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Synthesis and characterisation of some azo-containing phosphine complexes of Au(I): crystal and molecular structure of $[Au(C{\equiv}CPh)\{6\text{-}P(Ph)_2\text{-}1\text{-}(4\text{-}Me_2N\text{–}C_6H_4N_2)\text{–}C_{10}H_5\text{-}2\text{-}OH\}]\cdot CHCl_3$

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Abstract

Reduction of $Na[AuCl_4]$ followed by in situ addition of a stoichiometric amount of L{L = 1-(4-R–C_6H_4)-2-OR′-6-Ph_2P–$C_{10}H_5$; R′ = H, R = Me (**I**); R = NMe_2 (**II**); R = NO_2 (**III**); R′ = C(O)Me; R = Me (**IV**); R = NMe_2 (**V**)} affords the Au(I) complexes [LAuCl] **1a**–**1e** (L = **I**, **1a**; **II**, **1b**; **III**, **1c**; **IV**, **1d**; **V**, **1e**) in good yield. Treatment of **1a**–**1c** with two molar equivalents of LiC≡CR″ (R″ = Ph, ^{n}Bu) affords the acetylide containing complexes [Au(C≡CR″)L] **2a**–**2f** {R = Ph, L = **I**, **2a**, L = **II**, **2b**, L = **III**, **2c**; R = ^{n}Bu, L = **I**, **2d**, L = **II**, **2e**, L = **III**, **2f**} in good yield. The reaction of **1d** or **1e** with LiC≡CPh affords **2a** and **2b**, respectively, in which reaction of the acetylide ion with the complex takes place both at the metal centre and the ester group of the phosphine ligand. All of the compounds have been fully characterised by spectroscopic techniques and **2b**·$CHCl_3$ by a single crystal X-ray diffraction study. The solid state structure of **2b**·$CHCl_3$ shows a close $Cl_3CH\cdots C{\equiv}C$ π-interaction and no Au···Au interaction.

Keywords: Gold; Alkynyl; Crystal structure

1. Introduction

The first reported alkynyl gold compound dates from 1900 [1] and since that date many compounds have been prepared [2]. Current interest in Au(I) compounds derives from the observation of close Au···Au interactions [3] which have recently led to the synthesis, in association with Au–S interactions, to homoleptic gold thiolate catenanes [4]. Other gold-containing catenane systems are known and are derived from acetylide based systems [5] and strategies for synthesising large rings have been described [6], and some of the compounds prepared show luminescent properties. In addition to the interest in Au···Au interactions a series of alkynylgold phosphine complexes have been prepared and their non-linear optical properties assessed [7].

We recently reported the synthesis of a series of azo-containing phosphines [8] and have been investigating their coordination chemistry [9]. In this paper, we describe the preparation of a series of azo-containing phosphine complexes of gold(I).

2. Results and discussion

2.1. Preparation of azo-containing phosphine–gold(I) chloride complexes

The azo-containing phosphines L {L = 1-(4-R–C_6H_4)-2-OR′-6-Ph_2P–$C_{10}H_5$; R′ = H, R = Me (**I**); R = NMe_2 (**II**); R = NO_2 (**III**); R′ = C(O)Me; R = Me (**IV**); R = NMe_2 (**V**)} Fig. 1, were added, dissolved in $CHCl_3$, to a reduced solution of $Na[AuCl_4]$ using the

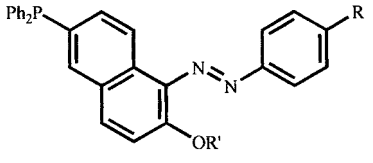

Fig. 1. Azo-containing phosphines L. R′ = H, R = Me (**I**), NMe_2 (**II**), NO_2 (**III**); R′ = C(O)Me, R = Me (**IV**), NMe_2 (**V**).

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Table 1
Physical [a] and analytical data [b] for complexes **1a**–**1e** and **2a**–**2f**

Compound	Colour	Yield	m.p. (°C)	Microanalysis ((%))		
				C	H	N
1a·0.5$CHCl_3$	Red	83	256	48.4 (48.0)	2.9 (3.2)	3.6 (3.8)
1b	Red	73	258	50.1 (50.9)	3.4 (3.7)	5.2 (5.9)
1c	Black	85	210	47.4 (47.3)	3.7 (3.0)	6.2 (6.2)
1d	Red	72	236	52.5 (51.6)	3.2 (3.5)	3.5 (3.9)
1e	Black	59	222	52.0 (52.3)	4.0 (3.8)	5.0 (5.7)
2a·$CHCl_3$	Red	64	218	53.0 (52.8)	3.4 (3.4)	2.7 (3.2)
2b·0.8$CHCl_3$	Red	93	180	53.6 (53.6)	2.8 (3.6)	4.7 (4.7)
2c	Black	78	196	55.4 (55.8)	3.7 (3.3)	4.4 (5.3)
2d·0.5$CHCl_3$	Red	71	150	55.1 (54.6)	3.5 (4.1)	3.7 (3.6)
2e·$CHCl_3$	Red	94	232	51.3 (50.9)	3.1 (3.7)	5.1 (4.8)
2f·0.25$CHCl_3$	Black	59	262	52.5 (52.4)	3.5 (3.8)	4.8 (5.3)

[a] All compounds soften before melting.
[b] Calculated values in parentheses.

