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Structural studies of two-coordinate complexes of tris(2-methoxylphenyl)phosphine and tris(4-methoxyphenyl)phosphine with gold(I) halides

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Abstract

A series of five gold(I) halide complexes with the two isomeric methoxy-substituted triarylphosphines, tris(2-methoxyphenyl)phosphine [P(oanis)$_3$], [AuP(oanis)$_3$X] [for X = Cl, (**1**); X = Br, (**2**) and X = I, (**3**)] and tris(4-methoxyphenyl)phosphine [P(panis)$_3$], [AuP(panis)$_3$X] [for X = Br (**4**) and X = I (**5**)] have been synthesized and characterized by single crystal X-ray diffraction and solution ^{31}P{^{1}H} NMR spectroscopy. The structure determinations confirm the expected presence of linear two-coordination about the gold centres in all five complexes with bond distance and angle data typical of this type of compound [Au–P, 2.239(2)–2.259(3) Å; Au–Cl, 2.294(2) Å; Au–Br, 2.385(2)–2.402(2) Å; Au–I, 2.546(1)–2.554(1) Å; P–Au–X; 175.3(1)–180°]. All analogues except the iodo complex **5** crystallize with one complex molecule in the crystallographic asymmetric unit. The bromo and iodo complexes **2** and **3** constitute a trigonal isomorphous set while the bromo complex **4** is also isomorphous with the previously determined chloro complex [AuP(panis)$_3$Cl]. The 2-methoxy analogues are stabilized by significant methoxy-O···Au interactions.

Keywords: Gold(I) phosphine halides; Crystal structures; Metal complexes

1. Introduction

The linear two-coordinate complexes of the gold(I) halides with the tertiary-substituted arylphosphines of the type [AuP(Ar)$_3$X] (where X = Cl, Br, I) have received considerable attention with respect to the steric influence of substituent groups on the aryl groups of the phosphine and the variable electron donor properties of the chloride, bromide and iodide anions. To date a large number of crystal structures of this type of compound have been published, for example [1–20]. It has been observed that steric factors exert the most important influence on the packing environment about the Au centres, with possible Au···Au interactions only being reasonable in gold(I) halide complexes with small alkyl substituted phosphines, e.g. [P(Me)$_3$] and [P(Et)$_3$]. Thus among the total set of gold complexes of this type, only the isomorphous pair [AuP(Me)$_3$Cl] [17–19] and [AuP(Me)$_3$Br] [17–19] and [AuP(Et)$_3$Cl] [20] have short Au···Au interactions, varying from 3.27–3.98 Å. It was therefore very unusual to encounter in our previous series of compounds [6] a sterically encumbered ring-substituted triarylphosphinegold(I) complex, that with tris(4-methylphenyl)phosphine, [AuP(ptol)$_3$Cl] which had similar Au···Au interactions [3.375(1) Å], considering that the corresponding unsubstituted phosphine complex [AuP(Ph)$_3$Cl] [1–3] had none. Furthermore, a feature of that entire series of compounds was the common occurrence of isomorphous crystal sets among the halide complexes particularly with the bromide and iodide members, although isomorphous series which include all three halide homologues are known, e.g. with [P(Ph)$_3$] [1,2,19] and [P(otol)$_3$] [otol = tris(2-methylphenyl)phosphine] [6]. In addition, there is a high incidence of examples in which

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there are two complex molecules in the crystallographic asymmetric unit, a phenomenon which appears to be a consequence of the conformational variability possible particularly in the aryl substituents on the phosphine ligand. This factor may be controlled to some extent by energetics, e.g. method of synthesis together with the conditions and solvents employed both in the synthesis and in recrystallization, e.g. [AuP(otol)$_3$Cl] gives a monoclinic modification (the α-polymorph) from ethanol [5] while the orthorhombic β-polymorph [6] is obtained from dimethylformamide, and a similar dimorphism is observed with the isomeric [AuP(p-tol)$_3$Cl] set [6,7].

