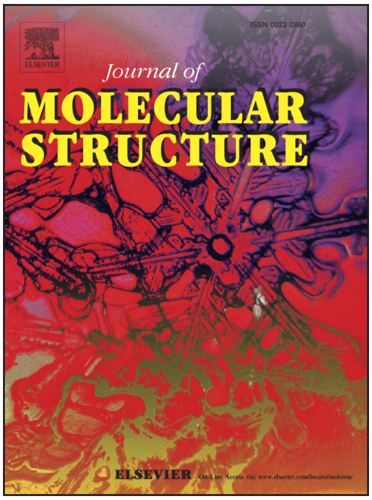


Isomorphism in the structural chemistry of two-coordinate adducts of diphenyl(2-formylphenyl)phosphine and triphenylphosphine with gold(I) halides

Samuel P.C. Dunstan, Peter C. Healy, Alexandre N. Sobolev, Edward R.T. Tiekink, Allan H. White, Michael L. Williams

PII: S0022-2860(14)00504-3
DOI: http://dx.doi.org/10.1016/j.molstruc.2014.05.020
Reference: MOLSTR 20619

To appear in: *Journal of Molecular Structure*

Received Date: 28 March 2014
Revised Date: 1 May 2014
Accepted Date: 9 May 2014

Please cite this article as: S.P.C. Dunstan, P.C. Healy, A.N. Sobolev, E.R.T. Tiekink, A.H. White, M.L. Williams, Isomorphism in the structural chemistry of two-coordinate adducts of diphenyl(2-formylphenyl)phosphine and triphenylphosphine with gold(I) halides, *Journal of Molecular Structure* (2014), doi: http://dx.doi.org/10.1016/j.molstruc.2014.05.020

Isomorphism in the structural chemistry of two-coordinate adducts of diphenyl(2-formylphenyl)phosphine and triphenylphosphine with gold(I) halides.

Samuel P. C. Dunstan[a], Peter C. Healy[a,*], Alexandre N. Sobolev[b], Edward R. T. Tiekink[c], Allan H. White[b], Michael L.Williams[a]

[a] *School of Biomolecular and Physical Sciences, Griffith University, Brisbane, Qld 4111, Australia*
[b] *School of Chemistry and Biochemistry M310, The University of Western Australia, Crawley, WA 6009, Australia*
[c] *Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

ABSTRACT

Single crystal X-ray structure determinations are recorded for diphenyl(2-formylphenyl)phosphine gold(I) halides [Ph_2(Ph-CHO)PAuX], X = Cl, Br and I, and for redeterminations of enhanced precision for triphenylphosphine gold(I) halides [Ph_3PAuX], X = Cl, Br, I, and $SCN_{0.91}Br_{0.09}$. These complexes, other than [Ph_2(Ph-CHO)PAuCl], together with a diverse array of other structures, crystallize as an isomorphous series in the orthorhombic space group $P2_12_12_1$ a = 9.804(1) – 11.906(3), b = 11.771(2) – 12.996(3) and c = 12.871(1) – 14.169(3) Å. In these complexes, introduction of the formyl group results in only minor differences between the conformations of the two phosphine ligands and the corresponding Au-P, Au-X, and Au-P-X bond lengths and angles. The crystal packings of [Ph_3PAuX] for X = Cl, Br, I and of [Ph_2(Ph-CHO)PAuX] for X = Br and I show that, while these structures are isomorphous, different supramolecular synthons may be present, suggesting global packing considerations are all-important rather than specific supramolecular interactions. This is borne out by the different packing found for the centrosymmetric [Ph_2(Ph-CHO)PAuCl] structure. Crystallization of the mixed anion structure [$Ph_3PAuSCN_{0.91}Br_{0.09}$] in the above $P2_12_12_1$ lattice rather than the $P2_1$/c lattice reported for pure [Ph_3PAuSCN] suggest that co-crystallization with bromide may impose constraints on packing considerations which favour crystallization in the $P2_12_12_1$ lattice.

Keywords: Gold(I) complexes; Phosphine ligands; Crystal structures; Isomorphism.