Table 2
$^{31}P\{^1H\}$-NMR [a] and proton [b] data for complexes **1a**–**1e** and **2a**–**2f**

Complex	^{31}P (δ ppm)	^1H (δ ppm)
1a	34.1	16.1 (s, 1H, O*H*); 8.7 (dd, [J_{HH} = 8.5 Hz, J_{HH} = 2.3 Hz], 1H, aryl-*H*); 7.9 (dd, [J_{PH} = 14.8 Hz, J_{HH} = 1.5 Hz], 1H, aryl-*H*); 7.7–7.3 (bm, 16H, aryl-*H*); 7.1 (d, [J_{HH} = 9.1 Hz], 1H, aryl-*H*); 2.4 (s, 3H, CH_3)
1b	34.1	16.2 (s, 1H, O*H*); 8.4–7.4 (bm, 18H, aryl-*H*); 6.7 (d, [J_{HH} = 9.8 Hz], 1H, aryl-*H*)
1c	34.2	16.0 (s, 1H, O*H*); 8.6 (d, [J_{HH} = 6.5 Hz], 1H, aryl-*H*); 7.9–7.5 (bm, 17H, aryl-*H*); 7.0 (d, [J_{HH} = 9.5 Hz], 1H, aryl-*H*); 3.2 (s, 6H, CH_3)
1d	34.1	8.7 (d, [J_{HH} = 6.8 Hz], 1H, aryl-*H*); 8.2 (d, [J_{PH} = 15.6 Hz], 1H, aryl-*H*); 7.9–7.8 (bm, 3H, aryl-*H*); 7.6–7.3 (bm, 14H, aryl-*H*); 2.5 (s, 3H, CH_3); 2.3 (s, 3H, CH_3)
1e	33.3	8.7 (dd, [J_{HH} = 8.7 Hz, J_{HH} = 2.0 Hz], 1H, aryl-*H*); 8.1 (d, [J_{PH} = 14.3 Hz], aryl-*H*); 7.9–7.3 (bm, 12H, aryl-*H*); 6.8 (d, [J_{HH} = 9.3 Hz], 2H, aryl-*H*); 3.1 (s, 6H, CH_3); 2.3 (s, 3H, CH_3)
2a	43.3	16.2 (s, 1H, O*H*); 8.7 (d, [J_{HH} = 8.3 Hz], 1H, aryl-*H*); 8.1–7.0 (bm, 24H, aryl-*H*); 2.4 (s, 3H, CH_3)
2b	43.3	16.0 (s, 1H, O*H*); 8.5 (d, [J_{HH} = 7.0 Hz], 1H, aryl-*H*); 8.3 (d, [J_{HH} = 8.5 Hz], 1H, aryl-*H*); 7.9–6.9 (bm, 21H, aryl-*H*); 6.8 (d, [J_{HH} = 9.5 Hz], 1H, aryl-*H*)
2c	43.6	15.7 (s, 1H, O*H*); 8.9 (d, [J_{HH} = 7.3 Hz], 1H, aryl-*H*); 8.7 (d, [J_{HH} = 6.8 Hz], 1H, aryl-*H*); 8.2–7.2 (bm, 21H, aryl-*H* 6.8 (dd, [J_{HH} = 9.3 Hz, J_{HH} = 2.0 Hz], 1H, aryl-*H*); 3.1 (s, 6H, CH_3)
2d	30.8	16.1 (s, 1H, O*H*); 8.7 (dd, [J_{HH} = 8.4 Hz, J_{HH} = 2.0 Hz], 1H, aryl-*H*); 7.9 (d, [J_{PH} = 14.0 Hz], 1H, aryl-*H*); 7.7–7.3 (bm, 16H, aryl-*H*); 7.0 (d, [J_{HH} = 8.6 Hz], 1H, aryl-*H*); 2.4 (s, 3H, CH_3); 2.4 (t, [J_{HH} = 7.0 Hz], 2H, CH_2); 1.5 (m, [J_{HH} = 7.0 Hz], 4H, CH_2); 0.6 (t, [J_{HH} = 6.8 Hz], 3H, CH_3)
2e	30.1	16.0 (s, 1H, O*H*); 8.5 (d, [J_{HH} = 8.3 Hz], 1H, aryl-*H*); 8.3 (d, [J_{HH} = 9.0 Hz], 1H, aryl-*H*); 7.7–7.4 (bm, 16H, aryl-*H*); 6.8 (d, [J_{HH} = 9.8 Hz], 1H, aryl-*H*); 2.4 (t, [J_{HH} = 5.8 Hz], 2H, CH_2); 1.5 (m, [J_{HH} = 6.0 Hz], 4H, CH_2); 0.6 (t, [J_{HH} = 6.0 Hz], 3H, CH_3)
2f	29.8	15.6 (s, 1H, O*H*); 8.8 (d, [J_{HH} = 8.3 Hz], 1H, aryl-*H*); 8.6 (d, [J_{HH} = 10.5 Hz], 1H, aryl-*H*); 8.2–7.2 (bm, 16H, aryl-*H*); 6.8 (dd, [J_{HH} = 9.3 Hz, J_{HH} = 2.3 Hz], 1H, aryl-*H*); 3.1 (s, 6H, CH_3); 2.4 (t, [J_{HH} = 7.0 Hz], 2H, CH_2); 1.5 (m, [J_{HH} = 4.5 Hz], 4H, CH_2); 0.6 (t, [J_{HH} = 6.8 Hz], 3H, CH_3)

