A Distorted Trigonal-bipyramidal Phosphorane with a Diequatorial Four-membered Ring; *X*-Ray Crystal Structure of 4-*p*-Bromophenyl-2′,2′,3′,4′,4′-pentamethyl-3,3,6,6-tetrakistrifluoromethyl-2,7-dioxa-1-phospha(v)bicyclo[3,2,0]hept-4-ene-1-spiro-1′-phosph(v)etan

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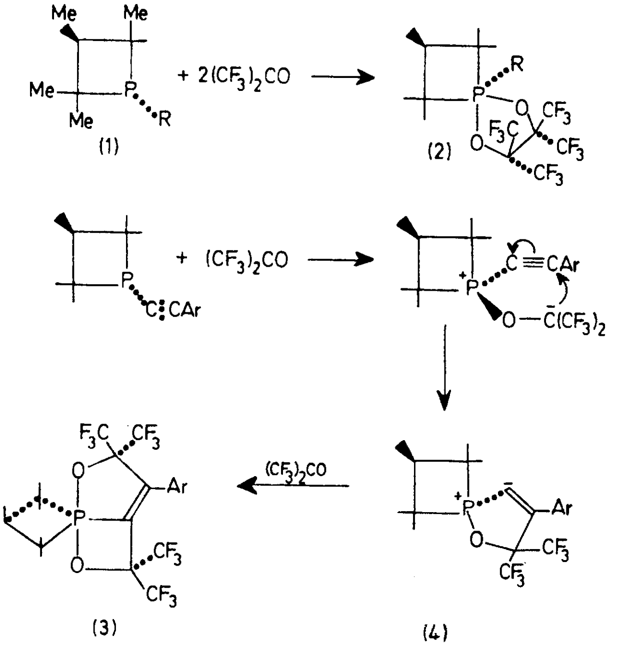
Summary Hexafluoroacetone and 1-phenylethynylphosphetan gave a 2:1 adduct shown by *X*-ray structure analysis to be a five-co-ordinate phosphorane having distorted trigonal bipyramidal geometry with a diequatorial phosphetan ring.

PREVIOUSLY[1] we have treated a number of phosphetans (**1**) with hexafluoroacetone (HFA) and studied the variable temperature ^{1}H n.m.r. spectra of the resulting adducts (**2**) in order to obtain data on the relative apicophilicities of the groups R. In continuation of these studies, the *trans*-phenylethynylphosphetan (**1**; R = PhC⋮C) was treated with an excess of HFA at −78 °C in dichloromethane. The major product, m.p. 160 °C, was a 1:2 adduct† [τ(CDCl$_3$) 2·6—3·15 (5H, m), 7·72—7·98 (1H, m), 8·62 (6H, d, *J* 24 Hz), 8·70 (6H, d, *J* 24 Hz), and 9·10 (3H, dd, *J* 7 and 1·5 Hz), ^{31}P (CDCl$_3$) 31·6 p.p.m. downfield from external 85% H$_3$PO$_4$, ^{19}F (CDCl$_3$) 9·70 (6F, s) and 11·52 (6F, d, *J* 4 Hz) p.p.m. upfield from internal PhCF$_3$], which showed no acetylenic absorption in its i.r. spectrum. We were unable to assign a convincing structure to this adduct and accordingly prepared the analogous *p*-bromophenyl compound,† m.p. 176—177 °C ^{31}P (CDCl$_3$) 30 p.p.m. downfield from external 85% H$_3$PO$_4$,‡ and submitted it to single crystal *X*-ray analysis.



Crystal data: C$_{22}$H$_{20}$BrF$_{12}$O$_2$P, $M = 655$, orthorhombic, $Pca2_1$, $a = 17{\cdot}77$, $b = 8{\cdot}71$, $c = 16{\cdot}51$ Å, $U = 2555$ Å^3, $Z = 4$, $D_c = 1{\cdot}70$ g cm^{-3}. 890 Unique reflection intensities were measured between $0{\cdot}1 < \sin\theta/\lambda < 0{\cdot}63$ using monochromatic Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation and have been refined to $R = 0{\cdot}062$ with anisotropic thermal parameters for P, Br, and F atoms, and all hydrogen atoms included.

