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Unusual Formation of a λ^6P-Tetrafluorophosphate Involving Intramolecular Donor–Acceptor Interaction; X-ray Crystal Structure Analysis and Temperature-Dependent NMR-Spectra

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ABSTRACT

The N,N,N′-*trimethylethylenediaminetetrafluorophosphate,* **4**, *was formed in the unusual reaction of* N,N,N′-*trimethyl*-N′-*trimethylsilylethylenediamine,* **1**, *with the N—P-bonded tetrafluorophosphoranes, dimethylaminotetrafluorophosphorane,* **2**, *or morpholinotetrafluorophosphorane,* **3**. *There was no evidence for the cleavage of a P—F bond in the tetrafluorophosphoranes (with formation of* Me_3SiF*); instead, the Si—N compounds,* R_2N—$SiMe_3$ (R_2 = Me_2 *or* $O(CH_2CH_2)_2$) *were formed. The* ^{19}F *and* ^{31}P *NMR spectra of* **4** *at room temperature indicated dynamic behavior. The X-ray crystal structure analysis of* **4** *revealed the presence of a five-membered ring, formally as a result of intramolecular donor–acceptor interaction (P—N = 196.5 pm) between the nitrogen atom of the* Me_2N *group and phosphorus.*

INTRODUCTION

It is well known that phosphorus pentafluoride, PF_5, displays acceptor (Lewis acid) properties toward bases, e.g. OR_2, SR_2, NR_3, and PR_3 [1]. In general uncharged adducts involving hexacoordinate (λ^6) phosphorus, e.g. $Me_2O{\cdot}PF_5$ [2], $Me_2S{\cdot}PF_5$ [3], $Me_3N{\cdot}PF_5$ [4], $C_5H_5N{\cdot}PF_5$ [4], or $Me_3P{\cdot}PF_5$ [5, 6] are formed. In the case of oxygen, sulfur, and phosphorus as donor atoms the stability of these adducts is relatively low. The adducts undergo rapid decomposition upon gentle warming with formation of the very stable, highly symmetric hexafluorophosphate anion $[PF_6]^-$ or, in the case of $Me_2O{\cdot}PF_5$, with formation of the λ^4P species $P(:O)F_3$ [7] (Equation 1).

$$3Me_2O{\cdot}PF_5 \longrightarrow 2Me_3O^+PF_6^- + F_3P{=}O \quad (1)$$

Apart from *inter*molecular formation of adducts as mentioned above, cases are known in which neutral compounds involving hexacoordinate (λ^6) phosphorus are formed as a result of *intra*molecular donor–acceptor interaction [8–10]. The first reports in this area included the investigation of the products from the reactions of 8-trimethylsiloxyquinoline and its 2-methyl derivative with fluorophosphoranes [8, 9]. Initially, no detailed NMR studies on these products were conducted but, subsequently, a detailed discussion of the NMR spectra of the λ^6P-tetrafluorophosphate **5** involving intramolecular donor–acceptor interaction has been presented [10].

In the following we report the unusual formation of a tetrafluorophosphate involving a hexacoordinate (λ^6) phosphorus atom, which was formed in the reaction of some aminotetrafluorophosphoranes with *N,N,N*′-trimethyl-*N*′-trimethylsilylethylenediamine, **1**.

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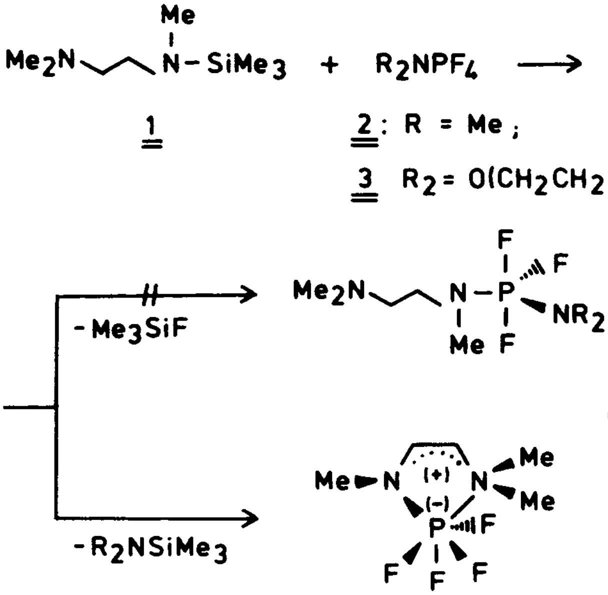
DISCUSSION