It has also been noted that the methoxy oxygen atoms in tris(2,4,6-trimethoxylphenyl)phosphine [P(tmp)$_3$] affect both the basicity of the ligand and the gold environment in the [AuP(tmp)$_3$X] complexes [3,12]. Previously, it was also observed that the presence of *ortho*-methyl substituents in the [P(otol)$_3$] complexes gave Au···H(methyl) interactions, resulting in regularity in the disposition of the phosphine phenyl rings [6]. We therefore were interested in determining the effect of a single methoxy substituent on both the intramolecular interactions (2-methoxy-O···Au) as well as upon intermolecular associations and crystal packing. With the unsymmetrically substituted complexes chloro(2-hydroxyphenyl)diphenylphosphinegold(I) [13], and iodo(2-aminophenyl)diphenylphosphinegold(I) [14], both the hydroxy oxygen and the amino proton give significant short Au···O [3.160(7) Å] and Au···N [3.61(3) Å] interactions. This effect is not present in the analogous but sterically demanding *ortho*-substituted phosphine complex, chloro[(2-trimethylsiloxyphenyl)diphenylphosphine]gold(I) [13] where no substituent group interaction is found. Similar steric effects are seen with the 2-iodo-substituted analogues iodo(2-iodophenyl)diphenylphosphinegold(I) [15] and iodo(2-iodo-3-methylphenyl)diphenylphosphinegold(I) [16].

We therefore set out to look at the structural effects of both *ortho*- and *para*-methoxy phosphine substitution on a series of gold(I) complexes. Reported here is the synthesis, the X-ray structures and solution $^{31}P\{^1H\}$ NMR spectra of the series of five halo-gold(I) complexes with the *ortho*- and *para*-anisyl-substituted phosphines, tris(2-methoxyphenyl)phosphine [P(oanis)$_3$], [AuP(oanis)$_3$X] [Series A: compounds **1**–**3**] and tris(4-methoxyphenyl)phosphine [P(panis)$_3$], [AuP(panis)$_3$X] [Series B: compounds **4**, **5**] (X = Br, I). The structure of the Series B chloro analogue [AuP(panis)$_3$Cl] has been previously reported [11].

2. Experimental

2.1. Preparation of compounds

The complexes [AuP(oanis)$_3$X] [Series A: for X = Cl (**1**); X = Br (**2**); X = I (**3**)] and [AuP(panis)$_3$X] [Series B: for X = Br (**4**); X = I (**5**)] were synthesized using a previously described procedure [6] by the interaction of equimolar quantities of [Bu$_4$N][AuX$_2$] (0.50 mmol; Cl, 0.255 g; Br, 0.300 g; I, 0.346 g) and the appropriate phosphine (0.50 mmol, 0.152 g) dissolved in 5 mL of dimethylformamide at ca. 50 °C. The resultant solutions were cooled to room temperature and allowed to stand for several days to yield well-formed colourless crystals of the expected complexes. Yields were 96%, 93%, 96%, 95% and 88% for **1**–**5**, respectively. Melting points and ν(Au–X) stretching frequencies obtained from FT raman data for **1**–**5** are listed in Table 1. No chemical analyses were completed.

Just as for the analogous Au(I) complex series with the isomeric *ortho*- and *para*-tolylphosphines [6,24], the chloride and bromide complexes **1**, **2** and **4** but not the iodide complexes **3** and **5** may be synthesized using either potentiostatic methods or galvanostatic methods.

2.2. Spectroscopy

Solution $^{31}P\{^1H\}$ NMR spectra were recorded in CDCl$_3$ solution on a Varian Gemini-2000 spectrometer at 80.86 MHz with 256 transients collected. Spectra were referenced internally to 85% H$_3$PO$_4$.

2.3. X-ray structure determinations

X-ray crystal data indicated that the Series A bromide and iodide complexes with [P(oanis)$_3$] (**2** and **3**) appeared to comprise a trigonal isomorphous set. Similarly, in the Series B set the bromo complex with [P(panis)$_3$] (**4**) had cell parameters and space group which indicated that it was isomorphous with the previously reported chloro analogue [11]. Both of these isomorphous series were confirmed in the structure analyses. With the iodo complex of [P(panis)$_3$] (**5**), although having four molecules in a centrosymmetric triclinic cell could not be transformed into a higher symmetry cell, and this was subsequently justified in the analysis with the presence of two conformationally dissimilar molecules in the asymmetric unit.

Unique data sets for all compounds were measured at 297(2) K within the specified $2\theta_{max}$ limit using a Rigaku AFC 7R four-circle diffractometer [θ–2θ scan mode, monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å), from a 12 kW rotating anode source] yielding N independent reflections, N_0 with $I > 3.0\sigma(I)$ (compounds **1**, **4** and **5**) or $I > 2.0\sigma(I)$ (compounds **2** and **3**) being considered 'observed' and used in the expression of the conventional refinement residual R. Crystal decay was negligible in most cases [1.5% maximum in **5**] and in the worst cases was allowed for by using a linear correction. The structures were solved by direct methods and refined by full-matrix least-squares refinement {on F for **1**, **4** and **5** or on F^2 for **2** and **3** (the latter using SHELX-97) [25]} after semi-empirical absorption corrections based on ψ-scans. Anisotropic thermal parameters were refined for all non-hydrogen atoms while $(x, y, z, U_{iso})_H$ were included and constrained at estimated values. Neutral atom complex scattering factors were employed while computation used the TeXsan

