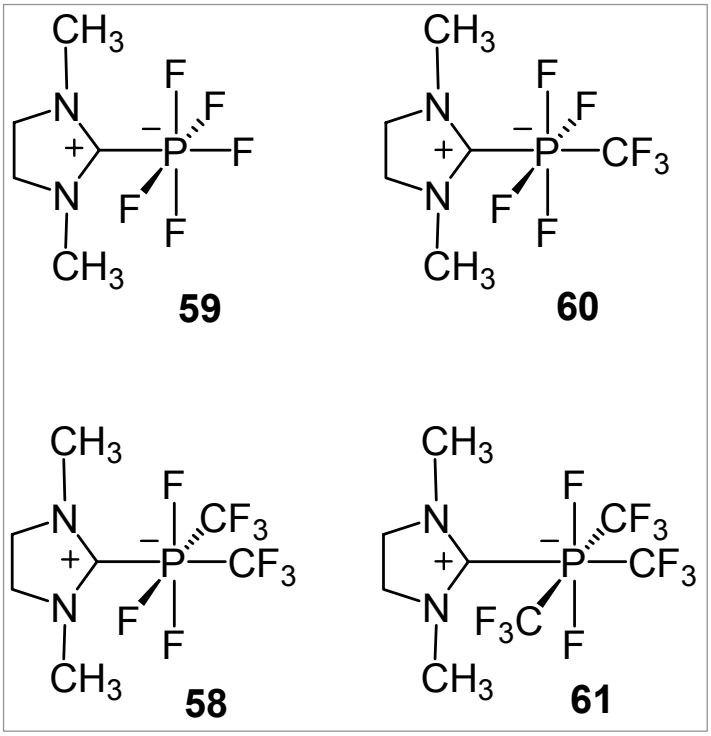
Figure 22

Figure 22 confirming our initial suggestion. The structure shows the expected octahedral geometry at phosphorus. There is a visible distortion of the octahedral environment - the flat heterocycle is not coaxial with opposite trifluoromethyl group, the C7-P1-C1 angle being 174.1º. It would be possible to explain this fact as the result of repulsion between two neighboring bulky substituents but nearly the same angle was found in the structure of Arduengo's perphosphoranide (177.2º, *Scheme 42*) where $^{(C6)}CF_3$ group is substituted by fluorine and the real reason of this phenomenon is not clear. The dihedral angle N1-C1-P1-F2 is 38.7º; this really reduces the repulsion forces between the substituents and allows closer packing of the elementary cell. Distortion from 45º could be attributed to the H···F interactions (average distance between the protons of N-Me groups and F3 or F2 is 211.4 pm, comparable with F···H bonds in ammonium monofluoroacetate (229 pm)[140] and in 4,4,8,8-tetrafluoropyrazabole (218.4 and 223.9 pm)[141]) as well as non symmetrical environment. The three fluorine atoms and the $^{(C6)}CF_3$ group are almost in plane. The bonds P1-F1, P1-F2, P1-F3 are not equal (161.76[12] pm), 161.62[10] pm and 162.93[11] pm, respectively),

unfortunately the high statistical error does not allow to make definitive conclusions, but we expect that F2 and F3 atoms being bounded to P by one 3c-4e bond should be equidistant. Also the bond P1-C7 (192.8[2] pm) was expected to be shorter than P1-C6 (192.7[2] pm) since it was known that, for instance, the formation of the P-N coordinate bond reduced the length of the *trans* P-F bond in PF_5•py, as was reported by Scheldrick and co-workers[142].

C4.2. Synthesis of other perphosphoranides.

Corresponding perphosphoranides were obtained in reactions of trifluorophosphine and difluoro(trifluoromethyl)phosphine with DFI™ (*Figure 23*). In the case of perphosphoranides **59** and **60** yields are quantitative but for the perphosphoranide **61** the situation is quite different. First of all, we should note that namely compound **61** was neither isolated nor even detected by NMR spectrometry. This derivative is supposed to be only an intermediate product. Very bulky electronegative trifluoromethyl groups impart outstanding properties to tris(trifluoromethyl) phosphine and its reaction with DFI proved to be much more sophisticated compared to that of other trifluoromethyl phosphines.



When phosphine **11** was added to an equimolar amount of **23** solid charge transfer complex **61A** formed. Gentle heating of this complex up to 39ºC led to

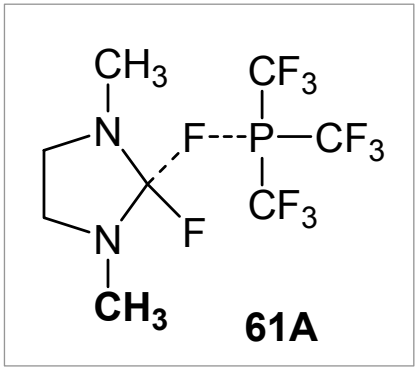


Figure 23

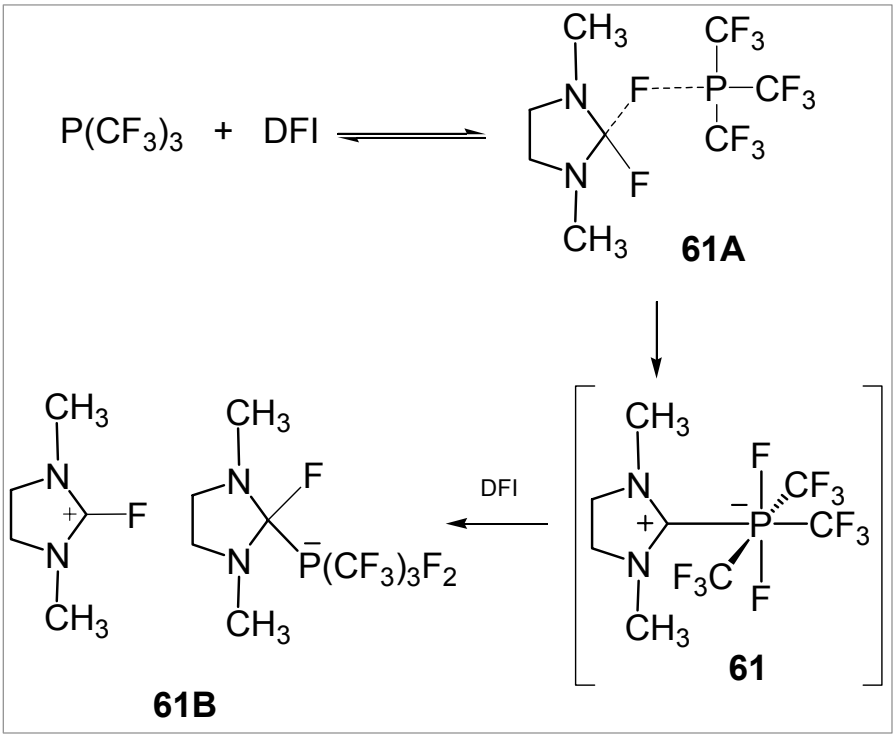
formation of two transparent immiscible liquid phases – starting compounds, which gave a homogeneous solution at 67ºC. Complex **61A** is readily soluble either in polar or in non polar solvents and its reactivity strongly depends on the polarity of the reaction media. Thus, absolutely no reaction products were detected in MG after two weeks at ambient temperature but stirring the mixture of precursors in acetonitrile during the same period of time allowed us to detect the six-coordinate phosphorus species in solution (relative intensity *ca.* 0.8% *vs.* phosphine **11** by ^{31}P NMR). Twelve milligrams of sticky, very sensitive to moisture solid were obtained after removing of the solvent and the starting

Perphosphoranide	^{19}F NMR data	^{31}P NMR data
58 ($DMSO_{d6}$)	δ=-81.2 ppm(d,d,sep, 2F)J_{PF}= 858.1 Hz, $^{2}J_{FF}$= 41.3 Hz, $^{3}J_{FF}$= 11.4 Hz δ= -69.12 ppm(d,d,t,q, 3F), $^{2}J_{PF}$= 126.5 Hz; $^{3}J_{FF(1)}$= 11.4 Hz, $^{3}J_{FF(2)}$= 6.8 Hz δ= -69.4 ppm(d,d,t,q, 3F), $^{2}J_{PF}$= 108.4 Hz, $^{3}J_{FF(1)}$= 17.2 Hz, $^{3}J_{FF(2)}$= 11.4 Hz δ= -43.2 ppm(d, t, q, q, 1F), J_{PF}= 859.7 Hz, $^{2}J_{FF}$= 41.3 Hz, $^{3}J_{FF(1)}$= 17.2 Hz, $^{3}J_{FF(2)}$= 6.8 Hz	δ= -157 ppm(q,q,q), J_{PF}= 859.5 Hz, $^{2}J_{PF(1)}$= 108.4 Hz, $^{2}J_{PF(2)}$= 126.5 Hz;
59 ($DMSO_{d6}$)	δ=-71.9 ppm(d,p, 1F), J_{PF}= 754.3 Hz, $^{2}J_{FF}$= 51.6 Hz δ=-55.6ppm(d,d, 4F), J_{PF}= 799.1 Hz, $^{2}J_{FF}$= 51.6 Hz	δ= -149.3 ppm(d,p), $J_{PF(1)}$= 799.5 Hz, $J_{PF(2)}$= 754.5 Hz
60 ($DMSO_{d6}$)	δ=-69.3 ppm(d,p, 3F), J_{PF}= 148.6 Hz, $^{2}J_{FF}$= 13.8 Hz δ=-61.7ppm(d,q, 4F), J_{PF}= 877.1 Hz, $^{2}J_{FF}$= 13.8 Hz	δ= -152.0 ppm(p,q), J_{PF}= 878.0 Hz, $^{2}J_{PF}$= 149.9Hz
61B (not resolved properly, CD_3CN)	δ=-89,1 ppm (s, 1F) δ=-66.2 ppm (d,m, 6F), J_{PF}=73.4Hz δ=-62.9 ppm (d,m, 3F), J_{PF}=122.7Hz δ=-57.8 ppm (d,d,m, 2F), J_{PF}= 805.96 Hz, $^{2}J_{PF}$=119.9 Hz	δ= -170.3 ppm(t,m), J_{PF}= 805.98 Hz,

Table 8

compounds. Lack of substance and the presence of impurities did not let us to characterize this compound comprehensively but its structure was supposed from NMR spectra. Characteristic high-field shift and multiplicity of the signal in

^{31}P NMR spectra, signals of two types of CF_3 groups with correct ratio to each other and relative to two equal fluorine atoms by ^{19}F NMR spectra clearly indicate a structure very close to **61** (*Table 8*). However, two fluorine atoms appears in

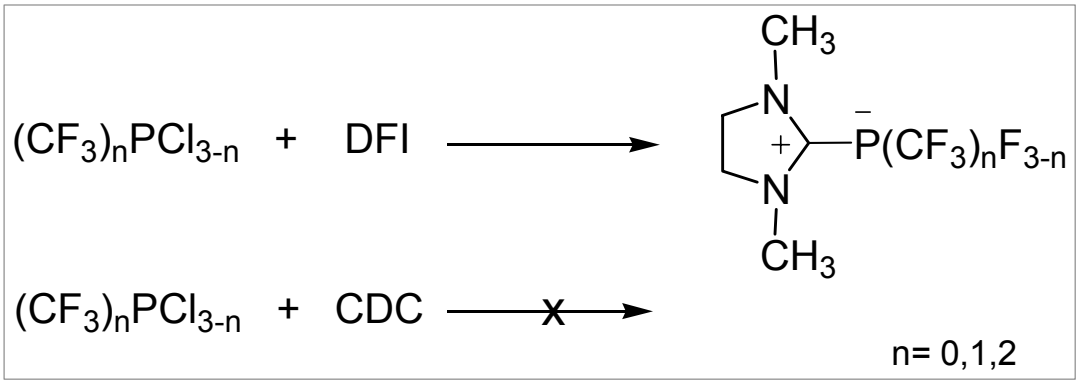


Scheme 44

the ^{19}F spectrum as a doublet of doublets of multiplets and a sharp singlet at -90 ppm is present which relative intensity corresponds to one fluorine atom. Taking into account the reaction conditions and constant excess of reagents with regard to the product following reaction scheme was proposed (*Scheme 44*).

Thus, compound **61B** is believed to be a 2-fluoro-1,3-dimethylimidazolinium salt, this fact is obviously responsible for its high reactivity towards water while perphosphoranides **58-60** are hydrolytically stable. The lower reactivity of phosphine **11** is evident – the tris(trifluoromethyl)fluorophosphoranide anion formed tends to detach the fluoride ion and fluorinate the 2-fluoro-1,3-dimethylimidazolidinium cation to give starting DFI™ (*Scheme 31*). Moreover, bulky substituents cause high steric hindrance in **61** what implies high energetic barrier and therefore low rate to the reaction discussed; for the same reason neither tetrakis(trifluoromethyl)phosphoranide nor tris(trifluoromethyl)fluorophosphoranide do react with trifluoromethylphosphines to give phosphinoperphosphoranides (*see chapter C3*).

An attempt to extend the reaction discussed to chlorophosphines was undertaken and quite interesting and unexpected results were obtained. Initially, the reactivity of phosphorus trichloride and trifluoromethylchlorophosphines towards DFI™ was investigated. No mixed chlorofluoroperphosphoranides were obtained. It was revealed that rapid fluorination of the corresponding chlorophosphine occurred even at about -90ºC, immediately after melting the



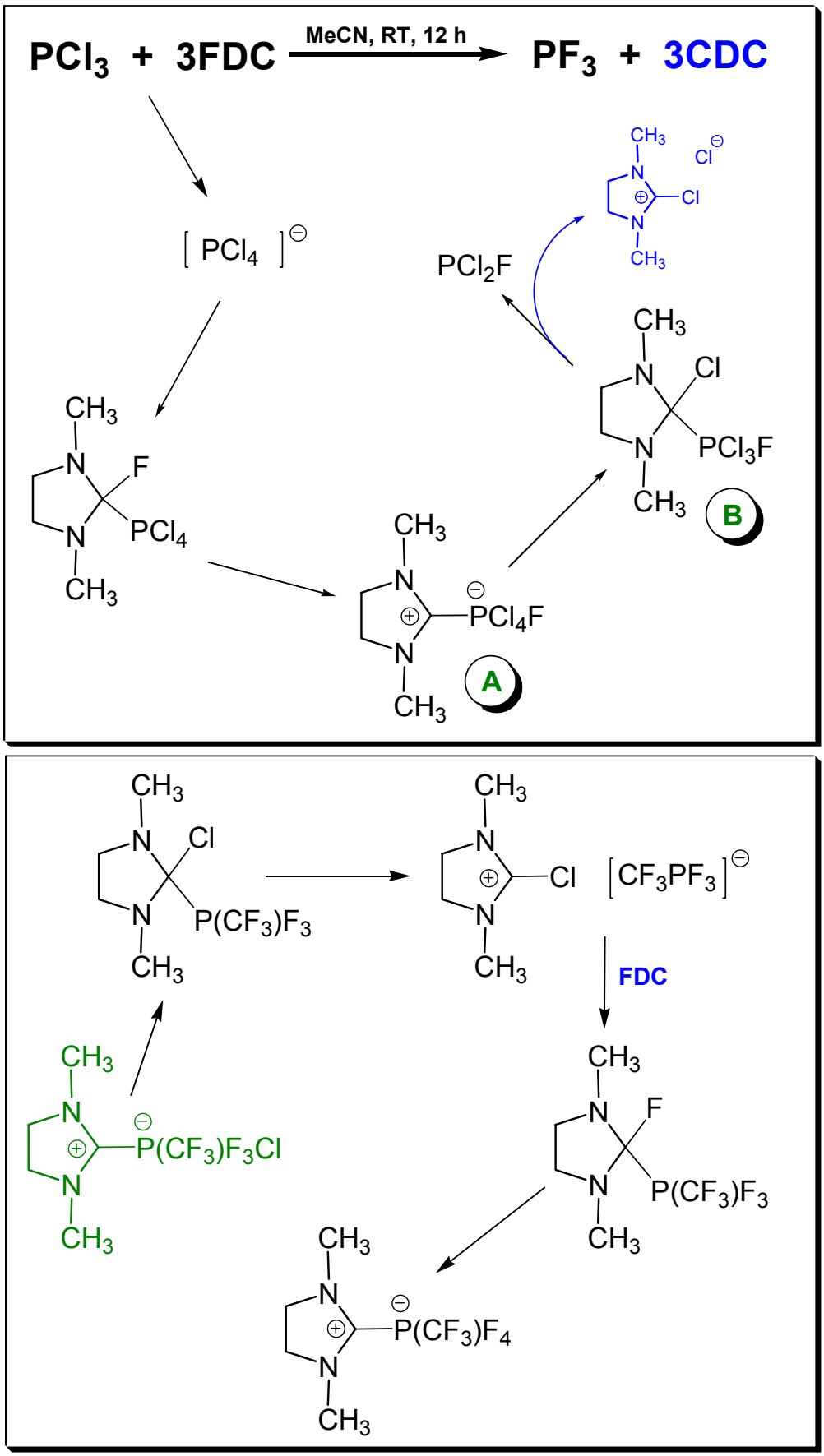
Scheme 45

solvent used for this reactions - MG or ether in the presence of significant excess of the precursor (*Scheme 45*). The reaction went quantitatively and even traces of by - product were not detected.

To reduce the reactivity of the electrophilic center, 2-chloro-1,3-dimethylimidazolinium chloride (CDC) was taken as a substrate. In contrast to DFI, CDC is an ionic compound and easily gives chloride ions in polar media. According to Dillon *et al.*[143] formation of the whole array of chlorophosphoranide ions was postulated starting from high – field shifts of signals observed relative to the precursor phosphines in the ^{31}P NMR spectra. Despite the phosphoranide generation no coupling products were detected in acetonitrile after stirring at ambient temperature for 24 h.

Surprisingly, a relatively fast reaction occurred when phosphorus trichloride was added to a solution of 2-fluoro-1,3-dimethylimidazolinium chloride (FDC) in acetonitrile. Immediately after mixing of the starting compounds in 1:3 ratio, small amounts of PF_3 were detected as well as intermediate PF_2Cl and PCl_2F and 12 h later conversion reached 100% (*Scheme 46*). No doubt, the tetrachlorophosphoranide ion is formed in the first step of the process and reacts

with FDC to give the corresponding phosphorane and finally the perphosphoranide. The key point of the process is transformation of six-coordinate derivative **A** into five-coordinate derivative **B**. The high electrophilicity of the positively charged carbon atom and relatively weak P-Cl bond are probably prerequisites for this rearrangement. The mechanism proposed seems to be common since in the reaction between PF_3, CF_3PF_2, CF_3PCl_2 and $(CF_3)_2PCl$ with FDC perphosphoranides **59, 60** and **58** were isolated. In the case of PF_3, the process of perphosphoranide formation is very smooth and the final product was isolated in 94% yield after 24 hrs at RT. The reaction between CF_3PF_2 and FDC should be carried out with care while gradual warming of the reaction mixture up from -50ºC to RT during 16 h. Otherwise, only traces of the product were detected together with at least three non identified by-products. In the case of CF_3PCl_2 or $(CF_3)_2PCl$ the rearrangement is very slow; stirring of the reaction mixture during one week at room temperature led to only 17%-20% conversion of the starting phosphine.

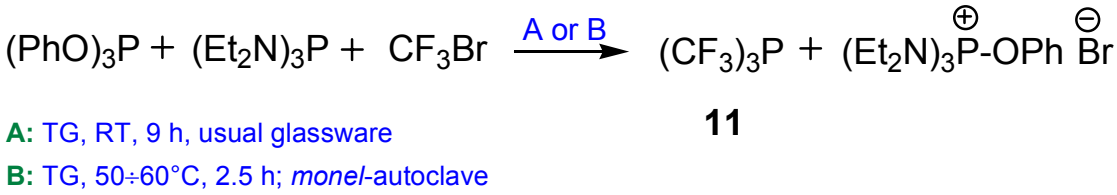

PCl3 + 3FDC
MeCN, RT, 12 h
PF3 + 3CDC
[PCl4]⊖
PCl2F
CH3
Cl⊖
N
Cl
N
CH3
CH3
N
F
PCl4
N
CH3
CH3
N
Cl
N
PCl3F
CH3
B
CH3
N
PCl4F
N
CH3
A
CH3
N
Cl
N
P(CF3)F3
CH3
CH3
N
Cl
[CF3PF3]⊖
N
CH3
FDC
CH3
N
P(CF3)F3Cl
N
CH3
CH3
N
F
N
P(CF3)F3
CH3
CH3
N
P(CF3)F4
N
CH3

Scheme 46

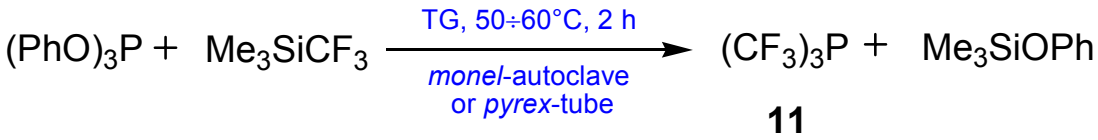
D. Conclusion

As it happens very often, answering the questions put on leads to discovering new unexpected compounds and fields of chemistry. Therefore, both planned and not planned research was done supplementing each other.

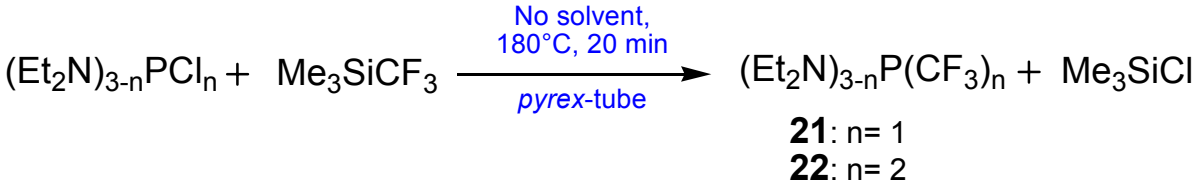
Syntheses of starting compounds were optimized significantly and new ease routes to ones were also found. Thus, $(CF_3)_3P$ was synthesized on simplified method in usual laboratory glassware or in an autoclave by using the Ruppert - system [*$(Et_2N)_3P/CF_3Br$*]. The phosphine mentioned can be also prepared using



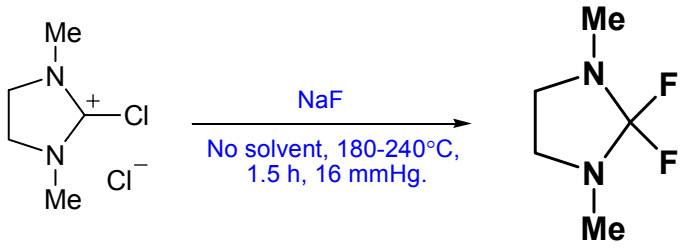
Ruppert reagent (*Me_3SiCF_3*) either in glass tubes with Teflon™ stop-cocks or in an autoclave. Taking into account the gradually decreasing price of the Ruppert reagent, this method can be considered as the easiest and cheapest route to trifluoromethyl phosphines in general. Syntheses of phosphines **21** and **22** were



carried out as the proof of the assertion. Applicability of the Grobe – method in synthesis of trifluoromethyl phosphines was evaluated. Unfortunately, side reactions prevailed over the target product formation and phosphines **11**, **21**, **22** were obtained in low yields.



Excellent results were obtained while optimizing the synthetic procedures for preparing DFI and DFTMU. A low cost and experimentally simple method was elaborated which could make these fluorinating agents available in everyday laboratory use. However, attempt to apply this approach for the synthesis of other N-CF_2 reagents failed. Very good yield might be accessible in the case of $(Et_2N)_3PF_2$ – a mild fluorinating agent.



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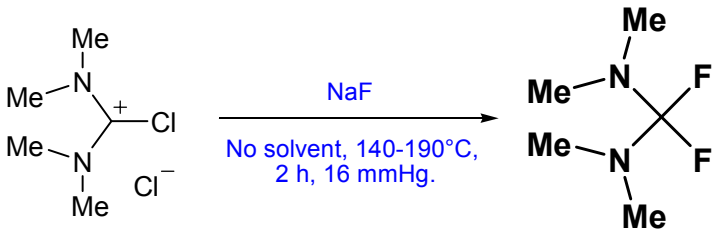

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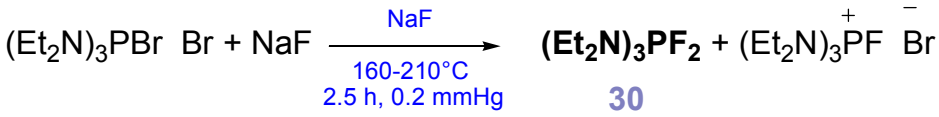
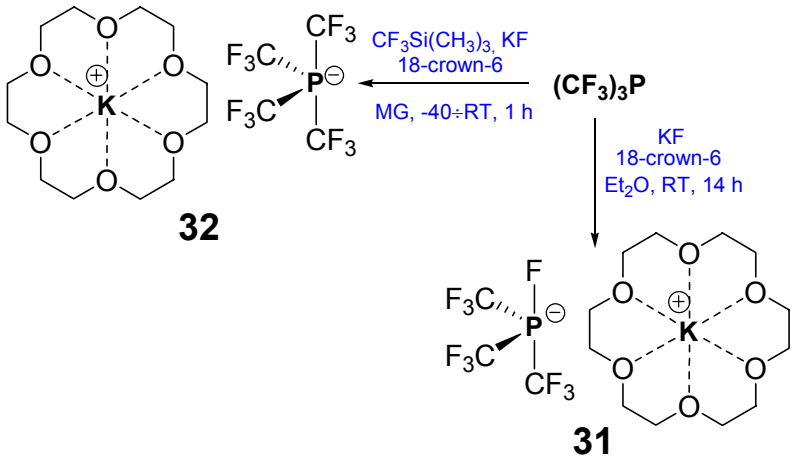
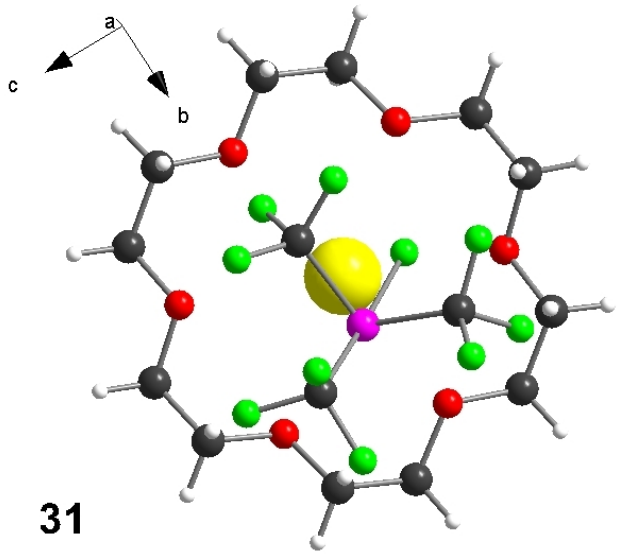


30

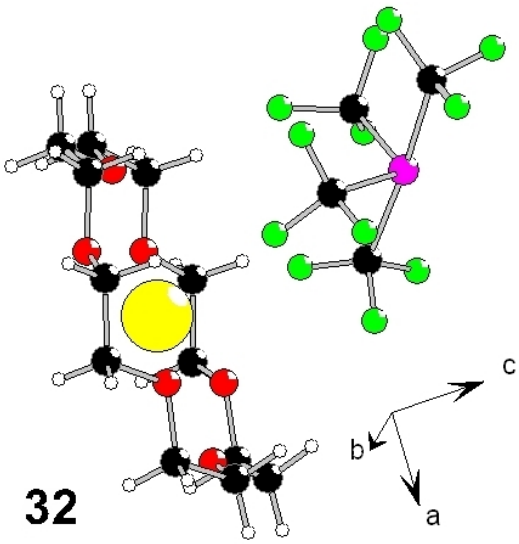
The new tris(trifluoromethyl)fluorophosphoranide (**31**) and tetrakis(trifluoromethyl)phosphoranide (**32**) salts were synthesized. High relative stability of these derivatives allowed theirs full characterization including X-Ray analysis as well as comprehensive studying of theirs chemical properties.



