# Phosphorus–Fluorine Chemistry. Part XXXVII.[1] Preparation and Crystal and Molecular Structure of the Product of the Reaction of Tetrafluoro(phenyl)phosphorane with 2-Methyl-8-trimethylsiloxyquinoline

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Tetrafluoro(phenyl)phosphorane reacts with 2-methyl-8-trimethylsiloxyquinoline to yield an intramolecular complex (2b) $F_3PhP(oxMe)$ (oxMe = 2-methyl-8-hydroxyquinoline), containing an N→P co-ordinate bond. Crystals of the complex are orthorhombic, space group *Pnam*, with $a = 21\cdot672(6)$, $b = 9\cdot451(3)$, $c = 6\cdot816(2)$ Å $Z = 4$. The phenyl group bonded to phosphorus is situated opposite the N→P co-ordinate bond. The molecule possesses a crystallographic plane of symmetry with the oxMe grouping lying in the mirror plane and perpendicular to the benzene ring. Considerable distortion from perfect octahedral co-ordination is observed at phosphorus with the P–O and P–F bonds being displaced away from the P–C bond at angles of 92·1, 95·5, and 93·5(1)°. The N→P co-ordinate bond length is 1·980(3) Å. The structure was solved by Patterson and Fourier methods and refined to R 0·040 for 986 diffractometer measured unique reflections.

WE have described previously [2] the reaction of PF_5 and some of its monosubstituted derivatives, RPF_4 (R = Me, Et, or Ph), with 8-trimethylsiloxyquinolines, which invariably yields not the expected monosubstituted phosphorane derivatives (1) but intramolecular donor–acceptor complexes of type (2) (R^1 = F, Me, Et, or Ph; R^2 = H or Me).

(2a) R^1 = F, R^2 = Me
(2b) R^1 = Ph, R^2 = Me
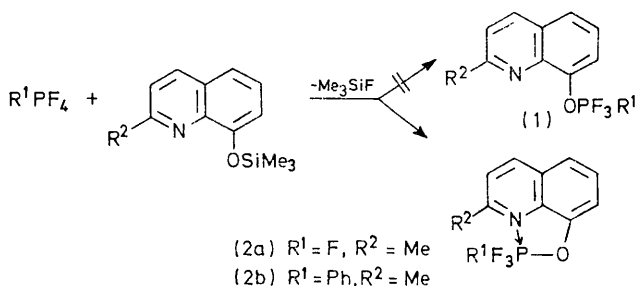
The stereochemistry of complexes of type (2) has been studied by ^{19}F and ^{31}P n.m.r. spectroscopy and, in addition, for (2a) the molecular structure has been confirmed by single-crystal X-ray diffraction.[2] In some cases, however, owing to the very poor solubility of the products, n.m.r. spectra could not be observed, as for *e.g.* (2b), the concentration of a saturated solution in acetonitrile at 25 °C being only *ca.* 0·04 mol l⁻¹. Three isomers are conceivable for this molecule, namely with the phenyl group opposite either nitrogen, oxygen, or fluorine in the co-ordination octahedron at phosphorus. In order to distinguish between these possible isomers, the molecular structure of (2b) has been determined by single-crystal X-ray diffraction. An additional objective of this work was to compare the N→P co-ordinate bond length in (2b) with that in $F_4P(oxMe)$, in which F_4PO displays stronger Lewis-acid acceptor properties than the PhF_3PO grouping.

EXPERIMENTAL

Preparation.—The usual precautions required in the handling of moisture-sensitive compounds were observed when $PhPF_4$ (ref. 3) (6·0 g, 0·032 mol) was added, by use of a syringe, to 2-methyl-8-trimethylsiloxyquinoline [2] (7·5 g,

0·032 mol) at liquid nitrogen temperature in a heavy-walled glass tube, which was subsequently sealed under vacuum. The temperature of the reaction mixture was slowly raised to 25 °C and maintained at 90—100 °C for 24 h to give fluorotrimethylsilane (90%), and light yellow crystals (7·5 g, 72%) of (2b) (m.p. 253 °C) which were recrystallised from acetonitrile (Found: C, 59·5; H, 4·9; P, 10·3%; M (mass spectrometry), 323. $C_{16}H_{13}F_3NOP$ requires C, 59·45; H, 4·05; P, 9·60%; M, 323·3).

