

Short communication

Low temperature neutron and X-ray diffraction study of  
imino(triphenyl)phosphorane <sup>1</sup>

Matthew G. Davidson <sup>a,\*</sup>, Andrés E. Goeta <sup>a</sup>, Judith A.K. Howard <sup>a,2</sup>, Christian W. Lehmann <sup>a</sup>,  
Garry M. McIntyre <sup>b</sup>, Richard D. Price <sup>a</sup>

<sup>a</sup> University of Durham, Department of Chemistry, Science Site, Durham, DH1 3LE, UK

<sup>b</sup> Institut Laue Langevin, B.P. 156, Grenoble 38042, Cedex 9, France

Received 2 April 1997

Abstract

The structure of imino(triphenyl)phosphorane, Ph<sub>3</sub>PNH **1** has been determined by low-temperature X-ray and neutron diffraction. This dual study is the first such for an iminophosphorane. From the neutron diffraction data, the P–N bond length is 1.582(2) Å and the P–N–H angle is 115.0(2)°. © 1998 Elsevier Science S.A.

*Keywords:* Iminophosphorane; Phosphorus; X-ray and neutron diffraction

1. Introduction

During our work on the interactions of phosphonium ylides and iminophosphoranes with s-block metals [1–3] and organic acids [4], we isolated imino(triphenyl)phosphorane, Ph<sub>3</sub>PNH **1**.

Although iminophosphoranes are commonly represented with a P=N double bond **1a**, their chemical and structural similarity to isoelectronic phosphonium ylides [5] suggests that a dipolar ylidic representation **1b** is equally valid (Scheme 1). The molecular structure of **1**, shown in Fig. 1, is of interest in order to probe the nature of this P–N bonding both by accurate structural studies and by comparison with *N*-substituted, -complexed, -protonated, and -metallated derivatives.

2. Experimental

2.1. Synthesis of imino(triphenyl)phosphorane **1**

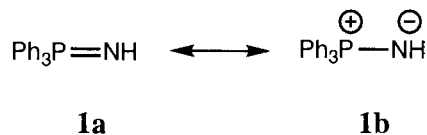
All solvents were freshly distilled over appropriate drying agents prior to use.

Ph<sub>3</sub>PNH was prepared by modification of a method described previously [6]: 15 g (57.3 mmol) Ph<sub>3</sub>P were placed in a 1000 ml round-bottomed Schlenk vessel and dried in vacuo before addition of acetonitrile (100 ml). A total of 3 ml bromine in 45 ml acetonitrile were added dropwise over a period of 45 min via a pressure-equalising funnel and ammonia was then bubbled through the reaction mixture for 4 h. The resulting solution was stirred at ambient temperature overnight and after removal of the solvent in vacuo the residue was extracted with chloroform and the undissolved NH<sub>4</sub>Br removed by filtration. Precipitation by addition of diethyl ether yielded 33.5 g (82%) Ph<sub>3</sub>PNH<sub>2</sub>Br which was subsequently dried in vacuo and stored under N<sub>2</sub>. 15 g (42 mmol) Ph<sub>3</sub>PNH<sub>2</sub>Br and 1.01 g (42 mmol) NaH were placed in a round-bottomed Schlenk vessel under a dry N<sub>2</sub> atmosphere and 50 ml toluene added. The reaction mixture was stirred at 100°C for 48 h and

\* Corresponding author. Fax: +44-0191-386-1127; e-mail: m.g.davidson@durham.ac.uk.

<sup>1</sup> Dedicated to Prof. Ken Wade on the occasion of his 65th birthday with sincere thanks for stimulating and fruitful collaborations in elucidation of the beautiful and complex structures that stem from a unique and extensive chemistry.

<sup>2</sup> Also corresponding author.



Scheme 1.

then filtered hot to remove NaBr. Cooling the resulting pale brown solution to room temperature overnight yielded 7.7 g (66%) colourless crystals of **1** which were isolated and stored under N<sub>2</sub> in a glove box. Crystals for the diffraction studies were obtained by similar reactions performed on a 5 mmol scale using 15 ml toluene.

