FULL PAPER

www.rsc.org/dalton

Effects of diphosphine structure on aurophilicity and luminescence in Au(1) complexes[†][‡]

Aranzazu Pintado-Alba,^{*a*} Héctor de la Riva,^{*a*} Mark Nieuwhuyzen,^{*a*} Delia Bautista,^{*b*} Paul R. Raithby,^{*cd*} Hazel A. Sparkes,^{*c*} Simon J. Teat,^{*d*} José M. López-de-Luzuriaga^{*e*} and M. Cristina Lagunas^{**a*}

- ^a School of Chemistry, The Queen's University of Belfast, Belfast, UK BT9 5AG.
 E-mail: c.lagunas@qub.ac.uk; Fax: +44 (0)2890 382117; Tel: +44 (0)2890 974436
- ^b Servicio Universitario de Instrumentación Científica, Universidad de Murcia, E-30100 Murcia, Spain
- ^c Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY. E-mail: p.r.raithby@bath.ac.uk; Fax: +44 (0)1225 386231; Tel: +44 (0)1225 383183
- ^d CCLRC Daresbury Laboratory, Warrington, UK WA4 4AD
- ^e Departamento de Química, Universidad de La Rioja, UA-CSIC, E-26004 Logroño, Spain

Received 12th July 2004, Accepted 14th September 2004 First published as an Advance Article on the web 27th September 2004

The effects of diphosphine flexibility and bite angle on the structures and luminescence properties of Au(1) complexes have been investigated. A range of diphosphines based on heteroaromatic backbones [bis(2-diphenylphosphino)phenylether (dpephos), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos), and 4,6-bis(diphenylphosphino)dibenzofuran (dbfphos)] has been used to prepare mono- and digold derivatives. A clear relationship between the presence of aurophilic contacts and the emission properties of dinuclear complexes has been observed, with one of the complexes studied, [Au₂Cl₂(μ -xantphos)], exhibiting luminescence thermochromism.

Introduction

The rich photochemistry exhibited by many Au(I) complexes and the potential applications derived therefrom (e.g., development of molecular sensors and switches or energy storage devices) has triggered numerous studies focused on clarifying the relationships between the structures and the optical properties of the compounds.¹⁻⁶ Particularly interesting are the connections found between the emission bands of the complexes and the presence of weak interactions (2.7-3.5 Å) between neighbouring Au atoms (aurophilicity).² In some cases, however, no clear relation between Au...Au distances and emission properties has been found.3 In this context, dinuclear Au(I) complexes with bridging diphosphines of variable length have been extensively studied.4-6 Most of these contain non-rigid diphosphines [e.g., of the type $R_2P(CH_2)_pPR_2$] which do not allow great control on the geometry adopted by the complexes. The use of more rigid phosphines is therefore desirable.

In this work, three diphosphine ligands derived from rigid heteroaromatic backbones [bis(2-diphenylphosphino)phenyl 4,6-bis(diphenylphosphino)dibenzofuran ether (dpephos),7 (dbfphos),⁷⁻⁹ and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos),10 Chart 1] have been used to prepare monoand digold(I) derivatives. It has been shown that the small variations in the backbones of these ligands affect their bite angles, while keeping electronic effects very similar (Chart 1).7 The influence of the variable flexibility and bite angles of the diphosphines on the structures of the new Au(I) complexes prepared has been analysed. In addition, the relationship between aurophilic interactions and optical properties of dinuclear [(AuCl)2(µdiphos)] species has been studied. While preparing this paper, the synthesis and optical properties at room temperature of one of the compounds reported here, [(AuCl)₂(µ-xantphos)], were published.11 However, low-temperature luminescence, NMR and crystallographic data, which are included in the present work, have not been previously reported.



Chart 1 Ligands used for the synthesis of Au(1) complexes. Bite angles obtained from ref. 7

Results

Synthesis

Complexes $[(AuCl)_2(\mu-diphos)] \cdot CH_2Cl_2$ (diphos = dpephos, 1; xantphos, 2; dbfphos, 3; Scheme 1) were readily prepared by reacting the corresponding diphosphine with two equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) in dichloromethane.

Attempts to isolate annular species of the type $[Au_2(\mu - diphos)_2]X_2$ (X = OTf, ClO₄) by reacting 1 or 2 with the



Scheme 1 Synthesis of complexes; adpephos or xantphos.

of 1-6. See http://www.rsc.org/suppdata/dt/b4/b410619a/

[†] Electronic supplementary information (ESI) available: UV-Vis spectra

[‡] Dedicated to Prof. José Vicente on the occasion of his 60th birthday.

corresponding free phosphine and AgOTf or NaClO₄ in molar ratio 1:1:2 failed. Various mixtures of products that could not be separated resulted in all cases. In order to clarify these processes, the reactions of the digold chloride complexes **1** or **2** with free ligand were studied by NMR spectroscopy, as described in the next section.

Complexes $[Au(diphos)_2][SbF_6]$ [diphos = dpephos (4), xantphos (5), dbfphos (6)] were obtained by reacting 1, 2 or 3 with the corresponding free diphosphine and NaSbF₆ in molar ratio 1:3:2 (Scheme 1). Complex 6 gave partial decomposition in solution, as shown by the presence of a small amount of diphosphine oxide in its ³¹P{¹H} NMR spectrum.

NMR spectroscopy

The NMR spectra of the complexes are consistent with the proposed structures. The presence of one molecule of CH₂Cl₂ in solid samples of 1–3 was confirmed by their ¹H and ¹³C{¹H} NMR spectra. In the aromatic regions of the ¹H NMR spectra, the signal at the lowest frequency (6.4–7.0 ppm), which appears as a ddd (1, 2) or a dd (3), has been assigned to the *ortho*-H atoms of the organic backbone, with ³*J*(PH) coupling constants in the range 11.9–13.4 Hz.

In the ¹³C{¹H} NMR spectrum of **3**, the *ipso-*, *ortho-* and *meta-*C atoms of the Ph₂P groups each appears as a doublet with J(PC) of 64, 15 or 12 Hz, respectively, whereas the *para-*C atoms give a singlet. Three other signals corresponding to C atoms of the diphenyl ether backbone also give doublets, with that of highest coupling constant (58 Hz) being assigned to the *ipso-*C atom.

Based on the assignment made for 3, the ${}^{13}C{}^{1}H$ NMR spectra of 1 and 2, which are more complicated, were analysed. The spectrum of complex 1 shows two types of Ph groups. These could indicate that the rigid structure of 1 in the solid state, with a Au...Au interaction (see below), is retained in solution. However, a locked conformation of the Ph groups could also occur without the need for an aurophilic interaction. The resonances of the Ph₂P ortho-, meta- and ipso-C atoms in the spectrum of 2 appear as multiplets or apparent triplets. The ¹³C{¹H} NMR spectrum of free xantphos, which also shows apparent triplets for some of its C atoms, has been analysed as an AA'X system (A = A' = ${}^{31}P$, X = ${}^{13}C$) with a large coupling between the two ³¹P nuclei, which results from the orientation of the P lone pairs and the short PP distance.^{7,10} The observed spectra of 2 can be rationalised in an analogous way, with a large ³¹P³¹P coupling transmitted through the organic backbone and/or the Au…Au interaction. The latter mechanism requires the assumption that the structure of 2 in solution is similar to that of the crystal, with the aurophilic interaction remaining in solution (see below).