X-Ray Diffraction.—A prismatic crystal of (2b), *ca.* $0\cdot20 \times 0\cdot20 \times 0\cdot45$ mm, was sealed in a Lindemann glass capillary tube. Intensity data were collected on a Philips PW 1100 four-circle diffractometer by use of graphite monochromated Mo-K_α radiation. Measurements were carried out with standard background counts (15 s) and θ—2θ scan of fixed range (30 s) for $2\theta \leqslant 50°$. Three standard reflections, monitored at regular intervals, showed no significant variations during data collection. A standard deviation $\sigma(I) = [N_s + N_b + (0\cdot01N_p)^2]^{1/2}$ was assigned to each net intensity I, where N_s is the gross count, N_b the background count corrected to cover the same time span as N_s, and $N_p = N_s - N_b$. 986 Reflections having $I \geqslant 2\cdot0\sigma(I)$, of the 1453 unique reflections measured, were considered observed. Lorentz and polarisation but no absorption corrections were then applied. Accurate unit-cell dimensions were obtained from measurements of 16 high-angle 2θ reflections by use of Mo-$K_{\alpha 1}$ ($\lambda = 0\cdot70926$ Å) radiation.

Crystal Data.—$C_{16}H_{13}F_3NOP$, $M = 323\cdot3$, Orthorhombic, $a = 21\cdot672(6)$, $b = 9\cdot451(3)$, $c = 6\cdot816(2)$ (Å), $U = 1396\cdot1(3)$ Å^3, $Z = 4$, $D_c = 1\cdot54$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å, μ(Mo-K_α) = 2·4 cm⁻¹. Systematic absences ($h0l$ with h odd, $0kl$ with $k + l$ odd) were consistent with space groups $Pna2_1$ (No. 33) and $Pnam$ (No. 62). The distribution of normalised structure factors (E values) was typically hypercentric, thereby favouring the centrosymmetric $Pnam$, in which the molecules must lie on crystallographic mirror planes at $z/c = 0\cdot25$ and $0\cdot75$. The subsequent successful refinement of the structure confirmed this interpretation.

Structure Solution and Refinement.—A three-dimensional Patterson synthesis was interpreted to yield a self-consistent set of co-ordinates for the phosphorus and the remaining heavy atoms were located from subsequent difference-Fourier syntheses. Positional parameters, together with

[1] Part XXXVI, G. V. Röschenthaler and R. Schmutzler, *J. Inorg. Nuclear Chem.*, in the press.

[2] K.-P. John, R. Schmutzler, and W. S. Sheldrick, *J.C.S. Dalton*, 1974, in the press.

[3] R. Schmutzler, *Inorg. Synth.*, 1967, **9**, 63.

TABLE 1

Hydrogen atom co-ordinates and isotropic vibrational amplitudes ($Å^2 \times 10^3$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U
H(3)	$-0.1239(17)$	$0.3732(40)$	0.25	$25(12)$
H(4)	$-0.0838(16)$	$0.6110(37)$	0.25	$16(11)$
H(5)	$0.0136(15)$	$0.7766(34)$	0.25	$7(10)$
H(6)	$0.1186(15)$	$0.7974(36)$	0.25	$13(11)$
H(7)	$0.1808(15)$	$0.5974(35)$	0.25	$8(10)$
H(12)	$0.1786(12)$	$0.0567(28)$	$-0.0517(43)$	$31(9)$
H(13)	$0.2552(12)$	$-0.0959(27)$	$-0.0334(48)$	$31(9)$
H(14)	$0.3078(20)$	$-0.1943(46)$	0.25	$49(15)$
H(21)	$-0.1008(19)$	$0.1391(43)$	0.25	$35(13)$
H(22)	$-0.0464(12)$	$0.0790(28)$	$0.1262(45)$	$41(9)$

anisotropic temperature-factor components, were refined by full-matrix least-squares in the space group $Pnam$. At this stage of the refinement the generalised index $R_G \{= [\Sigma w \Delta^2 / \Sigma w F_o^2]^{1/2}, \ \Delta = F_o - F_c\}$ had converged to 0.069 with a corresponding weighted index $R' [= \Sigma w^{1/2} \Delta / \Sigma w^{1/2} F_o]$ of 0.063. A difference-Fourier synthesis then revealed the positions of all hydrogen atoms, which were then included in the least-squares refinement with isotropic temperature factors. Complex neutral-atom scattering factors [4,5] were employed for all atoms. The terminal value of R_G was 0.035 with R' 0.037 and the corresponding unweighted index, R, 0.040. A final difference-Fourier synthesis displayed no unexpected

