The Crystal and Molecular Structure of (Pentane-2,4-dionato)-tetrafluorophosphorane

W. S. Sheldrick
GeSELLschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig-Stöckheim and
M. J. C. Hewson
Lehrstuhl B für Anorganische Chemie der Technischen Universität Braunschweig, Pockelstraße 4, D-3300 Braunschweig

Z. Naturforsch. 33b, 834–837 (1978); received June 5, 1978

X-ray, Hexa-coordinate Phosphorus Complex, Acetylacetone Chelate, $^{31}$P NMR, $^{31}$P NMR

(Pentane-2,4-dionato)-tetrafluorophosphorane crystallises in the space group $P2_1/c$, $Z = 8$, with $a = 8.889(2)$, $b = 13.760(4)$, $c = 13.316(2)$ Å, $\beta = 93.42(3)^\circ$. The structure was refined to $R = 0.053$ for 2445 reflections. Small but significant differences are observed in the bond angles at phosphorus and in the chelate ring conformations of the two independent molecules. These display an approximate mirror plane perpendicular to the chelate rings, which are in the boat form with $P$ and $C(3)$ displaced from the plane of the remaining ring atoms. The average $P$–O distance of 1.719(2) Å is similar to that for a $\sigma$-bond. $^{19}$F and $^{31}$P NMR and mass spectral data are reported. The basis peak is formed by the cleavage of the two P–O bonds resulting in the ion $PF_4^+$ ($m/e$ 107).

Introduction

The only acyclic hexa-coordinate phosphorus species which have been characterised by X-ray structural analysis are the anions $PF_6^-$ [1] and $PCl_6^-$ (in $PCl_4^+PCl_6^-$) [2] and the neutral adduct $F_3P:pyridine$ [3]. Inclusion of the phosphorus atom in one or more four- or five-membered rings leads to an increased relative stability of derivatives with the coordination numbers 5 and 6 vs. 4, as a result of the trigonal bipyramidal or octahedral rather than a tetrahedral geometry at phosphorus. Two examples of the stabilisation of hexa-coordinate phosphorus in a non-halogen derivative are provided by the $2,2'$-bipyridine-$bis(o$-phenylenedioxy)phosphonium cation and the $tris(o$-phenylenedioxy)phosphate anion, both of which owe their stability to the inclusion of phosphorus in 3 five-membered rings. Both of these species have been characterised by X-ray analysis, as the hexafluorophosphate [4] and the triethylammonium salt [5], respectively. X-ray analyses have also been performed on the following neutral hexa-coordinate phosphorus adducts with one chelated ligand (the remaining four ligands being $F$ or $Cl$): $F_2P(2$-methyl-8-oxycarbon-2-yl)phosphine $N$-pyridine [6], $F_3(Ph)P(2$-methyl-8-oxycarboxyl)phosphine $N$-pyridine [7], $ClF(N(CH_3)C(Cl)N(CH_3))$ [8] and $CH_3(CF_3)PF(OC(N(CH_3))O)$ [9]. The $N$–P distances of 1.911(4) and 1.980(3) Å in 2 and 3 allow the characterisation of this as a weak coordinate bond, whereas the corresponding $O$–P distances of 1.678(3) and 1.689(3) Å are typical for a $\sigma$-bond. The Schomaker-Stevenson corrected sums of the covalent radii are respectively 1.75 and 1.71 Å for the $N$–P and $O$–P bonds [10]. In contrast, the nature of the $N$–P and $O$–P bonding in 4 and 5 is less clear. The values of 1.91(4) and 1.85(6) Å for the $N$–P bonds in 4 were obtained with visually estimated data ($R = 0.13$) and do not allow a conclusion as to their equivalence or as to their strength in comparison to the $N$–P coordinate bonds in 2 and 3. However, they do suggest that the bonding in the chelate ring is best described by the assumption of two boundary structures with a betaine formulation $i.e.$ $N^+P-NC$ and $NP-N^+C$ [8]. The P–O and C–O bond lengths of 1.89, 1.82, 1.29 and 1.30 Å in the OPOC ring of 5 also indicate mesomeric betaine contributions. The observed difference of 0.07 Å in...
the P-O distances is presumably a consequence of the relative inductive character of the opposite substituent at phosphorus, the shorter bond being opposite to the more electronegative CF$_3$-group. A similar, though less pronounced trend has been observed in 2 and 3 [10]. This structural study of the title compound 1 was undertaken in order to provide more information about the nature of the bonding in such chelates. The presence of four fluorine ligands and reduced ring strain in the six-membered ring plus the possibility of enhanced π-delocalisation over the acetylacetone chelate system would be expected to lead to a significant shortening of the P-O bonds in 1 in comparison to 5.

Experimental

The usual precautions were employed in the handling of moisture sensitive compounds. $^1$H, $^{19}$F and $^{31}$P NMR spectra were recorded at room temperature on a Varian HA/HR-60 at 60 (internal standard Me$_4$Si), 56.4 (internal standard CCl$_3$P) and 26.3 MHz (external standard 85% H$_3$PO$_4$), respectively. Mass spectral data were collected on an A. E. I. MS 9 (direct-inlet or reservoir system) spectrometer.