Table 1
Crystal and physical data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Compound identity	[AuP(oanis)$_3$Cl]	[AuP(oanis)$_3$Br]	[AuP(oanis)$_3$I]	[AuP(panis)$_3$Br]	[AuP(panis)$_3$I]
Formula	$C_{21}H_{21}AuClO_3P$	$C_{21}H_{21}AuBrO_3P$	$C_{21}H_{21}AuIO_3P$	$C_{21}H_{21}AuBrO_3P$	$C_{21}H_{21}AuIO_3P$
FW	584.79	629.24	676.24	629.24	676.24
Melting point (°C)	239–241	242–245	242	200–203	194–196
ν(Au–X) (cm^{-1})	330	231	149	231	150
CCDC reference	211 590	211 591	211 592	211 593	211 594
Temperature (K)	297(2)	297(2)	297(2)	297(2)	297(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	trigonal	trigonal	monoclinic	triclinic
Space group	$P\bar{1}$	$R\bar{3}$	$R\bar{3}$	$C2/c$	$P\bar{1}$
a (Å)	10.384(2)	13.509(3)	13.6159(6)	14.337(5)	10.778(2)
b (Å)	12.309(3)	13.509(3)	13.6159(6)	14.770(7)	20.163(2)
c (Å)	8.599(2)	20.027(7)	20.367(2)	20.511(5)	10.623(2)
α (°)	92.14(2)	90	90	90	95.45(1)
β (°)	101.29(1)	90	90	101.72(2)	95.60(1)
γ (°)	96.46(2)	120	120	90	101.600(9)
V (Å^3)	1069.0(4)	3165.0(9)	3270.0(4)	4253(3)	2235.0(6)
Z	2	6	6	8	4
D_x (Mg m^{-3})	1.817	1.981	2.060	1.965	2.010
μ (Mo Kα) (mm^{-1})	7.12	8.99	8.26	8.89	8.08
Crystal size (mm^3)	0.25 × 0.25 × 0.10	0.25 × 0.20 × 0.20	0.27 × 0.20 × 0.06	0.25 × 0.20 × 0.15	0.30 × 0.25 × 0.15
Crystal decay (%)	0.06	0.18	0.96	0.43	1.53
N (total)	4011	1416	1416	10 336	8323
N (unique)	3781	1285	1291	4904	7865
N_0 [$I > n(I)$]	3180 ($n = 3.0$)	1245 ($n = 2.0$)	1018 ($n = 2.0$)	2505 ($n = 3.0$)	3865 ($n = 3.0$)
$2\theta_{max}$ (°)	50	50	50	55	50
R[a]	0.050	0.032	0.026	0.037	0.034
R_w[b], wR_2[c]	0.078[b]	0.084[c]	0.074[c]	0.041[b]	0.032[b]

[a] $R = (\sum|F_o| - |F_c|)/\sum|F_o|$.
[b] $R_w = \{\sum w(F_o - F_c)^2/\sum w(F_o)^2\}^{1/2}$, $\{w^* = [\sigma^2(F_o)]^{-1}\}$.
[c] $wR_2 = \{\sum w[(F_o^2 - F_c^2)]^2/\sum[w(F_o^2)^2]\}^{1/2}\}$, $\{w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ {where $P = [(\max F_o^2, 0) + 2(F_c^2)]/3\}$.

crystallographic software package of Molecular Structure Corporation [26].

3. Results and discussion

3.1. Structural chemistry

The series of five substituted triarylphosphine gold(I) halide complexes of the type [AuP(Ar)$_3$X] with isomeric tris(2-methoxyphenyl)phosphine [P(oanis)$_3$] and tris(4-methoxyphenyl)phosphine [P(panis)$_3$] have been characterized by X-ray diffraction and $^{31}P\{^1H\}$ NMR spectroscopy. Selected interatomic bond lengths and interbond angles for [AuP(oanis)$_3$X] (for X = Cl, Br and I) (Series A: compounds **1**–**3**) and [AuP(panis)$_3$X] (for X = Cl, Br and I) (Series B: compounds **4** and **5**) together with comparative data for the analogous [AuP(Ph)$_3$X] [1–3] and some mono-*ortho*-substituted phenyl phosphine complexes of the type [AuP(YPh)(Ph)$_2$X] (where Y = an interactive substituent, e.g. –OH, –NH$_2$), –OSi(Me)$_3$ [13,14], are given in Table 2.

