

## A triphospholyl-substituted phosphine

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Received 20 February 1996

### Abstract

Tris(2,3,4,5-tetramethylphospholyl)phosphine (**1**) has been prepared via the reaction of Li(PC<sub>4</sub>Me<sub>4</sub>) with PCl<sub>3</sub>. The structure of **1** was determined by single-crystal X-ray diffraction: triclinic, space group *P* $\bar{1}$  with *a* = 8.795(2), *b* = 11.489(2), *c* = 14.557(3) Å,  $\alpha$  = 72.89(3),  $\beta$  = 88.92(3),  $\gamma$  = 67.69(3)°, *V* = 1293.4(7) Å<sup>3</sup> and *Z* = 2.

**Keywords:** Tetrphosphine; Phospholyl; X-ray structure

### 1. Introduction

The parent *iso*-tetrphosphine, P(PH<sub>2</sub>)<sub>3</sub>, has been prepared (for reviews see Ref. [1]) in admixture with *n*-P<sub>4</sub>H<sub>6</sub>. In subsequent work, Baudler et al. [2] discovered that a *t*-butyl-substituted derivative of *iso*-tetrphosphine, P(P(*t*Bu)H)<sub>3</sub>, can be obtained in a pure state [2] and Fritz and coworkers [3,4] have isolated several *iso*-tetrphosphines bearing trimethylsilyl and/or hydrocarbyl groups. One such compound, P[P(SiMe<sub>3</sub>)Me]<sub>3</sub>, has been characterized by X-ray crystallography [3]. It occurred to us that an alternative way to stabilize the *iso*-P<sub>4</sub> skeleton might be realized by incorporation of the peripheral phosphorus atoms into a cyclic ligand system.

### 2. Experimental

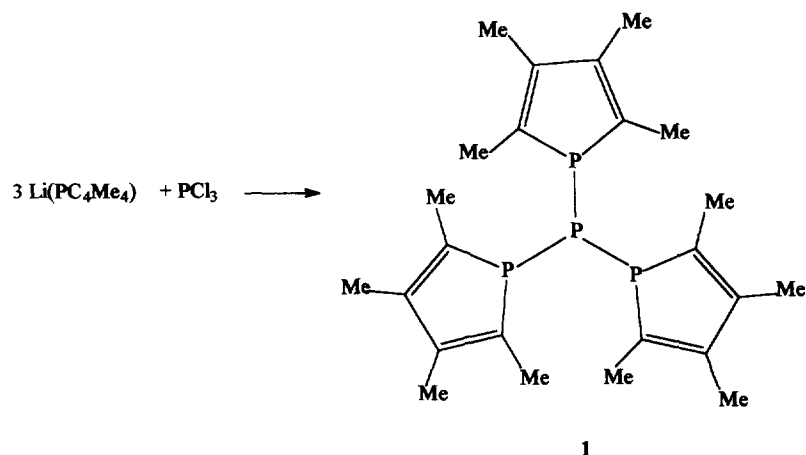
A solution of Li(PC<sub>4</sub>Me<sub>4</sub>) [5] was prepared by treatment of 1-phenyl-2,3,4,5-tetramethylphosphole (0.86 g, 4.0 mmol) in THF (50 ml) with a slurry of Li powder (0.11 g, 16.0 mmol) in THF (150 ml). The solvent was removed in vacuo and the resulting residue was extracted with Et<sub>2</sub>O. The ethereal extract was added via

cannula to a solution of PCl<sub>3</sub> (0.18 g, 1.3 mmol) in Et<sub>2</sub>O (25 ml) at –78 °C. The stirred reaction mixture was allowed to warm to 25 °C over a 4 h period, following which the solvent and volatiles were removed under reduced pressure and the resulting solid residue was extracted with hexane (50 ml). After filtration, the filtrate was concentrated and stored at –30 °C, resulting in a 23% yield of yellow crystalline P(PC<sub>4</sub>Me<sub>4</sub>)<sub>3</sub> (**1**) (Scheme 1), m.p. 145 °C. Anal. Found: C, 64.88; H, 8.10. C<sub>24</sub>H<sub>36</sub>P<sub>4</sub>. Calc.: C, 64.28; H, 8.09%. HRMS: found 448.1755; calcd 448.1767.

