The synthesis and structural characterisation of some azo-containing phosphine chalcogenides and comparison to non-phosphorus-containing analogues

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p-HO-Ph(Ph_2)P(E) (E = S, **1b**, Se, **1c**) reacts with the diazonium salts [4-R-PhN=N][BF_4] (R = H, Me, Et, ^{i}Pr, ^{t}Bu, NMe_2, NO_2) to afford the new compounds [1-HO-2-(4-R-PhN=N)-4-Ph_2P(E)C_6H_3] (E = S, R = H, **2a**; Me, **2b**; Et, **2c**; ^{i}Pr, **2d**; ^{t}Bu, **2e**; NMe_2, **2f**; NO_2, **2g**; E = Se, R = H, **2h**; Me, **2i**) in acceptable yield. Similarly *m*-HO-Ph(Ph_2)P(S) **3** reacts with two molar equivalents of the diazonium salts [4-R-PhN=N][BF_4] (R = H, Me, NMe_2, NO_2) to give the new compounds 1-HO-2,4-(4-R-PhN=N)-3-Ph_2P(S)-C_6H_2 **4a**–**d** (R = H, **4a**; Me, **4b**; NMe_2, **4c**; NO_2, **4d**). All of the new compounds have been characterised by elemental analysis, ^{1}H, ^{31}P-{^{1}H}, ^{13}C-{^{1}H}-NMR spectroscopy and in selected cases UV–visible spectroscopy. The selectivity in the substitution reactions of **3** with the diazonium salts is influenced not only by the steric bulk of the Ph_2PS moiety but by the *ortho*-effect too. These data have been compared to those obtained from analogous coupling reactions between *m*-cresol and one and two molar equivalents of [4-Me-PhN=N][BF_4] which afford 1-HO-3-CH_3-4-(4-Me-PhN=N)C_6H_3 **5** and 1-HO-3-CH_3-2,4-(4-Me-PhN=N)C_6H_2 **6** respectively. The compounds **2b**·0.55CH_2Cl_2·0.2C_6H_{14}, **4b**·CH_2Cl_2, **5** and **6b** have been further characterised by X-ray crystallography.

Introduction

Phosphorus(v) species that contain the azo (N=N) moiety have been known since the mid-1950s,[1] and since then sporadic reports of this class of compound have appeared in the literature,[2] see Fig. 1 for an illustration of representative examples. Recent interest has been shown in these types of compounds because of their potential opto-electronic properties.[2g–l] We recently reported[3] an efficient synthesis of the azo-containing phosphines **I**, Fig. 2, and have subsequently described some facets of their coordination chemistry.[4] We were curious to see if the deprotonation of a hydroxy group bound to a phenyl ring of a triarylphosphine would suitably activate the ring to a C–N azo-coupling reaction as in the naphthyl system,[2] or whether the simple P–N Lewis acid–Lewis base adduct would form preferentially,[5] in which case it would be necessary to protect the lone pair of electrons at phosphorus. Herein we report that deprotonation of the hydroxy group is not sufficient to activate the ring to undergo a C–N coupling reaction with a diazonium tetrafluoroborate salt, but that coupling readily takes place between *p*-hydroxyphenyl(diphenyl)phosphine sulfide or selenide and *m*-hydroxyphenyl(diphenyl)phosphine sulfide with a range of diazonium tetrafluoroborate salts to afford azo-containing phosphine chalcogenides.

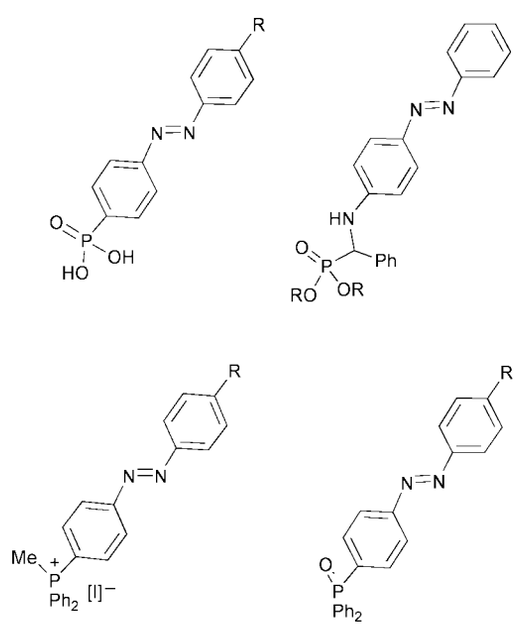
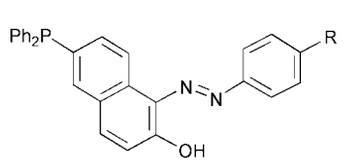


Fig. 1 Representative examples of azo-containing phosphorus(v) species.



I

R = H, Me, Et, ^{i}Pr, ^{t}Bu, NMe_2, NO_2.

Fig. 2 Azo-containing naphthylphosphines.

Results and discussion

It is well known that a deprotonated hydroxy group is an *ortho*/*para* director in electrophilic aromatic substitution reactions;[6] for example, in the reaction between [C_6H_5N=N][BF_4] and phenol,[7] the *para*-product is predominant (99.1% in H_2O; and 86.7% in C_5H_5N). Initial work, therefore, focused on coupling reactions between *p*-hydroxyphenyl(diphenyl)phosphine and diazonium salts so that only one product was likely, namely where coupling should occur *ortho* to the hydroxy group, since the *para*-position was blocked. Thus, dissolution of *p*-hydroxyphenyl(diphenyl)phosphine in dry THF and addition of NaH led to gas evolution and the generation of the phenoxide anion. Cooling of the solution to 0–5 °C and addition of a stoichiometric amount of [C_6H_5N=N][BF_4] did not lead to the