[a] Spectra recorded in $CDCl_3$ (298 K) and referenced to 85% H_3PO_4.
[b] Spectra recorded in $CDCl_3$ (298 K) and referenced to $CHCl_3$, J = Hz; s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

method of Parish et al. [10]. After stirring for 2 h and recrystallisation [AuCl(L)] **1a**–**1e** (L = **I**, **1a**; **II**, **1b**; **III**, **1c**; **IV**, **1d**; **V**, **1e**) were obtained in good yield. All of the compounds were characterised by elemental analysis (C, H, N) (Table 1); ^1H-, $^{31}P\{^1H\}$-NMR spectroscopy (Table 2); $^{13}C\{^1H\}$-NMR spectroscopy (Table 3); and UV–vis spectroscopy (Table 4).

The ^1H-NMR spectra for **1a**–**1e** are little perturbed from those observed for the free azo-containing phosphines [8]. For example, compounds **1a**–**1c** show a distinctive sharp singlet at ca. 16 ppm which disappears on addition of D_2O and is indicative of the strongly hydrogen-bonded OH proton; whereas, compounds **1d**–**1e** display a singlet resonance at 2.3 ppm indicative of the methyl group of acetyl ester.

All of the compounds showed a sharp singlet ca. 34 ppm in their $^{31}P\{^1H\}$-NMR spectrum which is at significantly higher frequency than the parent phosphines [8] and comparable to that observed for [AuCl(PPh_3)] [11].

The $^{13}C\{^{1}H\}$-NMR spectra have all been fully assigned with the aid of DEPT 135 data, the assigned spectra of **I**–**V** [8], published substituent effects [12] and the spin coupling to ^{31}P, see Fig. 2 for the numbering scheme. It is apparent from the data that the position of the hydroxyazo-ketohydrazone tautomerisation, that takes place in these phosphine ligands is little perturbed on complexation to the Au(I) centre in **1a**–**1c**. This can be deduced from the position of the resonance assigned to C(2) which is sensitive to the position of the equilibrium [8a,13] and this is consistent with observations made on complexation of these ligands to other metal centres [9]. For **1d**–**1e** resonances at 169.4 and 20.9 ppm are observed for the (CO) and (CH_3) groups of the ester moiety, respectively.

The UV–vis spectra of **1a**–**1e** all displayed absorption bands in similar positions to those observed for the free phosphines [8a] and the molar absorption coefficients for both the hydrazone- and azo-tautomer were calculated from the relative position of the equilibrium using the equation: $K = [\{\text{l}80 - \delta C(2)\}/\delta C(2) - \{\delta C(2) - \delta C(2)_{ester} + 11\}]$ [8a]. An additional band at ca. 290 nm observed for **1a**–**1c** has been assigned to a $\sigma(Au \leftarrow P) \rightarrow \pi^*(Np)$ (Np = naphthalene) transition and is consistent with the assignment of similar absorption bands in a series of ethynylgold(I) naphthylphosphine complexes [14b].

