Reactions of Fluorophosphoranes with *N,N,N'*-Trimethyl-*N'*-(trimethylsilyl)ethylenediamine – Intramolecularly Stabilized Azonium Hexafluorophosphates by Fluoride Abstraction from *N,N,N'*-Trimethylethylenediamine-Substituted Fluorophosphoranes with Phosphorus Pentafluoride[1)]

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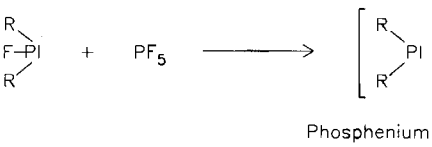
The reaction of the tetrafluorophosphoranes RPF_4 [R = CH_3, C_6H_5, C_6F_5, $(CH_3)_3SiCH_2$, and 2,5-$(CH_3)_2C_6H_3$] with *N,N,N'*-trimethyl-*N'*-(trimethylsilyl))ethylenediamine (**1**) yields the corresponding trifluorophosphoranes **2**–**6** by cleavage of the Si–N bond and elimination of $(CH_3)_3SiF$. In an analogous reaction the difluorophosphoranes $R^1R^2PF_2N(CH_3)CH_2CH_2N(CH_3)_2$ (R^1 = R^2 = C_6H_5, **7**: R^1 = C_6H_5, R^2 = C_4H_4N, **8**) are formed. Some of these *N,N,N'*-trimethylethylenediamine-substituted di- and trifluorophosphoranes react with PF_5 as a Lewis acid to form the corresponding azonium hexafluorophosphates **9**–**12** as a result of fluoride abstraction and intramolecular $(CH_3)_2N\rightarrow P$ donor-acceptor interaction. Compound **13** shows dynamic behaviour in solution. An exchange process is observed for the axial and equatorial fluorine atoms by ^{19}F- and ^{31}P-NMR spectroscopy. An X-ray structure analysis of the compounds **10**–**12** reveals the expected trigonal-bipyramidal geometry at phosphorus. The ethylenediamine ligand is found to form a chelate ring, whereby one axial and one equatorial site are bridged. The coordinative P–N bonds are very long (up to 207 pm).

The formation of trifluorophosphoranes (and fluorotrimethylsilane) in the reaction of alkyl- and aryltetrafluorophosphoranes with trimethylsilylamines is well known[2–9)]. Because of the trigonal-bipyramidal geometry around the five-coordinate phosphorus atom in the tetrafluorophosphoranes, substitution may occur at either an axial or an equatorial site. In the reaction of tetrafluorophosphoranes RPF_4 (R = alkyl or aryl) with silylamines an equatorial fluorine atom is generally substituted in preference to an axial fluorine atom. Axial positions are preferably occupied by the more electronegative substituents (i.e. fluorine)[2,10,11)]. This principle has been confirmed in the synthesis of compounds **2**–**6**.

$$RPF_4 + Me_3SiNR_2 \xrightarrow[-\,Me_3SiF]{} RPF_3NR_2 \qquad (1)$$

The potential of phosphorus pentafluoride as a Lewis acid acceptor is well established[2)]. Specifically, the reaction of phosphorus pentafluoride with certain substituted fluorophosphanes and -phosphoranes, forming the corresponding alkylphosphenium or alkylphosphonium cations and hexafluorophosphate, has repeatedly been described[12–15)].

Phosphorus pentafluoride exhibits the highest affinity for fluoride ion[16)] of all phosphorus compounds. In the present case it was of particular interest to establish whether ring closure (through interaction of the phosphorane phosphorus atom with the nitrogen atom of the Me_2N group) can be effected, as shown in eq. (3), by the reaction of compounds **2**–**6** with PF_5 as fluoride abstractor.



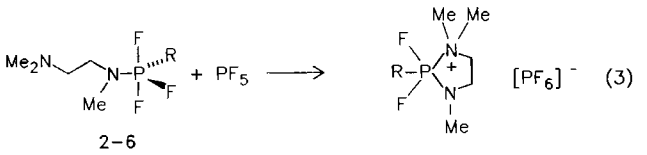
Phosphenium cation

(2)

(n = 1-3) Phosphonium cation

R = alkyl, aryl, dialkylamino, diarylamino

This type of intramolecular donor-acceptor interaction has previously been described in a number of cases involving phosphorus(III)[17–22)] and phosphorus(V)[23–27)]. Here we wished to determine if (as in the case of four-membered PNPN ring systems involving λ^5P) the nitrogen atoms preferably occupy one axial and one equatorial position at λ^5P[28,29)]. This would require abstraction of an axial fluorine atom, which may be demonstrated by ^{19}F-NMR spectroscopy. It was of interest, furthermore, to find out (a), whether an intramolecular donor-acceptor interaction between the nitrogen atom of the Me_2N-group and λ^5P is established spontaneously during the reaction of tetrafluorophosphoranes with **1** and (b), whether there is an influence of the group R in **2**–**6**. Finally, we have investigated whether, as



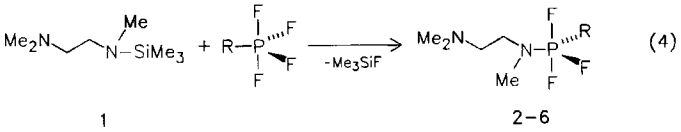
2–6

a result of the abstraction of fluoride from **2**–**6** by PF_5, compounds are formed that can be characterized unambiguously by room temperature NMR spectra; it might alternatively be the case[30] that interactions between cation and anion give rise to dynamic behaviour, as a result of which unambiguous NMR spectra are observed only at reduced temperature.

Discussion

1. Reaction of *N,N,N'*-Trimethyl-*N'*-(trimethylsilyl)-ethylenediamine with Organotetrafluorophosphoranes

In accord with the criteria set out in the foregoing, the Si–N cleavage reactions of *N,N,N'*-trimethyl-*N'*-(trimethylsilyl)ethylenediamine[31] (**1**) with tetrafluorophosphoranes RPF_4 eliminated fluorotrimethylsilane and produced the corresponding trifluorophosphoranes **2**–**6** in good yield (eq. (4)).



1 2–6

	2	3	4	5	6
R	CH_3	$(CH_3)_3SiCH_2$	C_6H_5	C_6F_5	2,5-$(CH_3)_2C_6H_3$

The reaction was followed by ^{1}H-NMR spectroscopy, confirming the formation of fluorotrimethylsilane. The products **2**–**6** are colourless, distillable liquids that are rapidly decomposed by moisture with the formation of brown oils. Compound **4** has been prepared previously[32], but in view of the absence of an elemental analysis and ^{13}C-NMR data the synthesis has been repeated and is included here with a full characterization of the product.

NMR Spectra of 2–6

In the ^{31}P-NMR spectra of **2**–**6** a doublet of triplets is observed. This is due to unequal coupling of the central phosphorus atom to one equatorial and two axial fluorine atoms. In accord with expectation, the ^{19}F-NMR spectra exhibit a doublet of doublets and a doublet of triplets. In the ^{19}F-NMR spectra $\delta(F^a)$ values are consistently more positive then $\delta(F^e)$ values[33] (see Table 1).

The ^{31}P-NMR spectrum of **5** is more complicated. The basic doublet of triplets shows fine structure arising from the coupling between ^{31}P and fluorine atoms of the pentafluorophenyl ring. This leads to a broadening of the ^{31}P signals. The ^{31}P-^{19}F(arom.) coupling constants cannot be accurately determined.

The ^{19}F-NMR spectrum of **5** displays a distinct splitting pattern. A doublet of doublets of triplets at $\delta = -28.7$ arises from the coupling of the axial fluorine atoms to phosphorus, to the single equatorial fluorine atom, and to the *ortho*-fluorine atoms of the C_6F_5 substituent. The appearance of the axial ^{19}F resonance of **5** as a doublet with $J = 817$ Hz originates from the coupling between F^a and P. Further fine structure is caused by the coupling F^aF^e giving rise to a doublet with $^2J(F^aF^e) = 66$ Hz. Finally, the FF coupling $^4J(F^aF^{arom.})$ is observed between the two axial fluorine atoms and the *ortho*-fluorine atoms of the C_6F_5 group (13 Hz). An analogous splitting pattern is observed for the resonance of the equatorial fluorine atom in **5**. The assignment of ^{19}F resonances to the aromatic C_6F_5 ring is based on the data for the compound $C_6F_5PF_4$, which we have described previously[34].

Table 1. ^{31}P- and ^{19}F-NMR data of the trifluorophosphoranes $Me_2NCH_2CH_2N(Me)PF_3(R)$ (**2**–**6**)

	^{31}P			^{19}F				
R	δ(P)	$^1J(PF_{ax})$	$^1J(PF_{eq})$	$\delta(F_{ax})$	$\delta(F_{eq})$	$^1J(PF_{ax})$	$^1J(PF_{eq})$	$^2J(FF)$
Me **2**	*-35.61*	*809*	*970*	*- 29.7*	*- 68.1*	*809*	*970*	*54*
Me_3SiCH_2 **3**	*-33.0*	*805*	*958*	*- 28.5*	*-67.0*	*805*	*958*	*51*
C_6H_5 **4**	*-52.0*	*819*	*966*	*-42.3*	*-52.0*	*819*	*966*	*56*
C_6F_5 **5**	*-58.0*	*817*	*962*	*- 28.7*	*-59.5*	*817*	*962*	*66*
2,5-$(CH_3)_2$ $-C_6H_3$ **6**	*-44.5*	*823*	*981*	*-33.4* -36.2**	*-66.0**	*817* 816**	*981**	*59*

*) Recorded at −30 °C.