32 **31**

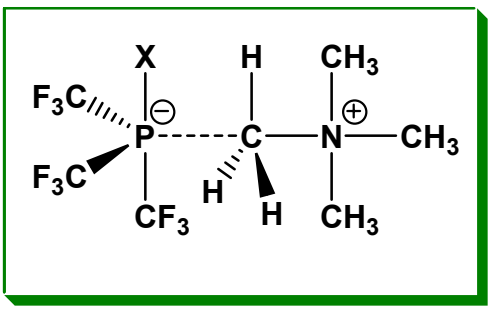


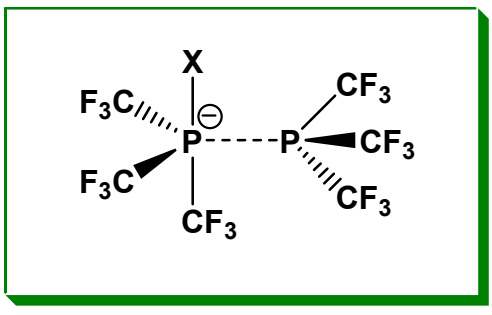
31



32

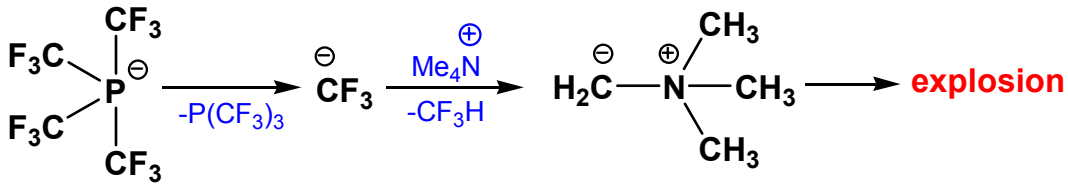
Thermal stability and fluxional behavior of salts **7**, **8**, **9**, **31**, **32** in solution in dependence on the nature of cation were investigated. Strong dissimilarity of TMA and (K^+)*18-crown-6 salts was supposed to be a result of coordination of TMA cation on the lone electron pair of phosphorus (tight ionic pair) while (K^+)*18-crown-6 cation was bound to the anion more loosely (solvent-separated ionic pair). The coordination of the cation, as well as $(CF_3)_3P$ to phosphorus (*vide infra*) is accompanied by a higher pseudorotation barrier what results in the resolution of NMR spectra at higher temperatures than in the case of the absence of coordination. Addition of phosphine **11** to solutions of the phosphoranides **7**, **8**, **31**, **32** was found to increase their stability and the same but significantly weaker effect was also found for Me_3SiCF_3 (it is true for salts **7**,



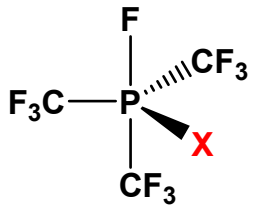


32; salts **8** and **31** are quickly trifluoromethylated by Ruppert reagent). It is very tempting to suggest that in general, Lewis acids may possess such a stabilizing effect. However, there is no possibility to check this suggestion due to high reactivity of the title phosphoranides towards electrophilic substrates to give

fluorinated or trifluoromethylated products (*vide infra*). TMA salts of trifluoromethyl phosphoranides proved to be much less stable than the corresponding (K^+)*18-crown-6 salts also in the solid state. Here, the formation of a highly unstable nitrogen ylide can be presumed to explain this phenomenon.

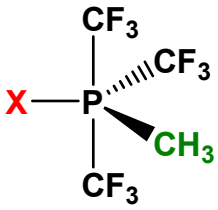


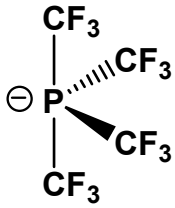
Energy barriers to pseudorotation in trifluoromethyl phosphoranides were compared with those for trifluoromethyl phosphoranes. These barriers turned out to be not regular for the phosphoranides – too low for salts **8**, **31** and too high for salts **7**, **32**. Steric factor ought to be crucial in the case of tetrakis(trifluoromethyl)-phosphoranides but the fluxional behavior of tris(trifluoromethyl)fluoro derivatives has still stayed inexplicable.



8 -60°C / 31 < -90°C

X= Me_2N / -40°C
MeO / -80°C
MeS / -70°C

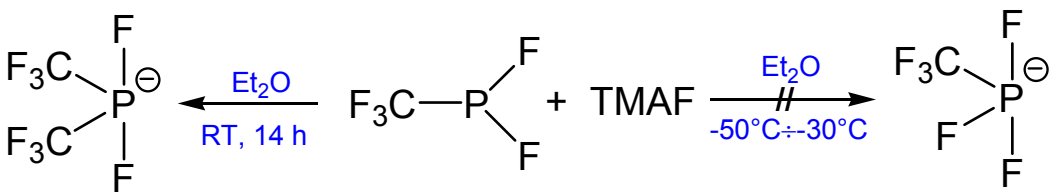




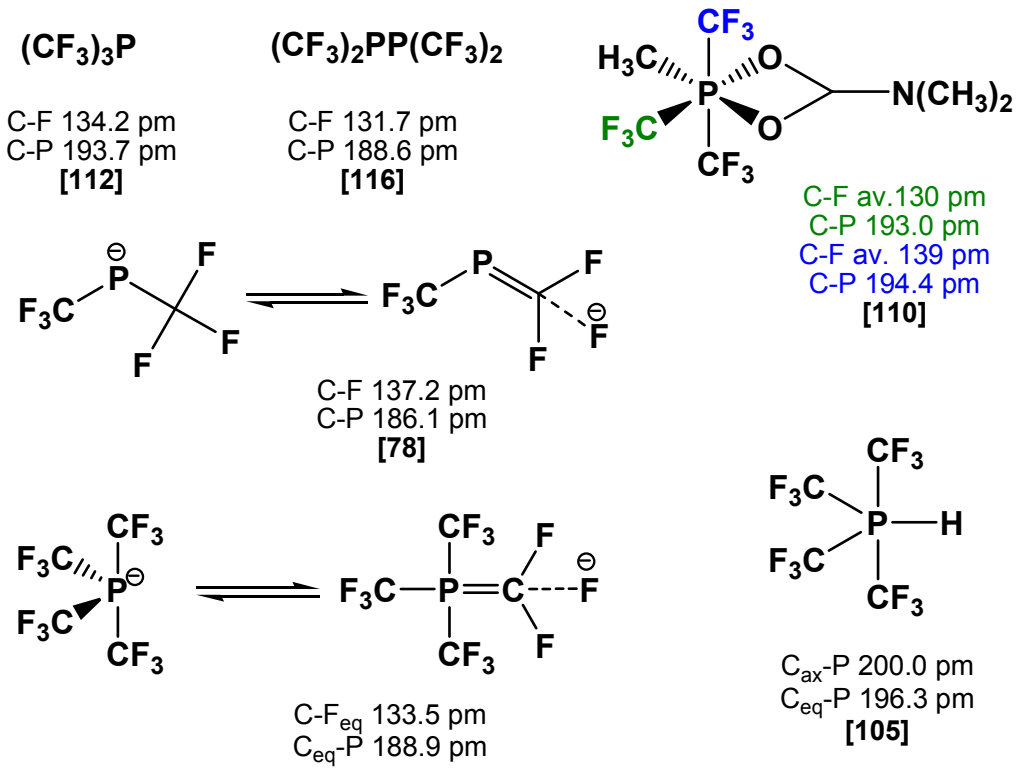
32 -50°C / 7 -45°C

X=	NMe_2	SCH_3	OCH_3	F	Cl
	33°C	-10°C	-40°C	-90°C	-100°C

Opposite to direct synthesis of salts **7**, **8**, **31** and **32**, phosphoranide **9** was obtained as the product of symmetrization reaction. Previously reported synthetic method for this compound implying simple decomposition of **8** was found to yield a mixture containing less than 50% of the phosphoranide desired.

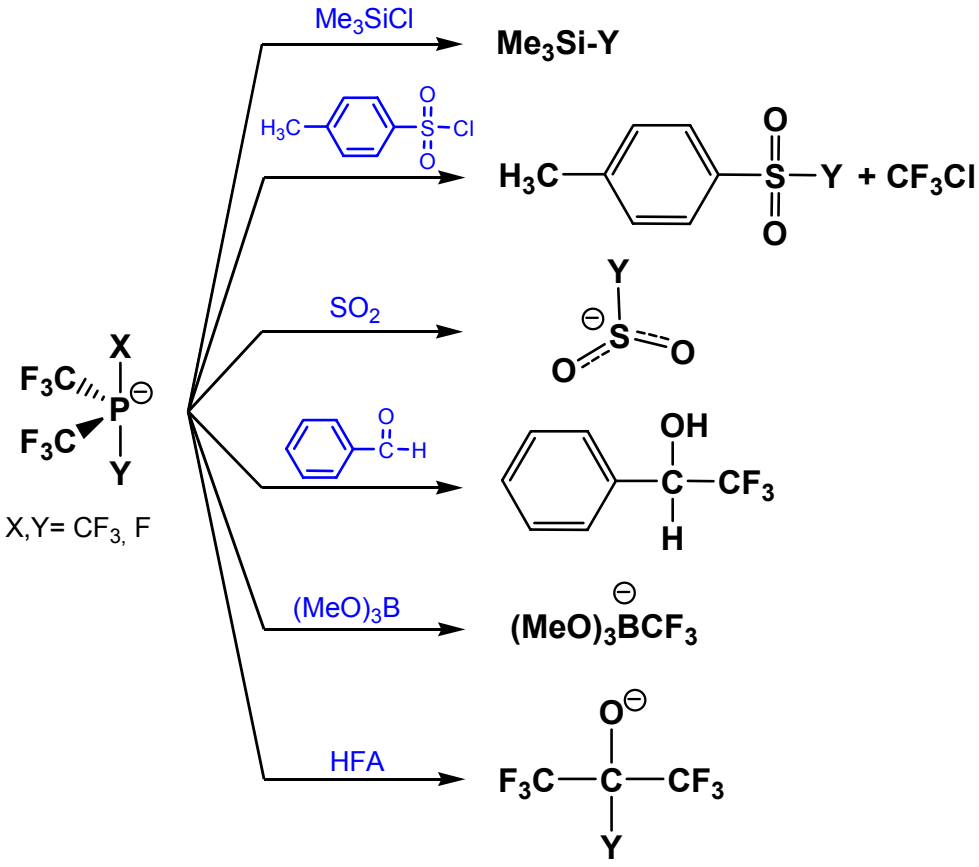


Ab-initio calculations of electronic and geometrical parameters as well as selected gas-phase acidities for phosphoranides were performed and close interrelationships of different parameters for each group of substituents (axial, equatorial) were established. One of the most important results obtained after comprehensive analysis of X-Ray and ab-initio calculations data is a discovery of the participation of equatorial groups in phosphoranide ion's negative charge delocalization. This is supported by C_{eq}-P bonds shortening and F-C_{eq} bond slight elongation.

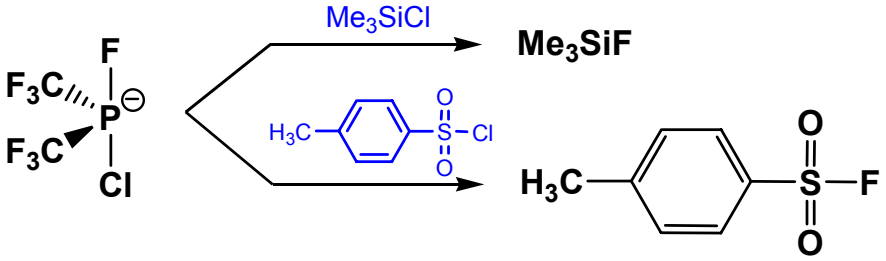


Since we have not managed to obtain MS spectra of trifluoromethyl phosphoranides, MS investigations of starting $(CF_3)_3P$ and $(CF_3)_2PCl$ were done. Fragments corresponding to $[(CF_3)_3PF]^-$ and $[(CF_3)_2PF_2]^-$ were detected. Fragment corresponding to $[(CF_3)_4P]^-$ was revealed in MS spectra of $[(CF_3)_5PF]^-$ TMA^+ [nnn].

Chemical properties of the phosphoranides were investigated. As expected, trifluoromethyl phosphoranides trend to loose an apical ligand serving as fluorinating or trifluoromethylating agents. Halogenophilic reaction of tetrakis-(trifluoromethyl)- derivatives with sulfonyl chlorides should be pointed out.

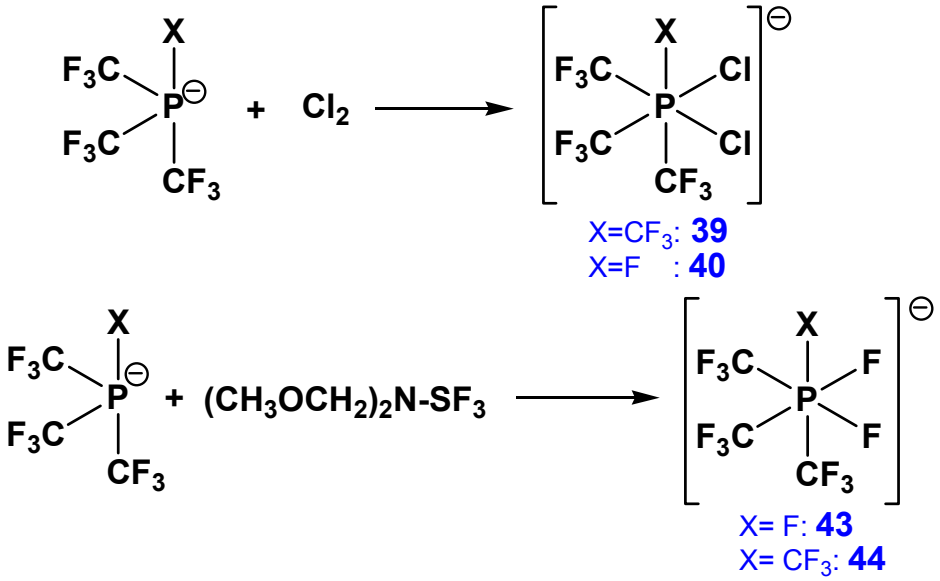


Surprisingly, phosphoranide **10** was revealed to act as a fluorinating agent. The equilibrium between the dissociated and non dissociated form is strongly shifted towards the formation of $(CF_3)_2PCl$ due to the immediate reaction of fluoride with a substrate.

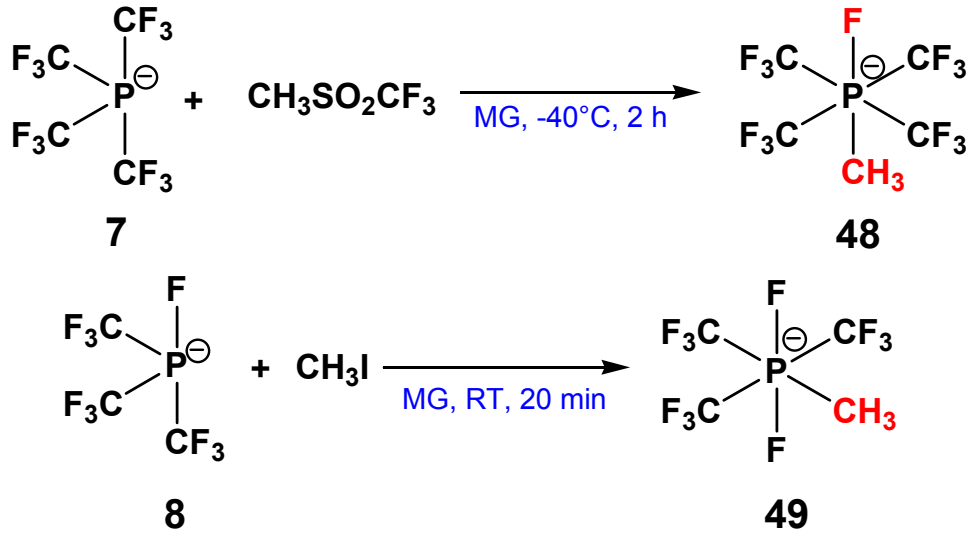


$$(CF_3)_2PF + Cl^{\ominus} \rightleftharpoons (CF_3)_2PFCl^{\ominus} \rightleftharpoons (CF_3)_2PCl + F^{\ominus}$$

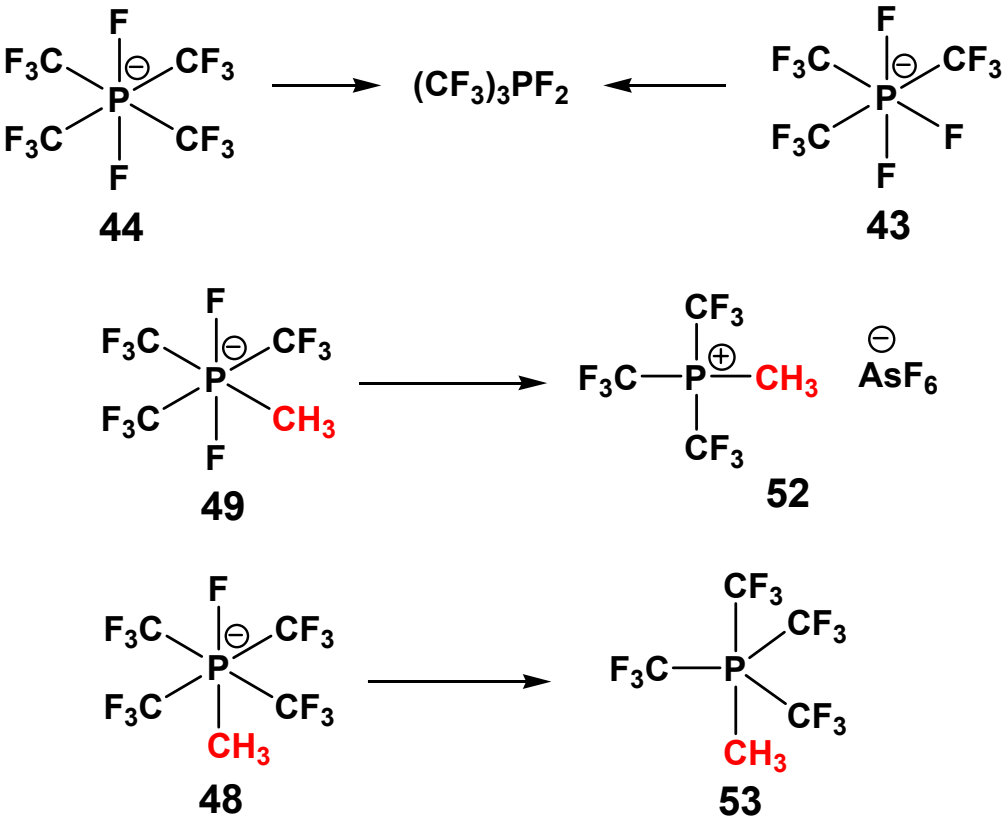
The title phosphoranides were oxidized by elemental chlorine or by Deoxo-Fluor™. However, yields of $[(CF_3)_4PF_2]^-$ TMA^+ were very low due to prevailing the reaction of Deoxo-Fluor™ trifluoromethylation over the fluorination reaction.



Phosphoranides **7** and **8** were successfully methylated and contrary to previously reported results, six-coordinate products **48** and **49** were isolated. Compounds **39**, **44**, **48** are the first compounds of six-coordinate phosphorus containing four trifluoromethyl groups to be isolated and completely described.

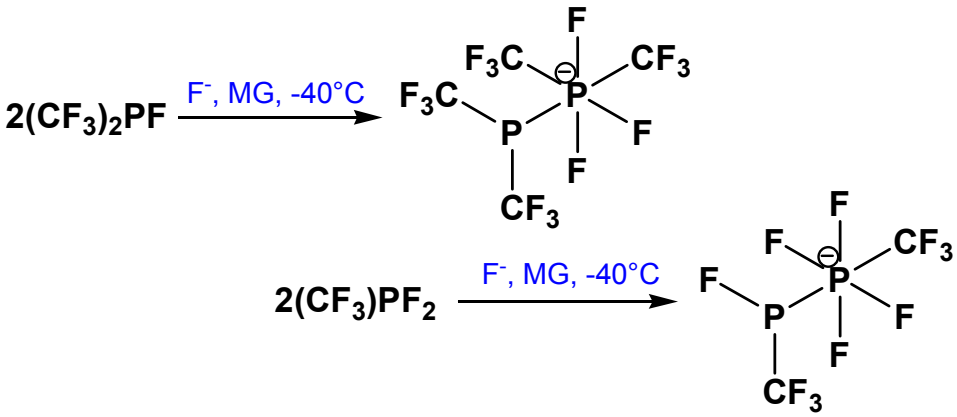


Using a strong Lewis acid and fluoride ion acceptor – AsF_5, we managed to abstract fluorine from the whole array of phosphate salts synthesized. High stability of the products obtained in liquid SO_2 should be pointed out. Such a stabilization effect was due to the solvent coordination on the very electronegative phosphorus atom.



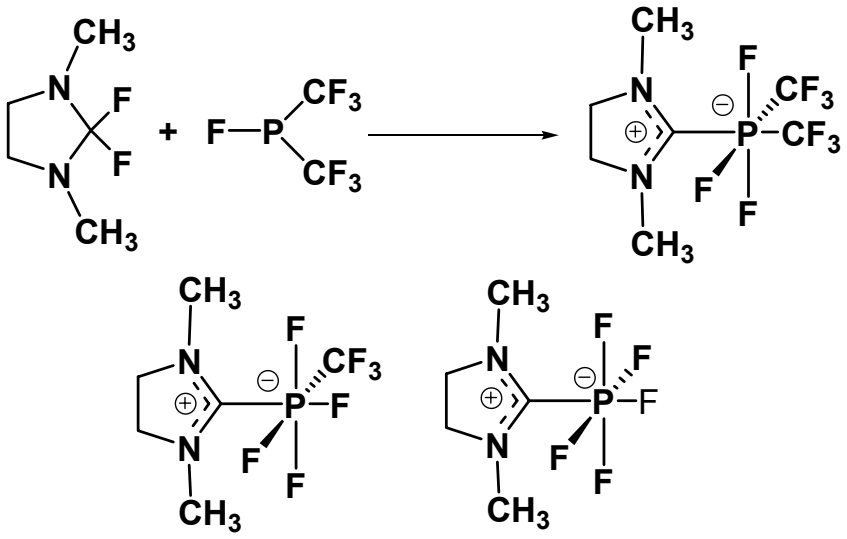
Conditions: **SO_2** as a solvent; for compounds **44**, **43**, **49** - stochiometric amount, for **48** - excess of **AsF_5** was taken; temperature range - from -78°C till RT

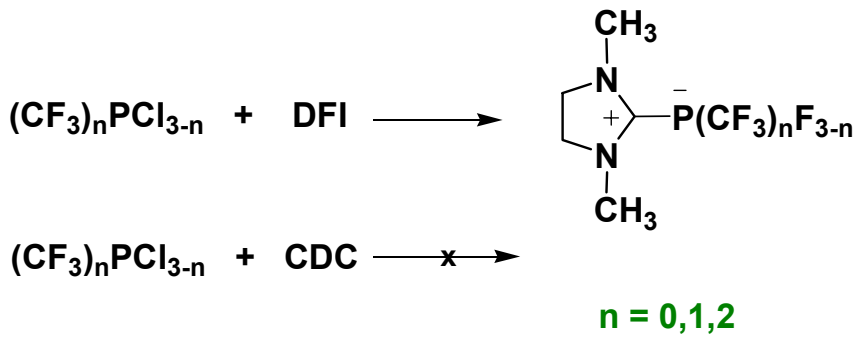
A new class of compounds was discovered during studying the chemistry of phosphoranides. Mixed-valence species (λ3σ3P-λ5σ6P system) **55**, **57** were unexpectedly obtained in the reactions of trifluoromethylphosphoranides with fluoride ion sources in monoglyme. These derivatives were characterized by



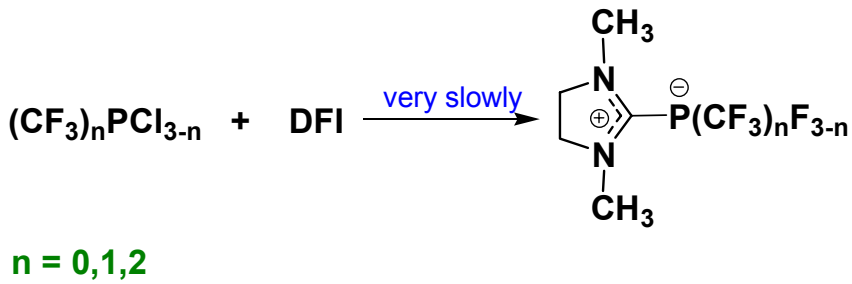
NMR and MS spectral methods however, numerous attempts to grow single crystals applicable for X-Ray analysis failed – compounds quickly decomposed in solution even at -40ºC to give phosphate salts: $[CF_3PF_5]^-$ $[(Et_2N)_3PF]^+$ (**57A**) and $[(CF_3)_2PF_4]^-$ $[(Et_2N)_3PF]^+$ (**55A**).

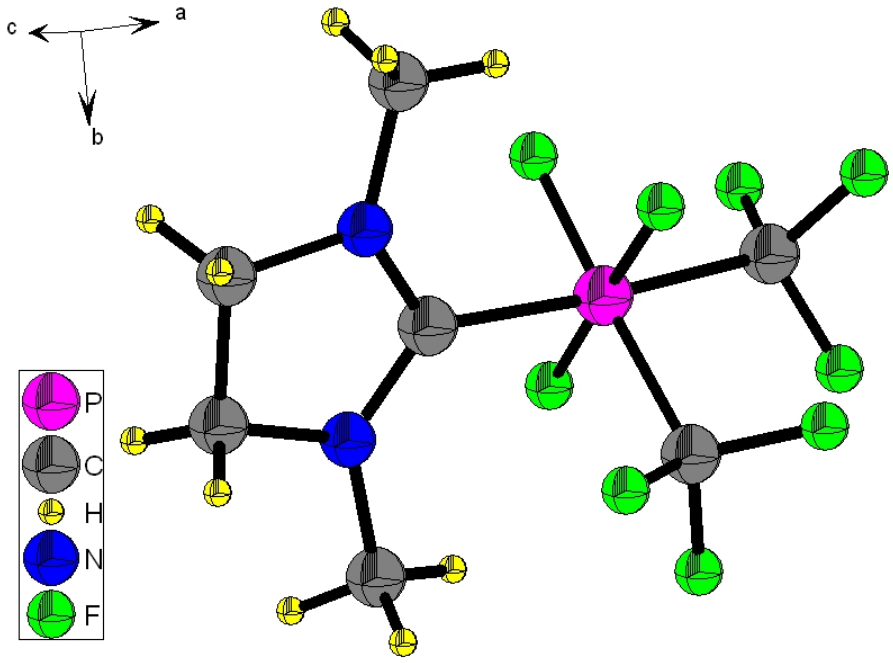
Perphosphoranides **58**, **59**, **60** were obtained in very high yields in the reaction of corresponding trifluoromethyl phosphines with DFI™. These compounds were fully described including X-Ray analysis (for perphosphoranide **58**). No perchloro- or mixed F-Cl perphosphoranides were synthesized. An



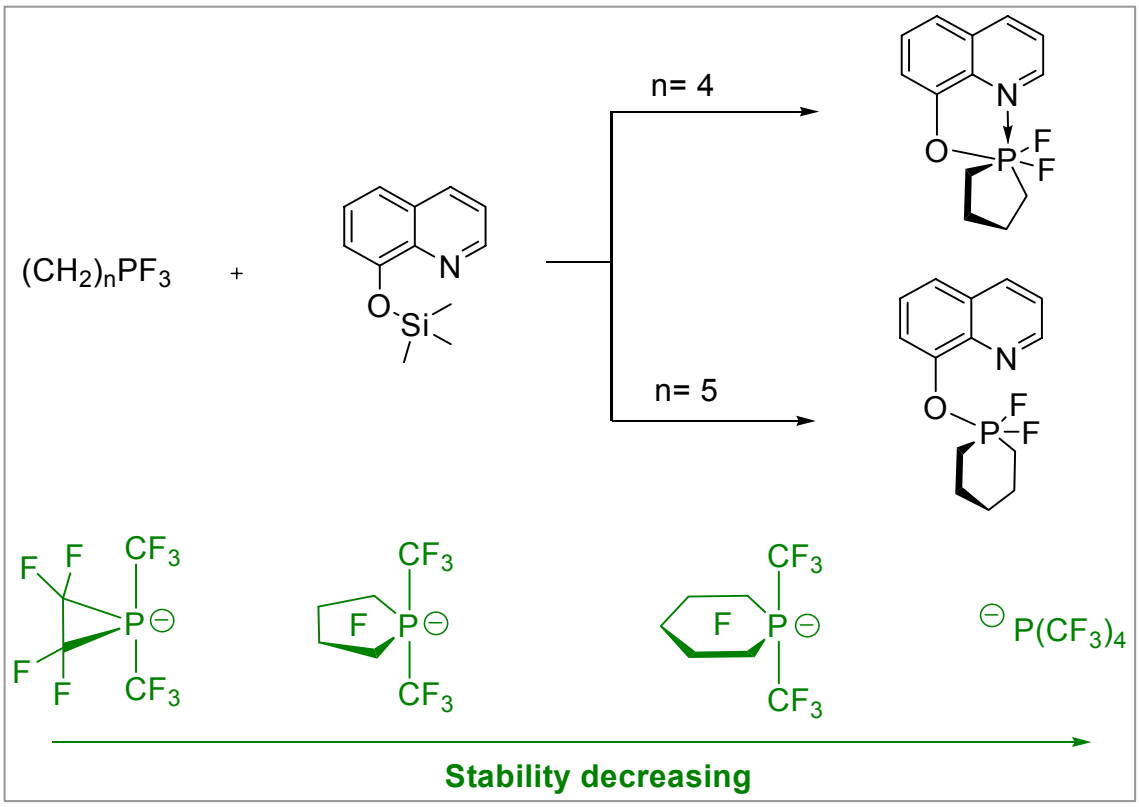


interesting transformation of difluoromethylchlorophosphines into perphosphoranides containing no Cl atoms under the influence of FDC was revealed and the mechanism of this process proposed.




c
a
b
P
C
H
N
F

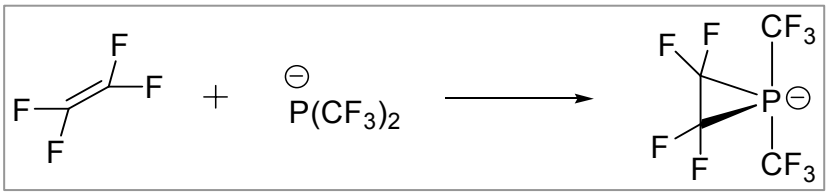
E. Future perspectives



Scheme 47

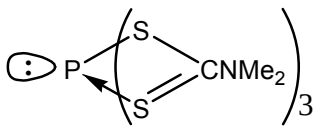
The chemistry of trifluoromethyl hypervalent phosphorus derivatives described here can be extended to longer chain perfluoroalkyl groups. The electrophilicity of P(III), P(IV) and P(V) centers is the key property defining reactivity and stability of corresponding species and so longer perfluoroalkyl chains being more electrophilic than the simple trifluoromethyl group should increase the stability of negatively charged hypervalent compounds. Moreover, the geometry of the perfluoroalkyl substituent can also play an important role. Thus reactions of $(CH_2)_nPF_3$ (n = 4 or 5) with 8-(trimethylsiloxy)quinaldine afforded six- and five-coordinated phosphorus (V) compounds, respectively[144]. The complex $(CH_2)_4PF_2L$, where L = oxinato, shows sixfold coordination at phosphorus, whereas $(CH_2)_5PF_3$ does not form the respective species at room temperature (*Scheme 47*). The difference in behavior was attributed to a difference in the Lewis acidity of the phosphorus center in $(CH_2)_5PF_3$ compared *to* $(CH_2)_4PF_3$, the latter being a stronger acid as the result of the ring strain. At

the same time it was noticed that the reaction between dimethyltrifluoro phosphorane and 8-(trimethylsiloxy)-quinoline produced a clean compound but with no evidence of a six-coordinate phosphorus(V) center[145]. Taking these results into consideration it is possible to predict higher stability for the phosphoranide ion $[(CF_2)_2P(CF_3)_2]^-$ compared to phosphoranide ion $[(CF_2)_4P(CF_3)_2]^-$ and both the phosphoranide ions ought to be more stable than trifluoromethyl derivative **7** (*Scheme 47*). The phosphoranide with smallest three-membered ring could be synthesized by an oxidation process presented on the *Scheme 48.* Such the method is not common for phosphoranide formation and only a few examples of its utilization are known by far[146,147]. Subsequent reactions of $P(CF_3)_2^-$ ion[78] to halogens, pseudohalogens, HFA or electrophilic P(III) centers with formation of corresponding phosphoranides could be also interesting.

