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Azo-phosphine containing complexes of Group 6 metal carbonyls: crystal and molecular structure of $[Mo(CO)_5\{1\text{-}(4\text{-ethylphenylazo})\text{-}6\text{-diphenylphosphino-naphthalen-}2\text{-ol}\}]$[1]

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

Department of Chemistry, UMIST, PO Box 88, Manchester, M60 1QD, UK

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Abstract

Treatment of the compounds $[M(CO)_5(NCMe)]$ (M = Cr, Mo, W) with the phenylazonaphthylphosphines $4\text{-R–PhN}_2\text{-1-C}_{10}H_5\text{-2-OR}'\text{-6-PPh}_2$ $\{R' = H$, $R = H$ (**I**), $R = Me$ (**II**), $R = Et$ (**III**), $R = Pr^i$ (**IV**) $R = Bu^t$ (**V**); $R' = C(O)Me$, $R = Me$ (**VI**)$\}$ afforded the mono-substituted products $[M(CO)_5(L)]$ (**1-8**) (M = Cr, L = **II**, **1**; M = Mo, L = **I**–**VI**, **2**–**7**; M = W, L = **II**, **8**). Further reaction of *cis*-$[Mo(CO)_4(\text{piperidine})_2]$ with the azo-phosphines **I**–**V** afforded the di-substituted complexes *cis*-$[Mo(CO)_4(L)_2]$ (**9**–**13**); whereas, reaction with **VI** afforded *cis*-$[Mo(CO)_4(\mathbf{II})_2]$ **10** rather than the expected compound *cis*-$[Mo(CO)_4(\mathbf{VI})_2]$ (**14**). **14** can, however, be prepared by esterification of **10**. The observed non-innocence of piperidene on displacement from *cis*-$[Mo(CO)_4(\text{piperidine})_2]$ has been further investigated. Thus, treatment of **7** with piperidene yielded **3** as a result it becomes apparent that the potential reactivity of the displaced ligand needs to be considered carefully when carrying out simple substitution reactions. The molecular structure of **4** is also reported. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Azo-phosphines; Chromium; Molybdenum; Tungsten

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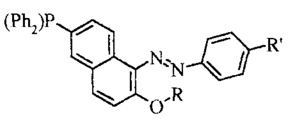
1. Introduction

We recently reported the synthesis of some azo-functionalised phosphines by hydroxyl activated C–N coupling between a diazonium salt and a hydroxy functionalised phosphine. [1] Having prepared these compounds we decided to investigate their coordination chemistry and have prepared a series of complexes derived from Group 6 metal carbonyls. Generally, in attempts to carry out carbonyl substitution reactions in Group 6 metal carbonyls with phosphine based ligands to get the reaction proceed smoothly it is often common to prepare either $[M(CO)_5(THF)]$ [2], $[M(CO)_5(NCMe)]$ [3], $[M(CO)_4(pip)_2]$ [4] or $[M(CO)_3(NCMe)_3]$ [5], as these compounds tend to give better yields of purer products than simple thermolysis of the metal hexacarbonyl in the presence of the ligand at high temperature alone. Recent examples where simple substitution reactions have occurred include: the preparation of $[M(CO)_5(\eta^1\text{-P–P})]$ (P–P = dppe, dppp, dppb) leading to the preparation of the heterobimetallic complexes $[(CO)_5M(\mu\text{-P–P})M'(CO)_5]$ (M, M′ = Cr, Mo, W, M ≠ M) [3]; reaction between



R = H, R' = H (**I**), Me (**II**), Et (**III**), Pr^i (**IV**), Bu^t (**V**); R = C(O)Me, R' Me (**VI**)

Fig. 1. Compounds **I**–**VII**.

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* Corresponding author. Tel.: +44 161 2004538; e-mail; k.r.flower@umist.ac.uk

[1] Paper dedicated to Professor W.R. Roper FRS on the occassion of his 60th birthday.

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Table 1
Physical and analytical data for complexes **1**–**14**[a]

Complex	Colour	Yield (%)	C (%)	H (%)	N (%)
1	Red	47	57.7 (58.1)	4.0 (3.5)	3.4 (3.8)
2	Red	72	59.3 (59.2)	2.6 (3.1)	4.2 (4.2)
3	Red	34	59.7 (59.8)	3.3 (3.4)	4.0 (4.1)
4	Red	50	60.1 (60.4)	3.4 (3.6)	4.1 (4.0)
5	Red	31	61.0 (60.9)	4.0 (3.8)	3.6 (3.9)
6	Red	32	62.1 (61.3)	4.6 (4.0)	3.7 (3.9)
7	Red	60	59.4 (60.0)	3.8 (3.5)	3.9 (3.9)
8	Red	30	52.9 (53.0)	3.0 (3.0)	3.5 (3.6)
9	Red	54	66.2 (62.5)	4.1 (3.9)	5.1 (4.9)
10	Red	42	67.8 (67.8)	4.4 (4.2)	5.3 (5.1)
11	Red	75	63.4 (63.8)	4.1 (4.2)	4.2 (4.6)
12	Red	56	67.4 (67.6)	4.7 (4.7)	4.6 (4.8)
13	Red	57	64.7 (67.7)	4.7 (4.9)	4.6 (4.6)
14	Red	54	59.8 (60.0)	3.8 (3.5)	3.9 (3.9)

[a] Calculated values in parentheses.

