Preparative and Structural Studies of Diazadiphosphetidines. Part 9.[1] *X*-Ray and Nuclear Magnetic Resonance Investigations of $(Ph_2FPNMe)_n$

By **Robin K. Harris** and **Mohamed I. M. Wazeer**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Ottfried Schlak and **Reinhard Schmutzler**,* Lehrstuhl B für Anorganische Chemie der Technischen Universität, 33 Braunschweig, Pockelstraße 4, Germany
William S. Sheldrick, Gesellschaft für Biotechnologische Forschung mbH, 33 Braunschweig-Stöckheim, Mascheroder Weg 1, Germany

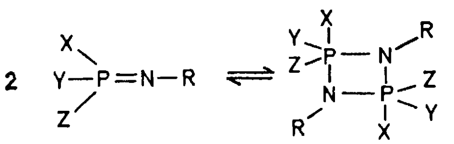
It has been established by *X*-ray and n.m.r. analyses that the compound $(Ph_2FPNMe)_n$ can be prepared as a dimer with a diazadiphosphetidine ring. The ^1H spectrum of the NMe group may be explained in terms of a slow pseudorotation between two conformations. The two values of $^3J_{PH}$ (16.78 and 6.17 Hz) are considerably different, and involve coupling paths through axial and equatorial P–N bonds. Crystals of $(Ph_2FPNMe)_2$ are triclinic, space group $P\bar{1}$, with $a = 9.849(2)$, $b = 14.858(3)$, $c = 8.236(1)$ Å, $\alpha = 93.53(2)$, $\beta = 94.70(2)$, $\gamma = 104.04(2)°$, $Z = 2$. There are two independent crystallographically centrosymmetric molecules within the unit cell. Distorted trigonal-bipyramidal co-ordination is observed at phosphorus with mean bond lengths; P–F 1.683(3), P–N_{eq} 1.652(3), P–N_{ax} 1.780(1), and P–C 1.835(4) Å. The structure was solved by direct methods and refined to R 0.063 for 3 299 diffractometer-measured unique reflections.

THE reaction of phosphorus pentafluoride and some of its substituted derivatives, $R^1_nPF_{5-n}$ (R^1 = hydrocarbon group; $n = 1$ or 2), with *N*-substituted hexamethyldisilazanes, $R^2N(SiMe_3)_2$, has been shown to give rise to the new class of phosphoranes, the 1,3-diaza-2,4-diphosphetidines (see, *e.g.* refs. 2—6), *i.e.* reaction (1). However,

$$2\ R^1_nPF_{5-n} + 2\ R^2N(SiMe_3)_2 \longrightarrow (R^1_nF_{3-n}PNR^2)_2 + 4\ Me_3SiF \quad (1)$$

the reaction of diphenyltrifluorophosphorane, Ph_2PF_3, with heptamethyldisilazane, $MeN(SiMe_3)_2$, in particular, was found [5,6] to give a monomeric fluorophosphine imide, Ph_2FPNMe, instead of the expected dimer, $(Ph_2FPNMe)_2$. The identity of this fluorophosphine imide has been established by a determination of its molecular weight [5,6] and, especially, from an *X*-ray structure determination [7,8] of the monoclinic crystals. It has been found to be impossible, in more recent work,[9] to repeat the earlier preparation [5,6] of Ph_2FPNMe, and the dimer has invariably been observed. Furthermore, it has become apparent that the n.m.r. data originally reported for the compound shown to be Ph_2FPNMe from its crystal structure determination,[5,6] are those of the dimer, $(Ph_2FPNMe)_2$, as will be shown.

The question arises, therefore, if there is a possibility of interconversion of phosphine imide monomers and dimers, with an equilibrium of the type shown in reaction



(2)

(2) being established. No clear evidence for the equilibrium (2) could be obtained for fluorophosphine imides. Attempted pyrolysis of fluorodiazadiphosphetidines, monitored by high-temperature ^{19}F n.m.r. spectroscopy, for example, was found to lead to irreversible changes, usually redistribution of groups at five-co-ordinate phosphorus.[9] A monomer–dimer equilibrium has been postulated [10,11] for a number of chlorophosphine imides, especially of aniline derivatives of type $Cl_3P{:}NAr$, and the stability of monomers, relative to dimers, has been discussed both in terms of the basicity of the aniline, $ArNH_2$, and of steric effects, *e.g.* in the case of *ortho*-substituted anilines.[11]

It may be noted that the chloro-analogue, $(Ph_2ClPNMe)_2$ ($\delta_P - 22.3$ p.p.m.), of our diphenylfluorophosphine imide dimer has been synthesized from diphenylchlorophosphine and methyl azide.[12] Reaction of the chlorophosphorane Ph_2PCl_3 with aniline hydrochloride in the melt has furnished [13] a monomeric $Ph_2ClPNPh$ ($\delta_P + 14$ p.p.m.), while no defined product was obtained when Ph_2PCl_3 and $MeNH_3Cl$ were fused together.[13]

In summary, it would appear that subtle effects, as yet unrecognised, are operative in the interconversion of halogenophosphine imides to the corresponding dimers.