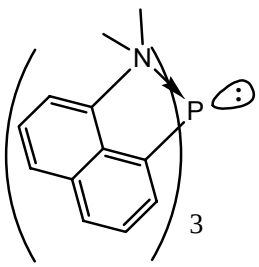


Scheme 48

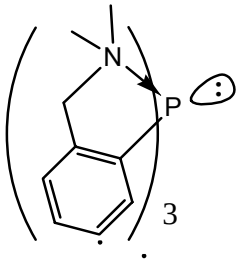
As was mentioned above, pseudo-heptacoordinate and heptacoordinate phosphorus derivatives are quite rare. Though pseudo-heptacoordinate phosphines **62**, **63**, **64** are characterized by X-Ray analysis, nothing is known about structure of heptacoordinate phosphonium salt **65**. Therefore the synthesis and analysis of the heptacoordinate phosphorane **66** could be of great interest. This idea is inspired by the synthesis of pseudo-pentacoordinate stabilized phosphenium salts successfully carried out by Carre and co-workers[148] *(Scheme 49)*. As pseudo-coordinated phosphines have tri-capped tetrahedron structure and such the type of structure is also supposed for the salt **65**, it is possible to predict di-capped trigonal bipyramide for heptacoordinate derivative **66**.



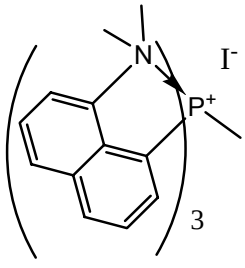
62



63

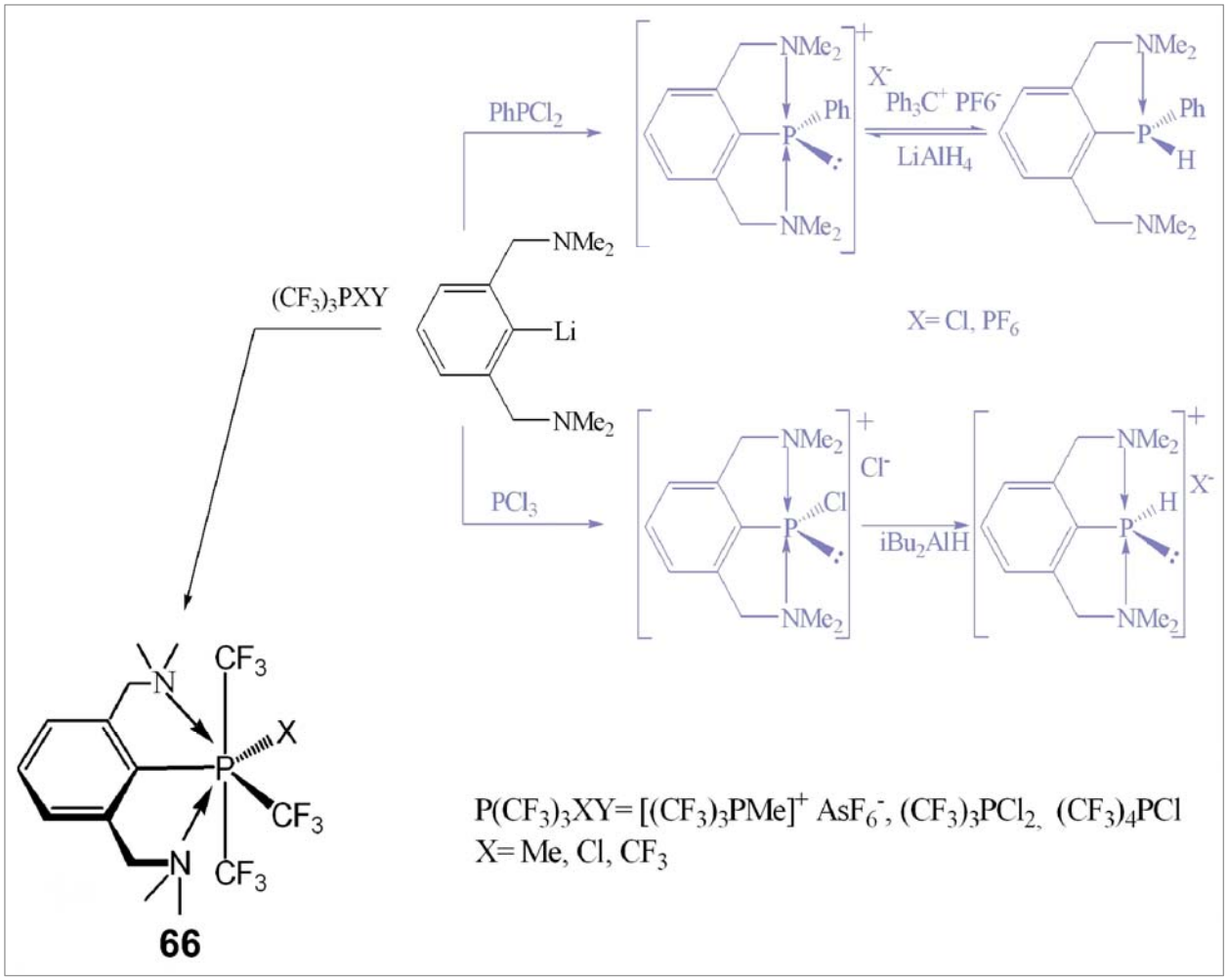


64



65

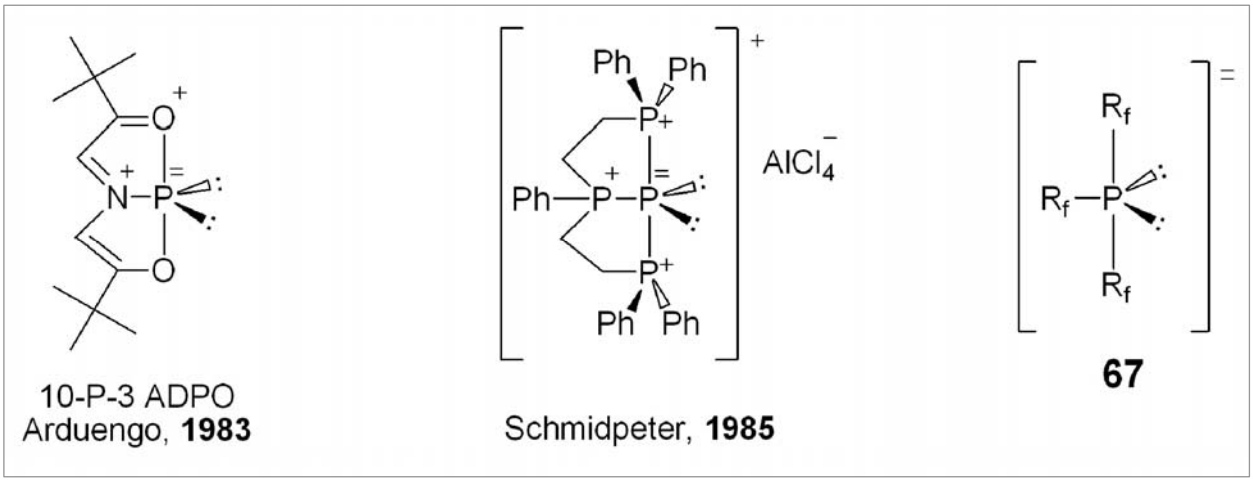
A very interesting class of hypervalent compounds with T-shaped 10-P-3 geometry was discovered by Schmidpeter *et al.* and Arduengo *et al.* in the early 80's[149, 150] (*Scheme 50*). The atom in apical position of a ψ-tbp structure must be effectively electronegative in order to accommodate the increased electron



Scheme 49

density in these positions and thus stabilizes the linear 3c-4e (hypervalent) bond. That is why the 10-P-3 ADPO structure is a minimum on the potential energy surface whereas Schmidpeter's salt is just a transition state. Utilization of perfluoroalkyl radicals as electronegative ligands in such the system could lead to formation of non-cyclic phosphorandiides **67** which are not known by far. X-Ray analysis of ADPO shows that P-O bond distances are only slightly longer (<6%) than the corresponding apical P-O distances in 10-P-5 centers and the large upfield shift of ^{17}O relative to diketoamine starting ligand was observed. This implies a very high degree of interaction between the phosphorus and oxygen centers. The ^{15}N-^{31}P coupling constants are around 80 Hz and are

generally consistent with three-coordinate phosphorus atoms[151a]. Therefore one can suggest relatively high stability to *tris(perfluoroalkyl)phosphorandiides* **67** though lower than of corresponding isoelectronic

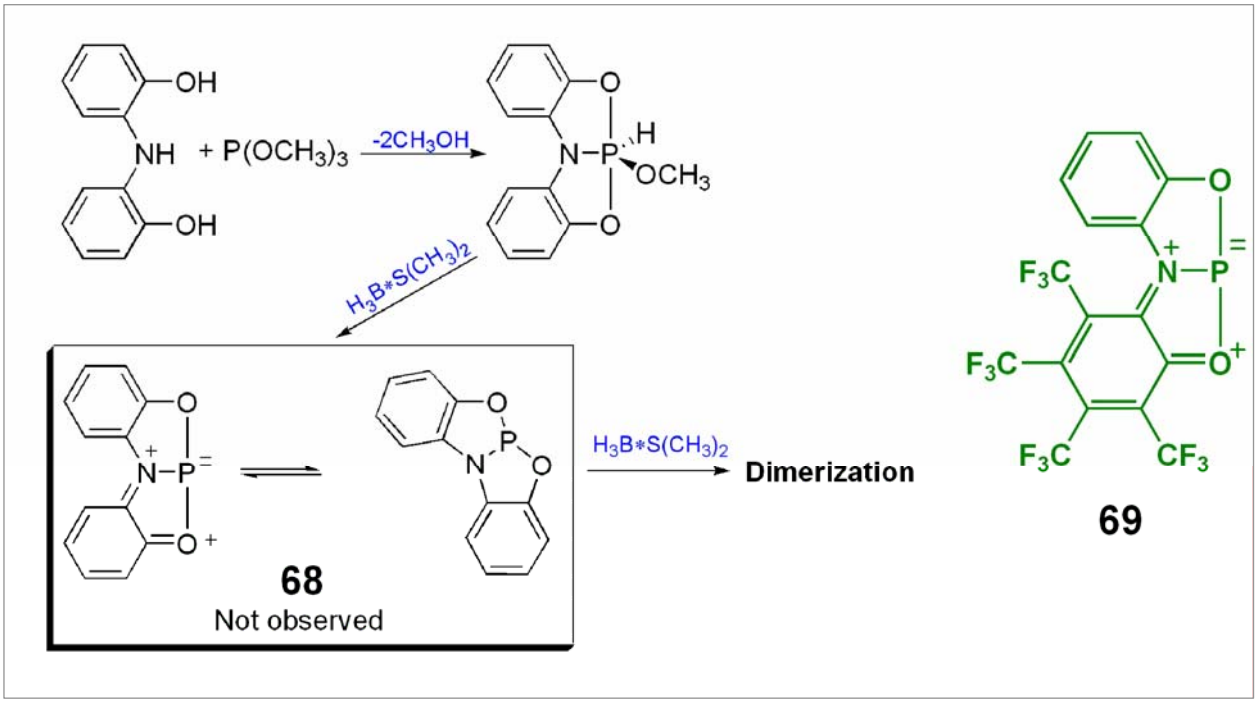


Scheme 50

tetrakis(perfluoroalkyl)phosphoranides.

The unsuccessful attempt to synthesize the “dibenzo”-ADPO ring system **68** was described in the literature[151b] (*Scheme 51*). The apparent lack of stability of **68** is consistent with the close energy relation between planar 10-P-3 and folded 8-P-3 structures with higher stability of the last. As one can see the folded structure has an intact aromatic system therefore it is more preferable.

It is known[152] that in hexa(trifluoromethyl) benzene the *π*-electron density is partly localized due to strong CF_3 group influence. In case of one aromatic ring of the planar 10-P-3 ADPO molecule being tetra(trifluoromethyl) substituted, the folded structure ought to be found less stable since aromaticity disruption effect is not so crucial and phosphorandiide **69** could be isolated. As typical ADPO systems are quite stable to dimerization besides, indirectly obtained dimers undergoe slow conversion to a bicyclic ring system[151], no dimerization products could be expected for **69**.


OH
NH
OH
+ P(OCH3)3
-2CH3OH
O
N–P
H
OCH3
O
H3B*S(CH3)2
O
N–P
O+
O
P
N
O
68
Not observed
H3B*S(CH3)2
Dimerization
O
N–P
O+
F3C
F3C
F3C
CF3
69

Scheme 51

F. Experimental part

F1. General procedures

All reactions and manipulations were conducted under atmosphere of dry nitrogen. The glassware to be used was usually kept overnight in drying oven at 160ºC and then cooled in the flow of dry nitrogen. Reactions with gases were carried out using standard vacuum techniques in a system made of Pyrex® glass and glassy stopcocks lubricated with “Waker” medium duty silicon grease, thick-walled round-bottom Pyrex® tubes with a Teflon® stop-cocks served as reaction vessels. Nonvolatile air and moisture sensitive materials were handled in inert atmosphere (glove box “M. Braun Unilab 1200/780” with integrated fridge and gas purifying unit) for a short time at room temperature, but stored in a fridge at -30ºC.

F2. Materials

The trifluoromethylphosphorus compounds and other reagents required for these studies were prepared according to indicated in literature methods: $(CF_3)_2PCl$[64], $(CF_3)_2PF$[153], CF_3PCl_2[64], CF_3PF_2[154], CF_3SiMe_3[60], TMAF[68], $(Et_2N)_3P$[155], $(Et_2N)_2PCl$[156], $(Et_2N)PCl_2$[157], $(Et_2N)_3PF_2$[68], $CF_3SO_3CH_3$[158], PF_3[159].

Solid fluorides and solvents used were purified, dried and degassed by standard methods. Commercially available chemicals of ”reagent grade” were used without further purification.

Following commercially available chemicals were used: $(PhO)_3P$, PCl_3, Et_2NH, 18-crown-6, ZnF_2 (Apollo PC8030), NaF (Fluka 71522), KF (Aldrich 30,759-9), AsF_5 (ABCR F01150), SbF_3 (Apollo PC1140), CF_3Br (generous gift of *Bayer AG*), MeI, NMP. DMI, $(COCl)_2$, $(Me_2N)_2CO$, $(CF_3)_2CO$, $ClC_6H_4SO_3Cl$, $CH_3C_6H_4SO_3Cl$, Cl_2, HCl, $(CH_3OCH_2)_2NSF_3$ (generous gift of *Hansa Fine Chemicals GmbH*), SO_2, PhCOH

F3. Physical methods

Mass spectra (70 eV) were carried out on a MAT 8200 type spectrometer (Varian MAT) as well as FAB measurements. High resolution mass spectra were carried out on a Finnigan MAT 8222 spectrometer using Peak-Matching Method.

The X-ray structural study was carried out on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 71.073 pm). While measuring crystals were cooled down till -100ºC with the low-temperature nozzle Siemens LTII. The diffractometer was operated by XSCAnS program.

NMR spectra were obtained on a Bruker DPX-200 spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, 188.31 MHz for ^{19}F and 81.01 MHz for ^{31}P, and Bruker AMX-360 spectrometer operating at 360.0 MHz for ^{1}H, 90.56 MHz for ^{13}C, 188.31 MHz for ^{19}F and 145.79 MHz for ^{31}P. As internal standard for ^{1}H and ^{13}C measurements Me_4Si was used, for ^{19}F and ^{31}P measurements CCl_3F and 85% H_3PO_4 were used correspondingly.

Melting points were estimated on Jürgens Electrothermal Melting Point Instrument with working range from 20ºC till 360ºC. The temperatures are uncorrected.

Element analyses were performed by Beller Microalanalytisches Laboratorium, Göttingen, Germany.

F4. Synthesis of compounds

*4.1. Synthesis of tris(trifluoromethyl)phosphine (**11**) in usual laboratory glassware*

Round-bottom one-neck 2 L flask equipped with magnetic stirring bar, dropping funnel with pressure-equalizing arm and vacuum adapter with stopcock was charged by 400 ml of dry triglyme, 50 g (0.16 mol) of triphenylphosphite and 120.8 g (0.49 mol) of hexaethylphosphorus amidite. The system was evacuated (water-aspirating or oil pump) and stirred in dynamic vacuum for 5 min to degas the reaction mixture completely. Then 79.2 g (0.53 mol) of trifluorobromomethane weighed in a rubber balloon were driven into the reactor portionwise (3×26.4 g) with time interval approximately 1 h depending on the reaction rate under constant stirring at ambient temperature. The reaction process was accompanied by gas absorbing, darkening of the mixture and mild exothermic effect. After consuming all trifluorobromomethane vacuum created in the reaction vessel was spoiled by dry nitrogen then, the closed system was stirred for 4-6 h additionally and connected to a trap cooled by liquid nitrogen. All volatiles were pumped off from the reaction mixture while it's moderate heating by a heat gun. The mixture of gases obtained was distilled trap-to-trap in 150 mmHg. The target phosphine was trapped at -40ºC and -60ºC and CF_3Br at -196ºC. Two fractions were combined to give 31.8 g (yield: 83%) of $(CF_3)_3P$ of 97.8% purity.

*Analysis of **11**:* C_3F_9P, FW 237.99 g/mol, b.p.= 17ºC; ^{19}F-NMR ($CDCl_3$): δ = -51.3 (d, $^2J_{PF}$ = 83.2 Hz), ^{31}P-NMR ($CDCl_3$): δ = -2.3 (dec); in good agreement with [52, 53, 55]

Attention! Phosphine **11** as well as other trifluoromethylhalogenophosphines, is a highly flammable liquid with low boiling point (17ºC) readily exploding in liquid state under contact with air, quite long induction time could be possible in this case. Avoid leaks and use steel clamps for safety. Be attentive - CF_3Br may initially mask ignition of the phosphine that may cause very intensive flame after disappearing of the main amount of the freon.

*4.2. Synthesis of tris(trifluoromethyl)phosphine (**11**) in autoclave*

To degassed solution of 20 g (0.064 mol) of triphenylphosphite and 48.32 g (0.195 mol) of hexaethylphosphorus amidite in 100 ml of dry triglyme placed in 300 ml monel autoclave 28.8 g (0.193 mol) of trifluorobromomethane were condensed. The autoclave was closed and warmed up to room temperature. A wall of the vessel was shortly heated up to 60 by a heat gun to initiate the reaction. In the case of carrying out the reaction at ambient temperature long induction period could be possible. Reaction began and finished in approximately 1 h with strong elision of heat therefore autoclave was continuously shaken and periodically cooled down by cold water until 40-50ºC. After disappearing the exothermic effect autoclave was placed in oil bath and heated at 60ºC during 1.5 h. Isolation and purification is described above. Yield: 77% - 11.8 g.

*4.3. Synthesis of tris(trifluoromethyl)phosphine (**11**) starting from Ruppert reagent - Me_3SiCF_3*

To solution of 10 g (0.032 mol) of triphenylphosphite and 15.1 g (0.106 mol) of Ruppert reagent in 50 ml of dry triglyme placed in 300 ml thick-walled round-bottom Pyrex® tube with a Teflon® stop-cock and cooled by ice, 0.42 g (0.0032 mol) of potassium phenolate was added. The reaction mixture was warmed up till RT and stirred at 50ºC during 2.5 h and then cooled down. All volatiles were pumped off into usual flask and distilled with Vigreux column at atmospheric pressure to give 6.1 g (Yield: 80%).

Analysis of **17**: $C_9H_5F_8OP$, FW 312.1 g/mol; ^{19}F-NMR (TG, without lock, field drift ≤ 1 Hz h^{-1}): δ = -51.8 (d.t, 6F, $^2J_{PF}$ = 79.3 Hz, $^4J_{FF}$ = 7.76 Hz), δ = -51.8 (d.sep, 2F, $^2J_{PF}$ = 81.03 Hz), ^{31}P-NMR (TG): δ = 0.93 (no, $^2J_{PF}$ = 79.08 Hz); MS: (EI, 70 eV, 200 °C, Matrix: isobutane) m/z (%): 312 (2) M^+, 293 (3) $[M\text{-}F]^+$, 262 (7) $[M\text{-}CF_2]^+$, 169 (12) $[M\text{-}PhOCF_2]^+$, 69 (17) $[CF_3]^+$, 178 (100) $[TG]^+$ and other fragments.

*4.4. Synthesis of tris(trifluoromethyl)phosphine (**11**) starting from CF_3Br and Al-powder*

To suspension of 1 g (0.037 mol) of Al-powder in 70 ml of dry NMP placed in 300 ml thick-walled round-bottom Pyrex® tube with a Teflon® stop-cock, 3.8 g (0.012 mol) of $P(OPh)_3$ was added. To degassed mixture of the reagents 9.1 g (0.06 mol) of CF_3Br was condensed. Reaction mixture was quickly warmed till RT and then stirred at 60ºC during 3 h. Gradual viscosity raising together with darkening of the reaction mixture were observed and at the end of the process very viscous and dark-brown mass was obtained. All the volatiles were pumped off and distilled trap-to-trap as previously described to give 0.34 g (0.0015 mol; yield: 12.7%) of the target phosphine.

NMR spectra of the reaction mixture: $(PhO)_3P$, ^{31}P-NMR (NMP, without lock, field drift ≤ 1 Hz h^{-1}): δ = 130.16 (br.s); $(PhO)_2PCF_3$, ^{19}F-NMR: δ = -75.86 (br.d, $^2J_{PF}$ = 89.2 Hz), ^{31}P-NMR: δ = 134.47 (q); $PhOP(CF_3)_2$, ^{19}F-NMR: δ = -64.9 (br.d, $^2J_{PF}$ = 78.5 Hz), ^{31}P-NMR: δ = 86.7 (sep); enamine **20**, ^{19}F-NMR: δ = -65.8 (br.s; *complete NMR description see below*), CF_3H, ^{19}F-NMR: δ = -81 (br.d, $^2J_{HF}$ = 76.7 Hz); CF_3Br, ^{19}F-NMR: δ = -23.24 (br.s); and other not identified products

To suspension of 0.4 g (0.015 mol) of Al-powder in 40 ml of dry NMP 1 g (0.0074 mol) of PCl_3 was added. To degassed mixture of the reagents 5.5 g (0.037 mol) of CF_3Br was condensed. Reaction mixture was quickly warmed till RT. After short inductive period intensive elision of heat was detected and the mixture turned black in 10-15 min. A mixture of gases presumably consisting of CF_3H and CF_3Br was obtained. No volatile phosphorous containing compounds were isolated.

NB: Other solvents and conditions were used as it was mentioned in the *Chapter C 1.1.* No reaction was detected for both the starting phosphines in MG or DG at any conditions used.

*4.5. Synthesis of bis(diethylamino)trifluoromethylphosphine (**21**) starting from CF_3Br and Al-powder*

Synthetic procedures for this reaction are identical to that of reaction of synthesis of phosphine **11** from $(PhO)_3P$ in NMP at 60ºC (*Clause 4.4*). The only difference is lower viscosity of the reaction mixture at the end of the process. 1.5 g (0.007 mol) of $(Et_2N)_2PCl$, 0.96 g (0.036) of Al-powder, 5.3 g (0.036) of CF_3Br and 50 ml of dry NMP were taken. Following compounds were identified in the reaction mixture: $(Et_2N)_2PCF_3$ (**21**, NMR yield: 31%), $(Et_2N)_2PF$, CF_3H, unreacted starting $(Et_2N)_2PCl$, CF_3Br

NMR spectra of the reaction mixture: $(Et_2N)_2PCl$, ^{31}P-NMR (NMP, without lock, field drift ≤ 1 Hz h^{-1}): δ = 160.1 (br.s); **21A**, ^{19}F-NMR: δ = -66.25 (br.s), ^{31}P-NMR: δ = 54.6 (br.s); **21**, ^{19}F-NMR: δ = -63.57 (br.d, $^2J_{PF}$ = 94.07 Hz), ^{31}P-NMR: δ = 76.0 (q); $(Et_2N)_2PF$, ^{19}F-NMR: δ = -78.6 (br.d, J_{PF} = 1759.92 Hz), ^{31}P-NMR: δ = 17.3 (br.d); CF_3H, ^{19}F-NMR: δ = -81.33 (br.d, $^2J_{HF}$ = 76.7 Hz); CF_3Br, ^{19}F-NMR: δ = -23.24 (br.s)

NB: **a)** Following the synthetic procedure described above, reaction of $(Et_2N)_2PCl$ with Al-powder and CF_3Br was carried out in DMF. Target product – **21** was detected to form in 6% NMR yield. Compound **21B** as byproduct was also detected and described by ^{19}F and ^{31}P NMR spectroscopy: ^{19}F-NMR (DMF, without lock, field drift ≤ 1 Hz h^{-1}): δ = -67.31 (br.d.d, $^3J_{FH}$ = 61.95 Hz, $^4J_{PF}$ = 6.88 Hz), ^{31}P-NMR: δ = 53.57 (non *or* und, $^3J_{PH}$ = 15.26 Hz)

b) Other solvents and conditions were used as it was mentioned in the *Chapter C 1.1*

*4.6. Synthesis of bis(diethylamino)trifluoromethylphosphine (**21**) and bis(trifluoromethyl)diethylaminophosphine (**22**) starting from Ruppert reagent: typical procedures*

Mixture consisting of 5 g (0.029 mol) of $(Et_2N)PCl_2$, 12.26 g (0.086 mol) of Me_3SiCF_3 and 0.48 g (0.003 mol) of CDC placed in 300 ml thick-walled round-bottom Pyrex® tube with a Teflon® stop-cock and a magnetic stirring bar was heated till 180ºC and kept at this temperature for 2 h under constant stirring. The mixture obtained was distilled in vacuum to give 6.4 g of **22** (0.027 mol; 93% yield).

