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A one step nickel(II)-catalysed synthesis of *tris*-{2-(2-benzothiazolyl)phenyl}phosphine from *tris*(hydroxymethyl)phosphine. Crystallographic evidence of intramolecular nitrogen to phosphorus coordination

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Abstract

Heating together 2-(2-bromophenyl)benzothiazole with *tris*-(hydroxymethyl)phosphine (generated in situ from *tetrakis*-(hydroxymethyl)phosphonium chloride and base) and nickel(II)bromide in aqueous ethanol results in the formation of the title triarylphosphine, isolated in a 20% yield. An X-ray crystallography study reveals that all three heterocyclic nitrogen atoms are involved in coordinative interactions with phosphorus, the average N–P distance (2.974 Å) being significantly smaller than the sum of the Van der Waals radii. Normal pyramidal geometry at phosphorus is observed. The crystal structure of the related *tris*-{2-(2-benzothiazolyl)phenyl}phosphine oxide is also reported. In this molecule, only one short nitrogen to phosphorus interaction is observed (2.888 Å). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydroxymethyl phosphines; Triarylphosphines; Kinetic template effect; Metal ion catalysis

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1. Introduction

There is renewed interest in the chemistry of hydroxymethylphosphines, and in particular that of *tris*-(hydroxymethyl)phosphine. This surprisingly air-stable, water-soluble phosphine is easily accessible by treatment of *tetrakis*-(hydroxymethyl)phosphonium chloride (commercially available as an aqueous solution (80% w/v), with one equivalent of a base [1]. Its water-soluble nickel, palladium, and platinum complexes have been investigated recently with respect to their application in homogeneous catalysis [2–4]. The presence of the reactive hydroxymethyl functionality enables the further derivatisation of the phosphine, enabling the synthesis of new functional phosphines. Thus, its reaction with ferrocenylmethyltrimethylammonium iodide has given ferrocenylmethyl-*bis*-(hydroxymethyl)phosphine [5], which can be transformed into the remarkably air-stable primary phosphine, ferrocenylmethylphosphine, simply by treatment with sodium metabisulphite [6].

We have explored metal ion-promoted reactions of phosphines with aryl halides which bear a suitably disposed potential donor ligand group, usually imino- or azo-nitrogen, in the *ortho* position to the halogen. The donor group acts as a kinetic template in facilitating the introduction of the phosphine into the carbon–halogen bond, ultimately to give an arylphosphonium salt [7]. In an extension of this work, we were interested in exploring the related reactions of *tris*-(hydroxymethyl)phosphine, in the hope of isolating new hydroxymethylphosphonium salts which could be the precursor of new hybrid imino/azo-phosphine hybrid

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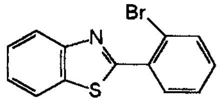
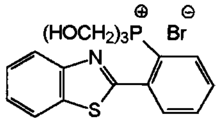
ligands. Accordingly, we studied the reaction of 2-(2-bromophenyl)benzothiazole (**1**) with *tris*-(hydroxymethyl)phosphine in the presence of nickel(II)-bromide, in refluxing ethanol, anticipating the formation of the phosphonium salt (**2**) *via* involvement of the sp^2-nitrogen of the heterocyclic ring as a template for the metal ion, facilitating introduction of phosphorus into the carbon–bromine bond.



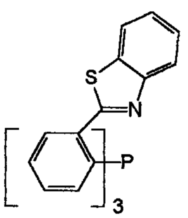
(**1**)



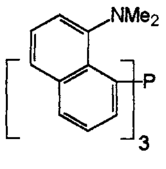
(**2**)

2. Results and discussion

When the above reactants were heated together under nitrogen in ethanol, for several hours, a pale brown solution resulted which, on cooling, deposited needle-like crystals. Examination by thin layer chromatography indicated that although the crystals consisted of a single component, the substance was significantly less polar than the anticipated phosphonium salt would have been, and had a pattern of development in iodine vapour reminiscent of a *tertiary* arylphosphine. The ^{31}P-NMR spectrum consisted of a single peak at -17.0 ppm, again suggestive of a triarylphosphine environment with some additional shielding. The ^{1}H-NMR spectrum showed only complex multiplets arising from aromatic hydrogen. The mass spectrum showed a low intensity apparent molecular ion at m/z 661, with a base peak at m/z 451, suggesting that the product is the triarylphosphine (**3**) which, under mass spectrometric conditions, loses one aryl residue to form the related diarylphosphenium ion, Ar_2P^+. Microanalytical data were consistent with the triarylphosphine (**3**). The identity of this material was unequivocally determined by a single crystal X-ray analysis.



