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FULL PAPER

Azo-containing tertiary phosphines: synthesis, reactivity and structural characterisation

Mark J. Alder, Wendy I. Cross, Kevin R. Flower * and Robin G. Pritchard

Department of Chemistry, UMIST, PO Box 88, Manchester, UK M60 1QD.
E-mail: k.r.flower@umist.ac.uk

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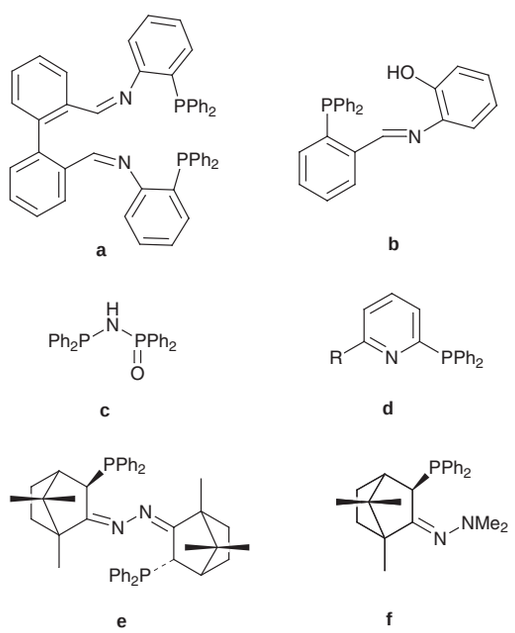
6-Bromo-2-methoxynaphthalene **1** was converted into 6-diphenylphosphanyl-2-methoxynaphthalene **2a** by preparing its Grignard and quenching with PPh_2Cl. Compound **2a** was demethylated on refluxing in HBr yielding 6-(diphenylphosphanyl)naphthalen-2-ol **2b** in good yield. Oxidation of **2b** with either H_2O_2 or S_8 afforded the corresponding phosphine oxide **3a** or sulfide **3b** respectively. Treatment of **2b** with a stoichiometric amount of NaH and quenching of the anion with $[4\text{-R-}C_6H_4N_2][BF_4]$ (R = H, Me, Et, ^{i}Pr, ^{t}Bu, NO_2 or NMe_2) yielded the C–N coupled azo-containing phosphines in good yield; similar coupling reactions of **3a**, **3b** afforded analogous compounds, again in good yield. Evidence is presented that shows the coupling reaction does not proceed through a P–N coupled intermediate, which would subsequently need to rearrange to the observed C–N coupled products. The latter all exist as tautomeric mixtures of the azo and hydrazone forms. The tautomerisation in some cases was suppressed on conversion into their acetic acid esters by reaction with NaH followed by acetyl chloride. All of the new compounds have been characterised by elemental analysis (C, H, N), FAB mass spectrometry, ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H} NMR and in selected cases by Uv-visible spectroscopy. The position of the C(2) resonance in the ^{13}C-{^{1}H} NMR spectra has been used to calculate the position of the azo/hydrazone equilibrium and hence the mole fraction of each tautomer present in solution. These data were used to interpret the Uv-visible data. In addition, three compounds have been further characterised by single crystal X-ray diffraction studies.

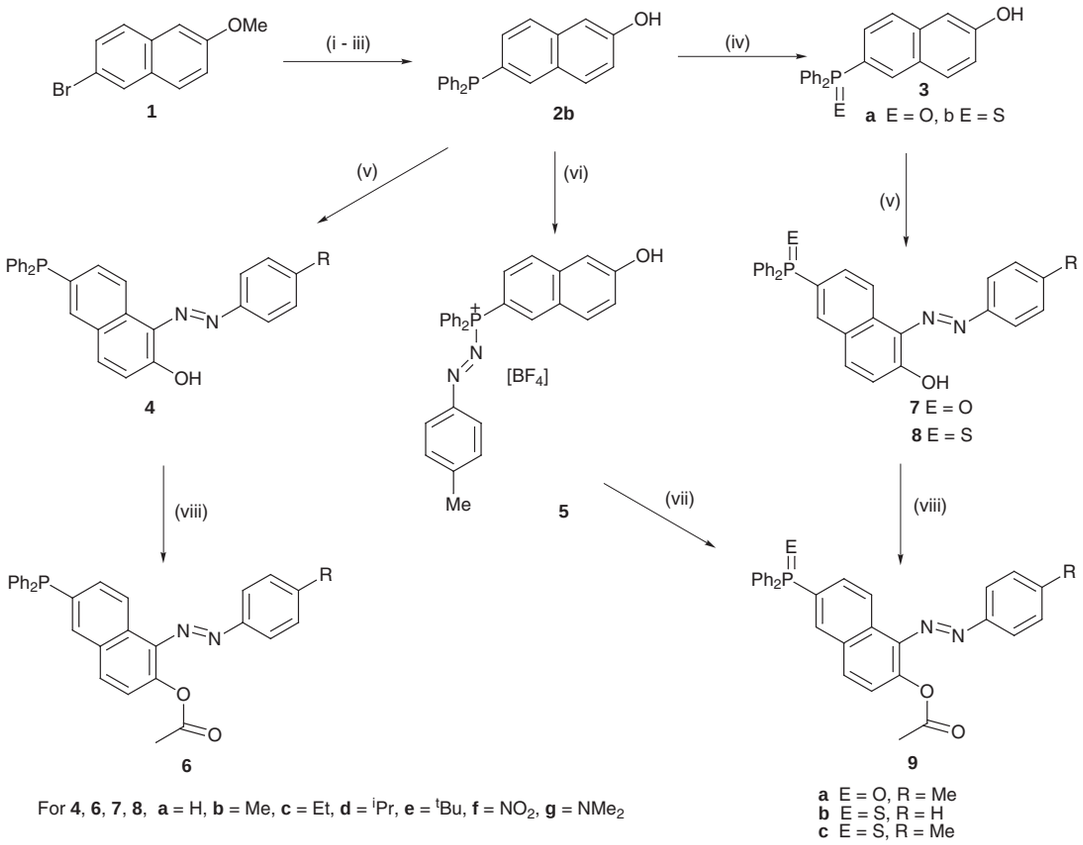
Introduction

A wide range of functionalised tertiary phosphines have been prepared and their use as ancillary ligands in transition metal chemistry is well documented.[1] Indeed there are many different types of phosphines that contain nitrogen functional groups,[2] see below for an illustration of current representative examples. Perusal of the literature for phosphines that contain a N–N/N=N bond showed that Shaw and co-workers have reported the synthesis of azine[2e] and hydrazone[2f] containing phosphines, and thoroughly investigated their chemistry over the last 10 years.[3] There are some reports of phosphorus(v) species that contain an azo (RN=NR) moiety,[4] the first dating from 1953. Allen's group have recently prepared a series of phosphonium salts that contained an azo moiety *via* nickel catalysed coupling reactions between triphenylphosphine and halogenophenylazophenols.[5] The groups of Lequan and Lambert have reported the preparation of phosphorus(v) compounds containing an azo moiety and investigated their non-linear optical properties.[4j–l] These compounds were synthesized by low temperature lithium/halogen exchange on halogenophenylazobenzenes and quenching with chlorophosphines. From these reactions they only managed to isolate phosphine oxides and phosphonium salts, after adding suitable oxidising agents, from purported phosphorus(iii) precursors due to the oxidative sensitivity of the azo-containing phosphines.[4j–l]

We considered the possibility of preparing azo-containing phosphines by standard azo coupling reactions rather than the metallation approach used by Lequan and Lambert's groups. There are, on reflection, however several potential pitfalls in this approach, namely the nucleophilicity of phosphorus(iii) precursors, as witnessed by the reaction of tertiary phosphines with diazo compounds and azides,[6] the strongly oxidising conditions used to generate diazonium salts (HONO)[7] will readily oxidise the phosphorus centre, and the conditions normally required to reduce phosphine oxides back to P^{III} are likely to reduce the azo moiety as well;[8] the reaction between triphenylphosphine and a diazonium salt under aqueous conditions has been shown to yield triphenylphosphine oxide and quaternised products caused by hydrolysis of an initially formed P–N coupled product or direct nucleophilic displacement of dinitrogen.[9]



In a recent short communication we reported[10] the preparation of a phosphine that contained an azo moiety and the



Scheme 1 (i) Mg, THF; (ii) PPh_2Cl; (iii) HBr, NaOH, $MeCO_2H$; (iv) H_2O_2 or S_8; (v) NaH, $[4\text{-}RC_6H_4N_2][BF_4]$; (vi) $[4\text{-}RC_6H_4N_2][BF_4]$; (vii) NaH, $[4\text{-}RC_6H_4N_2][BF_4]$, H_2O; (viii) NaH, MeCOCl.

molecular structure of its oxide, followed by some preliminary complexation studies of these phosphines towards Group 6 metal carbonyls.[11] Herein, we report an improvement in the synthetic procedure for the preparation of this class of compound, their tautomeric behaviour in solution and the solid state and their reactivity towards oxidising agents.

Results and discussion

It is well known that deprotonated hydroxyl groups can be used to activate an aromatic ring to undergo a C–N coupling reaction with an aromatic diazonium salt, for example in the dye industry the use of naphthalen-2-ol in coupling reactions with diazonium salts is extensive. A characteristic of this reaction is the rate of coupling to a diazonium salt is much faster than that of the corresponding phenols. An azo coupling reaction with naphthalen-2-ol precipitates the product almost immediately on addition of diazonium salt, whereas, when the reaction is carried out with a corresponding phenol, careful control of the pH is required and the reaction can take several hours to go to completion. We reasoned then that if the azo coupling reaction was to take place in a molecule that contained a phosphorus(III) moiety then the use of the naphthalen-2-ol system would be a good place to start as the rate of C–N coupling may be comparable or even faster than previously observed P–N couplings between diazonium salts and triarylphosphines.[9] Since hydrolysis of P–N coupled products was shown to yield phosphine oxides[9c] we decided to carry out the coupling reaction in non-aqueous solvents to circumvent this.

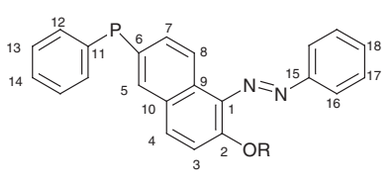
Our initial coupling reactions were carried out in ethanol using NaOH as the base;[10] we found that the purity of the product was dependent upon how rigorously the ethanol had been dried. As a result of this the decision was taken to modify the solvent system and the base used to generate the anion, *i.e.* to remove as much water from the system as possible. Thus, deprotonation of **2b**, which was prepared in two steps from commercially available 6-bromo-2-methoxynaphthalene **1**, with NaH in dry THF generated the naphthalide anion which was quenched with 4-R-phenyldiazonium tetrafluoroborate (where R = H, Me, Et, ^{i}Pr, ^{t}Bu, NO_2 or NMe_2), Scheme 1, affording the C–N coupled azo-containing phosphines **4a**–**4g** in good yield. These compounds were all fully characterised by microanalysis and multinuclear NMR studies, see Table 1 for physical data, Table 2 for ^{1}H and ^{31}P-{^{1}H} NMR, Table 3 for ^{13}C-{^{1}H} NMR and Table 4 for Uv-visible data. In addition **4b** was characterised by a single crystal X-ray diffraction study; see Table 5 for selected bond lengths and angles.