N.m.r. and *X*-ray evidence for the dimeric nature, $(Ph_2FPNMe)_2$, of the product of the reaction of Ph_2PF_3 with $MeN(SiMe_3)_2$ is now given.

N.M.R. Spectra.—The compound is not very soluble, and hence good ^{19}F and ^{31}P spectra were not available when the sample was first prepared.[5,6] The ^1H n.m.r. spectrum (Figure 1 shows a spectrum recorded during the more recent work) appeared to be difficult to interpret on the basis of either monomeric or dimeric structures.

Recently, however, further n.m.r. information has become available which throws light on the structure of the compound. First, the compound $(Me_2FPNMe)_2$

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has been prepared and examined by n.m.r.[14] It is certain that this compound is a dimer. Its ^1H n.m.r. spectrum (NMe region) bears a very close resemblance indeed to that of $(Ph_2FPNMe)_n$. Secondly, improved instrumentation (including facilities for noise decoupling of the protons) has allowed the ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ spectra of a fresh sample of the phenyl compound to be recorded (Figure 2). These spectra can be readily seen to be characteristic of an $[AX]_2$ spin system, as expected for the dimeric formulation.

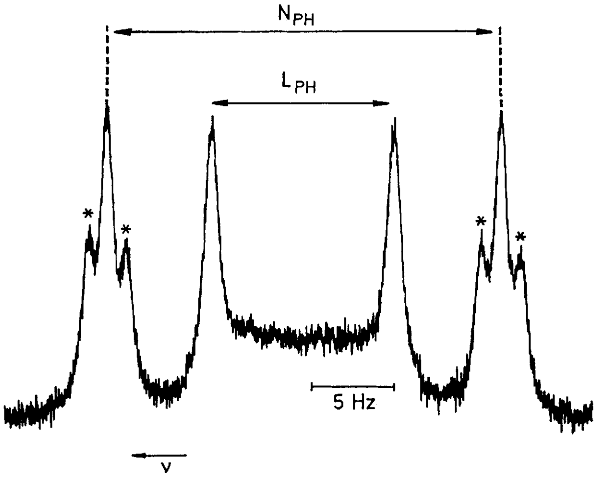


FIGURE 1 Observed 100 MHz ^1H spectrum for the NMe region of $(Ph_2FPNMe)_2$. *N* lines are indicated by asterisks

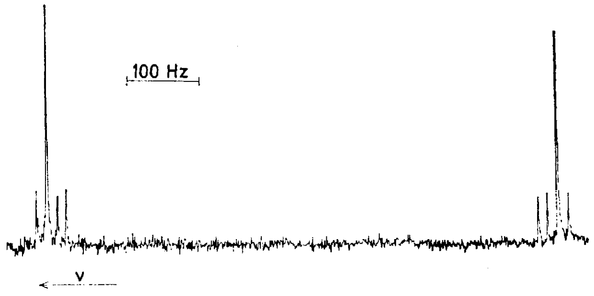


FIGURE 2 Observed 40.5 MHz ^{31}P-$\{^1H\}$ n.m.r. spectrum of $(Ph_2FPNMe)_2$

The ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ n.m.r. spectra were recorded at 94.155 and 40.5 MHz with Varian HA 100 and XL 100 spectrometers, respectively, as described earlier,[4] in the continuous-wave frequency-sweep mode with ^1H noise decoupling. The ^1H n.m.r. spectrum was obtained by use of the HA 100 spectrometer at 99.90 MHz. Both spectrometers were used at ambient probe temperature (*ca.* 35 °C). The compound was dissolved in $CDCl_3$. Tetramethylsilane and $CFCl_3$ were added to separate 5-mm n.m.r. tubes to provide field–frequency locks and references for the ^1H and ^{19}F work, respectively. The ^{31}P work was done by use of a 12-mm n.m.r. tube. The ^2H signal of the $CDCl_3$ provided the lock, and the ^{31}P shifts were calculated indirectly, as outlined previously.[14]

The n.m.r. parameters obtained from the ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ spectra are given in Table 1. The signs of the coupling constants and the assignments of $^2J_{PP}$ and $^4J_{FF}$ are taken from the earlier work on the methylated fluorodiazadiphosphetidines.[14] The spectral analysis yields the fact that the signs of $^1J_{PF}$ and $^3J_{PF}$ are the same. The data are comparable to the corresponding results for $(Me_2FPNMe)_2$, as shown in Table 1. Although there is a substantial difference between the two values of $^1J_{PF}$, the remaining parameters are all as close as may be expected (the chemical shifts and coupling constants are all known to be very sensitive to the nature and extent of substitution). The n.m.r. parameters, as well as the spin system itself, show clearly that the compound is the dimer $(Ph_2FPNMe)_2$.