(**3**)



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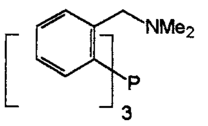


(**5**)

2.1. Crystal structure of the phosphine (3)

The X-ray structure of *tris*-{2-(2-benzothiazolyl)phenyl}phosphine (**3**) is shown in Fig. 1. In spite of the bulky substituents about phosphorus, the usual pyramidal configuration is retained, with C–P–C angles of 99.8(2), 100.1(2), and 101.0(2)° (average value 100.3°). These values are very similar to those for triphenylphosphine [8] in which the average C–P–C angle is 103.4°. However, the most interesting feature of the structure is the apparent interaction of the benzothiazolyl sp^2-N atoms with phosphorus, since all three N–P distances [2.966(5), 2.851(5) and 3.105(5) Å] are significantly shorter than the sum of the Van der Waals radii (3.4 Å). Although much longer than a covalent N–P bond (1.77 Å) [9], these distances are consistent with weak coordinate interactions between the heterocyclic nitrogens and the phosphorus atom. The apparent coordination from nitrogen appears to take place *trans* to a C–P bond, with C–P–N angles of 172.4(2), 173.0(2) and 175.4(2), average 173.6°. The N–P–N angles are 103.9(2), 105.3(2) and 110.4(2), average 106.5°. The planarity of the benzothiazolyl system is undisturbed, but the torsion angles between the phenyl ring and the heterocyclic substituent vary considerably [15.3(9), 30.3(8) and 53.6(8)°] to reduce inter-ring steric interactions. The corresponding bond lengths and angles in the three chemically equivalent benzothiazolylphenyl systems are mutually comparable and have values as expected for this type of species.

The structural arrangement about phosphorus in (**3**) is very similar to those reported for the triarylphosphines (**4**) and (**5**), in which comparable P–N interactions are apparent, involving average N–P distances of 2.834 Å in (**4**) and 3.026 Å in (**5**) [10]. Thus the structures of the phosphines (**3**), (**4**), and (**5**) all have very similar features, in spite of the variation in the nature of the potential N donor from dialkylarylamine to trialkylamine to heterocyclic sp^2-N. All involve formally seven coordinate phosphorus with three σ-bonds to carbon, three coordinate bonds from N to P, and the phosphorus lone pair. The overall geometry may be described as distorted octahedron, with an additional seventh site (centered on the N_3 trigonal face) being occupied by the lone pair. It is of interest to compare the environment about phosphorus in these phosphines to that in *tris*(2-hydroxymethylphenyl)phosphine (**6**), in which although all three oxygens are located on the same side of the molecule as the phosphorus lone pair, the phosphorus–oxygen distances are all longer than the sum of the Van der Waals radii [11].