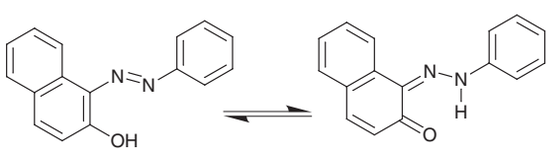
The ^{1}H NMR data (Table 2) are consistent with compounds **4a**–**4g** being azo-containing phosphines. Of particular note is the singlet observed in each spectrum around δ 16.1 which is assigned to the formal 'OH' proton on the naphthalene ring. This proton readily exchanges on addition of D_2O and these values are comparable to that observed for 1-phenylazonaphthalen-2-ol where δ 16.1.[12] The ^{31}P-{^{1}H} NMR (Table 2) all show a single resonance around δ −5 which is shifted slightly but comparable with that of **2a**, and infer no oxidation took place during the coupling procedure; when the preparation of **4a**–**4g** was carried out in ethanol the ^{31}P-{^{1}H} NMR spectra of the crude materials often showed additional resonances at *ca.* δ 25 and 30 corresponding to quaternised and oxidised products. The ^{13}C-{^{1}H} NMR spectra have been assigned (Table 3), see below for the numbering scheme, with the aid of DEPT 135 spectra, previously reported assignments of non-phosphorus containing 1-phenylazonaphthalen-2-ols[13] and substituent effects.[14] We are confident in our assignments as the process of assignment was further aided by observed coupling to the spin active phosphorus nucleus. The position of the C(2) resonance varies from δ 156.4 for **4f** to δ 179.8 for **4g** and this wide range of values is a result of the well known azo/hydrazone tautomerisation, see below. These data are also consistent with the non-phosphine containing 1-(4-R-phenylazo)naphthalen-2-ols[13] and will be discussed further later.

Table 1 Physical and analytical data for compounds **4**–**9c**[a]

Compound	Colour	Yield(%)	*m*/*z*[b]	mp/°C	Analysis (%)		
					C	H	N
4a	Red	49	433(MH^+, 100)	116	77.5 (77.8)	4.9 (4.9)	6.2 (6.5)
4b	Red	66	447(MH^+, 80)	145	77.5 (78.0)	5.2 (5.2)	5.8 (5.8)
4c	Red	35	461(MH^+, 100)	105	78.0 (78.2)	5.5 (5.4)	6.6 (6.1)
4d	Red	72	475(MH^+, 100)	130	78.2 (78.4)	5.7 (5.7)	5.9 (5.9)
4e	Red	35	489(MH^+, 42)	151	78.6 (78.8)	6.1 (6.0)	5.5 (5.7)
4f	Red	71	478(MH^+, 100)	202	68.1 (68.2)	4.4 (4.1)	7.5 (8.5)
4g	Black	64	475(M^+, 80)	194	75.7 (75.8)	5.5 (5.5)	8.9 (8.8)
6a	Orange	55	475(MH^+, 100)	126	76.1 (75.9)	4.8 (4.9)	5.8 (5.9)
6b	Red	56	489(MH^+, 40)	171	75.9 (76.2)	5.0 (5.1)	5.5 (5.7)
6c	Red	62	503(MH^+, 70)	138	75.8 (76.7)	5.5 (5.4)	5.5 (5.6)
6d	Red	52	517(MH^+, 100)	124	76.6 (76.7)	5.9 (5.7)	5.4 (5.4)
6e	Red	66	530(MH^+, 100)	120	77.1 (77.1)	5.8 (5.8)	5.6 (5.3)
6f	Black	61	518(MH^+, 22)	167	72.6 (72.0)	5.4 (5.7)	7.6 (7.8)
7a	Red	74	449(MH^+, 100)	190	68.6 (68.5)	4.5 (4.5)	5.7 (5.5)
7b	Red	59	463(MH^+, 38)	214	73.3 (75.3)	4.8 (5.0)	5.8 (6.0)
7c	Red	80	477(MH^+, 100)	196	73.2 (73.1)	5.4 (5.2)	5.6 (5.6)
7d	Red	73	491(MH^+, 100)	226	75.6 (75.9)	5.6 (5.5)	5.6 (5.7)
7e	Red	60	505(MH^+, 100)	162	73.8 (73.6)	5.6 (5.6)	5.3 (5.3)
8a	Red	80	465(MH^+, 62)	130	71.5 (72.4)	4.5 (4.6)	6.0 (6.0)
8b	Red	60	479(MH^+, 60)	183	73.0 (72.8)	5.1 (4.8)	5.6 (5.9)
8c	Red	58	491(MH^+, 100)	176	73.8 (73.8)	5.6 (5.6)	5.3 (5.3)
8d	Red	65	507(MH^+, 100)	161	73.7 (73.6)	5.7 (5.4)	5.4 (5.5)
8e	Red	48	521(MH^+, 100)	172	73.9 (73.8)	5.5 (5.6)	5.7 (5.4)
8f	Red	52	510(MH^+, 100)	300	65.7 (66.0)	4.0 (4.0)	8.2 (8.0)
8g	Black	59	508(MH^+, 100)	245	71.1 (71.0)	5.0 (5.2)	8.3 (8.3)
9a	Orange	71	507(MH^+, 100)	156	70.9 (71.1)	4.9 (5.6)	5.3 (5.6)
9b	Red	83	505(MH^+, 45)	197	72.9 (73.8)	4.8 (5.0)	5.3 (5.3)
9c	Red	77	521(MH^+, 35)	165	70.6 (71.5)	4.8 (4.8)	5.3 (5.4)

[a] Calculated values in parentheses. [b] Relative intensity in parentheses.





Final confirmation of the formulation of compounds **4a**–**4g** was obtained from a single crystal X-ray diffraction study carried out on **4b**. An ORTEP[15] representation of the molecule with the atomic numbering scheme is given in Fig. 1. The structure reveals several points of interest. First, in the solid state the compound exists primarily as the hydrazone tautomer as shown by the following bond lengths: C(2)–O(1) 1.262(6); C(1)–N(1) 1.323(8); N(1)–N(2) 1.306(6); N(2)–C(11) 1.394(8) Å. These data show there is significant elongation of the N–N bond and contraction of the C(2)–O(1) bond. Secondly the formal 'OH' proton was located on N(2), thus confirming a preference for the hydrazone tautomer in the solid state. Finally, there is a strong intramolecular hydrogen bond[16] N(2)–H · · · O(1): N(2)–

Table 2 ^{1}H NMR [a] (δ) and ^{31}P-{^{1}H} NMR data [b] (δ) for compounds **2**–**9c**