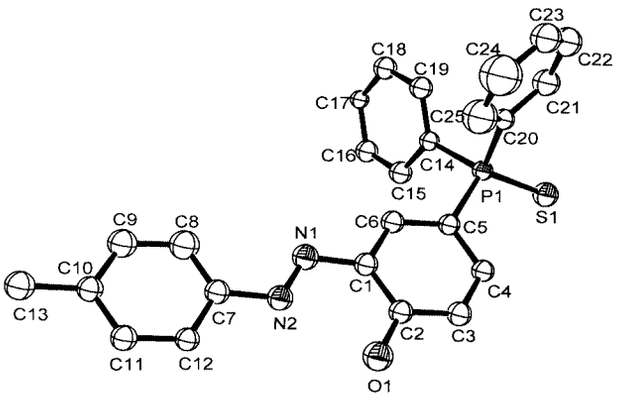
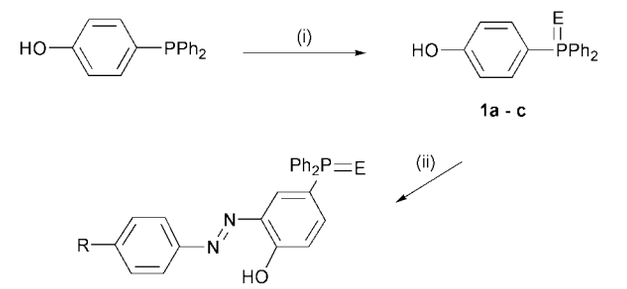


Fig. 3 ORTEP representation of compound **2b** showing the atomic numbering scheme.



E = S, R = H, **2a**; Me, **2b**, Et, **2c**; ^{i}Pr, **2d**; ^{t}Bu, **2e**; NMe_2, **2f**; NO_2, **2g**; E = Se, R = H, **2h**; Me, **2i**.

Scheme 1 (i) H_2O_2, acetone; S_8, THF; grey Se, toluene; (ii) NaH, [4-R-PhN=N][BF_4], THF.

characteristic orange colour of a phenylazo-containing compound, even on stirring for several days. After addition of water and work up *p*-hydroxyphenyl(diphenyl)phosphine oxide was isolated and this is consistent with the formation of a P–N coupled adduct which is hydrolysed on addition of water.[5] This observation is also consistent with our previous report where we have shown that the P–N adduct is not an intermediate in the formation of azo-containing phosphines, but is an undesired competing pathway.[4b] It was obvious, therefore, that deprotonation of the hydroxy group on the phenyl ring does not activate the ring sufficiently to compete with the P–N adduct forming reaction. We then turned our attention to protecting the phosphorus and investigating the coupling reactions with aryldiazonium salts. The phosphine chalcogenides *p*-HO-Ph(Ph_2)P(E) (E = O, S, Se) **1a**–**c** were prepared, Scheme 1, by reaction of the *p*-HO-Ph(Ph_2)P with the appropriate chalcogen in good yield, Table 1. To facilitate the coupling reactions **1a**–**c** were dissolved in THF and then reacted with a molar equivalent of NaH to generate the phenoxide ion. The anion generated from **1a** (the phosphine oxide) was found to precipitate from solution and not to undergo the expected coupling reaction; however, on deprotonation of **1b** or **1c** a soluble phenoxide ion was generated and these ions did readily couple with the diazonium salts [4-R-PhN=N][BF_4] (R = H, Me, Et, ^{i}Pr, ^{t}Bu, NMe_2, NO_2) to afford the new compounds [1-HO-2-(4-R-PhN=N)-4-Ph_2P(E)C_6H_3] (E = S, R = H, **2a**; Me, **2b**; Et, **2c**; ^{i}Pr, **2d**; ^{t}Bu, **2e**; NMe_2, **2f**; NO_2, **2g**; E = Se, R = H, **2h**; Me, **2i**) in acceptable yield, Scheme 1. All of the new compounds have been characterised by elemental analysis, Table 1, ^{1}H, ^{31}P-{^{1}H}, Table 2, and ^{13}C-{^{1}H} NMR spectroscopy, Table 3, and in selected cases UV–visible spectroscopy, Table 4, and compound **2b** by a single crystal X-ray diffraction study, see Fig 3 for an ORTEP[8] representation of the molecule.

The ^{1}H NMR data (Table 2) are consistent with the compounds **2a**–**i** being azo-containing phosphine chalcogenides. Of particular note is the singlet around 13.4 ppm which is assigned

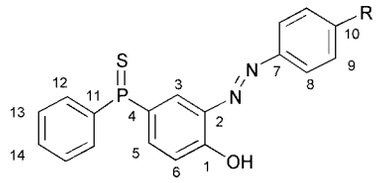
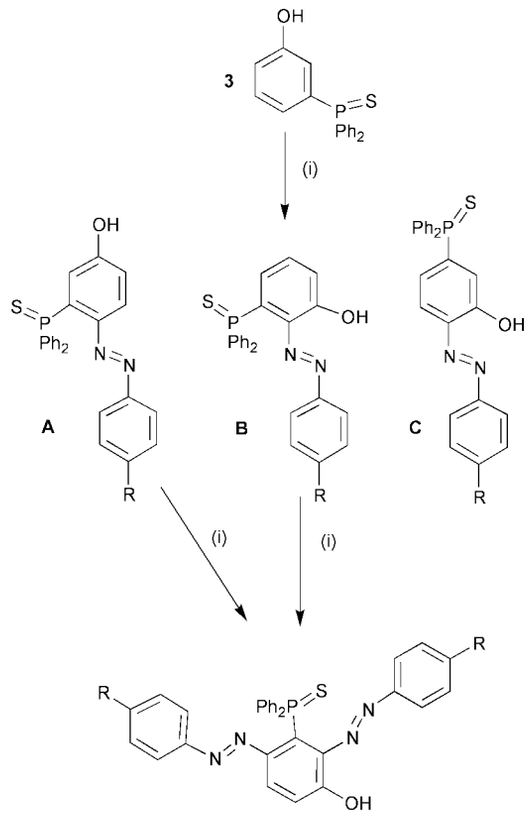


Fig. 4 ^{13}C-{^{1}H} NMR numbering scheme for **2a**–**i**.



R = H, **4a**; Me, **4b**; NMe_2, **4c**; NO_2, **4d**

Scheme 2 (i) NaH, [4-R-PhN=N][BF_4], THF.

to OH resonance and is indicative of a proton in a strongly bound hydrogen-bonded environment,[9] and this proton readily exchanges on addition of D_2O. The ^{31}P-{^{1}H} NMR data for **2a**–**g** all show a singlet resonance around 43 ppm which is as expected for phosphine sulfides and compounds **2h** and **2i** display singlets around 35 ppm straddled by satellites *J*(P–Se) of average value 732.2 Hz. The ^{13}C-{^{1}H} NMR spectra (Table 3), see Fig. 4 for the numbering scheme, have been assigned with the aid of DEPT 135 spectra, substituent effects[10] and coupling to the spin active ^{31}P nucleus.