$[Cp_2Rh_2(CO)\{\eta^1\text{-}Ph_2P(CH_2)_nPPh_2\}(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]$ ($n = 1$–4) and $[Cr(CO)_5(THF)]$ afforded the trimetallic species $[Cp_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}Cr(CO)_5]$ [6]; the water soluble compounds $[W(CO)_4(L)_2]$ ($L = 3\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_4N$, $3,5\text{-}(NaO_2C)_2C_5H_4N$, $3\text{-}NaO_3SC_5H_4N$) were prepared by displacement of piperidine from $[W(CO)_4(pip)_2]$ [7]; and a series of multimetallic species based upon complexation of the non-coordinated phosphorus in $[WI_2(CO)\{\eta^2\text{-}Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2\}(\eta^2\text{-}RC_2R)]$ with $[M(CO)_5(NCMe)]$ (M = Cr, Mo, W), $[M(CO)_4(pip)_2]$ (M = Mo, W) and $[Mo(CO)_3(NCMe)_3]$. [8] Herein, we report the reactions between the azophosphines $4\text{-}R\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OR'\text{-}6\text{-}PPh_2$ ($R' = H$, $R = H$ (**I**), $R = Me$ (**II**), $R = Et$ (**III**), $R = Pr^i$ (**IV**) $R = Bu^t$ (**V**); $R' = C(O)Me$, $R = Me$ (**VI**)) and the metal carbonyl compounds $[M(CO)_5(NCMe)]$ (M = Cr, Mo, W) and $[Mo(CO)_4(pip)_2]$ yielded the compounds $[M(CO)_5(L)]$ (**1**–**8**) (M = Cr, L = **II**, **1**; M = Mo, L = **I**–**VI**, **2**–**7**; M = W, L = **II**, **8**) and the di-substituted complexes *cis*-$[Mo(CO)_4(L)_2]$ (**9**–**13**). Furthermore, we report that on displacement of piperidine from *cis*-$[Mo(CO)_4(pip)_2]$ by **VI** affords **10** by a de-esterification process facilitated by the piperidene.

2. Results and discussion

The compounds **I**–**VI**, Fig. 1, react with $[M(CO)_5(NCMe)]$ to yield the mono-substituted products $[M(CO)_5(L)]$ **1**–**8** in good yield. All new compounds have been characterised by elemental analysis, ^{1}H-, $^{31}P\{^1H\}$-NMR and infrared spectroscopy (Tables 1–3). Compound **4** was further characterised by a single crystal X-ray diffraction study (Tables 4–8; see later for structure discussion).

The infrared spectra of compounds **1**–**8** (Table 2) all show the expected three carbonyl stretching bands for localised C_{4v}. [9].

The ^{1}H-NMR spectra, Table 3, all show the expected resonances for the phosphines which are little peturbed on complexation. The ^{31}P-NMR spectra for **1**–**7** all show a singlet resonance shifted downfield from the free phosphine; **8** shows a singlet resonance straddled by the expected tungsten satellites, $^1J_{W\text{-}P} = 242$ Hz.

In an attempt to prepare a series of bisphosphine complexes the compound $[Mo(CO)_4(pip)_2]$ was prepared and treated with **I**–**V** affording the expected di-substituted compounds $[Mo(CO)_4(L)_2]$ **9**–**13** in good yield. All of the compounds have been characterised by elemental analysis ^{1}H-, $^{31}P\{^1H\}$-NMR and infrared spectroscopy (Tables 1–3).

The infrared spectra (Table 2) all display three strong carbonyl bands rather than the expected four where a

Table 2
Infrared data for complexes **1**–**14**[a]

Complex	ν(CO) (cm^{-1})	ν(C=O) (cm^{-1})
1	2065(s), 1982(w), 1930(brs)	
2	2080(s), 1995(w), 1940(brs)	
3	2078(s), 1990(sh), 1948(brs)	
4	2079(s), 1989(w), 1945(brs)	
5	2078(s), 1988(w), 1950(brs)	
6	2079(s), 1990(w), 1948(brs)	
7	2080(s), 1995(w), 1935(brs)	1750(m)
8	2079(s), 1985(w), 1942(brs)	
9	2023(s), 1920(brs), 1880(brs)	
10	2022(s), 1915(brs), 1871(brs)	
11	2021(s), 1920(brs), 1870(brs)	
12	2021(s), 1920(brs), 1876(brs)	
13	2022(s), 1930(brs), 1870(brs)	
14	2025(s), 1921(brs), 11876(brs)	1745(s)

s, Strong; m, medium; sh, shoulder; br, broad.
[a] Spectra recorded as KBr discs.