Compound	^{31}P	^{1}H
2a	−4.5	7.8–7.4 (br m, 15 H, aryl H); 7.2 (d, J_{HH} 6, aryl H); 3.9 (s, 3 H, CH_3)
2b	−4.5	7.8–7.6 (br m, 3 H, aryl H); 7.4–7.3 (br m, 12 H, aryl H)
3b	44.3	8.0 (d, J_{PH} 15.4, 1 H, aryl H); 7.8–7.4 (br m, 13 H, aryl H); 7.0 (s, 2 H, aryl H)
4a	−5.2	16.1 (s, 1 H, OH); 8.5 (d, J_{HH} 8.2, 1 H, aryl H); 7.8–7.3 (br m, 17 H, aryl H); 6.9 (d, J_{HH} 9.6, aryl H)
4b	−5.2	16.2 (s, 1 H, OH); 8.6 (d, J_{HH} 8.4, 1 H, aryl H); 7.7–7.3 (br m, 17 H, aryl H); 6.9 (d, J_{HH} 9.4, 1 H, aryl H), 2.4 (s, 3 H, CH_3)
4c	−5.1	16.2 (s, 1 H, OH); 8.6 (d, J_{HH} 8.4, 1 H, aryl H); 7.7–7.3 (br m, 17 H, aryl H); 6.9 (d, J_{HH} 9.4, 1 H, aryl H); 2.7 (q, J_{HH} 7.4, 2 H, CH_2); 1.3 (t, J_{HH} 7.4, 3 H, CH_3)
4d	−5.1	16.2 (s, 1 H, OH); 8.6 (d, J_{HH} 8.2, 1 H, aryl H); 7.8–7.3 (br m, 17 H, aryl H); 6.9 (d, J_{HH} 9.2, 1 H, aryl H); 3.0 (m, J_{HH} 6.8, 1 H, CH); 1.3 (d, J_{HH} 6.8, 6 H, CH_3)
4e	−5.1	16.2 (s, 1 H, OH); 8.6 (s, J_{HH} 8.2, 1 H, aryl H); 7.7–7.3 (br m, 17 H, aryl H); 6.9 (d, J_{HH} 9.4, 1 H, aryl H); 1.4 (s, 9 H, CH_3)
4f	−5.4	16.1 (s, 1 H, OH); 8.3 (d, J_{HH} 9.0, 1 H, aryl H); 8.2 (dd, J_{HH} 8.8, 3.2, 2 H, aryl H); 8.1 (dd, J_{HH} 7.0, 2.0, 2 H, aryl H); 7.7–7.3 (br m, 12 H, aryl H); 6.7 (d, J_{HH} 9.6, 1 H, aryl H); 6.6 (dd, J_{HH} 7.0, 2.0, 2 H, aryl H)
4g	−5.2	15.6 (s, 1 H, OH); 8.8 (d, J_{HH} 8.3, 1 H, aryl H); 7.0, (d, J_{HH} 2.0, 2 H, aryl H); 7.8–7.4 (br m, 15 H, aryl H); 7.1 (d, J_{HH} 9.0, 2 H, aryl H); 6.8 (d, J_{HH} 9.0, 1 H, aryl H); 3.1 (s, 6 H, CH_3)
6a	−4.9	8.6 (d, J_{HH} 8.6, 1 H, aryl H); 8.0–7.3 (br m, 18 H, aryl H); 2.3 (s, 3 H, CH_3)
6b	−4.8	8.6 (d, J_{HH} 8.8, 1 H, aryl H); 7.9–7.3 (br m, 18 H, aryl H); 2.5 (s, 3 H, CH_3); 2.3 (3 H, CH_3)
6c	−4.9	8.6 (d, J_{HH} 9.3, 1 H, aryl H); 7.9–7.3 (br m, 18 H, aryl H); 2.8 (q, J_{HH} 7.8, 2 H, CH_2); 2.3 (s, 3 H, CH_3); 1.3 (t, J_{HH} 7.8, 3 H, CH_3)
6d	−5.0	8.6 (s, J_{HH} 8.6, 1 H, aryl H); 7.7–7.3 (br m, 18 H, aryl H); 3.0 (m, 1 H, J_{HH} 6.7, CH); 2.3 (s, 3 H, CH_3); 1.3 (d, 6 H, J_{HH} 6.7, CH_3)
6e	−5.0	8.6 (d, J_{HH} 7.8, 1 H, aryl H); 7.9–7.2 (br m, 18 H, aryl H); 2.3 (s, 3 H, CH_3); 1.4 (s, 9 H, CH_3)
6g	−5.0	8.6 (d, J_{HH} 9.0, 1 H, aryl H); 7.9–7.7 (br m, 5 H, aryl H); 7.4–7.3 (br m, 11 H, aryl H); 6.8 (d, J_{HH} 9.0, 2 H, aryl H); 3.0 (s, 6 H, CH_3); 2.3 (s, 3 H, CH_3)
7a	30.1	16.3 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.4, J_{PH} 2.8, 1 H, aryl H); 8.0 (d, J_{PH} 12.8, 1 H, aryl H); 7.8–7.4 (br m, 17 H, aryl H); 7.0 (d, J_{HH} 9.2, 1 H, aryl H)
7b	29.8	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.6, J_{PH} 2.6, 1 H, aryl H); 8.1 (d, J_{PH} 13.0, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.2, 1 H, aryl H); 2.4 (s, 3 H, CH_3)
7c	30.1	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.4, J_{PH} 2.4, 1 H, aryl H); 8.1 (d, J_{PH} 12.8, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.2, 1 H, aryl H); 2.7 (q, J_{HH} 7.6, 2 H, CH_2); 1.3 (t, J_{HH} 7.6, 3 H, CH_3)
7d	29.9	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.4, J_{PH} 2.6, 1 H, aryl H); 8.1 (d, J_{PH} 12.8, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H); 3.0 (m, J_{HH} 6.8, 1 H, CH); 1.3 (d, J_{HH} 6.8, 6 H, CH_3)
7e	29.9	16.3 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.2, J_{PH} 2.6, 1 H, aryl H); 8.1 (d, J_{PH} 12.8, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (dd, J_{HH} 9.4, J_{PH} 1.6, 1 H, aryl H); 1.4 (s, 9 H, CH_3)
8a	43.6	16.3 (s, 1 H, OH); 8.6 (dd, J_{HH} 8.4, J_{PH} 2.8, 1 H, aryl H); 8.1 (d, J_{PH} 12.8, 1 H, aryl H); 7.8–7.3 (br m, 17 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H)
8b	43.7	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.6, J_{PH} 2.8, 1 H, aryl H); 8.1 (d, J_{PH} 13.2, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H); 2.4 (s, 3 H, CH_3)
8c	43.7	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.6, J_{PH} 2.8, 1 H, aryl H); 8.1 (d, J_{PH} 13.0, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H); 2.7 (q, J_{HH} 7.6, 2 H, CH_2); 1.3 (t, J_{HH} 7.6, 3 H, CH_3)
8d	43.7	16.2 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.4, J_{PH} 2.8, 1 H, aryl H); 8.1 (d, J_{PH} 14.6, 1 H, aryl H); 7.8–7.3 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H); 3.0 (m, J_{HH} 7.0, 1 H, CH); 1.3 (d, J_{HH} 7.0, 6 H, CH_3)
8e	43.7	16.3 (s, 1 H, OH); 8.7 (dd, J_{HH} 8.4, J_{PH} 3.0, 1 H, aryl H); 8.1 (d, J_{PH} 14.6, 1 H, aryl H); 7.8–7.5 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.4, 1 H, aryl H); 1.4 (s, 9 H, CH_3)
8f	44.0	16.2 (s, 1 H, OH); 8.5 (dd, J_{HH} 8.5, J_{PH} 3.0, 1 H, aryl H); 8.3 (d, J_{HH} 9.0, 2 H, aryl H); 8.1 (d, J_{PH} 14.0, 1 H, aryl H); 7.8–7.5 (br m, 16 H, aryl H); 6.8 (d, J_{HH} 9.5, 1 H, aryl H)
8g	44.4	15.7 (s, 1 H, OH); 8.8 (d, J_{HH} 7.5, 1 H, aryl H); 8.2 (d, J_{PH} 15.6, 1 H, aryl H); 7.8–7.5 (br m, 16 H, aryl H); 7.0 (d, J_{HH} 9.5, 1 H, aryl H); 3.1 (s, 6 H, CH_3)
9a	29.6	8.7 (dd, J_{HH} 8.8, J_{PH} 2.7, 1 H, aryl H); 8.4 (d, J_{PH} 13.7, 1 H, aryl H); 8.0–7.3 (br m, 17 H, aryl H); 2.5 (s, 3 H, CH_3); 2.3 (s, 3 H, CH_3)
9b	44.4	8.7 (dd, J_{HH} 8.7, J_{PH} 2.5, 1 H, aryl H); 8.4 (d, J_{PH} 13.6, 1 H, aryl H); 8.0–7.3 (br m, 17 H, aryl H); 2.3 (s, 3 H, CH_3)
9c	43.8	8.7 (dd, J_{HH} 8.6, J_{PH} 2.8, 1 H, aryl H); 8.4 (d, J_{PH} 15.6, 1 H, aryl H); 8.0–7.3 (br m, 17 H, aryl H); 2.5 (s, 3 H, CH_3); 2.3 (s, 3 H, CH_3)

[a] Spectra recorded in $CDCl_3$ and referenced to $CHCl_3$; coupling constants in Hz. [b] Spectra recorded in $CDCl_3$ and referenced to 85% H_3PO_4; coupling constants in Hz.

H 0.93(6), N(2)–O(1) 2.520(7), O(1)–H 1.75(7) Å, N–H–O 138(5)°.

All of the spectroscopic and crystallographic data confirmed that an azo moiety had been introduced into a phosphorus(III) species *via* a classical azo coupling reaction. One question that remained to be answered was: does the coupling proceed through a P–N coupled intermediate? Anecdotal evidence was obtained to show that this is not the case, Scheme 1. Addition of 4-methylphenyldiazonium tetrafluoroborate to **2a** in dry THF afforded the P–N coupled product **5** which displayed a ^{31}P-{^{1}H} NMR resonance at δ 40. Deprotonation of this adduct with NaH afforded a pale yellow solution which did not go the characteristic deep red associated with an azo coupling reaction, even over a period of two weeks; however, after this period, on addition of an additional molar equivalent of 4-methylphenyldiazonium fluoroborate to this deprotonated adduct the solution immediately became a deep red. After removal of solvent the crude material displayed a resonance at δ 40 in its ^{31}P-{^{1}H} NMR spectrum, indicative of a P–N coupled product, and the characteristic singlet at δ 16 for a 1-phenylazonaphthalen-2-ol in its ^{1}H NMR spectrum which was indicative of a C–N coupling. Hydrolysis of this compound afforded the phosphine oxide **7b**.[10] From these observations it is clear that the reaction does not proceed through a P–N coupled intermediate as these adducts appear indefinitely stable under the reaction conditions, but rather directly through a C–N coupling pathway which must be faster than the P–N coupling reaction.

Since the principal objective of this work was to prepare a phosphorus(III) compound that contained an azo moiety the presence of the tautomeric mixture was somewhat of a disappointment. So, we decided to prevent the tautomeric process