Having established that *p*-hydroxyphenyl(diphenyl)phosphine chalcogenides readily undergo azo-coupling reactions we decided to investigate the coupling reaction with *m*-hydroxyphenyl(diphenyl)phosphine sulfide **3**, Scheme 2. In these coupling reactions, unlike those for the *p*-hydroxyphenyl-(diphenyl)phosphine chalcogenides, there is the distinct possibility of the generation of isomeric products, Scheme 2, due to the *meta*-disposition of *ortho*/*para*-(OH) and *meta*-($SPPh_2$) directing groups.[11] Normally the incoming group goes *ortho* to the *meta*-directing moiety, rather than *para*[12] which implies that either isomer **A** or **B** should result rather than **C**. Further, where the groups are sterically demanding **A** should be favoured.[12] These observations were further developed by Kruse and Cha who suggested,[13] that substitution *ortho* to the *meta*-director could be explained by consideration of the relative resonance energies of the potential transition states which they approximated as σ-complexes and in the absence of overwhelming steric effects they suggested that the reaction will occur

Table 1 Physical and analytical data for compounds **1a**–**6**[a]

Compound	Colour	Yield (%)	Mp/°C	Analysis (%) C	H	N	S
1a	White	69	158	73.4 (73.5)	4.7 (5.1)		
1b	White	69	158	69.4 (69.7)	4.9 (5.4)		10.1 (10.3)
1c	Off-white	85	178	60.0 (60.5)	3.6 (4.2)		
2a	Orange	60	92	68.6 (69.6)	4.7 (4.6)	6.7 (6.8)	7.4 (7.7)
2b·0.5CH_2Cl_2	Orange	68	80	64.9 (65.2)	5.0 (4.7)	5.9 (5.9)	6.3 (6.5)
2c	Orange	51	142	70.3 (70.6)	5.4 (5.2)	6.2 (6.2)	7.1 (7.3)
2d	Orange	63	126	70.8 (71.1)	5.4 (5.5)	6.1 (6.1)	6.8 (7.0)
2e	Orange	42	150	69.4 (69.1)	5.9 (5.6)	5.5 (5.7)	5.9 (6.8)
2f	Red	62	90	67.7 (68.3)	5.3 (5.3)	9.2 (9.2)	6.4 (7.0)
2g·0.25$CHCl_3$	Yellow	54	190	59.4 (59.7)	3.3 (3.8)	8.3 (8.3)	6.3 (6.6)
2h·0.25CH_2Cl_2	Orange	23	100	59.8 (59.8)	4.0 (4.0)	5.9 (5.7)	
2i·0.25CH_2Cl_2	Orange	16	162	61.2 (61.4)	4.4 (4.4)	5.4 (5.6)	
3	White	62	132	69.7 (68.4)	4.9 (4.9)	0 (0)	9.3 (10.0)
4a	Brown	58	226	68.8 (69.5)	4.5 (4.5)	10.8 (10.8)	5.7 (6.2)
4b	Brown	51	253	70.9 (70.3)	4.7 (5.0)	10.1 (10.2)	6.1 (5.9)
4c	Brown	53	224	67.0 (67.5)	5.8 (5.5)	13.1 (13.9)	5.0 (5.3)
4d·0.5CH_2Cl_2	Brown	45	200	56.3 (56.5)	3.0 (3.4)	12.3 (12.9)	5.7 (4.9)
5	Orange	56	95	74.2 (74.3)	6.1 (6.2)	12.3 (12.4)	
6	Brown	40	102	72.9 (73.2)	5.5 (5.9)	16.0 (16.3)	

[a] Calculated values in parentheses.

mutually *ortho* to both substituents. Applying their interpretation to the reaction between **3** and diazonium salts the most likely product is **B**, Scheme 2, since the transition states for **A** and **C** are "cross-conjugated".

Treatment of **3** with one molar equivalent of NaH in THF led to effervescence and generation of the phenoxide anion, which on reaction with a stoichiometric amount of [4-Me-PhN=N][BF_4] led to an orange solution, which after work-up, afforded an orange powder. The ^{31}P-{^{1}H} NMR spectrum displayed two equal intensity resonances at 44.7 and 44.3 ppm. This observation suggested that coupling had occurred to afford isomers **A** and **B**, Scheme 2. The presence of **B** was to be expected, and evidence for its presence came from the ^{1}H NMR spectrum which displayed a sharp singlet around 14 ppm (this is indicative of an azo group *ortho* to the hydroxy moiety). The presence of **A** must be a result of the large steric requirement of the Ph_2PS moiety. From the integration of the ^{31}P-{^{1}H} NMR spectrum it was apparent that a roughly 50 : 50 mixture of the two isomers was present. Either treatment of the crude mixture with a second equivalent of NaH followed by [4-Me-PhN=N]-[BF_4] or reaction of **3** with two molar equivalents of NaH followed by two molar equivalents of [4-Me-PhN=N][BF_4] led to the isolation of **4b**, Scheme 2. Compound **4b** displays a single resonance at 37.9 ppm in its ^{31}P-{^{1}H} NMR spectrum and three singlets at 14.2, 2.36 and 2.355 ppm (integral ratio 1 : 3 : 3) corresponding to the OH and the two different CH_3 moieties respectively in its ^{1}H NMR spectrum: this is consistent with a double coupling reaction having taken place. Compound **3** also reacts in an analogous manner with two molar equivalents of [4-R-PhN=N][BF_4] (R = H, NMe_2, and NO_2) to afford the new compounds 1-HO-2,4-(4-R-PhN=N)-3-Ph_2P(S)-C_6H_2, **4a**, **c**, **d** (R = H, **4a**; NMe_2, **4c**; NO_2 **4d**). Due to similar R_f and solubility properties of the mono-substituted isomers it has, to-date, not been possible to isolate any in an analytically pure state. All of the new compounds **4a**–**d** have been characterised by elemental analysis, Table 1, ^{1}H, ^{31}P-{^{1}H} NMR spectroscopy, Table 2, ^{13}C-{^{1}H} NMR spectroscopy, Table 3, see Fig. 5 for the numbering scheme, and in selected cases UV–visible spectroscopy, Table 4, and the data are consistent with their formulation. Compound **4b** was further characterised by a single crystal X-ray diffraction, see Fig. 6 for ORTEP[8] representation of the molecule showing the atomic numbering scheme.