Table 3
Proton[a] and ^{31}P-NMR data[b] (d) for complexes 1–**14**

Complex	^{31}P (δ) ppm	^{1}H (δ) ppm
1	56.3	16.1 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.8, Ar–H); 7.8–7.3 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.4, Ar–H); 2.4 (s, 3H, CH_3)
2	38.1	16.1 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.7, Ar–H); 7.8–7.3 (m, 18H, Ar–H); 7.0 (d, 1H, J_{HH} 9.7, Ar–H).
3	38.1	16.1 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 6.9, Ar–H); 7.8–7.3 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.3, Ar–H); 2.4 (s, 3H, CH_3)
4	38.1	16.1 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.7, Ar–H); 7.8–7.3 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.3, Ar–H); 2.7 (q, 2H, J_{HH} 7.8, CH_2); 1.3 (t, 3H, J_{HH} 7.8, CH_3)
5	38.1	16.2 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.9, Ar–H); 7.8–7.3 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.3, Ar–H); 3.0 (sp, 1H, J_{HH} 6.7, CH); 1.3 (d, 6H, J_{HH} 6.7, CH_3)
6	38.1	16.2 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.7, Ar–H); 7.8–7.4 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.3, Ar–H); 1.4 (s, 9H, CH_3)
7	38.7	8.7 (d, 1H, J_{HH} 6.9, Ar–H); 8.0 (d, 1H, J_{HH} 12.0, Ar–H); 7.8 (d, 1H, J_{HH} 8.4, Ar–H); 7.6–7.3 (m, 16H, Ar–H); 2.5 (s, 3H, OCCH_3); 2.3 (s, 3H, CH_3)
8	21.1 $^1J_{W\text{-}P}$ 242.6	16.1 (s, 1H, OH); 8.7 (d, 1H, J_{HH} 8.6, Ar–H); 7.8–7.3 (m, 17H, Ar–H); 7.0 (d, 1H, J_{HH} 9.5, Ar–H); 2.4 (s, 3H, CH_3)
9	38.7	16.1 (s, 2H, OH); 8.3 (d, 2H, J_{HH} 8.7, Ar–H); 7.7 (d, 2H, J_{HH} 8, Ar–H); 7.5–7.3 (m, 34H, Ar–H); 6.7 (d, 2H, J_{HH} 9.7, Ar–H).
10	38.6	16.0 (s, 2H, OH); 8.3 (d, 2H, J_{HH} 7.6, Ar–H); 7.6–7.2 (m, 34H, Ar–H); 6.8 (d, 2H, J_{HH} 9.3, Ar–H); 2.4 (s, 6H, CH_3)
11	38.6	16.1 (s, 2H, OH); 8.3 (d, 2H, J_{HH} 8.7, Ar–H); 7.6 (d, 2H, J_{HH} 10, Ar–H); 7.6–7.3 (m, 32H, Ar–H); 6.8 (d, 2H, J_{HH} 9.4, Ar–H); 2.7 (q, 4H, J_{HH} 7.6, CH_2); 1.3 (t, 3H, J_{HH} 7.6, CH_3)
12	38.6	16.1 (s, 2H, OH); 8.4 (d, 2H, J_{HH} 8.7, Ar–H); 7.7–7.2 (bm, 34H, Ar–H); 6.8 (d, 2H, J_{HH} 9.3, Ar–H); 6.8 (d, 2H, J_{HH} 9.3, Ar–H); 2.7 (sp, 2H, J_{HH} 6.6, CH); 1.3 (d, 12H, J_{HH} 6.6, CH_3)
13	38.6	16.1 (s, 2H, OH); 8.4 (d, 2H, J_{HH} 8.9, Ar–H); 7.7–7.2 (bm, 34H, Ar–H); 6.8 (d, 2H, J_{HH} 9.4, Ar–H); 1.4 (s, 18H, CH_3)
14	38.9	8.4 (d, 1H, J_{HH} 8.8, Ar–H); 7.8 (d, 1H, J_{HH} 8.3, Ar–H); 7.6–7.3 (bm, 17H, Ar–H); 2.5 (s, 3H, OCCH_3); 2.3 (s, CH_3)

J, Hz; s, singlet; d, doublet; t, triplet; sp, septet; m, multiplet; b, broad.

[a] Spectra recorded in $CDCl_3$ (298 K) and referenced to $CHCl_3$.

[b] Spectra recorded in $CDCl_3$ (298 K) and referenced to 85% H_3PO_4.

cis-orientation of the phosphine ligands leads to localised C_{2v} symmetry. On heating several of the compounds for extended periods only the initial *cis* isomer was recovered: there was no evidence for the formation of the *trans* isomer. Cotton et al. reported that the isomerisation process between the *cis* and *trans* isomers is dependent upon the steric and electronic properties of the phosphines [10], it is apparent for these azo-phosphines the *cis*-orientation is preferred.

As for **1**–**8** the ^{1}H-NMR spectra of **9**–**13** displayed the expected resonances for the phosphine ligands; and the ^{31}P{^{1}H}-NMR spectra all of the compounds exhibited the expected singlet resonance downfield from the uncomplexed phosphine.