The reactions of dimethylamino-, **2**, and morpholinotetrafluorophosphorane, **3**, with *N,N,N'*-trimethyl-*N'*-trimethylsilylethylenediamine, **1**, proceeded under relatively mild conditions at room temperature. The silylated diamine, **1**, was added dropwise with stirring to the solutions of the tetrafluorophosphoranes, **2** or **3**, in dichloromethane. In both cases a colorless solid was left after volatile products had been removed in vacuo. After addition of diethyl ether the product was collected by filtration. The ^1H NMR spectra of the volatile product, mostly dichloromethane, demonstrated the absence of trimethylfluorosilane, Me_3SiF. The ^1H NMR spectra contained two sets of signals; on the basis of their δ(H) values, these were assigned to the known compounds $Me_2N—SiMe_3$ and $O(CH_2CH_2)_2N—SiMe_3$, respectively.



(2)

4

The NMR spectroscopic investigation of the product, formed according to Equation 2, confirmed the presence of **4**.

The ^1H NMR spectrum, recorded at 200.1 MHz, revealed three sets of signals for the protons of the Me_2N, the —N(Me), and the $—CH_2CH_2$ groups. The NMR signal of the protons of the Me_2N group bonded to phosphorus was split into a doublet of quintets, at room temperature. The coupling constant, 6.13 Hz, is characteristic of $^3J(PH)$ when a $(CH_3)_2N$ group is coordinatively bonded via nitrogen to phosphorus [10]. The protons of the $(CH_3)N$ group in **4** were found to give a doublet of triplets, with $^3J(PH)$ amounting to 17.18 Hz. The fine structure observed for these signals is due to HF coupling ($^4J(FH)$) between ^1H and ^{19}F bonded to phosphorus. The coupling constant $^4J(FH)$ for the Me_2N group (1.5 Hz) is larger than the value for the MeN group (0.6 Hz).

The ^{19}F and ^{31}P NMR spectra of solutions of **4** in dichloromethane-d_2 at room temperature suggest that the solution structure is dynamic, and temperature-dependent NMR spectra were therefore recorded. The room temperature ^{19}F NMR spectrum of **4** revealed a very broad doublet, a doublet of doublets, and a doublet of triplets, indicating the presence of three chemically nonequivalent types of fluorine atoms. The ^{19}F NMR spectrum of **4** at −30°C (cf. Figure 1) corresponds to an A_2BCX system. Its line shape resembles that of the product **5** formed in the reaction between phosphorus pentafluoride and 2-(*N,N*-dimethylamino)acetoxytrimethylsilane [10] (Table 1).

Long range coupling, $^4J(FH)$, between F(A) and F(B) and the protons of the Me_2N groups, in contrast to the observations on **5**, is not seen in the case of **4**. At −30°C the line shape of all ^{19}F NMR signals is sharp and unambiguous.

The ^{31}P NMR spectrum of **4** in CD_2Cl_2 displays a sharp triplet at δ −120.84 and two broad signals at δ −111.04 and −130.53 (cf. Figure 2). The line broadening again serves to illustrate the dynamic behavior of **4** in solution at room temperature. The triplet fine structure is not due to $^1J(PF)$ coupling; the observed coupling constant of 1613 Hz would be unusually large for direct P—F coupling.

A ^{31}P NMR spectrum recorded at −45°C revealed a signal at δ −121.86, split into a sharp doublet of doublets of triplets [11]. The δ(P) value, compared to that of PF_5 (−80.3) was found at higher field by 41.6 ppm. High-field shifts of such magnitude were also observed for the products of the reaction of fluorophosphoranes with 8-trimethylsiloxyquinoline [7], and with amines, e.g. pyridine [12], trimethylamine [13], and ammonia [14, 15]. They are typical of hexacoordinate (λ^6) phosphorus. J(PF) coupling constants of 843, 756, and 769 Hz were observed. They were assigned by comparison with the values obtained from the ^{19}F NMR spectrum, as follows: $^1J(PF_A)$ 843 Hz; $^1J(PF_B)$ 769 Hz; $^1J(PF_C)$ 756 Hz.