The ${}^{31}P{}^{1}H{}$ NMR spectra of 1–3 showed a single resonance in the range 21–26 ppm. Coordination to Au(I) produced the expected downfield shift (*ca.* 40 ppm) with respect to the free ligands.

As mentioned above, the stepwise addition of free dpephos or xantphos to a solution of 1 or 2 was followed by ${}^{31}P{}^{1}H$ NMR. This type of titration reaction has been used in the past to investigate the formation of three- and fourcoordinated Au(I) species in solution.12-14 For example, the spectra of complexes [(AuCl)₂(µ-diphosphine)] (diphosphine = $Ph_2P(CH_2)_nPPh_2$, n = 2, 3 or *cis*-Ph_2PCH=CHPPh_2)^{13} showed, upon addition of less than 1 equiv. of free phosphine, the formation of significant quantities of a bis-chelated [Au(diphosphine)₂]⁺ species, whose resonance was generally broadened through exchange with other species in solution (e.g., tri-coordinated $[(AuCl)_2(\mu-diphosphine)_2]$). The fact that separate resonances for [Au(diphosphine)₂]⁺ and free phosphine could be seen in the spectra upon addition of ≥ 3 equivalents of ligand, indicated that only slow exchange between free and bound phosphine occurred in solution. The authors attributed this exceptional stability of the bis-chelated Au(I) complexes View Article Online

in solution to the formation of five- or six-membered chelate rings, since no evidence of analogous species was found when diphosphines leading to four- or seven-membered rings [*i.e.*, $Ph_2P(CH_2)_nPPh_2$, n = 1 or 4] were used.¹³

An analogous behaviour has been found in the reaction between complex 1 and free dpephos, performed in CDCl₃ or CD₂Cl₂. Upon addition of 0.5 equiv. of ligand, the initial singlet corresponding to 1 (21.4 ppm) disappeared and two new very broad resonances at 22.4 and 18.1 ppm appeared. The signal at 18.1 ppm increased in intensity at the expense of the other when more dpephos (i.e., Au: dpephos ratio of 1:1) was added, and has been tentatively assigned to a tri-coordinated 1:1 complex, [(AuCl)₂(µ-dpephos)₂] (A, Scheme 1). Further addition of free phosphine resulted in a unique (sharper) intermediate resonance at 21.9 ppm, which has been assigned to a bis-chelated species (C, Scheme 1). Complex [Au(dpephos)₂][SbF₆] (4) was later isolated, and its ³¹P{¹H} NMR spectrum at r.t. showed a singlet at 18.2 ppm which remained sharp at 213 K. The slightly different chemical shift of this signal with respect to that found during the titration (21.9 ppm) may be due to the influence of the anion

The addition of free xantphos to complex 2 was also followed by ³¹P{¹H} NMR spectroscopy in CDCl₃, with comparable results (Fig. 1). Upon addition of 0.5 equiv. of free diphosphine, three signals at 27.7, 22.9, and 5.8 (br) ppm appeared in the spectrum, in addition to that corresponding to 2 (24.7 ppm). The latter decreased gradually in intensity with the subsequent addition of diphosphine (up to 1.5 equiv.), while the singlets at 27.7 and 5.8 ppm increased, and the smallest signal at 22.9 ppm remained almost unchanged. On further addition of xantphos, the broad peak at 5.8 ppm was virtually the only signal remaining, until a singlet at -17.2 ppm, corresponding to the free ligand, appeared at a 2: xantphos ratio of ca. 1:3. The signal at 5.8 ppm was assigned to a bischelated species $[Au(xantphos)_2]^+$ (C), which was later isolated as its $[SbF_6]^-$ salt (5, Scheme 1) and characterised by X-ray diffraction (Fig. 10). The singlets at 27.7 and 22.9 ppm have been assigned to three-coordinated 1:1 Au:xantphos species [(AuCl)₂(xantphos)₂] (A) and [AuCl(xantphos)] (B). At 213 K, the signal at 5.8 ppm gave an AA'BB' pattern (Fig. 2). The two Me groups of the backbone also become inequivalent in the ¹H NMR spectrum at low temperature. This behaviour is consistent with the solid-state structure of 5 (Fig. 10), in which the two P atoms of each xantphos unit are in different chemical environments. As represented in Fig. 3, P1 is opposite to the aromatic backbone of the other xantphos unit, whereas P2 is opposite the phenyl groups. At higher temperatures, the four P atoms become equivalent, indicating that a fluxional process involving flipping of the xantphos conformation takes place



Fig. 1 ${}^{31}P{}^{1}H$ NMR spectra of complex 2 in CDCl₃ in the presence of free xantphos.

on the NMR timescale (Fig. 3). This may or may not involve de-coordination from the metal. Analogous behaviour can be assumed for complex **6**, whose ${}^{31}P{}^{1}H$ NMR at r.t. shows a very broad peak, which splits into two broad singlets at 213 K. The fact that all P centers in complex **4** remain equivalent at 213 K on the NMR timescale suggests that in this case the analogous fluxional behaviour is faster. This is consistent with the higher flexibility of dpephos with respect to xantphos or dbfphos.



Fig. 2 Observed (above) and simulated (below) ${}^{31}P{}^{1}H{}$ NMR spectra of complex 5 at 213 K, showing AA'BB' pattern [J(AA') = 22.2 Hz, J(AB) = 24.2 Hz, J(AB') = 13.3 Hz, J(BB') = 18.5 Hz].



Fig. 3 Proposed fluxional behaviour for complexes 4–6 in solution.

Crystal structures

The crystal structures complexes 1-3, and 5 were determined, in addition to that of free dpephos, which had not been previously reported (Figs. $4-10^{15}$). Crystal data and selected bond lengths and angles are included in Tables 1 and 2, repectively.

Dpephos. The crystal structure of the free phosphine is shown in Fig. 4. The distance between the two P atoms (4.876 Å) is shorter than that found in dbfphos [5.741(1) Å]⁹ and larger than those of xantphos, for which three different crystal structures have been reported [P–P = 4.045(1) Å,¹⁰ 4.080 Å,⁷ or 4.155(1) Å (xantphos·THF)¹⁰]. The two phenyl rings in the backbone of dpephos form an angle of *ca*. 67°, with the lone pairs of the P atoms pointing away from each other.

 $[(AuCl)_2(\mu-dpephos)] \cdot CH_2Cl_2$ (1). Complex 1 shows a Au...Au interaction of 3.0038(6) Å (Fig. 5). This seems to be easily accommodated within the bite angle of the



Fig. 4 Crystal structure of dpephos.



Fig. 5 Crystal structure of 1 (solvent molecules and H atoms are omitted for clarity).



Fig. 6 Crystal structure of $\mathbf{2}$ (solvent molecules and H atoms are omitted for clarity).