2.2. Preparation of azo-containing phosphine–gold(I) alkynyl complexes

The compounds **2a**–**2f** were prepared from the chlorogold(I) precursors **1a**–**1c** on reaction with two molar equivalents of LiC≡CR″ (R″ = Ph or ^{n}Bu). It was

Table 3
$^{13}C\{^{1}H\}$-NMR data [a] for compounds **1a**–**1e** and **2a**–**2f**

Compound	
1a [b]	166.0 (s, C(2)); 144.2 (s, C(15)); 139.9 (s, C(18)); 137.5 (s, C(4)); 135.8 (d, [J = 16.0 Hz], C(5)); 134.1 (d, [J = 13.8 Hz], C(12)); 132.0 (s, C(17)); 131.7 (d, [J = 11.6 Hz], C(7)); 130.4 (s, C(14)); 129.3 (d, [J = 11.6 Hz], C(13)); 124.4 (s, C(3)); 122.7 (d, [J = 10.9 Hz], C(8)); 120.0 (s, C(16)); 20.4 (s, *C*H3)
1b [b]	178.3 (s, C(2)); 147.7 (s, C(18)); 145.1 (s, C(1)); 142.5 (s, C(4)); 135.3 (d, [J = 16.7 Hz], C(5)); 134.0 (d, [J = 14.5 Hz], C(12)); 133.3 (d, [J = 12.4 Hz], C(7)); 129.2 (d, [J = 10.9 Hz], C(13)); 128.6 (s, C(14)); 126.9 (s, C(3)); 125.6 (s, C(17)); 122.8 (d, [J = 10.2 Hz], C(8)); 117.2 (s, C(16))
1c [b]	157.2 (s, C(2)); 152.1 (s, C(18)); 139.4 (s, C(15)); 136.0 (d, [J = 15.3 Hz], C(5)); 134.1 (d, [J = 13.8 Hz], C(12)); 133.4 (s, C(4)); 132.1 (d, [J = 10.2 Hz], C(7)); 131.9 (d, [J = 2.9 Hz], C(14)); 129.2 (d, [J = 11.6 Hz], C(13)); 123.6 (s, C(16)); 123.1 (d, [J = 11.6 Hz], C(8)); 122.5 (s, C(3)); 112.0 (s, C(17)); 40.3 (s, *C*H_3)
1d [b]	169.4 (s, *C*O); 151.3 (s, C(15)); 142.8 (s, C(18)); 139.1 (s, C(1)); 138.4 (s, C(2)); 135.9 (d, [J = 15.9 Hz], C(5)); 134.1 (d, [J = 13.8 Hz], C(12)); 132.1 (d, [J = 2.2 Hz], C(14)); 131.6 (d, [J = 13.1 Hz], C(7)); 131.4 (s, C(9)); 131.1 (s, C(4)); 129.3 (d, [J = 11.6 Hz], C(13)); 125.6 (d, [J = 10.9 Hz], C(8)); 122.8 (s, C(16)); 119.7 (s, C(3)); 21.5 (s, *C*H_3); 20.9 (s, *C*H_3)
1e [b]	169.4 (s, *C*O); 153.0 (s, C(18)); 144.5 (s, C(2)); 139.2 (s, C(15)); 138.8 (s, C(1)); 135.7 (d, [J = 15.3 Hz], C(5)); 134.1 (d, [J = 13.8 Hz], C(12)); 132.1 (d, [J = 10.2 Hz], C(10)); 131.8 (d, [J = 2.2 Hz], C(14)); 131.5 (d, [J = 13.8 Hz], C(7)); 129.4 (s, C(4)); 129.2 (d, [J = 11.8 Hz], C(13)); 125.8 (d, [J = 10.9 Hz], C(8)); 123.6 (s, C(16)); 122.4 (s, C(3)); 111.4 (s, C(17)); 40.3 (s, *C*H_3); 20.9 (s, *C*H_3)
2a [b]	166.8 (s, C(2)); 143.9 (s, C(15)); 139.7 (s, C(18)); 137.8 (s, C(4)); 136.0 (d, [J = 17.4 Hz], C(5)); 134.2 (d, [J = 14.5 Hz], C(12)); 132.4 (s, C(21)): 132.1 (d, [J = 13.5 Hz], C(7)); 131.6 (s, C(17)); 130.3 (s, C(14)); 130.1 (s, C(1)); 129.2 (d, [J = 11.6 Hz], C(13)); 127.9 (s, C(22)); 126.8 (s, C(23)); 124.8 (s, C(20)); 124.8 (s, C(3)); 122.6 (d, [J = 10.6 Hz], C(8)); 119.8 (s, C(16)); 21.3 (s, *C*H_3)
2b [b]	178.0 (s, C(2)); 147.8 (s, C(18)); 145.3 (s, C(1)); 142.0 (s, C(4)); 135.5 (d, [J = 16.7 Hz], C(5)); 134.2 (d, [J = 14.5 Hz], C(12)); 133.6 (d, [J = 10.2 Hz], C(7)); 132.4 (s, C(21)); 129.3 (d, [J = 10.9 Hz], C(13)); 127.9 (s, C(22)); 127.2 (s, C(23)); 126.8 (s, C(3)); 125.7 (s, C(17)); 124.7 (s, C(20)); 123.0 (d, [J = 10.2 Hz], C(8)); 117.4 (s, C(16)); 104.3 (bs, C(19))
2c [b]	156.9 (s, C(2)); 152.0 (s, C(18)); 139.4 (s, C(15)); 136.0 (d, [J = 16.0 Hz], C(5)); 134.4 (d, [J = 17.4 Hz], C(12)); 133.6 (s, C(4)); 133.1 (s, C(9)); 132.4 (s, C(21)); 132.0 (d, [J = 8.8 Hz], C(7)); 132.0 (d, [J = 2.2 Hz], C(14)); 129.1 (d, [J = 11.6 Hz], C(13)); 127.9 (s, C(22)); 126.8 (s, C(23)); 124.8 (s, C(20)); 123.5 (s, C(16)); 122.9 (d, [J = 10.2 Hz], C(8)); 122.2 (s, C(3)); 104.0 (bs, C(19)); 40.2 (s, *C*H_3)
2d [b,c]	166.4 (s, C(2)); 143.8 (s, C(15)); 139.6 (s, C(18)); 137.5 (s, C(4)); 135.7 (d, [J = 16.4 Hz], C(5)); 134.0 (d, [J = 13.5 Hz], C(12)); 131.9 (d, [J = 15.4 Hz], C(7)); 131.7 (s, C(17)); 130.2 (s, C(14)); 129.8 (s, C(1)); 129.5 (d, [J = 15.5 Hz], C(13)); 124.7 (s, C(3)); 122.5 (d, [J = 10.5 Hz], C(8)); 119.7 (s, C(16)); 105.7 (bs, C(19)); 30.4 (s, *C*(21), CH_2); 21.8 (s, C(22), *C*H_2); 21.3 (s, *C*H_3); 18.2 (s, C(20), *C*H_2); 13.7 (s, C(23), *C*H_3)
2e [b,c]	178.6 (s, C(2)); 147.7 (s, C(18)); 145.2 (s, C(1)); 142.4 (s, C(4)); 135.6 (d, [J = 15.5 Hz], C(5)); 134.1 (d, [J = 13.5 Hz], C(12)); 133.7 (d, [J = 9.7 Hz], C(7)); 132.3 (d, [J = 2.5 Hz], C(14)); 129.3 (d, [J = 12.6 Hz], C(13)); 127.1 (s, C(3)); 125.7 (s, C(17)); 123.1 (d, [J = 10.6 Hz], C(8)); 117.3 (s, C(16)); 29.6 (s, C(21)); 22.2 (s, C(22), *C*H_2); 18.2 (s, C(20), *C*H_2); 13.1 (s, C(23), *C*H_3)
2f [b]	157.0 (s, C(2)); 152.1 (s, C(18)); 139.4 (s, C(15)); 136.0 (d, [J = 15.3 Hz], C(5)); 134.1 (d, [J = 13.8 Hz], C(12)); 133.6 (s, C(4));132.1 (d, [J = 10.2 Hz], C(7)); 131.8 (s, C(14)); 129.6 (s, C(1)), 129.2 (d, [J = 11.6 Hz], C(13)); 129.2 (d, [J = 43.6 Hz], C(6)); 123.6 (s, C(16)); 123.1 (d, [J = 11.6 Hz], C(8)); 122.4 (s, C(3)); 112.0 (s, C(17)); 40.3 (s, *C*H_3); 31.5 (s, C(21), *C*H_2); 22.6 (s, C(22), *C*H_2); 19.2 (s, C(20), *C*H_2); 14.1 (5, C(23), *C*H^2)