(Pentane-2,4-dionato)-tetrafluorophosphorane (1) [11]

A solution of freshly distilled acetylacetone (10.0 g, 0.1 mole) in 100 ml of dry ether was saturated with phosphorus pentafluoride at $-70^\circ$C and then allowed to warm up to room temperature. The solvent was removed under vacuum to leave a thick yellow oil which was extracted with several 20 ml portions of dry ether. The combined portions were reduced in volume by approximately half and the remaining solution left at $-25^\circ$C for several days to yield white prismatic crystals of 1. Yield 12.6 g (61%), m.p. 85°C. MS: m/e = 206 (M$, 12.8\%$), 191 (M$-$CH$_3$, 91%), 187 (M$-$F, 61%), 107 (PF$_3$, 100%). NMR: δF (axial) +49.7, δF (equatorial) +73.1, δP +148.2, δH(CH$_3$) −2.17, δH(CH) −5.82 ppm, $^1$J$_{PF}$ (axial) 823, $^1$J$_{PF}$ (equatorial) 762, $^2$J$_{PF}$ (axial) $^1$J$_{PF}$ (equatorial) 59.0, $^3$J$_{PF}$ (axial) H$^1$CH 3.0, $^3$J$_{PF}$ (equatorial) H$^1$CH 3.0, $^4$J$_{PF}$ (CH$_3$) 1.6 Hz.

X-ray analysis of 1

1 crystallises in the space group P2$_1$/c with $a = 8.896(2)$, $b = 13.760(4)$, $c = 13.316(2)$ Å, $\beta = 93.42(3)^\circ$, $Z = 8$, $D_x = 1.58$ g·cm$^{-3}$. Intensity data were collected on a Syntex P2$_1$ diffractometer (Mo-K$\alpha$, graphite monochromator) in the $\theta$—$2\theta$ mode for the range $2\theta < 60^\circ$. No absorption correction was applied [μ(Mo-K$\alpha$) = 3.0 cm$^{-1}$]. The structure was solved by the automatic centrosymmetric multisolution routine of SHELX (G. M. Sheldrick) and refined by full-matrix least-squares with anisotropic temperature factors for the non-hydrogen atoms. The H atoms were allowed to refine freely with individual temperature factors. The terminal reliability indices for 2445 reflections with $I > 2\sigma$ ($I$) were $R'$ = 0.050 and $R = 0.053$. Weights were given by $w = k (\sigma^2(F_0) + g F_0^2)^{-1}$ where $k$ and $g$ refined to 2.2411 and 0.000333 respectively. Tables of anisotropic temperature factors, hydrogen atom positions and observed and calculated structure factors are available from W. S. Sheldrick on request.

Discussion

The two independent molecules of 1 in the crystal lattice display similar molecular geometries. Whereas there are no significant differences in bond distances (Fig. 2), small but significant differences are to be observed in the bond angles at phosphorus and in the conformations of the six-membered chelate rings. For instance the endocyclic OPO angles of 95.2 and 94.1(1)$^\circ$ differ by 1.1°. The molecules display an approximate plane of symmetry perpendicular to the ring system i.e. in the plane...
P, F(1), F(4) and C(3). The six-membered rings are in a boat conformation with P(1) and C(3) displaced from the plane of the remaining four ring atoms. The distances from the weighted least-squares planes of these atoms O(1), C(2), C(4) and O(5) are: molecule 1, P(1) —0.216, O(1) 0.004, C(2) —0.005, C(4) 0.005, O(5) —0.004 Å and molecule 2, P(l)' —0.339, O(1) 0.002, C(2) —0.003, C(3) —0.003, C(4) 0.003, O(5) —0.002 Å. The shortest non-hydrogen atom intermolecular contacts are between C(3) and F(2) [3.18 Å] and similar to those of 1.723(7) and 1.711(8) Å in the trig-(o-phenylenedioxy)phosphate anion [5] and the Schomaker-Stevenson corrected sum of the covalent radii 1.71 Å. Within the ring the average C-O distance of 1.290(2) is somewhat longer than that of 1.27 Å obtained from a series of metal chelates of acetylacetone [12]. At the same time the average C-C distance of 1.361(3) is shorter than that of 1.39 Å in these metal chelates. The P-F distances of 1.568-1.588(2) are similar to that of 1.58 Å in PF$_6^-$ [11]. Considerable distortion from the perfect octahedral geometry is observed at phosphorus in 1. The endocyclic O(l)-P-0(5) 95.2(1) and 94.1(1) and the opposite F(2)-P-F(3) 92.4(1) and 92.3(1)° angles are widened with a concomitant decrease in the coplanar O(1)-P-F(3) [86.0(1) and 86.9(1)] and O(5)-P-F(2) [86.4(1) and 86.8(1)]° angles. The axial fluorine atoms with the respect to this (the equatorial) plane, F(l) and F(4), are displaced towards the bisector of the O(l)-P-0(5) angle, F(l)-P-F(4) being 175.8(1) and 176.6(1)°.

The δ$^{31}$P value of 148.2 ppm in 1 is typical for a...
hexa-coordinate derivative, which have typical phosphorus chemical shifts to the high field of

Fig. 3. $^{19}$F (a) experimental and (b) computed [16] NMR band shapes for the low field resonance of 1 at room temperature, showing one half of the A resonance of an A$_2$M$_2$XR spin system (A = F(axial), M = F(equatorial), X = P, R = H).

80 ppm [13]. The fluorine shifts are consistent with those previously reported [14]. Both proton signals are shifted significantly to lower field with respect to acetylacetone as would be expected on account of the Lewis acid strength of the PF$_4$ unit. The $^{19}$F spectrum shows a 24 line pattern which may be analysed in terms of the A$_2$M$_2$ part [15] of an A$_2$M$_2$XR spin system where A = F(axial), M = F(equatorial), X = P and R = H(CH), which reduces to an A$_2$X$_2$(A = F(axial), X = F(equatorial)) system doubled by both $^{31}$P and $^1$H. A doublet of triplets of doublets is observed for each of the F atom resonances. Fig. 3 shows the experimental and computed [16] band shapes for one half of one of the F atom resonances.

We are grateful to Mr. H. Steinert for recording the mass spectra and to Prof. R. Schmutzler for his support of this work.