The ^{19}F and ^{31}P NMR spectra observed experimentally were precisely reproduced by a computer simulation. The simulated NMR spectra are displayed together with the experimental spectra (Figures 1 and 2).

Since compound **4** displays dynamic behavior in solution, a single-crystal X-ray investigation was conducted in order to confirm the proposed structure.

The crystal structure determination (Figure 3) confirms the octahedral coordination at the phosphorus atom; the least ideal angle is F(3)—P—F(4) 173.8°. The P—N(2) bond is very long at 196.5 pm (cf. P—N(1) 172.5 pm) and the P—F bond trans to N(2) is the shortest at 160.4 pm. The coordination at N(1) deviates appreciably from planar; N(1) lies 33 pm out of the plane C(1), C(3), P (sum of angles at N(1): 333.9°). The five membered chelate ring

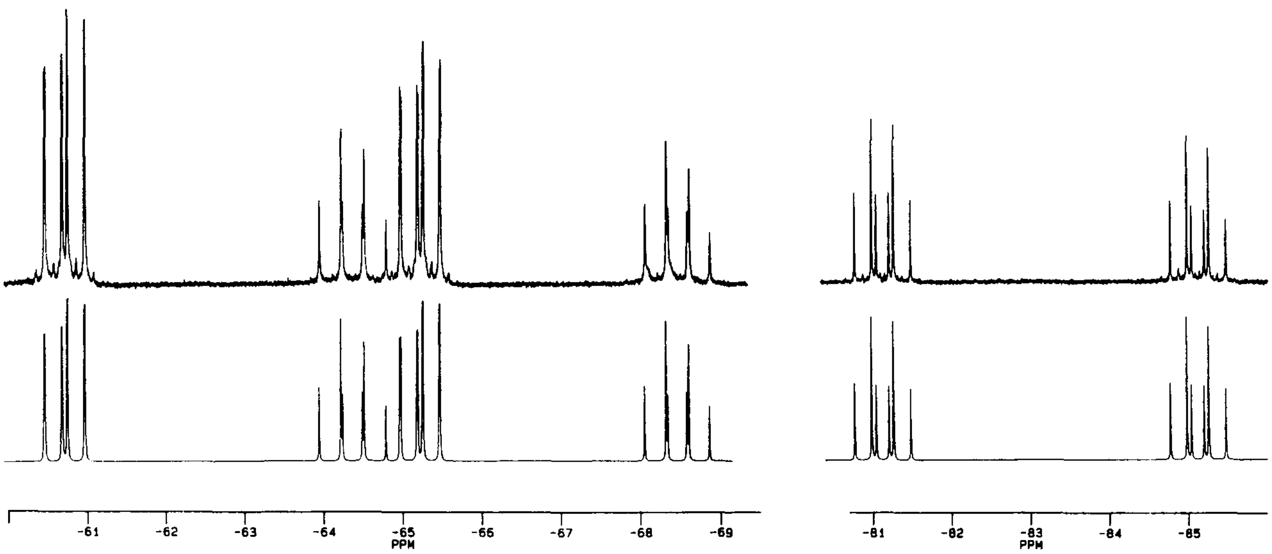


FIGURE 1 Temperature Dependent ^{19}F NMR Spectra of **4**. (Top: ^{19}F NMR spectra of **4** observed at −30°C; bottom: calculated ^{19}F NMR spectra of **4**.)

adopts an envelope conformation, with C(2) 61 pm out of the plane of the other atoms.