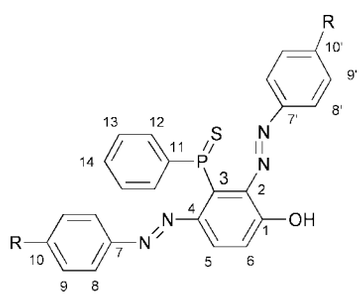


Fig. 5 ^{13}C-{^{1}H} NMR numbering scheme for **4a**–**d**.

Although the data collected for **4b** were not of high quality it confirmed that the coupling reaction had taken place in both positions *ortho* to the *meta*-directing group. Further, it was

Table 2 ^{1}H NMR [a] (δ) and ^{31}P-{^{1}H} NMR data [b] (δ) for compounds **1b**–**6**

Compound	^{31}P	^{1}H
1b	44.1	7.8–7.3 (br m, 12H, aryl H), 6.9 (dd, J_{HH} 8.5, J_{PH} 2.1, 2H, aryl H), 5.9 (br s, 1H, OH).
1c	35.4 ($^{1}J_{P\text{–}Se}$ 712.1)	7.8–7.7 (br m, 4H, aryl H), 7.6–7.3 (br m, 8H, aryl H), 6.8 (dd, J_{HH} 7.5, J_{PH} 2.0, 2H, aryl H), 5.8 (br s, 1H, O*H*).
2a	42.8	13.3 (s, 1H, OH), 8.3 (dd, J_{PH} 13.6, J_{HH} 1.9, 1H, aryl H), 7.9–7.3 (br m, 16H, aryl H), 7.1 (dd, J_{HH} 8.6, J_{HH} 2.5, 1H, aryl H).
2b	42.8	13.4 (s, 1H, OH), 8.3 (dd, J_{PH} 15.7, J_{HH} 2.2, 1H, aryl H), 7.9–7.3 (br m, 15H, aryl H), 7.1 (dd, J_{HH} 8.6, J_{HH} 2.5, 1H, aryl H), 5.29 (s, $\frac{1}{2}$ H, CH_2Cl_2), 2.4 (s, 3H, CH_3).
2c	42.9	13.4 (s, 1H, OH), 8.3 (dd, J_{PH} 13.6, J_{HH} 2.1, 1H, aryl H), 7.8–7.2 (br m, 15H, aryl H), 7.1 (dd, J_{HH} 8.6, J_{HH} 2.7, 1H, aryl H), 2.7 (q, J_{HH} 7.2, 2H, CH_2), 1.3 (t, J_{HH} 7.2, 3H, CH_3).
2d	42.9	13.4 (s, 1H, OH), 8.3 (dd, J_{PH} 15.7, J_{HH} 2.3, 1H, aryl H), 7.8–7.3 (br m, 15H, aryl H), 7.1 (dd, J_{HH} 8.6, J_{HH} 2.7, 1H, aryl H), 3.0 (m, J_{HH} 7.0, 1H, C*H*), 1.3 (d, J_{HH} 7.0, 6H, CH_3).
2e	42.9	13.4 (s, 1H, OH), 7.8 (dd, J_{PH} 14.7, J_{HH} 2.1, 1H, aryl H), 7.7–7.3 (br m, 15H, aryl H), 7.1 (dd, J_{HH} 8.5, J_{HH} 2.5, 1H, aryl H), 1.6 (s, 9H, CH_3).
2f	43.7	13.7 (s, 1H, OH), 8.2 (dd, J_{PH} 13.8,J_{HH} 2.0, 1H, aryl H), 7.8–7.5 (br m, 13H, aryl H), 7.0 (dd, J_{HH} 8.5, J_{HH} 3.0, 1H, aryl H), 6.7 (dd, J_{HH} 8.5, J_{HH} 3.0, 1H, aryl H), 3.1 (s, 6H, CH_3).
2g	43.2	12.9 (s, 1H, OH), 8.4–8.3 (br m, 3H, aryl H), 8.0 (d, J_{HH} 8.5, 2H, aryl H), 7.8–7.5 (br m, 10$\frac{1}{4}$ H, aryl H, $\frac{1}{4}$ $CHCl_3$), 7.1 (dd, J_{HH} 8.7, J_{HH} 2.8, 2H, aryl H).
2h	35.2 ($^{1}J_{P\text{–}Se}$ 731.7)	13.4 (s, 1H, OH), 8.3 (dd, J_{PH} 13.8, J_{HH} 2.0, 1H, aryl H), 7.8–7.5 (br m, 15H, aryl H), 7.1 (dd, J_{HH} 8.5, J_{HH} 2.5, 1H, aryl H), 5.29 (s, $\frac{1}{3}$ H, CH_2Cl_2).
2i	35.2 ($^{1}J_{P\text{–}Se}$ 732.7)	13.4 (s, 1H, OH), 8.3 (dd, J_{PH} 14.0, J_{HH} 2.0, 1H, aryl H), 7.8–7.7 (br m, 7H, aryl H), 7.5–7.4 (br m, 5H, aryl H), 7.3 (d, J_{HH} 8.5, 1H, aryl H), 7.1 (dd, J_{HH} 8.7, J_{HH} 2.6, 1H, aryl H), 5.29 (s, $\frac{1}{4}$ H, CH_2Cl_2), 2.4 (s, 3H, CH_3).
3	44.5	7.8–7.9 (br m, 4H, aryl H), 7.6–7.5 (br m, 7H, aryl H), 7.3–7.2 (br m, 3H, aryl H).
4a	37.9	14.2 (s, 1H, OH), 8.0–7.9 (br m, 6H, aryl H), 7.4–7.2 (br m, 16H, aryl H).
4b	37.9	14.2 (s, 1H, OH), 8.0–7.9 (br m, 5H, aryl H), 7.8–7.0 (br m, 15H, aryl H), 2.36 (s, 3H, CH_3), 2.355 (s, 3H, CH_3).
4c	37.8	14.3 (s, 1H, OH), 8.0–7.7 (br m, 8H, aryl H), 7.7–7.0 (br m, 7H, aryl H), 6.5–6.4 (br m, 5H, aryl H), 3.06 (s, 6H, CH_3), 3.04 (s, 6H, CH_3).
4d	38.0	14.0 (s, 1H, OH), 8.2–7.9 (br m, 10H, aryl H), 7.4–7.2 (br m, 10H, aryl H), 5.29 (s, $\frac{1}{2}$ H, CH_2Cl_2).
5		7.77 (d, J_{HH} 9.0, 2H, aryl H), 7.65 (d, J_{HH} 9.0, 1H, aryl H), 7.29 (d, J_{HH} 9.0, 2H, aryl H), 6.7 (m, 2H, aryl H), 5.1 (s, 1H, OH), 2.7 (s, 3H, CH_3), 2.42 (s, 3H, CH_3).
6		14.4 (s, 1H, OH), 7.8 (m, 5H, CH), 7.3 (m, 4H, CH), 6.9 (d, J_{HH} 9.0, 1H, CH), 3.1 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.44 (s, 3H, CH_3).