Table 2. ^{1}H-NMR data of the trifluorophosphoranes **2**–**6**

No.	$(CH_3)_2N$ δ	$(CH_3)_2NCH_2$ δ	$N(CH_3)P$ δ	$CH_2N(CH_3)P$ δ	R δ
2	2.18 (s)	2.36 (pt), N(PH) = 15	2.76 (dq), $^3J(PH)$ = 10, $^4J(FH)$ = 2.7	3.10 (m)	1.59 (ddt), $^2J(PH)$=20.1, $^3J(F_{eq}H)$=1.7, $^3J(F_{ax}H)$=12.4.
3	2.17 (s)	2.37 (pt), N(PH) = 15	2.74 (dq), $^3J(PH)$ = 10, $^4J(FH)$ = 3.0	3.07 (m)	0.09 (s), $(CH_3)_3Si$; 1.17(m), $SiCH_2$
4	2.24 (s)	2.49 (pt), N(PH) = 15	2.94 (dq), $^3J(PH)$ = 11, $^4J(FH)$ = 2.7	3.27 (m)	7.45 (m), H-aromatic, 7.74 (m), H-aromatic.
5	2.19 (s)	2.45 (pt), N(PH) = 15	2.91 (dq), $^3J(PH)$ = 12, $^4J(FH)$ = 3.0	3.24 (m)	----------
6	2.27 (s)	2.56 (pt), N(PH) = 15	3.00 (dq), $^3J(PH)$ = 11, $^4J(FH)$ = 3.0	3.30 (br)	2.34 (s), $C_6H_3CH_3$; 2.45 (s,br), $C_6H_3CH_3$; 7.12 (m), H-aromatic.

The resonances for the axial fluorine atoms in **6** do not exhibit sharp lines at room temperature. Two broad resonances are recorded and it is impossible to determine accurately either the δ(F) values or the multiplicity. On the other hand, the signals for F^e are sharp, appearing as a doublet of triplets with the expected δ(F) value. Since the broadening of the resonance for F^a suggests that a dynamic process occurs in solution at room temperature, a ^{19}F-NMR spectrum of **6** was recorded at −30°C. Two doublets of doublets are now observed for F^a, caused by the nonequivalence of the two axial fluorine atoms F^a and F'^a. A similar phenomenon has been described by Cowley[35] as a result of the different chemical environment of the axial fluorine atoms in $C_6H_5PF_3N(H)CH(Me)(C_6H_5)$. The nonequivalence of the axial fluorine atoms in **6** is believed to be caused by the difference in the chemical environment that is a consequence of the slower P−C rotation of the dimethyl-substituted phenyl ring on cooling. On the other hand, it is possible in the case of slow ligand exchange (relative to the NMR time scale) that the prochirality of phosphorus, as described in the literature[36], affects the nonequivalence of the axially substituted fluorine atoms. The coupling constants $^2J(F^aF^e)$ and $^2J(F'^aF^e)$ are identical.

The ^{1}H NMR spectra of **2**−**6** are as expected (see Table 2). The resonance for the $(CH_3)_2N$ protons does not indicate intramolecular donor-acceptor interactions between the nitrogen atom of the $(CH_3)_2N$ group and phosphorus; there is no splitting of the $(CH_3)_2N$ resonance by coupling to either ^{31}P or ^{19}F.

In contrast, the ^{1}H resonance of the $N(CH_3)P$ grouping is split into a doublet of quartets, resulting from ^3J(PH) and ^4J(FH). Thus, the nonequivalence of the three fluorine atoms, as seen in the ^{19}F- and ^{31}P-NMR spectra, is not reflected in the ^{1}H-NMR spectra.

From the FH coupling over four bonds in **2**−**6**, it is not possible to distinguish F^a and F^e bound to phosphorus by ^{1}H-NMR spectroscopy. The ^{1}H resonance of the CH_3 group in **2**, directly bound to ^{31}P, is split into a doublet of doublets of triplets. F^a and F^e are no longer equivalent. The value of ^2J(PH) of ca. 20 Hz is of the expected order of magnitude, as is $^3J(F^aH)$ (ca. 12 Hz). The value of $^3J(F^eH)$ (ca. 2 Hz), on the other hand, is small.

The proton resonances of the aromatic groups in **4** (R = C_6H_5) and in **6** [R = 2,5-$(CH_3)_2C_6H_3$] are split into multiplets and, because of ring-current effects[37], experience a low-field shift, relative to the aliphatic protons, in accord with expectation. The ^{1}H-NMR signals of *meta*- and *para*-protons in **4** (R = C_6H_5) appear at somewhat higher field than those for the *ortho*-protons.

The ^{1}H-NMR signal of the ring protons in **6** is slightly shifted to higher field, compared to the resonances of the phenyl protons in **4**. The influence of the two CH_3 groups in the substituted phenyl group is thought to reduce the ring current effect[37], as in a symmetric aromatic system, and thus causes a shift of δ(H) to smaller δ values.

The protons of the *ortho*-CH_3 group of the substituted phenyl group in **6** absorb at lower field than those of the *meta*-CH_3 group, in accord with expectation. This is presumably due to the stronger deshielding of the protons arising from the proximity of the electronegative fluorine atoms. The broadening of the ^{1}H-NMR signal of the *ortho*-CH_3 group presumably results from the interaction with ^{31}P and/or ^{19}F in **6**.

Table 3. ^{13}C-NMR data of the trifluorophosphoranes **2**−**6**

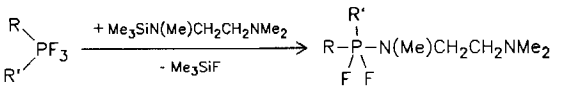
No.	$(\underline{C}H_3)_2N$ δ	$(CH_3)_2N\underline{C}H_2$ δ	$N(\underline{C}H_3)P$ δ	$\underline{C}H_2N(CH_3)P$ δ	R δ
2	45.7 (s)	58.6 (s)	39.0 (m)	51.4 (m)	17.29 (dd), ^1J(PC) = 203, ^2J(FC) = 12.
3	45.7 (s)	58.7 (s)	38.8 (m)	51.5 (m)	−0.55 (d), $\underline{C}H_3$, ^3J(PC) = 5; 21.5 (ddt), $\underline{C}H_2$, ^1J(PC) = 186, $^2J(F_{eq}C)$ = 41, $^2J(F_{ax}C)$ = 13.
4	45.8 (s)	58.7 (s)	39.7 (m)	51.9 (m)	128.1 (d, m-C, ^3J(PC) = 20); 131.5 (d, p-C, ^4J(PC) = 4); 132.2 (dt, o-C, ^2J(PC) = 12, ^3J(FC) = 8)
5	45.7 (s)	58.2 (s)	39.2 (m)	51.6 (m)	134.4 - 147.7 (m)
6	45.7 (s)	58.7 (s)	39.4 (m)	51.6 (m)	20.2 (d, o-$\underline{C}H_3$, ^3J(PC) = 6); 20.8 (s, m-$\underline{C}H_3$); 128.1 (d, m-$\underline{C}$); 131.5 (d, p-$\underline{C}$); 132.2 (dt, o-$\underline{C}$).

The ^{13}C-NMR parameters of **2**−**6** do not vary significantly with the substituent R. The values of both δ(C) and ^nJ(PC) are therefore observed within a narrow range (see Table 3).

2. Reaction of 1 with Trifluorodiphenylphosphorane and with Trifluorophenyl-1-pyrrolylphosphorane

Trifluorophosphoranes of the general type $R^1R^2PF_3$ have been known for some time[2,4,10,38]. The first aryl(dialkylamino)trifluorophosphoranes, $ArPF_3NR_2$, were synthesized by Ivanova and Kirsanov[39] by the reaction of arylchlorotrifluorophosphoranes, themselves not readily accessible, with secondary amines. An improved synthesis of trifluorophosphoranes of type $RPF_3NR'_2$ (R, R' = hydrocarbon groups) involves the reaction of tetrafluorophosphoranes with secondary amines or (diorganoamino)trimethylsilanes[7,40,41].

We have synthesized the difluorophosphoranes **7** and **8** by the reaction of the trifluorophosphoranes $(C_6H_5)_2PF_3$ and $C_6H_5(C_4H_4N)PF_3$ with **1**. This reaction proceeds with elim-



(5)

7: R = R' = Ph
8: R = Ph, R' =

ination of fluorotrimethylsilane at room temperature according to eq. (5).

Both **7** and **8** can readily be purified by distillation and are characterized by elemental analysis and by NMR spectroscopy (Tables 4 and 5).

Table 4. ^{31}P- and ^{19}F-NMR data of the difluorophosphoranes $RR'PF_2N(Me)CH_2CH_2NMe_2$ (**7**, **8**)

No.	^{31}P		^{19}F	
R, R'	δ(P)	^1J(PF)	δ(F)	^1J(PF)
R = R' = Ph **7**	-51.93	706	-37.5	706
R = Ph, R' =  **8**	-66.36	773	-40.2	773

Table 5. ^1H- and ^{13}C-NMR data of the difluorophosphoranes **7** and **8**. The ^{13}C-NMR values are printed in italics

	$(\underline{CH_3})_2N$ δ	$(CH_3)_2N\underline{CH_2}$ δ	$N(\underline{CH_3})P$ δ	$\underline{CH_2}N(CH_3)P$ δ	R δ
7	2.27 (s)	2.56 (pt), N= 15 Hz	3.02 (dt, ^3J(PH) = 10, ^4J(FH) = 3)	3.36 (m)	7.42 - 7.82 (m)
	45.68 (s)	*58.96 (s)*	*38.72 (m)*	*50.87 (m)*	*127.8 - 139.0 (m)*
8	2.26 (s)	2.49 (pt), N= 15 Hz	2.98 (dt, ^3J(PH) = 11, ^4J(FH) = 3)	3.28 (m)	6.33 - 7.71 (m)
	45.79 (s)	*58.78 (s)*	*39.25 (m)*	*51.56 (m)*	*111.7 - 140.5 (m)*

As expected for difluorophosphoranes, the δ(P) resonances of **7** and **8** are split into a triplet by coupling with the two axial fluorine atoms at the trigonal-bipyramidal phosphorus. A doublet is seen in the ^{19}F-NMR spectrum for the two (axial) fluorine atoms, which couple equally with phosphorus. The ^1J(PF) values, observed in the ^{19}F- and ^{31}P-NMR spectra, are in excellent agreement.