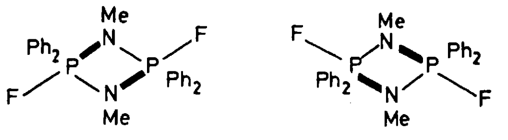
TABLE 1

^{19}F and ^{31}P n.m.r. parameters[a] for $(Ph_2FPNMe)_n$, compared to those for $(Me_2FPNMe)_2$

Parameter	$(Ph_2FPNMe)_n$	$(Me_2FPNMe)_n$
δ_F/p.p.m.[b]	-23.61 ± 0.01	-21.88
$^1J_{PF}$/Hz[c]	-689.2	-636.7
$^2J_{PP}$/Hz[c]	28.0	23.0
δ_P/p.p.m.[b]	-64.3 ± 0.2	-59.3
$^3J_{PF}$/Hz[c]	-5.8	-5.5
$^4J_{FF}$/Hz[c]	12.5	14.0

[a] From ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ double-resonance spectra. [b] With respect to the signals of internal $CFCl_3(\delta_F)$ and external 85% H_3PO_4 (δ_P): in each case a negative sign means the reference resonates to high-frequency of the sample. [c] Accurate to ±1.0 Hz.

We believe we now understand the curious ^1H spectrum illustrated in Figure 1*. Its appearance may be explained if the two NMe groups are chemically but not magnetically equivalent. If this is the case the appropriate spin system (ignoring the phenyl protons) is $[AMX_3]_2$, not $[AM]_2X_6$, where A = ^{31}P, M = ^{19}F, and X = ^1H. Such a system can arise because there are two isomers, (A) and (B), based on the diazadiphosphetidine structure previously established (see ref. 15 and refs. therein). For a given phosphorus atom one of the two N–P bonds will be axial and one equatorial, giving the following possibilities if the axial N–P bonds for the two P atoms are transoid:



Isomer (A) Isomer (B)

Axial N–P bonds are shown thicker

The interchange of analogous isomers for compounds of the type $(RF_2PNMe)_2$ has been discussed previously.[15] Our explanation of the ^1H n.m.r. spectrum of $(Ph_2FPNMe)_2$ indicates that the pseudorotation exchange

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* This was described earlier,[6] in an oversimplified fashion, as a doublet of doublets, with splittings *J* 17.4 and 6.3 Hz incorrectly assigned as J_{PH} and J_{FH} for the supposed monomeric species.

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$A \rightleftharpoons B$ is slow on the n.m.r. timescale at ambient probe temperature. Further evidence about this exchange for other compounds of the type $(R_2FPNMe)_2$ will be published later. Here we merely note that it involves intermediates with at least one R group axial, and is therefore likely to be a relatively high-energy process. Fast exchange would lead to an $[AM]_2X_6$ spin system. Slow exchange gives an $[AMX_3]_2$ system. In both cases proton decoupling would give ^{19}F and ^{31}P spectra characteristic of the simple $[AX]_2$ system, and these spectra, therefore, do not distinguish between the two exchange situations. However, only the $[AMX_3]_2$ case fits the observed ^1H spectrum, which may be explained as follows.

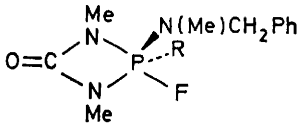
It may be assumed that the long-range (H,H) coupling constant, J_{XX}, is negligibly small and that $|J_{AM}|$ ($\equiv|^1J_{PF}|$) is much larger than any other coupling constant. The X spectrum may be discussed in terms of subspectra. When both fluorine nuclei are α (or both β) there is an $[ax_3]_2$ subsystem; correspondingly, when both phosphorus nuclei are α or both β there are $[mx_3]_2$ subsystems. Such systems with $J_{xx} = 0$ are well-known.[16] In the present instance there will be pairs of strong lines separated by $|N_{AX} + N_{MX}|$ and $|N_{AX} - N_{MX}|$ (where the parameters N are the sums of the appropriate long- and short-range coupling constants). The value of N_{AX} will be the sum of two three-bond (P,H) coupling constants, these being across axial and equatorial P–N bonds respectively. Thus N_{AX} is likely to be appreciable, whereas N_{MX}, which involves two values of $^4J_{FH}$, is expected to be much smaller. In fact the $[mx_3]_2$ subspectra are deceptively simple since $|J_{PP}| \gg |L_{FH}|$ (where L_{FH} is the difference in the two values of $^4J_{FH}$), giving the triplets at each end of the spectrum. The four N lines are thus the outer lines of these triplets, and immediately yield values for $|N_{FH}|$ and $|N_{PH}|$.