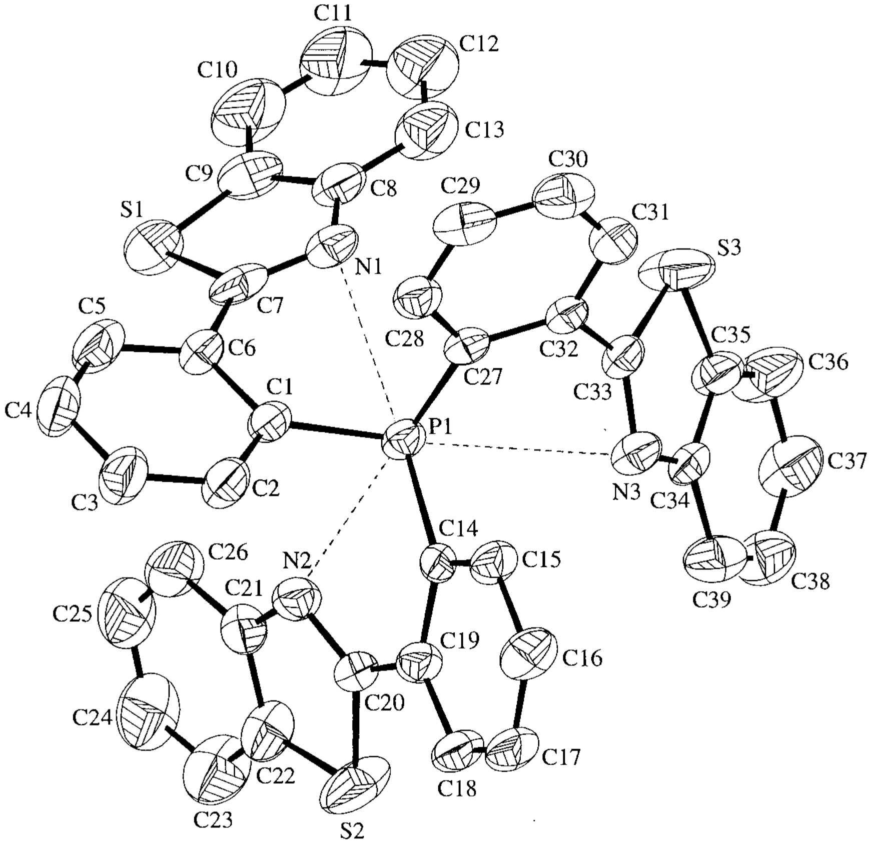
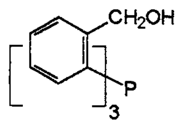


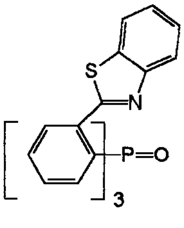
Fig. 1. X-ray structure of *tris*-{2-(2-benzothiazolyl)phenyl}phosphine (**3**) showing the crystallographic atom numbering scheme. The dashed lines indicate the P–N interactions. Thermal ellipsoids are drawn at 50% probability level. The hydrogen atoms are omitted for clarity.

2.2. Spectroscopic properties and reactivity of the phosphine (3)

The close approach of the three heterocyclic nitrogen atoms to phosphorus may account for the observed shielding of the ^{31}P nucleus (δ ^{31}P = -17 ppm) compared to that in triphenylphosphine (δ ^{31}P = -6 ppm). A similar effect has been noted for the phosphine (**5**) (δ ^{31}P = -34 ppm) but surprisingly not for phosphine (**4**), for which δ ^{31}P = 6.07 ppm [10]. We have briefly explored the reactivity of (**3**) towards electrophilic reagents. Oxidation with hydrogen peroxide in acetone gave the related triarylphosphine oxide (**7**), for which δ ^{31}P = 39.2 ppm, the phosphorus being somewhat deshielded compared to that in triphenylphosphine oxide (δ ^{31}P = 27 ppm). The identity of the oxide (**7**) was confirmed by an X-ray structure determination (see below). The phosphine was also heated with grey selenium in refluxing chloroform in the hope of isolating the related phosphine selenide, for which the coupling constant $^{1}J(^{31}\mathrm{P}-^{77}\mathrm{Se})$ would have given an indication of substituent effects at phosphorus [12]. However, the phosphine was recovered unchanged. It would be interesting to explore the use of the more reactive red form of selenium in this reaction. Similarly, it was also recovered unchanged from attempts to quaternize it with iodomethane or benzyl bromide in acetonitrile. The reduced reactivity at phosphorus is no doubt a reflection of steric crowding by the bulky *ortho*-substituents on the phenyl rings attached to phosphorus. The apparent formation of the diarylphosphenium ion (**8**) (*m*/*z* 451) as the base peak in the electron impact mass spectrum of the phosphine (**1**) is of considerable interest. Such a system is also likely to be stabilised by intramolecular coordination from the heterocyclic nitrogen atoms. Stable phosphenium ions of this type have recently been characterised [13]. It is of interest that the EI-MS of triphenylphosphine does not exhibit a simple M-phenyl fragment, the dibenzophospholium ion (**9**) (*m*/*z* 183) being the most significant fragment observed.



