A Rigid Double Spirocyclic λ^5P–O–λ^5P Oxydiphosphorane with a Boat-shaped Six-membered Ring; *X*-Ray Crystal Structure

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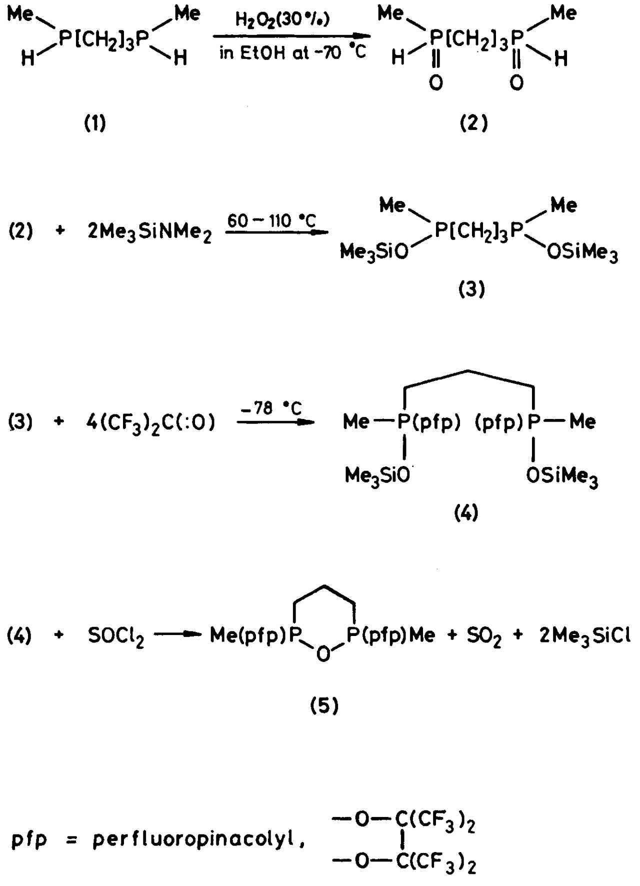
Summary Reaction of the bis(perfluoropinacolyl)bis(trimethylsilyloxy)-phosphorane (**4**) with thionyl chloride leads to formation of the title compound (**5**); its structure has been determined by *X*-ray diffraction.

A λ^5P–O–λ^5P bonded diphosphorane has recently been synthesized and characterized.[1,2] We now report the synthesis of a related compound, involving this novel structural element as part of a six-membered ring system as in (**5**). In contrast with the number of compounds containing the grouping λ^5E–O–λ^5E (E = pentaco-ordinate Sb and Bi),[3] the same type of compound with E = pentaco-ordinate P or As was unknown until our recent work,[1,2] and is still unknown for E = As. The detailed structural characterization of (**5**), as a stable λ^5P–O–λ^5P compound, by single-crystal *X*-ray diffraction appeared, therefore, particularly desirable, considering the importance of the phosphorus–oxygen linkage throughout the chemistry of phosphorus.

The synthesis of (**5**) is based on the di-secondary phosphine (**1**).[4] As set out in the Scheme, (**1**) was oxidized by H_2O_2 to the dioxide (**2**)[5] which, upon reaction with Me_3SiNMe_2, was converted into the bis(trimethylsilyl)phosphinous ester (**3**). Addition of 4 mol. equiv. of hexafluoroacetone to (**3**) proceeded with ease at −78 °C to give the bisphosphorane (**4**). Its reaction with $SOCl_2$ in a 1 : 1 molar ratio (70 °C; 5 h) finally furnished the novel diphosphorane (**5**).† Compound (**5**) was characterized by single-crystal *X*-ray diffraction, and by n.m.r. spectroscopy.‡



SCHEME

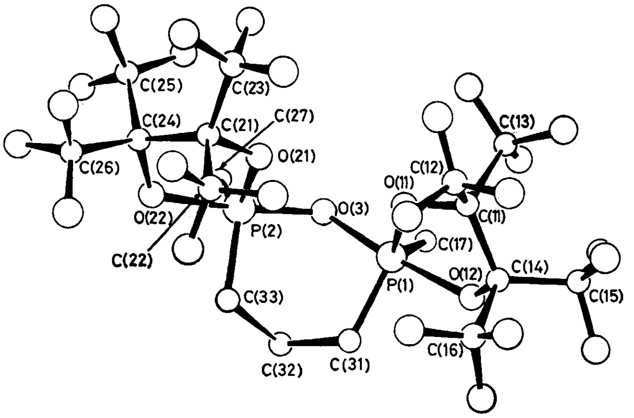


FIGURE. Crystal structure of (5).