[a] Spectra recorded in $CDCl_3$ (293 K) and referenced to $CDCl_3$ (δ 77.0); s = singlet, d = doublet.
[b] One or more resonances partially obscured due to overlap.
[c] Spectrum recorded at 100.6 MHz; see Fig. 2 for numbering scheme.

Table 4
UV–vis [a] data for complexes **1a**–**1e** and **2a**–**2f**

Complexes	Hydrazone-form λ [b]/ε [c]	Azo-form λ [b]/ε [c]	$\sigma(Au \leftarrow P) \rightarrow \pi^*(Np)$ λ [b]/ε [c]
1	491.5/18371	412.0/17659	299.5/10591
2	485.0/21258		282.0/13833
3		489.5/19561	280.0/17628
4		351.5/9017	[d]
		483.0/2436	
5		442.5/10485	[d]
6	490.5/16553	414.5/15237	296.5/11897
7	485.0/10204		282.0/13833
8		504.0/11778	280.0/17150
9	491.0/15285	412.0/14771	291.0/12493 (sh)
10	484.5/11000		280.0/11184 (sh)
11		504.0/16564	276.0/16898

[a] Spectra recorded in $CHCl_3$.
[b] λ_{max} = nm.
[c] $\varepsilon = dm^3\ mol^{-1}\ cm^{-1}$.
[d] Band obscured; sh = shoulder.