Fig. 7 Hydrogen bonding interactions in **2** (H atoms not involved in the interactions are omitted for clarity); Cl1…H15B: 2.726 Å, Cl1…C15: 3.654 Å, Cl1…H15B–C15: 158.4°; Cl1…H55: 2.788 Å, Cl1…C55: 3.554 Å, Cl1…H55–C55: 138.3°; Cl2…H99A: 2.646 Å, Cl2…C99: 3.619 Å, Cl2…H99A–C99: 168.0°; Cl4…H53: 2.898 Å, Cl4…C53: 3.746 Å, Cl4…H53–C53: 149.4°.

phosphine, as the conformation of the dpephos backbone in the complex is almost the same as in the free ligand (*i.e.*, the distance between the P atoms is 4.858 Å and the angle between the phenyl rings is of *ca*. 61°). The aurophilic interaction forces the Au coordination environments to deviate from linearity, with P–Au–Cl angles of 170.57(9) and 174.26(9)°. The P–Au–Cl fragments are almost perpendicular to each other [*e.g.*, the Cl(1)– Au(1)–Au(2)–Cl(2) torsion angle is 81°]. Short Au···O contacts in the range 3.04–3.25 Å have been shown to be important in

Table 1	Crystal	data for	dpephos	and complexes	1–3 and 5
---------	---------	----------	---------	---------------	-----------

	dpephos	1	2	3	5
Formula	$C_{36}H_{28}OP_2$	$C_{37}H_{30}Au_2Cl_4OP_2$	$C_{40}H_{34}Au_2Cl_4OP_2$	$C_{40}H_{36}Au_2Cl_2O_2P_2$	$C_{81}H_{67}AuCl_9F_6O_2P_4Sb$
M	538.52	1088.28	1128.34	1075.46	1947.99
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	Cc	$P2_1/c$	P1
aľÅ	13.8258(16)	8.9229(16)	10.4484(9)	12.6522(11)	12.8424(11)
b/Å	11.9848(14)	20.269(4)	24.8178(15)	10.8373(10)	15.0214(13)
c/Å	17.725(2)	19.987(4)	15.0035(9)	26.931(2)	21.1198(18)
$U/Å^3$	2830.5(6)	3526.8(12)	3804.7(5)	3689.5(5)	3967.0(6)
<i>T</i> /K	153(2)	150(2)	173(2)	150(2)	153(2)
Ζ	4	4	4	4	2
μ (Mo-K α)/mm ⁻¹	0.181	8.021	8.100	8.210	2.421
Refls. measured	30543	29760	6794	21155	44257
Unique refls. (R_{int})	6594 (0.0557)	10004 (0.0580)	6527 (0.0203)	8104 (0.0241)	17665 (0.0734)
$R(I \ge 2\sigma(I))$	0.0441	0.0465	0.0241	0.0336	0.0657
$wR(F^2)$ (all data)	0.1203	0.1185	0.0403	0.0793	0.1496

Table 2Selected bond lengths (Å) and angles (°) for 1–3 and 5

	1	2	3
$\overline{Au(1)}$ – $Au(2)$	3.0038(6)	2,9947(4)	
Au(1)-Cl(1)	2.300(2)	2.3009(17)	2.2879(15)
Au(2)-Cl(2)	2.310(2)	2.3071(16)	2.3004(13)
Au(1) - P(1)	2.234(2)	2.2347(17)	2.2257(13)
Au(2)-P(2)	2.235(2)	2.2410(16)	2.2315(13)
P(1)-Au(1)-Cl(1)	170.57(9)	173.07(6)	179.24(6)
P(2)–Au(2)–Cl(2)	174.26(9)	168.47(7)	179.20(5)

Au(1)–P(2)	2.474(2)	Au(1)–P(3)	2.4691(19)
Au(1)–P(1)	2.4771(19)	Au(2)-P(4)	2.471(2)
P(2)–Au(1)–P(1)	109.55(7)	P(2)-Au(1)-P(4)	107.76(7)
P(2)-Au(1)-P(3)	115.78(7)	P(1)-Au(1)-P(4)	109.02(7)
P(1)-Au(1)-P(3)	108.01(7)	P(3)-Au(1)-P(4)	106.56(7)



Fig. 8 Crystal structure of **3**' (most H atoms are omitted for clarity); O2…H26: 2.685 Å, O2…C26: 3.543 Å, O2…H26–C26: 150.7°.

the structures of organogold derivatives of diphenyl ether, $[(AuPPh_3)(C_6H_4OC_6H_5)]$ and $[(AuPPh_3)_2((C_6H_4)_2O)]$.¹⁶ In the case of complex 1, the distances between the metals and O are larger (*ca.* 3.5 Å), but may still have an influence on its structure.

 $[(AuCl)_2(\mu-xantphos)] \cdot CH_2Cl_2$ (2). The crystal structure of 2 (Fig. 6) shows a similar aurophilic interaction [2.9947(4) Å] and comparable P-Au-Cl angles [168.47(7) and 173.07(6)°] to those of 1. The angle between the P-Au-Cl fragments [Cl(1)-Au(1)-Au(2)-Cl(2) torsion angle: 90.7°] is slightly larger in 2. However, unlike complex 1, the diphosphine backbone



Fig. 9 Intermolecular interactions in **3**' [Au2···Cl2: 3.377 Å; Cl2···H36: 2.779 Å, Cl2···C36: 3.704 Å, Cl2···H36–C36: 164.52°] (the second molecule is related by the symmetry operation -x, -y, 1 - z; most H atoms are omitted for clarity).



Fig. 10 Crystal structure of the cation in 5 (solvent molecules and H atoms are omitted for clarity).

in 2 undergoes some distortion upon coordination. Thus, the distance between the P atoms (4.735 Å) is significantly larger in 2 than in the free xantphos (see above)^{7,10} and the xanthene backbone is both folded and twisted along the central ring, presumably to accommodate the two Au atoms at a close distance. Such distortion is not present in the free diphosphine, where the backbone is only slightly folded, with the two phenyl rings forming and angle of *ca.* 160°. Another difference with the structure of 1 resides in the distances between O and the Au atoms, which in 2 are 3.097 and 3.992 Å. The former indicates the presence of a weak Au…O interaction (*i.e.*, shorter than the sum of their van der Waals radii of *ca.* 3.2 Å). Additionally,

5

	$\lambda_{\rm abs}/{\rm nm}~(\varepsilon_{\rm max}/{\rm dm^3~mol^{-1}~cm^{-1}})$		$\lambda_{\rm em}/{ m nm} \left[au_0/\mu s ight]$
dpephos	262 sh (3359), 267 (4400), 274 (5025), 289 (5688)	Solid	440 (r.t.)
			441 (77 K)
		Cl_2CH_2	499 (r.t.)
			505 (77 K)
xantphos	262 (23667), 305 sh (9216)	Solid	436 (r.t.)
			447 (77 K)
		Cl_2CH_2	510 (r.t.)
			446 (77 K)
dbfphos	253 (44023), 297 (25368), 311 sh (14849), 322 sh (8306)	Solid	441 (r.t.)
			438 (77 K)
		Cl_2CH_2	521 (r.t.)
			445 (77 K)
1	248 sh (7912), 269 (3058), 277 (2993), 286 (2642), 293 (2409)	Solid	450 sh, 620 [12] (r.t.)
			628 (77 K)
		Cl_2CH_2	431, 654 (77 K)
2	261 (28548), 278 (25763)	Solid	449 sh, 620 [76] (r.t.)
			447, 621 (77 K)
		Cl_2CH_2	429, 507 sh (77 K)
3	245 sh (43802), 277 (8634), 298 (15389), 310 (11099)	Solid	429, 458, 488 sh [11] (r.t.)
			427, 456, 488 sh (77 K)
		Cl ₂ CH ₂	430, 450, 489 sh (r.t.)
		- 2 - 2	430, 454, 486 sh (77 K)
4	264 sh (64092)	Solid	485[12](r.t.)
			458 (77 K)
		Cl ₂ CH ₂	448 (77 K)
5	276 (72845)	Solid	491 [14] (r.t.)
	()		488 (77 K)
		Cl ₂ CH ₂	505 (r.t.)
			460 (77 K)
6	295 (92575)	Solid	470[8](rt)
-	()	20114	486 (77 K)
		Cl ₂ CH ₂	515 (rt)
		0120112	440 (77 K)
n Cl ₂ CH ₂ at r.t. ${}^b\lambda_{ex}$	= 290–340 nm.	0.201.2	440 (77 K)

Table 3 Absorption^{*a*} and emission^{*b*} data for the free phosphines and complexes 1-6

there is a network of hydrogen bonds in the crystal involving Cl atoms both from the complex and the solvent (Fig. 7).