Treatment of $[Mo(CO)_4(pip)_2]$ with **VI** did not, however, yield the expected complex $[Mo(CO)_4(\mathbf{VI})_2]$ **14** rather **10** was isolated in good yield. This result was initially a little perplexing, as **VI** was readily incorporated into the pentacarbonyl complexes by a simple ligand substitution reaction. On reflection, though, the reactivity observed could be easily rationalised using the following information. Reaction of **10** with a stoichiometric amount of NaH followed by an excess of MeC(O)Cl yielded $[Mo(CO)_4(\mathbf{VI})_2]$ **14** in good yield, which implies that this compound is not intrinsically unstable (see Tables 1–3 for characterising data). Treatment of **14** with **2** mole equivalents piperidine under the conditions used to prepare **9**–**13** readily afforded **10** and the amide $C_5H_9NHC(O)Me$ **VII**, whose spectroscopic data were compared with an authentic speciemen. [11] Further, treatment of **7** and **VI** with piperidene under the same reaction conditions led to the isolation of **3**, **II**, and **VII**, respectively, showing the de-esterification process by piperidine is quite general. If a slight excess of piperidine is added to a $CDCl_3$ solution of **II**, **7** or **14** and their ^{1}H-NMR spectra recorded immediately no evidence for the ester moiety is observed. The CH_3 signal at 2.5 ppm attributable to the ester moiety was replaced by a CH_3 signal at 1.98 ppm due to **VII**; however, the resonance due to the hydroxyl peak at 16.3 ppm is not observed as this is deprotonated by the excess piperidine. It is likely then that de-esterification begins immediately after the initial substitution of the piperidine ligand, with the displaced piperidine reacting with both complexed and uncomplexed azo-phosphine, implying that it is not an innocent spectator in these substitution reactions.

Although it is well known that amides can be prepared from esters, it can sometimes be difficult to achieve unless the ester is activated [12]. It is apparent that hydroxyazonaphthyl systems prefer to exist as the keto-hydrazone tautomer [1,13,14] and the rapidity of the de-esterification of the azo-phosphine and amide formation reported here, is presumably, facilitated by tautomerisation process activating the ester moiety to this reaction.

2.1. Molecular structure of **4**

The molecular structure and molecular numbering scheme for **4** can be found in Fig. 2. Of particular interest are the bond lengths around the formal azo link. Table 7 compares the accepted lengths of single and double bonds and the observed bond lengths in **4** ([15]). What becomes immediately apparent is that the azo-phosphine exists primarily as the keto-hydrazone tautomer not the hydroxy-azo tautomer (Fig. 3), since the C–O and N–C bonds lengths show some multiple bond character, whereas the N–N bond shows reduced double bond character. This is further supported by the location of H(2n) during the structural determination which was found to be 0.96 (8) Å from N(2) and is indicative of an N–H bond [15]. The data summarised in Table 8 shows that there is also an NH···O hydrogen bond [15]: an observation that has previously been made in hydroxyazonaphthalene systems [1,13,14]. All of the other bond lengths are as expected and warrant no further comment.

Table 4
Crystal data and structure refinement for 4

Empirical formula	$C_{35}H_{25}MoN_2O_6P$
Formula weight	696.48
Temperature (K)	203(2)
Wavelength (Å)	0.71069
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	11.054(2)
b (Å)	12.356(2)
c (Å)	12.761(2)
α (°)	98.005(15)
β (°)	108.620(16)
γ (°)	106.567(19)
V (Å^3)	1531.3(5)
Z	2
$D_{calc.}$ (mg m^{-3})	1.510
Absorption coefficient (mm^{-1})	0.531
F(000)	708
Crystal size (MM)	$0.30 \times 0.25 \times 0.20$
Theta range for data collection (°)	1.74–24.97
Limiting indices	$0 \le h \le 13$, $-14 \le k \le 14$, $-15 \le l \le 14$
Reflections collected/unique	5620/5311 [$R_{int} = 0.0280$]
Completeness to theta	24.97 (98.7%)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5311/0/482
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1105$
R indices (all data)	$R_1 = 0.0945$, $wR_2 = 0.1262$
Largest difference peak and hole (e Å^{-3})	0.443 and −0.350

