

SHORT PAPER

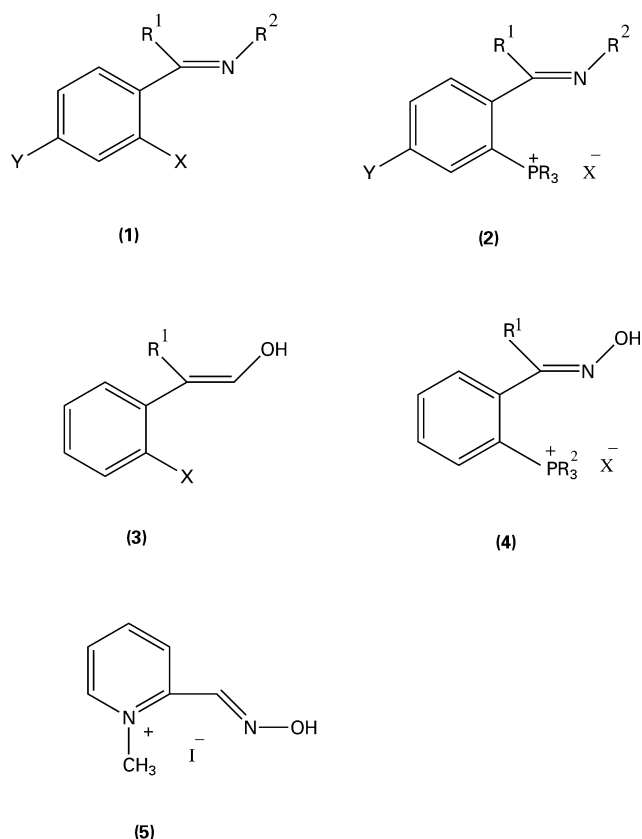
Hypervalent intramolecular coordination in main group chemistry: a template synthesis and crystal structure of an *ortho*-oximinoarylphosphonium salt[†]David W Allen^{a*}, Mark E Light^b and Michael B. Hursthouse^b^aChemistry Division, School of Science and Mathematics, Sheffield Hallam University, Sheffield S1 1WB, UK^bDepartment of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

The nickel(II)-catalysed reaction of triphenylphosphine with the oxime of *ortho*-bromoacetophenone gives an *ortho*-oximinoarylphosphonium salt, which shows a hypervalent intramolecular coordinative interaction between the oximino-nitrogen and the phosphonium centre.

Keywords: hypervalent intramolecular coordination, *ortho*-oximinoarylphosphonium salt

There is currently much interest in studies of coordination to main group elements, in particular that of p-block acceptors.^{1–4} We have a specific interest in systems involving intramolecular donation to the heavier Group 15 elements, notably phosphorus, arsenic, and antimony and have developed coordination template assisted syntheses of *ortho*-substituted aryl derivatives of these elements, which involve the presence of a donor atom, commonly nitrogen or oxygen, in the *ortho*-substituent.^{5,6} The donor atom is usually able to form a five-membered ring with the group 15 element, which may be in the trivalent state,⁷ or, more usually, in the form of a quadrivalent ‘onium species’.⁶

We have shown that when aryl halides bearing appropriate donor substituents in the *ortho* position are heated in ethanol



with a tertiary phosphine in the presence of nickel(II) or copper(II) catalysts, the halogen is replaced by the phosphine to form the related arylphosphonium salt. Thus, for example, the nickel(II)-catalysed reactions of the *ortho*-haloarylimines (1, $R^1 = \text{H}$ or Me ; $R^2 = \text{benzyl}$ or Ar ; $\text{X} = \text{Cl}$, Br , or I ; $\text{Y} = \text{H}$ or halogen) yield the phosphonium salts (2, $R^3 = \text{alkyl}$ or aryl).^{8,9} In the absence of the transition metal catalyst, these reactions do not occur. Similar substitution reactions have been achieved with *ortho*-haloaryl systems in which the key sp^2 -hybridised nitrogen atom is part of a heterocyclic ring system.^{10,11} A kinetic study of reactions of this type suggested that the mechanism involved initial reduction of nickel(II) to nickel(I), followed by oxidative insertion of the latter into the carbon-halogen bond to form an intermediate aryl-nickel(III) complex, stabilised by intramolecular coordination involving the sp^2 -hybridised nitrogen. Reductive elimination from the latter results in the arylphosphonium salt and regeneration of the nickel(I) species.¹²