[(AuCl)₂(µ-dbfphos)]. The crystal structures of [(AuCl)₂(µdbfphos)]·CH₂Cl₂ (3) and of the diethyl ether solvate (3') analogue were obtained. The structures of the two species were similar, and only the latter was fully refined (Fig. 8). The solid-state structure of [(AuCl)₂(µ-dbfphos)] is fundamentally different to that of 1 or 2. The two Au-Cl units in the former adopt an anti position that situates the metal atoms at a longer distance (7.21 Å) from each other, preventing the formation of an aurophilic contact. The geometry around the metals is almost perfectly linear, with P-Au-Cl angles of 179.24(6) and 179.20(5)°, and the distances between O and the Au atoms (4.116 and 3.990 Å) are too long to be considered as interactions. The dibenzofuran backbone is almost coplanar and the distance between the two P atoms (5.834 Å) is similar to that found in the free ligand.⁹ As in complex 1, the diphosphine is not distorted by coordination to the Au atoms. The O atom of the diethyl ether molecule forms a H-bonded interaction with one of the Ph groups, as represented in Fig. 8.

A close look at the way the molecules are packed in the crystal shows the presence of intermolecular Au…Cl and CH…Cl contacts (Fig. 9). Two Au-Cl units of adjacent molecules are situated in an anti-paralell manner, forming a rectangle through intermolecular Au...Cl contacts of 3.377 Å, slightly shorter than the sum of the van der Waals radii (3.41 Å). Analogous Au…Cl interactions have been previously described.¹⁷ Each of the two Cl atoms in the rectangle also forms an inter-molecular H-bond, as shown in Fig. 9.

[Au(xantphos)₂][SbF₆] (5). Complex 5 (Fig. 10) crystallises with three molecules of chloroform. The geometry around the metal is pseudo-tetrahedral with P-Au-P angles in the range 106.56(7)-115.78(7)°. The crystal structures of related

Au(I) four-coordinate complexes, such as [Au{o-phenylenebis-(dimethylarsine)}]+,18 [Au(dppe)2]+,12,19,21 and [Au{4-methyl-1,8bis(diphenylphosphino)naphthalene}2]+,20 show wider ranges of P-Au-P angles [86.7-121.8, 85.4(1)-129.6(1) and 86.9(2)-133.3(2)°, respectively], indicating tetrahedral geometries significantly more distorted than that of 5. The Au-P bond distances [2.4691(19)-2.4771(19) Å] are slightly longer in 5 than in $[Au(dppe)_2]^+$ [2.389(3)–2.416(3) Å]¹² and $[Au\{4-methyl-1,8$ bis(diphenylphosphino)naphthalene}2]+[2.379(6)-2.388(6) Å].²⁰ These bonds are also longer that the Au-P distances in twocoordinate derivatives 1-3.

The bite angles of the ligands, 106.56(7)° (P3-Au1-P4) and 109.55(7)° (P2-Au1-P1), are smaller than the calculated natural bite angle for free xantphos (111.7°),⁷ and the Au atom is situated at ca. 3.4 Å from each of the O atoms of the ligands. Each of the xantphos units in the complex is folded along the $O \cdots CMe_2$ imaginary line (*i.e.*, the angle between the two phenyl rings is ca. 145°), with the central ring adopting a boat-like conformation. The P1-P2 and P3-P4 distances are of 4.043 and 3.962 Å, respectively. These features are analogous to those found in the free ligand^{7,10} (see above), indicating that only little distortion occurs upon coordination of the gold atom in a chelating manner. This contrasts with the crystal structure of 2, in which the xantphos unit undergoes a high distortion when bridging between two metals. Finally, the C31C-C36C and C11A-C16A rings lie almost parallel to each other at a distance of *ca.* 3.8 Å, suggesting the presence of a phenylphenyl interaction. Ring stacking has also been observed in the structure of $[Au(dppe)_2]^+$ (inter-ring separation = 3.5 Å).²¹

Optical properties

The absorption and emission spectra of complexes 1-6 have been studied and compared to those of the free ligands. The photophysical data are summarised in Table 3.

The absorption spectra of all compounds were obtained from dichloromethane solutions (ESI†). The spectrum of dpephos exhibits a structured band between 250 and 325 nm, while xantphos presents a broad absorption band with a maximum at 262 nm and a shoulder at *ca.* 305 nm. An intense absorption at 253 nm and a broad band at 297 nm with tails into longer wavelengths are observed in the spectrum of dbfphos. The shapes of the electronic spectra for 1-3 resemble roughly that of the corresponding parent phosphine, whereas the four-coordinate complexes 4-6 exhibit broad more intense absorptions which tail to *ca.* 350 nm.

When excited at 300–330 nm, the emission spectra of the free phosphines at r.t. or 77 K consist of a broad emission band with λ_{max} in the 436–521 nm region.

The solid-state emission spectra of complexes 1 and 2^{11} at r.t. are similar to each other, exhibiting a broad band at 620 nm and a shoulder at *ca*. 450 nm (Fig. 11) when excited at 300 nm. Their spectra at 77 K, however, are quite different. While the spectrum of 1 does not change with temperature, the relative intensities of the two emissions of 2 change dramatically, with the high energy (HE) emission favoured at 77 K (Fig. 11). The excitation spectra monitored for both the HE and the LE emissions of 2 at 77 K are analogous. Complexes 1 and 2 are not luminescent in dichloromethane solution at r.t. but they emit at 77 K. Thus, a glassy solution of 1 gives two bands at 431 and 654 nm, whereas the xantphos derivative 2 shows mainly one broad band at 430 nm.



Fig. 11 Solid-state emission spectra ($\lambda_{exc} = 300$ nm) of complexes 1–3 at r.t. (left), and complex 2 at r.t. and 77 K (right).

The emission of 3 differs significantly from that of 1 or 2 (Fig. 11), and exhibits, both in the solid state and in dichloromethane, a structured band at 420-500 nm, which increases in intensity at low temperature.

Four-coordinate complexes 4-6 show solid-state emission at r.t. and 77 K, with a broad band in the region 458–491 nm when exited at 300–335 nm. Luminescence has been observed for the three complexes in degassed dichloromethane at 77 K, and in the case of 5 and 6, also at room temperature.