Because $|^1J_{PF}|$ is very large, the four types of spin state with zero spin-components for both the ^{31}P and the ^{19}F nuclear spin pairs (*i.e.* with basic product wavefunctions for PP'FF' $\alpha\beta\beta\alpha$, $\beta\alpha\alpha\beta$, $\alpha\beta\alpha\beta$, and $\beta\alpha\beta\alpha$) do not appreciably mix. They therefore give rise to 'first-order' pairs of lines separated by $|L_{AX} + L_{MX}|$ and $|L_{AX} - L_{MX}|$, where the parameters L are the differences of the appropriate long- and short-range coupling constants. Since L_{FH} is small, these four lines merge to give the two innermost peaks of Figure 1, the separation of which is therefore $|L_{PH}|$. The remaining lines (the so-called χ lines of the $[ax_3]_2$ subspectra[16]) will be appreciably weaker, though *in toto* constituting one quarter of the total intensity, than the lines already discussed. Moreover, the phenyl protons, ignored in the foregoing, will not[17,18] affect the N lines or L lines but will split or broaden the χ lines. Thus it is considered that the $[ax_3]_2$ χ lines form the broad background between the L lines. The curious appearance of the ^1H NMe spectrum of $(Ph_2FPNMe)_2$ is thus fully explained and is, of course, consistent with a dimeric but not a monomeric structure.

The appropriate ^1H n.m.r. parameters are: δ_H(NMe) 2.308, δ_H(PPh) $\approx$ 7.5 p.p.m.; $|^3J_{PH}|$ values: 16.78 and 6.17 Hz (they are the same sign); $|N_{FH}|$ 2.25 Hz; $|L_{FH}| \leqslant$ 0.6 Hz. The phenyl region of the ^1H spectrum does not yield well-defined parameters. The values of δ_H are relative to tetramethylsilane.

The striking variation between the two values of $^3J_{PH}$ is evidence for a big difference between the coupling paths, such as might be expected if the molecule is fixed in one of the conformations A or B so that one P–N bond is axial and the other equatorial.

We tentatively assign the smaller $^3J_{PH}$ to the coupling path involving an axial P–N bond, by reference to data[19] for compounds of type (I; R = Me or Ph), which give values of $^3J(PNCH_3)$ of magnitudes *ca.* 14, 7, and 12 Hz.



(I)

The 12 Hz coupling is assigned to the $N(Me)CH_2Ph$ side-chain, which must be equatorial, making it likely that the 14 Hz value is for equatorial and the 7 Hz coupling for axial NMe. The reasoning is not, however, definitive. The average value of $^3J_{PH}$ for $(Ph_2FPNMe)_2$, (12.0 Hz), is in the same range as those (10.9—12.5 Hz) reported[20] for compounds of the type $(RF_2PNMe)_2$ (R = Me, Et, Pr^i, or Bu^t) for which pseudorotation is rapid on the n.m.r. timescale at room temperature.

Detailed analysis of the n.m.r. spectra shows unambiguously that the compound under investigation is the dimer, $(Ph_2FPNMe)_2$. Presumably the original ^1H spectra, which appeared as in Figure 1, were also of the dimer, indicating a difference in solubility for the monomer and dimer or an interconversion consequent upon solution.

X-Ray Studies

Intensity data, from a tabular crystal sealed into a Lindemann glass-capillary tube and with dimensions *ca.* 0.22 × 0.04 × 0.16 mm, were collected on a Syntex $P2_1$ four-circle diffractometer by use of graphite-monochromated Mo-K_α radiation. Measurements were carried out in the θ—2θ mode ($3.0° \leqslant 2\theta \leqslant 50.0°$) at scan speeds varying linearly between 2.93° ($\leqslant$150 c/s) and 8.37° min^{-1} ($\geqslant$5 000 c/s). Scan and total background times were equal. Three standard reflections monitored at regular intervals showed no significant variations due to crystal deterioration during data collection. A standard deviation $\sigma(I) = t(N_s + N_b)^{1/2}$ was assigned to each net intensity I, with t being the scan rate, N_s the gross count and N_b the total background count. With the application of the rejection criterion $I \geqslant 2.0\sigma(I)$ and averaging of equivalencies, 3 299 reflections (one half of reciprocal space) were considered to be observed (internal consistency index R 0.010). Lorentz and polarisation but no absorption corrections were applied to the raw intensity data. Accurate unit-cell dimensions were obtained from

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measurements of 15 reflections ($\pm$ *hkl*) measured with Mo-K_α radiation.

TABLE 2

Atom positional parameters

(*a*) Non-hydrogen atom co-ordinates ($\times 10^4$)