The δ(H) values in the ^1H-NMR spectra of **7** and **8** are similar to those of **2**–**6**. They differ in their multiplicity, and the splitting pattern becomes simpler in the absence of a (nonequivalent) equatorial fluorine substituent. For the protons of the $(CH_3)_2N$ group only a singlet appears. No coupling ^3J(PH), which could result from intramolecular donor-acceptor interaction between the nitrogen of the $(CH_3)_2N$ group and phosphorus, is observed for **7** and **8**.

The splitting pattern of the signals of the aromatic protons in the phenyl ring of **7** and **8** is complicated, and only an unresolved multiplet appears. In the case of **8**, besides the multiplet at δ = 7.38 (from the ring protons), two further groups of signals are assigned to the hydrogen atoms of the pyrrolyl system. In accord with ref.[42] the multiplet at δ = 6.33 is assigned to the CH protons of the pyrrolyl ring distant from nitrogen. We suggest that the multiplet at δ = 7.71 arises from the pyrrolyl protons that are adjacent to nitrogen, with fine structure by coupling with ^{19}F and ^{31}P.

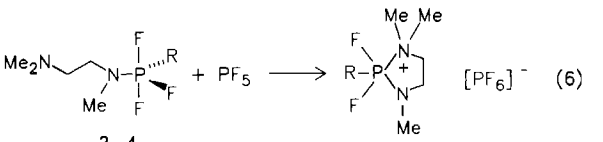
The ^{13}C-NMR signals in the aliphatic region of **7** and **8** are as expected and may be compared to those of **2**–**6**. In **7** the individual ^{13}C resonances of the phenyl group may be unambiguously assigned on the basis of their δ(C) values and multiplicity.

The ^{13}C-NMR signals of the two aromatic groups in **8** may also be assigned unambiguously. The doublet at δ = 111.48 [^3J(PC) = 12 Hz], because of its high-field shift and coupling constant, is assigned to the carbon atoms of the pyrrolyl group remote from nitrogen. The resonance with δ(C) = 126.2 is split into a doublet of triplets with ^2J(PC) = 8 and ^3J(FC) = 3 Hz; it is assigned to the C atoms next to the nitrogen of the pyrrolyl group.

All the ^{13}C-NMR signals of the phenyl ring exhibit the same splitting pattern and similar δ(C) values as those for **4**.

3. Reaction of {[2-(Dimethylamino)ethyl]methylamino}-alkyl(aryl)trifluorophosphoranes 2–4 with Phosphorus Pentafluoride; Synthesis of the Hexafluorophosphate Salts 9–11

It is known that phosphorus pentafluoride acts as a fluoride acceptor towards e.g. bis(dialkylamino)fluorophosphanes, $(R_2N)_2PF$, with formation of the bis(dialkylamino)-phosphenium cations, $[(R_2N)_2P]^+$, and $[PF_6]^-$ [12–15]. Also, some fluorophosphoranes are known to react with PF_5 with abstraction of F^- and formation of fluorophosphonium cations as $[PF_6]^-$ salts[13,14]. In the present investigation it is assumed that in the reaction of the trifluorophosphoranes **2**–**4** with PF_5 a fluorophosphonium cation is produced, which stabilizes itself by immediate ring closure as a result of intramolecular donor-acceptor interaction between the nitrogen atom of the $(CH_3)_2N$ group and phosphorus (eq. (6)).



2–4

9: R = CH_3
10: R = $(CH_3)_3SiCH_2$
11: R = C_6H_5

(6)

In the reaction of the trifluorophosphoranes **2**–**4** with PF_5 well-defined salt-like solids are precipitated during the reaction in nonpolar solvents, e.g. diethyl ether or petroleum ether, according to eq. (6). The salts **9**–**11** are obtained in good yields and mostly in analytical purity. They can be recrystallized if necessary.

NMR Spectra of 9–11

The observed δ(P) values are indicative of difluorophosphoranes (cf. Table 6).

Table 6. ^{31}P- and ^{19}F-NMR data of the hexafluorophosphate salts **9–11**

	^{31}P			^{19}F				
	δ(P)	$^1J(PF_{ax})$	$^1J(PF_{eq})$	δ(F_{ax})	δ(F_{eq})	$^1J(PF_{ax})$	$^1J(PF_{eq})$	$^2J(FF)$
9	-17.0	836	1044	-36.9	-82.9	836	1044	47
10	-13.33	850	1042	-34.0	-82.0	850	1042	45
11	-26.85	833	1059	-37.4	-86.5	834	1059	56

The ^{31}P-NMR signals of the methyl derivative **9** and of the phenyl derivative **11** are split into a doublet of doublets by coupling between ^{31}P and the axial and equatorial fluorine atoms. In the ^{31}P-NMR spectrum of the (trimethylsilyl)methyl-substituted compound **10** a pseudotriplet is observed at room temperature, which suggests that a dynamic process occurs in solution. At −30 °C the expected splitting pattern of the ^{31}P resonance, a doublet of doublets resulting from coupling of the ^{31}P nucleus to one axial and one equatorial fluorine atom, is seen. An intramolecular interaction of the trimethylsilyl group with one of the fluorine atoms is also observed by ^1H-NMR spectroscopy, which corroborates the effect observed in the ^{31}P-NMR spectra. Only at −30 °C is this interaction slowed down, and the ^{31}P-NMR spectrum exhibits the expected doublet of doublets.

The ^{19}F-NMR spectra of **9–11** show, as expected, one set of resonances at lower field for F^a and another set at higher field for F^e (cf. Table 6). The ^{19}F-NMR resonance lines for the cation of **10** are somewhat broadened, which may be caused by the intramolecular interaction discussed above for the ^{31}P- and ^1H-NMR spectrum.

The ^1H-NMR spectrum of **9** at room temperature indicates dynamic behaviour of the cation, and a pseudotriplet is observed for the protons of the methyl group directly bound to phosphorus. The coupling constants $^2J(PH)$ and $^3J(FH)$ cannot be determined from this resonance. Only a broad signal is recorded for the methyl protons of the $(CH_3)_2N$ group coordinatively bound to phosphorus. The coupling constant to ^{31}P and ^{19}F cannot be determined. Only the resonance for the protons of the $N(CH_3)P$ grouping, covalently bound to phosphorus, displays the expected splitting pattern of a doublet of triplets. It should be noted that F^a and F^e in the ^1H-NMR spectrum at room temperature appear to be magnetically equivalent, as only a doublet of triplets, and not a doublet of doublets of doublets, appears. The relevant NMR data are listed in Table 7.

Table 7. ^1H-NMR data of the hexafluorophosphate salts **9–11**

No.	$(CH_3)_2N$ δ	$(CH_3)_2NCH_2$ δ	$N(CH_3)P$ δ	$CH_2N(CH_3)P$ δ	R δ
9*	2.68 (dd, $^3J(PH)=5.8$, $^4J(FH)=1.9$) 2.74 (pt, $N(PH)=6.3$)	3.24 (m)	2.83 (dt, $^3J(PH)=12$, $^4J(FH)=3$)	3.24 (m)	2.05 (ddd, $^2J(PH)=17.0$, $^3J(F_{ax}H)=13.6$, $^3J(F_{eq}H)=3.5$)
10	2.71 (dt, $^3J(PH)=4.5$, $^4J(FH)=1.5$)	2.37 (m)	2.88 (dt, $^3J(PH)=11.8$, $^4J(FH)=3.2$)	3.33 (m)	0.22 (s, $(CH_3)_3Si$); 1.77 (dt, $(CH_3)_3SiCH_2$, $^2J(PH)=20.4$, $^3J(FH)=13$)
11	2.09 (d,br, $N(PH)=6$), 2.81 (t, br, $N(PH)=6$)	3.10 – 3.20 (m) obscured by $(CH_3)_2N$- resonance	3.11 (dt, $^3J(PH)=12$, $^4J(FH)=3.3$)	3.56 (m)	7.61 – 7.80 (m)

*) Recorded at −18 °C.

The broad resonance for the protons of the $(CH_3)_2N$ group coordinatively bound to phosphorus is split at −18 °C into a doublet of doublets and a pseudotriplet. The magnetic equivalence of the resonance of the $(CH_3)_2N$ protons noted at room temperature (broad singlet) is thus no longer observed at reduced temperature. Instead, two different resonances appear for the protons of the $(CH_3)_2N$ group. Their different chemical environment leads to a different splitting pattern of the NMR signals into a doublet of doublets and

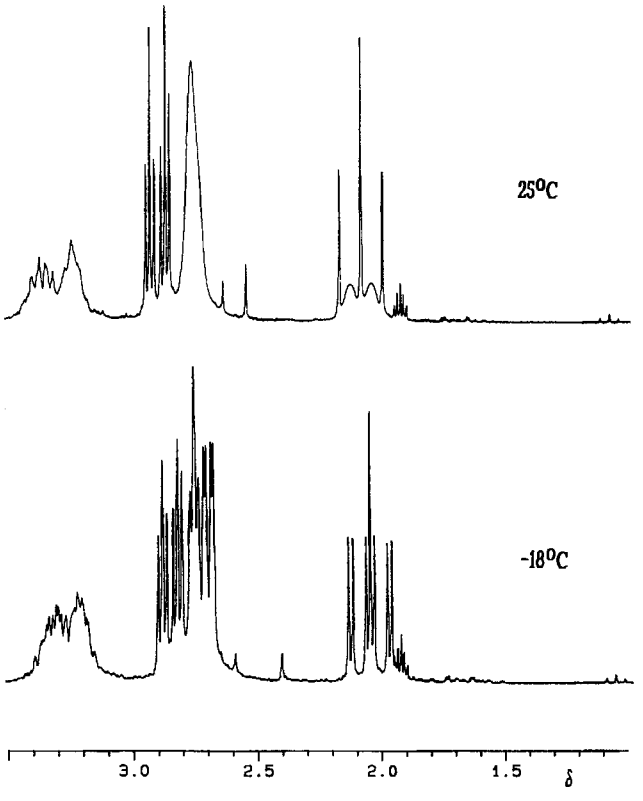


Figure 1. Room- and low-temperature ^1H-NMR spectra of **9**

a pseudotriplet, caused by coupling of the protons of each methyl group of the $(CH_3)_2N$ substituent coordinatively bound to phosphorus, with ^{31}P and ^{19}F. In the spectrum at $-18°C$ the resonance for the protons of the covalently bound $N(CH_3)P$ group appears as an unchanged doublet of triplets, with the same coupling constants as in the room temperature spectrum.