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **4**

Atom	x	y	z	U_{eq}
Mo(1)	4381(1)	2440(1)	9164(1)	30(1)
O(1)	8097(4)	6488(3)	4699(3)	47(1)
O(2)	7243(5)	4333(4)	9655(4)	70(1)
O(3)	4505(6)	3920(4)	11402(4)	72(1)
O(4)	5971(5)	1135(4)	10759(4)	60(1)
O(5)	2652(5)	3840(4)	7884(4)	66(1)
O(6)	1530(5)	636(4)	8852(4)	64(1)
N(1)	7981(4)	4110(3)	4329(3)	31(1)
N(2)	8576(5)	4777(4)	3802(3)	35(1)
P(1)	4549(1)	1420(1)	7363(1)	27(1)
C(1)	7470(5)	4599(4)	5021(4)	29(1)
C(8)	6897(5)	2732(4)	5594(4)	31(1)
C(7)	6249(5)	2020(4)	6130(4)	32(1)
C(6)	5500(5)	2386(4)	6712(4)	27(1)
C(5)	5486(5)	3507(4)	6782(4)	27(1)
C(4)	6180(6)	5427(4)	6350(4)	33(1)
C(3)	6839(6)	6157(4)	5871(4)	35(1)
C(2)	7509(5)	5789(4)	5179(4)	33(1)
C(9)	6846(5)	3848(4)	5615(4)	29(1)
C(10)	6155(5)	4248(4)	6248(4)	28(1)
C(11)	9052(5)	4268(4)	3027(4)	32(1)
C(12)	9852(6)	5024(5)	2603(5)	39(1)
C(13)	10386(6)	4577(5)	1879(5)	42(1)
C(14)	10153(6)	3407(5)	1560(5)	39(1)
C(15)	9324(7)	2674(5)	1987(6)	52(2)
C(16)	8787(6)	3100(5)	2711(5)	47(2)
C(17)	10766(8)	2940(6)	801(6)	55(2)
C(18)	10313(7)	3139(6)	−386(6)	54(2)
C(19)	5475(5)	412(4)	7614(4)	29(1)
C(20)	6773(6)	826(5)	8432(5)	44(1)
C(21)	7514(7)	97(6)	8656(6)	54(2)
C(22)	6954(8)	−1054(6)	8065(6)	53(2)
C(23)	5672(7)	−1477(5)	7262(5)	50(2)
C(24)	4935(6)	−750(5)	7028(5)	41(1)
C(25)	2980(5)	521(4)	6158(4)	31(1)
C(26)	2765(6)	606(5)	5041(4)	38(1)
C(27)	1588(6)	−157(5)	4154(5)	48(2)
C(28)	639(7)	−992(5)	4363(6)	51(2)
C(29)	843(6)	−1080(5)	5449(5)	47(1)
C(30)	2008(6)	−324(4)	6344(5)	39(1)
C(31)	6218(6)	3667(5)	9460(4)	39(1)
C(32)	4435(6)	3357(5)	10582(5)	45(1)
C(33)	2555(7)	1248(5)	8948(5)	44(1)
C(34)	5403(6)	1566(5)	10161(5)	42(1)
C(35)	3296(6)	3336(5)	8302(5)	41(1)

3. Conclusion

By simple ligand substitution reactions a series of azo-phophine Group 6 metal carbonyl complexes have been prepared. In carrying out these reactions care must be exercised to prevent the displaced ligand react-