All complexes have the expected linear two-coordination about the gold centres (see Figs. 1, 3, 5 and 6) with the mean P–Au–X bond angle [177.8°]. The largest deviation from linearity in the overall series of complexes of this type occurs with those members where packing allows short intermolecular Au···Au interactions, e.g. with the rare tris(4-methyltolyl)phosphine complex [AuP(ptol)$_3$Cl] [6] [Au···Au, 3.375(1) Å; P–Au–Cl, 173.2(2)°]. No examples of this type are found in the present Series A or B complexes. The mean Au–P and Au–X bond lengths are 2.25(1) Å (Au–P), 2.292(5) Å (Au–Cl), 2.394(5) Å (Au–Br) and 2.552(5) Å (Au–I) comparing with the series mean of 2.29(2), 2.29(2), 2.41(1) and 2.56(1) Å, respectively. With the Series A complexes (**1**–**3**), the *ortho*-substituted methoxy groups influence the conformational features of the substituted phosphine ligand. The triclinic chloro complex **1** [AuP(oanis)$_3$Cl] (Figs. 1 and 2), having one molecule in the asymmetric unit is significantly different from the bromo and iodo analogues (**2** and **3**) which constitute a trigonal isomorphous set, and have molecular C_3 symmetry coincident with crystallographic symmetry (Figs. 3 and 4), with the P–Au–X moiety lying on the three-fold axis and with the three methoxy groups in general positions. This implies that all methoxy groups adopt identical conformations in a perfect propeller conformation. It should be noted that although complexes **2** and **3** are isomorphous, the individual complex molecules in each have subtle conformational differences, one being right handed the other left [Fig. 1a and b]. This results from a simple rotation of the phenyl ring about the P1–C1 bond vector and is not a chiral relationship. In addition, the methoxy

Table 2
Important geometrical features [bond distances (Å) and angles (°)] for [AuP(anis)$_3$X] complexes (**1**–**5**), compared with [AuPPh$_3$X], [AuP(tmpp)$_3$X] (X = Cl, Br, I) and unsymmetrically substituted examples of the type [AuP(YPh)(Ph)$_2$I] (Y = interactive substituent group)

Compound	Au–P	Au–X	P–Au–X	τ_1[a]	τ_2	τ_3	Reference
[AuP(Ph)$_3$Cl]	2.235(3)	2.279(3)	179.6(1)	39(1)	58(1)	30(1)	[1]
[AuP(Ph)$_3$Br]	2.252(6)	2.407(6)	179.4(1)	44(2)	55(2)	33(2)	[2]
[AuP(Ph)$_3$I]	2.2499(2)	2.553(1)	175.65(9)	41(1)	58(1)	32(1)	[19]
[AuP(tmpp)$_3$Cl]	2.253(5)	2.303(6)	176.0(2)	−46(1)	−55(1)	−12(1)	[3]
[AuP(tmpp)$_3$Br]	2.255(5)	2.413(2)	175.9(1)	−48(1)	−55(1)	−16(1)	[3]
[AuP(tmpp)$_3$I]	2.239(7)	2.586(2)	177.7(2)	51(2)	54(2)	18(3)	[3]
[AuP(2-OHPh)(Ph)$_2$Cl][b]	2.226(2)	2.285(2)	176.8(1)	−42(1)	−56(1)	−41(1)	[13]
[AuP(2-OSiMe$_3$Ph)(Ph)$_2$Cl][c]	2.2295(8)	2.285(1)	177.3(1)	54.8(3)	43.3(3)	45.7(3)	[13]
[AuP(2-NH$_2$Ph)(Ph)$_2$I][d]	2.235(3)	2.553(1)	178.5(1)	41(1)	41(1)	41(1)	[14]
[AuP(oanis)$_3$Cl] (**1α**)	2.250(4)	2.294(5)	176.6(2)	56.3(15)	55.0(18)	−1.4(16)	this work
[AuP(oanis)$_3$Br] (**2β**)	2.244(3)	2.402(2)	180.0(6)	−46.3(8)	−46.3(8)	−46.3(8)	this work
[AuP(oanis)$_3$I] (**3β**)	2.259(3)	2.558(1)	180.0(1)	46.9(6)	46.9(6)	46.9(6)	this work
[AuP(panis)$_3$Cl]· · · (**α**)	2.235(2)	2.289(2)	176.1(1)	−29(1)	−62(1)	−3(1)	[11]
[AuP(panis)$_3$Br] (**4α**)	2.239(2)	2.385(2)	175.3(1)	−29.9(8)	−62.7(8)	−3.1(7)	this work
[AuP(panis)$_3$I] (**5β**$_1$)	2.259(3)	2.553(1)	176.9(1)	−4(1)	18(1)	80(1)	this work
[AuP(panis)$_3$I] (**5β**$_2$)	2.254(3)	2.546(1)	177.1(1)	−38(1)	−21(1)	−43(1)	

τ_m is defined by the torsion angle Au–P–C(*m*1)–C(*m*2).