Table 3 ^{13}C-{^{1}H} NMR [a] data (δ) for compounds **2a**–**9c**

Compound	
2a [b]	158.4 [s, C(2)]; 137.4 [d, *J* 10.6, C(11)]; 134.8 [s, C(9)]; 134.3 [d, *J* 24.2, C(5)]; 133.8 [d, *J* 18.9, C(12)]; 131.6 [d, *J* 9.1, C(6)]; 130.8 [d, *J* 16.6, C(7)]; 129.7 [s, C(4)]; 128.9 [d, *J* 8.4, C(10)]; 127.5 [s, C(14)]; 127.0 [d, *J* 6.8, C(13)]; 119.1 [s, C(3)]; 105.7 [s, C(1)]; 55.5 [s, CH_3]
3b [b,c]	156.2 [s, C(2)]; 136.0 [s, C(9)]; 133.8 [d, *J* 11.4, C(5)]; 132.7 [d, *J* 85.4, C(11)]; 132.3 [d, *J* 10.7, C(12)]; 131.3 [d, *J* 3.1, C(14)]; 130.6 [s, C(4)]; 128.5 [d, *J* 13.0, C(13)]; 128.0 [d, *J* 88.0, C(6)]; 127.4 [d, *J* 11.4, C(7)]; 126.8 [d, *J* 12.2, C(8)]; 119.2 [s, C(3)]; 109.3 [s, C(1)]
4a [b,c]	169.5 [s, C(2)]; 144.9 [s, C(15)]; 139.7 [s, C(4)]; 137.0 [d, *J* 10.5 C(11)]; 134.3 [d, *J* 22.4, C(5)]; 133.8 [s, C(10)]; 133.7 [d, *J* 16.7, C(12)]; 133.5 [d, *J* 17.8, C(7)]; 129.9 [s, C(1)]; 129.7 [s, C(17)]; 128.8 [s, C(14)]; 128.6 [d, *J* 9.5, C(6)]; 128.5 [d, *J* 7.3, C(13)]; 127.7 [s, C(9)]; 124.9 [s, C(3)]; 121.8 [d, *J* 6.2, C(8)]; 118.7 [s, C(16)]
4b [b,c]	167.9 [s, C(2)]; 143.6 [s, C(15)]; 138.7 [s, C(18)]; 138.6 [s, C(4)]; 137.1 [d, *J* 10.4, C(11)]; 134.4 [d, *J* 23.0, C(5)]; 133.7 [d, *J* 4.2, C(10)]; 133.7 [d, *J* 18.8, C(12)]; 133.2 [d, *J* 17.8, C(7)]; 130.2 [s, C(17)]; 129.6 [s, C(1)]; 128.8 [s, C(14)]; 127.9 [s, C(9)]; 128.6 [d, *J* 6.2, C(13)]; 124.2 [s, C(3)]; 121.8 [d, *J* 6.3, C(8)]; 119.3 [s, C(16)]; 21.3 [s, CH_3]
4c [b,c]	168.1 [s, C(2)]; 145.1 [s, C(18)]; 143.8 [s, C(15)]; 138.4 [s, C(4)]; 137.7 [d, *J* 11.4, C(11)]; 134.4 [d, *J* 22.9, C(5)]; 133.7 [d, *J* 4.6, C(10)]; 133.5 [d, *J* 19.1, C(12)]; 133.3 [d, *J* 17.9, C(7)]; 129.7 [s, C(1)]; 129.0 [s, C(17)]; 128.8 [s, C(14)]; 128.7 [d, *J* 8.4, C(13)]; 127.9 [s, C(9)]; 124.2 [s, C(3)]; 121.8 [d, *J* 6.8, C(8)]; 119.4 [s, C(16)]; 28.7 [s, CH_2]; 15.5 [s, CH_3]
4d [b,c]	167.9 [s, C(2)]; 149.9 [s, C(18)]; 143.9 [s, C(15)]; 138.6 [s, C(4)]; 137.1 [d, *J* 11.6, C(11)]; 134.4 [d, *J* 22.0, C(5)]; 133.8 [d, *J* 11.6, C(10)]; 133.7 [d, *J* 19.9, C(12)]; 133.2 [d, *J* 16.7, C(7)]; 129.7 [s, C(1)]; 128.8 [s, C(14)]; 128.6 [s, C(6)]; 128.0 [d, *J* 6.2, C(13)]; 127.6 [s, C(9)]; 127.6 [s, C(17)]; 124.2 [s, C(3)]; 121.8 [d, *J* 6.3, C(8)]; 119.4 [s, C(16)]; 33.8 [s, CH]; 23.7 [s, CH_3]
4e [b,c]	168.4 [s, C(2)]; 151.7 [s, C(18)]; 143.4 [s, C(15)]; 138.8 [s, C(4)]; 137.1 [d, *J* 10.6, C(11)]; 134.4 [d, *J* 22.0, C(5)]; 134.0 [s, C(10)]; 133.7 [d, *J* 18.8, C(12)]; 133.3 [d, *J* 16.7, C(7)]; 129.7 [s, C(1)]; 128.8 [s, C(14)]; 128.6 [s, C(6)]; 128.4 [d, *J* 6.2, C(13)]; 127.9 [s, C(9)]; 126.6 [s, C(17)]; 124.3 [s, C(3)]; 121.8 [d, *J* 6.3, C(8)]; 119.0 [s, C(16)]; 34.7 [s, CCH_3]; 31.3 [s, CH_3]
4f [d]	179.8 [s, C(2)]; 152.4 [s, C(15)]; 147.8 [s, C(18)]; 144.7 [s, C(1)]; 143.4 [s, C(4)]; 137.2 [d, *J* 12.5, C(11)]; 136.5 [d, *J* 10.6, C(6)]; 134.4 [d, *J* 18.4, C(5)]; 133.8 [d, *J* 19.3, C(12)]; 133.8 [s, C(9)]; 129.2 [d, *J* 14.4, C(7)]; 129.1 [s, C(14)]; 128.7 [d, *J* 7.7, C(13)]; 128.5 [d, *J* 6.8, C(10)]; 126.3 [s, C(3)]; 123.5 [s, C(17)]; 122.5 [d, *J* 5.8, C(8)]; 116.7 [s, C(16)]
4g [d]	156.4 [s, C(2)]; 151.7 [s, C(18)]; 139.6 [s, C(15)]; 137.3 [d, *J* 10.6, C(11)]; 134.4 [d, *J* 23.2, C(5)]; 133.9 [s, C(4)]; 133.7 [d, *J* 19.3, C(12)]; 133.1 [s, C(9)]; 132.2 [d, *J* 7.7, C(10)]; 131.9 [d, *J* 17.5, C(7)]; 129.2 [s, C(1)]; 128.7 [s, C(14)]; 128.5 [d, *J* 6.8, C(13)]; 128.1 [d, *J* 8.7, C(6)]; 123.2 [s, C(16)]; 121.9 [d, *J* 6.8, C(8)]; 121.3 [s, C(3)]; 112.0 [s, C(17)]; 40.3 [s, CH_3]
6a [b]	169.4 [s, CO]; 153.3 [s, C(15)]; 138.3 [s, C(1)]; 137.8 [s, C(2)]; 136.7 [d, *J* 10.6, C(11)]; 135.7 [d, *J* 11.7, C(6)]; 133.8 [d, *J* 19.3, C(12)]; 133.7 [d, *J* 12.5, C(5)]; 131.8 [s, C(18)]; 131.7 [d, *J* 17.4, C(7)]; 131.1 [s, C(4)]; 130.0 [s, C(9)]; 129.2 [s, C(17)]; 128.9 [s, C(14)]; 128.6 [d, *J* 6.8, C(13)]; 124.2 [d, *J* 6.8, C(8)]; 123.0 [s, C(16)]; 122.7 [s, C(3)]; 20.9 [s, CH_3]
6b [b]	169.4 [s, CO]; 151.5 [s, C(15)]; 142.3 [s, C(18)]; 138.5 [s, C(1)]; 137.7 [s, C(2)]; 136.7 [d, *J* 10.5, C(11)]; 135.6 [d, *J* 11.5, C(6)]; 133.8 [d, *J* 17.4, C(12)]; 132.1 [d, *J* 7.4, C(10)]; 131.6 [d, *J* 17.9, C(7)]; 130.8 [s, C(4)]; 130.0 [s, C(1)]; 129.8 [s, C(17)]; 128.9 [s, C(14)]; 128.6 [d, *J* 6.3, C(13)]; 124.2 [d, *J* 6.3, C(8)]; 123.0 [s, C(16)]; 122.8 [s, C(3)]; 21.5 [s, CH_3]; 20.9 [s, CH_3]
6c [d]	169.4 [s, CO]; 151.7 [s, C(15)]; 148.6 [s, C(18)]; 138.5 [s, C(1)]; 137.7 [s, C(2)]; 137.2 [d, *J* 10.6, C(11)]; 135.6 [d, *J* 11.6, C(6)]; 133.8 [d, *J* 19.3, C(12)]; 133.7 [d, *J* 13.5, C(5)]; 132.2 [d, *J* 7.7, C(10)]; 131.6 [d, *J* 17.4, C(7)]; 130.7 [s, C(4)]; 129.9 [s, C(9)]; 128.9 [s, C(14)]; 128.7 [s, C(17)]; 128.6 [d, *J* 6.8, C(13)]; 124.2 [d, *J* 6.8, C(8)]; 123.1 [s, C(16)]; 122.9 [s, C(3)]; 28.9 [s, CH_2]; 20.9 [s, CH_3]; 15.4 [s, CH_3]
6d [d]	169.4 [s, CO]; 153.1 [s, C(15)]; 151.3 [s, C(18)]; 138.5 [s, C(1)]; 137.7 [s, C(2)]; 136.7 [d, *J* 10.6, C(11)]; 135.6 [d, *J* 11.6, C(6)]; 133.8 [d, *J* 21.3, C(5)]; 133.8 [d, *J* 11.6, C(12)]; 132.2 [d, *J* 7.7, C(7)]; 131.6 [d, *J* 18.3, C(7)]; 130.7 [s, C(4)]; 129.9 [s, C(9)]; 128.9 [s, C(14)]; 128.6 [d, *J* 6.8, C(13)]; 127.2 [s, C(17)]; 124.2 [d, *J* 6.7, C(8)]; 123.1 [s, C(16)]; 122.9 [s, C(3)]; 34.1 [s, CH]; 23.8 [s, CH_3]; 20.9 [s, CH_3]
6e [d]	169.4 [s, CO]; 153.1 [s, C(18)]; 151.7 [s, C(15)]; 138.5 [s, C(1)]; 137.7 [s, C(2)]; 133.8 [d, *J* 19.3, C(12)]; 133.7 [d, *J* 19.3, C(5)]; 132.2 [d, *J* 7.7, C(10)]; 131.6 [d, *J* 17.4, C(7)]; 130.7 [s, C(4)]; 129.9 [s, C(9)]; 128.9 [s, C(14)]; 128.6 [d, *J* 6.8, C(13)]; 126.5 [s, C(17)]; 124.2 [d, *J* 6.8, C(8)]; 123.1 [s, C(16)]; 122.9 [s, C(3)]; 34.2 [s, CCH_3]; 23.8 [s, CH_3]; 20.9 [s. CH_3]
6g [d]	169.4 [s, CO]; 152.7 [s, C(2)]; 144.5 [s, C(18)]; 139.1 [s, C(15)]; 137.4 [s, C(10)]; 136.8 [d, *J* 10.6, C(11)]; 135.0 [d, *J* 11.6, C(6)]; 133.7 [d, *J* 19.3, C(12)]; 133.6 [d, *J* 18.4, C(5)]; 131.0 [d, *J* 17.4, C(7)]; 130.0 [s, C(4)]; 129.1 [s, C(1)]; 128.8 [s, C(14)]; 128.5 [d, *J* 7.7, C(13)]; 124.9 [s, C(16)]; 124.5 [d, *J* 6.8, C(8)]; 122.9 [s, C(3)]; 111.4 [s, C(17)]; 40.2 [s, CH_3]; 20.9 [s, CH_3]
7a [b,c,e]	170.1 [s, C(2)]; 145.0 [s, C(15)]; 139.3 [s, C(4)]; 135.8 [s, C(10)]; 133.6 [d, *J* 9.9, C(5)]; 132.3 [d, *J* 108.3, C(11)]; 132.1 [d, *J* 9.9, C(12)]; 132.1 [d, *J* 2.3, C(14)]; 130.7 [d, *J* 9.9, C(7)]; 129.6 [s, C(17)]; 129.4 [s, C(1)]; 128.6 [d, *J* 106.0, C(6)]; 128.6 [d, *J* 12.2, C(13)]; 128.4 [s, C(18)]; 127.5 [s, C(9)]; 125.4 [s, C(3)]; 121.9 [d, *J* 12.2, C(8)]; 119.2 [s, C(16)]
7b [b,c]	167.0 [s, C(2)]; 143.8 [s, C(15)]; 139.5 [s, C(18)]; 138.2 [s, C(4)]; 135.5 [d, *J* 3.2, C(10)]; 132.5 [d, *J* 104.3, C(11)]; 132.1 [d, *J* 10.5, C(12)]; 130.2 [s, C(17)]; 130.2 [d, *J* 10.5, C(7)]; 129.2 [s, C(1)]; 128.6 [d, *J* 12.6, C(13)]; 128.5 [d, *J* 106.3, C(6)]; 127.3 [s, C(9)]; 124.6 [s, C(3)]; 121.9 [d, *J* 11.6, C(8)]; 119.7 [s, C(16)]; 21.3 [s, CH_3]
7c [b,c,e]	167.3 [s, C(2)]; 145.8 [s, C(18)]; 143.9 [s, C(15)]; 138.3 [s, C(4)]; 135.8 [s, C(10)]; 133.6 [d, *J* 9.9, C(5)]; 132.3 [d, *J* 104.5, C(11)]; 132.2 [d, *J* 2.3, C(14)]; 132.1 [d, *J* 9.9, C(12)]; 130.3 [d, *J* 10.7, C(7)]; 129.3 [s, C(17)]; 128.6 [d, *J* 12.2, C(13)]; 128.2 [d, *J* 104.5, C(6)]; 127.4 [s, C(9)]; 124.8 [s, C(3)]; 121.9 [d, *J* 12.2, C(8)]; 119.8 [s, C(16)]; 28.6 [s, CH_2]; 15.3 [s, CH_3]
7d [b,c]	168.0 [s, C(2)]; 152.7 [s, C(18)]; 143.5 [s, C(15)]; 138.4 [s, C(4)]; 135.7 [d, *J* 2.1, C(10)]; 133.6 [d, *J* 9.5, C(5)]; 132.5 [d, *J* 105.5, C(11)]; 132.1 [d, *J* 11.6, C(12)]; 132.1 [s, C(14)]; 130.3 [d, *J* 10.5, C(7)]; 129.2 [s, C(1)]; 128.6 [d, *J* 111.5, C(6)]; 128.6 [d, *J* 12.6, C(13)]; 127.4 [s, C(9)]; 124.7 [s, C(3)]; 121.8 [d, *J* 11.6, C(8)]; 119.8 [s, C(16)]; 34.1 [s, CH]; 24.0 [s, CH_3]
7e [b,c]	168.0 [s, C(2)]; 152.7 [s, C(18)]; 143.5 [s, C(15)]; 138.4 [s, C(4)]; 135.8 [s, C(10)]; 133.6 [d, *J* 9.5, C(5)]; 132.5 [d, *J* 105.2, C(11)]; 132.1 [d, *J* 11.6, C(12)]; 132.1 [s, C(14)]; 130.3 [d, *J* 10.5, C(7)]; 129.2 [s, C(1)]; 129.6 [d, *J* 109.5, C(6)]; 128.6 [d, *J* 12.6, C(13)]; 127.4 [s, C(9)]; 124.9 [s, C(3)]; 121.8 [d, *J* 11.6, C(8)]; 119.4 [s, C(16)]; 35.1 [s, CCH_3]; 31.3 [s, CH_3]
8a [b,c]	170.2 [s, C(2)]; 145.0 [s, C(15)]; 139.4 [s, C(4)]; 135.5 [s, C(10)]; 133.7 [d, *J* 11.6, C(5)]; 133.4 [s, C(11)]; 132.2 [d, *J* 10.5, C(12)]; 131.6 [s, C(14)]; 130.8 [d, *J* 10.5, C(7)]; 129.8 [s, C(6)]; 129.6 [s, C(17)]; 129.4 [s, C(1)]; 128.6 [d, *J* 12.6, C(13)]; 128.3 [s, C(18)]; 127.3 [s, C(9)]; 125.3 [s, C(3)]; 121.8 [d, *J* 11.6, C(8)]; 119.1 [s, C(16)]
8b [b,c]	166.9 [s, C(2)]; 143.8 [s, C(15)]; 139.4 [s, C(18)]; 138.4 [s, C(4)]; 135.3 [s, C(10)]; 133.7 [d, *J* 10.5, C(5)]; 132.9 [d, *J* 85.3, C(11)]; 132.2 [d, *J* 10.5, C(12)]; 131.6 [s, C(14)]; 130.3 [d, *J* 11.6, C(7)]; 130.2 [s, C(17)]; 129.1 [s, C(1)]; 128.6 [d, *J* 87.3, C(6)]; 128.5 [d, *J* 12.6, C(13)]; 127.3 [s, C(9)]; 124.5 [s, C(3)]; 121.8 [d, *J* 11.6, C(8)]; 119.3 [s, C(16)]; 21.3 [s, CH_3]
8c [b,c]	167.3 [s, C(2)]; 145.8 [s, C(18)]; 144.0 [s, C(15)]; 138.3 [s, C(4)]; 135.4 [s, C(10)]; 133.7 [d, *J* 10.5, C(5)]; 132.2 [d, *J* 86.3, C(11)]; 132.2 [d, *J* 10.5, C(12)]; 131.6 [s, C(14)]; 130.3 [d, *J* 11.6, C(7)]; 129.2 [s, C(1)]; 129.1 [s, C(17)]; 128.9 [d, *J* 86.2, C(6)]; 128.6 [d, *J* 12.6, C(13)]; 127.4 [s, C(9)]; 124.6 [s, C(3)]; 121.8 [d, *J* 12.6, C(8)]; 119.8 [s, C(16)]; 28.6 [s, CH_2]; 15.3 [s, CH_3]
8d [b,c]	167.3 [s, C(2)]; 150.4 [s, C(18)]; 144.0 [s, C(15)]; 138.3 [s, C(4)]; 135.4 [s, C(10)]; 133.8 [d, *J* 11.6, C(5)]; 133.0 [d, *J* 86.3, C(11)]; 132.2 [d, *J* 10.5, C(12)]; 131.6 [d, *J* 3.2, C(14)]; 130.5 [d, *J* 11.6, C(7)]; 129.3 [s, C(1)]; 128.9 [d, *J* 86.6, C(6)]; 128.6 [d, *J* 12.6, C(13)]; 127.7 [s, C(17)]; 127.4 [s, C(9)]; 124.7 [s, C(3)]; 121.8 [d, *J* 11.6, C(8)]; 119.8 [s, C(16)]; 34.0 [s, CH]; 23.8 [s, CH_3]
8e [b,c]	167.6 [s, C(2)]; 152.6 [s, C(18)]; 143.5 [s, C(15)]; 138.4 [s, C(4)]; 135.5 [s, C(10)]; 133.8 [d, *J* 11.6, C(5)]; 133.0 [d, *J* 85.2, C(11)]; 132.3 [d, *J* 10.5, C(12)]; 131.6 [d, *J* 3.2, C(14)]; 130.5 [d, *J* 11.6, C(7)]; 129.4 [s, C(1)]; 129.0 [d, *J* 86.7, C(6)]; 128.6 [d, *J* 12.6, C(13)]; 127.4 [s, C(9)]; 126.6 [s, C(17)]; 124.8 [s, C(3)]; 121.8 [d, *J* 12.6, C(8)]; 119.4 [s, C(16)]; 34.8 [s, CCH_3]; 31.1 [s, CH_3]