	x	*y*	*z*
P(1)	6 095(1)	4 631(1)	221(1)
F(1)	7 652(2)	5 012(1)	1 369(2)
N(1)	5 626(3)	5 587(2)	807(3)
C(1)	6 437(5)	6 433(3)	1 758(5)
C(11)*	5 754(4)	3 578(2)	1 310(4)
C(12)	4 488(4)	3 264(3)	1 981(5)
C(13)	4 267(5)	2 519(3)	2 918(6)
C(14)	5 286(5)	2 042(3)	3 176(6)
C(15)	6 527(5)	2 325(3)	2 486(5)
C(16)	6 764(4)	3 079(3)	1 571(5)
C(21)	7 010(3)	4 519(2)	−1 606(4)
C(22)	8 376(4)	4 382(3)	−1 493(5)
C(23)	9 042(4)	4 274(3)	−2 872(5)
C(24)	8 397(4)	4 312(3)	−4 385(5)
C(25)	7 073(5)	4 473(3)	−4 539(5)
C(26)	6 388(4)	4 567(3)	−3 159(4)
P(2)	−113(1)	863(1)	5 357(1)
F(2)	880(2)	1 744(1)	6 637(2)
N(2)	979(3)	207(2)	5 785(3)
C(2)	2 399(5)	479(3)	6 612(6)
C(31)	−1 630(4)	948(3)	6 466(4)
C(32)	−2 071(5)	1 757(3)	6 567(5)
C(33)	−3 157(5)	1 833(4)	7 448(6)
C(34)	−3 812(5)	1 114(4)	8 277(6)
C(35)	−3 394(5)	292(4)	8 202(6)
C(36)	−2 308(5)	210(3)	7 270(6)
C(41)	106(4)	1 603(3)	3 636(4)
C(42)	520(4)	2 572(3)	3 919(5)
C(43)	680(5)	3 130(3)	2 622(7)
C(44)	442(5)	2 739(4)	1 048(6)
C(45)	44(5)	1 787(4)	750(5)
C(46)	−138(5)	1 255(3)	2 019(5)

(*b*) Hydrogen atom co-ordinates ($\times 10^3$) and isotropic temperature factors ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*
H(11)	585(4)	683(3)	189(5)	62(7)
H(12)	714(4)	676(3)	128(5)	62(7)
H(13)	687(4)	636(3)	276(5)	62(7)
H(121)	382(4)	362(3)	183(4)	47(4)
H(131)	344(4)	237(3)	334(4)	47(4)
H(141)	510(4)	151(3)	379(4)	47(4)
H(151)	718(4)	198(3)	266(4)	47(4)
H(161)	763(4)	326(2)	113(4)	47(4)
H(221)	883(4)	436(2)	−477(4)	47(4)
H(231)	989(4)	415(3)	−271(4)	47(4)
H(241)	881(4)	426(3)	−528(5)	47(4)
H(251)	664(4)	452(3)	−547(4)	47(4)
H(261)	559(4)	473(3)	−329(4)	47(4)
H(21)	300(5)	101(3)	609(5)	82(9)
H(22)	276(5)	−61(3)	675(5)	82(9)
H(23)	234(5)	74(3)	760(6)	82(9)
H(321)	−157(4)	227(3)	595(5)	69(4)
H(331)	−341(5)	238(3)	745(5)	69(4)
H(341)	542(5)	122(3)	887(5)	69(4)
H(351)	−381(4)	−17(3)	887(5)	69(4)
H(361)	795(5)	−30(3)	720(5)	69(4)
H(421)	74(5)	288(3)	493(5)	69(4)
H(431)	94(5)	374(3)	277(3)	69(4)
H(441)	56(4)	315(3)	22(5)	69(4)
H(451)	−20(5)	147(3)	972(5)	69(4)
H(461)	−47(4)	42(3)	171(5)	69(4)

* The first number of each carbon atom is that of the benzene ring to which it belongs.

Crystal Data.—$C_{26}H_{26}N_2F_2P_2$, $M = 466.5$, Triclinic, $a = 9.849(2)$, $b = 14.858(3)$, $c = 8.236(1)$ Å, $\alpha = 93.53(2)$, $\beta = 94.70(2)$, $\gamma = 104.04(2)°$, $U = 1\,161.2(4)$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ (Mo-K_α) = 1.76 cm^{-1}. The centrosymmetric space group $P\bar{1}$ was confirmed by the subsequent successful refinement of the structure.

Structure Solution and Refinement. The structure was solved, assuming space group $P\bar{1}$, by a multisolution technique,[21] in which 2^{20} sign permutations were expanded by the Σ_2 formula. A permutation is rejected in this method if its internal consistency falls at any stage below a preset value. Additionally, a similarity test is applied to avoid the calculation of too many closely similar E maps. In this case, only one E map was computed, which revealed the positions of all 32 heavy atoms in the asymmetric unit. There are two independent diphosphetidine molecules in the unit cell each of which lies about a crystallographic centre of symmetry (0.5,0.5,0 and 0,0,0.5 respectively). The phosphorus, fluorine, nitrogen, and carbon positional parameters, together with their associated anisotropic temperature factor components, were refined by full-matrix least-squares with the function $\Sigma w\Delta^2$ being minimised. At this stage of the refinement, a difference-Fourier synthesis clearly revealed the positions of the hydrogen atoms which were then included, together with group isotropic temperature factors, as parameters in the final cycles of refinement. The terminal value of the generalised index $R_G = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ was 0.054, with a weighted residual $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$ of 0.054 and a corresponding unweighted R of 0.063. The weights applied were given by the expression $w = k/[\sigma^2(F_o) + gF_o^2]$, where k and g refined to 1.9655 and 0.000208 respectively. A final difference-Fourier synthesis revealed one spurious peak 1.83 Å from P(2). Otherwise there were no peaks or troughs of density >0.44 eÅ^{-3}. Complex neutral-atom scattering factors were employed for the non-hydrogen atoms.[22,23] The results from the final least-