[a] **β**$_1$ and **β**$_2$ represent the two independent molecules in the crystallographic repeating unit.

[b] [P(2-OHPh)(Ph)$_2$] = (2-hydroxyphenyl)diphenylphosphine.

[c] [P(2-OSiMe3Ph)(Ph)$_2$Cl] = (2-trimethylsiloxyphenyl)diphenylphosphine.

[d] [P(2-NH$_2$Ph)(Ph)$_2$] = (2-aminophenyl)diphenylphosphine.

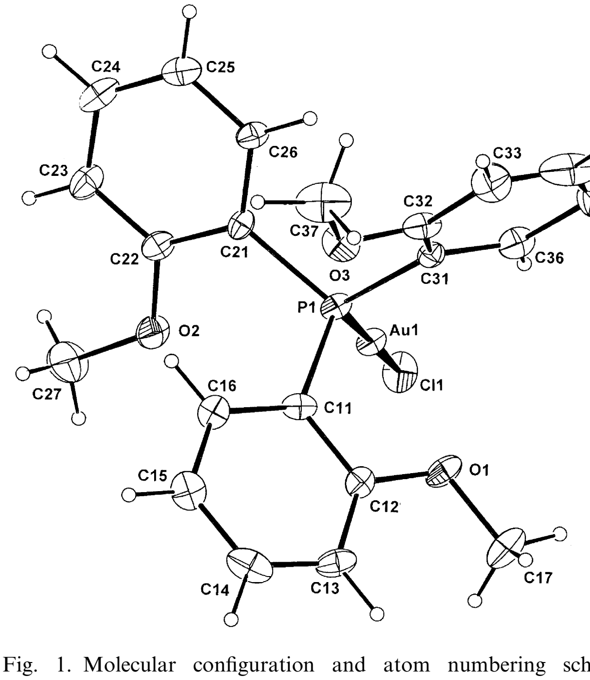

Fig. 1. Molecular configuration and atom numbering scheme for [AuP(oanis)$_3$Cl] (**1**) with non-hydrogen atoms shown as 30% probability ellipsoids [27].

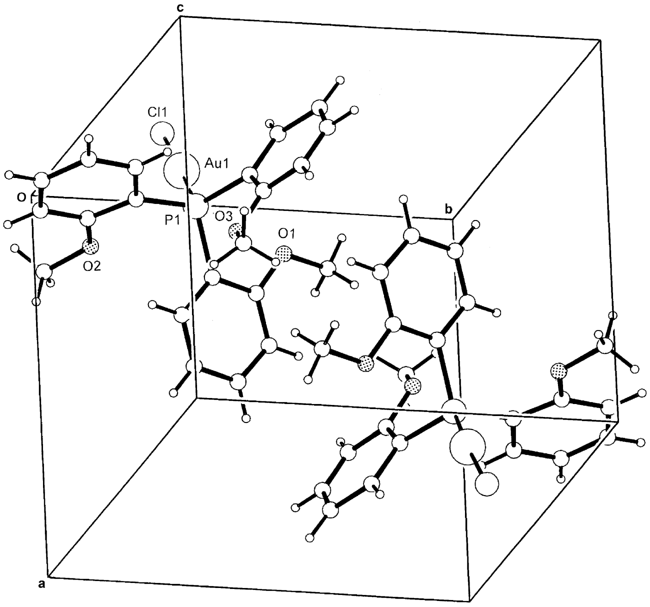

Fig. 2. Perspective view of the packing of **1** in the unit cell viewed down the approximate *c*-axial direction.

groups are essentially coplanar with the phenyl rings [torsion angle C1–C2–O2–C7, 178.1(8)° (**2**) and −177.2(7)° (**3**)] and have all three oxygen atoms directed towards the gold centre [Au· · ·O, 3.250(6) Å (**2**) and 3.239(7) Å (**3**)]. In contrast, complex **1** has two methoxy groups directed towards and one away from the gold centre [torsion angles ($\tau_1 - \tau_3$), 56°, 55°, 178(1)°]. The Au· · ·O distances for these *cis*-related methoxy groups are 3.27(1) and 3.36(1) Å indicating moderate interaction. Stronger interaction is certainly found with the (2-hydroxyphenyl)diphenylphosphinegold(I) chloride complex [13] where the single hydroxy group interacts with Au [Au· · ·O, 3.160(7) Å] and has the hydroxy-H directed away from Au. The more sterically demanding (2-trimethylsiloxyphenyl)diphenylphosphine ligand in the gold(I) chloride complex [13] has a somewhat longer but still significant Au· · ·O contact [3.353(2) Å]. With the corresponding tris(2,4,6-trimethoxy)phosphine analogues (Cl, Br, I) [3,12], one *o*-methoxy-O of each ring has an interactive Au· · ·O contact [2.92–3.14(1) Å (Cl); 2.96–3.13(1) Å (Br); 3.01–3.10(1) Å