The room-temperature ^1H-NMR spectrum of **10** is unremarkable (cf. Table 7), but its dynamic behaviour in solution is noteworthy. In all room-temperature ^1H-NMR spectra a doublet at $\delta = 0.16$ is observed. This suggests an interaction between one of the cationic phosphorus-bound fluorine atoms and the protons of the $(CH_3)_3Si$ group. The observed coupling $^3J(FH)$ (4.1 Hz) is too small for $(CH_3)_3SiF$, which might conceivably arise from an intramolecular interaction between the protons of the $(CH_3)_3Si$ group and a P(F) fluorine atom; furthermore, no resonance due to $(CH_3)_3SiF$ is observed in the ^{19}F-NMR spectrum.

The ^1H-NMR resonance of the $(CH_3)_2N$ group in **11** is split into two groups of signals. This may be attributed to an anisotropy effect[43–46]. The absorptions of the protons experience a high-field shift[47], as is observed for the resonance of the protons of the $(CH_3)_2N$ group. The molecular geometry is such that this grouping is placed directly above the phenyl ring. The ^1H-NMR signal is split into a doublet due to coupling with ^{31}P. The second methyl group in $(CH_3)_2N$ is not affected by the ring current effect and its resonance ($\delta = 2.81$) falls in the expected range; it is split into a pseudotriplet by coupling with ^{19}F and ^{31}P. The other ^1H resonances for **11** lie in the expected range (cf. Table 7). The proton resonances of the $-CH_2CH_2-$ group of compounds **9**–**11** are split into broad multiplets, exhibiting second-order effects.

Table 8. ^{13}C-NMR data of the hexafluorophosphate salts **9**–**11**

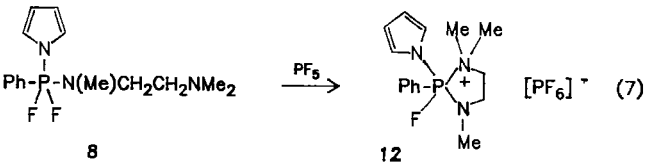
No.	$(\underline{C}H_3)_2N$ δ	$(CH_3)_2N\underline{C}H_2$ δ	$N(\underline{C}H_3)P$ δ	$\underline{C}H_2N(CH_3)P$ δ	R δ
9	47.05 (m)	46.47 (d, $^2J(PC)=9$)	37.63 (m)	54.83 (d, $^2J(PC)=8$)	14.47 (dd, $^1J(PC)=163.7$, $^2J(CF)=44.3$)
10	44.16 (d, $^2J(PC)=28$) 46.19 (s)	45.65 (d, $^2J(PC)=8$)	37.16 (s, br)	53.24 (d, $^2J(PC)=8$)	0.19 (d, $(\underline{C}H_3)_3Si$, $^3J(PC)=5$); 16.32 (dt, $\underline{C}H_2P$, $^1J(PC)=144$, $^2J(FC)=23$)
11	47.95 (m)	46.65 (d, $^2J(PC)=8$)	38.35 (m)	54.10 (d, $^2J(PC)=8$)	128.6 (m, m-$\underline{C}$, $^3J(PC)=13$; 130.7 (d, o-$\underline{C}$, $^2J(PC)=20$; 134.5 (d, p-$\underline{C}$, $^4J(PC)=3$)

In the ^{13}C-NMR spectrum of **9** (Table 8) a broad signal is displayed. In agreement with the ^1H-NMR spectrum, this suggests a dynamic behaviour of **9** at room temperature in solution. The ^{13}C resonance of the $N(CH_3)P$ group, coupling with ^{31}P and ^{19}F, is split into a doublet of doublets. It is noteworthy that coupling between ^{13}C and only one of the two fluorine nuclei is observed, and the signal is split only into a doublet. The values of the coupling constants are in the usual range.

The ^{13}C-NMR spectrum of **10** is normal. The δ(C) values for **9**–**11** and the various coupling constants are similar for all three compounds. A low-field shift of the ^{13}C resonance for the $(CH_3)_2NCH_2$ grouping in **9**–**11** of ca. 10 ppm, compared to **2**–**4**, is noteworthy. This low-field shift is believed to arise from the formation of a coordinative bond between the nitrogen atom of the $(CH_3)_2N$ group and phosphorus, following the abstraction of a fluoride ion by PF_5. This ring closure reaction removes electron density from the carbon atoms of the $(H_3C)_2N$ group. The carbon atom of the adjacent methylene group becomes electronically deshielded, which leads to a low-field shift of the ^{13}C signal.

4. Reaction of {[2-(Dimethylamino)ethyl]methylamino}difluorophenyl-1-pyrrolylphosphorane (8) with Phosphorus Pentafluoride; Formation of the Monofluoroazonium Hexafluorophosphate Salt 12 by Abstraction of a Fluoride Ion from 8

A fluoride ion is abstracted by PF_5 from **8** in a fashion similar to that described for compounds **9**–**11**. This fluoride abstraction is followed by an intramolecular ring closure reaction as a result of a donor-acceptor interaction between the nitrogen atom of the $(CH_3)_2N$ group and phosphorus. The salt **12** is similar to **9**–**11**. The formation of **12** is described in the Experimental Section.



8 **12** (7)

^{31}P NMR		^{19}F NMR	
δ(P)	$^1J(PF_{eq})$	δ(F)	$^1J(PF)$
−9.8	1037	−71.7	1043

Treatment of **7** with PF_5, even in excess and upon heating to 110°C in a heavy wall glass tube (2 h), does not lead to the same type of product. Besides large amounts of unreacted **7** the ^{31}P-NMR spectrum reveals only a mixture of unidentified products, and the reaction is not as clear-cut as the formation of **12**. We believe that the basicity of the phosphorus atom in **7** is not high enough to allow abstraction of a fluoride ion by PF_5. The electron-withdrawing effect of the phenyl groups reduces the electron density at phosphorus to such an extent that the formation of a coordinative bond, involving the nitrogen atom of the $(CH_3)_2N$ group after abstraction of a fluoride ion, will not compensate the decrease in the charge.

The basicity at phosphorus in compound **8** is believed to be higher than in **7**, in view of the nitrogen lone pair of the pyrrolyl group. Thus, the fluoride ion abstraction from **8** by the Lewis acid PF_5 is facilitated, and **12** is readily formed, in accord with eq. (7).

The δ(P) value of **12** (−9.8) is similar to the values of **9**–**11**. The signal is split into a doublet by coupling with the di-

rectly bound single fluorine atom. The observed value of ^1J(PF) (1037 Hz) falls in the upper end of the range typical of equatorial fluorine at trigonal-bipyramidal phosphorus. In the ^{19}F-NMR spectrum of **12** a doublet at $\delta = -71.7$ is observed. Both the values of δ(F) and ^1J(PF) suggest that the single fluorine substituent in **12** occupies an equatorial position at trigonal-bipyramidal phosphorus, unless there is a significant departure of the molecular geometry from trigonal-bipyramidal.

The axial positions of the two fluorine substituents in **8** have been established by both ^{19}F- and ^{31}P-NMR spectroscopy, and an axial fluorine atom is abstracted by PF_5. The subsequent ring closure apparently forces the second axial fluorine atom into an equatorial position. This is indicated by the ^{19}F-NMR parameters and confirmed for the solid state by a single-crystal X-ray diffraction study of **12** (see below). Possibly, electronic effects are responsible for the positional change of the fluorine substituent. Because of the strain in cyclic phosphoranes involving four- and five-membered ring systems, such rings preferentially occupy an axial and an equatorial position at trigonal-bipyramidal phosphorus[29,48,49]. As a result, only one axial position would be available to the remaining fluorine substituent. In the case of **12**, the pyrrolyl ligand is bound in the second axial position because of the higher group electronegativity[50,51] of this ligand compared to that of fluorine. The possibility of delocalisation of electron density over the aromatic system of the pyrrolyl group causes a more pronounced electronegative character of the pyrrolyl group than of the fluorine ligand.

Thus, the equatorial position of fluorine in **12** seems to contradict the electronegativity rule[2,10,11], according to which the axial positions at trigonal-bipyramidal phosphorus are always occupied by the (most electronegative) fluorine atoms, in accord with the Pauling electronegativity scale. Observations in which this rule is obeyed have repeatedly been reported[29,48,49].