*Analysis of **22***: $C_9H_{20}F_3N_2P$, FW 244.24 g/mol, bp= 45ºC (1 mmHg); ^{19}F-NMR ($CDCl_3$): δ = -66.4 (d, $^2J_{PF}$ = 93.1 Hz), ^{31}P-NMR ($CDCl_3$): δ = 74 (q); in good agreement with [64]

Compound **21** was synthesized in 89% yield. 10 g (0.047 mol) of $(Et_2N)_2PCl$, 20.25 g (0.14 mol) of Me_3SiCF_3 and 0.8 g (0.005 mol) of CDC were taken; 10.3 g (0.042 mol) of target phosphine was isolated.

*Analysis of **22***: $C_6H_{10}F_6NP$, FW 241.11 g/mol, bp= 60ºC (100 mmHg); ^{19}F-NMR ($CDCl_3$): δ = -59.8 (d, $^2J_{PF}$ = 86.6 Hz), ^{31}P-NMR ($CDCl_3$): δ = 42 (sep); in good agreement with [64]

*4.7. Synthesis of 1-methyl-5-(trifluoromethyl)-2,3-dihydro-1H-pyrrole (**20**) starting from CF_3Br, Al-powder and NMP*

To suspension of 6.7 g (0.05 mol) of $AlCl_3$ and 2.7 g (0.1 mol) of Al-powder in 70 ml of dry NMP placed in 300 ml thick-walled round-bottom Pyrex® tube with a Teflon® stop-cock and a magnetic stirring bar, 29.8 g (0.2 mol) of CF_3Br were condensed. The reaction mixture was quickly warmed up till 0ºC and left overnight with spontaneous warming up till RT and under constant stirring. After exposition of the reaction mixture at RT during 14 h excess of CF_3Br was evaporated at atmospheric pressure. The tube was connected to trap-to-trap system and the desired product was collected in trap cooled till -55ºC, CF_3Br at -196ºC, starting amide and byproducts were condensed at -10ºC (0.01 mmHg). 6.25 g (0.041 mol) of **20** were obtained (82% yield).

*Analysis of **20***: $C_6H_8F_3N$, FW = 151.13 g/mol, b.p.= 102ºC; ^{19}F-NMR ($CDCl_3$): δ = -64.7 (br. s), ^{1}H-NMR ($CDCl_3$): δ = 3.1 (s, CH_3), δ = 2.97 (br. s, CH_2), δ = 3.6 (br.s, CH_2), δ = 5.81 (s, =CH); in good agreement with [63]

*4.8. Synthesis of 2,2-difluoro-1,3-dimethylimidazolidine (DFI™) (**23**)*

30 g (0.177mol) of CDC and 74.3 g (1.77 mol) of NaF (*Aldrich 20,115-4; dried at 200ºC/0.01mmHg/16h*) thoroughly ground and mixed were placed in two-neck 0.5 L flask connected to usual distillation bridge with receiving 250ml flask attached i.e. standard distillation system. Pyrolysis was carried out while gradual raising the temperature from 180 till 240ºC during 1÷2 h in vacuum of water-aspirating pump. Since the target compound is quite volatile at the conditions described the receiving flask was cooled by liquid nitrogen. 22.2 g (0.163 mol) of the product as slightly pale liquid was obtained (92% yield).

*Analysis of **23***: $C_5H_{10}F_2N_2$, FW = 136.16 g/mol, b.p.= 47ºC (37 mmHg); ^{19}F-NMR ($CDCl_3$): δ = -73.9 (br. s), ^{1}H-NMR ($CDCl_3$): δ = 2.47 (br. s, 6H), δ = 2.97 (br.s, 4H), in good agreement with [66, 67a]

*4.9. Synthesis of Difluoro-N,N,N',N'-tetramethylmethanediamine (DFTMU) (**24**)*

50 g (0.29 mol) of TMCC and 197.35 g (4.7 mol) of dry NaF thoroughly ground and mixed were placed in two-neck 1 L flask connected to usual distillation bridge with receiving 250ml flask attached. Pyrolysis was carried out while gradual raising the temperature from 130 till 165ºC during 3.5 h in vacuum of water-aspirating pump, the receiving flask was cooled by liquid nitrogen. 36.34 g (0.26 mol) of the product as slightly pale liquid was obtained (90% yield).

*Analysis of **24***: $C_5H_{12}F_2N_2$, FW = 138.16 g/mol, b.p.= 100ºC; ^{19}F-NMR ($CDCl_3$): δ = -93.92 (br. s), ^{1}H-NMR ($CDCl_3$): δ = 2.26 (br. s), in good agreement with [67b]

NB: Since reactions occur in the solid phase and no mixing is possible, the reaction vessel was carefully shaken from time to time to provide better contact of the reagents. DFI™ as well as DFTMU can be used as fluorinating agents without further purification since they contain 1÷3% of corresponding mixed derivative as impurity. However, in separate cases distillation is necessary to obtain absolutely pure clear colorless liquid for a purpose to make a fine chemistry.

*4.10 Pyrolysis of 1,1-dichloro-N,N,N,N-tetramethylmethanediamine (TMCC) – synthesis of probably N, N, N'-trimethyl-chloroformamidine (**26**)*

The glassware used here is similar to that in the synthesis of DFTMU. Sample of TMCC (15 g, 0.88 mol; $m.p._{dec}$ 159ºC) was slowly heated from 100ºC till 180ºC. During Pyrolysis the main product was condensed in the receiving flask cooled by liquid nitrogen. However, less volatile white wool-like compound was condensed on the walls of the cooler. Amount of this byproduct (or polymerization product) was negligible therefore it could be ignored. Slightly pale colorless liquid was revealed in the receiving flask which was spontaneously solidified after 3-5 min exposition at RT to give white powder insoluble in common organic solvents. Attempts to dissolve the liquid obtained in different deuterated solvents led to either strong exothermic reaction ($DMSO_{d6}$, D_2O) or immediate solidification ($CDCl_3$, CD_3CN, C_6D_6) of the content of NMR tube. It was revealed that while warming the product till RT a gas elision from the liquid phase took place. Probably this gas is CH_3Cl but we did not manage to prove it unambiguously due to the problems discussed above.

*4.11. Synthesis of tris(diethylamino)difluorophosphorane (**30**)*

30 g (0.085 mol) of $[(Et_2N)_3PBr]^-$ Br+ and 35.9 g (0.85 mol) of NaF thoroughly ground and mixed were placed in two-neck 0.5L flask connected to usual distillation bridge with receiving 250ml flask attached. Pyrolysis was carried out while gradual raising the temperature from 160ºC till 210ºC during 2.5 h in vacuum of oil pump. The mixture consisting from **30** and **30A** as slightly yellow liquid was obtained. The mixture was dissolved in 100 ml of dry pentane and filtered under inert atmosphere from the mixed salt precipitated. The solvent was evaporated to give 10.19 g (0.044 mol) of difluorophosphorane ready to be used as fluorinating agent without further purification (84.5% conversion of starting dibromide, 52% yield, purity of the product – 97.4% by NMR).

*Analysis of **30***: $C_{12}H_{30}F_2N_3P$, FW = 285.36 g/mol, b.p.= 75ºC (0.02 mmHg); ^{19}F-NMR ($CDCl_3$): δ = -65 (d), ^{31}P-NMR ($CDCl_3$): δ = -60 (d.td, J_{PF} = 700 Hz, , $^3J_{PH}$ = 14.76 Hz), in good agreement with [68]

*4.12. Synthesis of N,2,2-trimethylpropanimidoyl chloride (**28**)- an attempt to obtain N-(1,1-difluoro-2,2-dimethylpropyl)-N,N-dimethylamine*

15 (0.081 mol) of 1,1-dichloro-*N,N*,2,2-tetramethyl-1-propanamine **27B** and 79 g (1.88 mol) of NaF thoroughly ground and mixed were placed in two-neck 250 ml flask connected to usual distillation bridge with receiving 250ml flask attached and cooled by liquid nitrogen. Reaction was carried out while gradual raising the temperature from 90 till 130ºC (m.p. of starting dichloride is 101ºC, decomposition temperature is 106ºC) during 1 h in vacuum of water-aspirating pump. 10.7 g (0.08 mol) of **28** were obtained (98.9% yield, traces of difluoroderivative were detected by ^{19}F NMR)

*Analysis of **28***: $C_6H_{12}ClN$, FW = 133.62 g/mol, b.p.= 63ºC (50 mmHg); ^{1}H-NMR ($CDCl_3$): δ = 1.23 (s, 9H), δ = 3.19 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 28.74 (s, 3×CH_3), δ = 40.36 (s, **C**$(CH_3)_3$), δ = 43.94 (s, CH_3), δ = 154.69 (s, -**C**=N-); MS: (EI, 70 eV, 200 °C) m/z (%): 133 (5) M^+, 118 (17) $[M\text{-}CH_3]^+$, 98 (57) $[M\text{-}Cl]^+$, 76 (9) $[M\text{-}tBu]^+$, 57 (27) $[tBu]^+$, 42 (100) $[tBu\text{-}CH_3]^+$ and other fragments, HRMS M^+ calc: 133.06583, found: 133.06581, R = 10 000.

NB: **a)** The same experiment was done in chlorobenzene as a solvent (*see Chapter C1.2*). The temperature regime was: 1) RT, 12h; 2) 50ºC, +16h; 3) 77ºC, +12h. CF_2 derivative formed was not isolated but its content in the reaction mixture was only analyzed by NMR. Maximum yield 26% was achieved after heating at 77ºC during 5 h, further heating did not result in increased yield indicating that all the starting compound had already reacted or decomposed.

b) Pyrolysis of the pure sample of *1,1-dichloro-N,N,2,2-tetramethyl-1-propanamine* made at 100÷120º/40 min/16 mmHg in the same glassware led to formation of **28** in 95% yield

c) Here and in the further attempts to synthesize CF_2 reagents discussed above starting from corresponding mixed derivatives, the temperature of reaction strictly depended on the melting points of precursors- it was found that decomposition temperatures were usually 4-10ºC higher than melting points.

4.13. Synthesis of N-[difluoro(pyridin-3-yl)methyl]-N,N-diethylamine

The glassware used here is similar to that in the synthesis of DFI™, the receiving flask was not cooled. 5 g (0.021 mol) *N*-[dichloro(pyridin-3-yl)methyl]-*N*,*N*-diethylamine were mixed with 10 gr (0.23 mol) of dry NaF. Reaction conditions: heating slowly from 90ºC till 200ºC, 2.5 h, 0.5 mmHg. Initial light-yellow color of the solid reaction mixture turned into dark-brown and not only liquid product but also mixed FCl derivative was revealed in the receiving flask. The mixture obtained was dissolved in ether, filtered under nitrogen and evaporated to give 0.6 g (0.003 mol) of target CF_2-reagent (14% yield) as yellowish liquid.

Analysis: $C_{10}H_{14}F_2N_2$, FW = 200.23 g/mol, b.p.= 55ºC (0.05 mmHg); ^{19}F-NMR ($CDCl_3$): δ = -75.64 (br. s), ^{1}H-NMR ($CDCl_3$): δ = 1.23 (t, 6H, CH_3, $^3J_{HH}$ = 7.33 Hz), δ = 3.65 (q, 4H), δ = 7.25 (d.d, 1H), δ = 8.14 (d, 1H, $^3J_{HH}$ = 8.31 Hz), δ = 8.57 (t, $^3J_{HH}$ = 0.98 Hz), δ = 9.1 (s, 1H) in good agreement with [76]

4.14 Synthesis of 4-(difluoromethyl)morpholine

The glassware used here is similar to that in the synthesis of DFI™, the receiving flask was cooled by liquid nitrogen. 15 g (0.09 mol) of 4-(dichloro-methyl)morpholine and 45.4 g (1.08 mol) of NaF were mixed and slowly heated from 80ºC till 190ºC for 2 h in 16 mmHg. During the pyrolysis process the solid within the reaction vessel turned black and viscous. No desired product was isolated. The main reaction products were HF and probably HCl. To prove the presence of the acids D_2O was added to cold receiving flask directly after carrying out the reaction. Acidic media was revealed by usual pH-indicators, ^{19}F NMR supported the presence of HF.

4.15. Synthesis of N-[difluoro(phenyl)methyl]-N,N-dimethylamine

The glassware used here is similar to that in the synthesis of DFI™, the receiving flask was cooled by liquid nitrogen. 4.2 g (0.02 mol) of *N*-[dichloro(phenyl)methyl]-*N*,*N*-dimethylamine and 17 g (0.41 mol) of NaF were mixed and heated from 80ºC till 190ºC for 2 h in 0.01 mmHg. During the pyrolysis process the solid within the reaction vessel turned black. Intensive formation of drops of colorless clear liquid was revealed on the walls of the reactor (probably volatile and low-melting mixed salt) however, side reactions seem to occur very fast and probably, CF_2 derivative formed decompose immediately to give black resin. HF was found to condense in the receiving flask.

*4.16. Pyrolysis of mixed FCl salts **23A**, **24A** and **27A** leading to formation of corresponding CF_2 derivatives*

Experimental procedures for these syntheses are similar to that in the synthesis of DFI™ or DFTMU. Conditions, yields and additional information are shown in *Table 9*.

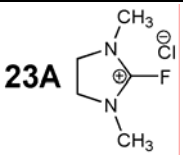
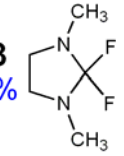
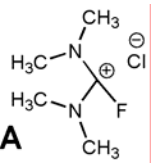
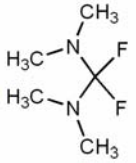
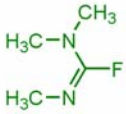
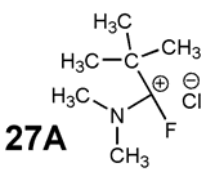
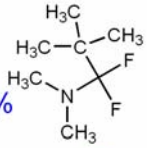
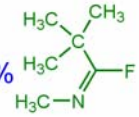
Starting compound	m.p. of starting compound	Reaction conditions	Products and yields
23A 	97ºC	Mixture of **23A** and 12-fold excess of NaF were heated at 140ºC for 1h in 16 mmHg.	**23** 97% 
24A 	95ºC	Mixture of **24A** and 12-fold excess of NaF were slowly heated up from 90º till 150ºC for 2.5h in 16 mmHg. Darkening of the reaction mixture occurred.	**24** 87%  **25** 8% 
27A 	130ºC	Mixture of **27A** and 12-fold excess of NaF were slowly heated up from 110º till 160ºC for 2h in 16 mmHg.	**27** 75.2%  **29** 13.5% 

Table 9

The mixtures of products were obtained and it was impossible to separate pure compounds due to negligible difference of boiling points between the mixture constituents.

Analysis of **25**: $C_4H_9F_2N_2$, FW = 104.13 g/mol; ^{19}F-NMR ($CDCl_3$): δ = -62.17 (br.s, $\Delta\nu_{½}$= 12 Hz), ^{1}H-NMR ($CDCl_3$): δ = 2.65 (br.d, 6H, CH_3, $^4J_{HH}$ = 4.9 Hz), δ = 2.26 (t, 3H, NCH_3, $^4J_{HH}$ = 2.4 Hz)

Analysis of **27**: $C_7H_{15}F_2N$, FW = 151.2 g/mol; ^{19}F-NMR ($CDCl_3$): δ = -97.53 (br.s), ^{1}H-NMR ($CDCl_3$): δ = 1.0 (br.s, 9H, CH_3), δ = 2.26 (t, 6H, $N(CH_3)$, $^4J_{HH}$ = 1.95 Hz)

Analysis of **29**: $C_6H_{12}FN$, FW = 117.17 g/mol; ^{19}F-NMR ($CDCl_3$): δ = -45.53 (br.s, $\Delta\nu_{½}$= 18 Hz), ^{1}H-NMR ($CDCl_3$): δ = 1.37 (br.d, 9H, CH_3, $^4J_{HH}$ = 1.96 Hz), δ = 3.61 (br.d, 3H, NCH_3, $^4J_{HH}$ = 3.42 Hz)

*4.17 Synthesis of tetrakis(trifluoromethyl)phosphoranide salts **7, 32***

The reaction was carried in Pyrex® λ-tube with a Teflon® stop-cock and equipped with magnetic stirring bar. To suspension of TMAF (0.5 g, 5.38 mmol) in 15 ml of dry ether Me_3SiCF_3 (0.8 g; 5.64 mmol) and $(CF_3)_3P$ (1.92 g; 8.1 mmol) were condensed. The mixture was quickly warmed up till -55ºC and was aged at this temperature (±5ºC) for 8 h under constant stirring. Finally, the precipitate was washed three times with ether by decantation and recondensation of the solvent back to the powder at -55ºC (standard λ-tube technique). Ether vas evaporated in high vacuum at -30ºC during 30 min to give 2 g (5.34 mmol) of slightly yellow powder - **7** in 100% yield. The phosphoranide obtained was noticed to explode spontaneously therefore should be handled carefully.

The reaction was carried out in 250 ml round bottom flask with side stopcock equipped with magnetic stirring bar and connected to vacuum manifold. To suspension of KF (0.4 g; 6.88 mmol) in solution of 18-crown-6 ether (2 g; 7.6

mmol) in 40 ml of dry monoglyme, Me_3SiCF_3 (1.1 g; 7.6 mmol) and $(CF_3)_3P$ (2.62 g; 11 mmol) were condensed. The mixture was quickly warmed up till 0ºC and was allowed to reach RT during 45 min under intensive stirring. Then 2/3 of the solvent were evaporated as quickly as possible in 0.01 mmHg while warming the reaction vessel by cold water-bath (10ºC÷RT); the suspension of phosphoranide obtained was cooled till -30ºC and the product was precipitated and washed by dry ether (100 ml for precipitation + 2×10 ml for washing, filtration at RT). The rest of ether was removed in high vacuum (5 min at RT) to give 3.87 g (6.33 mol; 92% yield; 93% purity) of white fluffy powder of **32** which should be stored at -40ºC in inert atmosphere as well as other phosphoranide salts.

Analysis of **7**: $C_8H_{12}F_{12}NP$, FW = 381.142 g/mol, m.p. = 93ºC$_{(dec)}$; ^{19}F-NMR (MG, int. Toluol-d8, 223K): δ = -51.7 (d.sep, CF_{eq}, 6F, $^2J_{PF}$= 68.9 Hz), δ = -63.0 (sep. d, CF_{ax}, 6F, $^2J_{PF}$= 2.5 Hz, $^4J_{FF}$= 8.5 Hz); ^{31}P-NMR (MG, int. Toluol-d8, 223K): δ = -49.48 (br.sep); ^{1}H-NMR (THF-d8, 223K): δ = 3.1 (s); ^{13}C{^{19}F}-NMR (MG, int. Toluol-d8, 223K): δ = 135.8 (d, CF_{eq}, $^1J_{PC}$= 195.1 Hz), δ = 129.5 (d, CF_{ax}, $^1J_{PC}$= 73.1 Hz), δ = 56.9 (s, (H_3**C**)N); Anal. Calcd. for brutto fomula: C, 25.21; H, 3.17; F, 59.82; N, 3.67; P, 8.13; Found: C, 25.28; H, 3.10; F, 59.36; N, 3.62; P, 8.24

Analysis of **32**: $C_{16}H_{24}F_{12}KO_6P$, FW = 610.411 g/mol, m.p. = 140ºC$_{(dec)}$; ^{19}F-NMR (THF-d8, 223K): δ = -53.85 (d.sep, CF_{eq}, 6F, $^2J_{PF}$= 68.73 Hz), δ = -65.38 (sep. d, CF_{ax}, 6F, $^2J_{PF}$= 2.06 Hz, $^4J_{FF}$= 8.25 Hz); ^{31}P-NMR (THF-d8, 223K): δ = -50 (br.sep.); ^{1}H-NMR (THF-d8, 293K): δ = 3.8 (s); Anal. Calcd. for brutto fomula: C, 31.48; H, 3.96; F, 37.35; P, 5.07; Found: C, 31.64; H, 3.89; F, 38.15; P, 5.21

NB: Desired product (**32**) can be obtained analytically pure but in lower yield (62%) if one would not remove a part of monoglyme from the reaction mixture. In this case phosphoranide should be precipitated by at least 200 ml of dry ether at -30ºC, filtered under nitrogen and washed by ether at RT to remove excess of 18-crown-6. High solubility of the compound discussed in the mixture ether/monoglyme led to partial lost of the substance. Tris(trifluoromethyl)-fluorophosphoranide salts and products of the reaction of trifluoromethyl anion and a solvent (*Figure 8*) were usually the main impurities identified by NMR.

*4.18 Synthesis of tris(trifluoromethyl)fluorophosphoranide salts **8**, **31***

The reaction was carried in Pyrex® λ-tube with a Teflon® stop-cock and equipped with magnetic stirring bar. To suspension of TMAF (0.5 g, 5.38 mmol) in 15 ml of dry ether $(CF_3)_3P$ (1.92 g; 8.1 mmol) was condensed. The mixture was quickly warmed up till -40ºC and was aged in the temperature range -50 ÷ -40ºCºC for 8 h under constant stirring. Finally, the precipitate was washed three times with ether by decantation and recondensation of the solvent back to the powder at -40ºC (standard λ-tube technique). Ether vas evaporated in high vacuum at -20ºC ÷ -10ºC during 30 min to give 1.71 g (5.16 mmol) of slightly yellow powder - **8** in 100% yield (analytically pure).

The reaction was carried out in 250 ml round bottom flask with side stopcock equipped with magnetic stirring bar and connected to vacuum manifold. To suspension of KF (0.5 g; 8.6 mmol) in solution of 18-crown-6 ether (2.9 g; 11.2 mmol) in 70 ml of dry ether $(CF_3)_3P$ (4.1 g; 17.2 mmol) was condensed. The mixture was quickly warmed up till RT and aged at this temperature for 16 h under intensive stirring. Heavy but mobile grains of KF were gradually substituted by friable flakes of phosphoranide formed. The solid formed was filtered under nitrogen, washed by 20 ml of dry ether and dried in high vacuum (10 min at RT) to give 4.73 g (8.43 mol; 98 % yield; 98.7% purity) of white fluffy powder of **31**.

Analysis of **8**: $C_7H_{12}F_{10}NP$, FW = 331.135 g/mol, m.p. = 127÷129ºC$_{(dec)}$; ^{19}F-NMR (MG, int. Toluol-d8, 223K): δ = -61.2 (br.m, CF_{ax}, 3F, $^1J_{PF}$= 28.57 Hz, $^2J_{(FF)trans}$= 38.24 Hz, $^3J_{(FF)cis}$= 9.63 Hz), δ = -53,95 (d.br.sep, CF_{eq}, 6F, $^1J_{PF}$= 85.3 Hz, $^2J_{(FF)cis}$= 10.87 Hz), δ = -14.13 (d.br.m, F_{ax}, 1F, $^1J_{PF}$= 384.82 Hz); ^{31}P-NMR (MG, int. Toluol-d8, 223K): δ = -54.87 (d.sep.q); ^{1}H-NMR (THF-d8, 223K): δ = 3.12 (s); ^{13}C/^{19}F-Cosy-NMR (MG, int. Toluol-d8, 223K): δ = 136.6 (d.d.t, C_{ax}, $^1J_{PC}$= 159.8 Hz, $^1J_{CF}$= 360.1 Hz, $^2J_{(CF)trans}$= 220.8 Hz), δ = 130.4 (d.d.t, C_{eq}, $^1J_{PC}$= 29.4 Hz, $^1J_{CF}$= 320.1 Hz, $^2J_{(CF)cis}$= 25.2 Hz), δ = 56.9 (s, (H_3**C**)N); Anal. Calcd. for brutto fomula: C, 25.39; H, 3.65; F, 57.37; N, 4.23; P, 9.35; Found: C, 25.71; H, 3.27; F, 57.65; N, 4.00; P, 9.01

Analysis of **31**: $C_{15}H_{24}F_{10}KO_6P$, FW = 560.4 g/mol, m.p. = 147ºC; ^{19}F-NMR (THF-d8, 183K): δ = -19.8 (br.s, F_{ax}, 1F, $\Delta\nu_{½}$= 32.9 Hz), δ = -59.27 (br.s., $CF_{3(eq+ax)}$, 9F, $\Delta\nu_{½}$ = 304.14 Hz); ^{31}P-NMR (THF-d8, 183K): δ = -61.9 (br.dec.); ^{1}H-NMR (THF-d8, 293K): δ = 3.8 (s); Anal. Calcd. for brutto fomula: C, 32.15; H, 4.32; F, 33.90; P, 5.53; Found: C, 32.22; H, 4.01; F, 33.97; P, 5.50

*4.19 Synthesis of bis(trifluoromethyl)difluorophosphoranide salt **9***

To suspension of 0.5 g (5.38 mmol) of TMAF in 20 ml of dry ether placed in 300 ml thick-walled round-bottom Pyrex® tube with a Teflon® stop-cock 1.85 g (13.44 mmol) of CF_3PF_2 was condensed. The vacuum within the tube was spoiled by dry nitrogen, the tube was closed and quickly warmed up till RT. Reaction mixture was stirred at this temperature during 16 h. White precipitate was filtered under nitrogen, washed by 10 ml of dry ether and dried in high vacuum (10 min at RT) to give 1.47 g (5.24 mol; 97.6 % yield; 99% purity) of white fluffy powder of **31**.

Analysis of **9**: $C_6H_{12}F_8NP$, FW = 281.13 g/mol, m.p. = 172ºC$_{(dec)}$; ^{19}F-NMR (MG, int. Toluol-d8): δ = -69.2 (d.sep, F_{ax}, 2F, $^{1}J_{PF}$= 312.06 Hz, $^{3}J_{PF}$= 13.77 Hz), δ = -63.89 (d.t, CF_{eq}, 6F, $^{2}J_{PF}$= 94.08 Hz); ^{31}P-NMR (MG, int. Toluol-d8): δ = -10.35 (d.t.sep.); ^{1}H-NMR (THF-d8, 223K): δ = 3.11 (s); ^{13}C-NMR (MG, int. Toluol-d8): δ = 128.64 (m), δ = 56.9 (s, (H_3**C**)N); Anal. Calcd. for brutto fomula: C, 25.63; H, 4.30; F, 54.06; N, 4.98; P, 11.02; Found: C, 26.64; H, 4.42; F, 54.37; N, 5.01; P, 11.07

*4.20 Reaction of TMAF with CF_3PF_2 in acetonitrile - detection of the signal corresponding presumably to (trifluoromethyl)trifluorophosphoranide salt **33***

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.03 g (0.32 mmol) of TMAF and attached to vacuum manifold. 1.5 ml of dry acetonitrile and of CF_3PF_2 (0.049 g, 0.352 mmol) were condensed to TMAF. The tube was warmed up till -38ºC carefully to avoid the NMR-tube destruction due to the

thermal expansion of its content, and low-temperature NMR measurements were done immediately. When removed from the NMR spectrometer at RT, the sample had dark-yellow color and contained some solid matter on the walls of the tube – probably products of reaction of hypervalent phosphorus species (or products of theirs decomposition) with the solvent.

Analysis of **33**: $C_5H_{12}F_6NP$, FW = 231.12 g/mol; ^{31}P-NMR (CH_3CH, 235K): δ = -10.35 (t.d.q., $^1J_{PF(ax)}$= 449.8 Hz, $^1J_{PF(eq)}$= 1236.8 Hz, $^2J_{PF}$= 80.31 Hz)

NB: **a)** The procedures described are typical for all the reaction made at low temperatures in NMR tube. The lowest temperature for NMR investigation depended on melting point of a solvent first. However, it was limited by technical parameters of NMR spectrometer (T_{min}= -60ºC for DPX-200, T_{min}= -90ºC for AMX-360).

b) The same reaction but carried out in Et_2O/CH_3CN (1 / 1) mixture at -40ºC yielded mixture containing $(CF_3)_2PF_2^-$, PF_4^-, $[(CF_3)FP\text{-}P(CF_3)F_4]^-$ salts (in 0.57 / 1 / 0.39 ratio correspondingly, $Q^+ = TMA^+$) and other not identified by-products.

*4.21 Reaction of PF_3 with tetramethylammonium bis(trifluoromethyl)trifluoromethylsiliconat – an attempt to obtain salt **33***

Thick-walled round-bottom 150 ml Pyrex® tube with a Teflon® stop-cock was charged with 0.3 g (3.22 mmol) of TMAF and 15 ml of monoglyme and cooled till -60ºC. 0.96 g (6.76 mol) of CF_3SiMe_3 was added to the mixture prepared and the content of the tube was stirred for 3 h at -55ºC (as described in [119]). After finishing the process of hypervalent Si-compound formation, reaction mixture was cooled by liquid nitrogen and 0.28 g (3.22 mmol) of PF_3 was condensed to it. The temperature of the mixture was allowed to rise slowly from -78ºC till -10ºC within 4 h. All the reaction products were identified by multinuclear NMR but not isolated.