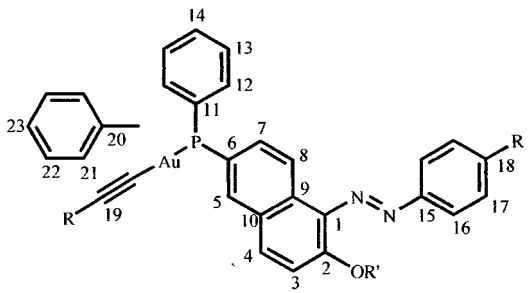

Fig. 2. Numbering scheme for $^{13}C\{^1H\}$-NMR data.

found that two molar equivalents of the lithium acetylide were required as deprotonation of the hydroxyl group as well as metathesis of the Au–Cl bond takes place. It appears, qualitatively at least, that the rates of the two competing reactions are comparable as on addition of a stoichiometric amount of lithium acetylide a 50:50 mixture of starting material and product are obtained; reprotonation of the hydroxyl group was effected by stirring with a saturated aqueous solution of NH_4Cl.

Similar reactions of **1d** and **1e** with a stoichiometric amount LiC≡CR″ (Rh″ = Ph, ″Bu) does not lead to an alkynylgold(I) species, rather compounds **1a** and **1b** are isolated. This presumably results from preferential acetylide attack on the ester moiety. In an attempt to prepare the ester containing alkynylgold(I) complexes compounds **2a** and **2b** were each reacted with one mole equivalent of NaH to generate the naphthalide anion, which imparted a deep red colouration to the solution, and then reacted with acetyl chloride; once again only **1a** and **1b** were isolated and this suggested that the gold complex acts as an efficient alkynylating agent and that complexes containing the ester-functionalised azo-containing phosphines are intrinsically unstable. This was simply confirmed by adding **IV** to **2a** and observing the formation of **I**, **1a** and PhCCC(O)Me [15]. Another example of Au(I) alkynyl complexes behaving in this manner is the reaction between [Au(C≡CPh)(PPh_3)] and $HgCl_2$ to give [$Hg(C{\equiv}CPh)_2$] [16].

All of the compounds **2a**–**2f** were characterised by elemental analysis (C, H, N) (Table 1); ^1H-, $^{31}P\{^1H\}$-NMR spectroscopy (Table 2); $^{13}C\{^1H\}$-NMR spectroscopy (Table 3); and UV–vis spectroscopy (Table 4).

The ^1H-NMR spectra for **2a**–**2f** are little perturbed from those observed for the free azo-containing phosphines [8a]. For example, all of the compounds show a distinctive sharp singlet at ca. 16 ppm which disappears on addition of D_2O and is indicative of the strongly hydrogen-bonded OH proton. The resonances at-

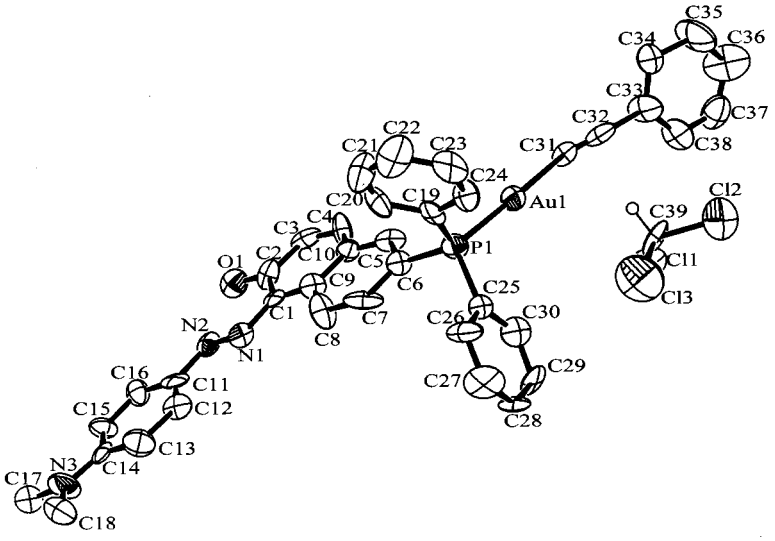

Fig. 3. ORTEP representation of **2c** showing the atomic numbering scheme.

tributable to the *n*-butyl moiety of the acetylide ligand appear where expected based upon substituent effects [17].