(**6**)



(**7**)

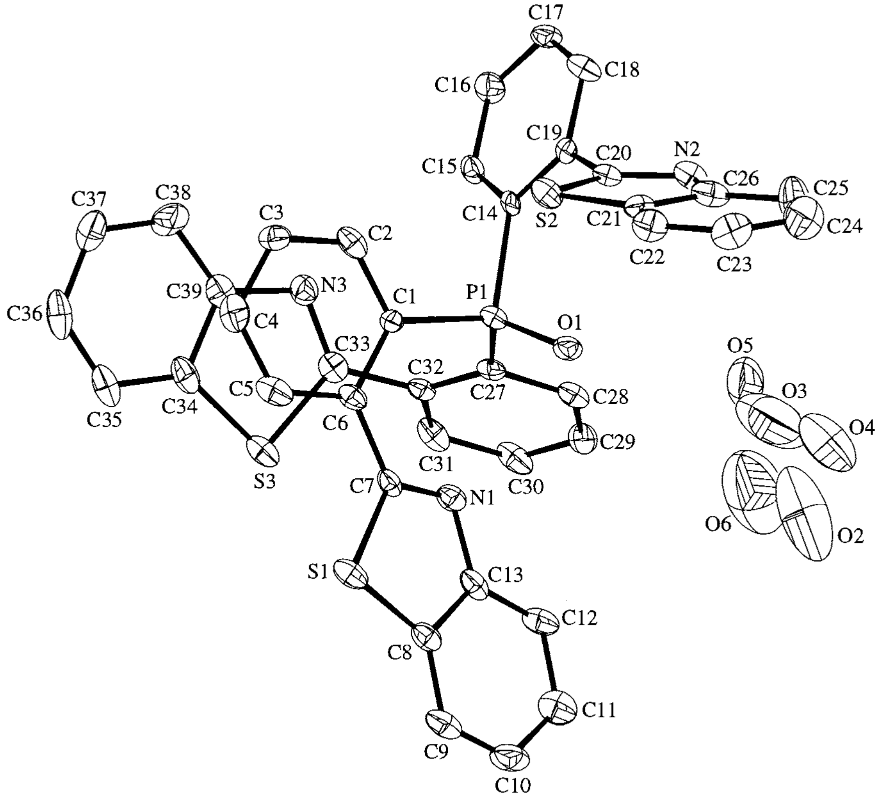
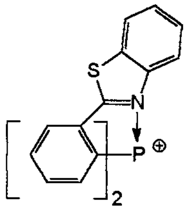
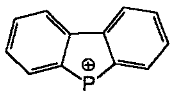


Fig. 2. X-ray structure of *tris*-{2-(2-benzothiazolyl)phenyl}phosphine oxide (**7**) showing the crystallographic atom numbering scheme. Thermal ellipsoids are drawn at 50% probability level. The hydrogen atoms are omitted for clarity.



(**8**)



(**9**)

2.3. Crystal structure of the phosphine oxide (7)

An X-ray structure determination of *tris*-{2-(2-benzothiazolyl)phenyl}phosphine oxide (**7**) confirmed the structure, shown in Fig. 2; the compound also contains 2.5 molecules of water (solvate) sited on several partially occupied positions and scattered about a centre of symmetry. One of these water molecules [O(5)] lies within the hydrogen bonded distance [2.867(8) Å] from the O(1) atom of the phosphine oxide.