Products detected: $[(CF_3)FP\text{-}P(CF_3)F_4]^-$, $(CF_3)_2PF_2^-$ and one not identified product in 1 / 0.22 / 0.16 (if it contains one P atom) ratio correspondingly.

4.22 Pyrolysis of trifluoromethylphosphoranides

Thick-walled round-bottom 150 ml Pyrex® tube with a Teflon® stop-cock was charged with 2÷5 mmol of phosphoranide (**7**, **8**, **9**, **31**, **32**) and slowly warmed up till decomposition of the compound investigated which usually occurred before melting. After finishing of the decomposition the temperature was raised slowly until complete destruction of the tube content which was accompanied by liquefying, changing of color and gas evolution. Then, the gas evolved was collected in Pyrex® NMR tube with a Teflon® stop-cock containing suitable solvent. Both gaseous and solid pyrolysis products were analyzed by NMR spectrometry (*See Table 7*).

4.23 Hydrolysis of trifluoromethylphosphoranides

2÷5 mmol of phosphoranide salt was dissolved in 15 ml dry monoglyme and cooled down till -20ºC. 35 mmol of degassed water was added to the solution and the mixture obtained was slowly warmed up till RT. Hydrolysis products were analyzed by NMR and MS spectrometry.

Analysis of **36**: $C_5H_{13}F_3NO_2P$, FW = 207.131 g/mol; ^{19}F-NMR (MG/H_2O): δ = -79.14 (d.d., CF_3, $^2J_{PF}$= 95.8 Hz, $^3J_{HF}$= 4.01 Hz), ^{31}P-NMR (MG/H_2O): δ = 1.98 (d.q., $^1J_{PH}$= 560.81 Hz) in good agreement with [160]

4.24 Reaction of trifluoromethylphosphoranides with Me_3SiCl

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.2÷0.4 mmol of phosphoranide salt (**7**, **8**, **31**, 32) and attached to vacuum manifold. Then 1.5 ml of dry monoglyme and 4-fold excess of Me_3SiCl were condensed to the phosphoranide. The tube was warmed up till RT and NMR measurements were done.

Depending on the phosphoranide taken, signals of Me_3SiF or Me_3SiCF_3 were revealed in NMR spectra of reaction mixture and theirs relative intensities were in proper ratio with that of $(CF_3)_3P$ (molar ratio 1 / 1).

4.25 Reaction of $(CF_3)_2PF_2^-$ TMA^+ (9) with Me_3SiCl

Round bottom 50 ml flask with side stopcock was charged with 0.5 g (1.78 mmol) of **9** and cooled down till -30ºC. Then 5 ml of dry monoglyme and 0.19 g (1.78 mmol) of Me_3SiCl were added to the substrate. The reaction mixture was kept at the temperature mentioned for 3 h under constant stiring. 1 ml of the mixture was taken for NMR measurements (-60ºC) and the rest was concentrated in high vacuum, the product was precipitateds by cold ether, filtered and dried to give 0.33 g (1.11 mmol, 78% yield) of **10B**.

Analysis of **10B**: $C_6H_{12}ClF_7NP$, FW = 297.58 g/mol; ^{19}F-NMR (MG, 213K): δ = -60.37 (d.d., $CF_{3(eq)}$, 6F, $^2J_{PF}$= 60.34 Hz, $^4J_{FF}$= 10.34 Hz), δ = -87.9 (d.sep., $F_{(ax)}$, 1F, $^1J_{PF}$= 504.36 Hz); ^{31}P-NMR (MG, 213K): δ = 11.97 (d.q.) in good agreement with [48]

NB: In the case of taking the starting silane in excess, $(CF_3)_2PCl$ as the only phosphorus containing reaction product together with Me_3SiF were identified by NMR spectroscopy

*4.26 Reaction of $(CF_3)_4P^-$ K^+*18-crown-6 (32) with Me_3SiCF_3*

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.12 g (0.2 mmol) of **32** and attached to vacuum manifold. Then 1.5 ml of dry monoglyme and 0.043 g (0.3 mmol) of Me_3SiCF_3 were condensed into the tube. The tube was warmed up till -55ºC carefully to avoid the NMR-tube destruction due to the thermal expansion of its content, and low-temperature NMR measurements (-55ºC÷RT) were done immediately.

Analysis of ^{19}F NMR spectra of the reaction mixture: (MG, 233K): δ = -52.85 (d.sept., $CF_{3(eq)}$, $^{2}J_{PF}$= 68.04 Hz, $^{4}J_{FF}$= 8.24 Hz), δ = -64.3 (sept.d., $CF_{3(ax)}$, $^{2}J_{PF}$= 2.06 Hz)

4.27 Reaction of trifluoromethylphosphoranides with SO_2

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.3 mmol of the phosphoranide investigated (**8**, **9**, **31**, **32**) and attached to vacuum manifold. Then 20 mmol of SO_2 were condensed into the tube - SO_2 was used as both a solvent and a reagent. The reaction mixture was warmed up till -78ºC quickly and then from -78ºC till RT within 1.5 h.

Reaction of **32** *with SO_2 - spectra of the reaction mixture*: ^{19}F-NMR (SO_2, 293K): δ = -50.66 (d., (C**F**$_3$)$_3$P, $^{2}J_{PF}$= 82.18 Hz), δ = -77.2 (br.s., C**F**$_3$$SO_2$TMA); ^{31}P-NMR ($SO_2$, 293K): δ = -0.73 (dec., (C**F**$_3$)$_3$P). After removing all the volatiles and dissolution of the rest in DMF signal at δ = -87 was revealed in ^{19}F-NMR spectra (in good agreement with [161])

Reaction of **31** *(or* **9***) with SO_2 - spectra of the reaction mixture*: only signals corresponding to $(CF_3)_3P$ were found in NMR spectra.

Thick-walled round-bottom 150 ml Pyrex® tube with a Teflon® stop-cock was charged with 1 g (3 mmol) of phosphoranide **8** and then 5 g (0.1 mol) of SO_2 was condensed into the tube. The reaction mixture was warmed up till -30ºC within 40 min and stirred for 30 min at this temperature. Excessive SO_2 was carefully removed under vacuum (approx. 20 mmHg, -30ºC). 0.45 g (2.9 mmol, 97.7% yield) of the creamy solid left after evaporation of the solvent was dissolved in CD_3CN at -30ºC. Low temperature NMR measurements were done.

Reaction of **8** *with SO_2 – spectrum of the solid obtained*: ^{19}F-NMR (CD_3CN, 243K): δ = 103.0 (br.s.); ^{1}H-NMR (CD_3CN, 243K): δ = 3.12 (s); in good agreement with [122].

*4.28 Reaction of phosphoranide salt **32** with 4-chlorobenzenesulfonyl chloride*

Usual NMR tube was charged with 0.183 g (0.3 mmol) of the phosphoranide investigated and cooled till -100ºC. Then 1.2 ml of MG and 0.13 g (0.6 mmol) of the reagent were added into the tube under inert atmosphere. The tube was closed and reaction mixture was warmed up till -78ºC and then from -78ºC till RT within 1.5 h (or within 5 min) shaking the tube periodically.

Reaction of **32** *with 4-chlorobenzenesulfonyl chloride (quick warming up til RT) - spectra of the reaction mixture*: ^{19}F-NMR (MG, 293K): δ = -29.7 (br.s., CF_3Cl; lit. [120] : δ_{CDCl_3} = -33), δ = -51.86 (br.d., (C**F**$_3$)$_3$P, $^2J_{PF}$= 80.46 Hz); ^{31}P-NMR (MG, 293K): δ = -2.97 (br.dec., (C**F**$_3$)$_3$P) ;NMR yiled: 100%

Reaction of **32** *with 4- chlorobenzenesulfonyl chloride (slow warming up til RT) - spectra of the reaction mixture*: ^{19}F-NMR (MG, 293K): δ = -76.35 (s., *4*-Cl-$C_6H_4SO_2CF_3$; lit. [162] : δ_{CDCl_3} = -74.98), δ = -51.29 (br.d., (C**F**$_3$)$_3$P, $^2J_{PF}$= 80.75) and signals of other not identified compounds, ^{31}P-NMR (MG, 293K): δ = -2.92 (br.dec., (C**F**$_3$)$_3$P) ;NMR yiled: 32%

NB: Phosphoranide **31** also reacts with 4- chlorobenzenesulfonyl chloride under the same conditions. In the spectra of the reaction mixture signal corresponding to *4*-Cl-$C_6H_4SO_2F$ {^{19}F-NMR (MG, 293K): δ = 64.59 (s., lit. [163] : δ_{CD_3CN} = 65.1)} and $(CF_3)_3P$ together with the signals of unidentified six-coordinate (^{31}P-NMR (MG, 293K): δ = -156.42, br.m) phosphorus compound were revealed. NMR yield of sulfonyl fluoride: 85%

*4.29 Reaction of $(CF_3)_4P^-K^+$*18-crown-6 (32) with PhCOH*

0.11 g (1 mmol) of behzaldehyde was added to solution of 0.5 g (0.82 mmol) of **32** in 7 ml of dry monoglyme at -40ºC and the reaction mixture was stirred at this temperature for 30 min. Several drops of aqueous 37% solution of HCl were added to the mixture and its temperature was allowed to rise till 25ºC. Reaction

product was not isolated but was analyzed by NMR spectrometry. NMR yield: 76.7%

Analysis of PhCH(CF$_3$)(OH): $C_8H_7F_3O$, FW = 176.14 g/mol; ^{19}F-NMR (MG, 293K): δ = -79.42 (br.d., CF_3; $^3J_{FH}$= 6.9 Hz; lit. [164] : δ_{CDCl_3} = -79.0, $^3J_{FH}$= 6.6 Hz)

*4.30 Reaction of $(CF_3)_4P^-K^+$*18-crown-6 (32) with $(MeO)_3B$*

To a stirred solution of **32** (0.5 g, 0.82 mmol) in 10 ml of dry monoglyme $(MeO)_3B$ (0.1 g, 0.98 mmol) was added at -70ºC. The reaction mixture was kept at the indicated temperature for 1 h and then allowed to warm up to 25ºC. Reaction product was not isolated but was analyzed by NMR and MS spectrometry (71.9% NMR yield).

*Analysis of $(MeO)_3BCF_3^-K^+$*18-crown-6*: $C_6H_{33}BF_3KO_9$, FW = 476.33 g/mol; ^{19}F-NMR (MG, 293K): δ = -71.1 (m., CF_3; lit. [165] : δ_{D_2O} = -75.9, m.); ^{11}B-NMR (MG, 293K): δ = -0.87 (q., $^2J_{BF}$ = 30.0 Hz; lit. [165] : δ_{D_2O} = -0.9, q., $^2J_{BF}$ = 29.5 Hz)

4.31 Reaction of trifluoromethylphosphoranides with 2-fluoro-1,3-dimethyl-imidazolidinium triflate

To a stirred solution of **32** (0.5 g, 0.82 mmol) in 10 ml of dry monoglyme 2-fluoro-1,3-dimethylimidazolidinium triflate (0.27 g, 1 mmol) was added at -40ºC. The reaction mixture was kept at the indicated temperature for 2 h and then allowed to warm up to 25ºC within 30 min. Reaction product was not isolated but was analyzed by NMR and MS spectrometry (89.6% NMR yield)

Analysis of the product: $C_6H_{10}F_4N_2$, FW = 186.15 g/mol; ^{19}F-NMR (MG, 293K): δ = -63.58 (s., CF_3, 3F; lit.[123] (for the analogous slat made from *DFTMU*): δ_{CDCl_3} = -73.37, s.), δ = -72.05 (s., 1F; lit.[123] : δ_{CDCl_3} = -139.31, br.s.); MS: (EI, 70 eV, 200 °C) m/z (%): 186 (15) M^+, 167 (47) $[M-F]^+$, 136 (9) $[M-CF_2]^+$, 117 (100) $[M-CF_3]^+$, 69 (17) $[CF_3]^+$, and other fragments.

NB: Under the same conditions, phosphoranide **31** (or **8**) reacts with the triflate salt mentioned above to produce DFI nearly quantitatively (evaluated by ^{19}F NMR) and traces of unidentified compound.

4.32 Reaction of trifluoromethylphosphoranides with $(CF_3)_2CO$

Thick-walled round-bottom 250 ml Pyrex® tube with a Teflon® stop-cock was charged with 1 mmol of phosphoranide and 12 ml of dry monoglyme. Then 1.3 mmol of HFA was condensed into the tube. The reaction mixture was warmed up till -30ºC and stirred for 30 min at this temperature and afterwards was allowed to warm up till 25ºC. The solvent and excess of reagent were pumped off in vacuum to give slightly-brown solid.

Reaction of **32** *with HFA*: ^{19}F-NMR (THF-d8, 293K): δ = -76.35 (br.s., 9F, $(C\mathbf{F}_3)_3CO^-$; lit. [166] : $\delta_{acetone\text{-}d6}$ = -76.0, s.); ^1H-NMR (THF-d8, 293K): δ = 3.8 (s.); isolated yiled: 95.7%

Reaction of **8** *with HFA*: ^{19}F-NMR (THF-d8, 293K): δ = -83.12 (br.s., 6F, $(C\mathbf{F}_3)_2FCO^-$; lit.[167] : δ_{CDCl_3} = -83.5), δ = -84.42 (br.s., 1F, $(CF_3)_2\mathbf{F}CO^-$; lit.[167] : δ_{CDCl_3} = -85.0); ^1H-NMR (THF-d8, 293K): δ = 3.12 (s.); isolated yiled: 98.9%

4.32 Oxidation of trifluoromethylphosphoranides with Cl_2

Thick-walled round-bottom 150 ml Pyrex® tube with a Teflon® stop-cock was used as a reaction vessel for these syntheses. To solution of 1 mmol of phosphoranide (pregenerated as described above, usually TMA salts) in 15 ml of dry monoglyme strictly equimolar amount of Cl_2 was condensed. The reaction mixture was warmed up till -50ºC and stirred at this temperature for 4 h. Then the solvent was pumped off while warming the reaction vessel by cold water. The powder obtained was washed with dry ether (2×5 ml), filtered under nitrogen and dried in high vacuum to give moisture sensitive white powder.

Analysis of **39**: $C_8H_{12}Cl_2F_{12}NP$; FW = 452.05 g/mol., m.p. = >360ºC; ^{19}F-NMR (THF-d8, 293K): δ = -63.85 (br.d., CF_3, $^2J_{PF}$ = 100.96 Hz); ^{31}P-NMR (THF-d8, 293K): δ = -167.76 (dec.); ^{1}H-NMR (THF-d8, 293K): δ = 3.1 (s.); MS: (FAB negativ, NBA, 300 °C) m/z (%): 377 (44) $[M]^-$, 323 (100) [unidentified fragment]$^-$, 361 (14) $[M\text{-}Cl+F]^-$, 311 (12) $[M\text{-}Cl\text{-}CF_2+F]^-$, 273 (9) $[M\text{-}Cl\text{-}CF_2\text{-}2F+F]^-$, 223 (1) $[M\text{-}Cl\text{-}2CF_2\text{-}2F+F]^-$, 201 (18) [unidentified fragment]$^-$, 69 (7) $[CF_3]^-$ and other fragments; HRMS M^- calculated: 376.89325, found: 376.89334, R = 5000; Anal. Calcd. for brutto fomula: C, 21.26; H, 2.68; Cl, 15.69; F, 50.43; N, 3.10; P, 6.85; Found: C, 21.31; H, 2.70; Cl, 15.54; F, 50.37; N, 3.12; P, 6.92; isolated yiled: 98.9%

Analysis of **40**: $C_7H_{12}Cl_2F_{10}NP$; FW = 402.04 g/mol.; m.p. = >360ºC, ^{19}F-NMR (THF-d8, 293K): δ = -2.29 (d.m., $^1J_{PF}$ = 982.1 Hz), δ = -34.02 (d.m., $^1J_{PF}$ = 883.4 Hz), δ = -36.02 (d.m., $^1J_{PF}$ = 943.1 Hz), δ = -51.4 (d.m., $^1J_{PF}$ = 885.7 Hz), δ = -62.11 ÷ -66.64 (set of multiplets), δ = -64.9 (d.q., $^2J_{PF}$ = 161.8 Hz, $^4J_{FF}$ = 13.8 Hz), δ = -64.9 (d.sept., $^2J_{PF}$ = 153.74 Hz, $^4J_{FF}$ = 12.62 Hz), δ = -85.9 (d.m., $^1J_{PF}$ = 836.36 Hz); ^{31}P-NMR (THF-d8, 293K): δ = 142.69÷173.37 (m.); MS: (ESI negativ, CH_3CN, 350 °C) m/z (%): 327 (100) $[M]^-$, 311 (61) $[M\text{-}Cl+F]^-$, 273 (5) $[M\text{-}Cl\text{-}2F+F]^-$, 201 (7) $[M\text{-}Cl\text{-}CF_3\text{-}2F+F]^-$, and other fragments; Anal. Calcd. for brutto fomula: C, 20.91; H, 3.01; Cl, 17.64; F, 47.25; N, 3.48; P, 7.70; Found: C, 21.07; H, 3.07; Cl, 14.81; F, 49.62; N, 3.51; P, 7.85; isolated yiled: 92% (mixture of isomers and probably $(CF_3)_3PF_2Cl^-$ TMA^+ as byproduct)

4.33 Oxidation of trifluoromethylphosphoranides with $(CH_3OCH_2)_2NSF_3$

To solution of 1 mmol of phosphoranide (*{K^+}*18-crown-6 salts*) in 20 ml of dry monoglyme 6-fold excess of Deoxo-Fluor™ was added at -35ºC. The reaction mixture was slowly warmed up till RT and stirred at the normal conditions for 1 h. The solid phase formed immediately after addition of fluorinating agent, gradually dissolved to produce slightly-brown clear solution at the end of the reaction. The solvent was removed in vacuum and the solid

obtained was washed with dry ether and dried in 0.01 mmHg to give white powder.

Analysis of **43**: $C_{15}H_{24}F_{12}KO_6P$; FW = 598.4 g/mol.; meridional (unsymmetrical) structure: ^{19}F-NMR (MG, int. Toluol-d8): δ = -60.6 (d.m., 1F, $^1J_{PF}$ = 884.49 Hz), δ = -68.5 (d.q.m., 6F, $^2J_{PF}$ = 125.86 Hz, $^4J_{FF}$ = 12.07 Hz), δ = -69.8 (d.m., 3F, $^2J_{PF}$ = 89.66 Hz), δ = -96.7 (d.m., 2F, $^1J_{PF}$ = 862.08 Hz); ^{31}P-NMR (MG, int. Toluol-d8): δ = -157.48 (d.t.q.sept); facial (symmetrical) structure: ^{19}F-NMR (MG, int. Toluol-d8): δ = -65.69 (d.q., 9F, $^2J_{PF}$ = 91.78 Hz, $^4J_{FF}$ = 11.47 Hz), δ = -78.9 (d.dec., 3F, $^1J_{PF}$ = 797.36 Hz); ^{31}P-NMR (MG, int. Toluol-d8): δ = -157.48 (q.dec.); ratio of the isomers mer./fac. = 1/1.4; yield: 95.2%

Analysis of **44**: $C_{16}H_{24}F_{14}KO_6P$; FW = 648.41 g/mol., m.p. = >360ºC; ^{19}F-NMR (THF-d8, 293K): δ = -62.6 (d.sept.m., 6F, CF_3, $^2J_{PF}$ = 102.16 Hz, $^4J_{FF}$ = 12.07 Hz), δ = -63.84 (d.sept.m., 6F, CF_3, $^2J_{PF}$ = 72.85 Hz), δ = -69.13 (d. m., 2F, $^1J_{PF}$ = 852.16 Hz); ^{31}P-NMR (THF-d8, 293K): δ = -165.40 (d.d.sept.sept); ^{1}H-NMR (THF-d8, 293K): δ = 3.6 (s.); yield (in the mixture with **43**, analyzed by NMR spectroscopy): 21.14%

4.34 Reaction of trifluoromethylphosphoranides with methyliodide

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.122 g (0.2 mmol) of **32** and attached to vacuum manifold. 1.5 ml of dry monoglyme and 0.23 g (1.6 mmol) of MeI were condensed into the tube. The reaction mixture was warmed up till -30ºC quickly and low temperature NMR measurements were done. Since it was revealed that reaction occurred very slowly at 0ºC, the NMR tube was left at RT for 12 h and then analyzed.

Phosphoranide **8** was pregenerated *[0.4 g (4.3 mmol) of TMAF+1.33 g (5.6 mmol) of $(CF_3)_3P$+30ml of MG / 45 min at -15ºC]* in 250 ml two-neck round bottom flask connected to a funnel for filtration under inert atmosphere and equipped with vacuum adapter with stopcock and magnetic stirring bar. To solution of the phosphoranide prepared 6.1 g (0.043 mol) of MeI was condensed.

The reaction mixture was warmed up till RT quickly and stirred at this temperature for 30 min. Intensive formation of creamy precipitate was revealed immediately after the reaction mixture temperature's running up to 10÷15ºC. Then, 2/3 of the solvent was removed in vacuum and the rest was solidified (20 ml) and washed (7 ml) by dry ether and finally, dried in high vacuum to give 1.49 g (4.1 mmol) of white powder (**49**; 95.2% yield)

*Analysis of the reaction of **32** with MeI*: main reaction products are $(CF_3)_3P$ and CF_3CH_3 (^{19}F-NMR (MG): δ = -61.97 (br.q., $^3J_{HF}$ = 12.64 Hz). Other unidentified products were also observed in ^{19}F and ^{31}P NMR spectra.

Analysis of **49**: $C_8H_{15}F_{11}NP$; FW = 365.17 g/mol., m.p. = >360ºC; *cis*-isomer (isolated as a powder): ^{19}F-NMR (THF-d8, 293K): δ = -50.47 (d.m., 1F, $^1J_{PF}$ = 772.69 Hz), δ = -55.79 (d.m., 1F, $^1J_{PF}$ = 745.16 Hz), δ = -64.51 (br.d.q.d.d., 6F, $^2J_{PF}$ = 88.34 Hz, $^4J_{FF}$ = 10.32 Hz, $^3J_{FF}$ = 14.92 Hz, $^3J_{FF}$ = 15.49 Hz), δ = -66.57 (br.d.sept., 3F, $^2J_{PF}$ = 60.81 Hz); ^{31}P{^{1}H}-NMR (THF-d8, 293K): δ = -165.04 (d.d.q.sept); ^{1}H-NMR (THF-d8, 293K): δ = 3.17 (s., 12H), δ = 1.15 (br.t, 3H, $^3J_{FH}$ = 9.6 Hz); ^{13}C-NMR (THF-d8, 293K): δ = 124.95÷135.84 (m.); MS: (FAB, negativ, NBA, 300 °C) m/z (%): 290.8 (100) $[M]^-$, 220.9 (3) $[M\text{-}CF_3H]^-$ and other minor fragments; HRMS M^- calculated: 291.97972, found: 291.97987, R = 6000; isolated yield: 95.2%; *trans*--isomer (observed in solution): ^{19}F-NMR (MG): δ = -45.33 (br.d., 2F, $^1J_{PF}$ = 830.63 Hz), δ = -62.59 (br.d.m., 3F, $^2J_{PF}$ = 114.73 Hz), δ = -65.34 (br.d.m., 6F, $^2J_{PF}$ = 50.48 Hz); ^{31}P{^{1}H}-NMR (MG): δ = -158.5 (br.d.d.m.)

4.35 Reaction of $(CF_3)_4P^-$ TMA^+ (7) with methyltriflate

The glassware used to carry out this reaction was similar to that in the synthesis of **49**. To 0.62 g (6.67 mmol) of TMAF 15 ml of dry monoglyme, 2.06 g (8.67 mmol) of tris(trifluoromethyl)phosphine and 0.99 g (7 mmol) of Ruppert reagent were condensed. The mixture was warmed up till -50ºC and stirred at the temperature range from -55 till -50ºC for 2 hour. To pale solution of the phosphoranide salt formed 1.85 g (9.98 mmol) of methyltriflate was added in one portion. Reaction mixture was warmed up till -40ºC and stirred at this

temperature for 2 hours. Then the temperature was allowed to rise up to 0ºC within 20 min and the reaction mixture was filtered under nitrogen. Filtrate was evaporated, solidified and washed by dry ether (2×9 ml) to give 0.7 g (1.69 mmol) of white powder (**48**; 51% yield, not optimized).

Analysis of **48**: $C_9H_{15}F_{13}NP$; FW = 415.16 g/mol., m.p. = 273ºC$_{(dec.)}$; ^{19}F-NMR (THF-d8): δ = -49.60 (d.tridec.q., 1F, $^1J_{PF}$ = 752.9 Hz, $^3J_{FF}$ = 11.19 Hz, $^3J_{HF}$ ≈ 1.15 Hz), δ = -65.54 (d.d., 12F, $^2J_{PF}$ = 72.85 Hz); ^{31}P{^{1}H}-NMR (THF-d8): δ = -175.60 (d.tridec.{or probably higher multiplicity}); ^{1}H-NMR (THF-d8): δ = 3.17 (s., 12H), δ = 1.29 (br.d, 3H, $^3J_{FH}$ = 7.93 Hz); ^{13}C-NMR (THF-d8): δ = 137.64÷121.2 (m.); MS: (FAB, negativ, NBA, 300 °C) m/z (%): 340.9 (100) $[M]^-$; HRMS M^- calculated: 340.97910, found: 340.97907, R = 6000 ; isolated yield: 51.07%

4.36 Fluoride ion abstraction from phosphates 43, 44, 48, 49 by using very strong Lewis acid – AsF_5

All the reactions with AsF_5 participation were carried out in SO_2 serving a role of moderately coordinating solvent able to stabilize highly electrophilic phosphorus centers. A typical reaction vessel was Pyrex® NMR tube with a Teflon® stop-cock. Due to extreme instability of the compounds synthesized (when not stabilized by a solvent) products were not isolated but were only characterized by multinuclear NMR spectrometry.

Typical procedures: To 0.146 g (0.4 mmol) of **48**, 0.96 g (20 mmol) of SO_2 and 0.12 g (0.7 mmol) of AsF_5 were condensed. The reaction mixture was warmed up till RT within 30 min. 100% NMR yield of **53** was revealed.

Analysis of **53**: $C_5H_3F_{12}P$; FW = 322.03 g/mol.; ^{19}F-NMR (SO_2): δ = -60.74 (br.d., $^2J_{PF}$ = 77.59 Hz); ^{31}P{^{1}H}-NMR (SO_2): δ = -65.96 (undec.{lines of low intensity is difficult to detect}); ^{31}P-NMR (SO_2): δ = -65.96 (undec.q., $^2J_{PH}$ = 11.88 Hz); ^{1}H-NMR (SO_2): δ = 3.47 (br.s., 12H), δ = 1.35 (br.s., 3H); ^{13}C-NMR (SO_2): δ = 125.82 (d.q.m., $^1J_{CF}$ = 341.66 Hz, $^1J_{PH}$ = 109.46 Hz), δ = 10.59 (d., **C**H_3, $^1J_{PC}$ = 66.34 Hz); NMR yield: quantitatively

Analysis of **52**: $C_4H_3AsF_{15}P$; FW = 441.94 g/mol.; ^{19}F-NMR (SO_2): δ = -50.36 (br.d., 9F, CF_3, $^2J_{PF}$ = 125.48 Hz), δ = -53.79 (br.s., $[AsF_6]^-$ + AsF_5); ^{31}P{^{1}H}-NMR (SO_2): δ = 42.38 (dec.); ^{31}P-NMR (SO_2): δ = 42.38 (dec.q., $^2J_{PH}$ = 16.33 Hz), ; ^{1}H-NMR (SO_2): δ = 3.73 (br.s., 12H), δ = 3.92 (br.d., 3H); ^{13}C-NMR (SO_2): δ = 120.29 (d.q., **C**F_3, $^1J_{CF}$ = 321.72 Hz, $^1J_{PH}$ = 145.23 Hz), δ = 14.47 (d., **C**H_3, $^1J_{PC}$ = 119.5 Hz); NMR yield: quantitatively

*Fluoride ion abstraction from **43** (strong distortion of NMR spectra)*: ^{19}F-NMR (SO_2): δ = -58.21 (br.dec., $^2J_{PF}$ = 17.21 Hz), δ = -63.35 (br.m.), δ = -64.19 (br.t., $^2J_{PF}$ = 16.63 Hz); ^{31}P-NMR (SO_2): δ = -57.4 (t.m., $^1J_{PF}$ = 991.82 Hz)

4.37 Synthesis of phosphinoperphosphoranides - typical synthetic procedures

To 1.1 mmol of fluoride ion source (KF+18-crown-6, TMAF, $(Et_2N)_3PF_2$) suspended or dissolved in 30 ml of dry monoglyme, exactly 2 mmol of starting phosphine was condensed. The reaction mixture was warmed up till -30ºC quickly and then from -30ºC till 0ºC slowly within 40 min. After finishing the reaction cooled down till -20ºC reaction mixture was filtered under nitrogen, 5/4 of the solvent was removed in high vacuum at RT within 10÷15 min and the substance obtained was solidified (-40ºC, 20 ml) and washed (RT, 2×10 ml, decantation) by dry ether. The product obtained was dried in high vacuum at -10ºC for 30 min.