We were interested in exploring the related reactions of *ortho*-haloaryl oxime templates (3), that would provide the cationic oxime system (4), of possible interest as an analogue of the pyridinium oxime (5), an antidote for poisoning by organophosphate nerve-agents, which functions by enabling nucleophilic displacement of organophosphate moieties from phosphorylated (acetyl)cholinesterases by the oxime unit, the cationic charge of the N-methyl pyridinium centre facilitating binding to the active site of the enzyme.¹³

When the oxime of 2'-bromoacetophenone (3, $R^1 = \text{Me}$, $\text{X} = \text{Br}$) was heated with triphenylphosphine and nickel(II) bromide in ethanol overnight, the arylphosphonium salt (4, $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $\text{X} = \text{Br}$) was formed in modest yield (25%). Clearly the *ortho*-bromoaryloxime is providing an appropriate coordination template for the nickel-catalysed replacement of halogen by phosphorus under mild conditions.

The structure was confirmed by microanalytical data, ³¹P and ¹H NMR spectroscopy, and the results of a single crystal X-ray structural study.

The structure of the salt is displayed in Fig. 1, and the compound exists in the solid state as a hydrogen bonded dimer (Fig. 2) via a four membered $\text{Br} - \text{H}_2\text{O} - \text{Br} - \text{H}_2\text{O}$ ring, with the water molecules hydrogen bonded to the oxime OH. Selected bond lengths and bond angles are given in Table 1. Hydrogen bond parameters are detailed in Table 2.

The oximino nitrogen interacts strongly with the phosphonium centre with the N–P distance being 2.781(4) Å (well within the sum of the Van der Waals radii of 3.40 Å). This flattens three of the tetrahedral angles around the phosphorus (115.44(11), 113.37(10), 110.82(10)) leading to a more trigo-

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

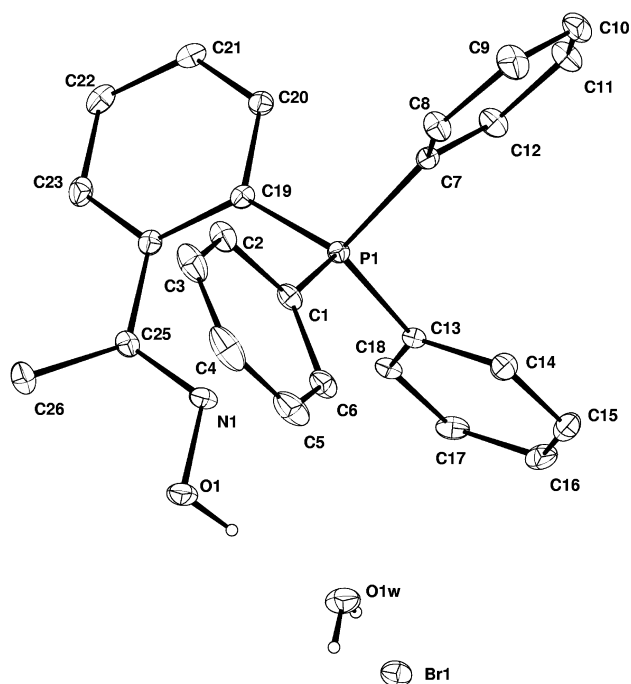


Fig. 1 Structure of the *o*-oximinoarylphosphonium salt.

nal bipyramidal geometry with N1 occupying an apical site (Fig. 3) ($N1-P1-C7 = 178.67(11)$). This interaction is very similar to that previously observed in the salt (2, $R^1 = H$; $R^2 = p\text{-MeOC}_6\text{H}_4$; $R^3 = \text{Ph}$; $Y = \text{H}$; $X = \text{I}^-$),⁶ and in other related compounds.^{10,11,14-16} Salt (2, $R^1 = H$; $R^2 = p\text{-MeOC}_6\text{H}_4$; $R^3 = \text{Ph}$; $Y = \text{H}$; $X = \text{I}^-$) showed an N-P distance of 2.757 Å with bond angles at P clearly distorted from tetrahedral and approaching a trigonal bipyramidal arrangement, coordination from N essentially creating a five-membered ring which spans apical-equatorial positions, the N-P-phenyl apical axis being almost linear ($N-P-C15$ 176.9°).