Table 9. ^{1}H- and ^{13}C-NMR data of **12**

	^{1}H	^{13}C
δ $(\underline{CH_3})_2N$	2.25 (dd), ^3J(PH) = 3.1, ^4J(FH) = 2.0	46.83 (d), ^2J(PC) = 2.0
δ $(CH_3)_2N\underline{CH_2}$	2.92 (m)	48.92 (d), ^2J(PC) = 4.7
δ $N(\underline{CH_3})P$	2.37 (dd), ^3J(PH)=14.2	37.47 (d), ^2J(PC) = 3.5
δ $\underline{CH_2}N(CH_3)P$	3.51 (m)	52.57 (d), ^2J(PC) = 7.0
δ N-C(H)=$\underline{C}$(H)	6.26 (m)	113.78 (d), ^3J(PC) = 8.7
δ N-$\underline{C}$(H)=C(H)	6.70 (m)	124.20 (dd), ^2J(PC) = 5.0, ^3J(FC) = 3.0
δ ($\underline{C_6}H_5$)	7.76 (m)	130.49 (m), o-, m-$\underline{C}$, 135.2 (d), p-$\underline{C}$, ^4J(PC) = 4

The ^{1}H-NMR spectrum of **12** is similar to the spectra of compounds **9**–**11**. The proton resonance for the $N(CH_3)P$ grouping is slightly shifted to higher field, compared to the resonances of the difluoroazonium salts **9**–**11**. The coupling constant ^3J(PH) is slightly increased, the ^4J(FH) coupling constants are comparable. All further δ(H) values and coupling constants (Table 9) are in agreement with the values observed for **9**–**11**. The resonances are mostly split into multiplets, because of coupling of ^{1}H to phosphorus and fluorine.

The splitting pattern of the ^{13}C-NMR signals in **12** is more clear-cut than that of the ^{1}H-NMR spectrum. By comparison of the δ(C) values of **12** with those of **8**–**11**, the NMR data can be assigned unambiguously (cf. Table 9).

5. Discussion of the X-Ray Structure Analyses of 10–12

The X-ray analyses of compounds **10**–**12** confirm the expected trigonal-bipyramidal geometry at phosphorus; the least ideal angles are (**10**) N(2)–P(1)–C(9) 130.7°, (**11**) F(1)–P(1)–N(1) 169.5°, (**12**) N(1)–P(1)–N(3) 169.2°. The $CH_3NCH_2CH_2N(CH_3)_2$ ligand forms a chelate ring in each case, whereby one axial $[N(CH_3)_2]$ and one equatorial site (NCH_3) are bridged. The P–N bonds to the $N(CH_3)_2$ group

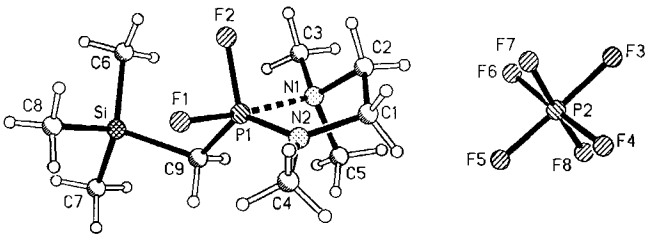


Figure 2. Formula unit of compound **10** in the crystal, showing the atom numbering scheme. Radii are arbitrary. Only one position of the disordered anion is shown. The long P–N bond is indicated by a broken line

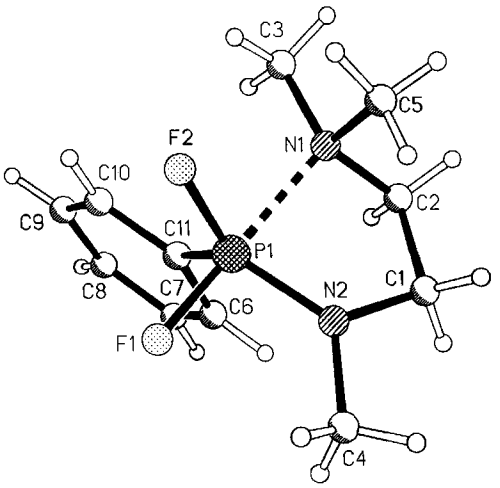


Figure 3. Cation of compound **11** in the crystal, showing the atom numbering scheme. Radii are arbitrary. The long P–N bond is indicated by a broken line

are all very long; (**10**) 199.1(3), (**11**) 199.6(3), (**12**) 207.0(3) pm [cf. 163.0(3), 161.3(3), 161.3(3) to the NCH_3 groups and 173.0(3) pm to the axial nitrogen of **12**].

The exceptionally long P—N bond in **12** is consistent with the decreased Lewis acid character of phosphorus bearing only one F substituent. The chelate rings all adopt an envelope conformation, with the nitrogen of $N(CH_3)_2$ lying 80, 76, and 72 pm, respectively, out of the plane of the other four atoms. The equatorial P—F bond lengths are all similar [156.5(2), 155.8(2), 157.4(2) pm], as are the equatorial P—C bond lengths [177.0(3), 179.7(3), 178.6(3) pm], despite the different substituents, viz. $CH_2Si(CH_3)_3$ in **10** and phenyl in **11** and **12**].

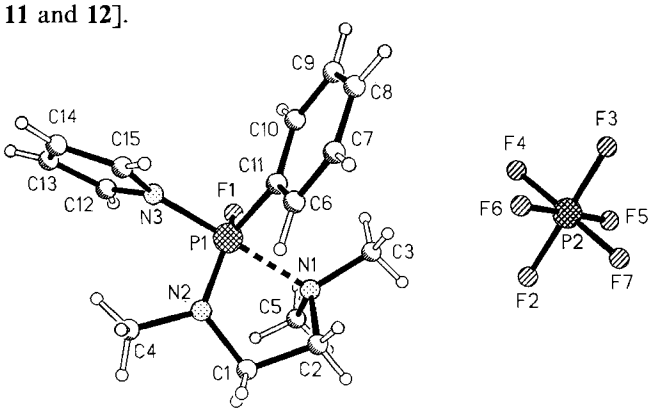
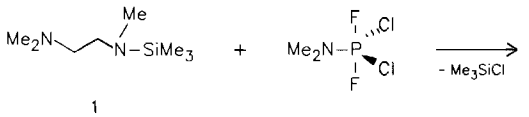


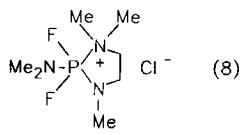
Figure 4. Formula unit of compound **12** in the crystal, showing the atom numbering scheme. Radii are arbitrary. The long P—N bond is indicated by a broken line

6. Reaction of Dichloro(dimethylamino)difluorophosphorane with *N,N,N'*-Trimethyl-*N'*-(trimethylsilyl)ethylenediamine (1)

Compound **13** [R = $(CH_3)_2N$], analogous to **9**—**11**, cannot be synthesized by the reaction of (dimethylamino)tetrafluorophosphorane with **1** followed by treatment with phosphorus pentafluoride. The unusual reaction of $(CH_3)_2NPF_4$ with **1** yields an intramolecularly stabilized tetrafluorophosphate[52] and (dimethylamino)trimethylsilane. For this reason the synthesis of **13** was attempted by the reaction of the dimethylamino-substituted chlorofluorophosphorane $(CH_3)_2NPF_2Cl_2$ with **1**. Dichloro(dimethylamino)difluorophosphorane is synthesized in analogy to the ethyl derivative, as described in the literature[53]. The mixed halogenated (dialkylamino)phosphorane is unstable[54—56] and is therefore allowed to react with **1** immediately after its synthesis, eq. (8).



1



(8)

13

The starting materials are allowed to react in a molar ratio of 1:1. The white solid isolated is investigated by NMR spectroscopy. The data confirm the proposed structure of **13**. In the first reaction step, *N,N,N'*-trimethylethylenediamine is bound to phosphorus with formation of $(CH_3)_3SiCl$, confirmed by ^{1}H-NMR spectroscopy. In a second step, an intramolecular donor-acceptor interaction between nitrogen and phosphorus [$(CH_3)_2N$ group] follows immediately, displacing Cl^-. Displacement of F^- as anion and subsequent intramolecular donor-acceptor interaction has not been observed in solution, probably because of the limited polarizability of the F^- anion.

In the ^{31}P-NMR spectrum of **13** a triplet at $\delta = -30$ is observed, instead of a doublet of doublets, as obtained for **9**—**11**. This is due to the equivalence of the two fluorine atoms in **13**. The ^{19}F-NMR spectrum reveals a doublet at $\delta(F) = -75.3$. The coupling constants $^1J(PF)$ (938 Hz), determined from both the ^{31}P- and the ^{19}F-NMR spectra, are in good agreement.

The $\delta(F)$ value and the magnitude of $^1J(PF)$ indicate rapid exchange[2] of the two fluorine atoms at trigonal-bipyramidal phosphorus in **13**. Because the ethylenediamine ligand is attached axially/equatorially, as observed in **9**—**11**, it may be assumed that the fluorine atoms occupy one axial and one equatorial position at trigonal-bipyramidal phosphorus. This would cause the splitting of the ^{19}F resonance into a doublet of doublets.

We assume the dynamic exchange process, mentioned above, to be fast compared to the NMR time scale. Thus, only a mean value for both the expected fluorine resonances can be observed. The $^1J(PF)$ coupling constant (938 Hz) displays a mean value between $^1J(PF^a)$ and $^1J(PF^e)$ observed for **9**—**11**.

The ^{13}C-NMR spectrum of **13** reveals a multiplet at $\delta = 38.2$ for the $N(CH_3)P$ group. The covalent, phosphorus-bound $(CH_3)_2N$ group gives rise to a singlet at $\delta = 38.8$, and the resonance is slightly shifted to higher field compared with the resonance of the coordinatively bound $(CH_3)_2N$ group at $\delta = 46.4$ (singlet). Two doublets are observed for the ethylene group. The ^{13}C resonance at $\delta = 44.9$ [$^2J(PC) = 12$ Hz] is assigned to the carbon atom adjacent to the coordinatively bound $(CH_3)_2N$ group, and the resonance at $\delta = 51.4$ [$^2J(PC) = 12$ Hz] to the carbon atom adjacent to the covalently bound $N(CH_3)P$ group.