EXPERIMENTAL

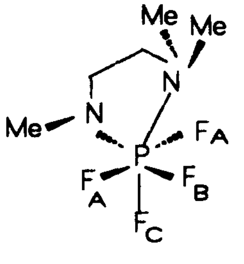
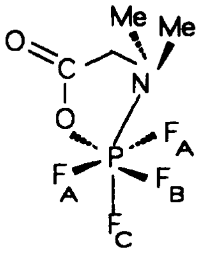
The reactions of **1** with **2** or **3** were conducted, with exclusion of moisture, in sealed systems in an atmosphere of dried nitrogen (BASF BTS catalyst). Solvents were dried by standard procedures [16].

NMR spectra: Spectrometer BRUKER AC 200 (^{1}H at 200.1 MHz; ^{13}C at 50.3 MHz; ^{19}F at 188.0 MHz; ^{31}P at 81.3 MHz). Reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C); $CFCl_3$ ext. (^{19}F), and 85% H_3PO_4 ext. (^{31}P). High field shifts were given negative, low field shifts positive signs. For the simulation of the NMR spectra the program PANIC (BRUKER) was used.

Mass spectrum: Spectrometer FINNIGAN MAT 8430; E.I. at 70 eV.

Materials: The silylated trimethylethylenediamine, $Me_2NCH_2CH_2N(Me)SiMe_3$ [17], and dimethylaminotetrafluorophosphorane [18] were synthesized according to procedures reported in the

TABLE 1 ^{19}F NMR Data of *N,N,N'*-trimethylethylenediaminetetrafluorophosphate, **4**, and 2-(N,N-dimethylamino)acetoxytetrafluorophosphate, **5**

 **4**		 **5**
δ F(A) = −62.4	(ddd),	δ F(A) = −65.8,
δ F(B) = −66.3	(ddt),	δ F(B) = −76.8,
δ F(C) = −82.5	(ddt).	δ F(C) = −81.4.
J(F(A)P) = 843 Hz,		J(F(A)P) = 851 Hz,
J(F(B)P) = 769 Hz,		J(F(B)P) = 840 Hz,
J(F(C)P) = 758 Hz.		J(F(C)P) = 751 Hz.
^2J(F(A)F(B)) = 55 Hz,		^2J(F(A)F(B)) = 69 Hz,
^2J(F(A)F(C)) = 41 Hz,		^2J(F(A)F(C)) = 47 Hz,
^2J(F(B)F(C)) = 51 Hz.		^2J(F(B)F(C)) = 65 Hz.