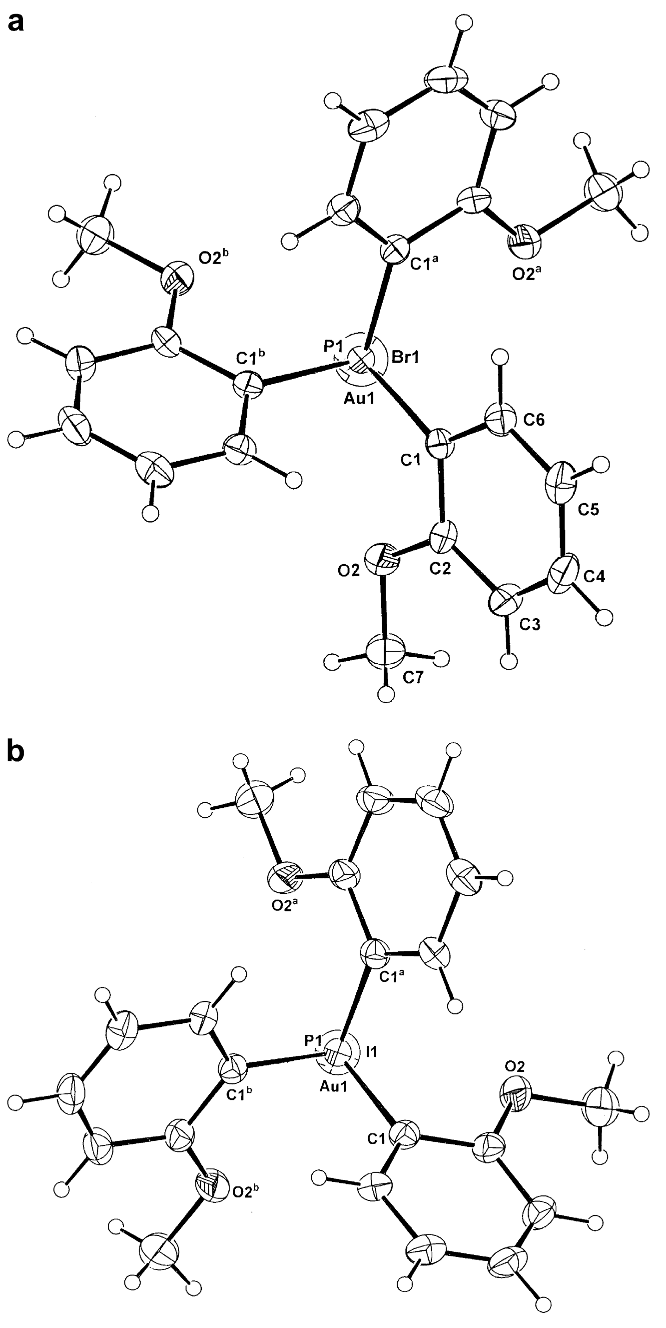

Fig. 3. Molecular configuration for the molecules of the isomorphous complexes (a) [AuP(oanis)$_3$Br] (**2**), and (b) [AuP(oanis)$_3$I] (**3**) viewed down molecular the C_3 axis of each, showing the subtle conformational difference between the two.

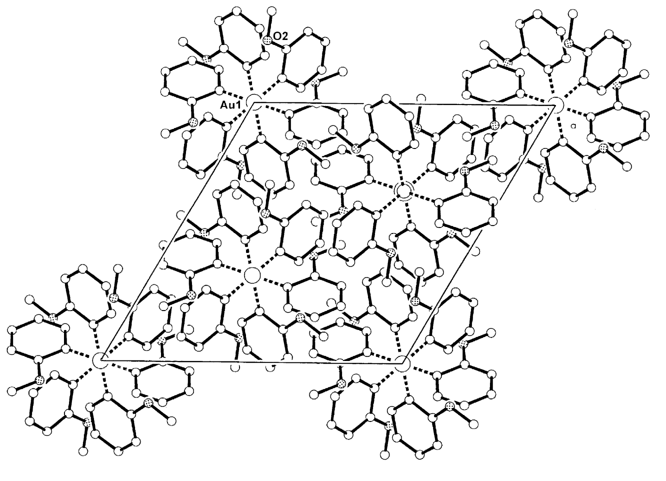

Fig. 4. Packing of the molecules of **2** in the unit cell viewed down the *c*-axial direction.