---

[*] Corresponding author. Tel +617 3735 7442
E-mail address: P.Healy@griffith.edu.au

1. Introduction

Structural studies of the neutral 1:1 complexes of the univalent coinage metal halides with monodentate tertiary aryl-phosphine ligands, $[R_3P\text{-}M\text{-}X]_n$ (M = Cu, Ag, Au; X = Cl, Br, I) have shown that adducts with M = Cu and Ag crystallize as three- and four- coordinate molecular oligomeric clusters (most notably for n = 4 as 'cubane' and 'step' M_4X_4 tetramers for triphenylphosphine [1]) with two-coordinate monomeric $[R_3P\text{-}M\text{-}X]$ isolated only with highly sterically hindered ligands such as tris(trimethylphenyl)phosphine or tris(trimethoxyphenyl)phosphine [2]. By contrast, the analogous complexes with M = Au crystallize exclusively as $[R_3P\text{-}Au\text{-}X]$ monomers with the P-Au-X bond angle deviating only slightly from linearity, irrespective of the steric or electronic properties of the phosphine [3]. For these complexes, formal charges on the gold and halide atoms are +1 and -1 respectively. However, density functional calculations on $[Ph_3PAuCl]$ [4] have suggested that electron density is transferred from phosphorus to gold with the resultant charges on the P, Au and Cl atoms calculated to be 1.135, 0.003 and -0.963 (electron units) respectively, with the possibility that the charge on the phosphorus may be further delocalized to result in increased positive charge on the phenyl hydrogen atoms [5]. Thus, rather than the formation of oligomeric clusters through inter-molecular M...X bonding as found for the copper and silver complexes, aggregation of the gold complexes in crystalline solids has been found to occur through a range of intermolecular interactions including Au...X interactions, aurophilic Au...Au and Au...π interactions, which, together with C-H...X, X... π and π..π interactions results in the formation of diverse arrays of supramolecular crystal structures [6, 7].

A survey of the literature shows that the triphenylphosphine gold(I) halide complexes, $[Ph_3PAuX]$, are members of an isomorphous series of $[R_3L\text{-}M\text{-}X]$ compounds for L = P, As; M = Au, I, Br; X = monovalent anion, which crystallize in the orthorhombic space group $P2_12_12_1$ Z = 4 with unit cell dimensions *a* = 9.804(1) – 11.906(3), *b* = 11.771(2) – 12.996(3) and *c* = 12.871(1) – 14.169(3) Å (labelled here as the alpha series). Complexes currently identified as belonging to this series include $[Ph_3P\text{-}Au\text{-}X]$ for X = Cl, Br, I, *C*N, *C*NO, *N*CO, *S*CN, $O_2CCH_3$and O_2CCF_3 [4, 8]; $[Ph_2(2\text{-}NH_2Ph)P\text{-}Au\text{-}I]$, $[Ph_2(1\text{-Me-imidazole})P\text{-}Au\text{-}Cl]$, [*m*-tolyl$_3$P-Au-X] for X = Cl and *C*N, [(*m*-FPh)$_3$P-Au-Cl] [9]; $[Ph_3As\text{-}Au\text{-}X]$ for X = Cl and Br [10]; and $[Ph_3P\text{-}Br\text{-}Br]$, $[Ph_3P\text{-}I\text{-}I]$ [11]. A second, closely related, series of isomorphous structures in the space group $P2_12_12_1$ with unit cell dimensions *a* = 11.5642(1) – 12.689(4), *b* = 12.622(2) – 13.963(3) and *c* = 10.974(2) – 11.403(1) Å (beta series) have been recorded for the complexes $[Ph_3As\text{-}Au\text{-}Cl]$ [10a], $[Ph_3P\text{-}Au\text{-}N_3]$ [12a] $[Ph_3P\text{-}Au\text{-}(1,2,3\text{-triazolate})]$ [12b], $[Ph_3P\text{-}Au\text{-}(\text{perfluorovinyl}))]$ [12c] and $Ph_3As\text{-}I\text{-}I$ [12d], with polymorphs of $[Ph_3AsAuCl]$ represented in both α and β series.

In this present study, we have determined single crystal structures of the diphenyl(2-formylphenyl)phosphine complexes [Ph_2(Ph-CHO)AuX] for X = Cl, Br and I. The bromide and iodide complexes in this series crystallize as new members of the α-series, while, as also reported previously [13], the chloride crystallizes in the centrosymmetric space group $P\bar{1}$ with two independent molecules comprising the asymmetric unit. As part of this work we have also re-determined the crystal structures of the gold triphenylphosphine complexes [Ph_3P-Au-X] for X = Cl, Br, I and *S*CN with the aim of providing structural data of comparable precision for these compounds.