Discussion

The lack of aurophilic interaction in $[(AuCl)_2(\mu-dbfphos)](3, 3')$ contrasts with the structures of complexes 1 and 2, and it may be attributed to the rigid conformation of dbfphos, whose large bite angle would not accommodate comfortably an Au---Au fragment. In fact, in two analogous complexes recently prepared by us, $[{Au(SC_6H_4Cl-4)}_2(\mu-dbfphos)]$ and $[{Au(CCPh)}_2(\mu-dbfphos)]$ dbfphos)],²² it has been found that dbfphos only allows very weak Au…Au contacts (of ca. 3.4 Å). In the case of [(AuCl)₂(µ-dbfphos)], such weak aurophilic interaction would be in competition with intermolecular Au…Cl and CH…Cl interactions (Fig. 9) which, as a whole, seem to have a greater influence on the overall structure of the complex. In complexes 1 and 2, the shorter aurophilic contact (of *ca.* 3.0 Å) allowed by the diphosphine ligands, is strong enough to prevail over competing intermolecular interactions. In addition, weak intramolecular Au...O contacts may contribute to stabilise the Au…Au bonded conformation of these two compounds, in particular in the case of **2**, which presents the shortest Au···O distance (*ca.* 3.1 Å). A number of intermolecular hydrogen bonds are also present in **2** (Fig. 7). The importance of the cumulative contribution to the stabilisation energy of weak interactions in a crystalline solid has been recently highlighted in the literature.²³ The competition between aurophilic and other secondary interactions in the crystal packing of Au complexes has also been analysed.²⁴

It is interesting to note that the three diphosphines are able to stabilise eight-membered chelate rings with Au(I) in a pseudotetrahedral environment (complexes 4-6). This contrasts with the behaviour of more flexible diphosphines, for which fourcoordinate chelated Au(I) complexes containing large rings (*i.e.*, >six-membered rings) have been found to be unstable.¹³ The preference of xantphos to coordinate in a chelate manner has been pointed out before as a result of the phosphine's bite angle.7 The fact that this ligand adopts a less strained conformation in complex 5 than in 2 agrees with its predicted preference for chelating. The stability of unusually large chelated rings is more surprising in the case of dbfphos, whose large bite angle has been suggested to not favour ring closure.7 In fact, metal complexes containing dbfphos in a chelating coordination mode are scarce and only a few Re and Ru compounds in which the metal also coordinates to the O atom of the diphosphine have been described.²⁵ As in complexes 1 and 2, the presence of weak Au...O interactions (of ca. 3.4 Å) in the structure of 5 could contribute to the stabilisation energy of the crystal. Similar contacts may also be present in 4 and 6.

Previous studies have established that the lowest energy absorption for any phosphines is associated with a $1 \rightarrow a_{\pi}$ (or $n \to \pi^*)$ transition involving the promotion of an electron from the lone pair orbital (l) on phosphorus to an empty antibonding orbital of π origin on a phenyl ring.^{26,27} Such transition can be buried under the tail of more intense $\pi \to \pi^*$ bands.²⁶ The $l \to a_{\pi}$ transition, which becomes a $\sigma \rightarrow a_{\pi}$ transition on coordination, should shift to higher energy as the electron pair is stabilised by the metal, but examples in which it remains unchanged or shifts to lower energies have also been reported.27 In the latter cases, the transition energy has been suggested to be modified by metalphosphorus π -backbonding or alterations on the angle between the P l-orbital and the axis of the adjacent C 2pπ-orbital upon coordination.²⁷ Luminescence arising from the $l \rightarrow a_{\pi}$ state has been described for a number of aryl mono- and di-phospines,²⁶ whereas emission bands arising from $\sigma \rightarrow a_{\pi}$ transitions (often label as ILCT transitions) are shown by some of their d¹⁰ metal complexes, including four-coordinate Au(1) derivatives.^{27,28} In some cases, this emission has been proposed to have a mixed ILCT/MLCT [d (metal) $\rightarrow \pi^*$ (phosphine)] character.

According to this interpretation, the intense absorptions that the three diphosphines exhibit in the 250–300 nm region have been assigned to $\pi \to \pi^*$ transitions localised on the aromatic groups, while the tails at longer wavelengths may be associated with the $1 \to a_{\pi}$ transition. This transition shifts slightly to higher energy upon coordination in 2 and 3, does not change significantly in the case of 1, and it moves to lower energy in 4–6. The emission observed for the free diphosphines at 436–447 nm is suggested to arise from the $1 \to a_{\pi}$ transition.

The HE emissions in 1 and 2, which are similar in energy and shape to those of the free ligands, may be associated with an ILCT ($\sigma \rightarrow a_{\pi}$) transition. The same origin can be assumed for the emission of 3, which appears in the same region. However, given the distinctive vibrational structure of this band, a different origin cannot be ruled out. The difference in energy between the two sharper vibrational peaks in the emission spectrum of 3 (solid state at r.t.) is of 1476 cm⁻¹, which corresponds closely to a peak at 1478 cm⁻¹ of medium intensity found in its IR spectrum in Nujol. This band has been assigned to an aromatic C–C stretching frequency, suggesting a $\pi \rightarrow \pi^*$ origin for the emission of 3. An emission of $\sigma \rightarrow$ a_{π} origin should show the vibrational structure of the P–Ph stretching frequency, which normally appears as a strong very sharp band at *ca.* 1440 cm⁻¹ (a band with these characteristics is found at 1435 cm⁻¹ in the IR spectrum of **3**). Mononuclear Au(I) complexes {(R_2PhP)AuX}_n (R = Me, Ph, X = Cl, Br) also exhibit a structured phosphorescence at *ca.* 360 nm that has been proposed to originate from a phenyl-localised ${}^3\pi\pi^*$ state.²⁹

The LE emission at 620 nm, which is not observed in the spectrum of **3** or the free ligands, can be related to the aurophilic interaction present in **1** and **2**. The nature of the lowest energy emissive state of polynuclear phosphine Au(I) complexes in which Au···Au interactions are present is normally considered to originate from a metal-centered (MC) transition modified by the aurophilic interaction $(d\sigma^*/d\delta^* \rightarrow$ $p\sigma/s\sigma$; where $d\sigma^*$ or $d\delta^*$ is generated by overlap of Au $5d_{z^2}$ or $5d_{x^2-y^2}$ orbitals, respectively) or a metal-metal to ligand charge transfer (MMLCT, $d\sigma^*/d\delta^* \rightarrow \pi^*$) transition.

The temperature dependence of the solid-state luminescence of **2** is indicative of a thermally activated energy transfer from the HE to the LE excited state, which may be closer in energy than the corresponding states in complex **1**. Analogous luminescence thermochromism has been found in other Au(I) complexes.^{5,29}

Loss of the aurophilic contacts in solution and/or solvent quenching may be responsible for the non-emissive nature of 1 and 2 at r.t. in dichloromethane. In the glassy state, however, a LE emission at 654 nm can still be seen in the spectrum of 1, indicating that some aurophilic contacts are present. The inequivalence of the Ph groups observed in the ¹³C NMR spectrum of 1 also supports this proposal.