In the salt (4, $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $X = \text{Br}$), the revealed (*E*)-configuration of the aryloxime moiety is such that the lone pair at nitrogen should be appropriately disposed to make such a coordinative interaction with the cationic centre possible.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data

Table 1 Selected bond lengths and angles around phosphonium centre [Å and °]

P1...N1	2.781(4)	P1-C1	1.793(2)
P1-C7	1.818(2)	P1-C13	1.797(2)
P1-C19	1.805(2)	N1-C25	1.271(3)
N1-O1	1.390(2)		
C1-P1-C13	115.44(11)	C1-P1-C19	110.82(10)
C13-P1-C19	113.37(10)	C1-P1-C7	105.02(10)
C13-P1-C7	102.00(10)	C19-P1-C7	109.32(10)
N1...P1-C7	178.67(11)	N1...P1-C13	77.97(10)
N1...P1-C1	73.85(10)	N1...P1-C19	71.85(11)

Table 2 Hydrogen bonds [Å and °]

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O1-H1...O1W	0.84	1.82	2.662(3)	175.3
O1W-H1W...Br1 ⁱ	0.71(3)	2.57(3)	3.277(2)	175(3)
O1W-H2W...Br1	0.86(4)	2.58(5)	3.433(2)	171(3)

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z+1$

Centre (CCDC). Any request to the CCDC for this information should quote the full literature citation and the reference number CCDC 179098.

Experimental

³¹P and ¹H NMR studies were carried out using a Bruker AC250 FTNMR spectrometer.

Preparation of N-[2-triphenylphosphoniophenyl- α -methylbenzylidene]hydroxylamine bromide: 2-Bromoacetophenone oxime (2.0 g, 9.3×10^{-3} moles), triphenylphosphine (4.9 g, 18.7×10^{-3} moles), and nickel(II) bromide (1.0 g, 4.6×10^{-3} moles) were heated together in ethanol (10 cm³) under nitrogen for 3h. The reaction mixture was poured into aqueous potassium bromide solution (10%, w/v), and then extracted with dichloromethane (3×10 cm³). The dried extract was evaporated and the residue triturated several times with dry diethylether to give the salt as a white solid, 1.25g (25%), m.p. 282–285°C. (Found: C, 64.1, H, 4.95, N, 2.65. $\text{C}_{26}\text{H}_{23}\text{BrNOP}$. $\text{H}_2\text{O}_{(0.5)}$ requires C, 64.3, H, 5.0, N, 2.9%). δ ³¹P(CDCl₃) 25.75ppm. δ ¹H(CDCl₃) 8.1–7.7(m, 19ArH), 2.1(s, 3H)ppm.

Crystal data for the salt N-[2-triphenylphosphoniophenyl- α -methylbenzylidene]hydroxylamine, (4, $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $X = \text{Br}$): these were collected on a Bruker Nonius Kappa CCD area detector diffractometer mounted at the window of a molybdenum rotating anode following standard procedures. Crystals of the salt were grown from dichloromethane-ether.