Analysis of **55**: $C_{16}H_{30}F_{16}N_3P_3$; FW = 661.33 g/mol., m.p. ≈ 7ºC; ^{19}F-NMR (THF-d8): δ = -19.1 (d.t.m., 1F, $^1J_{PF}$ = 1064.67 Hz, $^2J_{FF}$ = 78.02 Hz, $^3J_{FF(CF3)}$ ≈ 4.6 Hz), δ = -48.91 (d.m., 6F, $(CF_3)_{PIII}$, $^2J_{PF}$ = 60.86 Hz), δ = -68.3 (d.m., 6F, $(CF_3)_{PVI}$, $^2J_{PF}$ = 108.99 Hz), δ = -71.5 (d.t.m., 2F, $^1J_{PF}$ = 956.89 Hz, $^3J_{FF(CF3)}$ ≈ 9.2 Hz), δ = -81.23 (br.d., 1F, $(Et_2N)_3P$**F**, $^1J_{PF}$ = 966.6 Hz); ^{31}P-NMR (THF-d8): δ = 20.4 (d.sept.m., P(III), $^1J_{PP}$ ≈ 14.3 Hz), δ = -149.53 (d.t.m., P(VI)), δ = 42.82 (d.tridec., $(Et_2N)_3$**P**F, $^3J_{PH}$ = 12.9 Hz); MS: (FAB, negativ, NBA, 200 °C) m/z (%): 395 (54) $[M]^-$, 295 (43) $[M\text{-}2CF_2]^-$, 276 (14) $[M\text{-}2CF_2\text{-}19]^-$, 151 (100) [unidentified fragment] and other fragments; isolated yield: 94.7%

Analysis of **57**: $C_{14}H_{30}F_{12}N_3P_3$; FW = 561.31 g/mol., m.p. = 18ºC; ^{19}F-NMR (THF-d8): δ = -58.37 (d.d.q.q, 4F, $^1J_{PF}$ = 1035.99 Hz, $^2J_{PF}$ = 117.02 Hz), δ = -63.83 (d.d.quint.d., 3F, $CF_{3(P_{III})}$, $^2J_{PF}$ = 66.54 Hz, $^3J_{PF}$ = 31.55 Hz, $^3J_{FF}$ = 9.75 Hz, $^3J_{FF}$ = 5.2 Hz), δ = -69.8 (br.d.quint., 3F, $CF_{3(P_{VI})}$, $^2J_{PF}$ = 156.03 Hz, $^3J_{FF}$ = 14.95 Hz), δ = -234.95 (d.d.q., 1F, $^1J_{PF}$ = 875.37 Hz, $^2J_{PF}$ = 61.95 Hz), δ = -80.56 (d., 1F, $(Et_2N)_3P\mathbf{F}$, $^1J_{PF}$ = 969.45 Hz); ^{31}P-NMR (THF-d8): δ = 185.24 (d.quint.q.q.d., P(III)), δ = -138.6 (quint.q.d.q.d., P(VI), $^1J_{PP}$ = 9.8 Hz), δ = 42.82 (d.tridec., $(Et_2N)_3\mathbf{P}F$, $^3J_{PH}$ = 12.9 Hz); ^{1}H-NMR (THF-d8): δ = 3.15 (q.d.d., 12H, $^3J_{HH}$ = 6.06 Hz, $^3J_{PH}$ = 13.87 Hz, $^4J_{FH}$ = 1.32 Hz), δ = 1.21 (t, 18H); ^{13}C-NMR (THF-d): due to the complex structure of the signals corresponding to $\mathbf{C}F_3$ groups we did not manage to analyse ^{13}C-NMR spectra completely (compounds **55** – **61B** also) but only detected broad signal in the range δ = 141.15 ÷ 118.64; MS: (FAB, negativ, NBA, 300 °C) m/z (%): 295 (19) $[M]^-$, 195 (30) $[M\text{-}2CF_2]^-$, 151 (100) [unidentified fragment]$^-$ and other fragments; isolated yield: 95.7%

4.38 Decomposition of phosphinoperphosphoranides

2 g (3.56 mmol) of phosphinoperphosphoranide **57** was dissolved in 7 ml of dry monoglyme and stirred at RT for 4 d. Complete decomposition of the starting compound was revealed by NMR. The solvent was evaporated then the solid obtained was washed by 2×5 ml of dry ether and dried in high vacuum. 1.6 g (3.53 mmol) of **57A** was obtained.

1.7 g (2.57 mol) of phosphinoperphosphoranide **55** was dissolved in 10 ml of dry monoglyme, warmed up till 60ºC and kept at this temperature for 20 min. Complete decomposition of the starting compound was revealed by NMR. The solvent was evaporated then the solid obtained was washed by 2×5 ml of dry ether and dried in high vacuum to give 1.29 g (2.52 mmol) of **55A**.

Analysis of **55A**: $C_{14}H_{30}F_{11}N_3P_2$; FW = 511.34 g/mol.; m.p. = >360ºC, ^{19}F-NMR (THF-d8): δ = -68.10 (d.quint., 6F, $^2J_{PF}$ = 147.28 Hz, $^3J_{FF}$ = 14.08 Hz), δ = -78.73 (d.sept., 4F, $^1J_{PF}$ = 897.14 Hz), δ = -80.56 (br.d., 1F, $(Et_2N)_3P\mathbf{F}$, $^1J_{PF}$ = 969.32

Hz); ^{31}P-NMR (THF-d8): δ = -148.44 (quint.sept.), δ = 42.83 (d.tridec., $(Et_2N)_3$**P**F, $^3J_{PH}$ = 12.9 Hz); MS: (ESI negativ, CH_3CN, 350 °C) m/z (%): 245 (100) $[M]^-$, 195 (3) $[M\text{-}CF_2]^-$, 145 (15) $[M\text{-}2CF_2]^-$; Anal. Calcd. for brutto fomula: C, 32.88; H, 5.91; F, 40.87; N, 8.22; P, 12.11; Found: C, 32.85; H, 6.02; F, 40.92; N, 8.20; P, 12.12; isolated yiled: 98.2%

Analysis of **57A**: $C_{13}H_{30}Cl_2F_9N_3P_2$; FW = 461.33 g/mol.; m.p. = >360ºC, ^{19}F-NMR (THF-d8): δ = -69.91 (d.quint.d., $^2J_{PF}$ = 132.51 Hz, $^3J_{FF}$ = 13.19 Hz, $^3J_{FF}$ = 2.30 Hz), δ = -75.22 (d.m.[overlapping multiplets which were impossible to be analyzed in details: δ = -75.39 and δ = -75.22], 1F, $^1J_{PF}$ = 819.83 Hz), δ = -75.39 (d.m., 4F, $^1J_{PF}$ = 727.50 Hz), δ = -80.56 (d., 1F, $(Et_2N)_3$P**F**, $^1J_{PF}$ = 969.45 Hz); ^{31}P-NMR (THF-d8): δ = -147.78 (quint.d.q., $^1J_{PF}$ = 818.01 Hz, $^1J_{PF}$ = 12.62 Hz), δ = 42.83 (d.tridec., $(Et_2N)_3$**P**F, $^3J_{PH}$ = 12.9 Hz); ^{1}H-NMR (THF-d8): δ = 3.15 (q.d.d., 12H, $^3J_{HH}$ = 6.06 Hz, $^3J_{PH}$ = 13.87 Hz, $^4J_{FH}$ = 1.32 Hz), δ = 1.21 (t, 18H); MS: (ESI negativ, CH_3CN, 350 °C) m/z (%): 195 (100) $[M]^-$, 145 (10) $[M\text{-}CF_3]^-$; Anal. Calcd. for brutto fomula: C, 33.85; H, 6.55; F, 37.06; N, 9.11; P, 13.43; Found: C, 33.79; H, 6.50; F, 37.09; N, 9.66; P, 13.12; isolated yiled: 96.8%

4.39 Synthesis of perphosphoranides - typical synthetic procedures

Thick-walled round-bottom 150 ml Pyrex® tube with a Teflon® stop-cock was charged with 1.2 mmol of phosphine, 1 mol of DFI™ and 20 ml of dry ether. Reaction mixture was warmed up till -78ºC quickly and then was allowed to reach ambient temperature within 1.5 h under constant stirring. The white precipitate formed was filtered off under nitrogen, washed by ether (2×5 ml) and dried in high vacuum.

Analysis of **58**: $C_7H_{10}F_9N_2P$; FW = 324.13 g/mol.; m.p. = 146ºC, ^{19}F-NMR (DMSO-d6): δ = -81.2 (d.d.sep., 2F, $^1J_{PF}$ = 858.1 Hz, $^2J_{FF}$ = 41.3 Hz, $^3J_{FF}$ = 11.4 Hz), δ = -69.12 (d.d.t.q., 3F, CF_3, $^2J_{FF}$ = 126.5 Hz, $^3J_{FF}$ = 11.4 Hz, $^3J_{FF}$ = 6.8 Hz), δ = -69.4 (d.d.t.q., 3F, CF_3, $^2J_{PF}$ = 108.4 Hz, $^3J_{FF}$ = 17.2 Hz), δ = -43.2 (d.t.q.q., 1F, $^1J_{PF}$ = 859.7 Hz, $^2J_{FF}$ = 41.3 Hz); ^{31}P-NMR (DMSO-d6): δ = -157 (q.q.q.); ^{1}H-NMR (DMSO-d6): δ = 3.81 (br.s., 4H), δ = 3.25 (br.s., 6H); MS: (CI negativ, NH_3, 150

°C) m/z (%): 648 (42) $[2M]^{-\cdot}$, 324 (100) $[M]^{-\cdot}$, 225 (12) $[M\text{-}2CF_2]^{-\cdot}$ and other fragments; (EI, 70 eV, 200 °C) m/z (%): 305 (4) $[M\text{-}F]^{-\cdot}$, 255 (19) $[M\text{-}F\text{-}CF_2]^{-\cdot}$, 205 (100) $[M\text{-}F\text{-}2CF_2]^{-\cdot}$, 70 (60) $[CF_3H]^{-\cdot}$, 45 (26) $[CH_3]^{-\cdot}$ and other fragments; Anal. Calcd. for brutto fomula: C, 25.94; H, 3.11; F, 52.75; N, 8.64; P, 9.56; Found: C, 25.87; H, 3.07; F, 52.63; N, 8.48; P, 9.60; isolated yiled: 87.9%

Analysis of **59**: $C_5H_{10}F_5N_2P$; FW = 224.11 g/mol.; m.p. = 194ºC, ^{19}F-NMR (DMSO-d6): δ =71.9 (d.quint., 1F, $^1J_{PF}$ = 754.3 Hz, $^2J_{FF}$ = 51.6 Hz), δ = -55.6 (d.d., 4F, $^1J_{PF}$ = 799.1 Hz); ^{31}P-NMR (DMSO-d6): δ = -149.3 (d.quint.); ^{1}H-NMR (DMSO-d6): δ = 3.77 (br.s., 4H), δ = 3.13 (br.s., 6H); ^{13}C-NMR (DMSO-d6): δ = 174.45 (d.sept.(presumably, due to very low intensity it is quite difficult to describe the signal), $(R_2N)_2$**C**-PF_5 (C^2), $^1J_{PC}$ = 300.21 Hz, $^2J_{CF}$ = 59.55 Hz), δ = 52.37 (s., $C^{4,5}$), δ = 37.19 (s., N-CF_3); MS: (CI positiv, NH_3, 200 °C) m/z (%): 466 (14) $[2M+NH_4]^+$, 242 (100) $[M+NH_4]^+$, 205 (81) $[M\text{-}F]^+$, 70 (7) $[CF_3H]^+$ and other fragments; Anal. Calcd. for brutto fomula: C, 26.80; H, 4.50; F, 42.39; N, 12.50; P, 13.82; Found: C, 26.76; H, 4.57; F, 42.42; N, 12.43; P, 13.84; isolated yiled: 97.15%

Analysis of **60**: $C_6H_{10}F_7N_2P$; FW = 274.12 g/mol.; m.p. = 188ºC, ^{19}F-NMR (DMSO-d6): δ = -69.3 (d.quint., 3F, CF_3, $^2J_{PF}$ = 148.6 Hz, $^3J_{FF}$ = 13.8 Hz), δ = -61.7 (d.q., 4F, $^1J_{FF}$ = 877.1 Hz); ^{31}P-NMR (DMSO-d6): δ = -152 (quint.q.); ^{1}H-NMR (DMSO-d6): δ = 3.81 (br.s., 4H), δ = 3.15 (br.s., 6H); ^{13}C-NMR (DMSO-d6): δ = 174.45 (d.quint., $(R_2N)_2$**C**-P (C^2), $^1J_{PC}$ = 305.18 Hz, $^2J_{CF}$ = 57.06 Hz), δ = 133.27 ÷ 116.6 (m., CF_3), δ = 52.45 (s., $C^{4,5}$), δ = 37.03 (s., N-CF_3); MS: (EI, 70 eV, 149 °C) m/z (%): 255 (3) $[M\text{-}F]^+$, 205 (100) $[M\text{-}CF_3]^+$, 70 (7) $[CF_3H]^+$, 45 (17) $[CH_3]^+$ and other fragments; Anal. Calcd. for brutto fomula: C, 26.29; H, 3.68; F, 48.51; N, 10.22; P, 11.30; Found: C, 26.34; H, 3.57; F, 48.78; N, 10.01; P, 11.24; isolated yiled: 91.2%

Analysis of **61B**: ^{19}F-NMR (DMSO-d6): δ = -89.1 (s., 1F), δ = -66.2 (d.m., 6F, $^2J_{PF}$ = 73.4 Hz), δ = -62.9 (d.m., 3F, $^2J_{PF}$ = 122.7 Hz), δ = -57.8 (d.d.m., 2F, $^1J_{PF}$ = 805.96 Hz, $^3J_{FF}$ = 119.9 Hz); ^{31}P-NMR (DMSO-d6): δ = -170.3 (t.m.)

NB: **a)** The same synthetic procedures were applied while carrying out the reactions of trifluoromethylchlorophosphines with DFI™. Instead of the chlorofluoroperphosphoranides expected, fluoroperphosphoranides **58**-**61B** were isolated (*See chapter C4*).

b) No reaction between trifluoromethylchlorophosphines with CDC was detected at the same reaction conditions.

4.40 Reaction of trifluoromethylchlorophosphines with FDC

Pyrex® NMR tube with a Teflon® stop-cock was charged with 0.046 g (0.3 mmol) of FDC and attached to vacuum manifold. 1.5 ml of dry acetonitrile and 0.2 mmol of starting trifluoromethylchlorophosphine were condensed in the tube. Reaction mixture was accurately warmed up till RT and shaked for 2 weeks. Formation of reaction products was monitored by NMR spectrometry. Very slow formation of perphosphoranides **58**-**60** was observed, no presence of mixed perphosphoranides was revealed.

G. X-Ray data

Structures were solved by direct methods (SHELXS-97) and Fourier synthesis. The refinement was done by full matrix least squares (SHELXL-97) procedures using anisotropic thermal parameters. If nothing is noted, the H atom positions were taken from the difference Fourier card at the end of the refinement. Images inserted in this thesis were prepared using the program Diamond version 2.1e.

STRUCTURE 1. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $F(CF_3)_3P^-(K^+)$*18-CROWN-6 (31, *FIGURE 23*)

Identification code	ak26	
Empirical formula	$C_{15}H_{24}F_{10}KO_6P$	
Formula weight	560.41	
Temperature	173(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 889.7(4) pm	**α**= 90.552(14)°.
	b = 954.4(2) pm	**β**= 93.19(2)°.
	c = 1496.5(3) pm	**γ** = 115.168(17)°.
Volume	1.1474(6) nm^3	
Z	2	
Density (calculated)	1.622 Mg/m^3	
Absorption coefficient	0.411 mm^{-1}	
F(000)	572	
Crystal size	0.60 x 0.40 x 0.40 mm^3	
Theta range for data collection	2.54 to 26.00°.	
Index ranges	$-10 \le h \le 1$, $-11 \le k \le 11$, $-18 \le l \le 18$	
Reflections collected	5396	
Independent reflections	4413 [R(int) = 0.0335]	
Completeness to theta = 26.00°	98.2 %	
Absorption correction	None	
Max. and min. transmission	0.8529 and 0.7906	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4413 / 60 / 355	
Goodness-of-fit on F^2	1.064	

Final R indices [I>2sigma(I)]	R1 = 0.0649, wR2 = 0.1780
R indices (all data)	R1 = 0.0998, wR2 = 0.2059
Largest diff. peak and hole	0.689 and -0.585 e.Å^{-3}

Table 10

	X	Y	Z	U(eq)
F(1)	4558(3)	1989(3)	1699(2)	44(1)
P(1)	3665(1)	2676(1)	2545(1)	28(1)
C(1)	2320(6)	3214(6)	3371(3)	41(1)
F(10)	10647(4)	2687(5)	3293(3)	79(1)
F(11)	2652(5)	2881(5)	4205(2)	70(1)
F(12)	2873(5)	4776(4)	3389(3)	74(1)
C(2)	2689(5)	3267(4)	1554(3)	44(1)
F(20)	1614(9)	3831(10)	1701(5)	91(4)
F(21)	1951(8)	2177(6)	930(3)	53(2)
F(22)	3881(8)	4370(7)	1150(4)	75(3)
F(20A)	2510(20)	4520(14)	1774(8)	85(6)
F(21A)	1190(14)	2257(12)	1280(15)	201(15)
F(22A)	3530(20)	3610(20)	835(9)	186(15)
C(3)	2283(5)	549(5)	2659(2)	44(1)
F(30)	1114(14)	175(19)	3228(8)	91(6)
F(31)	1540(14)	-218(13)	1912(5)	54(3)
F(32)	3250(20)	-100(16)	2956(9)	91(5)
F(30A)	1650(20)	220(20)	3443(7)	72(4)
F(31A)	1000(20)	-21(18)	2072(10)	140(8)
F(32A)	3070(20)	-340(20)	2563(15)	135(8)
K(1)	7426(1)	2065(1)	2410(1)	30(1)
O(1)	8255(4)	3285(4)	712(2)	40(1)
C(4)	7217(6)	2152(7)	52(3)	53(2)
C(5)	7435(6)	719(7)	147(4)	56(2)
O(2)	6762(4)	27(4)	961(2)	44(1)
C(6)	6968(7)	-1351(7)	1142(4)	61(2)
C(7)	6078(7)	-2058(6)	1946(4)	56(2)
O(3)	6866(4)	-1038(4)	2697(3)	46(1)
C(8)	6058(7)	-1614(6)	3496(4)	57(2)
C(9)	6963(7)	-519(7)	4261(4)	53(1)
O(4)	6811(4)	892(4)	4141(2)	42(1)
C(10)	7646(7)	1981(7)	4853(3)	53(1)

C(11)	7447(7)	3417(7)	4698(3)	53(1)
O(5)	8285(4)	4116(4)	3931(2)	43(1)
C(12)	8137(7)	5496(6)	3749(4)	49(1)
C(13)	9083(7)	6200(6)	2959(4)	53(2)
O(6)	8283(4)	5210(4)	2193(2)	42(1)
C(14)	9109(7)	5768(6)	1397(4)	52(1)
C(15)	8135(7)	4711(7)	638(4)	55(2)

Table 11 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for **31**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z #2 x+1,y,z					
F(1)-P(1)	179.0(3)	K(1)-O(5)	283.6(3)	F(12)-C(1)-P(1)	107.6(3)
F(1)-K(1)	268.0(3)	K(1)-C(4)	352.7(5)	C(1)#2-F(10)-K(1)	156.4(3)
P(1)-C(2)	188.7(5)	O(1)-C(15)	141.4(6)	F(20)-C(2)-F(21)	105.0(4)
P(1)-C(3)	188.9(5)	O(1)-C(4)	142.3(6)	F(20)-C(2)-F(22)	104.8(4)
P(1)-C(1)	197.5(5)	C(4)-C(5)	146.7(9)	F(21)-C(2)-F(22)	104.4(4)
P(1)-K(1)	364.81(19)	C(5)-O(2)	142.8(7)	F(20)-C(2)-P(1)	118.4(4)
C(1)-F(11)	133.9(6)	O(2)-C(6)	143.0(7)	F(21)-C(2)-P(1)	114.7(4)
C(1)-F(10)#1	135.1(6)	C(6)-C(7)	148.2(9)	F(22)-C(2)-P(1)	108.3(4)
C(1)-F(12)	135.6(6)	C(7)-O(3)	141.8(6)	F(31)-C(3)-F(30)	105.5(4)
F(10)-C(1)#2	135.1(6)	O(3)-C(8)	142.2(7)	F(31)-C(3)-F(32)	105.2(4)
F(10)-K(1)	290.3(4)	C(8)-C(9)	148.6(9)	F(30)-C(3)-F(32)	104.9(4)
C(2)-F(22A)	130.6(5)	C(9)-O(4)	142.2(6)	F(31)-C(3)-P(1)	115.5(7)
C(2)-F(20)	130.9(4)	O(4)-C(10)	141.5(6)	F(30)-C(3)-P(1)	117.6(8)
C(2)-F(21A)	130.9(5)	C(10)-C(11)	147.4(8)	F(32)-C(3)-P(1)	107.0(8)
C(2)-F(21)	131.0(4)	C(11)-O(5)	141.6(6)	F(1)-K(1)-O(2)	78.60(9)
C(2)-F(20A)	131.1(5)	O(5)-C(12)	140.6(6)	F(1)-K(1)-O(6)	78.51(10)
C(2)-F(22)	131.6(5)	C(12)-C(13)	148.4(8)	O(2)-K(1)-O(6)	121.76(12)
C(3)-F(31)	130.9(5)	C(13)-O(6)	142.5(6)	F(1)-K(1)-O(1)	76.81(9)
C(3)-F(30)	131.2(5)	O(6)-C(14)	142.1(7)	O(2)-K(1)-O(1)	61.57(11)
C(3)-F(30A)	131.3(5)	C(14)-C(15)	147.7(9)	O(6)-K(1)-O(1)	61.33(11)
C(3)-F(31A)	131.4(5)	P(1)-F(1)-K(1)	107.72(13)	F(1)-K(1)-O(4)	106.78(10)
C(3)-F(32A)	131.4(5)	F(1)-P(1)-C(2)	83.42(15)	O(2)-K(1)-O(4)	119.23(11)
C(3)-F(32)	131.5(5)	F(1)-P(1)-C(3)	83.84(15)	O(6)-K(1)-O(4)	118.49(11)
K(1)-O(2)	276.3(3)	C(2)-P(1)-C(3)	104.76(16)	O(1)-K(1)-O(4)	176.37(10)
K(1)-O(6)	279.1(3)	F(1)-P(1)-C(1)	170.42(18)	F(1)-K(1)-O(3)	106.85(10)
K(1)-O(1)	280.9(3)	C(2)-P(1)-C(1)	91.03(19)	O(2)-K(1)-O(3)	60.33(11)

K(1)-O(4)	282.1(3)	C(3)-P(1)-C(1)	90.07(19)	O(6)-K(1)-O(3)	174.64(10)
K(1)-O(3)	282.8(3)	F(1)-P(1)-K(1)	44.42(9)	O(1)-K(1)-O(3)	119.37(11)
C(3)-P(1)-K(1)	93.59(12)	C(2)-P(1)-K(1)	122.44(12)	O(4)-K(1)-O(3)	60.42(11)
F(11)-C(1)-F(10)#1	104.5(4)	C(1)-P(1)-K(1)	143.84(15)	F(1)-K(1)-O(5)	105.06(9)
F(10)#1-C(1)-F(12)	103.6(4)	F(11)-C(1)-F(12)	105.0(4)	O(2)-K(1)-O(5)	176.32(10)
F(10)#1-C(1)-P(1)	125.5(3)	F(11)-C(1)-P(1)	109.0(3)	O(6)-K(1)-O(5)	59.96(11)
O(3)-K(1)-O(5)	117.64(11)	O(2)-K(1)-F(10)	110.18(10)	O(1)-K(1)-O(5)	119.29(11)
F(1)-K(1)-F(10)	170.02(10)	F(1)-K(1)-C(4)	66.35(11)	O(4)-K(1)-O(5)	59.66(11)
O(6)-K(1)-F(10)	92.51(12)	O(2)-K(1)-C(4)	41.79(13)	O(5)-K(1)-C(4)	139.85(14)
O(1)-K(1)-F(10)	102.83(11)	O(6)-K(1)-C(4)	79.99(13)	F(10)-K(1)-C(4)	116.74(12)
O(4)-K(1)-F(10)	73.54(11)	O(1)-K(1)-C(4)	22.52(12)	O(2)-C(5)-C(4)	108.8(4)
O(3)-K(1)-F(10)	82.15(12)	O(4)-K(1)-C(4)	159.55(13)	C(5)-O(2)-C(6)	113.7(4)
O(5)-K(1)-F(10)	66.20(10)	O(3)-K(1)-C(4)	102.02(14)	C(5)-O(2)-K(1)	115.3(3)
F(1)-K(1)-P(1)	27.86(6)	O(2)-K(1)-P(1)	104.94(7)	O(6)-K(1)-P(1)	72.04(7)
O(1)-K(1)-P(1)	97.26(7)	F(10)-K(1)-P(1)	144.63(8)	C(4)-O(1)-K(1)	108.4(3)
O(4)-K(1)-P(1)	85.98(7)	C(4)-K(1)-P(1)	92.29(10)	O(1)-C(4)-C(5)	110.1(4)
O(3)-K(1)-P(1)	112.66(8)	C(15)-O(1)-C(4)	112.8(4)	O(1)-C(4)-K(1)	49.1(2)
O(5)-K(1)-P(1)	78.63(7)	C(15)-O(1)-K(1)	111.2(3)	C(5)-C(4)-K(1)	81.4(3)
C(6)-O(2)-K(1)	115.4(3)	O(2)-C(6)-C(7)	109.1(4)	O(3)-C(7)-C(6)	108.5(4)
C(7)-O(3)-C(8)	112.1(4)	O(4)-C(9)-C(8)	109.2(4)	O(4)-C(10)-C(11)	109.6(4)
C(7)-O(3)-K(1)	113.8(3)	C(10)-O(4)-C(9)	111.8(4)	C(12)-O(5)-K(1)	112.8(3)
C(8)-O(3)-K(1)	112.9(3)	C(10)-O(4)-K(1)	115.1(3)	C(11)-O(5)-K(1)	113.7(3)
O(3)-C(8)-C(9)	109.6(4)	C(9)-O(4)-K(1)	114.6(3)	O(5)-C(12)-C(13)	109.1(4)
O(5)-C(11)-C(10)	109.0(4)	C(12)-O(5)-C(11)	111.6(4)	O(6)-C(13)-C(12)	108.4(4)
C(14)-O(6)-C(13)	113.0(4)	C(14)-O(6)-K(1)	112.8(3)	C(13)-O(6)-K(1)	115.7(3)
O(6)-C(14)-C(15)	108.7(4)	O(1)-C(15)-C(14)	109.6(4)		

Table 12 *Bond lengths [pm] and angles [°] for **31**.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	41(2)	61(2)	39(2)	-9(1)	5(1)	30(1)
P(1)	25(1)	34(1)	27(1)	-7(1)	-2(1)	14(1)
C(1)	47(3)	44(3)	36(3)	-2(2)	8(2)	23(2)
F(10)	47(2)	116(3)	89(3)	-14(2)	17(2)	49(2)
F(11)	106(3)	98(3)	30(2)	2(2)	15(2)	67(2)
F(12)	118(3)	51(2)	66(2)	-9(2)	31(2)	47(2)
C(2)	61(3)	47(3)	37(3)	-3(2)	-1(2)	36(3)
F(20)	122(7)	183(11)	44(4)	-26(5)	-25(4)	140(8)