The emission of each of the tetrahedral compounds **4–6** is closely related to that of the corresponding free phosphine, with the solid-state bands in the complexes red-shifted 20–40 nm with respect to those in the ligands. The mechanism for the emission in **4–6** is thus considered to involve $\sigma \rightarrow a_{\pi}$ transitions. An analogous assignment has been done for the emission of related bis(diphenylphosphino)naphthalene complexes.²⁰ Luminescence of four-coordinated Au(I)–phosphine complexes is rare, in particular in fluid solution, but it has been shown to be enhanced when stacked P–phenyl groups are present, with low energy transitions (*i.e.*, 520–620 nm) associated with intra- and/ or inter-molecular Ph–Ph excited dimers.²¹ Although a weak Ph–Ph interaction has been identified in the crystal structure of **5**, evidence of excimer formation has not been found.

The lifetime of complexes 1–6, measured in the solid state at room temperature, are in the microsecond range (Table 3), indicating that the emissions occur from excited states of triplet parentage and probably phosphorescent. This is in agreement with the assignments of the bands.

Conclusions

The use of three diphosphines with various bite angles and flexibilities allows for some control over the structures of Au(I) complexes, which, in turn, have a strong influence on the optical properties of the compounds.

In the digold(I) derivatives, the aurophilic interactions determine the emission of the complexes, with a distinctive low energy band clearly associated with the presence of Au…Au contacts. The more flexible dpephos allows the establishment of such Au...Au (and Au...O) contacts in the solid state while remaining relatively unconstrained, as indicated by the crystallographic data of 1. This lack of constraint may allow the structure of 1 to remain largely unchanged in solution, as optical and ¹³C{¹H} NMR studies suggest. As the flexibility of the phosphine decreases (and the bite angle increases), the aurophilic interaction becomes less favoured. Thus, the xantphos ligands in complex 2 adopt a distorted conformation with respect to that of the free ligand or complex 5. Although an aurophilic interaction is observed for 2 in the solid state, presumably also favoured by the presence of Au…O and hydrogen-bonding interactions, its luminescence shows no evidence of the interaction remaining in solution. Finally, complex **3**, with the more rigid dbfphos, adopts a structure in the solid state in which intermolecular $Au\cdots Cl$ contacts prevail over potentially very weak intramolecular $Au\cdots Au$ interactions.

The three phosphines are able to form stable four-coordinate derivatives (4–6) which are highly luminescent both in the solid state and in solution. These are notable in that only a few other emissive tetrahedral Au(I) complexes have been described to date, with only two showing emission at r.t. in solution.²⁰

Experimental

General

Literature methods were followed for the syntheses of the diphosphine ligands.7 An alternative method to that described below for the synthesis of [(AuCl)₂(u-xantphos)] has recently been published.^{11 31}P{¹H} NMR (referenced to external 85% H_3PO_4), and ¹H- and ¹³C{¹H} NMR (standard SiMe₄) spectra were recorded on a Brüker Advance DPX 300 or DPX 500, at r.t. using CDCl₃ as solvent, unless otherwise stated. Elemental analyses (CHN) were performed in ASEP (School of Chemistry, Queen's University Belfast). Electrospray mass spectra were obtained on a VG Quattro spectrometer. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. The electronic absorption spectra were recorded on a Perkin Elmer UV/Vis spectrometer Lambda800. The emission spectra were recorded on a Perkin Elmer LS55 luminescence spectrometer equipped with a R928 photomultiplier and a lowtemperature accessory. For the luminescence measurements in dichloromethane, the solvent was previously degassed and the concentration of the solutions used was of ca. 10-3 M. Emission lifetimes were recorded on a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter equipped with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube with a flash rate between 0.05 and 25 Hz. The data were fitted using the Jobin-Yvon software package and the Origin 6.1 program.

Crystal structures

Single crystals of dpephos and complexes 1–3 and 5 were obtained by slow diffusion of hexane or diethyl ether in dichloromethane solutions of the compounds.

Crystals of 1 and 3' were mounted in inert oil on glass fibres, and data were measured using a Bruker AXS SMART CCD area detector, fitted with an Oxford Cryostream low-temperature attachment, on Station 9.8 of the CCLRC Daresbury Laboratory using an X-ray wavelength of $\lambda = 0.6892$ Å (for 1) and $\lambda = 0.6898$ Å (for 3').³⁰ The two structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).³¹ The structure of 1 was found to be twinned and in order to obtain a satisfactory refinement the twin matrix -100; 0-10; 101, obtained using the ROTAX program,³² was applied with a refined scale factor of 0.232 for the two components. For both structures, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model. Weighting schemes were introduced to give flat analyses of variance and refinement continued until convergence was reached.

Crystals of **2** were mounted in inert oil on a glass fiber and transferred to a Siemens P4 diffractometer with an LT2 low-temperature attachment. The unit cell parameters were determined from a least-squares fit of 100 accurately centered reflections (9.8 < 2θ < 24.9). The structure was solved by the heavy-atom method and refined anisotropically on $F^{2,31}$ Hydrogen atoms were included using a riding method. The absolute structure parameter³³ is -0.022(5).

Crystallographic data for dpephos and complex **5** were collected using a Bruker SMART diffractometer with graphite

monochromated Mo-K α radiation. The crystal stability was monitored and there was no significant decay ($\pm 1\%$). Data were collected at low temperature (ca. 153 K). Omega-phi scans were employed for data collection and Lorentz and polarisation corrections were applied. The structures were solved by direct methods and all non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atom positions were located from a Fourier difference map and refined with isotropic atomic displacement parameters for dpephos. Hydrogen atoms for 5 were added at idealised positions, subsequent refinement uses a riding model with atomic displacement parameters fixed at $1.2U_{eq}$ of the atom to which they are attached $(1.5U_{eq}$ for methyl groups). The function minimised for wR2 was $\sum [w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_0|^2 + (g_1 P)^2 + g_2 P]$ where $P = [\max |F_0|^2 + 2|F_0|^2]/3$ for all F^2 and the function minimised for R1 was $\Sigma[w(|F_o| - |F_c|)]$. The SAINT³⁴ and SHELXTL³⁵ PC packages were used for data collection, reduction, structure solution and refinement.

CCDC reference numbers 244462-244466.

See http://www.rsc.org/suppdata/dt/b4/b410619a/ for crystallographic data in CIF or other electronic format.

Syntheses

[(AuCl)₂(μ -diphos)]·CH₂Cl₂ [diphos = dpephos (1), xantphos (2), dbfphos (3)]. To a solution of the corresponding diphosphine [0.4 g, 0.742 mmol (1), 0.3 g, 0.519 mmol (2); 0.4 g, 0.743 mmol (3)] in 15 cm³ of dichloromethane, two equivalents of [AuCl(tht)] were added. The resulting solution was stirred at room temperature under an atmosphere of dinitrogen for 2 h, and then concentrated to dryness. To the residue, a mixture of acetone–ether (1:15, *ca.* 15 cm³) was added, and the resulting suspension filtered. The resulting white solid was air-dried.

