

Preparation and Crystal Structure Determination of a Diphosphorus Compound with a Direct $\lambda^5\text{P}-\lambda^4\text{P}$ Bond

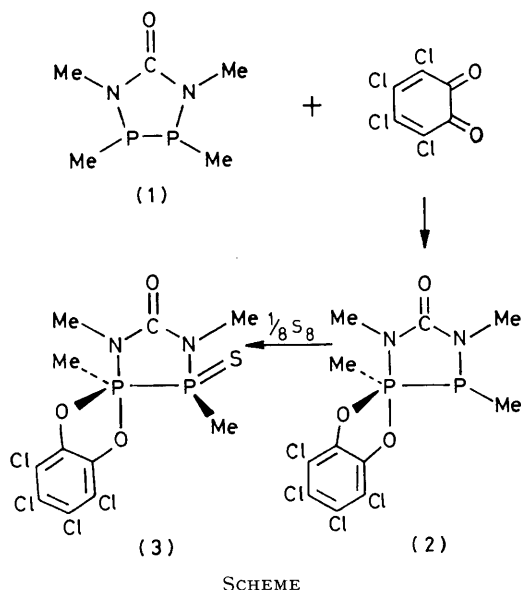
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Summary The synthesis of the first example of a $\lambda^5\text{P}-\lambda^4\text{P}$ diphosphorus compound is described; its structural characterization is based on spectroscopic and single-crystal X-ray diffraction studies.

ORGANODIPHOSPHORUS compounds with trivalent phosphorus atoms directly bonded have been known for more than 90 years.¹ Oxidation of one or two of the phosphorus atoms in such compounds is possible, and both $\lambda^4\text{P}-\lambda^3\text{P}$ and $\lambda^4\text{P}-\lambda^4\text{P}$ compounds are well established.² In the former type of compound the $\lambda^3\text{P}$ atom may display donor properties towards transition metals.³ The synthesis of $\lambda^5\text{P}-\lambda^3\text{P}$ ^{4,5} and

$\lambda^5\text{P}-\lambda^5\text{P}$ ⁶ compounds, however, has been reported only very recently. We now report the synthesis and structural characterization of a novel $\lambda^5\text{P}-\lambda^4\text{P}$ diphosphorus compound (**3**). As shown in the Scheme, the $\lambda^5\text{P}-\lambda^3\text{P}$ diphosphorus compound (**2**) is readily obtained by the oxidative addition of 1 equiv. of tetrachloro-*o*-benzoquinone to the *NN'*-dimethylurea-bridged diphosphine (**1**).⁷ Addition of elemental sulphur to the λ^3 phosphorus atom in (**2**) furnishes the $\lambda^5\text{P}-\lambda^4\text{P}$ -diphosphorus compound (**3**) in high yield. The chemical and thermal stability of (**3**) is noteworthy: the compound is stable to both air and moisture; thermal decomposition commences only at temperatures in excess of 160 °C.



The structural proof for (3) rests on analytical and spectroscopic data, as well as on a single-crystal *X*-ray diffraction study.[†] The mass spectrum exhibits molecular ion peaks at *m/e* 454/456/458/460, with the isotopic distribution characteristic of four chlorine atoms. In the {¹H}-³¹P n.m.r. spectrum of (3) the pattern expected for an AX spin system is observed [$\delta(\lambda^5\text{P}) - 16.5$ p.p.m.; $\delta(\lambda^4\text{P}) + 54.9$ p.p.m.; $J_{\text{PP}} 232$ Hz]. The ¹H n.m.r. spectrum of (3) in dichloromethane may be interpreted in terms of a first-order system: $\delta(\text{NCH}_3)$ 3.09; $J(\text{PNCH}_3)$ 5.6 Hz; $\delta(\text{N}'\text{CH}_3)$ 2.96; $J(\text{PN}'\text{CH}_3)$ 8.6 Hz; $\delta(\text{PCH}_3)$ 2.17; $^2J(\text{PCH}_3)$ 13.5 Hz; $^3J(\text{PP}'\text{CH}_3)$ 7.5 Hz; $\delta(\text{P}'\text{CH}_3)$ 2.08; $^2J(\text{P}'\text{CH}_3)$ 13.5 Hz; $^3J(\text{P}'\text{PCH}_3)$ 9.3 Hz.[‡]