## 2.2. X-ray crystal and molecular structure determination of **1**

The X-ray diffraction study was performed at 150(2) K on a Siemens SMART-CCD diffractometer [7] using graphite-monochromated Mo-K $\alpha$  X-radiation ( $\lambda = 0.71073$  Å). Unit cell parameters were obtained from 267 reflections ( $17 < \theta < 24$ ). Empirical formula: C<sub>18</sub>H<sub>16</sub>NP,  $M = 277.29$ . A white crystal of  $0.2 \times 0.2 \times 0.1$  mm was used. Space group  $P2_1/c$  (Monoclinic) with  $a = 14.587(9)$  Å,  $b = 9.597(6)$  Å,  $c = 10.965(7)$  Å,  $\beta = 90.428(6)^\circ$ ,  $V = 1535(2)$  Å<sup>3</sup>,  $\mu = 0.168$  mm<sup>-1</sup>,

$Z = 4$ . 6376 reflections, from which 2577 were unique ( $R_{\text{int}} = 0.0282$ ), were collected to a maximum  $2\theta$  of  $51^\circ$ ,  $-17 < h < 15$ ,  $-10 < k < 10$ ,  $-7 < l < 13$ ; no absorption correction was applied. The structure was solved by direct methods and 2545 reflections were used for the least squares refinement [8]. H(1) was located from a difference Fourier map and freely refined, all other H atoms were placed at calculated positions and refined using a riding model with their individual isotropic displacement parameter set to 1.2 times that of the attached C atom. Refinement was on  $F^2$  and converged to a  $wR_2 = 0.1149$ , goodness of fit = 1.112 for all data, and conventional  $R_1 = 0.0479$  for [2077 reflections with  $F > 4\sigma(F)$ ], 185 parameters. Residual electron density,  $+0.14/-0.21$  e Å<sup>-3</sup>.

## 2.3. Neutron diffraction study of **1**

The neutron diffraction experiment was performed on the D10 four-circle diffractometer [9] at the Institut Laue Langevin using a wavelength of 1.2658(4) Å obtained by a Cu(200) monochromator. The air-sensitive crystals were manipulated in a glove-box under an atmosphere of dry, oxygen-free N<sub>2</sub>. A sample was mounted on an aluminium pin using a low temperature (4K) epoxy glue (Oxford Instruments, TRZ0004) and

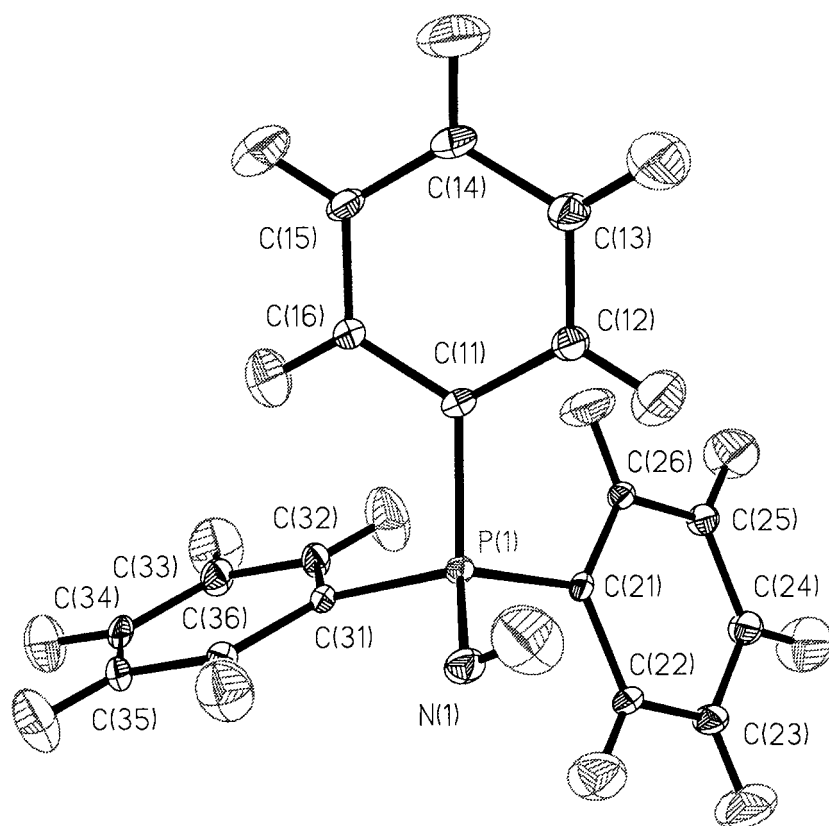


Fig. 1. Ortep plot of **1** with thermal ellipsoids at 70% level (derived from neutron diffraction data).