We are indebted to Dr. *R. Wiesboeck* (US Steel Corp., Decatur, Ga., U.S.A.), *BASF AG*, *Bayer AG*, and *Hoechst AG* for generous supplies of chemicals and to *Fonds der Chemischen Industrie* for financial support.

Experimental

All experiments were conducted in conventional glass apparatus under dry nitrogen. Solvents were purified and dried by standard procedures[57] and were stored over molecular sieves. — NMR: Bruker AC 200, ^{1}H (200.13 MHz), ^{13}C (50.32 MHz), ^{19}F (188.31 MHz), ^{31}P (81.02 MHz); Bruker AM 400, ^{1}H (400.1 MHz); Jeol JNMC 60 HL, ^{31}P (24.3 MHz); Perkin Elmer R 24 B, ^{1}H (60 MHz). Reference substances: ^{1}H, ^{13}C, CH_2Cl_2 int. ($\delta = 5.35$), $CHCl_3$ int. ($\delta = 7.27$), and TMS int. ($\delta = 0$); ^{19}F, CCl_3F ext. ($\delta = 0$); ^{31}P, 85% H_3PO_4

ext. ($\delta = 0$). Coupling constants J are given in Hertz. All NMR spectra were recorded in $CDCl_3$ as a solvent, unless stated otherwise. – Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen.

The following starting materials were synthesized by the procedures indicated: $C_6H_5(C_4H_4N)PF_3$[7]; $Me_2NCH_2CH_2N(Me)SiMe_3$[31] (**1**); $C_6F_5PF_4$[34]; $Me_2NPF_2Cl_2$[53]; $MePF_4$[58]; $PhPF_4$[58]; $2,5\text{-}(CH_3)_2C_6H_3PF_4$[58]; Ph_2PF_3[58]; $Me_3SiCH_2PF_4$[59].

Synthesis of the Trifluorophosphoranes **2**–**6**: These compounds were prepared by the reaction of *N,N,N'*-trimethyl-*N'*-(trimethylsilyl)ethylenediamine (**1**) with the appropriate tetrafluorophosphorane, eliminating fluorotrimethylsilane. The synthesis of **2** is described as a typical example:

{[2-(Dimethylamino)ethyl]methylamino}trifluoromethylphosphorane (**2**): A solution of **1** (9.96 g; 57.2 mmol) in 20 ml of dichloromethane was placed in a heavy-wall glass tube fitted with a Teflon® stopcock. At −196°C tetrafluoromethylphosphorane (7.0 g; 57.2 mmol) was condensed onto this solution. The reaction mixture was allowed to reach 25°C within 0.5 h, and the solvent was subsequently removed by pumping it off in vacuo (0.1 Torr/25°C). The remaining liquid product was distilled through a Vigreux column. The product **2** was obtained as a colourless liquid of b.p. 57°C/9 Torr; yield 7.8 g (67%).

The other trifluorophosphoranes **3**–**6** were prepared in a similar fashion. All the relevant experimental data are listed in Table 10; NMR data: Tables 1–3.

Reaction of Trifluorodiphenylphosphorane, $(C_6H_5)_2PF_3$, and Trifluorophenyl-1-pyrrolylphosphorane, $C_6H_5(C_4H_4N)PF_3$, with **1**: *Synthesis of the Difluorophosphoranes* **7** *and* **8**: The preparation of **7** is described as a typical example. Compound **8** was prepared in an analogous fashion. A solution of 9.9 g (57 mmol) of **1** in 10 ml of dichloromethane was added dropwise with stirring to a solution of 13.8 g (57 mmol) of trifluorodiphenylphosphorane in 10 ml of dichloromethane. A ^{1}H-NMR spectrum recorded at this stage revealed that there had been no reaction; the reaction was found to be complete after 3 h reflux. All products volatile in vacuo (0.1 Torr/25°C) were pumped off. The residue was twice distilled in vacuo; b.p. 124°C/10^{-3} Torr, yield 13.5 g (73%). For preparative data cf. Table 10; NMR data see Tables 4 and 5.

Reaction of **2**–**4** *and* **8** *with PF_5: Synthesis of the Hexafluorophosphate Salts* **9**–**12**: These compounds were prepared in a similar fashion by fluoride abstraction from **2**–**4** and **8** with phosphorus pentafluoride. The synthesis of **9** is described as typical: Phosphorus pentafluoride (3.5 g; 24.5 mmol) was condensed onto a solution of 5.0 g (24.5 mmol) of **2** in 50 ml of diethyl ether, contained in a heavy-wall glass tube at −196°C. The mixture was allowed to reach

Table 10. Trifluorophosphoranes $RPF_3N(Me)CH_2CH_2NMe_2$ (**2**–**6**) and difluorophosphoranes $RR'PF_2N(Me)CH_2CH_2NMe_2$ (**7** and **8**)

Compound	Reactants	Reaction conditions	Yield g (%)	B.p. °C (Torr)	Formula Mol. weight	Analyses
$MePF_3N(Me)CH_2CH_2NMe_2$ **2**	**1** (9.96g; 57.2 mmol) $MePF_4$ (7.0g; 57.2 mmol)	−196 to 25°C within 0.5 h	7.8 (67)	57 (9)	$C_6H_{16}F_3N_2P$ 204.2	Calcd. C 35.30 H 7.90 F 27.9 Found. C 35.27 H 7.73 F 27.3
$Me_3SiCH_2PF_3N(Me)\text{-}CH_2CH_2NMe_2$ **3**	**1** (10.8g; 62 mmol) $Me_3SiCH_2PF_4$ (12.0g; 62 mmol)	50 ml CH_2Cl_2; 25°C; stirring for 0.5 h	13.2 (77)	76 (1.5)	$C_9H_{24}F_3N_2PSi$ 276.4	Calcd. C 39.12 H 8.75 F 20.6 Found. C 39.12 H 8.78 F 20.8
$C_6H_5PF_3N(Me)CH_2CH_2NMe_2$ **4**	**1** (8.0g; 45.9 mmol) $C_6H_5PF_4$ (8.5g; 46 mmol)	20 ml Et_2O; 0°C; 0.5 h at 25°C	5.14 (42)	71 (0.05)	$C_{11}H_{18}F_3N_2P$ 266.3	Calcd. C 49.62 H 6.81 F 21.4 Found. C 48.88 H 6.98 F 21.0
$C_6F_5PF_3N(Me)CH_2CH_2NMe_2$ **5**	**1** (3.62g; 20.8 mmol) $C_6F_5PF_4$ (5.7g; 20.8 mmol)	40 ml CH_2Cl_2; 0.5 h at 25°C	4.1 (56)	52 (0.1)	$C_{11}H_{13}F_8N_2P$ 356.2	Calcd. C 37.09 H 3.68 F 42.7 Found. C 37.25 H 3.71 F 42.5
$2,5\text{-}(CH_3)_2C_6H_3PF_3N(Me)\text{-}CH_2CH_2NMe_2$ **6**	**1** (17.4g; 0.1 mol) $2,5\text{-}(CH_3)_2C_6H_3PF_4$ (21.2g; 0.1 mol)	60 ml CH_2Cl_2; 1.0 h at 25°C	13.5 (46)	71 (0.07)	$C_{13}H_{22}F_3N_2P$ 294.3	Calcd. C 53.06 H 7.53 F 19.4 Found. C 52.95 H 7.50 F 19.6
$(C_6H_5)_2PF_2N(Me)\text{-}CH_2CH_2NMe_2$ **7**	**1** (9.9g; 57 mmol) Ph_2PF_3 (13.8g; 57 mmol)	20 ml CH_2Cl_2; 3 h reflux	13.5 (73)	124 (10^{-3})	$C_{17}H_{23}F_2N_2P$ 324.4	Calcd. C 62.95 H 7.15 P 9.55 Found. C 62.49 H 6.96 P 9.29
$(C_6H_5)(C_4H_4N)PF_2N(Me)\text{-}CH_2CH_2NMe_2$ **8**	**1** (11.4g; 64 mmol) $Ph(C_4H_4N)PF_3$ (14.8g; 64 mmol)	40 ml CH_2Cl_2; 2 h at 25°C	14.5 (72)	112 (0.15)	$C_{15}H_{22}F_2N_3P$ 313.3	Calcd. C 57.50 H 7.08 F 12.13 Found. C 57.27 H 7.11 F 12.30

Table 11. Hexafluorophosphate salts $[R\overline{PF_2N(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$ and $[R,R'\overline{PFN(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$

Compound	Reactants	Reaction conditions	Yield g (%)	M.p. °C	Formula Mol. weight	Analyses
$[\overline{MePF_2N(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$ **9**	**2** (5.0g; 24.5 mmol) PF_5 (3.5g; 24.5 mmol)	50 ml Et_2O; 15 h at 25°C	6.3 (74)	61	$C_6H_{16}F_8N_2P_2$ 330.1	Calcd. C 21.83 H 4.88 F 46.0 Found. C 21.79 H 4.96 F 45.5
$[\overline{Me_3SiCH_2PF_2N(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$ **10**	**3** (5.76g; 20.9 mmol) PF_5 (3.8g; 20.9 mmol)	40 ml Et_2O; 1 h at 25°C	5.2 (62)	63	$C_9H_{24}F_8N_2P_2Si$ 402.3	Calcd. C 26.87 H 6.01 N 6.96 Found. C 26.1 H 6.26 N 7.02
$[\overline{PhPF_2N(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$ **11**	**4** (6.1g; 23 mmol) PF_5 (2.9g; 23 mmol)	30 ml CH_2Cl_2 2 h at 25°C	7.8 (86)	139	$C_{11}H_{18}F_8N_2P_2$ 392.2	Calcd. C 33.69 H 4.63 F 38.8 Found. C 33.33 H 4.67 F 39.2
$[\overline{Ph(C_4H_4N)PFN(Me)CH_2CH_2NMe_2}]^+ [PF_6]^-$ **12**	**8** (12.4g; 39.6 mmol) PF_5 (5.0g; 39.6 mmol)	40 ml CH_2Cl_2 2 h at 25°C	12.9 (74)	121	$C_{15}H_{22}F_7N_3P_2$ 439.3	Calcd. C 41.01 H 5.05 N 9.57 Found. C 41.19 H 5.33 N 9.48

room temp. in the course of 16 h. Formation of a colourless solid was noted in the reaction mixture, which was stirred at room temp. for 2 h. The product was subsequently collected by filtration through a sintered glass disc, washed with three 5-ml portions of diethyl ether and dried in vacuo (0.1 Torr/25°C). Details of the preparation of **9**–**12** are listed in Table 11, NMR data in Tables 6–9.