As illustrated in the Figure the geometry around the pentacoordinate phosphorus atom in (3) is about halfway between that of a trigonal bipyramid (TBP) and a square pyramid (SP). Analysis of interplanar angles⁸ indicates a 56% C_{2v} distortion of the TBP in the direction of SP. The comparably large difference between the axial and equatorial P–O bond lengths [1.768(5) and 1.658(4) Å, respectively] shows the residual TBP character of the bonding around P(1). The $\lambda^5\text{P}-\lambda^4\text{P}$ bond [2.216(3) Å] is slightly longer than published values for a $\lambda^5\text{P}-\lambda^3\text{P}$ [2.195(2) Å]⁴ and a $\lambda^4\text{P}-\lambda^3\text{P}$

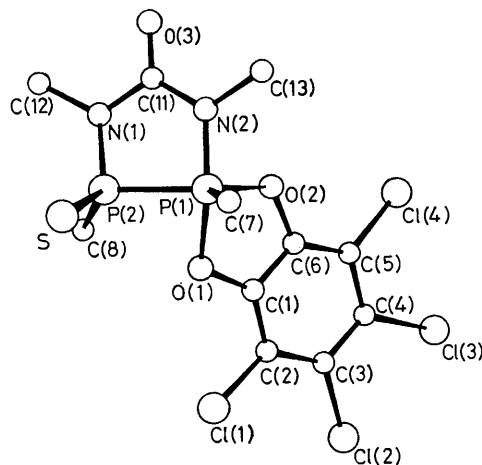


FIGURE. The structure of (3).

(2.193 Å)⁹ bond. The NMeC(:O)NMe group exhibits only a minute deviation from planarity [sum of angles at N(1) and C(11) 360.0°; at N(2) 358.7°].

The geometry at the $\lambda^4\text{P}$ atom is distorted tetrahedral, with the endocyclic angle N(1)–P(2)–P(1) reduced to 94.8(2)°. The rather large P=S bond length [1.929(2) Å] is comparable with that of similar bond lengths in phosphorothioates.¹⁰

The $\lambda^5\text{P}-\text{C}$ and $\lambda^4\text{P}-\text{C}$ bond lengths are nearly identical [1.781(9) and 1.783(7) Å]. The two methyl groups are 'trans,' relative to the five-membered ring. The n.m.r. spectra give no indication of the existence of (3) as two isomers (*cis* and *trans*), and it appears that sulphur attacks the $\lambda^3\text{P}$ atom exclusively at the geometrically less crowded side of the ring.

Bond lengths and angles not mentioned are in the normally observed and/or geometrically required range.

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[†] *Crystal data*: triclinic; space group $P\bar{1}$; $a = 9.484(3)$; $b = 13.045(4)$; $c = 8.695(2)$ Å; $\alpha = 102.64(2)$; $\beta = 119.92(2)$; $\gamma = 84.32(2)$; $Z = 2$; $D_c = 1.613$ g cm⁻³. The intensity data were collected on a Syntex P2, diffractometer using Cu- $K\alpha$ radiation by the $\theta-2\theta$ scan technique at a scan rate of 2.93–29.30°/min, depending on the intensity of the reflection. 3216 unique reflections were measured in the range $3^\circ \leq 2\theta \leq 135^\circ$. The structure was determined by direct methods and difference Fourier synthesis (SHELX-76; G. M. Sheldrick). Least-squares refinement using 2313 reflections with $I \geq 2\sigma(I)$ led to $R = 0.063$.

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.

[‡] ³¹P and ¹H n.m.r. spectra were obtained at 24.3 and 60 MHz, respectively, on a JEOL 60 HL instrument, with 85% H₃PO₄ (external) and Me₄Si (internal) as references; high-field shifts are negative.

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