then, whilst still in the glove-box, sealed under a quartz dome in order to maintain the inert atmosphere around the crystal during subsequent transport and measurement. Data collection was carried out at 20(1)K using a liquid-He flow cryostat. Unit cell parameters were determined from 25 reflections,  $a = 14.301(5)$  Å,  $b = 9.541(4)$  Å,  $c = 10.686(3)$  Å,  $\beta = 90.72(3)^\circ$ ,  $V = 1458(1)$  Å<sup>3</sup>. A crystal of  $3.5 \times 3 \times 1$  mm was used to collect 3412 reflections ( $\theta_{\max} = 50.74$ ),  $-17 < h < 17$ ,  $-11 < k < 3$ ,  $-7 < l < 12$ ; 2716 unique reflections ( $R_{\text{int}} = 0.023S$ ) were used for the refinement. Data were corrected for absorption using a Gaussian grid integration [10] ( $T_{\max} = 0.8318$  and  $T_{\min} = 0.5878$ ). Heavy atom positions from the X-ray model were used as a starting point for the refinement. Hydrogen atom positions were located from subsequent difference Fourier maps. All atoms were refined with anisotropic atomic displacement parameters. Refinement [8] was on  $F^2$  and converged to a  $wR_2 = 0.0435$ , goodness of fit = 1.149 for all data and conventional  $R_1 = 0.0389$  for [2083 reflections with  $F > 4\sigma(F)$ ], 326 parameters.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry are available from the authors on request.

### 3. Results and discussion

An X-ray structure of **1**, determined at 203 K, has also recently been reported by Grün et al. [11]. Comparison with that presented here shows a disagreement in the cell parameters, in particular  $b$  and  $\beta$ .<sup>3</sup> In order to investigate the possibility of a phase transition occurring between 203 and 150 K, we remeasured our cell parameters of **1** at 203 K, obtaining  $a = 14.508(4)$ ,  $b = 9.557(2)$ ,  $c = 10.893(2)$ ,  $\beta = 90.29(1)$ . We can, therefore, discount a phase transition as being responsible for the discrepancy and instead attribute it to the characterisation of two different polymorphs of Ph<sub>3</sub>PNH. This possibility is supported by a number of observations. Firstly, the ambiguous nature of the ylidic P–N bond in **1** is consistent with the existence of different molecular geometries of similar energy: the main difference in the geometries of the two polymorphs is in the length of the P–N bond [1.524(3) and 1.582(2) Å, Grün et al. [11] and this (neutron) work, respectively]. Secondly, polymorphism has been observed in similar compounds: for example, three polymorphs of Ph<sub>3</sub>P=O, which is isoelectronic and isonuclear with **1** are known [12–14]. Thirdly, samples of **1** were obtained by different synthetic procedures and crystallised from different solvents.

<sup>3</sup> Cell parameters from Ref. [11]:  $a = 14.604(9)$ ,  $b = 9.289(6)$ ,  $c = 10.966(6)$  Å,  $\beta = 93.35(5)^\circ$  at  $T = 203$  K.

While Grün et al. [11] mention the non-existence of intermolecular N–H...N bridges, they omit to report the existence of three intermolecular C–H...N contacts (see Table 1) which form layers of molecules parallel to the  $bc$ -plane. One hydrogen bond forms chains along the  $c$ -axis, while the other two intermolecular hydrogen interactions form chains along  $b$ , the links of which are tetrameric. Layers formed by the combination of these interactions have a thickness of two molecules, approximately the length of the  $a$ -axis. One such layer is shown in Fig. 2.