Table 6
Bond lengths (A) and angles (°) for 4

Mo(1)–C(32)	1.970(5)
Mo(1)–C(35)	2.031(6)
Mo(1)–C(33)	2.039(6)
Mo(1)–C(31)	2.039(6)
Mo(1)–C(34)	2.055(6)
Mo(1)–P(1)	2.5500(13)
O(1)–C(2)	1.275(6)
O(2)–C(31)	1.120(6)
O(3)–C(32)	1.141(6)
O(4)–C(34)	1.122(6)
O(5)–C(35)	1.132(7)
O(6)–C(33)	1.126(7)
N(1)–N(2)	1.300(5)
N(1)–C(1)	1.353(6)
N(2)–C(11)	1.414(7)
P(1)–C(25)	1.824(5)
P(1)–C(19)	1.825(5)
P(1)–C(6)	1.827(4)
C(1)–C(9)	1.440(6)
C(1)–C(2)	1.442(7)
C(8)–C(7)	1.369(7)
C(8)–C(9)	1.393(7)
C(7)–C(6)	1.398(7)
C(6)–C(5)	1.379(6)
C(5)–C(10)	1.401(6)
C(4)–C(3)	1.335(7)
C(4)–C(10)	1.436(7)
C(3)–C(2)	1.426(7)
C(9)–C(10)	1.407(7)
C(11)–C(16)	1.360(7)
C(11)–C(12)	1.386(7)
C(12)–C(13)	1.378(8)
C(13)–C(14)	1.370(8)
C(14)–C(15)	1.393(8)
C(14)–C(17)	1.489(8)
C(15)–C(16)	1.369(8)
C(17)–C(18)	1.515(9)
C(19)–C(20)	1.373(8)
C(19)–C(24)	1.380(7)
C(20)–C(21)	1.381(8)
C(21)–C(22)	1.370(9)
C(22)–C(23)	1.353(9)
C(23)–C(24)	1.378(8)
C(25)–C(30)	1.376(7)
C(25)–C(26)	1.392(7)
C(26)–C(27)	1.387(8)
C(27)–C(28)	1.370(9)
C(28)–C(29)	1.356(9)
C(29)–C(30)	1.383(8)
C(32)–Mo(1)–C(35)	87.6(2)
C(32)–Mo(1)–C(33)	90.3(2)
C(35)–Mo(1)–C(33)	86.8(2)
C(32)–Mo(1)–C(31)	86.9(2)
C(35)–Mo (1)–C(31)	93.7(2)
C(33)–Mo (1)–C(31)	177.1(2)
C(32)–Mo(1)–C(34)	87.2(2)
C(35)–Mo(1)–C(34)	174.2(2)
C(33)–Mo(1)–C(34)	90.7(2)
C(31)–Mo(1)–C(34)	88.6(2)
C(32)–Mo(1)–P(1)	173.96(17)
C(35)–Mo(1)–P(1)	92.59(15)
C(33)–Mo(1)–P(1)	95.72(16)
C(31)–Mo(1)–P(1)	87.08(15)
C(34)–Mo(1)–P(1)	92.82(15)
N(2)–N(1)–C(1)	117.0(4)
N(1)–N(2)–C(11)	117.9(4)
C(25)–P(1)–C(19)	102.4(2)
C(25)–P(1)–C(6)	103.3(2)
C(19)–P(1)–C(6)	101.9(2)
C(25)–P(1)–Mo(1)	118.81(16)
C(19)–P(1)–Mo(1)	113.40(15)
C(6)–P(1)–Mo(1)	115.01(15)
N(1)–C(1)–C(9)	115.9(4)
N(1)–C(1)–C(2)	124.2(4)
C(9)–C(1)–C(2)	119.9(4)
C(7)–C(8)–C(9)	121.5(5)
C(8)–C(7)–C(6)	121.0(5)
C(5)–C(6)–C(7)	118.3(4)
C(5)–C(6)–P(1)	120.1(4)
C(7)–C(6)–P(1)	121.6(4)
C(6)–C(5)–C(10)	121.3(4)
C(3)–C(4)–C(10)	122.4(5)
C(4)–C(3)–C(2)	121.5(5)
O(1)–C(2)–C(3)	120.6(5)
O(1)–C(2)–C(1)	121.5(5)
C(3)–C(2)–C(1)	117.9(4)
C(8)–C(9)–C(10)	117.9(4)
C(8)–C(9)–C(1)	122.8(5)
C(10)–C(9)–C(1)	119.3(4)
C(5)–C(10)–C(9)	119.9(4)
C(5)–C(10)–C(4)	121.4(5)
C(9)–C(10)–C(4)	118.7(4)
C(16)–C(11)–C(12)	119.9(5)
C(16)–C(11)–N(2)	123.4(5)
C(12)–C(11)–N(2)	116.8(5)
C(13)–C(12)–C(11)	119.1(5)
C(14)–C(13)–C(12)	122.2(5)
C(13)–C(14)–C(15)	116.9(5)
C(13)–C(14)–C(17)	121.7(5)
C(15)–C(14)–C(17)	121.4(5)
C(16)–C(15)–C(14)	121.8(6)
C(11)–C(16)–C(15)	120.1(5)
C(14)–C(17)–C(18)	114.6(6)
C(20)–C(19)–C(24)	118.1(5)
C(20)–C(19)–P(1)	118.6(4)
C(24)–C(19)–P(1)	123.4(4)
C(19)–C(20)–C(21)	120.8(6)
C(22)–C(21)–C(20)	120.0(6)
C(23)–C(22)–C(21)	120.0(6)
C(22)–C(23)–C(24)	120.2(6)
C(19)–C(24)–C(23)	121.0(6)
C(30)–C(25)–C(26)	118.4(5)
C(30)–C(25)–P(1)	119.0(4)
C(26)–C(25)–P(1)	122.4(4)
C(27)–C(26)–C(25)	119.5(5)
C(28)–C(27)–C(26)	120.8(6)
C(29)–C(28)–C(27)	120.0(6)
C(28)–C(29)–C(30)	119.9(6)
C(25)–C(30)–C(29)	121.4(5)
O(2)–C(31)–Mo(1)	177.9(5)
O(3)–C(32)–Mo(1)	177.4(5)
O(6)–C(33)–Mo(1)	176.5(5)
O(4)–C(34)–Mo(1)	176.0(5)
O(5)–C(35)–Mo (1)	174.8(5)

Table 7
Comparison of formal bond lengths and those observed in **4**

	C–O (Å)	N–N (Å)	N–C (Å)
Double bond	1.23 ± 1	1.24 ± 1	1.352 ± 5[a]
Single bond	1.36 ± 1	1.44 ± 4	1.426 ± 12
4	1.275(6)	1.300(5)	1.353(6)

[a] Shortened partial double bond in heterocyclic systems, e.g. C_5H_5N [16].

ing with the incoming phosphine. These azo-phosphines exist as the expected keto-hydrazone tautomer.

4. Experimental

All solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. The azo-phosphines were prepared by the published method [1] as were $[M(CO)_5(NCMe)]$ (M = Cr, Mo, W) and $[Mo(CO)_4(pip)_2]$ [3,4]; all other chemicals were purchased from commercial sources and used as received. ^1H-NMR (200.2 MHz) and $^{31}P\ \{^1H\}$-NMR (81.3 MHz) were recorded on a Bruker AC200 spectrometer. ^1H were referenced to $CHCl_3$ ($\delta = 7.26$) and $^{31}P\ \{^1H\}$-NMR were referenced externally to 85% H_3PO_4. Elemental analyses were performed by the Microanalytical service, Department of Chemistry, UMIST. The synthesis of all the carbonyl complexes were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Work-ups were generally carried out under dinitrogen unless otherwise stated, although work-up in the open is possible in some cases, and chromatographic separations were carried out on silica 60 mesh using CH_2Cl_2 as eluent.