TABLE 2

Atom co-ordinates and anisotropic vibrational amplitudes ($Å^2 \times 10^3$),* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	$0.1001(1)$	$0.1806(1)$	0.25	$33(1)$	$21(1)$	$39(1)$	0	0	$-1(1)$
F(1)	$0.0939(1)$	$0.1885(2)$	$0.0149(2)$	$58(1)$	$71(1)$	$34(1)$	$-9(1)$	$-4(1)$	$20(1)$
F(2)	$0.0547(1)$	$0.0482(2)$	0.25	$37(1)$	$24(1)$	$117(2)$	0	0	$-5(1)$
O	$0.1421(1)$	$0.3311(3)$	0.25	$30(1)$	$23(1)$	$79(2)$	0	0	$0(1)$
N	$0.0267(1)$	$0.3053(3)$	0.25	$31(2)$	$26(2)$	$32(2)$	0	0	$2(1)$
C(2)	$-0.0335(2)$	$0.2808(4)$	0.25	$35(2)$	$34(2)$	$37(2)$	0	0	$-5(2)$
C(3)	$-0.0752(2)$	$0.3966(4)$	0.25	$34(2)$	$44(2)$	$38(3)$	0	0	$3(2)$
C(4)	$-0.0552(2)$	$0.5328(4)$	0.25	$42(2)$	$39(2)$	$36(3)$	0	0	$10(2)$
C(5)	$0.0368(2)$	$0.6957(4)$	0.25	$53(3)$	$25(2)$	$42(3)$	0	0	$8(2)$
C(6)	$0.0996(2)$	$0.7060(4)$	0.25	$61(3)$	$22(2)$	$50(3)$	0	0	$-5(2)$
C(7)	$0.1379(2)$	$0.5863(4)$	0.25	$38(2)$	$26(2)$	$58(3)$	0	0	$-9(2)$
C(8)	$0.1113(2)$	$0.4554(4)$	0.25	$37(2)$	$26(2)$	$38(2)$	0	0	$3(2)$
C(9)	$0.0469(2)$	$0.4426(3)$	0.25	$34(2)$	$22(2)$	$27(2)$	0	0	$-2(2)$
C(10)	$0.0086(2)$	$0.5607(4)$	0.25	$42(2)$	$28(2)$	$28(2)$	0	0	$3(2)$
C(21)	$-0.0604(2)$	$0.1340(4)$	0.25	$34(2)$	$39(2)$	$92(4)$	0	0	$-12(2)$
C(11)	$0.1697(2)$	$0.0702(4)$	0.25	$32(2)$	$19(2)$	$60(3)$	0	0	$-1(2)$
C(12)	$0.1946(1)$	$0.0219(3)$	$0.4236(5)$	$64(2)$	$50(2)$	$77(3)$	$-19(2)$	$-30(2)$	$20(2)$
C(13)	$0.2440(2)$	$-0.0735(4)$	$0.4202(7)$	$73(3)$	$63(2)$	$117(4)$	$-18(3)$	$-55(3)$	$22(2)$
C(14)	$0.2689(2)$	$-0.1218(5)$	0.25	$41(3)$	$46(3)$	$144(6)$	0	0	$8(2)$

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

TABLE 3

Interatomic distances (Å) and bond angles (°)

(a) Distances

P–F(1)	$1.610(2)$	P–F(2)	$1.593(2)$
P–O	$1.689(3)$	P–N	$1.980(3)$
P–C(11)	$1.833(4)$	C(11)–C(12)	$1.378(4)$
C(12)–C(13)	$1.400(4)$	C(13)–C(14)	$1.358(4)$
N–C(2)	$1.326(4)$	N–C(9)	$1.368(4)$
C(2)–C(3)	$1.420(4)$	C(3)–C(4)	$1.359(5)$
C(4)–C(10)	$1.408(4)$	C(5)–C(10)	$1.414(4)$
C(5)–C(6)	$1.365(4)$	C(6)–C(7)	$1.403(4)$
C(7)–C(8)	$1.365(4)$	C(8)–C(9)	$1.401(4)$
C(9)–C(10)	$1.392(4)$	C(8)–O	$1.352(4)$
C(2)–C(21)	$1.504(4)$	C(12)–H(12)	$1.00(3)$
C(13)–H(13)	$0.84(4)$	C(14)–H(14)	$1.09(4)$
C(3)–H(3)	$1.08(4)$	C(4)–H(4)	$0.96(4)$
C(5)–H(5)	$0.92(3)$	C(6)–H(6)	$0.96(3)$
C(7)–H(7)	$0.94(3)$	C(21)–H(21)	$0.88(4)$
C(21)–H(22)	$1.04(3)$		