F(21)	67(4)	75(4)	30(3)	-17(2)	-24(3)	45(3)
F(22)	85(5)	69(4)	50(5)	32(3)	1(4)	13(4)
F(20A)	169(16)	76(8)	54(7)	-4(6)	-29(9)	99(11)
F(21A)	157(16)	63(8)	340(30)	-29(14)	-220(20)	39(10)
F(22A)	320(40)	390(40)	22(7)	41(14)	44(13)	310(30)
C(3)	53(3)	32(2)	45(3)	0(2)	3(2)	17(2)
F(30)	115(10)	42(6)	90(9)	-5(7)	74(9)	0(7)
F(31)	77(6)	30(4)	46(5)	-16(3)	4(4)	14(4)
F(32)	126(10)	66(7)	110(10)	19(6)	-25(8)	72(6)
F(30A)	103(9)	49(6)	52(5)	19(4)	18(6)	19(6)
F(31A)	124(11)	63(8)	133(12)	32(7)	-88(10)	-44(7)
F(32A)	166(16)	57(7)	220(20)	27(11)	99(13)	75(10)
K(1)	38(1)	31(1)	25(1)	-3(1)	-1(1)	18(1)
O(1)	31(2)	61(2)	30(2)	7(2)	0(1)	22(2)
C(4)	32(3)	94(4)	20(2)	3(2)	0(2)	14(3)
C(5)	32(3)	88(4)	39(3)	-32(3)	0(2)	17(3)
O(2)	40(2)	58(2)	40(2)	-23(2)	-7(2)	30(2)
C(6)	56(3)	64(4)	77(4)	-48(3)	-30(3)	45(3)
C(7)	54(3)	31(2)	84(4)	-17(3)	-22(3)	23(2)
O(3)	44(2)	32(2)	62(2)	-3(2)	-8(2)	18(2)
C(8)	53(3)	35(3)	85(4)	23(3)	7(3)	21(3)
C(9)	53(3)	57(3)	58(3)	25(3)	6(3)	30(3)
O(4)	46(2)	52(2)	34(2)	11(2)	3(2)	25(2)
C(10)	57(3)	83(4)	26(2)	-2(2)	4(2)	36(3)
C(11)	60(3)	81(4)	27(2)	-13(2)	6(2)	40(3)
O(5)	43(2)	50(2)	39(2)	-15(2)	2(2)	23(2)
C(12)	44(3)	39(3)	62(3)	-27(2)	-5(2)	17(2)
C(13)	38(3)	29(2)	85(4)	-14(3)	-4(3)	9(2)
O(6)	40(2)	28(2)	57(2)	7(2)	11(2)	12(1)
C(14)	44(3)	38(3)	80(4)	27(3)	23(3)	22(2)
C(15)	49(3)	78(4)	54(3)	37(3)	23(3)	41(3)

Table 13 *Anisotropic displacement parameters ($pm^2x\ 10^{-1}$) for **31**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	x	y	z	U(eq)
H(4A)	7506	2552	-553	57(4)
H(4B)	6039	1934	120	57(4)

H(5A)	6854	-5	-368	57(4)
H(5B)	8632	953	158	57(4)
H(6A)	8165	-1099	1246	57(4)
H(6B)	6514	-2092	622	57(4)
H(7A)	4899	-2231	1863	57(4)
H(7B)	6110	-3070	2043	57(4)
H(8A)	6035	-2643	3611	57(4)
H(8B)	4895	-1735	3429	57(4)
H(9A)	6491	-977	4829	57(4)
H(9B)	8153	-318	4293	57(4)
H(10A)	8843	2211	4892	57(4)
H(10B)	7180	1546	5426	57(4)
H(11A)	6250	3177	4605	57(4)
H(11B)	7917	4138	5226	57(4)
H(12A)	8582	6226	4274	57(4)
H(12B)	6951	5274	3627	57(4)
H(13A)	9109	7236	2869	57(4)
H(13B)	10243	6322	3054	57(4)
H(14A)	10243	5813	1455	57(4)
H(14B)	9208	6826	1291	57(4)
H(15A)	6955	4533	642	57(4)
H(15B)	8567	5183	66	57(4)

Table 14 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (pm^2x 10^{-1}) for **31**.*

STRUCTURE 2. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $(CF_3)_4P^-(K^+)$*18-CROWN-6 (32, *FIGURE 23*)		
Identification code	os5a	
Empirical formula	$C_{16}H_{24}F_{12}KO_6P$	
Formula weight	610.42	
Temperature	163(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P\,2_1/c$	
Unit cell dimensions	a = 1463.3(2) pm	**α**= 90°.
	b = 3525.5(6) pm	**β**= 98.39(3)°.
	c = 1461.9(6) pm	**γ** = 90°.
Volume	7.46(1) nm^3	
Z	12	
Density (calculated)	1.630 Mg/m^3	
Absorption coefficient	0.398 mm^{-1}	
F(000)	3720	
Crystal size	0.80 x 0.50 x 0.40 mm^3	
Theta range for data collection	2.23 to 27.51°.	
Index ranges	$-18 \le h \le 1$, $-24 \le k \le 1$, $-18 \le l \le 1$	
Reflections collected	14417	
Independent reflections	12345 [R(int) = 0.0172]	
Completeness to theta = 27.51°	72.0 %	
Absorption correction	None	
Max. and min. transmission	0.8572 and 0.7415	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12345 / 0 / 974	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1047	
R indices (all data)	R1 = 0.0761, wR2 = 0.1205	
Largest diff. peak and hole	0.324 and -0.314 e.$Å^{-3}$	

Table 15

	x	y	z	U(eq)
P(1)	2916(1)	1766(1)	7138(1)	31(1)
C(1)	2331(2)	1262(1)	7472(2)	38(1)
F(1)	1488(1)	1342(1)	7720(2)	66(1)
F(2)	2701(2)	996(1)	8078(1)	57(1)
F(3)	2113(2)	1070(1)	6662(1)	55(1)
C(2)	3546(3)	2264(1)	6897(3)	53(1)
F(4)	3673(2)	2271(1)	6003(2)	84(1)
F(5)	4322(2)	2425(1)	7342(2)	79(1)
F(6)	2872(2)	2537(1)	6958(2)	83(1)
C(3)	2870(2)	1941(1)	8362(2)	44(1)
F(7)	2752(2)	1670(1)	8968(1)	71(1)
F(8)	3609(2)	2138(1)	8731(2)	66(1)
F(9)	2158(2)	2177(1)	8373(2)	82(1)
C(4)	4043(2)	1505(1)	7229(3)	41(1)
F(10)	3939(2)	1176(1)	6767(2)	62(1)
F(11)	4405(1)	1416(1)	8099(2)	61(1)
F(12)	4713(2)	1693(1)	6893(2)	79(1)
P(2)	8118(1)	1572(1)	12872(1)	27(1)
C(5)	8710(2)	2064(1)	12473(2)	40(1)
F(13)	8348(2)	2309(1)	11803(1)	57(1)
F(14)	9572(1)	1981(1)	12268(1)	56(1)
F(15)	8888(2)	2284(1)	13246(1)	55(1)
C(6)	7486(2)	1080(1)	13153(2)	36(1)
F(16)	6695(1)	921(1)	12708(1)	51(1)
F(17)	8135(1)	801(1)	13141(2)	53(1)
F(18)	7343(1)	1097(1)	14051(1)	49(1)
C(7)	6970(2)	1826(1)	12665(2)	39(1)
F(19)	6623(1)	1856(1)	11765(1)	56(1)
F(20)	7037(2)	2181(1)	13000(2)	59(1)
F(21)	6315(1)	1658(1)	13073(2)	60(1)
C(8)	8265(2)	1362(1)	11698(2)	41(1)
F(22)	7586(2)	1128(1)	11338(1)	54(1)
F(23)	8351(2)	1613(1)	11034(1)	62(1)
F(24)	9044(2)	1151(1)	11791(2)	69(1)
P(3)	2555(1)	-110(1)	2925(1)	25(1)
C(9)	3208(2)	368(1)	2531(2)	34(1)

F(25)	3391(1)	593(1)	3297(1)	47(1)
F(26)	2881(1)	614(1)	1845(1)	46(1)
F(27)	4065(1)	269(1)	2350(1)	47(1)
C(10)	1864(2)	-591(1)	3189(2)	35(1)
F(28)	1058(1)	-736(1)	2730(1)	48(1)
F(29)	2479(1)	-884(1)	3181(2)	49(1)
F(30)	1704(1)	-575(1)	4084(1)	49(1)
C(11)	2695(2)	-329(1)	1752(2)	35(1)
F(31)	1988(1)	-545(1)	1383(1)	52(1)
F(32)	2831(2)	-81(1)	1098(1)	53(1)
F(33)	3442(2)	-557(1)	1858(2)	60(1)
C(12)	1438(2)	162(1)	2711(2)	35(1)
F(34)	1095(1)	192(1)	1812(1)	53(1)
F(35)	1549(1)	520(1)	3033(2)	50(1)
F(36)	763(1)	12(1)	3126(2)	57(1)
K(1)	2797(1)	787(1)	-55(1)	31(1)
O(1)	4684(1)	926(1)	16(1)	34(1)
C(13)	5096(2)	1126(1)	814(2)	46(1)
C(14)	4532(2)	1472(1)	919(3)	50(1)
O(2)	3642(1)	1352(1)	1087(2)	35(1)
C(15)	3076(2)	1662(1)	1267(2)	38(1)
C(16)	2187(2)	1512(1)	1497(2)	41(1)
O(3)	1704(1)	1328(1)	701(1)	36(1)
C(17)	843(2)	1180(1)	875(3)	45(1)
C(18)	394(2)	978(1)	40(3)	46(1)
O(4)	917(1)	648(1)	-112(2)	38(1)
C(19)	511(2)	431(1)	-883(3)	52(1)
C(20)	1083(2)	88(1)	-965(3)	49(1)
O(5)	1961(1)	203(1)	-1170(2)	35(1)
C(21)	2539(2)	-105(1)	-1327(2)	37(1)
C(22)	3417(2)	49(1)	-1584(2)	35(1)
O(6)	3896(1)	247(1)	-806(1)	31(1)
C(23)	4738(2)	409(1)	-1007(2)	41(1)
C(24)	5206(2)	604(1)	-163(3)	42(1)
K(2)	8260(1)	2440(1)	9894(1)	31(1)
O(7)	6395(1)	2249(1)	9716(2)	36(1)
C(25)	5770(2)	2554(1)	9795(3)	44(1)
C(26)	6151(2)	2801(1)	10590(3)	44(1)
O(8)	6995(1)	2965(1)	10409(2)	37(1)

C(27)	7368(2)	3222(1)	11125(2)	46(1)
C(28)	8289(3)	3359(1)	10929(2)	42(1)
O(9)	8912(2)	3050(1)	11006(1)	33(1)
C(29)	9841(2)	3165(1)	10966(2)	43(1)
C(30)	10433(2)	2821(1)	11011(2)	43(1)
O(10)	10173(1)	2606(1)	10197(1)	36(1)
C(31)	10729(2)	2276(1)	10151(3)	43(1)
C(32)	10404(2)	2070(1)	9273(2)	43(1)
O(11)	9511(1)	1914(1)	9329(1)	34(1)
C(33)	9123(2)	1732(1)	8490(2)	37(1)
C(34)	8240(2)	1548(1)	8640(2)	36(1)
O(12)	7591(1)	1838(1)	8756(1)	32(1)
C(35)	6728(2)	1688(1)	8939(3)	43(1)
C(36)	6064(2)	2007(1)	8965(2)	43(1)
K(3)	2812(1)	882(1)	4948(1)	32(1)
O(13)	3196(2)	247(1)	6028(1)	35(1)
C(37)	4064(3)	67(1)	5965(2)	46(1)
C(38)	4805(2)	357(1)	6068(2)	44(1)
O(14)	4653(1)	606(1)	5302(1)	35(1)
C(39)	5357(2)	883(1)	5319(2)	41(1)
C(40)	5140(2)	1132(1)	4497(2)	42(1)
O(15)	4304(1)	1334(1)	4563(1)	35(1)
C(41)	4046(2)	1573(1)	3788(2)	42(1)
C(42)	3190(3)	1790(1)	3925(2)	45(1)
O(16)	2440(2)	1526(1)	3873(1)	37(1)
C(43)	1585(3)	1712(1)	3966(2)	51(1)
C(44)	832(2)	1421(1)	3853(2)	51(1)
O(17)	985(1)	1163(1)	4603(2)	41(1)
C(45)	276(2)	881(1)	4570(3)	52(1)
C(46)	491(2)	623(1)	5376(2)	51(1)
O(18)	1332(2)	430(1)	5312(2)	41(1)
C(47)	1582(3)	175(1)	6060(2)	49(1)
C(48)	2462(3)	-21(1)	5940(2)	47(1)

Table 16 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for 32. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1 #2 x,-y+1/2,z+1/2 #3 x,y,z-1 #4 x,-y+1/2,z-1/2					
P(1)-C(4)	187.6(4)	F(10)-K(3)	309.6(3)	F(23)-K(2)	335.3(3)
P(1)-C(3)	190.3(4)	P(2)-C(7)	188.9(4)	P(3)-C(12)	188.1(3)
P(1)-C(2)	203.7(5)	P(2)-C(8)	191.0(3)	P(3)-C(11)	191.8(3)
P(1)-C(1)	206.0(4)	P(2)-C(6)	203.8(4)	P(3)-C(10)	204.0(4)
C(1)-F(2)	135.0(4)	P(2)-C(5)	206.0(4)	P(3)-C(9)	206.1(4)
C(1)-F(3)	136.1(4)	C(5)-F(13)	135.4(4)	C(9)-F(26)	136.0(4)
C(1)-F(1)	136.6(4)	C(5)-F(15)	136.5(4)	C(9)-F(27)	136.4(3)
F(2)-K(1)#1	281.0(2)	C(5)-F(14)	136.9(4)	C(9)-F(25)	136.8(4)
F(3)-K(3)	291.6(2)	F(13)-K(2)	281.3(2)	F(25)-K(3)	285.9(2)
C(2)-F(4)	134.8(4)	F(15)-K(2)#2	287.0(2)	F(26)-K(1)	282.8(2)
C(2)-F(5)	134.9(5)	C(6)-F(18)	136.2(4)	C(10)-F(30)	136.3(4)
C(2)-F(6)	139.0(5)	C(6)-F(16)	136.3(4)	C(10)-F(28)	136.7(4)
C(3)-F(7)	133.1(4)	C(6)-F(17)	136.8(4)	C(10)-F(29)	137.1(4)
C(3)-F(8)	133.3(4)	C(7)-F(21)	133.8(4)	C(11)-F(32)	133.0(4)
C(3)-F(9)	133.7(4)	C(7)-F(20)	134.2(4)	C(11)-F(31)	133.5(4)
C(4)-F(12)	133.6(4)	C(7)-F(19)	134.4(4)	C(11)-F(33)	134.9(4)
C(4)-F(10)	134.0(4)	F(20)-K(2)#2	334.7(3)	C(12)-F(34)	134.1(4)
C(4)-F(11)	134.0(4)	C(8)-F(23)	133.4(4)	C(12)-F(36)	134.1(4)
C(15)-C(16)	148.8(5)	C(8)-F(22)	133.8(4)	C(12)-F(35)	135.0(4)
C(16)-O(3)	142.7(4)	C(8)-F(24)	135.1(4)	F(35)-K(3)	337.2(3)
O(3)-C(17)	141.9(4)	K(2)-O(8)	279.7(2)	K(1)-O(2)	277.1(2)
C(17)-C(18)	148.1(5)	K(2)-O(11)	281.2(2)	K(1)-O(4)	278.4(2)
C(18)-O(4)	142.6(4)	K(2)-O(10)	283.0(2)	K(1)-O(1)	279.2(2)
O(4)-C(19)	141.9(4)	K(2)-F(15)#4	287.0(2)	K(1)-O(5)	279.5(2)
C(19)-C(20)	148.6(6)	K(2)-F(20)#4	334.7(3)	K(1)-F(2)#3	281.0(2)
C(20)-O(5)	142.1(4)	O(7)-C(36)	142.0(4)	K(1)-O(6)	281.5(2)
O(5)-C(21)	141.6(4)	O(7)-C(25)	142.7(4)	K(1)-O(3)	281.8(2)
C(21)-C(22)	149.3(5)	C(25)-C(26)	149.3(5)	O(1)-C(24)	141.4(4)
C(22)-O(6)	142.7(4)	C(26)-O(8)	142.2(4)	O(1)-C(13)	141.9(4)
O(6)-C(23)	142.8(4)	O(8)-C(27)	143.0(4)	C(13)-C(14)	149.4(5)
C(23)-C(24)	148.9(5)	C(27)-C(28)	149.9(5)	C(14)-O(2)	142.4(4)
K(2)-O(9)	277.7(2)	C(35)-C(36)	148.8(5)	O(2)-C(15)	142.0(4)
K(2)-O(12)	278.5(2)	K(3)-O(13)	274.9(2)	C(40)-O(15)	143.0(4)
K(2)-O(7)	278.6(2)	K(3)-O(16)	276.9(3)	O(15)-C(41)	141.9(4)
C(28)-O(9)	141.7(4)	K(3)-O(18)	280.1(2)	C(41)-C(42)	150.6(5)
O(9)-C(29)	142.7(4)	K(3)-O(15)	282.5(2)	C(42)-O(16)	143.1(4)
C(29)-C(30)	148.7(5)	K(3)-O(17)	282.5(2)	O(16)-C(43)	143.7(4)
C(30)-O(10)	141.5(4)	K(3)-O(14)	284.1(2)	C(43)-C(44)	149.8(6)
O(10)-C(31)	142.5(4)	O(13)-C(48)	142.2(4)	C(44)-O(17)	141.6(4)
C(31)-C(32)	149.2(5)	O(13)-C(37)	143.6(4)	O(17)-C(45)	143.3(4)
C(32)-O(11)	143.1(4)	C(37)-C(38)	148.2(5)	C(45)-C(46)	148.6(5)
O(11)-C(33)	142.8(4)	C(38)-O(14)	141.5(4)	C(46)-O(18)	142.1(4)
C(33)-C(34)	149.0(5)	O(14)-C(39)	141.9(4)	O(18)-C(47)	142.2(4)
C(34)-O(12)	142.3(4)	C(39)-C(40)	148.5(5)	C(47)-C(48)	149.3(5)
O(12)-C(35)	142.9(4)	F(4)-C(2)-P(1)	108.2(3)	F(6)-C(2)-P(1)	104.1(3)
C(4)-P(1)-C(3)	104.05(16)	F(5)-C(2)-P(1)	130.6(3)	F(7)-C(3)-F(8)	106.3(3)
C(4)-P(1)-C(2)	91.15(18)	F(2)-C(1)-P(1)	128.0(2)	F(7)-C(3)-F(9)	105.2(3)
C(3)-P(1)-C(2)	87.81(17)	F(3)-C(1)-P(1)	106.0(2)	F(8)-C(3)-F(9)	104.9(3)
C(4)-P(1)-C(1)	87.22(16)	F(1)-C(1)-P(1)	107.9(3)	F(7)-C(3)-P(1)	114.8(3)

C(3)-P(1)-C(1)	89.06(16)	C(1)-F(2)-K(1)#1	141.2(2)	C(8)-F(23)-K(2)	159.9(2)
C(2)-P(1)-C(1)	176.02(15)	C(1)-F(3)-K(3)	142.53(18)	C(12)-P(3)-C(11)	105.05(15)
F(2)-C(1)-F(3)	104.2(3)	F(4)-C(2)-F(5)	103.5(3)	C(12)-P(3)-C(10)	90.74(16)
F(2)-C(1)-F(1)	105.0(3)	F(4)-C(2)-F(6)	104.4(3)	C(11)-P(3)-C(10)	87.53(15)
F(3)-C(1)-F(1)	103.2(3)	F(5)-C(2)-F(6)	103.4(4)	C(12)-P(3)-C(9)	87.91(15)
F(8)-C(3)-P(1)	114.4(2)	F(15)-C(5)-F(14)	103.4(3)	C(11)-P(3)-C(9)	87.91(14)
F(9)-C(3)-P(1)	110.4(3)	F(13)-C(5)-P(2)	127.2(2)	C(10)-P(3)-C(9)	174.74(13)
F(12)-C(4)-F(10)	106.2(3)	F(15)-C(5)-P(2)	106.3(2)	F(26)-C(9)-F(27)	104.7(2)
F(12)-C(4)-F(11)	104.7(3)	F(14)-C(5)-P(2)	108.8(3)	F(26)-C(9)-F(25)	103.8(3)
F(10)-C(4)-F(11)	106.1(3)	C(5)-F(13)-K(2)	141.1(2)	F(27)-C(9)-F(25)	103.3(2)
F(12)-C(4)-P(1)	114.5(3)	C(5)-F(15)-K(2)#2	147.39(19)	F(26)-C(9)-P(3)	126.9(2)
F(10)-C(4)-P(1)	110.8(2)	F(18)-C(6)-F(16)	103.8(2)	F(27)-C(9)-P(3)	108.8(2)
F(11)-C(4)-P(1)	113.8(2)	F(18)-C(6)-F(17)	104.4(3)	F(25)-C(9)-P(3)	106.9(2)
C(4)-F(10)-K(3)	136.9(2)	F(16)-C(6)-F(17)	104.0(3)	C(9)-F(25)-K(3)	148.32(17)
C(7)-P(2)-C(8)	104.79(16)	F(18)-C(6)-P(2)	107.2(2)	C(9)-F(26)-K(1)	145.27(19)
C(7)-P(2)-C(6)	90.97(16)	F(16)-C(6)-P(2)	129.3(2)	F(30)-C(10)-F(28)	103.4(2)
C(8)-P(2)-C(6)	87.91(16)	F(17)-C(6)-P(2)	105.8(2)	F(30)-C(10)-F(29)	104.2(3)
C(7)-P(2)-C(5)	87.52(17)	F(21)-C(7)-F(20)	105.6(3)	F(28)-C(10)-F(29)	103.7(3)
C(8)-P(2)-C(5)	88.05(16)	F(21)-C(7)-F(19)	106.1(3)	F(30)-C(10)-P(3)	107.8(2)
C(6)-P(2)-C(5)	175.18(13)	F(23)-C(8)-F(22)	105.4(3)	F(28)-C(10)-P(3)	129.2(2)
F(13)-C(5)-F(15)	104.0(3)	F(23)-C(8)-F(24)	105.8(3)	F(29)-C(10)-P(3)	106.2(2)
F(13)-C(5)-F(14)	104.7(3)	F(22)-C(8)-F(24)	105.6(3)	F(32)-C(11)-F(31)	105.9(3)
F(20)-C(7)-F(19)	106.4(3)	F(23)-C(8)-P(2)	115.5(3)	F(32)-C(11)-F(33)	105.7(3)
F(21)-C(7)-P(2)	113.4(3)	F(22)-C(8)-P(2)	114.7(2)	F(31)-C(11)-F(33)	105.8(3)
F(20)-C(7)-P(2)	111.6(2)	F(24)-C(8)-P(2)	109.2(2)	F(32)-C(11)-P(3)	115.2(3)
F(19)-C(7)-P(2)	113.1(2)	F(34)-C(12)-P(3)	113.3(2)	F(31)-C(11)-P(3)	114.4(2)
C(7)-F(20)-K(2)#2	132.5(2)	F(36)-C(12)-P(3)	113.8(3)	F(33)-C(11)-P(3)	109.1(2)
F(35)-C(12)-P(3)	111.2(2)	C(12)-F(35)-K(3)	131.81(18)	F(34)-C(12)-F(36)	106.3(3)
O(2)-K(1)-O(4)	119.75(7)	O(4)-K(1)-O(1)	179.57(7)	F(34)-C(12)-F(35)	105.9(3)
O(2)-K(1)-O(1)	59.93(7)	O(2)-K(1)-O(5)	178.50(7)	F(36)-C(12)-F(35)	105.7(3)
O(4)-K(1)-O(5)	60.47(7)	O(4)-K(1)-F(2)#3	96.17(7)	O(1)-K(1)-O(6)	61.02(7)
O(1)-K(1)-O(5)	119.85(7)	O(1)-K(1)-F(2)#3	84.22(7)	O(5)-K(1)-O(6)	60.05(6)
O(2)-K(1)-F(2)#3	110.56(7)	O(5)-K(1)-F(2)#3	70.77(7)	F(2)#3-K(1)-O(6)	75.46(7)
O(4)-K(1)-O(6)	119.22(7)	O(2)-K(1)-O(6)	119.38(7)	O(2)-K(1)-O(3)	60.41(7)
O(4)-K(1)-O(3)	60.97(7)	F(2)#3-K(1)-F(26)	177.19(7)	O(6)-K(1)-F(26)	107.00(7)
O(1)-K(1)-O(3)	118.78(7)	O(3)-K(1)-F(26)	72.92(7)	C(13)-O(1)-K(1)	114.64(18)
O(5)-K(1)-O(3)	120.15(7)	C(24)-O(1)-C(13)	112.0(2)	O(1)-C(13)-C(14)	108.4(3)
F(2)#3-K(1)-O(3)	104.62(7)	C(24)-O(1)-K(1)	114.16(19)	O(2)-C(14)-C(13)	107.8(3)
O(6)-K(1)-O(3)	179.79(7)	C(15)-O(2)-C(14)	112.0(3)	C(14)-O(2)-K(1)	116.72(19)
O(2)-K(1)-F(26)	67.15(7)	C(15)-O(2)-K(1)	116.36(18)	O(2)-C(15)-C(16)	108.8(3)
O(4)-K(1)-F(26)	83.83(7)	O(3)-C(16)-C(15)	108.8(3)	O(3)-C(17)-C(18)	109.1(3)
O(1)-K(1)-F(26)	95.76(7)	C(17)-O(3)-C(16)	111.6(2)	O(4)-C(18)-C(17)	109.6(3)
O(5)-K(1)-F(26)	111.55(7)	C(18)-O(4)-K(1)	113.76(19)	C(19)-O(4)-C(18)	113.0(3)
C(17)-O(3)-K(1)	113.0(2)	O(4)-C(19)-C(20)	109.2(3)	C(19)-O(4)-K(1)	114.52(18)

C(16)-O(3)-K(1)	112.69(17)	C(20)-O(5)-K(1)	114.8(2)	O(6)-C(22)-C(21)	108.6(2)
O(5)-C(20)-C(19)	108.8(3)	O(5)-C(21)-C(22)	108.5(3)	O(9)-K(2)-O(12)	178.99(7)
C(21)-O(5)-C(20)	113.3(3)	C(22)-O(6)-C(23)	111.7(2)	O(9)-K(2)-O(7)	119.33(7)
C(21)-O(5)-K(1)	116.03(17)	C(22)-O(6)-K(1)	113.55(17)	O(12)-K(2)-O(7)	60.38(7)
O(12)-K(2)-O(8)	118.42(7)	C(23)-O(6)-K(1)	111.7(2)	O(9)-K(2)-O(8)	61.02(7)
O(7)-K(2)-O(8)	60.46(7)	O(6)-C(23)-C(24)	108.7(3)	O(11)-K(2)-F(13)	104.21(7)
O(9)-K(2)-O(11)	119.94(7)	O(1)-C(24)-C(23)	109.2(3)	O(9)-K(2)-O(10)	60.11(7)
O(12)-K(2)-O(11)	60.60(6)	O(8)-K(2)-F(13)	77.17(7)	O(12)-K(2)-O(10)	120.25(7)
O(7)-K(2)-O(11)	118.92(7)	O(7)-K(2)-O(10)	175.88(7)	O(12)-K(2)-F(15)#4	83.34(7)
O(8)-K(2)-O(11)	178.53(7)	O(8)-K(2)-O(10)	120.02(7)	O(7)-K(2)-F(15)#4	115.62(7)
O(9)-K(2)-F(13)	65.46(7)	O(11)-K(2)-O(10)	60.70(7)	O(8)-K(2)-F(15)#4	107.93(7)
O(12)-K(2)-F(13)	115.36(7)	F(13)-K(2)-O(10)	88.72(7)	O(11)-K(2)-F(15)#4	71.03(6)
O(7)-K(2)-F(13)	87.44(7)	O(9)-K(2)-F(15)#4	96.02(7)	F(13)-K(2)-F(15)#4	156.14(7)
C(36)-O(7)-K(2)	115.87(17)	O(10)-K(2)-F(20)#4	116.41(7)	O(10)-K(2)-F(15)#4	68.37(7)
C(25)-O(7)-K(2)	116.15(19)	F(15)#4-K(2)-F(20)#4	50.86(6)	O(9)-K(2)-F(20)#4	105.79(7)
O(7)-C(25)-C(26)	109.3(3)	O(9)-K(2)-F(23)	113.39(7)	O(12)-K(2)-F(20)#4	73.20(7)
O(8)-C(26)-C(25)	109.1(3)	O(12)-K(2)-F(23)	67.58(7)	O(7)-K(2)-F(20)#4	67.71(6)
C(26)-O(8)-C(27)	111.7(3)	O(7)-K(2)-F(23)	78.65(7)	O(8)-K(2)-F(20)#4	70.35(7)
C(26)-O(8)-K(2)	114.1(2)	O(8)-K(2)-F(23)	114.91(7)	O(11)-K(2)-F(20)#4	108.20(7)
C(27)-O(8)-K(2)	114.74(18)	O(11)-K(2)-F(23)	65.93(6)	F(13)-K(2)-F(20)#4	145.85(7)
O(8)-C(27)-C(28)	108.9(3)	F(13)-K(2)-F(23)	51.02(6)	O(9)-C(29)-C(30)	108.6(3)
O(9)-C(28)-C(27)	108.7(3)	O(10)-K(2)-F(23)	97.76(7)	O(10)-C(30)-C(29)	108.4(3)
C(28)-O(9)-C(29)	112.6(3)	F(15)#4-K(2)-F(23)	135.84(6)	C(30)-O(10)-C(31)	113.0(3)
C(28)-O(9)-K(2)	112.81(18)	F(20)#4-K(2)-F(23)	137.36(6)	C(30)-O(10)-K(2)	112.38(17)
C(29)-O(9)-K(2)	116.3(2)	C(36)-O(7)-C(25)	111.5(2)	C(31)-O(10)-K(2)	112.57(18)
C(34)-O(12)-K(2)	115.91(18)	O(13)-K(3)-O(15)	118.30(7)	O(10)-C(31)-C(32)	108.9(3)
C(35)-O(12)-K(2)	114.40(19)	O(16)-K(3)-O(15)	61.19(7)	O(11)-C(32)-C(31)	108.5(3)
O(12)-C(35)-C(36)	108.9(3)	O(18)-K(3)-O(15)	179.39(7)	C(33)-O(11)-C(32)	112.0(2)
O(7)-C(36)-C(35)	108.9(3)	O(13)-K(3)-O(17)	119.78(7)	C(33)-O(11)-K(2)	110.88(17)
O(13)-K(3)-O(16)	179.34(8)	O(16)-K(3)-O(17)	60.62(7)	C(32)-O(11)-K(2)	113.7(2)
O(13)-K(3)-O(18)	61.75(7)	O(16)-K(3)-F(3)	103.68(7)	O(11)-C(33)-C(34)	108.3(2)
O(16)-K(3)-O(18)	118.76(7)	O(13)-K(3)-F(3)	76.12(7)	O(12)-C(34)-C(33)	108.3(3)