The molecular geometry of **1** is largely as expected (values quoted for **1** are derived from the neutron diffraction experiment). The P atom has a slightly distorted tetrahedral geometry with C–P–N angles ranging from 109.1(1) to 115.6(1)°. The P–N bond length in **1** [1.582(2) Å] is in the range of those reported for N-substituted imino(triphenyl)phosphoranes: in Ph<sub>3</sub>PN(*p*-BrC<sub>6</sub>H<sub>4</sub>) the P–N bond length is 1.567(6) Å [15] and in Ph<sub>3</sub>PNPh, 1.602(3) Å [16]. The P–N–H bond angle in **1** [115.0(2)°] is more acute than the corresponding P–N–C angles in either of the above-mentioned *N*-aryl substituted derivatives [124.2(5)° and 130.4(3)° for Ph<sub>3</sub>PN(*p*-BrC<sub>6</sub>H<sub>4</sub>) and Ph<sub>3</sub>PNPh, respectively]. Whether this is simply a steric effect or, more significantly, indicative of pyramidalisation of N such as it is found for the ylidic carbon atom in the isoelectronic unsubstituted phosphonium ylide, Ph<sub>3</sub>PCH<sub>2</sub> [17], remains unclear. The P–N bond length in **1** is also concordant with the decrease in P–X distance along the isoelectronic and isonuclear series of Ph<sub>3</sub>PX compounds from Ph<sub>3</sub>PBH<sub>3</sub> to Ph<sub>3</sub>PO [P–X distances for X = BH<sub>3</sub> [18], CH<sub>2</sub> [16], NH (this work) and O [12–14] are 1.917 (average), 1.661 (average), 1.582(2) and 1.494 (average) Å, respectively]. This reduction in P–X bond length from B to O can be attributed to a combination of factors: a decrease in covalent radius; an increase in electronegativity (and a possible increase in the degree of electrostatic shortening in the bond); and a possible increase in P–X multiple bonding. The relative contribution of each of these factors, which is not necessarily constant throughout the series, has yet to be satisfactorily resolved.

To further elucidate the nature of the P–N bond in iminophosphoranes in particular, and ylidic P–X (where

Table 1  
Geometries of intermolecular C–H...N contacts found in **1**, derived from neutron diffraction data

D–H...A	D–H	H...A	D...A	D–H...A
C(14)–H(14)...N(1) <sup>i</sup>	1.082(3)	2.410(4)	3.331(2)	142.1(3)
C(26)–H(26)...N(1) <sup>ii</sup>	1.081(3)	2.484(3)	3.534(2)	163.5(3)
C(34)–H(34)...N(1) <sup>iii</sup>	1.088(4)	2.599(4)	3.439(2)	133.4(3)

Symmetry Codes: (i)  $1 - x, 0.5 + y, 1.5 - z$ ; (ii)  $x, 0.5 - y, 0.5 + z$ ; (iii)  $x, -0.5 - y, 0.5 + z$ .