TABLE 3

Bond lengths (Å)

P(1)–N(1)$_{eq}$	1.654(3)	P(1)–N(1)$_{ax}$	1.779(3)
N(1)–C(1)	1.456(5)	P(1)–F(1)	1.686(2)
P(1)–C(11)	1.825(4)	P(1)–C(21)	1.835(4)
C(11)–C(12)	1.393(5)	C(12)–C(13)	1.372(6)
C(13)–C(14)	1.373(8)	C(14)–C(15)	1.373(7)
C(15)–C(16)	1.384(6)	C(16)–C(11)	1.388(6)
C(21)–C(22)	1.405(5)	C(22)–C(23)	1.377(6)
C(23)–C(24)	1.363(6)	C(24)–C(25)	1.379(7)
C(25)–C(26)	1.384(6)	C(26)–C(21)	1.386(5)
C(1)–H(11)	0.93(5)	C(1)–H(12)	0.88(4)
C(1)–H(13)	0.92(4)	C(12)–H(121)	0.94(4)
C(13)–H(131)	0.90(4)	C(14)–H(141)	0.95(4)
C(15)–H(151)	0.92(4)	C(16)–H(161)	0.94(4)
C(22)–H(221)	0.92(4)	C(23)–H(231)	0.90(4)
C(24)–H(241)	0.88(4)	C(25)–H(251)	0.86(4)
C(16)–H(261)	0.88(4)		
P(2)–N(2)$_{eq}$	1.649(3)	P(2)–N(2)$_{ax}$	1.780(3)
N(2)–C(2)	1.456(5)	P(2)–F(2)	1.680(2)
P(2)–C(31)	1.839(4)	P(2)–C(41)	1.842(4)
C(31)–C(32)	1.373(6)	C(32)–C(33)	1.363(7)
C(33)–C(34)	1.360(7)	C(34)–C(35)	1.379(8)
C(35)–C(36)	1.391(8)	C(36)–C(31)	1.376(6)
C(41)–C(42)	1.397(8)	C(42)–C(43)	1.388(7)
C(43)–C(44)	1.365(7)	C(44)–C(45)	1.373(8)
C(45)–C(46)	1.375(7)	C(46)–C(41)	1.392(5)
C(2)–H(21)	1.00(4)	C(2)–H(22)	0.96(5)
C(2)–H(23)	0.89(5)	C(32)–H(321)	1.00(4)
C(33)–H(331)	0.97(4)	C(34)–H(341)	0.97(5)
C(35)–H(351)	0.94(4)	C(36)–H(361)	0.86(5)
C(42)–H(421)	0.91(4)	C(43)–H(431)	0.88(4)
C(44)–H(441)	0.94(4)	C(45)–H(451)	0.93(4)
C(46)–H(461)	1.17(4)		

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TABLE 4

Bond angles (°)

F(1)–P(1)–N(1)$_{ax}$	169.3(1)	F(1)–P(1)–N(1)$_{eq}$	90.7(1)
F(1)–P(1)–C(11)	89.1(1)	F(1)–P(1)–C(21)	90.3(1)
N(1)$_{ax}$–P(1)–N(1)$_{eq}$	78.6(1)	N(1)$_{ax}$–P(1)–C(11)	95.6(1)
N(1)$_{ax}$–P(1)–C(21)	96.7(1)	N(1)$_{eq}$–P(1)–C(11)	123.8(2)
N(1)$_{eq}$–P(1)–C(21)	123.3(1)	C(11)–P(1)–C(12)	113.0(2)
P(1)–N(1)$_{eq}$–P(1)′	101.4(1)	P(1)′–N(1)$_{eq}$–C(1)	128.2(3)
P(1)–N(1)$_{eq}$–C(1)	130.1(3)	P(1)–C(11)–C(12)	121.2(3)
P(1)–C(11)–C(16)	121.7(3)	C(12)–C(11)–C(16)	117.0(3)
C(13)–C(12)–C(11)	121.7(4)	C(14)–C(13)–C(12)	120.3(4)
C(15)–C(14)–C(13)	119.4(4)	C(16)–C(15)–C(14)	120.3(5)
C(11)–C(16)–C(15)	121.2(4)	P(1)–C(21)–C(22)	121.5(3)
P(1)–C(21)–C(26)	121.6(3)	C(22)–C(21)–C(26)	116.9(3)
C(23)–C(22)–C(21)	121.2(4)	C(24)–C(23)–C(22)	120.6(4)
C(25)–C(24)–C(23)	119.8(4)	C(26)–C(25)–C(24)	119.8(4)
C(21)–C(26)–C(25)	121.6(4)		
F(2)–P(2)–N(2)$_{ax}$	168.6(1)	F(2)–P(2)–N(2)$_{eq}$	91.0(1)
F(2)–P(2)–C(31)	88.4(1)	F(2)–P(2)–C(41)	90.6(1)
N(2)$_{ax}$–P(2)–N(2)$_{eq}$	78.1(1)	N(2)$_{ax}$–P(2)–C(31)	95.1(1)
N(2)$_{ax}$–P(2)–C(41)	97.9(1)	N(2)$_{eq}$–P(2)–C(31)	125.9(2)
N(2)$_{eq}$–P(2)–C(41)	121.0(2)	C(31)–P(2)–C(41)	113.0(2)
P(2)–N(2)$_{eq}$–P(2)′	101.8(1)	P(2)′–N(2)$_{eq}$–C(2)	128.4(1)
P(2)–N(2)$_{eq}$–C(2)	128.8(1)	P(2)–C(31)–C(32)	121.0(3)
P(2)–C(31)–C(36)	120.2(3)	C(32)–C(31)–C(36)	118.7(4)
C(33)–C(32)–C(31)	121.0(4)	C(34)–C(33)–C(32)	120.7(5)
C(35)–C(34)–C(33)	119.8(5)	C(36)–C(35)–C(34)	119.3(5)
C(31)–C(36)–C(35)	120.5(5)	P(2)–C(41)–C(42)	120.6(3)
P(2)–C(41)–C(46)	121.7(3)	C(42)–C(41)–C(46)	117.7(4)
C(43)–C(42)–C(41)	120.6(4)	C(44)–C(43)–C(42)	120.5(4)
C(45)–C(44)–C(43)	119.6(5)	C(46)–C(45)–C(44)	120.7(4)
C(41)–C(46)–C(45)	120.9(4)		