*4.1. $[Cr(CO)_5(4\text{-}Me\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OH\text{-}6\text{-}PPh_2)]$ (**1**)*

To $[Cr(CO)_6]$ (0.058 g, 0.26 mmol) dissolved in NCMe (10 cm^3) was added $Me_3NO.2H_2O$ (0.029 g, 0.26 mmol) and the solution was stirred under reduced pressure for 45 min. To the resulting solution **II** (0.13 g, 0.29 mmol) was added and the solution stirred for 2 h. After removal of the solvent in vacuo the crude product was passed down a silica column 2 × 8 cm with CH_2Cl_2:hexane (9:1) as eluent. Removal of the solvent afforded analytically pure $\mathbf{1}\cdot CH_2Cl_2$. (See Table 1 for physical and analytical data).

Table 8
Hydrogen bond data for **4**

D–H···A	d (D–H) (Å)	d (H···A) (Å)	d (D···A) (Å)	∠(DHA) (°)
N(2) –H···O(1)	0.96(8)	1.69(8)	2.532(6)	145(7)

*4.2. $[Mo(CO)_5(PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OH\text{-}6\text{-}PPh_2)]$ (**2**)*

To $[Mo(CO)_6]$ (0.07 g, 0.27 mmol) dissolved in NCMe (10 cm^3) was added $Me_3NO\cdot 2H_2O$ (0.03 g, 0.29 mmol) and the solution was stirred under reduced pressure for 45 min. To the resulting solution **I** (0.13g, 0.29 mmol) was added and the solution stirred for 2 h. After removal of the solvent in vacuo the crude product was passed down a silica column 2 × 8 cm with CH_2Cl_2:hexane (9:1) as eluent. Removal of the solvent afforded analytically pure **2**.

In analogous reactions treatment of $[Mo(CO)_5(NCMe)]$ generated in situ with an equimolar quantity of L ($L = 4\text{-}R\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OR'\text{-}6\text{-}PPh_2$; R′ = H, R = Me, Et, Pr^i, Bu^t; R′ = C(O)Me, R = Me) afforded the complexes $[Mo(CO)_5L]$ **3**–**7**. (See Table 1 for physical and analytical data).

*4.3. $[W(CO)_5(4\text{-}Me\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OH\text{-}6\text{-}PPh_2)]$ (**8**)*

To $[W(CO)_6]$ (0.11 g, 0.31 mmol) dissolved in NCMe (10 cm^3) was added $Me_3NO\cdot 2H_2O$ (0.34 g, 0.31 mmol) and the solution was stirred under reduced pressure for 45 min. To the resulting solution **II** (0.15 g, 0.34 mmol) was added and the solution stirred for 2 h. After removal of the solvent in vacuo the crude product was passed down a silica column 2 × 8 cm with CH_2Cl_2:hexane (9:1) as eluent. Removal of the solvent afforded analytically pure **8.** (See Table 1 for physical and analytical data).

*4.4. $[Mo(CO)_4(PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OH\text{-}6\text{-}PPh_2)]$ (**9**)*

To *cis*-$[Mo(CO)_4(pip)_2]$ (0.044 g, 0.12 mmol) dissolved in $CHCl_2$ (25 cm^3) was added **I** (0.1 g, 0.24 mmol) and the solution heated to reflux for 2 h. After cooling HCl (0.2 cm^3) was added and the solution filtered and the solvent removed under reduced pressure. The crude product was then passed down a short silica column 2 × 8 cm with CH_2Cl_2 as eluent. Removal of the solvent afforded analytically pure $\mathbf{9}\cdot\frac{3}{4}CH_2Cl_2$.

In analogous reactions treatment of $[Mo(CO)_4(pip)]$ with two molar equivalents of L ($L = 4\text{-}R\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OH\text{-}6\text{-}PPh_2$; R = Me, Et, Pr^i, Bu^t) afforded the complexes $[Mo(CO)_5L]$ **10**–**13.** (See Table 1 for physical and analytical data).

*4.5. $[Mo(CO)_4\{4\text{-}Me\text{–}PhN_2\text{-}1\text{-}C_{10}H_5\text{-}2\text{-}OC(O)\text{-}Me\text{-}6\text{-}PPh_2\}]$ (**14**)*

To **10** (0.14 g, 0.13 mmol) dissolved in THF (15 cm^3) NaH (0.02 g, 0.26 mmol) under a stream of dry N_2 was added and allowed to stir. After 1 h MeC(O)Cl (0.05 g,