[a] Spectra recorded in $CDCl_3$ (293 K) and referenced to $CHCl_3$; coupling constants in Hz. [b] Spectra recorded in $CDCl_3$ (293 K) and referenced to 85% H_3PO_4; coupling constants in Hz.

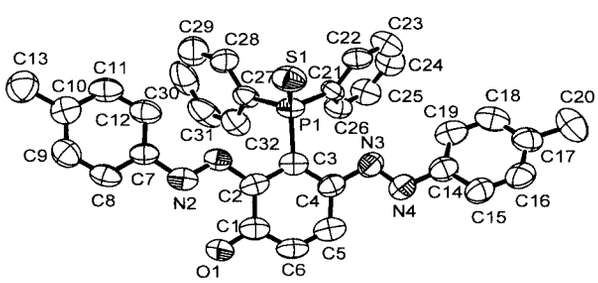


Fig. 6 ORTEP representation of compound **4b** showing the atomic numbering scheme.

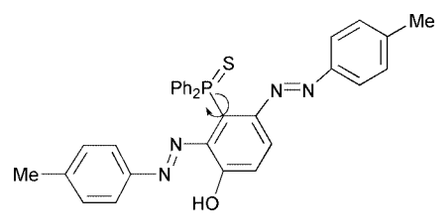


Fig. 7 Representation of the rotation about P–C bond observed in molecular structure of **4b**.

evident that there is a strong hydrogen bond[14] present in the molecule: O(1)–H···N(2) with O(1)–H 0.753(2), O(1)–N(2) 2.578(2), N(2)–H 1.994(2) Å, O–H–N 134.6(11) which is common in these types of compounds.[15] Since **4b** contains two azo-moieties, of which only one is *ortho* to the hydroxy group, direct structural evidence for the presence of hydroxyazo–ketohydrazone tautomerisation in phenol based systems should be possible.[15] Unfortunately in the crystal, rotation about the P(1)–C(3) bond, Fig. 7, was evident about 20% of the time which means that the bond lengths around each azo-moiety in the final structural model contain a contribution from both types of azo environment and so no such interpretation can be made.

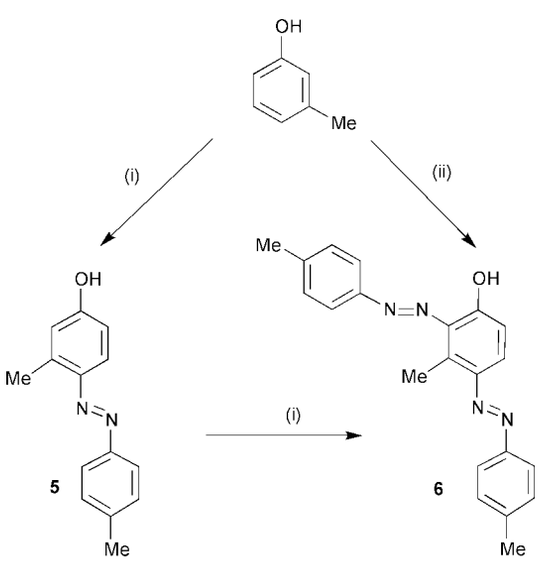
Since the coupling reaction of **3** with diazonium salts had occurred at the expected *ortho*-positions to the *meta*-directing Ph_2PS group, we were curious as to whether replacing the Ph_2PS moiety with the formally *ortho*/*para*-directing methyl group, and carrying the reaction out under identical conditions would lead to (i) exclusively mono-substitution *para* to the hydroxy group and (ii) on reaction of a second equivalent to substitution at the sterically least hindered site *ortho* to the hydroxy group, since the *ortho*-effect should no longer be operating.

Treatment of *m*-cresol with a stoichiometric amount of NaH in THF led to effervescence and the generation of the phenoxide ion, which on cooling to 0–5 °C and addition of [4-Me-PhN=N][BF_4] led exclusively, as expected, to formation of 1-HO-3-CH_3-4-(4-Me-PhN=N)-C_6H_3 **5**, *i.e.* the *para*-coupled product and no evidence for any *ortho*-coupled product either at the 2- or 6-position was obtained, Scheme 3, see Tables 1–3 for characterising data. Treatment of **5** with a stoichiometric amount of NaH followed by [4-Me-PhN=N][BF_4] led to the isolation of the brown solid 1-HO-3-CH_3-2,4-(4-Me-PhN=N)-C_6H_2 **6** where a second coupling reaction had occurred and once again exclusively in the sterically most congested *ortho*-position; Scheme 3, see Tables 1–3 for characterising data. The second coupling in the 2-position is clear from the proton NMR spectrum by the presence of a doublet at 6.9 ppm J_{HH} 9.0 Hz (the other expected doublet is obscured under the multiplet centred at 7.32 ppm), whereas if coupling had occurred in the 6-position lower frequency long range coupling would of been evident for the two protons on the substituted ring: no evidence for this product was seen in the crude ^{1}H NMR spectrum. This