O(18)-K(3)-O(17)	59.74(8)	O(13)-K(3)-O(14)	60.48(7)	C(34)-O(12)-C(35)	112.3(3)
O(15)-K(3)-O(17)	120.36(8)	O(14)-K(3)-F(25)	68.98(7)	O(17)-K(3)-F(10)	114.08(7)
O(16)-K(3)-O(14)	119.12(7)	O(18)-K(3)-F(3)	65.73(6)	O(14)-K(3)-F(10)	65.53(6)
O(18)-K(3)-O(14)	120.61(8)	O(15)-K(3)-F(3)	114.89(7)	F(25)-K(3)-F(10)	131.09(6)
O(15)-K(3)-O(14)	59.29(7)	O(17)-K(3)-F(3)	68.47(7)	F(3)-K(3)-F(10)	52.84(6)
O(17)-K(3)-O(14)	179.52(8)	O(14)-K(3)-F(3)	111.32(7)	O(13)-K(3)-F(35)	102.15(7)
O(13)-K(3)-F(25)	97.71(7)	F(25)-K(3)-F(3)	171.95(7)	O(16)-K(3)-F(35)	78.48(7)
O(16)-K(3)-F(25)	82.55(7)	O(13)-K(3)-F(10)	74.96(7)	O(18)-K(3)-F(35)	66.28(6)
O(18)-K(3)-F(25)	106.91(7)	O(16)-K(3)-F(10)	104.42(8)	O(15)-K(3)-F(35)	113.17(6)
O(15)-K(3)-F(25)	72.48(6)	O(18)-K(3)-F(10)	110.92(7)	O(17)-K(3)-F(35)	66.09(6)
O(17)-K(3)-F(25)	111.29(7)	O(15)-K(3)-F(10)	69.63(7)	O(14)-K(3)-F(35)	114.31(6)
C(48)-O(13)-K(3)	113.6(2)	O(14)-C(39)-C(40)	109.0(3)	F(25)-K(3)-F(35)	50.11(5)
C(37)-O(13)-K(3)	115.66(19)	O(15)-C(40)-C(39)	108.8(3)	F(3)-K(3)-F(35)	125.53(6)
O(13)-C(37)-C(38)	109.2(3)	C(41)-O(15)-C(40)	111.8(2)	F(10)-K(3)-F(35)	176.84(7)
O(14)-C(38)-C(37)	108.6(3)	C(41)-O(15)-K(3)	111.80(17)	C(48)-O(13)-C(37)	111.3(3)
C(38)-O(14)-C(39)	112.6(3)	C(40)-O(15)-K(3)	115.3(2)	O(16)-C(42)-C(41)	108.0(3)
C(38)-O(14)-K(3)	113.10(17)	O(15)-C(41)-C(42)	108.9(3)	C(44)-O(17)-K(3)	113.69(18)
C(39)-O(14)-K(3)	115.71(19)	C(42)-O(16)-C(43)	111.7(3)	C(45)-O(17)-K(3)	115.1(2)
O(16)-C(43)-C(44)	108.2(3)	C(42)-O(16)-K(3)	114.64(19)	O(17)-C(45)-C(46)	109.3(3)
O(17)-C(44)-C(43)	108.9(3)	C(43)-O(16)-K(3)	115.0(2)	O(18)-C(46)-C(45)	109.0(3)
C(44)-O(17)-C(45)	112.8(3)	C(46)-O(18)-C(47)	112.3(3)	C(46)-O(18)-K(3)	116.2(2)
C(47)-O(18)-K(3)	112.76(18)	O(18)-C(47)-C(48)	109.4(3)	O(13)-C(48)-C(47)	109.6(3)

Table 17 *Bond lengths [pm] and angles [°] for **31**.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	34(1)	31(1)	26(1)	1(1)	-2(1)	-1(1)
C(1)	35(2)	45(3)	33(2)	-2(2)	5(1)	-3(2)
F(1)	40(1)	86(2)	76(2)	-7(1)	23(1)	-16(1)
F(2)	78(2)	44(2)	47(1)	16(1)	4(1)	-10(1)

F(3)	63(1)	58(2)	43(1)	-11(1)	4(1)	-26(1)
C(2)	72(3)	48(4)	39(2)	0(2)	3(2)	-11(2)
F(4)	147(3)	63(2)	43(1)	10(1)	18(2)	-41(2)
F(5)	96(2)	67(2)	69(2)	-2(1)	3(1)	-49(2)
F(6)	113(2)	33(2)	101(2)	11(2)	6(2)	3(2)
C(3)	42(2)	49(3)	43(2)	-10(2)	15(2)	-2(2)
F(7)	113(2)	73(2)	30(1)	-7(1)	20(1)	-22(2)
F(8)	62(1)	91(2)	47(1)	-33(1)	12(1)	-28(1)
F(9)	72(2)	78(2)	106(2)	-23(2)	46(2)	18(2)
C(4)	41(2)	37(3)	48(2)	-7(2)	15(2)	-5(2)
F(10)	53(1)	59(2)	77(2)	-31(1)	20(1)	2(1)
F(11)	47(1)	62(2)	67(2)	0(1)	-14(1)	16(1)
F(12)	51(1)	80(2)	117(2)	0(2)	46(1)	-15(1)
P(2)	27(1)	31(1)	23(1)	1(1)	3(1)	-6(1)
C(5)	44(2)	47(3)	30(2)	2(2)	5(1)	-13(2)
F(13)	76(2)	49(2)	43(1)	18(1)	3(1)	-15(1)
F(14)	42(1)	72(2)	57(1)	6(1)	15(1)	-22(1)
F(15)	75(2)	48(2)	41(1)	-10(1)	4(1)	-30(1)
C(6)	35(2)	37(3)	35(2)	4(2)	3(1)	-9(2)
F(16)	48(1)	51(2)	52(1)	0(1)	0(1)	-26(1)
F(17)	53(1)	35(2)	72(2)	6(1)	9(1)	-3(1)
F(18)	59(1)	51(2)	37(1)	9(1)	10(1)	-18(1)
C(7)	38(2)	41(4)	40(2)	1(2)	8(1)	0(2)
F(19)	42(1)	74(2)	49(1)	13(1)	-8(1)	6(1)
F(20)	61(1)	45(2)	76(2)	-10(1)	20(1)	9(1)
F(21)	38(1)	65(2)	84(2)	20(1)	29(1)	3(1)
C(8)	40(2)	49(3)	35(2)	-5(2)	14(1)	-7(2)
F(22)	63(1)	60(2)	40(1)	-22(1)	11(1)	-23(1)
F(23)	89(2)	71(2)	28(1)	-3(1)	22(1)	-24(1)
F(24)	55(1)	83(2)	76(2)	-16(1)	32(1)	15(1)
P(3)	25(1)	27(1)	23(1)	0(1)	3(1)	-1(1)
C(9)	33(2)	40(3)	28(2)	-1(2)	7(1)	0(2)
F(25)	60(1)	44(2)	39(1)	-12(1)	9(1)	-21(1)
F(26)	59(1)	39(2)	40(1)	13(1)	8(1)	-5(1)
F(27)	32(1)	56(2)	56(1)	-2(1)	15(1)	-10(1)
C(10)	35(2)	37(3)	32(2)	-3(2)	3(1)	-8(2)
F(28)	40(1)	51(2)	49(1)	1(1)	-1(1)	-20(1)
F(29)	51(1)	29(2)	66(1)	7(1)	4(1)	0(1)
F(30)	66(1)	51(2)	32(1)	5(1)	12(1)	-20(1)

C(11)	37(2)	34(3)	36(2)	-7(2)	12(1)	-4(2)
F(31)	59(1)	59(2)	40(1)	-22(1)	12(1)	-22(1)
F(32)	79(2)	54(2)	28(1)	-5(1)	19(1)	-17(1)
F(33)	53(1)	60(2)	75(2)	-9(1)	30(1)	16(1)
C(12)	32(2)	31(3)	42(2)	4(2)	9(1)	0(2)
F(34)	42(1)	61(2)	49(1)	2(1)	-13(1)	13(1)
F(35)	51(1)	31(2)	70(2)	-11(1)	19(1)	7(1)
F(36)	35(1)	56(2)	89(2)	5(1)	32(1)	1(1)
K(1)	24(1)	38(1)	31(1)	-9(1)	4(1)	1(1)
O(1)	27(1)	40(2)	34(1)	-3(1)	1(1)	4(1)
C(13)	28(2)	58(3)	49(2)	-11(2)	-2(1)	-7(2)
C(14)	41(2)	54(4)	54(2)	-15(2)	5(2)	-22(2)
O(2)	35(1)	33(2)	38(1)	-4(1)	4(1)	1(1)
C(15)	52(2)	31(3)	31(2)	-1(2)	3(1)	7(2)
C(16)	55(2)	43(3)	26(2)	-5(2)	6(1)	21(2)
O(3)	34(1)	43(2)	32(1)	3(1)	10(1)	9(1)
C(17)	41(2)	42(3)	57(2)	5(2)	24(2)	12(2)
C(18)	24(2)	50(3)	65(2)	12(2)	8(2)	9(2)
O(4)	26(1)	49(2)	38(1)	1(1)	1(1)	5(1)
C(19)	23(2)	74(4)	55(2)	-8(2)	-3(2)	-6(2)
C(20)	34(2)	56(3)	56(2)	-6(2)	4(2)	-17(2)
O(5)	31(1)	34(2)	38(1)	-4(1)	2(1)	-4(1)
C(21)	47(2)	34(3)	29(2)	-7(2)	1(1)	-3(2)
C(22)	46(2)	36(3)	25(2)	-5(2)	7(1)	8(2)
O(6)	31(1)	37(2)	27(1)	-2(1)	8(1)	2(1)
C(23)	35(2)	45(3)	49(2)	-5(2)	22(2)	2(2)
C(24)	24(2)	46(3)	57(2)	-2(2)	6(1)	5(2)
K(2)	26(1)	35(1)	33(1)	-10(1)	3(1)	0(1)
O(7)	25(1)	40(2)	41(1)	-7(1)	1(1)	2(1)
C(25)	27(2)	48(3)	59(2)	-7(2)	8(2)	4(2)
C(26)	39(2)	45(3)	51(2)	-9(2)	15(2)	11(2)
O(8)	37(1)	38(2)	36(1)	-10(1)	5(1)	2(1)
C(27)	49(2)	45(3)	41(2)	-15(2)	2(2)	13(2)
C(28)	60(2)	20(3)	43(2)	-6(2)	-1(2)	-4(2)
O(9)	39(1)	25(2)	35(1)	-2(1)	5(1)	-6(1)
C(29)	45(2)	45(3)	41(2)	-3(2)	9(2)	-24(2)
C(30)	33(2)	60(3)	36(2)	2(2)	0(1)	-13(2)
O(10)	29(1)	40(2)	36(1)	1(1)	0(1)	-1(1)
C(31)	24(2)	43(3)	59(2)	12(2)	3(1)	4(2)

C(32)	26(2)	54(3)	52(2)	5(2)	15(1)	8(2)
O(11)	29(1)	42(2)	33(1)	1(1)	7(1)	4(1)
C(33)	44(2)	38(3)	30(2)	-2(2)	9(1)	13(2)
C(34)	49(2)	27(3)	32(2)	-6(2)	2(1)	8(2)
O(12)	34(1)	23(2)	38(1)	-8(1)	2(1)	1(1)
C(35)	39(2)	39(3)	49(2)	-10(2)	1(2)	-15(2)
C(36)	28(2)	49(3)	49(2)	-12(2)	-2(1)	-8(2)
K(3)	26(1)	38(1)	32(1)	8(1)	5(1)	3(1)
O(13)	45(1)	30(2)	30(1)	2(1)	7(1)	0(1)
C(37)	67(2)	36(3)	36(2)	7(2)	17(2)	24(2)
C(38)	44(2)	58(3)	30(2)	12(2)	7(1)	23(2)
O(14)	33(1)	44(2)	29(1)	7(1)	3(1)	8(1)
C(39)	23(1)	61(3)	39(2)	-5(2)	4(1)	4(2)
C(40)	27(2)	59(3)	42(2)	-2(2)	11(1)	-6(2)
O(15)	33(1)	44(2)	30(1)	6(1)	7(1)	-2(1)
C(41)	48(2)	42(3)	38(2)	6(2)	10(2)	-14(2)
C(42)	69(2)	26(3)	39(2)	6(2)	7(2)	1(2)
O(16)	42(1)	34(2)	34(1)	3(1)	8(1)	11(1)
C(43)	66(3)	52(3)	39(2)	9(2)	17(2)	36(2)
C(44)	36(2)	80(4)	37(2)	8(2)	5(2)	28(2)
O(17)	31(1)	58(2)	34(1)	-1(1)	1(1)	12(1)
C(45)	20(2)	84(4)	49(2)	-26(2)	1(1)	3(2)
C(46)	29(2)	81(4)	44(2)	-17(2)	10(2)	-14(2)
O(18)	36(1)	52(2)	34(1)	-2(1)	8(1)	-9(1)
C(47)	54(2)	54(3)	39(2)	-1(2)	10(2)	-28(2)
C(48)	71(3)	32(3)	38(2)	-4(2)	6(2)	-10(2)

Table 18 *Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2} U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	x	y	z	U(eq)
H(13A)	5736	1199	747	47(1)
H(13B)	5117	963	1368	47(1)
H(14A)	4831	1628	1442	47(1)
H(14B)	4476	1627	349	47(1)
H(15A)	2959	1828	716	47(1)
H(15B)	3391	1814	1790	47(1)
H(16A)	2307	1330	2016	47(1)

H(16B)	1809	1723	1688	47(1)
H(17A)	441	1389	1029	47(1)
H(17B)	942	1003	1406	47(1)
H(18A)	-241	903	123	47(1)
H(18B)	355	1148	-504	47(1)
H(19A)	475	585	-1454	47(1)
H(19B)	-123	356	-801	47(1)
H(20A)	1158	-56	-378	47(1)
H(20B)	776	-78	-1464	47(1)
H(21A)	2228	-267	-1833	47(1)
H(21B)	2672	-262	-762	47(1)
H(22A)	3806	-160	-1762	47(1)
H(22B)	3281	224	-2116	47(1)
H(23A)	4607	593	-1521	47(1)
H(23B)	5143	208	-1197	47(1)
H(24A)	5260	429	371	47(1)
H(24B)	5835	682	-256	47(1)
H(25A)	5162	2452	9894	47(1)
H(25B)	5683	2705	9217	47(1)
H(26A)	5703	3004	10675	47(1)
H(26B)	6262	2649	11164	47(1)
H(27A)	7439	3092	11731	47(1)
H(27B)	6944	3439	11147	47(1)
H(28A)	8228	3468	10298	47(1)
H(28B)	8524	3560	11375	47(1)
H(29A)	10059	3335	11490	47(1)
H(29B)	9873	3304	10383	47(1)
H(30A)	11091	2895	11060	47(1)
H(30B)	10352	2668	11562	47(1)
H(31A)	10682	2109	10687	47(1)
H(31B)	11384	2351	10171	47(1)
H(32A)	10368	2247	8742	47(1)
H(32B)	10842	1865	9181	47(1)
H(33A)	9558	1538	8316	47(1)
H(33B)	9007	1920	7984	47(1)
H(34A)	8003	1388	8101	47(1)
H(34B)	8343	1385	9197	47(1)
H(35A)	6815	1553	9539	47(1)
H(35B)	6484	1506	8449	47(1)

H(36A)	6003	2150	8377	47(1)
H(36B)	5449	1906	9042	47(1)
H(37A)	4037	-62	5360	47(1)
H(37B)	4196	-127	6458	47(1)
H(38A)	4799	500	6649	47(1)
H(38B)	5415	232	6094	47(1)
H(39A)	5962	758	5312	47(1)
H(39B)	5394	1036	5891	47(1)
H(40A)	5651	1314	4471	47(1)
H(40B)	5066	978	3926	47(1)
H(41A)	3924	1419	3217	47(1)
H(41B)	4554	1752	3723	47(1)
H(42A)	3281	1916	4536	47(1)
H(42B)	3054	1986	3441	47(1)
H(43A)	1451	1911	3488	47(1)
H(43B)	1628	1833	4582	47(1)
H(44A)	225	1546	3841	47(1)
H(44B)	830	1283	3262	47(1)
H(45A)	239	734	3989	47(1)
H(45B)	-329	1004	4586	47(1)
H(46A)	550	771	5958	47(1)
H(46B)	-15	437	5382	47(1)
H(47A)	1086	-15	6076	47(1)
H(47B)	1663	316	6652	47(1)
H(48A)	2599	-221	6414	47(1)
H(48B)	2398	-142	5323	47(1)

Table 19 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (pm^2x 10^{-1}) for **31**.*

STRUCTURE 3. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PERPHOSPHORANIDE 58 (*FIGURE 42*)		
Identification code	olegpc2	
Empirical formula	C7 H10 F9 N2 P	
Formula weight	324.14	
Temperature	173(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 980.40(10) pm	**α**= 90°.
	b = 1310.00(10) pm	**β**= 90°.
	c = 1773.2(2) pm	**γ**= 90°.
Volume	2.2774(4) nm^3	
Z	8	
Density (calculated)	1.891 Mg/m^3	
Absorption coefficient	0.351 mm^{-1}	
F(000)	1296	
Crystal size	0.70 x 0.55 x 0.40 mm^3	
Theta range for data collection	2.84 to 27.49°.	
Index ranges	-12≤h≤12, -17≤k≤5, -11≤l≤23	
Reflections collected	3400	
Independent reflections	2614 [R(int) = 0.0321]	
Completeness to theta = 27.49°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2614 / 0 / 177	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1115	
R indices (all data)	R1 = 0.0479, wR2 = 0.1163	
Extinction coefficient	0.0130(11)	
Largest diff. peak and hole	0.578 and -0.389 $e.Å^{-3}$	

Table 20

	x	y	z	U(eq)
P(1)	1765(1)	702(1)	3778(1)	19(1)
C(1)	-191(2)	776(1)	3883(1)	19(1)
C(2)	-732(2)	-1035(2)	3475(1)	36(1)
C(3)	-2449(2)	246(2)	3893(1)	28(1)
C(4)	-2375(2)	1338(2)	4170(1)	28(1)
C(5)	-484(2)	2578(2)	4386(2)	45(1)
C(6)	1863(2)	1906(2)	3156(1)	28(1)
C(7)	3720(2)	543(2)	3768(1)	31(1)
N(1)	-1017(2)	14(1)	3706(1)	24(1)
N(2)	-895(2)	1550(1)	4171(1)	25(1)
F(1)	1673(1)	-346(1)	4259(1)	30(1)
F(2)	1605(1)	74(1)	2999(1)	25(1)
F(3)	1947(1)	1357(1)	4553(1)	29(1)
F(4)	2773(1)	1784(1)	2588(1)	40(1)
F(5)	2223(1)	2772(1)	3505(1)	44(1)
F(6)	659(1)	2092(1)	2813(1)	39(1)
F(7)	4381(1)	1441(1)	3762(1)	45(1)
F(8)	4205(1)	8(1)	3184(1)	45(1)
F(9)	4176(1)	63(1)	4389(1)	52(1)

Table 21 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for* ***58.*** *U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z #2 x+1,y,z			
P(1)-F(2)	161.62(10)	C(7)-F(8)	133.8(2)
P(1)-F(1)	161.76(12)	C(7)-F(7)	134.4(3)
P(1)-F(3)	162.93(11)	C(7)-F(9)	134.5(2)
P(1)-C(6)	192.7(2)	F(2)-P(1)-F(1)	90.75(6)
P(1)-C(7)	192.8(2)	F(2)-P(1)-F(3)	178.58(6)
P(1)-C(1)	192.85(17)	F(1)-P(1)-F(3)	90.50(6)
C(1)-N(1)	132.3(2)	F(2)-P(1)-C(6)	86.10(7)

C(1)-N(2)	132.9(2)	F(1)-P(1)-C(6)	176.85(8)
C(2)-N(1)	146.0(2)	F(3)-P(1)-C(6)	92.66(8)
C(3)-N(1)	147.4(2)	F(2)-P(1)-C(7)	91.89(7)
C(3)-C(4)	151.4(3)	F(1)-P(1)-C(7)	88.22(8)
C(4)-N(2)	147.7(2)	F(3)-P(1)-C(7)	87.47(7)
C(5)-N(2)	145.6(3)	C(6)-P(1)-C(7)	91.91(9)
C(6)-F(5)	133.9(2)	F(2)-P(1)-C(1)	90.67(6)
C(6)-F(6)	135.0(2)	F(3)-P(1)-C(1)	90.09(6)
C(6)-F(4)	135.5(2)	C(6)-P(1)-C(1)	93.64(7)
F(1)-P(1)-C(1)	86.37(6)	C(7)-P(1)-C(1)	174.04(8)
N(1)-C(1)-N(2)	110.38(15)	F(4)-C(6)-P(1)	111.25(13)
N(1)-C(1)-P(1)	123.22(13)	F(8)-C(7)-F(7)	106.33(16)
N(2)-C(1)-P(1)	126.31(13)	F(8)-C(7)-F(9)	105.77(17)
N(1)-C(3)-C(4)	102.87(14)	F(7)-C(7)-F(9)	104.77(17)
N(2)-C(4)-C(3)	102.98(14)	F(8)-C(7)-P(1)	114.67(13)
F(5)-C(6)-F(6)	106.55(16)	F(7)-C(7)-P(1)	112.64(14)
F(5)-C(6)-F(4)	105.66(15)	F(9)-C(7)-P(1)	111.92(13)
F(6)-C(6)-F(4)	105.18(15)	C(1)-N(1)-C(2)	131.20(16)
F(5)-C(6)-P(1)	116.23(14)	C(1)-N(1)-C(3)	111.96(15)
F(6)-C(6)-P(1)	111.22(12)	C(2)-N(1)-C(3)	116.07(15)
C(1)-N(2)-C(5)	131.48(16)	C(1)-N(2)-C(4)	111.52(15)
C(5)-N(2)-C(4)	116.46(15)		

Table 22 *Bond lengths [pm] and angles [°] for olegpc2.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	16(1)	26(1)	16(1)	-1(1)	-1(1)	1(1)
C(1)	19(1)	23(1)	16(1)	1(1)	-1(1)	1(1)
C(2)	37(1)	23(1)	47(1)	-5(1)	4(1)	-6(1)
C(3)	15(1)	42(1)	26(1)	3(1)	1(1)	-3(1)
C(4)	17(1)	40(1)	28(1)	4(1)	3(1)	5(1)
C(5)	34(1)	35(1)	65(2)	-23(1)	2(1)	6(1)
C(6)	22(1)	32(1)	30(1)	5(1)	-2(1)	-6(1)
C(7)	20(1)	48(1)	23(1)	-3(1)	-1(1)	4(1)
N(1)	18(1)	27(1)	28(1)	0(1)	1(1)	-3(1)
N(2)	18(1)	29(1)	29(1)	-6(1)	1(1)	3(1)
F(1)	26(1)	34(1)	29(1)	9(1)	1(1)	8(1)
F(2)	23(1)	33(1)	21(1)	-8(1)	1(1)	-1(1)
F(3)	21(1)	45(1)	21(1)	-11(1)	-3(1)	1(1)
F(4)	33(1)	55(1)	31(1)	11(1)	6(1)	-10(1)
F(5)	44(1)	30(1)	60(1)	-3(1)	0(1)	-12(1)
F(6)	30(1)	44(1)	44(1)	20(1)	-9(1)	-3(1)
F(7)	21(1)	62(1)	52(1)	-9(1)	-3(1)	-10(1)
F(8)	22(1)	72(1)	41(1)	-17(1)	6(1)	10(1)
F(9)	24(1)	95(1)	37(1)	16(1)	-6(1)	16(1)

Table 23 *Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for olegpc2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$*

	x	y	z	U(eq)
H(2A)	217	-1087	3307	70(4)
H(2B)	-1342	-1226	3061	70(4)
H(2C)	-880	-1495	3903	70(4)
H(3A)	-2795	-215	4291	34(3)
H(3B)	-3041	189	3443	34(3)
H(4A)	-2866	1806	3826	34(3)
H(4B)	-2763	1402	4684	34(3)
H(5A)	503	2594	4470	70(4)
H(5B)	-957	2775	4851	70(4)
H(5C)	-723	3056	3982	70(4)

Table 24 *Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($pm^2 x\ 10^{-1}$) for olegpc2.*

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I. Appendix

I1. Posters and oral presentations

1. New trifluoromethyl phosphoranides

   O. A. Shyshkov, A. A. Kolomeitsev, B. Hoge and G.-V. Röschenthaler, 10. Deutscher Fluortag, Schmitten, Germany, **2002**

2. New trifluoromethyl phosphoranides

   O. A. Shyshkov, A. A. Kolomeitsev, B. Hoge and G.-V. Röschenthaler, 16th Winter Fluorine Conference, St. Petersburg Beach, USA, January 12-17, **2003**

3. Unusual transformations of perfluoroalkyl phosphorus(III) derivatives (Poster)

   O. A. Shyshkov, A. A. Kolomeitsev, B. Hoge and G.-V. Röschenthaler, Third RSC Fluorine Subject Group Postgraduate Meeting, St. Andrews, Scotland. September 3-15, **2003**

4. Trifluoromethyl phosphoranides and perphosphoranides

   O. A. Shyshkov, A. A. Kolomeitsev, I. Koppel, B. Hoge, E. Lork, N. Kalinovich and G.-V. Röschenthaler, 11. Deutscher Fluortag, Schmitten, Germany, **2004**

5. Trifluoromethyl phosphoranides and perphosphoranides

   A. A. Kolomeitsev, O. A. Shyshkov, I. Koppel, B. Hoge, E. Lork, N. Kalinovich and G.-V. Röschenthaler, 14th European Symposium on Fluorine Chemistry, Poznan, Poland, July 2-16, **2004**

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I3. Curriculum vitae

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Education:

1983-1993	12th Secondary school of Bila Tserkva
1993-1999	Student at the National Technical University of Ukraine (*Former Kiev Polytechnic Institute*). Specialty: Chemical Technology of Basic Organic Synthesis and Petrochemistry. 1998-Bachelor Degree, 1999-Certificate of Engineer.
1998-1999	Diploma work at the Institute of Organic Chemistry, Ukrainian Academy of Science, Kiev, Ukraine. Theme: "Synthesis and characterization of Diethyl-1,1-difluoro-3-trimethylylsilyl-propynephosphonate – new synthon for synthesis of biologically active compounds " (*Scientific advisers: Dr. A. A. Kolomeitsev, Prof. Dr. L. M. Yagupolskii*).
1999-2000	Practice at "Biocide" Inc, Kiev, Ukraine. Position: Engineer.
2000-2005	Ph. D. student at the University of Bremen. Scientific advisers: Prof. Dr. G.-V. Röschenthaler, Dr. A. A. Kolomeitsev.
2003-2005	Scientific cooperation with "MCS Microcarrier Systems" GmbH, Germany on the theme: "Lipid derivated Bisphosphonic Acids" under the supervision of Prof. Dr. G.-V. Röschenthaler. Two patents are issued (WO 2005/070952, DE 102004032781).

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