The *X*-ray crystal structure of (**5**)§ (see Figure) suggests that the geometry at both pentaco-ordinate phosphorus atoms may be described as distorted trigonal-bipyramidal, with one five- and one six-membered ring each spanning one axial and one equatorial position at each of the two phosphorus atoms. As the direction and extent of the distortion are approximately the same for both phosphorus atoms it is concluded that intermolecular interactions are of minor importance.

The most interesting feature of the structure of (**5**) is the effect imposed upon the geometry around phosphorus by the six-membered ring. The six-membered ring is in the boat conformation which leads to a rather short non-bonding distance between O(3) and H(321) of 2·47 Å. The methyl substituents at phosphorus are *cis* with respect to the ring, so that the molecule displays approximate C_s symmetry. In most spirophosphoranes a local C_{2v} distortion of the trigonal bipyramid in the direction of a rectangular pyramid is observed, with the exocyclic ligand occupying the axial position in the latter.[6,7] This is not the case for (**5**); as the endocyclic angles O(3)–P(1)–C(31) and O(3)–P(2)–C(33) are significantly greater than 90° [95·9(2) and 96·4(2)°, re-

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† Compound (5) and its precursors have been characterized by elemental analysis and mass spectroscopy. While a molecula ion peak for (5) (*m/e* 814) was not seen intense fragment ions at *m/e* 799 ($M^+ - CH_3$), 795 ($M^+ - F$), and 745 ($M^+ - F - CF_2$), confirmed by a metastable peak at M^* 694·6, were observed. We are indebted to Dr. H. M. Schiebel (Technische Universität Braunschweig) for these measurements.

‡ Because of the asymmetry at both phosphorus atoms of (5) a pair of diastereomers is to be expected and, indeed, is observed [δ (P) + 4·7; δ (P′) + 5·3 p.p.m. downfield from ext. 85% H_3PO_4]. The ^{19}F n.m.r. spectrum of (5), in agreement with earlier findings on perfluoropinacolyl-substituted phosphoranes, showed a single resonance at −68·4 p.p.m. (upfield from int. CCl_3F); there was no change with temperature in the range investigated: +25 to −78 °C. In the $^1H\{^{31}P\}$ n.m.r. spectrum of (5) (in CH_2Cl_2) a $[CH_2]_3$ multiplet at δ 2·4 as well as two singlets at δ 1·80 and 1·90 (intensity ratio *ca.* 1 : 10) were observed; the latter correspond to the methyl groups in the *trans*- and *cis*-configuration of (5).

§ *Crystal data:* $C_{17}H_{12}F_{24}O_5P_2$, orthorhombic; space group $Pna2_1$; $a = 16{\cdot}281(2)$; $b = 13{\cdot}861(1)$; $c = 11{\cdot}911(1)$ Å; $Z = 4$; $D_c = 2{\cdot}012$ g cm^{-3}. The intensity data were collected on a Stoe STADI 4 diffractometer, using Mo-K_α radiation, by the θ–2θ scan technique at a scan rate of 3°/min in the range $3° \leqslant 2\theta \leqslant 50°$. The structure was determined by direct methods and difference Fourier synthesis (SHELX-76; G. M. Sheldrick). Least squares refinement using 3443 reflections with $I \geqslant 3\sigma(I)$ led to $R = 0{\cdot}042$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

spectively], and the planarity of the equatorial plane at phosphorus is retained, a distortion towards a square-pyramidal structure is no longer possible.

The P–C bond lengths [P–CH_3 1·792(6) and 1·807(6) Å; P–CH_2 1·810(6) and 1·792(6) Å] are in the usual range whereas the axial P–O bond distances in the five-membered rings are strikingly large [1·815(3) and 1·809(3) Å] compared with values found for a similar perfluoropinacolyl-substituted diphosphorane, [(pfp)(F)(Me_3SiN)P]$_2$ (1·704 Å).[8] The angle at the bridging oxygen [P–O(3)–P 142·3°] is significantly larger than the 'tetrahedral VSEPR value'.[9]

Much higher strain in the twisted five-membered ring, as against the six-membered ring, is suggested by the observation that the equatorial P–O bond in the former is of about the same length as the axial P–O bond in the six-membered ring [1·650(3) and 1·652(3) Å compared with 1·639(3) and 1·657(3) Å, respectively].

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