Table 3 ^{13}C-{^{1}H} NMR data (δ)[a] for compounds **1b**–**6**

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7) C(7′)	C(8) C(8′)	C(9) C(9′)	C(10) C(10′)	C(11)	C(12)	C(13)	C(14)	Others
1b[b]	159.3	115.8	134.1	122.4							132.9	132.1	128.5	131.6	
	J 3.1	*J* 13.6	*J* 12.6	*J* 91.0							*J* 84.7	*J* 12.6	*J* 3.1	*J* 3.1	
1c[b]	159.2	115.8	134.5	121.3							131.8	132.5	128.5	131.6	
	J 2.2	*J* 13.8	*J* 12.4	*J* 83.6							*J* 77.8	*J* 10.9	*J* 13.1	*J* 2.9	
2a[b]	155.6	136.5	136.4	123.8	137.9	119.0	150.2	122.5	129.5	131.9	132.9	132.2	128.6	131.6	
	J 2.1	*J* 15.1	*J* 11.6	*J* 91.5	*J* 12.6	*J* 13.7					*J* 86.3	*J* 10.5	*J* 12.6	*J* 3.1	
2b[b]	155.6	136.2	136.0	123.6	137.5	118.9	148.2	122.5	130.1	142.7	133.1	132.2	128.6	131.6	21.7
	J 2.1	*J* 15.7	*J* 11.5	*J* 91.5	*J* 12.6	*J* 13.7					*J* 86.3	*J* 10.5	*J* 12.6	*J* 3.1	(CH_3)
2c[b]	155.6	136.5	136.0	123.6	137.6	118.9	148.4	122.5	128.9	149.0	133.1	132.2	128.6	131.6	28.9 15.3
	J 2.1	*J* 15.8,	*J* 11.6	*J* 90.5	*J* 12.6	*J* 13.7					*J* 86.3	*J* 10.5	*J* 12.6	*J* 2.7	(CH_2) (CH_3)
2d[b]	155.6	136.6	136.0	123.6	137.6	118.9	148.5	122.6	127.5	153.5	133.1	132.2	128.6	131.6	34.3 23.8
	J 2.1	*J* 15.8	*J* 11.6	*J* 90.5,	*J* 12.6	*J* 13.7					*J* 86.3	*J* 10.5	*J* 12.6	*J* 3.2	(CH) (CH_3)
2e[b]	155.6	136.6	136.0	123.4	137.7	118.9	148.0	122.2	126.4	155.8	133.1	132.2	128.6	131.6	35.3 31.2
	J 2.1	*J* 15.7	*J* 11.6	*J* 90.5	*J* 12.6	*J* 13.7					*J* 86.3	*J* 10.5	*J* 12.6	*J* 3.2	(CCH_3) (CH_3)
2f[c]	155.6	136.7	134.2	122.7	136.0	118.4	140.0	124.5	111.6	152.7	133.1	132.1	128.5	131.4	40.1
	J 1.9	*J* 15.5	*J* 11.6	*J* 91.8	*J* 12.6	*J* 13.5					*J* 86.0	*J* 10.6	*J* 12.6	*J* 2.9	(CH_3)
2g[c,d]	155.6	136.9	137.8	124.2	138.8	119.3	153.5	123.1	125.0	149.0	133.1	132.2	128.7	131.6	
	J 2.1	*J* 15.5	*J* 10.6	*J* 80.2	*J* 9.7	*J* 12.6					*J* 86.3	*J* 10.6	*J* 12.6		
2h[b]	155.6	136.4	134.6	122.4	136.7	115.7	150.1	122.4	129.4	131.7	131.8	132.5	128.6	131.7	
	J 1.9	*J* 15.3	*J* 12.3	*J* 82.1	*J* 12.4	*J* 14.5					*J* 77.8	*J* 10.9	*J* 13.1	*J* 2.9	
2i[b,d]	155.6	136.4	136.3	122.8	137.9	118.9	148.1	122.4	130.1	142.7		132.5	128.6	131.6	21.5
	J 2.2	*J* 15.3	*J* 11.6	*J* 82.8	*J* 12.4	*J* 14.5						*J* 10.9	*J* 13.1	*J* 3.6	(*C*H_3)
3[c,d]	156.0		132.3	124.0	129.7	119.8					133.6	132.1	128.4	131.6	
	J 10.1		*J* 86.0	*J* 9.7	*J* 15.5	*J* 2.6					*J* 85.0	*J* 10.6	*J* 12.6	*J* 2.2	
4a[c,d]	156.1	135.3	134.0	146.8	122.2	123.6	151.9	123.5	128.9	131.7	138.3	130.1	128.6	129.6	
	J 7.7		*J* 80.2		*J* 8.7	*J* 1.9	149.4	123.2	128.4	131.1	*J* 88.9	*J* 10.6	*J* 12.6	*J* 2.9	
4b[c,d]	157.4	135.6	133.3	147	121.9		150.1	123.5	129.6	142.6	138.5	130.0	128.0	129.1	21.5 21.4
	J 7.7		*J* 80.2		*J* 8.7		147.6	123.2	129.0	141.7	*J* 88.9	*J* 10.6	*J* 13.8	*J* 3.9	(CH_3) (CH_3)
4c[c,d]	154.5	136.0	134.2	147.7	119.8	122.8	143.5	125.7	111.2	152.6	139.1	130.0	128.6	129.1	40.18 40.15
	J 10.3		*J* 90.5		*J* 9.7		140.4	125.4	110.7	152.2	*J* 88.9	*J* 10.6	*J* 12.6	*J* 2.9	(CH_3) (CH_3)
4d[c,d]	157.4	135.6	136.8	146.6			154.7	124.1	124.7	148.8	137.9	130.1	128.4		
	J 7.7		*J* 77.3				152.6	123.8	124.0	148.7	*J* 89.8	*J* 10.6	*J* 13.6		
5[b]	157.9	117.2	140.8	145.2	117.3	113.6	151.4	122.6	129.7	140.7					21.4 17.5
															(CH_3) (CH_3)
6[b]	156.4	142.6	135.0	144.0	121.7	116.4	151.1	122.7	129.6	140.7					21.5 21.4 11.9
							148.4	121.2	130.0	141.8					(CH_3) (CH_3) (CH_3)

[a] Spectra recorded in $CDCl_3$ (293 K) and referenced to $CDCl_3$ (δ 77.0); (J_{C-P}) coupling constants in Hz. [b] Spectrum recorded at 75.6 MHz. [c] Spectrum recorded at 100.6 MHz. [d] One or more resonances obscured or partially obscured by overlapping with other signals; see Fig. 5 for the numbering schemes.