Table 3 (*Contd.*)

Compound	
8g[d]	157.1 [s, C(2)]; 152.0 [s, C(18)]; 139.4 [s, C(15)]; 134.5 [d, *J* 1.9, C(10)]; 134.2 [s, C(4)]; 133.9 [d, *J* 11.6, C(5)]; 133.2 [d, *J* 85.7, C(11)]; 132.3 [d, *J* 10.6, C(12)]; 131.5 [d, *J* 2.9, C(14)]; 129.0 [d, *J* 10.6, C(7)]; 129.0 [s, C(1)]; 128.5 [d, *J* 12.6, C(13)]; 127.5 [d, *J* 87.9, C(6)]; 127.3 [s, C(9)]; 123.5 [s, C(16)]; 122.1 [d, *J* 11.6, C(8)]; 122.0 [s, C(3)]; 112.0 [s, C(17)]; 40.3 [s, CH_3]
9a[b]	169.3 [s, CO]; 151.4 [s, C(15)]; 142.6 [s, C(18)]; 138.7 [s, C(1)]; 137.4 [s, C(2)]; 133.7 [d, *J* 9.5, C(5)]; 132.1 [d, *J* 10.8, C(11)]; 132.1 [d, *J* 19.5, C(12)]; 132.1 [d, *J* 2.1, C(14)]; 131.5 [s, C(4)]; 131.4 [s, C(9)]; 130.2 [s, C(1)]; 130.2 [d, *J* 104.2, C(6)]; 129.9 [s, C(7)]; 128.6 [d, *J* 11.6, C(13)]; 128.6 [d, *J* 10.5, C(7)]; 124.6 [d, *J* 11.6, C(8)]; 122.8 [s, C(16)]; 119.7 [s, C(3)]; 21.5 [s, CH_3]; 20.9 [s, CH_3]
9b[d]	169.2 [s, CO]; 153.2 [s, C(15)]; 139.1 [s, C(1)]; 138.3 [s, C(2)]; 133.9 [d, *J* 11.6, C(5)]; 132.7 [d, *J* 8.5, C(11)]; 132.4 [d, *J* 10.6, C(10)]; 132.3 [d, *J* 10.6, C(12)]; 131.9 [d, *J* 10.6, C(7)]; 131.7 [d, *J* 2.9, C(14)]; 131.4 [s, C(9)]; 130.7 [d, *J* 85.0, C(6)]; 129.3 [s, C(18)]; 128.7 [s, C(17)]; 128.6 [d, *J* 12.6, C(13)]; 124.6 [d, *J* 12.6, C(8)]; 123.0 [s, C(16)]; 120.0 [s, C(3)]; 20.9 [s, CH_3]
9c[b]	169.2 [s, CO]; 151.4 [s, C(15)]; 142.6 [s, C(18)]; 138.9 [s, C(1)]; 138.3 [s, C(2)]; 133.8 [d, *J* 10.5, C(5)]; 132.3 [d, *J* 10.5, C(12)]; 131.7 [d, *J* 3.2, C(14)]; 131.2 [s, C(9)]; 130.8 [d, *J* 89.7, C(6)]; 129.9 [s, C(17)]; 128.6 [d, *J* 13.7, C(13)]; 124.6 [d, *J* 12.6, C(8)]; 122.8 [s, C(16)]; 119.7 [s, C(3)]; 21.5 [s, CH_3]; 20.9 [s, CH_3]

[a] Spectra recorded in $CDCl_3$ and referenced to $CDCl_3$ (δ 77.0); coupling constants in Hz. [b] Spectrum recorded at 75.45 MHz. [c] One or more resonances obscured or partially obscured by overlapping with other signals. [d] Spectrum recorded at 100.5 MHz. [e] Spectrum recorded at 50.5 MHz.

Table 4 Uv-visible data for selected compounds **4a**–**9c**[a]

		λ/nm (ε/dm^3 mol^{-1} cm^{-1})	
Compound	K[b]	Hydrazone form	Azo form
4a	0.53	491.5 (26134)	408.0 (24288), 328.0 (21503)
4b	0.66	493.5 (16912)	415.5 (24286), 328.5 (27899)
4c	0.65	497.5 (21425)	420.5 (25285), 331.0 (31201)
4d	0.66	497.0 (20024)	421.0 (25084), 330.5 (31378)
4e	0.62	496.5 (23091)	421.0 (23729), 331.0 (29186)
4f		500.5 (30527)	
4g			504.5 (24555)
6a			484.0 (2340), 354.0 (10740)
6b			478.0 (2028), 353.0 (10394)
6c			464.5 (1176), 349.5 (13647)
6d			469.5 (1820), 349.5 (13450)
6e			491.5 (3683), 352.0 (13734)
6f			426.0 (19183)
7b	0.78	490.0 (12397)	415.0 (34944), 318.0 (27300)
8b	0.79	491.0 (14095)	414.0 (40534), 323.0 (40973)
9b			477.5 (1584), 355.0 (12513)
9c			477.5 (1736), 356.5 (13824)

[a] Spectra recorded in $CHCl_3$. [b] Calculated from $K = \{180 - \delta C(2)\}/\{\delta C(2) - [\delta C(2)_{ester} + 12]\}$.