X-Ray Structure Determinations of **10**–**12**: Single crystals were mounted in inert oil and rapidly transferred to the cold gas stream (−95°C) of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). Measurements were performed using monochromated Mo-K_α radiation. Cell constants were refined from setting angles of ca. 50 reflections in the 2-Θ range 20–24°. Structures were solved by routine direct methods and subjected to a full-matrix least-squares refinement on *F*. Hydrogen atoms were located in difference syntheses and included in the refinements using a riding model. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed.

Special features of the refinements: In compound **10**, the $[PF_6]^-$ ion is disordered; two components with a common phosphorus site were refined, with the s.o.f. of the major component refining to 0.770(4). The refinement of compound **11** was somewhat unsatisfactory in two respects; a moderate difference peak near C1, possibly arising from a minor unidentified twinning or disorder component, and the incomplete convergence of the methyl group at C4, indicating rotational disorder of this group.

The program system was "Siemens SHELXTL PLUS". Crystal data are listed in Table 12, atomic coordinates, bond lengths, and angles in Tables 13–18. Further details of the structure determinations (H atom coordinates, structure factors, temperature factors) have been deposited with the Fachinformationszentrum Karlsruhe,

Table 12. Crystal data for the compounds **10**–**12**

Compound	**10**	**11**	**12**
Formula	$C_9H_{24}F_8N_2P_2Si$	$C_{11}H_{18}F_8N_2P_2$	$C_{15}H_{22}F_7N_3P_2$
M_r	402.3	392.2	439.3
Crystal habit	Colourless plate	Colourless tablet	Pale brown prism
Crystal size (mm)	0.8 x 0.7 x 0.15	0.8 x 0.6 x 0.3	0.65 x 0.5 x 0.4
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
Cell constants :			
a (pm)	883.5(4)	1184.0(4)	2289.4(10)
b (pm)	913.2(4)	1183.2(4)	1281.4(5)
c (pm)	1225.4(5)	1150.6(4)	1651.9(6)
α (°)	73.50(3)		
β (°)	70.41(3)	102.77(3)	126.83(3)
γ (°)	74.74(3)		
V (nm^3)	0.8776	1.5720	3.879
Z	2	4	8
D_x (Mg m^{-3})	1.523	1.657	1.504
F(000)	416	800	1808
μ (mm^{-1})	0.38	0.35	0.29
$2\theta_{max}$ (°)	55	50	50
No. of reflections :			
measured	5143	4550	5453
independent	4017	2763	3416
R_{int}	0.016	0.023	0.017
observed [>4 $\sigma(F)$]	2987	2419	2435
R	0.045	0.059	0.036
wR	0.054	0.083	0.039
g	0.0003	0.0002	0.00015
No. of parameters	237	217	253
S	2.0	4.0	1.7
Max. Δ/σ	0.007	0.7	0.002
Max. $\Delta\rho$ (e Å^{-3})	0.6	1.2	0.2

Table 13. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors [pm^2] for compound **10**. s.o.f. F(3–8) 0.770(4), F(3′–8′) 0.230(4)

	x	y	z	U(eq)
P(1)	4822.8(8)	6866.2(8)	3345.7(1)	271(3)
F(1)	4502(2)	7808(2)	4346(1)	433(7)
F(2)	6199(2)	5660(2)	3828(1)	360(7)
N(1)	5182(3)	5473(3)	2258(2)	302(9)
N(2)	2994(3)	6449(3)	3865(2)	337(9)
Si	7435(1)	9098(1)	2221.7(7)	308(3)
C(1)	2689(4)	5042(4)	3693(3)	405(13)
C(2)	4310(4)	4205(3)	3073(3)	387(12)
C(3)	6925(4)	4833(4)	1707(3)	466(14)
C(4)	1586(4)	7308(4)	4621(3)	509(15)
C(5)	4364(4)	6251(4)	1297(3)	398(13)
C(6)	9279(3)	7538(4)	2086(3)	445(13)
C(7)	7712(4)	10719(3)	904(3)	406(13)
C(8)	6990(5)	9800(5)	3598(3)	540(16)
C(9)	5599(3)	8388(3)	2194(2)	295(10)
P(2)	1671(1)	2099(1)	1873.7(7)	346(3)
F(3)	1818(5)	252(3)	2064(3)	696(16)
F(4)	-216(3)	2206(5)	2510(3)	867(18)
F(5)	1556(6)	3884(3)	1726(5)	966(24)
F(6)	3572(3)	1935(5)	1324(4)	979(18)
F(7)	2008(5)	1735(5)	3142(3)	854(20)
F(8)	1338(6)	2368(5)	652(3)	860(25)
F(3′)	994(13)	651(13)	2238(9)	514(16)
F(4′)	275(11)	3038(11)	2674(8)	514(16)
F(5′)	2524(12)	3637(13)	1289(8)	514(16)
F(6′)	3176(11)	1347(11)	850(8)	514(16)
F(7′)	2776(12)	1599(13)	2694(10)	514(16)
F(8′)	779(16)	2821(16)	850(13)	514(16)

Table 14. Bond lengths [pm] and angles [°] for the cation of compound **10**

P(1)-F(1)	160.0 (2)	P(1)-F(2)	156.5 (2)
P(1)-N(1)	199.1 (3)	P(1)-N(2)	163.0 (3)
P(1)-C(9)	177.0 (3)	N(1)-C(2)	149.3 (4)
N(1)-C(3)	149.0 (3)	N(1)-C(5)	149.6 (4)
N(2)-C(1)	146.4 (5)	N(2)-C(4)	146.5 (4)
Si-C(6)	185.6 (3)	Si-C(7)	185.1 (3)
Si-C(8)	185.6 (4)	Si-C(9)	191.2 (3)
C(1)-C(2)	149.6 (4)		

F(1)-P(1)-F(2)	90.2(1)	F(1)-P(1)-N(1)	173.2(1)
F(2)-P(1)-N(1)	85.9(1)	F(1)-P(1)-N(2)	92.8(1)
F(2)-P(1)-N(2)	116.7(1)	N(1)-P(1)-N(2)	84.0(1)
F(1)-P(1)-C(9)	92.5(1)	F(2)-P(1)-C(9)	112.3(1)
N(1)-P(1)-C(9)	94.1(1)	N(2)-P(1)-C(9)	130.7(1)
P(1)-N(1)-C(2)	101.4(2)	P(1)-N(1)-C(3)	115.4(2)
C(2)-N(1)-C(3)	110.7(2)	P(1)-N(1)-C(5)	111.5(2)
C(2)-N(1)-C(5)	108.7(3)	C(3)-N(1)-C(5)	108.8(2)
P(1)-N(2)-C(1)	120.5(2)	P(1)-N(2)-C(4)	124.9(3)
C(1)-N(2)-C(4)	114.3(3)	C(6)-Si-C(7)	110.6(1)
C(6)-Si-C(8)	110.1(2)	C(7)-Si-C(8)	110.7(2)
C(6)-Si-C(9)	110.9(2)	C(7)-Si-C(9)	103.3(1)
C(8)-Si-C(9)	111.0(2)	N(2)-C(1)-C(2)	106.4(3)
N(1)-C(2)-C(1)	104.3(2)	P(1)-C(9)-Si	119.5(2)

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Table 15. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors [pm^2] for compound **11**

	x	y	z	U(eq)
P(1)	1696.4(7)	971.5(7)	5079.1(7)	239(3)
F(1)	905(2)	1605(2)	5823(2)	409(7)
F(2)	1354(2)	-177(2)	5566(2)	387(7)
N(1)	2440(2)	-9(3)	4049(3)	312(9)
N(2)	1109(3)	1604(3)	3853(3)	373(10)
C(1)	1649(4)	1538(4)	2814(4)	597(17)
C(2)	2752(5)	792(4)	3192(4)	605(18)
C(3)	3424(4)	-710(4)	4672(5)	609(17)
C(4)	158(3)	2426(3)	3669(4)	465(13)
C(5)	1544(4)	-776(5)	3337(4)	554(16)
C(6)	3511(3)	2472(3)	5627(3)	297(10)
C(7)	4537(3)	2899(3)	6331(3)	369(12)
C(8)	5072(3)	2339(3)	7353(3)	386(12)
C(9)	4598(3)	1365(4)	7712(3)	401(12)
C(10)	3577(3)	922(3)	7007(3)	341(11)
C(11)	3046(3)	1477(3)	5964(3)	267(10)
P(2)	7792.0(9)	4251.6(8)	5520.3(8)	373(3)
F(3)	7408(2)	3538(3)	6535(3)	687(11)
F(4)	8275(3)	5186(3)	6464(3)	829(13)
F(5)	8979(2)	3601(3)	5773(3)	795(13)
F(6)	7285(3)	3336(3)	4547(3)	1004(15)
F(7)	6546(3)	4849(3)	5289(3)	769(12)
F(8)	8176(4)	5001(3)	4542(3)	992(17)