2. Experimental

2.1. Preparation and crystallization of compounds.

The ligands Ph_2(Ph-CHO)P and Ph_3P were obtained commercially. [Ph_2(Ph-CHO)PAuX] for Cl, Br and I and [Ph_3PAuBr] were prepared by dissolution of equimolar quantities of [NBu_4][AuX_2] and the phosphine ligand in warm dimethylformamide to give clear solutions from which slow evaporation of solvent yielded colourless air-stable crystals. *[Ph_2(Ph-CHO)PAuCl]* [Bu_4N][$AuCl_2$] (0.112 mg, 0.22 mmol) and Ph_2(Ph-CHO)P (64 mg, 0.22 mmol), m.p. 196-197°C. Anal. Found C 43.82, H 2.87; Calc. for $C_{19}H_{15}AuClOP$ C 43.66, H 2.89%. *[Ph_2(Ph-CHO)PAuBr]* [Bu_4N][$AuBr_2$] (0.114 g, 0.19 mmol) and Ph_2(Ph-CHO)P (54 mg, 0.19 mmol), m.p. 201-203°C. Anal. Found C 40.26, H 2.58; Calc. for $C_{19}H_{15}AuBrOP$ C 40.24, H 2.67%. *[Ph_2(Ph-CHO)PAuI]* [Bu_4N][AuI_2] (0.130 g, 0.19 mmol) and Ph_2(Ph-CHO)P (54 mg, 0.19 mmol), m.p. 202-204°C. Anal. Found C 36.99, H 2.35; Calc. for $C_{19}H_{15}AuIOP$ C 37.16, H 2.85%. *[Ph_3PAuBr]* [Bu_4N][$AuBr_2$] (0.300 g, 0.50 mmol) and Ph_3P (0.138g, 0.53 mmol) m.p 253-254°C.

Crystals of [Ph_3PAuCl] were obtained by recrystallization from dichloromethane of a sample previously prepared by the addition of chloroauric acid to triphenylphosphine according to the method of ref. [14]. Crystals of [Ph_3PAuI] were obtained from a sample prepared previously [8a] which had been crystallized from an acetone solution of Ph_3PAuCl and hydro-iodic acid according to the method of ref. [15]. Synthesis of both the chloride and iodide adducts by the reaction of Ph_3P and [NBu_4][AuX_2], X = Cl, I, followed by re-crystallization from a range of organic solvents and determination of unit cell dimensions revealed no evidence for polymorphism in the resultant crystal lattices. A crystal of '[$Ph_3PAuSCN$]' was retrieved from the original sample prepared by crystallization from a solution of Ph_3PAuBr and KSCN [8a] and, as discussed below, has been modelled in a subsequent improved redetermination as a SCN/Br co-crystal with 91% [$Ph_3PAuSCN$] and 9% [Ph_3PAuBr].

2.2 X-ray structure determinations

CCD area-detector diffractometer data sets were measured at *ca.* 153 and 223 K (monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{(\mathrm{total})}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multi-scan absorption correction (proprietary software), N_o with $I > 2\sigma(I)$ being considered 'observed'; all data were used in the full-matrix least-squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a 'riding' model; reflection weights were $[\sigma^2(F_o^{\,2}) + (aP)^2 + (bP)]^{-1}$ $[P = (F_o^{\,2} + 2F_c^{\,2})/3]$. Friedel data were retained distinct and x_{abs} refined in all cases. Computation used SHELX 97, ORTEP-3 for Windows and PLATON [16]. Pertinent results are given below and in the Tables and Figures, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Crystal data and final refinement details are given in Table 1. The phenyl carbon atoms of the phosphine ligands are labelled (*mn* where *m* is the ring number (1-3) and *n* the atom number (1-6). Atom 1 is the *ipso* carbon and atom 2 the *ortho* carbon endo to the gold coordination sphere. Full .cif files have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 638229 – 638232 for [PPh_3AuX], X = Cl, Br, I, SCN and 969332 - 969334 for [Ph_2(Ph-CHO)PAuX], X = Cl, Br, I**.** Copies can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int. (1223)336-033; e-mail for inquiry: fileserv@ccdc.clam.ac.uk.

Variata. The structure determination of [$Ph_3PAuSCN$] recorded in ref. [8a] was less satisfactory at that time than those of the chloride and bromide, with limited data supporting only isotropic displacement parameter refinement for the peripheral non-hydrogen atoms. Redetermination of the structure using the data acquired in the present study yielded a model in which it became evident that the thiocyanate sulfur site was overlaid with another heavy atom component. Trial refinement as bromide, presumably originating from the starting materials and noted earlier as 'minor impurities', refined to 9% occupancy, yielding a credible model in terms of associated geometry and displacement parameter refinement. With the results of this experiment in mind, particular attention was paid to the modelling of the halide throughout the other structures reported here, but in no case was anything other than a homogeneous model with occupancy of unity for the anion considered necessary.