Scheme 3 (i) NaH, [4-R-PhN=N][BF_4], THF; (ii) 2 NaH, 2 [4-R-PhN=N][BF_4], THF.

result was somewhat surprising, however, reaction at the 2-position in competition with the 6- is not without precedent in related systems. For example, the reaction of 1-hydroxy-3-methyl-4-nitrobenzene with either HNO_3 or Cl_2 affords substitution at the 2-position (66 and 80% respectively),[16,17] and the only explanation offered for these observations was: electronic rather than steric effects dominate.[13]

Table 4 UV–visible data[a] for selected compounds **2a**–**4d**

Compound	λ[b]	ε[c]
2a	324	10426
	377	5260
2b	337	15870
	380	11270
2f	469	37470
2g	336	16790
	399	8200
2h	324	14420
	380	7460
2i	336	21490
	380	13510
4a	358	24040
	430	9930
4b	349	67120
	427	23040
4d	374	14040

[a] Spectra recorded in $CHCl_3$. [b] λ_{max}/nm. [c] ε/dm^3 mol^{-1} cm^{-1}.

Compounds **5** and **6** were also characterised by single crystal X-ray diffraction studies, see Figs. 8 and 9 for ORTEP[8] representations of the molecules showing the atomic numbering schemes. Compound **5** displays a strong intermolecular hydrogen bond O(1)–H(1)···N(2) where O(1)–H(1) 0.905, H(1)···N(2) 1.987, O(1)···N(2) 2.876 Å, O(1)–H(1)–N(2) 167.3°, whereas, compound **6** shows a strong intramolecular hydrogen bond O(1)–H(1) 1.183, H(1)···N(2) 1.487, O(1)···N(2)

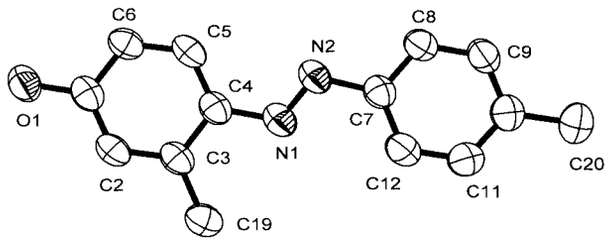


Fig. 8 ORTEP representation of compound **5** showing the atomic numbering scheme.

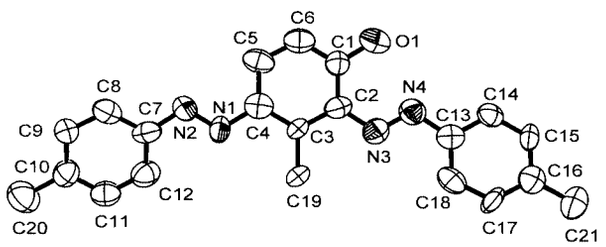


Fig. 9 ORTEP representation of compound **6** showing the atomic numbering scheme.

2.543 Å, O(1)–H(1)–N(2) 144.3° which is a common feature of *ortho*-hydroxyazo benzene systems.[14]

Conclusion

We have prepared a series of azo-containing phosphine chalcogenides by a classical azo-coupling reaction. Coupling in *m*-hydroxyphenyl(diphenyl)phosphine sulfide occurs at both positions *ortho* to the phosphine sulfide group qualitatively, at least, at the same rate and this is a result of the *ortho*-effect[11] and steric bulk of the (diphenyl)phosphine sulfide moiety. A similar coupling pattern is seen for *m*-cresol, although coupling in the sterically encumbered *ortho*-position only takes place once coupling *para*- to the hydroxy-group has occurred even though there is not a *meta*-disposition between an *ortho*/*para* and *meta*-directing groups.

Experimental

General considerations

All solvents, except water, were dried over an appropriate drying agent and distilled prior to use: THF (K); CH_2Cl_2 (P_2O_5); hexane (NaK). The aryldiazonium tetrafluoroborate salts,[18] *p*-methoxyphenyl(diphenyl)phosphine, *p*-hydroxyphenyl(diphenyl)phosphine and *p*-hydroxyphenyl(diphenyl)phosphine oxide,[19] *m*-methoxyphenyl(diphenyl)phosphine and *m*-hydroxyphenyl(diphenyl)phosphine[20] were prepared by the literature methods using reagents purchased from commercial sources. Melting points were recorded on a Griffin Melting Point Apparatus and are uncorrected. The ^{1}H (200.1 MHz) and ^{31}P-{^{1}H} NMR (81.3 MHz) were recorded on a Bruker DPX 200 spectrometer. ^{13}C-{^{1}H} NMR spectra (75.5, 100.5 MHz) were recorded on either a Bruker DPX 300 or DPX 400 spectrometer. ^{1}H and ^{13}C-{^{1}H} NMR 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. UV–visible spectra were recorded on a Shimadzu UV20101 PC spectrophotometer in $CHCl_3$ (AR) in 1 cm cuvettes. Elemental analyses, were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvents of crystallisation were confirmed by repeated elemental analysis and observation of relevant signals in the NMR spectra. Syntheses were carried out under a dinitrogen atmosphere using standard Schlenk techniques and subsequent workups were carried out in the open unless otherwise stated.

Preparations

***p*-Hydroxyphenyl(diphenyl)phosphine sulfide 1a.** To *p*-hydroxyphenyl(diphenyl)phosphine (1 g, 3.6 mmol) dissolved in THF (15 mL) with continuous stirring under dinitrogen was added S_8 (0.13 g, 3.6 mmol). When all of the S_8 had dissolved the solution was filtered through Celite and the solvent removed under reduced pressure. Recrystallisation of the crude material from CH_2Cl_2–hexane afforded **1a** as a white solid (1 g, 92%). In an analogous manner *m*-hydroxyphenyl(diphenyl)phosphine sulfide **3** was obtained; see Table 1 for physical and analytical data.

***p*-Hydroxyphenyl(diphenyl)phosphine selenide 1c.** To *p*-hydroxyphenyl(diphenyl)phosphine (1 g, 3.6 mmol) dissolved in toluene (15 mL) with continuous stirring under dinitrogen was added grey Se (0.32 g, 4 mmol) and the mixture refluxed for 3 h. The solution was cooled, filtered through Celite and the solvent removed under reduced pressure. Recrystallisation of the crude material from CH_2Cl_2–hexane afforded **1c** as an off-white solid (1.1 g, 85%); see Table 1 for physical and analytical data.