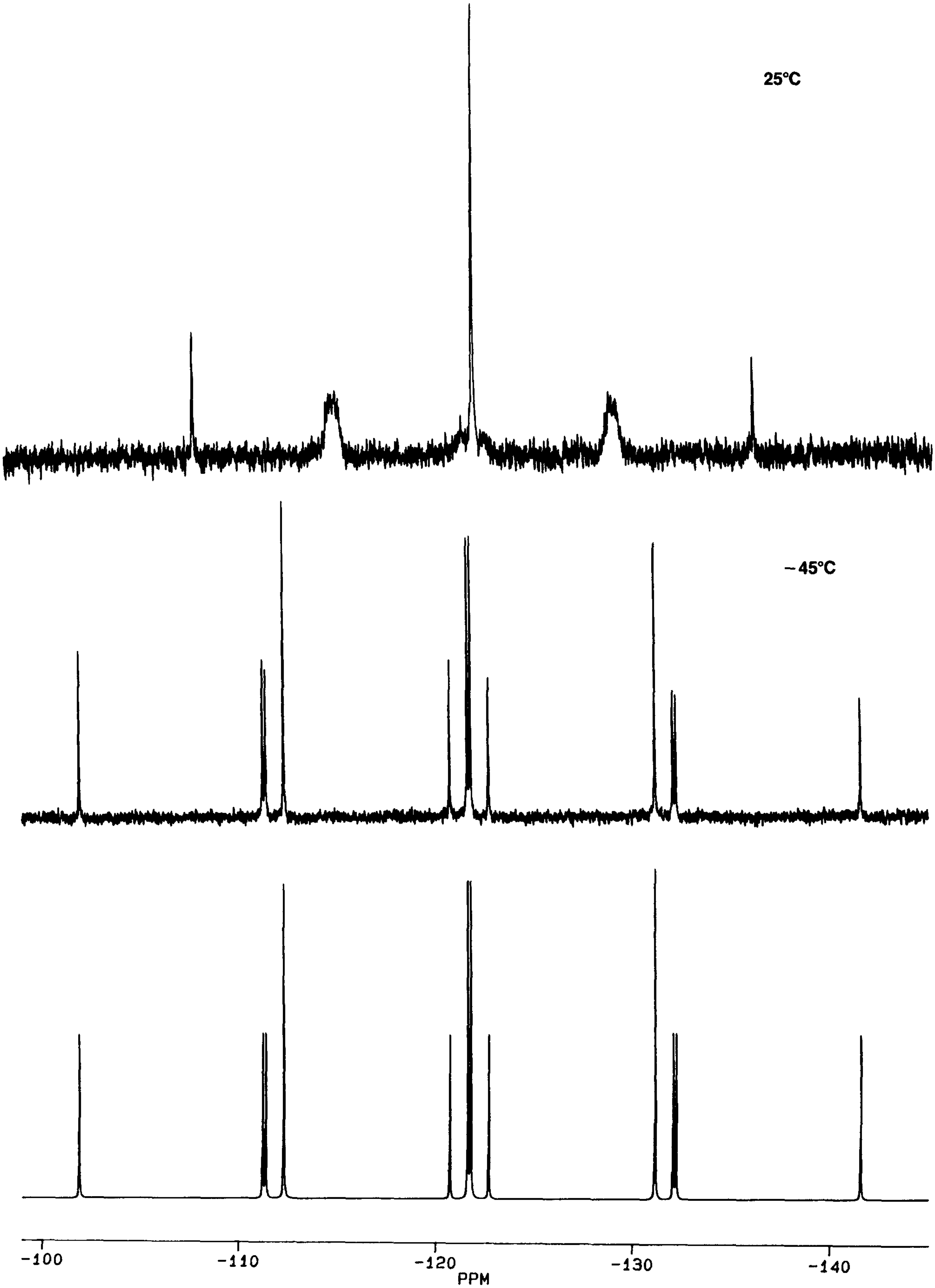


FIGURE 2 Temperature Dependent ^{31}P NMR Spectra of **4**. (Top: ^{31}P NMR spectra of **4** at room temperature and −45°C, respectively; bottom: calculated ^{31}P NMR spectra of **4**.)

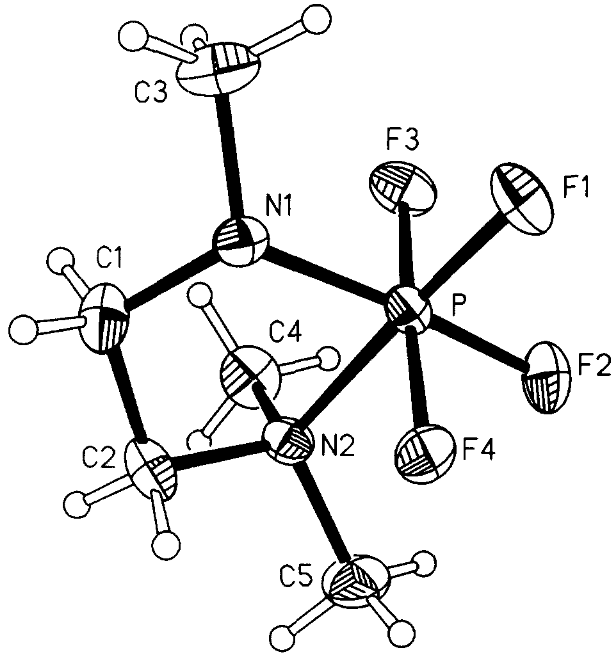


FIGURE 3 The Molecule of Compound **4** in the Crystal, Showing the Atom Numbering Scheme. Thermal ellipsoids represent 50% probability limits. H atom radii are arbitrary.

literature. *N*-morpholinotetrafluorophosphorane is new, and the compound was synthesized as described in the following.