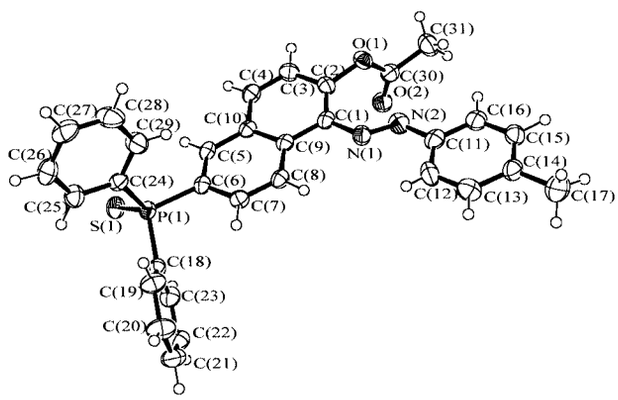


Fig. 1 An ORTEP representation of compound **4b** showing the atomic numbering scheme.

by functionalising the hydroxyl group as its acetic acid ester; another possibility was the preparation of the methyl ether, however, this would be unsatisfactory as the reaction would be accompanied by quaternisation at phosphorus. Treatment of **4a**–**4e**,**4g** with NaH in dry THF generated the naphthalide anions with liberation of dihydrogen. Quenching of the anions with acetyl chloride afforded the acetic acid esters **6a**–**6e**,**6g** in good yield. All of the compounds were fully spectroscopically characterised, see Tables 1–4. In addition **6a** was further characterised by a single crystal X-ray diffraction study, see Table 6 for selected bond lengths and angles.

The ^{1}H NMR spectra of compounds **6a**–**6e**,**6g** are consistent with their formulation as the acetic acid esters. The characteristic 'OH' resonance around δ 16 was replaced by a singlet resonance at δ 2.3, corresponding to the methyl of the acetyl group. In the ^{31}P-{^{1}H} NMR spectra a singlet resonance around δ −5 was seen which is consistent with their formulation as triarylphosphines.

The ^{13}C-{^{1}H} NMR spectra of **6a**–**6e**,**6g** are all consistent with their being the acetic acid esters of **4a**–**4e**,**4g**. Assignment was carried out with the aid of DEPT 135 spectra, previous assignments for 1-phenylazonaphthalen-2-ols,[13] substituent effects[14] along with the observed coupling to the spin active phosphorus nucleus. A characteristic resonance at δ 169 attributable to the ester CO carbon was clearly visible in all spectra. Assignment of C(5)–C(10) and C(11)–C(14) was aided by their coupling to phosphorus. Lycka *et al.*[13b] prepared a series of phenylazo containing compounds that were locked either in the azo or hydrazone form and showed that the carbon resonances for the 1-phenylazo ring differed noticeably on going between the respective tautomers. With the aid of these data and known substituent effects[14] we were able to calculate where the position of the 4-R-phenylazo ring carbons {C(15)–C(18)} might be and then assigned them. The only ring carbons left to assign were C(1), C(2), C(3), and C(4) and these were easily distinguished using the DEPT 135 spectra. In all cases except **6g** this left two quaternary resonances around δ 138.5 and 137.5. Looking at *ipso*- and *ortho*-substituent effects of azo and acetate moieties it is likely that the C(1) and C(2) carbon resonances will be shifted equally from the value of the analogous carbon in naphthalene, hence C(1) has been assigned to the higher frequency resonance. Two things are worth noting here: (i) the absolute values calculated using these effects did not correspond well with the observed and (ii) the positions of the resonances of these phosphine containing compounds are comparable with those of non-phosphine containing analogues.[17] Compound **6g** displays a C(2) resonance at δ 144.5 which is 7 ppm higher than that observed for **6a**–**6e** and is closer to the calculated value. The difference in the values for the C(2) resonances, we believe, must have something to do with conjugation between the strongly electron releasing dimethylamino group on the phenyl ring coupled with the strongly electron accepting azo moiety. Olivieri *et al.*[18a] calculated K for the azo/hydrazone tautomerisation in 1-phenylazonaphthalen-2-ols using the equation $K = [\{180 - \delta C(2)\}/\{\delta C(2) - 147\}]$ where 180 is the position ascribed to C(2) for the hydrazone tautomer and 147 the value calculated for C(2) of the azo tautomer based upon substituent effects. Considering the position of the C(2) resonance of **6g** is δ 144.5 this equation seems reasonable, until one

Table 5 Selected bond lengths (Å) and angles (°) for compound **4b**

P(1)–C(6)	1.809(6)	P(1)–C(24)	1.813(6)	P(1)–C(18)	1.821(6)
N(1)–N(2)	1.306(6)	N(1)–C(1)	1.323(8)	N(2)–C(11)	1.394(8)
O(1)–C(2)	1.262(6)	C(1)–C(2)	1.440(8)	C(1)–C(9)	1.445(7)
C(2)–C(3)	1.436(9)	C(3)–C(4)	1.329(8)	C(4)–C(10)	1.422(7)
C(5)–C(6)	1.376(7)	C(5)–C(10)	1.382(7)	C(6)–C(7)	1.390(8)
C(7)–C(8)	1.368(7)	C(8)–C(9)	1.398(7)	C(9)–C(10)	1.403(8)
C(11)–C(16)	1.379(8)	C(12)–C(13)	1.359(9)	C(13)–C(14)	1.380(8)
C(14)–C(15)	1.370(8)	C(14)–C(17)	1.491(8)	C(15)–C(16)	1.356(9)
C(6)–P(1)–C(24)	102.3(3)	C(6)–P(1)–C(18)	99.9(3)		
C(24)–P(1)–C(18)	103.3(3)	N(2)–N(1)–C(1)	117.7(5)		
N(1)–N(2)–C(11)	120.0(5)	N(1)–C(1)–C(2)	124.8(6)		
N(1)–C(1)–C(9)	115.8(5)	C(2)–C(1)–C(9)	119.4(6)		
O(1)–C(2)–C(3)	120.7(6)	O(1)–C(2)–C(1)	120.7(7)		
C(5)–C(6)–P(1)	117.3(6)	C(7)–C(6)–P(1)	125.3(4)		
C(12)–C(11)–N(2)	116.4(6)	C(16)–C(11)–N(2)	124.3(6)		
C(23)–C(18)–P(1)	125.0(6)	C(19)–C(18)–P(1)	118.0(5)		
C(29)–C(24)–P(1)	125.3(5)	C(25)–C(24)–P(1)	117.2(4)		

realises that the position of the equilibrium calculated using it does not compare favourably with data obtained from UV-visible spectroscopy which suggest the compound exists essentially as the azo tautomer. The ^{13}C-{^{1}H} NMR data also support the presence of essentially the azo tautomer when the positions of C(15)–C(18) for the naphthol and ester forms are compared. Atom C(15) which is directly attached to the azo/hydrazone moiety will be most sensitive to conversion into the pure azo form on esterification. It can be seen that on esterification of **4a**–**4e** the C(15) resonance shifts approximately 8 ppm to higher frequency, whereas esterification of **4f** shifts the resonance only 0.4 ppm, suggesting the presence of only a small amount of hydrazone tautomer. Based on the work of Lycka *et al.*[13b] this suggests that **4g** exists as >95% azo tautomer. This would imply a value closer to δ 155.5 for the C(2) resonance of the azo tautomer of **4g** rather than δ 147.[18a] This value is, of course, based upon the assumption that the value of 180 for the C(2) resonance of the hydrazone tautomer is correct. In the hydrazone tautomer the ring substituents in the 4 position of the phenylazo ring are not in conjugation with the naphthalene ring, so their influence on the C(2) resonance should be limited, hence the use of this value is reasonable. The difference in the C(2) resonance of the naphthol and ester forms of the azo tautomer appears to be approximately 11 ppm. This could not be predicted from tabulated substituent effects, which suggest a difference of 4 ppm for phenyl systems on conversion of the phenol into the ester and the fact that the C(2) resonance of naphthalen-2-ol shifts from δ 153 to 134.5 on conversion into its acetic acid ester.[14] The validity of this prediction, however, lies in its compatibility with other measurements. Calculation of the equilibrium constant and the percentages of each tautomer in solution using this methodology affords roughly 33% azo and 67% hydrazone tautomer for **4a** which is essentially the same as calculated from ^{15}N–H and ^{14}N–H coupling constant measurements, for the non-phosphorus analogues:[19] these are considered to be a reasonable reflection of the position of the equilibrium.[20] On reflection, the fact that the C(2) resonance position varies for the azo tautomer depending upon the substituents attached to the phenylazo ring is not surprising, as this is what makes this kind of spectroscopy useful. We suggest that the position of the equilibrium can be calculated using ^{13}C NMR based upon a predicted position of the C(2) resonance for the azo tautomer, but before this can be done it is necessary to prepare a derivative such as the ester.

A single crystal X-ray diffraction study carried out on compound **6b** confirmed the spectroscopic data that an ester moiety had been introduced into the molecule, the tautomerisation suppressed and the molecule locked in the *trans*-azo form, see Fig. 2 for an ORTEP representation of the molecule with the atomic numbering scheme. This can clearly be seen from the following bond lengths: C(2)–O(1) 1.389(4); C(1)–N(1) 1.413(4); N(1)–N(2) 1.246(4); N(2)–C(11) 1.433(4) Å. In addition the C–C bond lengths around the naphthalene ring are as to be expected rather than the distorted values seen in **4b**. The most noticeable change is in the C(3)–C(4) bond length changing from 1.329(8) in **4b** to 1.366(5) in **6b**.

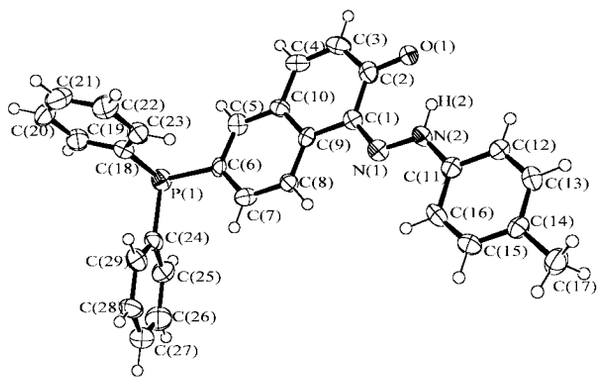


Fig. 2 An ORTEP representation of compound **6b** showing the atomic numbering scheme.

Oxidation of compounds **4a**–**4e** with H_2O_2 or **4a**–**4g** with S_8 readily affords the phosphine oxides **7a**–**7e** and the phosphine sulfides **8a**–**8g** in good yield; they can also be prepared by deprotonation of either **3a** or **3c** and quenching the naphthalide anion with the relevant 4-R-phenyldiazonium salt. They have all been characterised by microanalysis, and multinuclear NMR spectroscopy, see Tables 1–4. Compound **7b** has previously been characterised by a single crystal X-ray diffraction study;[10] a summary of pertinent bond lengths for the purpose of the discussion can be found in Table 8.

As in compounds **4a**–**4g**, **7a**–**7e** and **8a**–**8g** exist as a tautomeric mixture of the azo and hydrazone form. All display a singlet in the ^{1}H NMR spectrum which is assigned to the formal 'OH' proton. Successful oxidation was confirmed from the ^{31}P-{^{1}H} NMR spectra. The resonances for **7a**–**7e** at around δ 30 and for **8a**–**8g** around δ 44 are consistent with those usually observed for phosphine oxides and sulfides. Oxidation had a noticeable effect on the ^{13}C-{^{1}H} NMR spectra. The resonances assigned to C(11)–C(14) and C(5)–C(10) which are constituents of the aromatic rings directly bound to the phosphorus were noticeably shifted, which is not surprising considering the change in oxidation state at phosphorus. The other resonances were little affected. Further, oxidation of the phosphorus had no apparent effect on the position of the azo/hydrazone tautomerisation: the C(2) resonances appear in essentially the same position as for the parent phosphines **4a**–**4g**.

