A Three-membered Phosphorus Ring: $(C_2F_5P)_3$

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Summary The synthesis of tris(pentafluoroethyl)cyclotriphosphine is described.

WITH the possible exception of the dianion $(PhP)_3^{2-}$ (whose structure is not well established[1]) no three-membered tricovalent phosphorus ring compound has been described. We report the preparation of tris(pentafluoroethyl)cyclotriphosphine. Curiously this also appears to be the first report of a pentafluoroethyl-substituted phosphine.

The phosphorus(III) iodide, $C_2F_5PI_2$, was prepared by the reaction of C_2F_5I with red phosphorus (219°, 40 hr.).† The di-iodide, which condenses at −20°, was readily separated from the more volatile $(C_2F_5)_2PI$ and unused C_2F_5I. The action of an excess of mercury on $C_2F_5PI_2$ in an evacuated sealed tube for 24 hours produced a 2:3 mixture of $(C_2F_5P)_3$ (I) and $(C_2F_5P)_4$ (II). The colourless liquid (I) was separated from the white crystalline (II) (m.p. 23·5°) by fractional vacuum condensation, the former passing a −15° trap and condensing at −30°. The vapour pressure of (I) conforms to the equation $\log_{10}P_{\text{mm}} = 7{\cdot}831 - (2101{\cdot}9/T)$.

The formulation of (I) as tris(pentafluoroethyl)-cyclotriphosphine is based upon the following considerations. First the presence of the C_2F_5P moiety is established by elemental analysis (C and F), i.r., and n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum of (I) consists of complex CF_3 and CF_2 resonances at 36·9 and 19·2 p.p.m.‡ respectively. Secondly, the three-membered phosphorus ring of (I) is established by the mass spectrum, which cuts off at *m/e* 450, corresponding to $(C_2F_5P)_3^+$. Furthermore, peaks of significant intensity are observed at *m/e* 331, 143, 131, 119, 100, and 93 which are attributable to the anticipated fragments $(C_2F_5)_2P_3^+$, $CF_2P_3^+$, $C_2F_4P^+$, $C_2F_5^+$, $C_2F_4^+$, and P_3^+. This conclusion is supported by the experimental (immersible tensimeter) molecular weight of 446 and the vapour-phase u.v. spectrum which displays a broad singlet at 250 nm. U.v. absorption in this region seems to be characteristic of all P–P bonded polyphosphines.[2]

The chemistry of (I) appears to be similar to that of

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† The procedure is very similar to that employed in the synthesis of perfluoropropyliodophosphines: H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 1959, 375.

$(CF_3P)_4$ and $(CF_3P)_5$.[2] For example, (I) reacts with excess Me_3P to yield the phosphine–phosphinidene complex $Me_3PPC_2F_5$ [τ 8·38, δ (CF_2) 18·6 p.p.m.,‡ δ (CF_3) 20·9 p.p.m.,‡ J_{PCH} 12·4, J_{PPCH} 3·2, J_{PCF} 30·2, J_{PPCF} 26·6, J_{PPCCF} 3·8, J_{PCCF} 19·3, J_{FCCF} 6·9 Hz].

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‡ Relative to internal α,α,α-trifluorotoluene.

[1] K. Issleib and E. Fluck, *Angew. Chem. Internat. Edn.*, 1966, **5**, 587.

[2] A. B. Burg, *Accounts Chem. Res.*, 1969, **2**, 353; A. H. Cowley, *Chem. Rev.*, 1965, **65**, 617; L. Maier, *Fortschr. Chem. Forsch.*, 1967, **8**, 1.