The bond distances (Table 1) in (**7**) are comparable with the corresponding values in (**3**), but in this case only one possible P···N co-ordinative interaction is observed and somewhat larger angular distortions are observed around the phosphorus atom. The relative orientations of the benzothiazolyl groups are also significantly different due to greater steric crowding in the molecule. In particular, the much wider C(1)–P(1)–C(27) angle in (**7**), 113.1(3)° compared with 100.1(2)° in (**3**), seems to result from the close approaches of N(1) to O(1) [2.991(8) Å] and to P(1) [2.888(7) Å]. Similarly, the larger value for the torsion angle C(14)–C(19)–C(20)–N(2) in (**7**), 56.7(6)° compared with 15.3(9)° in (**3**), can be explained by the non-bonded contact between the O(1) and S(2) atoms [3.257(8) Å]. The P=O distance 1.483(4) Å is very close to the corresponding values in other *tertiary* phosphine oxides, e.g. 1.489, 1.474 and 1.483 Å in $Me_3P{=}O$ [14], $Me_2PhP{=}O$ [15] and $Ph_3P{=}O$ [16], respectively and seems to be unaffected by the possible hydrogen bonding with a half-occupied water solvate, or by the close approach of N(1) to phosphorus.

3. Experimental

^{31}P- and ^{1}H-NMR studies were carried out using a Bruker AC 250 FTNMR Spectrometer. Mass Spectra were recorded on a VG Micromass 7070F instrument.

3.1. Synthesis of the phosphine (**3**)

To a solution of *tetrakis*(hydroxymethyl)phosphonium chloride (80% w/v aqueous, 0.714 g) in ethanol (8 cm^3) was added aqueous sodium hydroxide (2.0 mol dm^{-3}, 1.5 cm^3), and the mixture swirled. To this was then added 2-(2-bromophenyl)-benzothiazole (0.29 g, 10^{-3} mol), followed by nickel(II)bromide (0.105 g, 5×10^{-4} mol), and the resulting system heated to reflux under nitrogen for 4 h. On cooling, a crystalline solid formed (61 mg, 21%), identified as *tris*-{2-(2-benzothiazolyl)phenyl}phosphine (**3**), m.p. 268°C (from ethanol). (Found: C, 70.05; H, 3.60; N, 6.25. $C_{39}H_{24}N_3PS_3$ requires C 70.75; H, 3.65; N, 6.35%). δ ^{31}P ($CDCl_3$) -17.0 ppm. δ ^1H ($CDCl_3$): 8.1 (m, 2H); 7.75 (m, 2H); 7.6–7.2 (m, 4H). *m*/*z* 661 (M^+, 3%); 451 (R_2P^+, 100%).

Treatment of the phosphine, dissolved in acetone, with aqueous hydrogen peroxide at room temperature gave *tris*-{2-(2-benzothiazolylphenyl}phosphine oxide (**7**), (90%), m.p. 168°C, (from ethanol). Found: C, 67.35; H, 3.90; N, 5.75. $C_{39}H_{24}N_3S_3PO \cdot H_2O$ requires C, 67.30; H, 3.75; N, 6.05%. δ ^{31}P ($CDCl_3$): 39.2 ppm. δ ^1H ($CDCl_3$): 7.92–7.78 (m, 2H); 7.72–7.56 (m, 2H); 7.54–7.40 (m, 2H); and 7.38–7.2 (m, 2H) ppm. *m*/*z* 667 (M^+, 30%); 467(R_2PO^+, 10%). IR ν_{max} 1150 cm^{-1} (P=O)

Table 1
Selected distances (Å) and angles (°) in (**3**) and (**7**)

	(**3**)	(**7**)
Bond distances (Å)		
P(1)–O(1)		1.483(4)
P(1)–C(1)	1.838(5)	1.817(5)
P(1)–C(14)	1.864(5)	1.845(5)
P(1)–C(27)	1.838(5)	1.836(6)
P(1)···N(1)	2.966(6)	2.888(7)
P(1)···N(2)	2.851(6)	
P(1)···N(3)	3.105(6)	
O(1)···N(1)		2.991(9)
O(1)···S(2)		3.257(7)
Bond angles (°)		
O(1)–P(1)–C(1)		114.7(2)
O(1)–P(1)–C(14)		108.8(2)
O(1)–P(1)–C(27)		111.8(2)
C(1)–P(1)–C(14)	101.0(2)	105.4(2)
C(1)–P(1)–C(27)	100.1(2)	113.1(3)
C(14)–P(1)–C(27)	99.8(2)	101.9(2)
N(1)–P(1)–C(14)	175.4(2)	
N(2)–P(1)–C27)	172.4(2)	
N(3)–P(1)–C(1)	173.0(2)	
N(1)–P(1)–N(2)	103.9(2)	
N(1)–P(1)–N(2)	105.3(2)	
N(2)–P(1)–N(3)	110.4(2)	
Torsional angles		
P(1)–C(1)–C(6)–C(7)	6.3(7)	4.7(8)
P(1)–C(14)–C(19)–C(20)	10.8(7)	10.6(8)
P(1)–C(27)–C(32)–C(33)	0.1(6)	2.3(7)
C(1)–C(6)–C(7)–N(1)	30.3(8)	10.9(9)
C(14)–C(19)–C(20)–N(2)	15.3(9)	56.7(6)
C(27)–C(32)–C(33)–N(3)	53.6(8)	66.7(8)