The tautomeric process in these phosphine oxides and sulfides can be suppressed in an analogous manner to that used for the free phosphines. Thus, treatment of compounds **7b**, **8a** and

Table 6 Selected bond lengths (Å) and angles (°) for compound **6b**

P(1)–C(6)	1.818(4)	P(1)–C(24)	1.819(4)	P(1)–C(18)	1.819(4)
N(1)–N(2)	1.246(4)	N(1)–C(1)	1.413(4)	N(2)–C(11)	1.433(4)
O(1)–C(30)	1.345(4)	O(1)–C(2)	1.389(4)	O(2)–C(30)	1.192(4)
C(1)–C(2)	1.369(5)	C(1)–C(9)	1.429(5)	C(2)–C(3)	1.391(5)
C(3)–C(4)	1.366(5)	C(4)–C(10)	1.404(5)	C(5)–C(6)	1.369(5)
C(5)–C(10)	1.415(5)	C(6)–C(7)	1.412(5)	C(7)–C(8)	1.353(5)
C(8)–C(9)	1.402(5)	C(9)–C(10)	1.413(5)	C(11)–C(16)	1.377(5)
C(11)–C(12)	1.381(5)	C(12)–C(13)	1.382(5)	C(13)–C(14)	1.381(5)
C(14)–C(15)	1.364(5)	C(14)–C(17)	1.504(6)	C(15)–C(16)	1.380(5)
C(30)–C(31)	1.475(6)				
C(6)–P(1)–C(24)	102.80(17)	C(6)–P(1)–C(18)	103.06(16)		
C(24)–P(1)–C(18)	101.84(17)	N(2)–N(1)–C(1)	115.7(3)		
N(1)–N(2)–C(11)	113.2(3)	C(30)–O(1)–C(2)	116.5(3)		
C(2)–C(1)–N(1)	125.5(3)	N(1)–C(1)–C(9)	114.9(3)		
C(1)–C(2)–C(3)	121.5(3)	O(1)–C(2)–C(3)	117.9(3)		
C(5)–C(6)–P(1)	124.8(3)	C(7)–C(6)–P(1)	117.2(3)		
C(16)–C(11)–N(2)	116.0(3)	C(12)–C(11)–N(2)	124.0(3)		
C(19)–C(18)–P(1)	117.2(3)	C(23)–C(18)–P(1)	124.7(3)		
C(25)–C(24)–P(1)	124.6(3)	C(29)–C(24)–P(1)	117.6(3)		
O(2)–C(30)–O(1)	121.4(4)	O(2)–C(30)–C(31)	126.8(4)		
O(1)–C(30)–C(31)	111.8(4)				

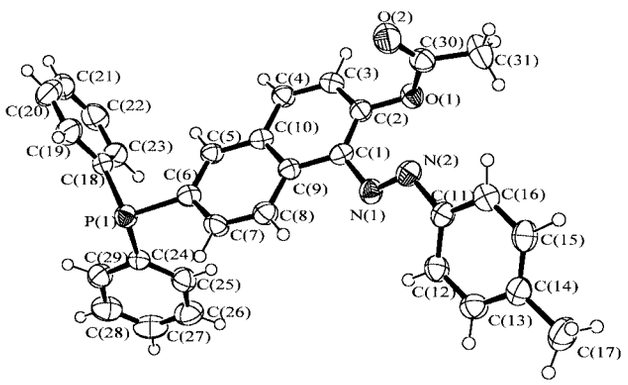


Fig. 3 An ORTEP representation of compound **9c** showing the atomic numbering scheme.

8b with NaH in dry THF followed by acetyl chloride afforded good yields of the acetic acid esters **9a**–**9c**. These compounds were fully characterised (see Tables 1–4). In addition **9c** has been characterised by a single crystal X-ray diffraction study, see Table 7 for selected bond lengths and angles. The physical and spectroscopic data are consistent with acylation of the hydroxyl group; a similar interpretation, as before, of the spectroscopic data can be applied to **9a**–**9c** as for **6a**–**6e**,**6g**.

The solid state structures of compounds **7b** and **9c** are consistent with the spectroscopic data in both cases, see Fig. 3 for **9c**. Compound **7b** was shown to exist primarily as the hydrazone tautomer[10] with bond lengths that were very similar to those for **4b**: N(1)–N(2) 1.306; C(1)–N(1) 1.365(6); N(2)–C(11) 1.419(6); C(2)–O(1) 1.277(5) Å. The X-ray data confirmed that **9c** had been locked in the *trans*-azo form on esterification of the hydroxyl group. This time the bond lengths are comparable with those observed for **6b**: N(1)–N(2) 1.227(3); C(1)–N(1) 1.426(3); N(2)–C(11) 1.445(3); C(2)–O(1) 1.390(3) Å. Compound **7b**, like **4b**, also shows the presence of a strong intramolecular hydrogen bond[16] N(2)–H · · · O(1): N(2)–H(2a) 1.24; H–O(1) 1.35; N(2)–O(2) 2.52 Å; N(2)–H(2a)–O(1) 153°. A summary of the pertinent bond lengths around the azo moiety for all the structurally characterised compounds can be found in Table 8.

The UV-visible data, Table 4, are consistent with the alkyl substituted compounds **4a**–**4e** existing as an equilibrium mixture of azo and hydrazone tautomers with maxima around 400 nm for the azo and 500 nm for the hydrazone tautomer. On esterification the band attributable to the hydrazone tautomer disappears. Compound **4f** shows only bands ascribed to the hydrazone tautomer; no evidence for the azo form was visible. The λ_{max} for **4g** at 504 nm is consistent with shifts normally observed for substituted benzenes that contain the NMe_2 functional group when compared to those that contain alkyl substituents.[21] Unfortunately the shift caused by the NMe_2 group causes the absorption to move to exactly the same position as that expected for the hydrazone tautomer and is exactly as observed by Burawoy *et al.*[22] when they measured the UV-visible spectra of 1-(4-aminophenylazo)naphthalen-2-ol thus preventing observation of this absorbance. As with all of the other spectroscopic data, the presence of the phosphine group does not appear to affect the position of the absorbances and the data obtained are consistent with those for the non-phosphorus containing analogues.

Conclusion

It is apparent, from this study and others, that tertiary phosphines react with diazonium salts in several ways: (i) *via* nucleophilic displacement of nitrogen, (ii) adduct formation and (iii) C–N coupling. Incorporation of a hydroxyl group, which can be used to activate and direct a C–N coupling reaction between a diazonium tetrafluoroborate salt and a phosphine, can be achieved if the hydroxyl group is part of a naphthalen-2-ol moiety. The spectroscopic data and the solid state structure of **4b** imply that the 6-(diphenyl)phosphanyl-1-(4-R-phenylazo)-naphthalen-2-ols have a tendency to tautomerise and exist primarily as the keto-hydrazone form, as do the phosphine sulfide and oxide analogues in the solid state. The tautomeric process can be prevented by functionalisation of the hydroxyl group. This has been successfully accomplished by esterification giving compounds **6a**–**6e**,**6g** and **9a**–**9c**. The spectroscopic and solid state structures of these esterified phosphines confirmed that the tautomerisation was suppressed and isomerically pure *trans*-azo containing phosphines were obtained. The position of the C(2) resonance of the esterified phosphines implies the resonance of the unobserved azo tautomer of the parent naphthalen-2-ols is influenced by the presence of additional substituents in the phenylazo ring. The position of the azo/hydrazone equilibrium can be calculated based on the predicted position of the C(2) resonance of the hydrazone and azo tautomers, but due care needs to be exercised in predicting the position of the C(2) resonance for the azo form of the parent naphthalen-2-ol. Calculation of K allows the molar absorption coefficients based on the mole fraction of each tautomer present in solution to be evaluated.

Table 7 Selected bond lengths (Å) and angles (°) for compound **9c**

S(1)–P(1)	1.9484(10)	N(1)–N(2)	1.227(3)	N(1)–C(1)	1.426(3)
N(2)–C(11)	1.445(3)	P(1)–C(24)	1.801(2)	P(1)–C(6)	1.807(2)
P(1)–C(18)	1.811(2)	O(1)–C(30)	1.358(3)	O(1)–C(2)	1.390(3)
O(2)–C(30)	1.192(3)	C(1)–C(2)	1.378(3)	C(1)–C(9)	1.429(3)
C(2)–C(3)	1.395(3)	C(3)–C(4)	1.356(4)	C(4)–C(10)	1.408(3)
C(5)–C(6)	1.362(3)	C(5)–C(10)	1.409(3)	C(6)–C(7)	1.408(3)
C(7)–C(8)	1.361(3)	C(8)–C(9)	1.412(3)	C(9)–C(10)	1.418(3)
C(14)–C(15)	1.375(4)	C(14)–C(17)	1.508(4)	C(15)–C(16)	1.370(4)
C(30)–C(31)	1.486(4)				
N(2)–N(1)–C(1)	116.0(2)	N(1)–N(2)–C(11)	112.8(2)		
C(24)–P(1)–C(6)	105.69(11)	C(24)–P(1)–C(18)	106.99(11)		
C(6)–P(1)–C(18)	105.29(10)	C(24)–P(1)–S(1)	112.78(8)		
C(6)–P(1)–S(1)	113.06(8)	C(18)–P(1)–S(1)	112.45(8)		
C(30)–O(1)–C(2)	117.01(18)	C(2)–C(1)–N(1)	127.5(2)		
N(1)–C(1)–C(9)	113.7(2)	C(1)–C(2)–O(1)	121.5(2)		
O(1)–C(2)–C(3)	116.3(2)	C(5)–C(6)–P(1)	118.89(17)		
C(7)–C(6)–P(1)	122.05(18)	C(16)–C(11)–N(2)	115.7(2)		
C(12)–C(11)–N(2)	123.9(2)	C(23)–C(18)–P(1)	117.51(19)		
C(29)–C(24)–P(1)	122.07(19)	C(25)–C(24)–P(1)	118.72(19)		
O(2)–C(30)–O(1)	122.7(2)	O(2)–C(30)–C(31)	126.9(2)		
O(1)–C(30)–C(31)	110.5(2)				

Table 8 Summary of selected bond lengths (Å) for compounds **4b**, **6b**, **7b** and **9c**

Compound	N=N	N(1)–C(1)	N(2)–C(11)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(2)–O(1)	Ref.
'Expected'	1.255	1.431	1.431	1.364	1.406	1.364	1.395	23
4b	1.306(6)	1.323(8)	1.394(8)	1.440(8)	1.436(9)	1.329(8)	1.262(6)	This work
6b	1.246(4)	1.413(4)	1.433(4)	1.369(5)	1.391(5)	1.366(5)	1.389(4)	This work
7b	1.306(5)	1.365(6)	1.419(6)	1.432(7)	1.430(6)	1.358(6)	1.277(5)	10
9c	1.227(3)	1.426(3)	1.445(3)	1.378(3)	1.395(3)	1.356(4)	1.390(3)	This work

Experimental

All solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. All the diazonium salts were prepared[7] from aromatic amines purchased from commercial sources and distilled prior to use; all other chemicals were from commercial sources and used as received. Melting points were measured on a Griffin Melting Point Apparatus and are uncorrected. The ^{1}H (200.2 MHz) and ^{31}P-{^{1}H} NMR (81.3 MHz) spectra were recorded on a Bruker AC200 spectrometer, ^{13}C-{^{1}H} NMR (50.5, 75.5 or 100.5 MHz) on either a AC200 or Bruker AC300 or Brucker DPX 400 spectrometer; ^{1}H and ^{13}C-{^{1}H} spectra were referenced to C*H*Cl$_3$ (δ 7.26) and *C*HCl$_3$ (δ 77.0) and ^{31}P-{^{1}H} NMR externally to 85% H_3PO_4. Positive FAB spectra were obtained on a Kratos MS50TC spectrometer in a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvates of crystallisation have been confirmed by NMR data and by repeated elemental analysis. The syntheses of all the tertiary phosphines were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Work-ups were generally carried out in the open unless otherwise stated and chromatographic separations were carried out on silica (60 mesh).