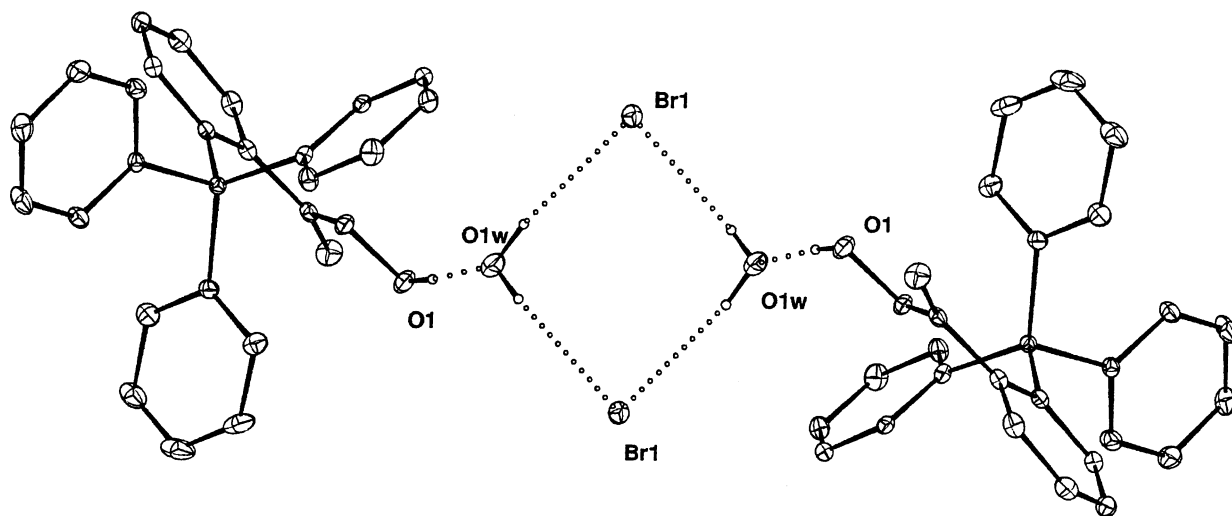


Fig. 2 Hydrogen bonding interactions.

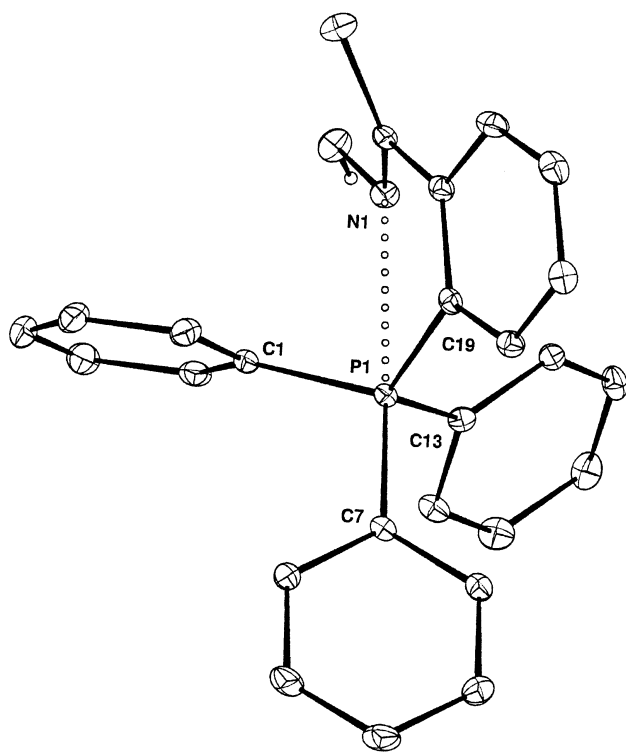


Fig. 3 Trigonal bipyramidal arrangement at phosphorus, showing apical nitrogen to phosphorus interaction.

Crystal data for $C_{26}H_{23}NOP \cdot H_2O \cdot Br$, $M_r = 494.35$, $T = 150(2)$ K, triclinic, space group $P-1$, $a = 10.1029(2)$, $b = 10.7903(2)$, $c = 11.8307(2)$ Å, $\alpha = 106.9004(9)$, $\beta = 97.0845(11)$, $\gamma = 105.9223(10)^\circ$,

$V = 1157.39(4)$ Å³, $\rho_{\text{calc}} = 1.419$ g cm⁻³, $\mu = 1.868$ mm⁻¹, $Z = 2$; reflections collected: 14732, independent reflections: 4054 ($R_{\text{int}} = 0.0528$), final R indices [$I > 2\sigma(I)$]: $R1 = 0.0295$, $wR2 = 0.0719$, R indices (all data): $R1 = 0.0343$, $wR2 = 0.0744$.

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