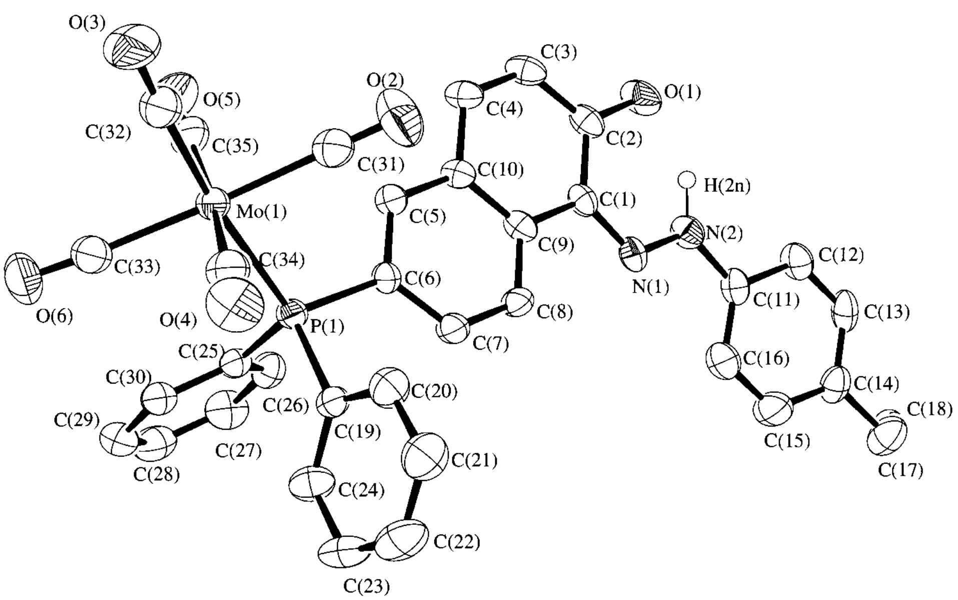

Fig. 2. ORTEP drawing for **4** showing the atomic numbering scheme.

64 mmol) was added and the resulting solution stirred for a further 2 h. After removal of solvent under reduced pressure the crude product was extracted into CH_2Cl_2 and filtered. Subsequent purification by passing the crude material through a short silica column afforded analytically pure **14**. (See Table 1 for physical and analytical data).

4.6. Crystallography

The X-ray diffraction experiment was carried out at 203 K on a Nonius MACH 4-circle diffractometer using graphite monochromated Mo–K_α radiation. Lattice constants were determined from the setting angles of 25 accurately controlled reflections $22.2 < 2\theta < 28.3°$. The $\omega/2\theta$ scan technique was used with ω scan width of $0.9° + 0.35 \tan\theta$ to collect 5620 reflections with $2\theta \leq 50°$. three standard reflections were measured every 3 h and showed no significant decay. The intensities were corrected for Lorenz and polarisation effects but absorbtion was ignored. Crystallographic data are summarised in Table 4; atom coordinates, bond lengths and angles are presented in Tables 5 and 6, respectively. The SHELX-97 suite of programs [16] was used to solve the structure by direct methods and refined using full-matrix least-squares.

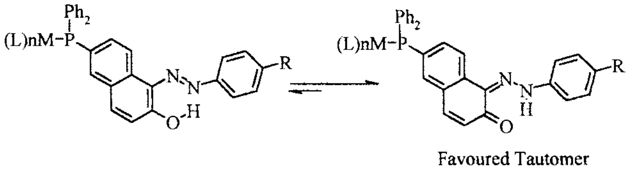

Fig. 3. Tautomerism displayed by the hydroxyazonaphthylphosphine complexes **1**–**6**, **8**–**13**.

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References

[1] M.J. Alder, K.R. Flower, R.G. Prichard, Tetrahedron Lett. 39 (1998) 3571.
[2] W. Strohmeier, K.L. Gerlach, Chem. Ber. 93 (1960) 2087.
[3] K.S. Gan, H.K. Lee, T.S.A. Hor, J. Organomet. Chem. 460 (1993) 197.
[4] M.A. Beckett, D.P. Cassidy, A.J. Duffin, Inorg. Chim. Acta 189 (1991) 229.
[5] D.P. Tate, W.R. Knipple, J.M. Augl, Inorg. Chem. 1 (1962) 433.
[6] G.R. County, R.S. Dickson, S.M. Jenkins, J. Johnson, O. Paravagna, J. Organomet. Chem. 530 (1997) 49.
[7] P.K. Baker, A.E. Jenkins, Polyhedron 16 (1997) 2279.
[8] P.K. Baker, M. Meehan, J. Organomet. Chem. 535 (1997) 129.
[9] F.A. Cotton, C.S. Kraihanzel, J. Am. Chem. Soc. 84 (1962) 4432.
[10] F.A. Cotton, D.J. Darrensbourg, S. Klein, B.W.S. Kolthammer, Inorg. Chem. 21 (1982) 2661.
[11] S. Fernandez, E. Menendez, V. Gotor, Synthesis (1991) 713.
[12] B.C. Challis, J.A. Challis in, Comprehensive Organic Chemistry, Pergamon, Oxford, 1979, p. 961.
[13] A. Whitaker, J. Soc. Dyers Colour. 94 (1978) 431.
[14] A.C. Olivieri, R.B. Wilson, I.C. Paul, D.Y. Curtin, J. Am. Chem. Soc. 111 (1989) 5525.
[15] International Tables for Crystallography, 3 (1968) 270.
[16] G.M Schedrick, Programs for crystal structure analysis (release 97–2), Göttingen, 1998.