3. Results and discussion

3.1. Gold coordination environments for [Ph_2(Ph-CHO)PAuX] and [Ph_3PAuX], X = Cl, Br, I.

Interatomic distances, bond angles and torsion angles for the complexes and related data for the parent ligands, Ph_2(Ph-CHO)P [17a] and Ph_3P [18] are presented in Tables 2 and

3. In the molecular structure of Ph_2(Ph-CHO)P [17a] the formyl group adopts the O-cis conformer and is co-planar with the phenyl ring with the C-C-C-O torsion angle 1.8(5)° (Fig. 1). The carbonyl oxygen atom is located above the plane of the three *ipso* carbons of the aromatic rings and acts as a donor to the phosphorus atom with the P...O distance 2.834(2) Å [19]. The P-C bond lengths and C-P-C bond angles are equivalent within experimental error to those reported for Ph_3P, with average P-C bond lengths and C-P-C angles of 1.837(3) Å and 102.4(5)° for Ph_2(Ph-CHO)P compared to 1.831(3) Å and 102.8(9)° for Ph_3P. The conformational structures of the phenyl rings in the two compounds are also similar, with the torsion angles between the normal to the plane of the three *ipso* carbons and the $C_{ipso} – C_{ortho}$ bonds -51.9, -44.8 and -27.9° for Ph_2(Ph-CHO)P and 55.9, 27.1, 24.7° for Ph_3P.

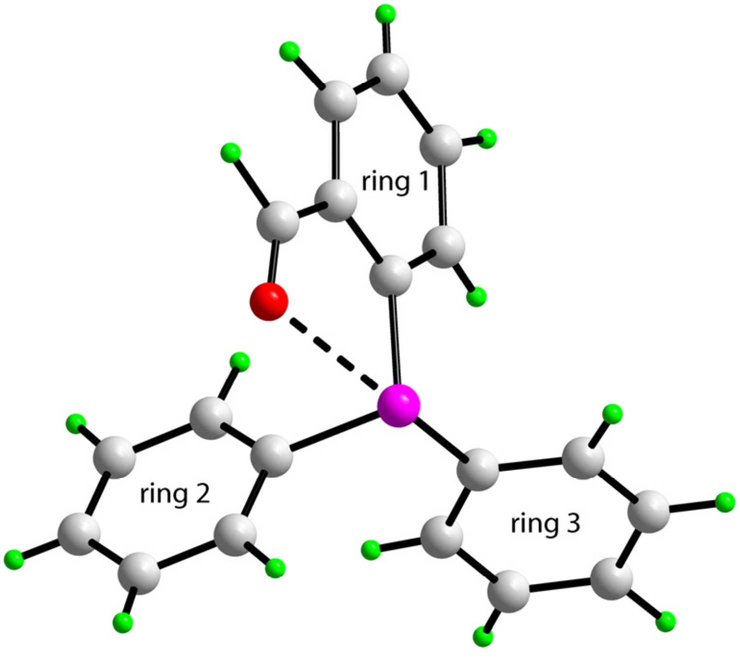


Fig. 1 Molecular structure of Ph_2(Ph-CHO)P showing the close O...P approach [17a].

For the [Ph_3PAuX] halide complexes, unlike the previous less precise structure determinations for the bromide and iodide [8a], it is now evident that the Au-P bond lengths show the expected monotonic increase [20] with values of 2.2280(11) Å (Cl), 2.2368(8) Å (Br) and 2.2533(5) Å (I).

For the [Ph_2(Ph-CHO)PAuX] halide complexes, the bromide and iodide are isomorphous with the α series. For the bromide, no significant difference compared to the [Ph_3PAuBr] counterpart is observed in either the Au-P or Au-Br bond lengths, while for the iodide complexes, there is a small difference of the order of 0.01 Å in the Au-I bond length. In contrast, as also previously reported [13], [Ph_2(Ph-CHO)PAuCl] crystallizes in the centrosymmetric triclinic space group $P\bar{1}$, with two independent molecules comprising the asymmetric unit. Nevertheless, with two independent determinations of comparable precision, the differences in the Au-P and Au-Cl with the [PPh_3AuCl] adduct are relatively minor. In both series of complexes, the P-Au-X angles lie above 178º, with only small differences between the angular parameters of Ph_2(Ph-CHO)P and PPh_3 (Tables 2, 3).