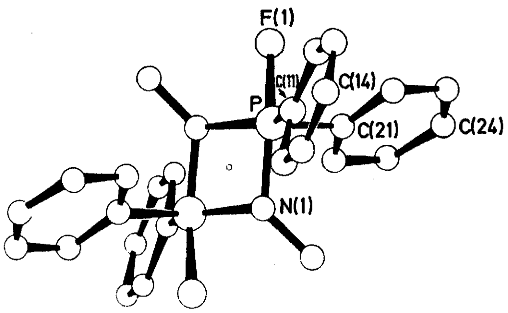

FIGURE 3 Molecule (1) of (Ph$_2$FPNMe)$_2$ in perspective, together with the numbering system used. That in molecule (2) is analogous

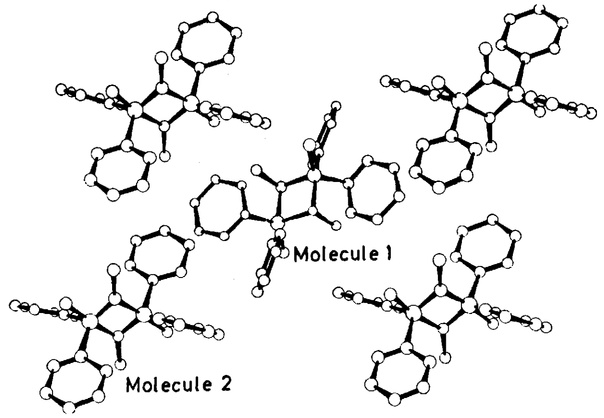

FIGURE 4 Projection of the unit-cell contents perpendicular to [001]

squares cycle, summarised in Table 2, were used, together with the full covariance matrix, to calculate bond lengths and angles, and their estimated standard deviations listed in Tables 3 and 4. Figure 3 shows the molecule in perspective, and Figure 4 the contents of the unit cell projected perpendicular to [001]. Observed and calculated structure factors and anisotropic temperature parameters for non-hydrogen atoms are listed in Supplementary Publication No. SUP 21916 (23 pp., 1 microfiche).*

DISCUSSION

The *X*-ray structure determination confirms that the compound (Ph$_2$FPNMe)$_n$ may be prepared as a dimer with a diazadiphosphetidine ring. Only a triclinic modification was observed, which, as would be expected, exhibits a higher density (1.33 g cm^{-3}) than the monoclinic monomer (1.25 g cm^{-3}). The earlier *X*-ray work by Adamson and Bart [7,8] reported the existence of two types of crystal, of which only the monoclinic form was examined in detail. Whether the triclinic form studied in the present work is identical with that observed by Adamson and Bart [7,8] is, however, unclear, as they reported no information about the relevant unit-cell parameters or density. There are no significant differences between the bond lengths of the two independent molecules in the triclinic unit cell. Small but significant differences are, however, observed in the bond angles, which presumably result from crystal-packing effects.