TABLE

Bond angles (°) about phosphorus atom in P(C$_3$HMe$_5$)[OC(CF$_3$)$_2$C(C$_6$H$_4$Br)CC(CF$_3$)$_2$O]. Estimated standard deviations are 0·9°.

Bonded atoms	Angle	Bonded atoms	Angle
O(1), O(2)	159·7	O(1), C(1)	101·0
C(1), C(3)	82·9	O(1), C(3)	99·0
C(1), C(6)	133·4	O(2), C(6)	71·6
C(3), C(6)	141·1	O(2), C(1)	94·3
O(1), C(6)	88·1	O(2), C(3)	96·0

The structure is shown in the Figure with selected bond lengths, and in formula (**3**). Despite the ^{31}P n.m.r. chemical shift the compound is a five-co-ordinate phosphorane. From the angles given in the Table the geometry round the phosphorus atom is that of a distorted trigonal bipyramid with the phosphetan ring occupying two equatorial positions. Obviously the equatorial angles depart from the ideal 120° values to accommodate the four-membered ring, otherwise distortions are small. The two apical atoms are bent slightly away from the phosphetan ring. The molecule has a plane of symmetry defined by the two apical and the third equatorial atoms and dictated by the CC double bond, the largest displacement out of this plane for the seven atoms of this PO$_2$C$_4$ system and the

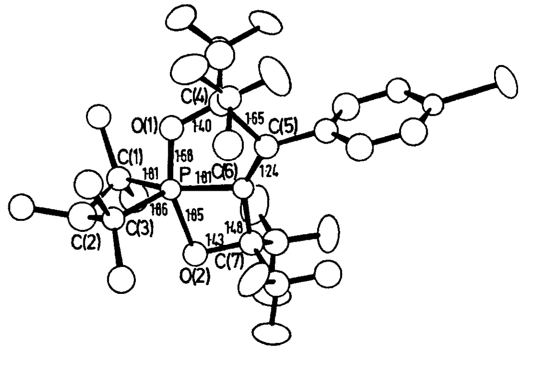


FIGURE. The molecular structure of P(C$_3$HMe$_5$)[OC(CF$_3$)$_2$-C(C$_6$H$_4$Br)CC(CF$_3$)$_2$O]. E.s.d.'s of bond lengths shown are P–O, 0·015; P–C 0·02 Å; C–O, C–C, 0·025 Å.

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† This compound gave correct elemental analysis and showed the expected mass peak and fragmentation pattern in its mass spectrum.

‡ The other spectral properties were similar to those of the phenyl analogue.

attached phenyl carbon being 0·06 Å. The phenyl ring is perpendicular to this plane (88·6°), presumably to minimise steric repulsions with the trifluoromethyl groups. Large variations in bond lengths within the rings is evidence of ring strain. The distortion from trigonal bipyramidal geometry is towards that of a 0° (2 + 3) structure[2] with the 'pair' being the O and C of the oxaphosphetan ring and the geometry could equally well be described in these terms.

The reaction between the phosphetans (**1** R = ArC⋮C) and HFA presumably proceeds *via* the ylides (**4**) as shown.[3]

We have postulated[1,4] that trigonal bipyramidal phosphoranes having four- or five-membered diequatorial rings are high energy intermediates or transition states in the Berry pseudo-rotations of a variety of spirophosphoranes, although the opinion has been expressed[2] that such diequatorial placement of small-membered rings is not possible and the turnstile rotation mechanism for the permutational isomerisation of phosphoranes was developed largely in order to avoid such placements. Ideal trigonal bipyramidal geometry was never assumed or expected in strained phosphoranes and structure (**3**) shows how little distortion from this is necessary in order to accommodate a diequatorial four-membered ring.

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