The compounds **2a**–**2c** showed a sharp singlet ca. 43 ppm which is at higher frequency than the chloro–phosphine complex and comparable to the value 43.1 ppm reported by Humphrey et al. for the analogous complex [Au(C≡CPh)(PPh_3)] [7]. The ^{n}Bu–acetylide complexes all show a resonance around 30 ppm which is at lower frequency than the parent chloro-containing complex and suggests that the nature of the acetylide affects the $^{31}P\{^1H\}$-NMR resonant frequency, whereas the R-groups on the 4-R-phenyl-azo groups appear to have no influence.

The $^{13}C\{^1H\}$-NMR spectra have all been assigned in a manner similar to that for the chloro-containing complexes **1a**–**1e**. The aurated C-atom of the acetylide-ligand was not observed for any of the compounds and this is presumably due to the quadrapolar broadening effect of the ^{197}Au (100%) nucleus. The non-aurated carbon C(19) for **2a**–**2c** appears ca. 104 ppm which is comparable to that observed in [Au(C≡CPh)(PPh_3)] [7].

The UV–vis spectra seem little affected on exchange of the chloride by acetylide and the molar extinction coefficients for the two tautomers were calculated assuming the position of the ketohydrazone/hydroxyazo tautomerisation was unaffected, by the chloride–acetylide exchange. This assumption is justifiable as the C(2) resonances for **2a**–**2f** are in the same position observed for the parent chloro-compounds **1a**–**1c** [8a].

2.3. Molecular structure of [Au(C≡CPh){6-P(Ph)$_2$-1-(4-Me$_2$N–C$_6$H$_4$N$_2$)-C$_{10}$H$_5$-2-OH}]·CHCl$_3$ (2c)

Little comment can be made about the solid state structure of **2c** due to the poor quality of the data, see Fig. 3 for the atomic numbering scheme. The structure confirms the spectroscopic data and shows that there are no close Au···Au interactions: the closest approach is 8.9 Å. The structure also confirms the $CHCl_3$ solvate of crystallisation and offers some explanation as to why the alkynyl-containing complexes **2a**–**2f** tenaciously hold onto chloroform. The chloroform solvate was located directly above the C≡C triple bond effecting a Cl_3CH···C≡C π-interaction. Although the H atom was not located the orientation of the three C–Cl bonds and the distance of the C(39) of the $CHCl_3$ solvate to C(31) and C(32)-atoms of the C≡C bond of 3.45 Å is comparable to that reported by Mingos et al. in the crystal structure of [{{Np(Ph)$_2$P}Au}$_2$(C≡C)] [14]. Calculations reported by Mingos et al. suggest that interactions of this nature have energies of ca. 25 kJ mol^{-1} and are comparable in strength to hydrogen-bonded systems [18] and offers a good explanation as to why these compounds tenaciously hold onto $CHCl_3$ on recrystallisation. The relevance of these types of interactions arises from the mode of electrophilic attack on the C≡C bond, i.e. the addition of HX to an alkyne, in which the first step is believed to be the formation of a weakly H-bound complex with a T-shaped configuration. Crystallographically characterised examples of these types of complex have been previously reported [14,19] and this structure offers another example.

3. Conclusions

A collection of new gold(I) azo-containing phosphine complexes have been prepared and characterised. The alkynyl-containing complexes have been shown to act as alkynylating agents towards the ester functional group in the ligated azo-containing phosphines.

4. Experimental

All solvents were dried by refluxing over an appropriate drying agent and distilled prior to use. All other chemicals were obtained from commercial sources and used as received except for Na[$AuCl_4$] which was loaned by Johnson Matthey. Melting points were measured on a Griffin Melting Point apparatus and are uncorrected. ^{1}H-NMR (200.2 MHz) and $^{31}P\{^1H\}$-NMR (81.3 MHz) spectra were recorded on a Bruker DPX 200 spectrometer and $^{13}C\{^1H\}$-NMR (75.6 or 100.6 MHz) spectra were recorded on either a Brucker DPX 300 or Brucker DPX 400 spectrometer. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were referenced to C*H*Cl$_3$ ($\delta = 7.26$) and *C*HCl$_3$ ($\delta = 77.0$) and $^{31}P\{^1H\}$-NMR was referenced externally to 85% H_3PO_4. Elemental analyses were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvates of crystallisation were confirmed by repeated elemental analysis. UV–vis spectra were recorded on a Shimadzu UV20101 PC spectrophotometer in $CHCl_3$ in 1 cm cuvettes. The syntheses of all complexes were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Work-ups were generally carried out in the open unless otherwise stated.