Table 16. Bond lengths [pm] and angles [°] for the cation of compound **11**

P(1)-F(1)	158.9 (2)	P(1)-F(2)	155.8 (2)
P(1)-N(1)	199.6 (3)	P(1)-N(2)	161.3 (3)
P(1)-C(11)	179.7 (3)	N(1)-C(2)	147.3 (6)
N(1)-C(3)	148.0 (5)	N(1)-C(5)	149.6 (5)
N(2)-C(1)	147.8 (6)	N(2)-C(4)	146.7 (5)
C(1)-C(2)	155.6 (7)	C(6)-C(7)	139.7 (4)
C(6)-C(11)	139.1 (5)	C(7)-C(8)	137.6 (5)
C(8)-C(9)	138.4 (6)	C(9)-C(10)	140.1 (5)
C(10)-C(11)	139.1 (5)		
F(1)-P(1)-F(2)	89.3(1)	F(1)-P(1)-N(1)	169.5(1)
F(2)-P(1)-N(1)	83.7(1)	F(1)-P(1)-N(2)	93.5(1)
F(2)-P(1)-N(2)	128.6(1)	N(1)-P(1)-N(2)	85.0(1)
F(1)-P(1)-C(11)	95.4(1)	F(2)-P(1)-C(11)	110.9(1)
N(1)-P(1)-C(11)	94.4(1)	N(2)-P(1)-C(11)	119.9(2)
P(1)-N(1)-C(2)	103.4(3)	P(1)-N(1)-C(3)	116.2(3)
C(2)-N(1)-C(3)	113.4(4)	P(1)-N(1)-C(5)	109.0(3)
C(2)-N(1)-C(5)	106.0(3)	C(3)-N(1)-C(5)	108.2(3)
P(1)-N(2)-C(1)	120.2(3)	P(1)-N(2)-C(4)	127.1(3)
C(1)-N(2)-C(4)	112.0(3)	N(2)-C(1)-C(2)	106.9(4)
N(1)-C(2)-C(1)	103.5(4)	C(7)-C(6)-C(11)	119.5(3)
C(6)-C(7)-C(8)	119.9(3)	C(7)-C(8)-C(9)	121.0(3)
C(8)-C(9)-C(10)	119.6(3)	C(9)-C(10)-C(11)	119.4(3)
P(1)-C(11)-C(6)	118.8(2)	P(1)-C(11)-C(10)	120.5(3)
C(6)-C(11)-C(10)	120.6(3)		

Reaction of Dichloro(dimethylamino)difluorophosphorane with **1**: *Preparation of 2-(Dimethylamino)-2,2-difluoro-1,1,3-trimethyl-1,3,2λ⁵-diazaphospholidinium Chloride* (**13**): A solution of 3.22 g (18.5 mmol) of **1** in 10 ml of dichloromethane was added dropwise with stirring at room temp. to a solution of 3.40 g (18.5 mmol) of (dimethylamino)dichlorophosphorane in 10 ml of dichloromethane. Stirring was continued for 0.5 h. Subsequently, the solvents were pumped off in vacuo (0.1 Torr/25 °C); then 30 ml of diethyl ether was added to the oily residue. Within 30 min a colourless solid was precipitated, which was filtered through a sintered glass disc and washed with three 5-ml portions of diethyl ether. The product was then dried in vacuo (0.1 Torr). – M.p. 92 °C; yield 3.90 g (84%). – ^{1}H NMR: δ = 2.63 [d, $(CH_3)_2N$; ^3J(PH) = 15 Hz]; 2.83 [d,

Table 17. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors [pm^2] for compound **12**

	x	y	z	U(eq)
P(1)	4140.1(3)	1796.7(5)	3985.4(5)	346(3)
F(1)	4354.3(7)	863(1)	4735(1)	422(8)
N(1)	4279(1)	2621(2)	5168(2)	483(14)
N(2)	3368(1)	2399(2)	3304(2)	438(13)
N(3)	3976(1)	916(2)	3076(1)	391(12)
C(1)	3213(2)	3314(2)	3683(2)	633(22)
C(2)	3904(2)	3619(2)	4679(3)	645(24)
C(3)	5044(2)	2800(3)	6062(2)	709(22)
C(4)	2742(1)	2135(3)	2258(2)	618(17)
C(5)	3889(2)	2076(2)	5523(2)	642(22)
C(6)	4916(1)	3321(2)	3807(2)	408(15)
C(7)	5543(2)	3715(2)	3963(2)	532(19)
C(8)	6185(2)	3153(3)	4525(2)	611(19)
C(9)	6206(2)	2194(3)	4914(2)	571(17)
C(10)	5588(1)	1795(2)	4760(2)	451(14)
C(11)	4940(1)	2365(2)	4218(2)	343(13)
C(12)	3654(1)	-61(2)	2874(2)	465(16)
C(13)	3511(2)	-435(2)	2007(2)	601(19)
C(14)	3742(2)	321(3)	1637(2)	696(22)
C(15)	4019(2)	1134(2)	2288(2)	571(19)
P(2)	6785.3(4)	4486.9(6)	8316.7(5)	433(4)
F(2)	5981(1)	4387(1)	8011(1)	612(10)
F(3)	7586(1)	4585(1)	8620(1)	738(12)
F(4)	6827(1)	3251(1)	8288(1)	736(14)
F(5)	7101(1)	4448(2)	9470(1)	736(11)
F(6)	6456(1)	4528(1)	7151(1)	705(12)
F(7)	6731(1)	5727(1)	8320(1)	688(12)

Table 18. Bond lengths [pm] and angles [°] for the cation of compound **12**

P(1)-F(1)	157.4 (2)	P(1)-N(1)	207.0 (3)
P(1)-N(2)	161.3 (2)	P(1)-N(3)	173.0 (3)
P(1)-C(11)	178.6 (3)	N(1)-C(2)	148.1 (4)
N(1)-C(3)	148.4 (3)	N(1)-C(5)	150.2 (6)
N(2)-C(1)	147.0 (5)	N(2)-C(4)	147.9 (3)
N(3)-C(12)	138.8 (3)	N(3)-C(15)	139.1 (5)
C(1)-C(2)	149.7 (4)	C(6)-C(7)	139.2 (5)
C(6)-C(11)	138.5 (4)	C(7)-C(8)	138.1 (4)
C(8)-C(9)	137.4 (5)	C(9)-C(10)	137.7 (5)
C(10)-C(11)	139.3 (3)	C(12)-C(13)	135.3 (5)
C(13)-C(14)	140.7 (6)	C(14)-C(15)	135.2 (4)
F(1)-P(1)-N(1)	81.2(1)	F(1)-P(1)-N(2)	127.4(1)
N(1)-P(1)-N(2)	84.2(1)	F(1)-P(1)-N(3)	89.4(1)
N(1)-P(1)-N(3)	169.2(1)	N(2)-P(1)-N(3)	97.4(1)
F(1)-P(1)-C(11)	110.2(1)	N(1)-P(1)-C(11)	91.8(1)
N(2)-P(1)-C(11)	120.6(1)	N(3)-P(1)-C(11)	96.5(1)
P(1)-N(1)-C(2)	102.4(2)	P(1)-N(1)-C(3)	116.1(2)
C(2)-N(1)-C(3)	111.2(2)	P(1)-N(1)-C(5)	109.9(2)
C(2)-N(1)-C(5)	109.2(3)	C(3)-N(1)-C(5)	107.8(3)
P(1)-N(2)-C(1)	121.9(2)	P(1)-N(2)-C(4)	126.5(2)
C(1)-N(2)-C(4)	111.6(2)	P(1)-N(3)-C(12)	127.2(3)
P(1)-N(3)-C(15)	125.5(2)	C(12)-N(3)-C(15)	106.4(2)
N(2)-C(1)-C(2)	108.0(3)	N(1)-C(2)-C(1)	105.0(2)
C(7)-C(6)-C(11)	119.7(2)	C(6)-C(7)-C(8)	120.0(3)
C(7)-C(8)-C(9)	120.3(3)	C(8)-C(9)-C(10)	120.2(3)
C(9)-C(10)-C(11)	120.2(3)	P(1)-C(11)-C(6)	121.3(2)
P(1)-C(11)-C(10)	118.9(2)	C(6)-C(11)-C(10)	119.6(3)
N(3)-C(12)-C(13)	109.3(3)	C(12)-C(13)-C(14)	107.5(3)
C(13)-C(14)-C(15)	107.7(4)	N(3)-C(15)-C(14)	109.1(3)

$(CH_3)_2N^+$; $^3J(PH)$ = 6 Hz]; 2.90 [dt, CH_3NP; $^3J(PH)$ = 12, $^4J(FH)$ = 1 Hz]; 3.44 (m, CH_2CH_2). – ^{13}C NMR: δ = 38.15 (s, CH_3NP); 38.75 [s, $(CH_3)_2N$]; 44.9 [d, CH_2CH_2, $^2J(PC)$ = 12 Hz]; 46.43 [s, $(CH_3)_2N^+$]; 51.4 [d, CH_2CH_2, $^2J(PC)$ = 6 Hz]. – ^{19}F NMR: δ = −75.34 [d, $^1J(PF)$ = 938 Hz]. – ^{31}P NMR: δ = −30 [t, $^1J(PF)$ = 938 Hz].

$C_7H_{19}ClF_2N_3P$ (249.7)
Calcd. C 33.68 H 7.67 N 16.83
Found C 32.90 H 7.94 N 16.45

CAS Registry Numbers

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[1] Dedicated to Professor *Rolf Appel* on the occasion of his 70th birthday.
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