(b) Angles

C(11)–P–F(1)	$95.5(1)$	C(11)–P–F(2)	$93.5(1)$
C(11)–P–O	$92.1(1)$	F(1)–P–F(2)	$89.1(1)$
F(1)–P–O	$90.3(1)$	N–P–F(1)	$84.5(1)$
N–P–F(2)	$88.3(1)$	N–P–O	$86.1(1)$
P–C(11)–C(12)	$120.7(2)$	C(11)–C(12)–C(13)	$119.9(4)$
C(12)–C(13)–C(14)	$122.3(4)$	C(13)–C(14)–C(13')	$117.4(4)$
C(12)–C(11)–C(12')	$119.4(4)$	P–O–C(8)	$117.7(2)$
P–N–C(2)	$133.3(2)$	P–N–C(9)	$107.9(2)$
O–C(8)–C(7)	$125.4(2)$	O–C(8)–C(9)	$114.6(2)$
C(9)–N–C(2)	$118.7(2)$	N–C(2)–C(3)	$119.4(2)$
C(2)–C(3)–C(4)	$121.9(3)$	C(3)–C(4)–C(10)	$119.4(3)$
C(4)–C(10)–C(9)	$115.8(3)$	C(10)–C(9)–N	$124.8(2)$
C(5)–C(10)–C(9)	$117.8(3)$	C(10)–C(5)–C(6)	$119.7(3)$
C(5)–C(6)–C(7)	$122.2(3)$	C(6)–C(7)–C(8)	$118.7(3)$
C(7)–C(8)–C(9)	$120.0(3)$	C(8)–C(9)–C(10)	$121.6(3)$

features. An attempt to describe rigid-body motion of the molecule in terms of the model of Schomaker and Trueblood [6] was unsatisfactory. Results from the final least-squares cycle are summarised in Table 1 and 2: these

TABLE 4

Intermolecular non-bonded distances (Å), <3.5 Å

F(1) $\cdots$ C(4^I)	3.301	F(1) $\cdots$ H4^I)	2.626
F(1) $\cdots$ H(5^I)	2.966	F(1) $\cdots$ H(22^I)	2.895
F(1) $\cdots$ H(14^{II})	3.004	F(2) $\cdots$ H(22^I)	2.838
O $\cdots$ C(13^{II})	3.457	O–H(13^{II})	2.758
C(12) $\cdots$ H(21^I)	3.376	C(12) $\cdots$ H(14^{II})	3.485
C(13) $\cdots$ H(7^{II})	3.212	C(14) $\cdots$ H(13^{III})	3.305
C(14) $\cdots$ H(4^{III})	3.195	C(2) $\cdots$ C(5^I)	3.416
C(2) $\cdots$ H(5^I)	3.478	C(21) $\cdots$ H(12^I)	3.411
C(4) $\cdots$ C(9^I)	3.421	C(4) $\cdots$ H(14^{III})	3.338
C(5) $\cdots$ H(22^I)	3.340	C(6) $\cdots$ H(22^I)	3.469
C(7) $\cdots$ H(3^I)	3.443	C(7) $\cdots$ H(13^{II})	3.242
C(8) $\cdots$ H(13^{II})	3.284		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, -y, -z$ III $0.5 + x, 0.5 - y, 0.5 - z$
II $0.5 - x, 0.5 + y, 0.5 + z$

results, together with the full covariance matrix, were used to calculate the bond lengths and angles, and their estimated standard deviations, presented in Table 3. The shortest non-bonded distances are summarised in Table 4. Figure 1 depicts the molecule in perspective, together with the numbering system, and Figure 2 the unit-cell contents

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[6] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

shown perpendicular to [001]. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21109 (7 pp., 1 microfiche).*
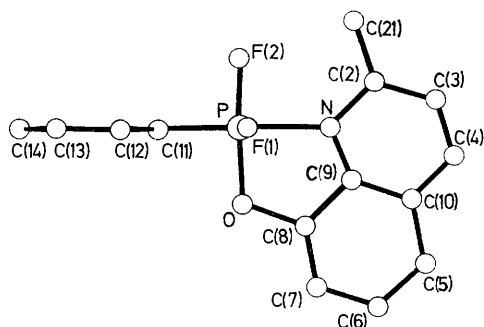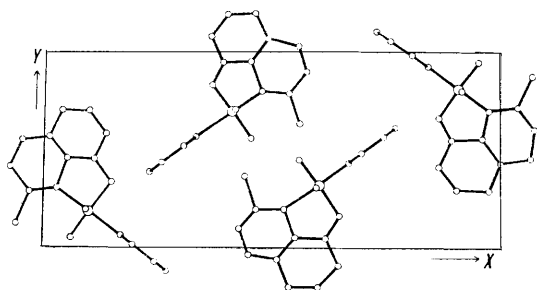

FIGURE 1 Atom numbering in the molecule

FIGURE 2 Projection of the unit-cell contents perpendicular to [001]

DISCUSSION

The molecules of (2b) lie on crystallographic planes of symmetry perpendicular to [001] with the oxMe grouping lying in the mirror plane and perpendicular to the benzene ring. A similar phenomenon was observed for $F_4P(oxMe)$, which crystallises in the space group $P2_1/m$ with the quinoline framework lying in the mirror plane perpendicular to [010]. In (2b) the phenyl group bonded to phosphorus occupies the most sterically favourable position, namely that opposite the N→P co-ordinate bond, thereby avoiding a potential interaction with the quinoline aromatic system.