1 (0.58 g, 72%) (Found: C, 40.63; H, 2.40. $C_{37}H_{30}Au_2Cl_4OP_2$ requires C, 40.83; H, 2.78%); v_{max}/cm^{-1} (AuCl) 320, 311 (Nujol); δ_H (300 MHz) 7.60–7.09 (26 H, m, Ph), 6.71 [2 H, ddd, ³*J*(HH) = 7.7 Hz, ⁴*J*(HH) = 1.5 Hz, ³*J*(HP) = 11.9 Hz, H(3)], 5.30 (2 H, s, CH₂Cl₂); δ_P (121.5 MHz) 21.7 (s); δ_C (75.4 MHz) 158.9 [2 C, d, *J*(CP) = 6 Hz, CO], 135.0 [4 C, d, *J*(CP) = 14 Hz, o-C₆H₃P], 134.2 (2 C, s, C₆H₄OP), 133.9 [2 C, d, *J*(CP) = 6 Hz C₆H₄OP], 133.1 [4 C, d, *J*(CP) = 14 Hz, *o*-C₆H₅P], 132.1 (2 C, s, *p*-C₆H₅P), 131.1 (2 C, s, *p*-C₆H₅P), 129.7 [4 C, d, *J*(CP) = 12 Hz, *m*-C₆H₅P], 129.2 [4 C, d, *J*(CP) = 12 Hz, *m*-C₆H₅P], 128.3 [2 C, d, ¹*J*(CP) = 64 Hz, *i*-C₆H₅P], 127.0 [2 C, d, ¹*J*(CP) = 65 Hz, *i*-C₆H₅P], 125.1 [2 C, d, *J*(CP) = 9 Hz, C₆H₄OP], 120.2 [2 C, d, *J*(CP) = 5 Hz, C₆H₄OP], 119.1 [2 C, d, ¹*J*(CP) = 62 Hz, *i*-C₆H₄OP], 53.4 (s, CH₂Cl₂).

2 (0.46 g, 79%) (Found: C, 42.86; H, 3.02. $C_{40}H_{34}Au_2Cl_4OP_2$ requires C, 42.58; H, 3.03%); v_{max}/cm^{-1} (AuCl) 318 (Nujol); δ_H (300 MHz) 7.62 [2 H, dd, ${}^{3}J$ (HH) = 7.7 Hz, ${}^{4}J$ (HH) = 1.2 Hz, H(1,8)], 7.44–7.25 (20 H, m, Ph), 7.06 [2 H, apparent t, ${}^{3}J$ (HH) = 7.7 Hz, H(2,7)], 6.44 [2 H, ddd, ${}^{3}J$ (HH) = 7.7 Hz, ${}^{4}J$ (HH) = 1.3 Hz, ${}^{3}J$ (HP) = 12.7 Hz, H(3,6)], 5.30 (2 H, s, CH₂Cl₂), 1.69 (6 H, s, 2 CH₃); δ_P (121.5 MHz) 24.0 (s); δ_C (125.7 MHz) 152.6 (2 C, s, CO), 134.4 (8 C, m, *o*-C₆H₃P), 133.1 (2 C, s, C₆H₃OP), 131.5 (4 C, s, *p*-C₆H₃P), 131.3 (2 C, s, C₆H₃OP), 129.6 (2 C, s, C₆H₃OP), 129.5 (2 C, s, C₆H₃OP), 128.9 (8 C, m, *m*-C₆H₅P), 124.4 (4 C, apparent t, *i*-C₆H₅P), 116.4 [2 C, d, ${}^{1}J$ (CP) = 58 Hz, *i*-C₆H₃OP], 34.6 (s, CMe₂), 31.6 (2 C, s, 2 CH₃), 53.4 (s, CH₂Cl₂).

3 (0.73 g, 91%) (Found: C, 40.79; H, 2.42. $C_{37}H_{28}Au_2Cl_4OP_2$ requires C, 40.90; H, 2.59%); ν_{max}/cm^{-1} (AuCl) 332, 321 (Nujol); δ_H (300 MHz) 8.17 [2 H, d, 3J (HH) = 7.8 Hz, H(1,9)], 7.61–7.46 (20 H, m, Ph), 7.41 [2 H, apparent t, 3J (HH) = 7.7 Hz, H(2,8)], 7.06 [2 H, dd, 3J (HH) = 7.7 Hz, 3J (HP) = 13.4, H(3,7)], 5.30 (2 H, s, CH₂Cl₂); δ_P (121.5 MHz) 25.2 (s); δ_C (125.7 MHz) 156.2 (2 C, s, CO), 134.3 [8 C, d, J(CP) = 15 Hz, $o - C_6H_5P$), 132.9 [2 C, d, J(CP) = 8 Hz, C_6H_3OP], 132.7 (4 C, s, $p - C_6H_5P$), 129.7 [8 C, d, J(CP) = 12 Hz, $m - C_6H_5P$), 127.2 [4 C, d, 1J (CP) = 64 Hz, $i - C_6H_3P$), 124.8 (2 C, s, C_6H_3OP], 113.6 [2 C, d, 1J (CP) = 58 Hz, $i - C_6H_3OP$], 53.4 (s, CH₂Cl₂). [Au(diphos)₂][SbF₆] [diphos = dpephos (4), xantphos (5), dbfphos (6)]. To a suspension of 1, 2 or 3 (0.075 mmol) in chloroform (15 cm³) was added the corresponding diphosphine (0.250 mmol). After stirring the resulting mixture for 0.5 h, a solution of NaSbF₆ (0.039 g, 0.149 mmol) in acetone (*ca.* 1 cm³) was added. After 0.5 h, the solvent was evaporated to dryness and dichloromethane (*ca.* 5 cm³) added to the resulting white residue. The suspension was filtered over Celite and the filtrate concentrated to dryness to give the product as a white (4, 5) or a yellow (6) solid. Complex 5 was washed with acetone–diethyl ether (1:15, *ca.* 5 cm³).

4 (0.08 g, 72%) (Found: C, 57.62; H, 3.80. $C_{72}H_{56}AuF_6O_2P_4Sb$ requires C, 57.27; H, 3.74%); δ_H (300 MHz) 7.91–6.65 (52 H, m, Ph), 6.28 [4 H, d, *J*(HH or HP) = 8 Hz, H(3)]; δ_P (121.5 MHz) 18.2 (s); *m/z* 1274 (M⁺).

5 (0.07 g, 58%) (Found: C, 58.74; H, 4.09. $C_{78}H_{64}AuF_6O_2P_4Sb$ requires C, 58.92; H, 4.06%); δ_H (500 MHz, 300 K) 7.51–6.73 (52 H, m, Ph), 1.59 (12 H, br s, 4 CH₃), (213 K) 7.55–6.15 (52 H, m, Ph), 1.83 (6 H, s, 2 CH₃) 0.88 (6 H, s, 2 CH₃); δ_P (202.5 MHz, 300 K) 5.8 (br s), (213 K) 5.5, 0.5 [4 P, AA'BB', *J*(AA') = 22.2 Hz, *J*(AB) = 24.2 Hz, *J*(AB') = 13.3 Hz, *J*(BB') = 18.5 Hz]; *m*/z 1354 (M⁺).

6 (0.11 g, 98%) (Found: C, 58.15; H, 3.87. $C_{72}H_{52}AuF_6O_2P_4Sb$ requires C, 57.43; H, 3.48%); δ_H (500 MHz) 8.06 [4 H, d, ${}^{3}J(HH) = 8$ Hz, H(1,9)], 7.35–7.12 (44 H, m, Ph), 6.99 [4 H, apparent t, J(HH or HP) = 8 Hz, H(3,7)]; δ_P (121.5 MHz, 300 K) 6.5 (br s), (202.5 MHz, 213 K) 34.1 (br s), -19.8 (br s); m/z 1270 (M⁺).