The impact of the carbonyl oxygen on the gold atom coordination environment in the [Ph_2(Ph-CHO)PAuX] complexes appears to be minor or non-existent. As for the parent ligand [17a], the 2-formyl group in the complexes exists as the O-cis isomer and is coplanar with the parent phenyl rings with τ(C-C-C-O): Cl (molecules 1, 2), 0.8(8)^o, 1.4(8)^o; Br; 1.8(11)^o; I, –0.6(8)º. The P…O distances are 2.890(4), 2.892(3) Å for molecules 1 and 2 of the chloride complex, 2.852(5) Å for the bromide complex and 2.815(3) Å for the iodide complex. The Au...O distances are 3.114(4), 3.120(3) Å (Cl), 3.112(5) Å (Br) and 3.136(4) Å (I) with only small, if any, impact on the associated phenyl ring dispositions. These distances may be compared with those found in other systems with an oxygen atom pendant from the 2-position in one of the phenyl rings: for systems immediately pendant, in the 2-OH/chloride complex [21], Au...O is 3.160(7) Å, comparable with the present structures, while with the more sterically demanding 2-Me_3SiO substituted ligand in the chloride and iodide arrays, the distances are appreciably longer 3.353(2), 3.297(7) and 3.251(7) Å [22]. In the 2-carboxymethyl/chloride complex with the oxygen atom further displaced, Au...O is 3.037(5) Å [21]; while in tris(2-methoxy-phenyl)phosphine gold chloride, bromide and iodide [7j], all Au...O distances are greater than 3.24 Å. In none of these structures, does the Au...O contact appear to have anything other than a minor impact on the P-Au-X angle.

3.2. Crystal packings for [Ph_3PAuX] and [Ph_2(Ph-CHO)PAuX], X = Cl, Br, I

As noted above, the [Ph_3PAuX] crystal structures for X = Cl, Br and I and the [Ph_2(Ph-CHO)PAuX] crystal structures for X = Br and I form part of the isomorphous α series. Cell dimensions for the full series of these compounds (transformed where required from the original data to form a consistent packing array), together with M-P bond lengths and M-P-C_{m1}-C_{m2} torsion angles, τ_m, (m = 1-3) are listed in Table 4. The atom numbering adopted globally for the present series of complexes, and to which the data of other studies, including free ligands, have been referred in making the present comparisons, is shown in Fig. 2.

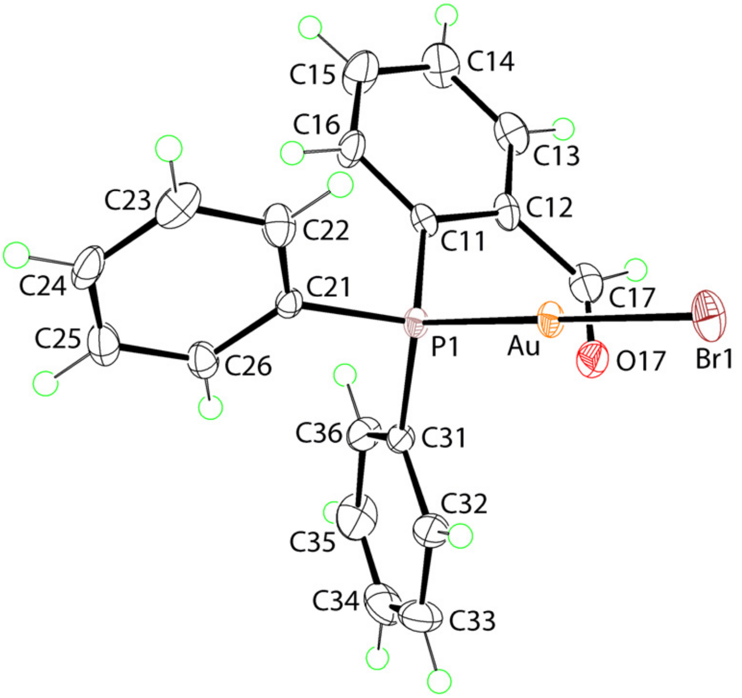


Fig. 2 Molecular projection of [Ph_2(Ph-CHO)PAuBr] showing the atom numbering scheme adopted in the description of the present comparative study of complexes and ligands.