(I)]. The tris(*o*-tolyl)phosphine examples [6] in which the methyl-H$\cdots$Au interactions are important in influencing conformation, have a mean Au$\cdots$C distance of 3.44(1) Å. The effect of this conformational control can be gauged by inspecting the comparative torsion angles ($\tau_1 - \tau_3$) [corresponding to the angle Au–P–C(*m*1)–C(*m*2)] (Table 2). In examples having interaction, the angles are more regular, e.g. a 41–59° range for the [AuP(otol)$_3$X] (X = Cl, Br and I) series cf. 17–57° for the [AuP(ptol)$_3$X] (X = Cl, Br and I series) [6]. With the previous series the values were usually ordered small–large–small as is the case with the parent [P(Ph)$_3$] [39°, 58°, 30° (X = Cl); 44°, 55°, 33° (X = Br); 41°, 58°, 32° (X = I) [1,2,19]. With the series (**1**–**5**) considered here, the same trend is observed, with values of 56.3(15)°, 55.0(18)°, −1.4(16)° for **1**, where only two methoxy groups are interactive [Au$\cdots$O1, 3.356(12) Å and Au1$\cdots$O2, 3.271(12) Å], compared to the constant values for the trigonal examples **2** [−46.3(8)°; Au$\cdots$O1, 3.250(6) Å] and **3** [47.4(7)°; Au$\cdots$O1, 3.239(7) Å]. In none of these three examples does the packing in the unit cell result in dimer formation through the back-to-back sextuple phenyl embrace (SPE) [6,21–23].

With the [AuP(panis)$_3$X] examples in the Series **B** set, the bromo analogue [AuP(panis)$_3$Br] (**4**) (Fig. 5) is found to be isomorphous with the previously reported first member of the series, [AuP(panis)$_3$Cl] [11]. Both crystallize in *C*-centred monoclinic cells {comparative cell data for the chloro analogue [11]: $a = 14.2875(4)$, $b = 14.5396(4)$,

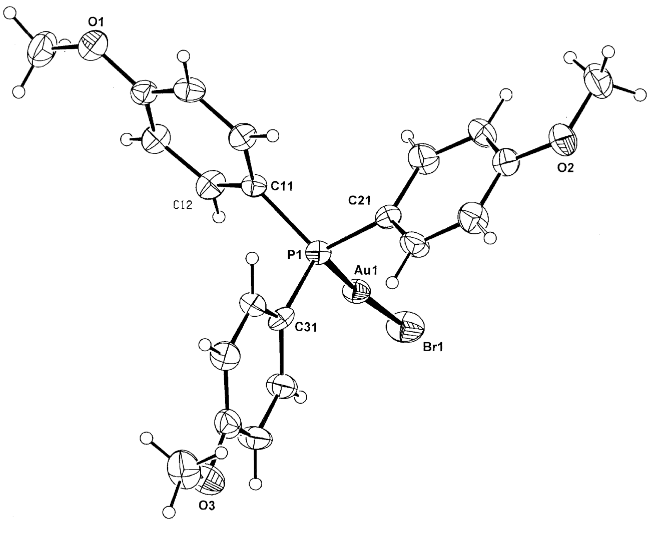

Fig. 5. Molecular configuration and naming scheme for the [AuP(panis)$_3$Br] (**4**). Non-hydrogen atoms are drawn as 30% probability displacement ellipsoids.

$c = 20.2212(6)$ Å, $\beta = 101.504(1)°$, $Z = 8$; space group, $C2/c$} with one molecule in the asymmetric unit. This contrasts with the iodo analogue [AuP(panis)$_3$I] (**5**) which has two conformationally different molecules in the asymmetric unit, as indicated by the variation in the $\tau_1 - \tau_3$ values [−4°, 18°, 80(1)° (molecule 1) (Fig. 6a) and −38°, −21°, −43(1)° (molecule 2)] (Fig. 6b). These values compare with −29°, −62°, −3° for the Series B chloro complex [5] and −29.9(8)°, −62.7(8)° and −3.1(7)° for **4**. This variation is possible with the greater conformational freedom afforded by the absence of Au···O(o-methoxy) interactions cf. the *ortho*-anisyl-substituted phosphines.