### 3. Results and discussion

The tetrphosphorus skeleton of **1** was evident from the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum which exhibits a quartet at  $\delta$  –51.06 (relative intensity 1) due to the central phosphorus atom and a doublet at  $\delta$  –9.55 (relative intensity 3) stemming from the peripheral (phospholyl) phosphorus atoms. The <sup>1</sup>J<sub>PP</sub> value of 292.3 Hz is consistent with P(III)–P(III) single bond formation [3,4]. The <sup>1</sup>H NMR spectrum of **1** is very simple and indicative of the equivalence of the three phospholyl rings ( $\delta$  2.15 (m, 6H, 2,5-Me);  $\delta$  2.28 (s, 6H, 3,4-Me)). Compound **1** was also characterized by EI mass spectrometry. The most intense peak occurs at *m/z* = 448 and corresponds to M<sup>+</sup>; the primary mode of fragmentation involves loss of phospholyl units.

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Scheme 1.

Confirmation of the above structure assignment was forthcoming from a single-crystal X-ray diffraction study.

*Crystal data:*  $\text{C}_{24}\text{H}_{36}\text{P}_4$ ,  $M = 448.4$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.795(2)$ ,  $b = 11.489(2)$ ,  $c = 14.557(3)$  Å,  $\alpha = 72.89(3)$ ,  $\beta = 88.92(3)$ ,  $\gamma = 67.69(3)^\circ$ ,  $V = 1293.4(7)$  Å<sup>3</sup>,  $D_c = 1.151$  g cm<sup>-3</sup>,  $Z = 2$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo K}\alpha) = 3.0$  cm<sup>-1</sup>. A total of 3268 independent reflections was collected on a Siemens P4 diffractometer at 298 K with  $2\theta$  between 3.5 and 45.0° using the  $\theta$ - $2\theta$  scan mode and a graphite monochromator. The data set was corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined (full-matrix least squares) to  $R$  and  $wR$  values of 0.0728 and 0.0902 respectively.

The X-ray analysis revealed that **1** is monomeric in the solid state (Fig. 1) and that there are no unusually short intermolecular contacts. The  $\text{P}_4$  skeleton is

arranged in a trigonal pyramidal fashion typical of a tertiary phosphine; the P–P–P bond angles fall within a narrow (4°) range and the average angle is 104.2(1)°. The average P–P bond distance of 2.223(5) Å is consistent with a bond order of unity. In turn, these metrical parameters are very similar to those for the *iso*-tetraphosphine  $\text{P}[\text{P}(\text{SiMe}_3)\text{Me}]_3$  for which the average P–P bond distance is 2.201(7) Å and the average P–P–P bond angle is 105.4(3)° [3]. The phospholyl ligands, each of which is planar within experimental error, are arranged around the central phosphorus atom in a propeller fashion; the dihedral angles between the P(2), P(3), and P(4) phospholyl rings and the P(2)–P(3)–P(4) plane are 71.8°, 53.4°, and 84.8° respectively. The metrical parameters for the phospholyl rings are very similar to those found for the corresponding benzyl phosphole [6] and each phospholyl phosphorus atom adopts a trigonal pyramidal geometry.

Finally, efforts are underway to synthesize the corresponding phospholyl derivatives of arsenic, antimony, and bismuth since such compounds might be able to function as photo or thermal single-source precursors to inter-Group 15 phases such as AsP, SbP, and BiP [7].

### Acknowledgements

We are grateful to the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

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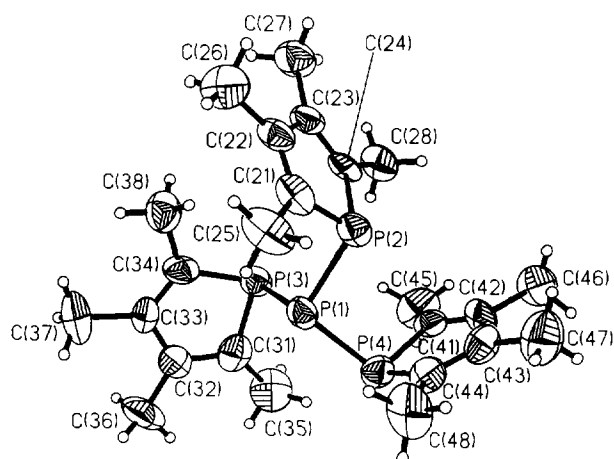


Fig. 1. Molecular structure of **1**. Important bond lengths (Å) and angles (deg): P(1)–P(2) 2.217(5), P(1)–P(3) 2.237(5), P(1)–P(4) 2.215(5), P(2)–P(1)–P(3) 106.4(2), P(2)–P(1)–P(4) 102.4(2), P(3)–P(1)–P(4) 103.8(2), P(1)–P(2)–C(21) 100.6(5), P(1)–P(2)–C(24) 110.5(4), P(1)–P(3)–C(31) 97.8(4), P(1)–P(3)–C(34) 96.2(5), P(1)–P(4)–C(41) 109.2(4), P(1)–P(4)–C(44) 96.7(4).

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