4.1. [AuCl{6-P(Ph)$_2$-1-(4-Me–C$_6$H$_4$N$_2$)–C$_{10}$H$_5$-2-OH}] (1a)

To Na[$AuCl_4$]·2H_2O (0.27 g, 0.67 mmol) dissolved in H_2O (30 cm^3) at 0°C was added 2,2′-thiodiethanol (0.25 g, 2.0 mmol) over 15 min. After stirring for 1 h, **I** (0.3 g, 0.67 mmol), dissolved in $CHCl_3$ (10 cm^3), was added at 0°C and stirred for a further 1 h. $CHCl_3$ (30 cm^3) was then added to the mixture and the organic layer was separated and dried over anhydrous $MgSO_4$. After

filtration and removal of the solvent under reduced pressure, recrystallisation of the crude material from $CHCl_3$–hexane afforded **1a**·0.25$CHCl_3$ as a red solid (0.38 g, 83%). In an analogous manner, complexes **1b**, **1c**, **1d** and **1e** were obtained; see Table 1 for physical and analytical data.

4.2. [Au(C≡CPh){6-P(Ph)$_2$-1-(4-Me–C$_6$H$_4$N$_2$)–C$_{10}$H$_5$-2-OH}] (2a)

To phenylethyne (0.1 cm^3, 0.88 mmol) dissolved in dry THF (10 cm^3), with continuous stirring under an atmosphere of dry dinitrogen, at 0°C was added ^{n}BuLi (0.35 cm^3, 2.5 M in hexanes, 0.88 mmol). After stirring for 10 min, **1a** (0.2 g, 0.29 mmol) was added and the mixture stirred for a further 2 h at 0°C. Saturated $NH_4Cl_{(aq)}$ solution (5 cm^3) was then added to the mixture and the solvent was removed in vacuo. The residue was extracted into CH_2Cl_2 (10 cm^3) and dried over anhydrous $MgSO_4$. Filtration followed by removal of the solvent under reduced pressure and recrystallisation from $CHCl_3$–hexane afforded **2a**·$CHCl_3$ as a red solid (0.14 g, 64%). In an analogous manner, complexes **2b**·0.8$CHCl_3$ and **2c** were prepared; see Table 1 for physical and analytical data. Single crystals of **2a** used in the diffraction study were grown by diffusion of hexane into a saturated solution of **2a** in $CHCl_3$.

4.3. [Au(C≡C^{n}Bu){6-P(Ph)$_2$-1-(4-Me–C$_6$H$_4$N$_2$)–C$_{10}$H$_5$-2-OH}] (2d)

To hex-1-yne (0.1 cm^{-3}, 0.88 mmol) dissolved in dry THF (10 cm^3), with continuous stirring under an atmosphere of dry dinitrogen, at 0°C was added ^{n}BuLi (0.35 cm^3, 2.5 M in hexanes, 0.88 mmol). After stirring for 10 min, **1a** (0.2 g, 0.29 mmol) was added and stirred for a further 2 h at 0°C. Saturated $NH_4Cl_{(aq)}$ solution (5 cm^3) was then added to the mixture and the solvent removed in vacuo and the residue extracted into CH_2Cl_2 (10 cm^3), dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent under reduced pressure and recrystallisation from $CHCl_3$–hexane afforded **2d**·0.5$CHCl_3$ as a red solid (0.15 g, 71%). In an analogous manner, complexes **2e**·$CHCl_3$ and **2f**·0.25$CHCl_3$ were prepared; see Table 1 for physical and analytical data.

4.4. Crystallography

A red plate ($0.25 \times 0.20 \times 0.15$ mm^3) of **2b**·$CHCl_3$: M_w 891.95 which was obtained by slow diffusion of *n*-hexane into a saturated $CHCl_3$ solution of **2b** was mounted on a Nonius MACH four-circle diffractometer using monochromated Mo–K_α (0.71069 Å) radiation. Lattice constants were determined from the setting angles of 25 accurately controlled reflections: triclinic $P\bar{1}$; $a = 8.887(7)$, $b = 12.241(8)$, $c = 16.939(5)$ Å; $\alpha = 101.75(3)$, $\beta = 92.85(5)$, $\gamma = 91.03(2)°$, $Z = 2$. The $\omega/2\theta$ scan technique was used with an ω scan width of $(0.9° + 0.35 \tan\theta)$ to collect reflections with $2\theta \leq 50°$. The intensities were corrected for Lorenz polarisation and absorption (4.386 mm^{-1}). The SHELX-97 suite of programs [20] were used to solve the structure by direct methods and refined using full-matrix least-squares based on F^2, hydrogen atoms were constrained to chemically reasonable positions: R $[I > 2\sigma(I)]$, $R_1 = 0.1138$, $wR_2 = 0.2135$; R (all data), $R_1 = 0.2365$, $wR_2 = 0.2742$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 158667. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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