The N→P co-ordinate bond length [1·980(3) Å] in (2b) is much longer than those of 1·898(4) (librationally corrected) and 1·911(4) Å previously observed for $F_5P(py)$ [7] (py = pyridine) and $F_4P(oxMe)$ respectively. These contrast with the N-P σ-bond distance of 1·769 Å.[8] The weakness of the N→P co-ordinate bond in (2b) is in accordance with the much weaker Lewis-acid acceptor properties exhibited by the PhF_3PO grouping in comparison with PF_5 or the F_4PO grouping. It has been demonstrated,[2] for instance, that the reactivity of fluorophosphoranes with 8-trimethylsiloxyquinolines to yield intramolecular complexes containing six-co-ordinate phosphorus, and the subsequent resistance of these products to hydrolysis, is in the order: $F_4P(ox) >$ $PhF_3P(ox) > MeF_3P(ox) \sim EtF_3P(ox)$. Furthermore, the reaction of Me_2PF_3 with 8-trimethylsiloxyquinoline

yields a white crystalline oxinatofluorophosphorane for which there is no evidence of an intramolecular N→P co-ordinate bond. In contrast to $F_4P(oxMe)$, considerable distortion from perfect octahedral co-ordination is observed at phosphorus in (2b) with P-O, P-F(1), and P-F(2) bonds being displaced away from the P-C bond at angles of 92·1(1), 95·5(1), and 93·5(1)°. A similar distortion of the coplanar fluorine atoms towards the nitrogen was observed in $F_5P(py)$; the mean F-P-F angle is 91·8(2)°. In the case of (2b) the phenomenon may be explained in terms of two complementary factors. (a) The electron density at phosphorus in the P-C bond of (2b) is higher than that in the P-F bonds opposite N in $F_4P(oxMe)$ and $F_5P(py)$, and will therefore exert a greater degree of repulsion upon the coplanar P-O and P-F bonds. (b) The N→P co-ordinate bond in (2b) is much weaker than in these other complexes, and the subsequent electron density at phosphorus and hence the degree of repulsion upon the coplanar P-O and P-F bonds will therefore be smaller.

The (F)-F and (O)P-F bond lengths [1·610(2) and 1·593(3) Å] in (2b) are significantly longer than the equivalent values [1·598(3) and 1·572(3) Å] observed in $F_4P(oxMe)$. This increase in the P-F bond lengths is to be expected, as the replacement of one fluorine by the phenyl group in (2b) will cause the P(3d) orbitals to become less energetically favourable for possible $p_\pi-d_\pi$ bonding from the F $2p_\pi$ orbitals. In a similar way, the P-O bond length [1·689(3) Å] is longer, albeit not significantly, than that [1·678(3) Å] in $F_4P(oxMe)$. In both compounds the (F)P-F bond length is significantly longer than the O(P)-F bond length, which may be associated with the lower electron density at phosphorus in the opposite bond of the octahedron. The values of the P-F bond length are close to those (1·58 Å) for the octahedral PF_6^- anion.[9]

The distortion of the angles at N and C(8), necessary to achieve octahedral co-ordination at phosphorus in (2b), leads to angles of 107·9(2) at N and 114·6(2)° at C(8) within the five-membered NPOCC ring, which are identical to those of 107·6(3) and 114·5(4)° in $F_4P(oxMe)$. The increased N→P bond length and decreased N-P-O bond angle in (2b) are balanced by an increase in the P-O-C(8) bond angle to 117·7(2), in contrast to that of 115·8(3)° in $F_4P(oxMe)$. There are no significant differences to be observed in the quinoline framework dimensions of the two complexes.

* See Notice to Authors No. 7 in J.C.S. Dalton, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[7] W. S. Sheldrick, J.C.S. Dalton, 1974, 1402.
[8] (a) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, Acta Cryst., 1953, 6, 621; (b) D. W. J. Cruickshank, ibid., 1964, 17, 671.
[9] H. Bode and H. Clausen, Z. anorg. Chem., 1952, 268, 20.