Reaction of N*-Trimethylsilylmorpholine,* **6** *with* PF_5*: Synthesis of* N*-Morpholinotetrafluorophosphorane,* **3**

A solution of *N*-trimethylsilylmorpholine, **6** (Aldrich Chemical Co.) (15.1 g; 0.095 mole) in 40 mL of dichloromethane was cooled to −196°C. After condensation of 12.0 g (0.095 mole) of PF_5 onto this solution the temperature of the reaction mixture was raised to room temperature within 30 min. The mixture was stirred magnetically at room temperature. Subsequently all products volatile at reduced pressure (40 mm) were pumped off. The remaining oily liquid product was distilled in vacuo; bp 55°C (32 mm); Yield 12.5 g (68%).

^{1}H-NMR spectrum in $CDCl_3$ (200.1 MHz): δ 3.42 (m, $N(CH_2CH_2)_2$); δ 3.65 (m, $O(CH_2CH_2)_2$). ^{31}P NMR spectrum in $CDCl_3$ (81.0 MHz): δ −73.18 (Quintet, $^1J(PF) = 855$ Hz). $C_4H_8F_4NOP$ (193.08): Found: C, 24.56; H, 4.11; F, 38.7. Calcd. C, 24.88; H, 4.18; F, 39.4.

Reaction of $Me_2NCH_2CH_2N(Me)SiMe_3$*,* **1** *with* **2***: Synthesis of* $Me_2\overline{NCH_2CH_2N(Me)P}F_4$*,* **4**

To a solution of 5.7 g (0.038 mole) of **2** in 30 mL of dichloromethane a solution of 6.57 g (0.038 mole) of **1** in 20 mL dichloromethane was added dropwise with stirring over 30 min. Stirring at room temperature was continued for another 30 min. Subsequently, volatile products were pumped off in vacuo (0.1 mm). The remaining colorless solid was recrystallized from diethyl ether/dichloromethane (4:1), mp 103°C (without dec.); Yield 6.0 g (75.5%). $C_5H_{13}F_4N_2P$ (208.14): Found, C 28.74, H 6.30; F 36.50; calc., C 28.85, H 6.30; F 36.51.

^{1}H NMR spectrum in CD_2Cl_2 (200.1 MHz, 25°C): δ 2.51 (dt, $CH_2N(CH_3)P$, $^3J(PH) = 17.18$ Hz); δ 2.71 (dquin, $(CH_3)_2N$, $^3J(PH) = 6.13$ Hz, $^4J(FH) = 1.50$ Hz); δ 2.80–3.05 (m, CH_2CH_2). ^{13}C NMR spectrum in CD_2Cl_2 (50.3 MHz, −30°C): δ 38.34 (d, $CH_2N(CH_3)P$, $^2J(PC) = 5.72$ Hz); δ 45.19 (m, $CH_2N(CH_3)P$); δ 48.91 (d, $(CH_3)_2N$, $^2J(PC) = 10.71$ Hz); δ 56.86 (d, $(CH_3)_2NCH_2$, $^2J(PC) = 14.85$ Hz). ^{31}P NMR spectrum in CD_2Cl_2 (81.3 MHz, −45°C): δ −121.86 (ddt, $^1J(PF_A) = 843.1$ Hz, $^1J(PF_B) = 769.2$ Hz, $^1J(PF_C) = 756.3$ Hz).

MS (*m/e*): 209 (M^+ + H, 3%); 189 (M^+ − F, 8%); 58 (Me_2NCH_2, 100%); 44 (Me_2N, 32%).

X-Ray Structure Analysis: 1) Crystal Data: $C_5H_{13}F_4N_2P$, $M_r = 208.15$, Orthorhombic, $Pna2_1$, $a = 1227.1(6)$, $b = 635.8(4)$, $c = 1082.1(6)$ pm, $U = 0.8442$ nm^3, $Z = 4$, $D_x = 1.64$ Mg*m^{-3}, λ(Mo Kα) = 71.069 pm, $\mu = 0.33$ mm^{-1}, $F(000) = 432$, $T = -95$°C.

2) Data Collection and Reduction: A colorless prism (ca. 0.8 × 0.5 × 0.4 mm) was mounted on a glass fiber in inert oil and rapidly transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment). A quadrant of data ($+h + k \pm l$, 1935 reflections) were collected to $2\Theta_{max}$ 55° with monochromated Mo Kα radiation. 1832 reflections with $F > 4\sigma(F)$ were used for all calculations (program system "Siemens SHELXTL Plus"). The orientation matrix was refined from setting angles of 46 reflections in the range 2Θ 20–25°.