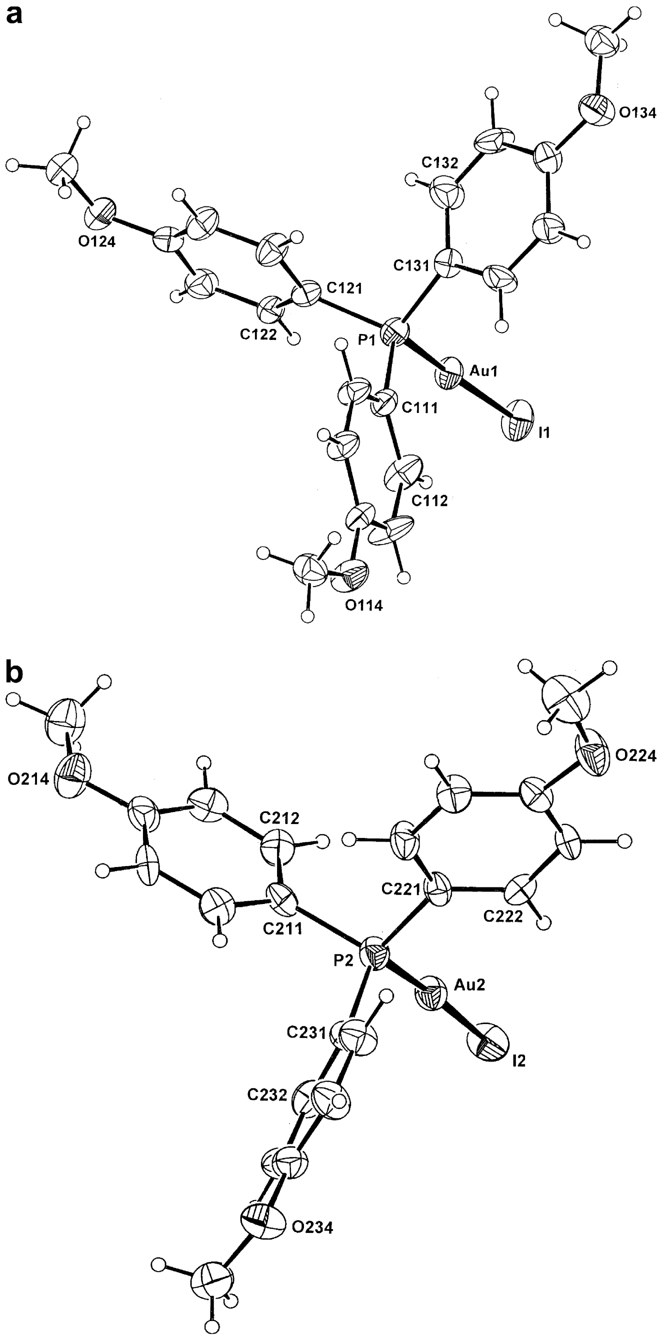

Fig. 6. The two conformationally different molecules of [AuP(panis)$_3$I] in the crystallographic asymmetric unit in **5**. (a) Molecule 1; (b) Molecule 2.

3.2. Solution NMR results

The solution ^{31}P{^{1}H} NMR spectra in CDCl$_3$ showed singlet peaks at 9.1, 12.6,19.1 ppm (Series A) and 32.2, 34.4, 38.9 ppm (Series B), respectively, which compare with 33.8, 34.6 and 38.4 ppm for the [P(Ph)$_3$] series of complexes (for X = Cl, Br, I, respectively) [1–3,6,17–19]. The corresponding coordination chemical shifts ($\Delta\delta = \delta$ complex − δ ligand), with the exception of that for **3** [38.1, 41.6, 48.1 ppm (Series A) and 39.4, 41.6, 45.7 ppm (Series B)] are similar to the [P(Ph)$_3$] complexes (38.5, 40.5, 43.1 ppm), respectively.

3.3. Conclusions

The presence of methoxy substituent groups in the triphenylphosphine molecule appears to have little influence on the nature of the gold(I) complex formed, but the presence of the *ortho*-methoxy substituent significantly affects the conformation of the phenyl rings, due to intramolecular methoxy-O···Au interactions. This is best seen with the isomorphous [AuP(oanis)$_3$Br] and [AuP(oanis)$_3$I] complexes where the rings adopt perfect C_3 symmetry. In addition the methoxy group appears to have less effect than the analogous methyl substituent group in triaryl phosphines upon the formation of crystals containing more than one independent complex molecule in the asymmetric unit. No short Au···Au interactions of the type found in [AuP(ptol)$_3$Cl] were expected or found in this series.

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Appendix A. Supplementary material

CCDC 211590, 211591, 211592, 211593 and 211594 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.01.014.

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