Acknowledgements

We are grateful to the EPSRC and the McClay Trust for their financial support, including PhD grants for H. de la R. and A. P.-A., respectively.

References

- V. W.-W Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, 28, 323;
 V. W.-W Yam, C.-L. Chan, C.-K. Li and K. M.-C. Wong, *Coord. Chem. Rev.*, 2001, 216–217, 173;
 W. E. van Zyl, J. M. López de Luzuriaga and J. P. Fackler, Jr., *J. Mol. Struct.*, 2000, 516, 99;
 P. Li, B. Ahrens, K.-H. Choi, M. S. Khan, P. R. Raithby, P. J. Wilson and W.-Y. Wong, *CrystEngComm*, 2002, 4, 405.
- 2 Z. Assefa, B. G. McBurnett, R. J. Staples, J. P. Fackler Jr., B. Assmann, K. Angermaier and H. Schmidbaur, *Inorg. Chem.*, 1995, **34**, 75; J. C. Vickery, M. M. Olmstead, E. Y. Fung and A. L. Balch, *Angew. Chem., Int. Ed. Eng.*, 1997, **36**, 1179; S. S. Tang, C.-P. Chang, I. J. B. Lin, L.-S. Liou and J.-C. Wang, *Inorg. Chem.*, 1997, **36**, 2294; B.-C. Tzeng, C.-K. Chan, K.-K. Cheung, C.-M. Che and S.-M. Peng, *Chem. Commun.*, 1997, 135.
- 3 W. B. Jones, J. Yan, R. Narayanaswamy, M. A. Young, R. C. Elder, A. E. Bruce and M. R. M. Bruce, *Inorg. Chem.*, 1995, 34, 1996.
- 4 J. M. Forward, J. P. Fackler, Jr. and Z. Assefa, in *Optoelectronic Properties of Inorganic Compounds*, ed. M. Roundhill and J. P. Fackler, Jr., Plenum Press, New York, 1999, ch. 6, pp. 195–229, and references therein.
- 5 H. Xiao, Y.-X. Weng, W.-T. Wong, T. C. W. Mak and C.-M. Che, J. Chem. Soc., Dalton Trans., 1997, 221.
- 6 A. Vogler and H. Kunkely, Coord. Chem. Rev., 2001, 219-221, 489.
- 7 M. Kranenburg, Y. E. M. van der Burgt, P. C. Kramer and P. W. N. M. van Leeuwen, *Organometallics*, 1995, **14**, 3081.
- 8 M. W. Haenel, D. Jakubik, E. Rothenberger and G. Schroth, *Chem. Ber.*, 1991, **124**, 1705.
- 9 E. M. Vogl, J. Bruckmann, C. Krüger and M. W. Haenel, J. Organomet. Chem., 1996, **520**, 249.
- 10 S. Hillebrand, J. Bruckmann, C. Krüger and M. W. Haenel, *Tetrahedron Lett.*, 1995, 36, 75.
- 11 V. Pawlowski, H. Kunkely and A. Vogler, *Inorg. Chim. Acta*, 2004, 357, 1309.
- 12 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, J. Chem. Soc., Dalton Trans., 1984, 969.
- 13 S. J. Berners-Price and P. J. Sadler, *Inorg. Chem.*, 1986, 25, 3822.
- 14 S. J. Berners-Price, R. J. Bowen, T. W. Hambley and P. C. Healy, J. Chem. Soc., Dalton Trans., 1999, 1337.
- 15 Ortep representations have been done using Ortep-3 for Windows (L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565). Ellipsoids are drawn at 30% probability.

- 16 T. V. Baukova, N. A. Oleinikove, D. A. Lemenovskii and L. G. Kuz'mina, *Russ. Chem. Bull.*, 1994, 43, 681.
- 17 W. J. Hunks, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2000, **39**, 2699.
- 18 R. Usón, A. Laguna, J. Vicente, J. García, P. G. Jones and G. M. Sheldrich, J. Chem. Soc., Dalton Trans., 1981, 655.
- 19 P. A. Bates and J. M. Walters, *Inorg. Chim. Acta*, 1991, **81**, 151; C. S. W. Harker, E. R. T. Tiekink and M. W. Whitehouse, *Inorg. Chim. Acta*, 1991, **181**, 23.
- 20 V. W.-W Yam, C.-L. Chan, S. W.-K. Choi, K. M.-C. Wong, E. C.-C. Cheng, S.-C. Yu, P.-K. Ng, W.-K. Chan and K.-K. Cheung, *Chem. Commun.*, 2000, 53.
- 21 C. D. Delfs, H. J. Kitto, R. Stranger, G. F. Swiegers, B. Wild, A. C. Willis and G. J. Wilson, *Inorg. Chem.*, 2003, **42**, 4469.
- 22 A. Pintado, H. de la Riva, M. Nieuwhuyzen, P. R. Raithby and M. C. Lagunas, unpublished work.
- 23 J.-A. van den Berg and K. R. Seddon, *Cryst. Growth Des.*, 2003, 3, 643.
 24 B. Ahrens, P. G. Jones and A. K. Fischer, *Eur. J. Inorg. Chem.*, 1999,
- 1103; M. Freytag, P. G. Jones, B. Ahrens and A. K. Fischer, *New J. Chem.*, 1999, **23**, 1137; M. Freytag and P. G. Jones, *Chem. Commun.*, 2000, 277.
- 25 S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, 41, 405.

- 26 D. J. Fife, K. W. Morse and W. M. Moore, J. Photochem., 1984, 24, 249.
- 27 C. Kutal, Coord. Chem. Rev., 1990, 99, 213.
- 28 A. Vogler and H. Kunkely, Coord. Chem. Rev., 2002, 230, 243.
- 29 B. Weissbart, D. V. Toronto, A. L. Balch and D. S. Tinti, *Inorg. Chem.*, 1996, **35**, 2490; L. J. Larson, E. M. McCauley, B. Weissbart and D. S. Tinti, *J. Phys. Chem.*, 1995, **99**, 7218.
- 30 Bruker, SMART, version 5.054, Bruker AXS Inc., Madison, Wisconsin, USA, 1998; Bruker, SAINT, version 5.00, Bruker AXS Inc., Madison, WI, 1997; Bruker, SAINT, version 6.36a, Bruker AXS Inc., Madison, Wisconsin, USA, 2002; G. M. Sheldrick, SADABS, Program for Siemens Area Detector Absorption Correction, University of Göttingen, 1996.
- 31 SHELXL-97, G. M. Sheldrick, programme for crystal structure refinement, University of Göttingen, 1997.
- 32 ROTAX, R. I. Cooper, R. O. Gould, S. Parsons and D. J. Watkin, J. Appl. Crystallogr., 2002, 35, 168.
- 33 H. D. Flack, Acta Crystallogr., Sect. A, 1983, 39, 876.
- 34 SMART Software Reference Manual, version 5.054, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998.
 35 G. M. Sheldrick, SHELXTL, An Integrated System for Data
- 35 G. M. Sheldrick, SHELXTL, An Integrated System for Data Collection, Processing, Structure Solution and Refinement, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998.