3) Structure Solution and Refinement: The structure was solved by routine direct methods and

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (pm^2) for Compound **4**

	x	*y*	*z*	*U*(eq)[a]
P	3703.1(3)	1979.6(5)	5000	197(1)
F(1)	2960(1)	657(2)	5931(1)	347(3)
F(2)	4641(1)	194(1)	5059(1)	336(3)
F(3)	4331(1)	3099(2)	6152(1)	313(3)
F(4)	3202(1)	733(2)	3828(1)	263(3)
N(1)	2762(1)	3964(2)	4855(1)	221(3)
N(2)	4625(1)	3448(2)	3802(1)	216(4)
C(1)	3023(1)	5589(3)	3959(2)	291(5)
C(2)	3823(1)	4688(3)	3049(2)	286(5)
C(3)	2272(2)	4847(3)	5970(2)	369(6)
C(4)	5438(2)	4917(3)	4377(2)	327(5)
C(5)	5253(2)	2033(3)	2952(2)	361(6)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3 Bond Lengths (pm) (Libration-Corrected Bond Lengths in Brackets) and Angles (°) in **4**

P—F(1)	159.8 (1)	(160.4)	P—F(2)	161.8 (1)	(162.5)
P—F(3)	162.9 (1)	(163.7)	P—F(4)	161.8 (1)	(162.5)
P—N(1)	171.7 (1)	(172.5)	P—N(2)	195.7 (2)	(196.5)
N(1)—C(1)	145.3 (2)	(145.9)	N(1)—C(3)	146.0 (2)	(146.7)
N(2)—C(2)	150.2 (2)	(150.8)	N(2)—C(4)	150.1 (2)	(150.8)
N(2)—C(5)	150.0 (3)	(150.7)	C(1)—C(2)	150.4 (2)	(151.0)

F(1)—P—F(2)	90.7(1)	F(1)—P—F(3)	91.0(1)
F(2)—P—F(3)	86.6(1)	F(1)—P—F(4)	91.1(1)
F(2)—P—F(4)	87.6(1)	F(3)—P—F(4)	173.8(1)
F(1)—P—N(1)	93.5(1)	F(2)—P—N(1)	175.9(1)
F(3)—P—N(1)	93.8(1)	F(4)—P—N(1)	91.9(1)
F(1)—P—N(2)	176.6(1)	F(2)—P—N(2)	87.1(1)
F(3)—P—N(2)	91.4(1)	F(4)—P—N(2)	86.2(1)
N(1)—P—N(2)	88.7(1)	P—N(1)—C(1)	115.8(1)
P—N(1)—C(3)	118.9(1)	C(1)—N(1)—C(3)	111.6(1)
P—N(2)—C(2)	103.4(1)	P—N(2)—C(4)	114.0(1)
C(2)—N(2)—C(4)	109.5(1)	P—N(2)—C(5)	114.6(1)
C(2)—N(2)—C(5)	108.6(1)	C(4)—N(2)—C(5)	106.6(1)
N(1)—C(1)—C(2)	108.1(1)	N(2)—C(2)—C(1)	105.8(1)

subjected to anisotropic full-matrix least-squares refinement on F. H atoms were included using a riding model. The absolute structure was determined by an η refinement, with $\eta = +0.93(21)$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$. An extinction correction of the form $F_{corr} = F/(1 + \kappa F^2/\sin 2\Theta)^{0.25}$ was applied; κ refined to $3.8(5) \times 10^{-6}$. The final R value was 0.0225, with R_w 0.027, for 118 parameters; $S = 1.24$; max. $\Delta/\sigma = 0.001$; max. $\Delta\rho = 0.55 \times 10^{-6}$ e pm^{-3}. Final atomic coordinates are given in Table 2, with derived bond lengths and angles in Table 3.

A rigid-body libration correction was performed ($R_{lib} = 0.06$).

Further details of the structure determination (H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54962.

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