2-Phenylazo-4-(diphenyl)phosphinothioylphenol 2a. To *p*-hydroxyphenyl(diphenyl)phosphine (0.3 g, 0.97 mmol) dissolved in THF (10 mL) with continuous stirring under dinitrogen NaH (60% w/w in mineral oil; 0.046 g, 1.16 mmol) was added and the mixture stirred for 1 h. The solution was then cooled to 0–5 °C and [PhN=N][BF_4] (0.2 g, 1.1 mmol) dissolved in NCMe (10 mL) was rapidly added. After stirring for 1 h, HCl (0.2 mL, 1 M) was added and the solvent was removed under reduced pressure. The crude material was then extracted into CH_2Cl_2 and filtered through Celite to remove $NaBF_4$. Reduction of the solvent volume to 1 mL, *in vacuo*, and passing the solution down a silica column (3 × 20 cm) with CH_2Cl_2 as eluent afforded **2a** as an orange solid (0.24 g, 60%) on removal of the solvent. In an analogous manner compounds **2b**–**i** were obtained; see Table 1 for physical and analytical data.

2,4-Bis(4-methylphenylazo)-3-(diphenyl)phosphinothioylphenol 4b. To **3** (0.3 g, 0.97 mmol) dissolved in dry THF (10 mL), with continuous stirring under an atmosphere of dry dinitrogen was added NaH (60% w/w in mineral oil; 0.12 g, 2.9 mmol). After stirring for 10 min, the solution was cooled to 0–5 °C and [4-CH_3-C_6H_4N=N][BF_4] (0.49 g, 2.4 mmol) was added and stirred for 2 h. HCl (1 M, 0.2 mL) was added and the solvent removed under reduced pressure, followed by extraction into CH_2Cl_2 (10 mL) and filtration through Celite to remove $NaBF_4$. The resulting solution, after reduction in volume to *ca.* 1 mL, was passed through a silica column with CH_2Cl_2–hexane (8 : 2) as eluent. Elution initially gave a light red band, which was a mixture of mono-substituted products (0.1 g). Further elution with CH_2Cl_2–hexane (8 : 2) gave a dark red–brown band, which on removal of the solvent under reduced pressure, followed by recrystallisation from CH_2Cl_2–hexane afforded **4b** as a brown solid (0.26 g, 51%). In an analogous manner, compounds **4a**, **4c**–**d** were obtained; see Table 1 for physical and analytical data.

3-Methyl-4-(4-methylphenylazo)phenol 5. To *m*-cresol (0.8 g, 7.39 mmol) dissolved in dry THF (10 mL), with continuous stirring under an atmosphere of dry dinitrogen, was added NaH (60% w/w in mineral oil; 0.30 g, 7.39 mmol). After stirring for 10 min, the solution was cooled to 0–5 °C and [4-CH_3-C_6H_4N=N][BF_4] (1.5 g, 7.39 mmol) was added and stirred for 2 h. HCl (1 M, 0.2 mL) was added and the solvent removed under reduced pressure, followed by extraction into CH_2Cl_2 (10 mL) and filtration through Celite to remove $NaBF_4$. The solvent was removed to yield a brown solid and purification was effected by passing down a silica column with Et_2O–hexane (1 : 1) as eluent affording **6** (0.93 g, 56%); see Table 1 for physical and analytical data.

Table 5 Crystallographic data for compounds **2b**, **4b**, **5**, and **6**

	2b·0.55CH_2Cl_2·0.2C_6H_{14}	**4b**·CH_2Cl_2	**5**	**6**
Formula	$C_{26.8}H_{29}Cl_{1.1}N_2OPS$	$C_{33}H_{29}Cl_2N_4OPS$	$C_{14}H_{14}N_2O$	$C_{21}H_{20}N_4O$
M	492.92	631.53	226.27	344.41
Space group	*P*-1	*P*21/*c*	*P*21/*n*	*Pna*21
T/K	203	293	293	293
a/Å	8.8661(12)	16.037(2)	5.809(4)	18.942(4)
b/Å	10.5570(18)	7.6280(10)	18.173(7)	20.515(3)
c/Å	14.267(3)	26.332(2)	11.540(5)	4.6558(10)
α/°	110.513(16)			90
β/°	94.713(13)	93.860(10)	96.99(4)	90
γ/°	91.063(12)			90
V/Å^3	1244.9(4)	3213.9(6)	1209.1(11)	1809.2(6)
Z	2	4	4	4
μ(Mo-Kα)/cm^{-1}	0.71069	0.70169	1.54178	1.54178
No. reflections	4676	5205	2194	6653
No. ind. reflections	4368	2744	1981	3048
R (%)	6.1	5.4	4.4	8.5
R_w (%)	18.1	10.8	7.5	16.5

2,4-Bis(4-methylphenylazo)-3-methylphenol 6. To **5** (0.5 g, 2.21 mmol) dissolved in dry THF (10 mL), with continuous stirring under an atmosphere of dry dinitrogen, was added NaH (60% w/w in mineral oil; 0.088 g, 2.21 mmol). After stirring for 10 min, the solution was cooled to 0–5 °C and [4-CH_3-C_6H_4N=N][BF_4] (0.46 g, 2.21 mmol) was added and stirred for 2 h. HCl (1 M, 0.2 mL) was then added and the solvent removed under reduced pressure, followed by extraction into CH_2Cl_2 (10 mL) and filtration through Celite to remove $NaBF_4$. Removal of the solvent under reduced pressure, followed by recrystallisation from EtOH afforded **6** as a brown solid (0.3 g, 40%); see Table 1 for physical and analytical data.

Crystallography †

All of the crystals were grown by slow diffusion of hexane into a saturated CH_2Cl_2 solution of **2b**, **4b**, **5**, or **6** at room temperature. The X-ray crystallography experiments for **2b** and **4b** were carried out on a Nonius Mach 4-circle diffractometer using Mo-Kα radiation and for **5** and **6** on a Rigaku AFC6S diffractometer using Cu-Kα radiation. Crystallographic data for compounds **2b**, **4b**, **5** and **6** are summarised in Table 5. The SHELX 97 suite of programs[21] was used to solve the structures by direct methods and refined them by full matrix least squares.

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† CCDC reference numbers 165166–165169. See http://www.rsc.org/suppdata/p1/b1/b104918f/ for crystallographic files in .cif or other electronic format.

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