Preparations

6-(Diphenylphosphanyl)-2-methoxynaphthalene 2a. To a 250 mL 3-necked round bottomed flask, equipped with a reflux condenser and mechanical stirrer, containing 6-bromo-2-methoxynaphthyl magnesium [prepared from magnesium turnings (5.6 g, 0.23 mmol) and 6-bromo-2-methoxynaphthalene (50 g, 0.21 mol)] in THF (100 mL), chlorodiphenylphosphine (46.3 g, 0.21 mol) in THF (15 mL) was added dropwise at such a rate to create a gentle reflux. The reaction was further refluxed for 1 h and cooled to room temperature. After addition of ice (80 g) and stirring for 1 h, toluene (100 mL) was added and the organic fraction collected. The aqueous layer was washed with toluene (2 × 50 mL). The organic fractions were then combined and dried over anhydrous $MgSO_4$. After filtration and removal of volatiles under reduced pressure compound **2a** was obtained as a yellow oil. Recrystallisation from methanol afforded **2a** (60.8 g, 85%), mp 100–103 °C (Found: C, 79.9; H, 5.5; P, 8.9. $C_{23}H_{19}OP$ requires C, 80.7; H, 5.6; P, 9.1%). *m*/*z* 342 (M^+, 100%).

6-(Diphenylphosphanyl)naphthalen-2-ol 2b. In a 100 mL 3-necked round bottomed flask, equipped with a reflux condenser and mechanical stirrer, compound **2a** (5g, 1.5 mmol) suspended in concentrated HBr (25mL) was heated to reflux for 4 h under dinitrogen. The solution was cooled and the white precipitate collected by filtration, washed with water, and dried *in vacuo* affording **2b** as its hydrobromide salt (5.67 g, 95%). To NaOH (1 g, 25 mmol) dissolved in ethanol was added the phosphonium salt (2.5 g, 6.1 mmol) which was left to stir until it had all dissolved. The resulting pale yellow solution was then treated with acetic acid until just acidic. Water (100 mL) was added and the precipitate collected by filtration. Recrystallisation of the crude material from methanol afforded **2b** (1.85 g, 92%), mp 206–207 °C (Found: C, 80.9; H, 5.4; P, 9.3. $C_{22}H_{17}OP$ requires C, 80.5; H, 5.6; P, 9.5%). *m*/*z* 328 (MH^+, 100%).

6-(Diphenylphosphinoyl)naphthalen-2-ol 3a. To compound **2b** (1 g, 3.05 mmol) dissolved in acetone (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added H_2O_2 (0.5 g, 27% w/w). After stirring for 20 min the solvent was removed under reduced pressure to afford an off-white solid. Recrystallisation of the crude material from methanol afforded **5**·0.75MeOH as a white solid (0.95 g, 86%), mp 149–150 °C (Found: C, 74.6; H, 4.8; P, 8.8. $C_{22}H_{17}O_2P$·0.75MeOH requires C, 74.7; H, 5.1; P, 8.4%). *m*/*z* 345 (MH^+, 70%).

6-(Diphenylphosphinothioyl)naphthalen-2-ol 3b. To compound **2b** (1 g, 3.05 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was

Table 9 Crystal data for compounds **4b**, **6b** and **9c**

	4b	**6b**	**9c**
Empirical formula	$C_{29}H_{23}N_2OP$	$C_{31}H_{25}N_2O_2P$	$C_{31}H_{25}N_2O_2PS$
M	446.46	488.8	520.56
T/K	203(2)	203(2)	203(2)
Crystal symmetry	Orthorhombic	Triclinic	Triclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$
a/Å	8.0770(10)	8.2523(16)	8.865(2)
b/Å	22.366(3)	10.0350(19)	12.054(3)
c/Å	25.317(4)	16.500(5)	13.935(3)
α/°		97.27(2)	107.558(17)
β/°		99.19(2)	94.483(18)
γ/°		108.358(16)	108.463(16)
U/Å^3	4573.5(11)	1257.2(5)	1321.5(5)
Z	8	2	2
μ/mm^{-1}	0.145	0.141	0.215
Reflections collected	9356	4412	4969
Independent reflections	3457	4412	4640
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0686, 0.1172	0.0581, 0.1117	0.0412, 0.0964
(all data)	0.2136, 0.1665	0.1221, 0.1417	0.0648, 0.1077

added S_8 (0.1 g, 3.05 mmol). When all of the sulfur had dissolved the solvent was removed under reduced pressure. Recrystallisation of the crude material from CH_2Cl_2–hexane afforded **6** as a white solid (1 g, 91%), mp 149–150 °C (Found: C, 73.4; H, 5.1; S, 8.6. $C_{22}H_{17}OPS$ requires C, 73.3; H, 4.8; S, 8.9%). *m*/*z* 361 (MH^+, 100%).

6-(Diphenylphosphanyl)-1-(phenylazo)naphthalen-2-ol 4a. To compound **2b** (0.5g, 1.5 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added NaH (0.079 g, 1.9 mmol). After stirring for 10 min the solution was cooled to 0–5 °C and phenyldiazonium tetrafluoroborate (0.29 g, 1.5 mmol) dissolved in acetonitrile (10 mL) added rapidly causing the solution immediately to turn red. After stirring for 45 min the solvent was removed under reduced pressure, the residue extracted into dichloromethane and filtered through a Celite pad to remove $NaBF_4$. The resulting solution after reduction in volume to *ca*. 5 mL was passed through a silica column with dichloromethane as eluent. After removal of the solvent under reduced pressure, recrystallisation of the crude material from dichloromethane–hexane afforded **4a** as a red solid (0.32 g, 49%). In an analogous manner compounds **4b–4g** were obtained; see Table 1 for physical and analytical data.

2-Acetoxy-6-(diphenylphosphanyl)-1-(4-methylphenylazo)-naphthalene 6b. To compound **4b** (0.3 g, 0.67 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added NaH (0.032 g, 0.81 mmol). After stirring for 10 min acetyl chloride (0.078 g, 1.0 mmol) was added. After stirring for 45 min the solvent was removed under reduced pressure and the crude material extracted into dichloromethane and filtered through a Celite pad to remove NaCl. Removal of the solvent under reduced pressure and recrystallisation of the crude material from butanol afforded **6b**. In an analogous manner compounds **6a**,**6c–6e**,**g** were obtained; see Table 1 for physical and analytical data.

6-(Diphenylphosphinoyl)-1-(phenylazo)naphthalen-2-ol 7a. To compound **3a** (0.15 g, 0.44 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added NaH (0.023 g, 0.57 mmol). After stirring for 10 min the solution was cooled to 0–5 °C and phenyldiazonium tetrafluoroborate (0.11 g, 0.57 mmol) dissolved in acetonitrile (10 mL) added rapidly causing the solution immediately to turn red. After stirring for 45 min the solvent was removed under reduced pressure, the residue extracted into dichloromethane and filtered through a Celite pad to remove $NaBF_4$. After removal of the solvent under reduced pressure, recrystallisation of the crude material from butanol followed by dichloromethane–hexane afforded **7a**·$\frac{2}{3}CH_2Cl_2$. In an analogous manner compounds **7b**, **7c**·0.25CH_2Cl_2, **7d** and **7e**·0.25CH_2Cl_2 were obtained; see Table 1 for physical and analytical data.

6-(Diphenylphosphinothioyl)-1-(phenylazo)naphthalen-2-ol 8a. To compound **3b** (0.15 g, 0.42 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added NaH (0.022 g, 0.55 mmol). After stirring for 10 min the solution was cooled to 0–5 °C and phenyldiazonium tetrafluoroborate (0.11 g, 0.55 mmol) dissolved in acetonitrile (10 mL) added rapidly causing the solution immediately to turn red. After stirring for 45 min the solvent was removed under reduced pressure, the residue extracted into dichloromethane and filtered through a Celite pad to remove $NaBF_4$. The resulting solution after reduction in volume to *ca*. 5 mL was passed through a silica column with dichloromethane as eluent. After removal of the solvent under reduced pressure, recrystallisation of the crude material from dichloromethane–hexane afforded **8a**. In an analogous manner compounds **8b**·0.25CH_2Cl_2, **8c**, **8d** and **8e** were obtained; see Table 1 for physical and analytical data.

2-Acetoxy-6-(diphenylphosphinoyl)-1-(4-methylphenylazo)-naphthalene 9a. To compound **6b** (0.25 g, 0.60 mmol) dissolved in THF (5 mL) with continuous stirring under an atmosphere of dry nitrogen was added H_2O_2 (0.1 g, 27% w/w). After stirring for 20 min the solvent was removed under reduced pressure and recrystallisation of the crude material from CH_2Cl_2–hexane afforded **9a**.

2-Acetoxy-6-(diphenylphosphinothioyl)-1-(4-methylphenylazo)naphthalene 9c. To compound **6b** (0.25 g, 0.60 mmol) dissolved in THF (10 mL) with continuous stirring under an atmosphere of dry nitrogen was added S_8 (0.023 g, 0.72 mmol). When all of the sulfur had dissolved the solvent was removed under reduced pressure. Recrystallisation of the crude material from CH_2Cl_2–hexane afforded **9c**. In an analogous manner compound **9b** was obtained; see Table 1 for physical and analytical data.

Crystallography

The X-ray diffraction experiments were carried out on a Nonius MACH 4-circle diffractometer using Mo-Kα radiation. Crystallographic data for compounds **4b**, **6b** and **9c** are summarised in Table 9. The SHELX 97 suite of programs[24] were used to solve the structures by direct methods and refine them using full matrix least squares.

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See http://www.rsc.org/suppdata/dt/1999/2563/ for crystallographic files in .cif format.

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