3.2. X-ray crystallography

Crystal data for (**3**): $C_{39}H_{24}N_3PS_3$, $Mr = 661.76$, triclinic, space group P-1 (no. 2), $a = 10.603(2)$, $b = 10.838(2)$, $c = 14.974(3)$ Å, $\alpha = 78.50(2)$, $\beta = 76.37(2)$, $\gamma = 82.740(8)°$, $V = 1633.0(4)$ $Å^3$, $Z = 2$, $D_{calc.} = 1.346$ Mg m^{-3}, $\mu(Mo–K_\alpha) = 0.310$ mm^{-1}, $F(000) = 684$, $T = 293(2)$ K, crystal size $0.18 \times 0.18 \times 0.12$ mm.

Crystal data for (**7**): $C_{39}H_{24}N_3OPS_3$, 2.5 H_2O, $Mr = 722.80$, triclinic, space group P-1 (no. 2), $a = 10.627(3)$, $b = 11.208(2)$, $c = 14.646(2)$ Å, $\alpha = 91.620(13)$, $\beta = 99.98(2)$, $\gamma = 91.820(14)°$, $V = 17.16.2(6)$ $Å^3$, $Z = 2$, $D_{calc.} = 1.399$ Mg m^{-3}, $\mu(Mo–K_\alpha) = 0.308$ mm^{-1}, $F(000) = 750$, $T = 150(2)$ K, crystal size $0.35 \times 0.24 \times 0.16$ mm.

All crystallographic measurements were made on a Delft Instruments FAST area detector diffractometer positioned at the window of a rotating anode generator with $Mo–K_\alpha$ radiation ($\lambda = 0.71069$ Å) by following procedures described elsewhere [17]. The cell parameters were determined by least-squares refinement of diffractometer angles for 250 reflections within$1.92 \leq \theta \leq 25.03°$ (**3**) and $1.82 \leq \theta \leq 25.08°$ (**7**). Both data sets were corrected for Lorentz and polarisation factors but not for absorption. The structures were solved by direct methods (SHELXS86) [18] and refined by full-matrix least-squares on F^2 using all unique data with intensities greater than zero (SHELXL93) [19]. In both cases, the non-hydrogen atoms were all anisotropic, but the displacement coefficients of the partially occupied oxygen atoms (water) were restrained [ISOR = 0.006] to prevent these atoms becoming 'non-positive-definite'. The hydrogen atoms on the heterocyclic rings in both structures were included in calculated positions (riding model); those on the water solvates in (**7**) were ignored. Final R_1 and wR_2 values are 0.0460 [1851 data with $I > 2\sigma(I)$] and 0.1150 (all 3886 data, 415 parameters), respectively for (**3**) and 0.0538 [2532 data with $I > 2\sigma(I)$] and 0.1197 (all 4564 data, 466 parameters), respectively for (**7**). The diagrams were drawn using SNOOPI [20]. Sources of scattering factor data are given in Ref. [19]. The calculations were done on a 200 MHz personal computer. Selected distances and angles for both (**3**) and (**7**) are presented in Table 1. The detailed crystallographic results for this study have been deposited with the Cambridge Crystallographic Data Centre and are available on request. Any such request should be accompanied by a full bibliographic reference for this work.

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