As in other diphosphetidines,[24-27] a distorted trigonal-bipyramidal geometry is found at phosphorus with a small mean N_{ax}–P–N_{eq} angle of 78.4(3)° necessitated by its inclusion in the four-membered (PN)$_2$ ring. A correlation between the increase in the P–N axial and equatorial bond lengths with decreasing electronegativity of the ligand R in the series (RF$_2$PNCH$_3$)$_2$ (R = F,[24] CCl$_3$,[25] C$_6$F$_5$,[26] Ph [27]) has been noted.[25,26] The coupling constant J_{PP} has also been found [15,26,28] to display a direct relationship to the electronegativity of R (*e.g.* J_{PP} 125 for R = CCl$_3$, 111 for R = C$_6$F$_5$, and 80 Hz for R = Ph). For (Ph$_2$FPNCH$_3$)$_2$ a value of 28.0 Hz was observed for J_{PP}, which is as would be expected upon replacement of a second fluorine by a phenyl substituent. As would be predicted on the basis of simple orbital overlap considerations, a good correlation is observed between the short P · · · P intramolecular distance and J_{PP} in the molecules (R^{1}R^{2}FPNMe)$_2$ [R^1 = F, R^2 = CCl$_3$ 2.579(2), R^2 = C$_6$F$_5$ 2.594(2), R^2 = Ph 2.61; R^1 = R^2 = Ph 2.659(3) Å]. The mean P–N bond lengths [1.780(1) and 1.652(3) Å] for the axial and equatorial nitrogen atoms respectively, are longer than those [1.750(4) and 1.631(4) Å] observed for R = C$_6$F$_5$, but not significantly different from those [1.78(2) and 1.64(2) Å] for R = Ph. However, in view of the large standard deviations associated with this earlier visual determination and the small nature of the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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variations in the bond lengths, these results do not necessarily prejudice the validity of the correlation previously drawn for these molecules. The long mean P–F_{ax} distance [1.683(3) Å] is similar [29] to that [1.685(1) Å] in Me_3PF_2.

It has been predicted, on the basis of symmetry considerations and semiempirical MO calculations, that an equatorial substituent with a single π system will prefer to have its acceptor orbital perpendicular to the equatorial plane or its donor orbital in that plane.[30] The crystal-structure analysis of 2-methyl-5-(tetrafluorophosphoranyl)pyrrole [31] has confirmed that the equatorially substituted pyrrole ring, which behaves as a π donor, does, in fact, lie in the axial plane of the trigonal bipyramid. However, the C_6F_5-groups in $[(C_6F_5)F_2PNMe]_2$ and $(C_6F_5)_3PF_2$ make dihedral angles [26,32] of 23.8 and 33.5—36.2°, with the equatorial plane. This position is obviously dictated by steric necessity on account of interaction between the *ortho*-substituted F atoms of the C_6F_5-groups and the axial F atoms of the trigonal bipyramid. Potential intramolecular contacts should be of lesser importance for equatorially substituted phenyl groups, and therefore their planes would be expected to take up positions much closer to the axial plane in a trigonal bipyramid. Dihedral angles of 71.5, 60.0, 74.3, and 62.1° for the benzene rings, numbered as in Table 2, with their respective equatorial planes of the trigonal bipyramid at phosphorus demonstrate that this does in fact occur. The individual rings make dihedral angles of 52.3 (1 and 2) and 57.8° (3 and 4) with one another.

The determination of the molecular weight of $(Ph_2FPNMe)_2$, by osmometry in benzene (found: 416), although giving a low value (calculated: 466.46), provides further support for the dimeric formulation; for the monomeric fluorophosphine imide, Ph_2FPNMe, a molecular weight of 210 (calc. 233.23) has been observed.[6] The i.r. spectrum of $(Ph_2FPNMe)_2$ was essentially superimposable on that observed for the monomer.[6]

Since there also appears to be no doubt concerning the result of the earlier [7,8] *X*-ray crystal-structure determination of the monomer, Ph_2FPNMe, our present findings can only be rationalized in terms of the existence of two structural isomers, a monomer and a dimer.

EXPERIMENTAL

The usual precautions in handling moisture-sensitive compounds were observed.

Preparation of $(Ph_2FPNMe)_2$.—The reaction of diphenyltrifluorophosphorane [33] with heptamethyldisilazane [34] was conducted in two separate runs, under somewhat differing conditions.

(*a*) A mixture of Ph_2PF_3 (29.8 g, 0.123 mol) and $MeN(SiMe_3)_2$ (21.6 g, 0.123 mol) was heated for 3 h/100 °C in a sealed heavy-walled glass tube. The solid product formed was recrystallised twice from toluene (m.p. 225—228 °C).

(*b*) A mixture of Ph_2PF_3 (6.6 g, 0.027 mol) and $MeN(SiMe_3)_2$ (4.8 g, 0.027 mol) was allowed to react at atmospheric pressure, in a round-bottom flask fitted with a reflux condenser which was topped by a drying tube. After heating (3 h, 120—130 °C) the product formed was recrystallised twice from toluene (46%; m.p. 227—229 °C).

For the monomer Ph_2FPNMe a m.p. 144—146.5 °C has been observed.[6] The mass spectrum of the dimer showed a fragmentation pattern typical of diazadiphosphetidines.[35] A molecular ion (*ca.* 3%) was found at *m/e* 466 (calc. 466.46). The transition $M]^+ \longrightarrow M/2 + 1]^+$ is established from the observation of a metastable signal.

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