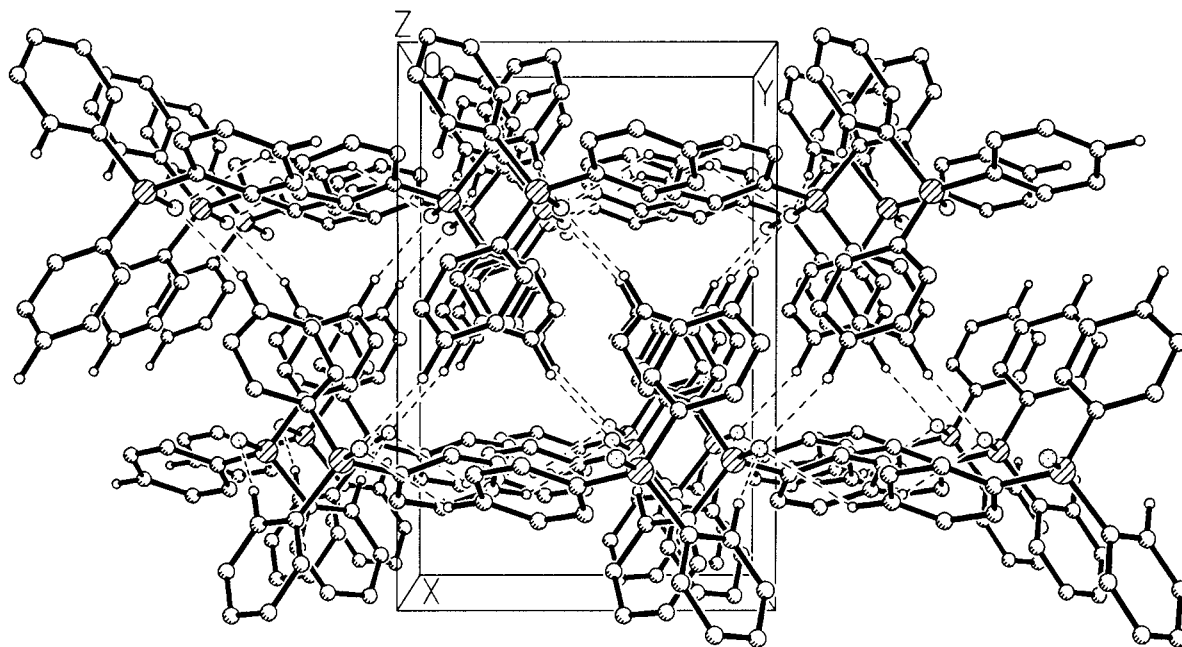


Fig. 2. Packing diagram of **1**, viewed down the crystallographic *c* axis, showing one polymeric layer of molecules parallel to the *bc* plane. H-atoms, except those involved in hydrogen bonding, omitted for clarity.

X = C, N or O) bonds in general, we plan to collect X-ray diffraction data at 20 K using the *Fddd* high intensity cryogenic diffractometer at Durham University [19] to complement the neutron diffraction study reported here and thereby perform charge density studies on **1**.

### Acknowledgements

A.E.G. and R.D.P. thank EPSRC for a Postdoctoral Fellowship and a Quota studentship, respectively. J.A.K.H. thanks The Royal Society for a Leverhulme Trust Senior Research Fellowship. The authors would like to acknowledge the Institut Laue Langevin for the beam time awarded in order to perform the neutron measurement.

### References

- [1] D.R. Armstrong, M.G. Davidson, D. Moncrieff, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 478.
- [2] A.S. Batsanov, M.G. Davidson, J.A.K. Howard, S. Lamb, R. Price, *Chem. Commun.* (1997) 1211.
- [3] A.S. Batsanov, P.D. Bolton, R.C.B. Copley, M.G. Davidson, J.A.K. Howard, C. Lustig, R.D. Price, *J. Organomet. Chem.*, 550 (1998) 445–448.
- [4] M.G. Davidson, *J. Chem. Soc., Chem. Commun.* (1995) 919.
- [5] A.W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993.
- [6] H.J. Cristau, J. Kadoura, L. Chiche, E. Torreilles, *Bull. Soc. Chim. Fr.* (1989) 515.
- [7] Program used for data collection: SMART (1995). Program used for data reduction: SAINT (1995). Siemens Analytical X-ray Instruments, Madison, WI, USA.
- [8] G.M. Sheldrick, SHELXTL, (1995). Ver. 5.03/VMS, Siemens Analytical X-ray Instruments, Madison, WI, USA.
- [9] Program used for data collection: MAD. A. Barthelemy, Technical Report 84BA15T (1984). Program used for data reduction: COLL5N. M.S. Lehmann, S. Wilson. College V, Data Reduction System: Treatment of Reflection Profiles (1987). Institut Laue Langevin, Grenoble, France.
- [10] P. Coppens, DATAP, The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis, in: F.R. Ahmed (Ed.), *Crystallographic Computing* (1970) Munksgaard.
- [11] M. Grün, K. Harms, R.M. zu Köcker, K. Dehnicke, H. Goemann, *Z. Anorg. Allg. Chem.* 622 (1996) 1091.
- [12] G. Bandoli, G. Bartolozzo, D.A. Clemente, U. Croatto, C. Panattoni, *J. Chem. Soc. A* (1970) 2778; Orthorhombic form.
- [13] G. Ruban, V. Zabel, *Cryst. Struct. Commun.* 5 (1976) 671, first monoclinic form.
- [14] A.L. Spek, *Acta Crystallogr.* C43 (1987) 1233, second monoclinic form.
- [15] M.J.E. Hewlins, *J. Chem. Soc. B* (1971) 942.
- [16] E. Böhm, K. Dehnicke, J. Beck, W. Hiller, J. Strähle, A. Maurer, D. Fenske, *Z. Naturforsch.* 43B (1988) 138.
- [17] H. Schmidbaur, J. Jeong, A. Schier, W. Graf, D.L. Wilkinson, G. Müller, *New J. Chem.* 13 (1989) 341.
- [18] J.C. Huffman, W.A. Skupinski, K.G. Caulton, *Cryst. Struct. Commun.* 11 (1982) 1435.
- [19] R.C.B. Copley, A.E. Goeta, C.W. Lehmann, J.C. Cole, D.S. Yufit, J.A.K. Howard, J.M. Archer, *J. Appl. Crystallogr.* 30 (1997) 413.