In these compounds, the three phenyl rings are numbered in a counter clock-wise direction viewed down the X-M-P axis with values of τ_m generally decreasing in the order $\tau_1 > \tau_2 > \tau_3$ with the range of values 54–71°, 21–50°, and 22–43° respectively. For the [Ph_2(Ph-CHO)PAuX] adducts , the 2-formyl group is located in ring 1. The similarities in the conformational structures of the Ph_2(Ph-CHO)P and Ph_3P ligands is reflected also in the small differences observed in the magnitudes of τ_m.

In the crystal lattices of these complexes, the Au...Au distances range from 6.8 - 7.6 Å. The P-Au-X vectors are directed along the [100] direction with inter-molecular C-H...X interactions in the Ph_3P complexes of 2.79 Å (Cl), 2.92 Å (Br) and 3.11 Å (I) between the halide and *para* proton H24 from ring in the molecule at (½+*x*, ½-*y*, -*z*). The anion environment is characterized by the P-Au-X vector lying approximately perpendicular to ring 1 of the molecule at (1+*x*, *y*, *z*) with X...Cg distances of 4.25 Å (Cl), 4.07 Å (Br) and 4.04 Å

(I), indicating increasing significance of these interactions in their respective crystal structures. Along the [010] direction, crystal packing for this structure consists of a helical chain of antiparallel monomers linked by $(EF)_3$ embraces [6]. Within this chain weak Au…π_{aryl} interactions, are also apparent between Au and ring 3 of the adjacent molecule at (-*x*, ½+*y*, ½-*z*) with Au….Cg distances (d) of 4.05 Å (Cl), 4.19 Å (Br), 4.26 Å (I), Fig. 3.

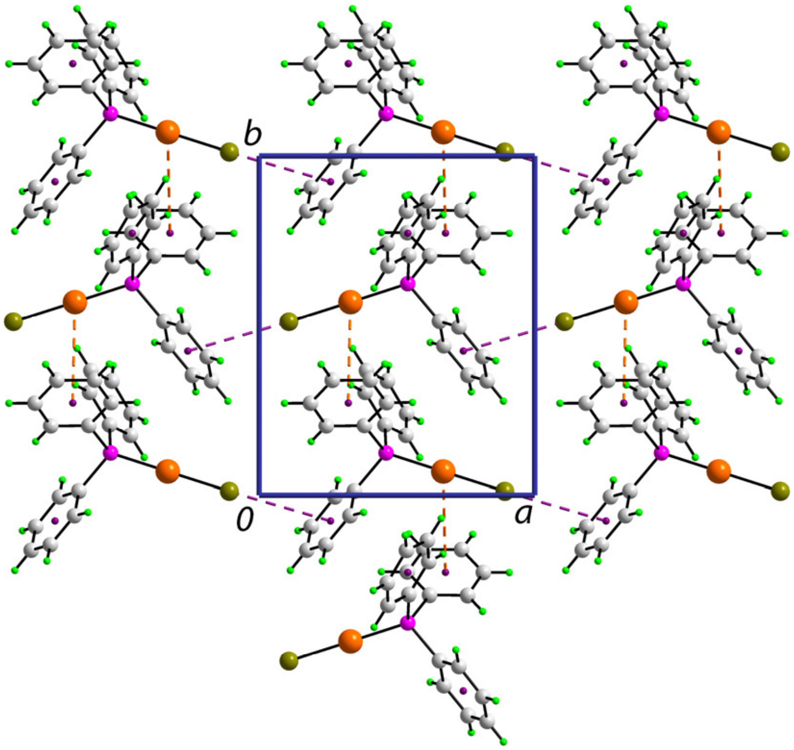


Fig. 3. View of the crystal packing down the *c*-axis for Ph_3PAuBr with Au...π and Br...π interactions shown as orange and purple dashed lines, respectively.

While crystallizing as members of the α series, the crystal packing of $[Ph_2(Ph\text{-}CHO)PAuX]$ for X = Br and I presents different features with the appearance of C-H...O contacts [H...O distances = 2.41 Å (Br) and 2.45 Å (I)], that lead to supramolecular chains along the *c* axis, and C-H...π(ring 1) [H...Cg distances = 2.89 Å (Br) and 2.93 Å (I)]; the Br...π(ring 1) contacts persist with Br….Cg distances (d) of 4.03 Å (Br) and 3.99 Å (I), (Fig. 4).

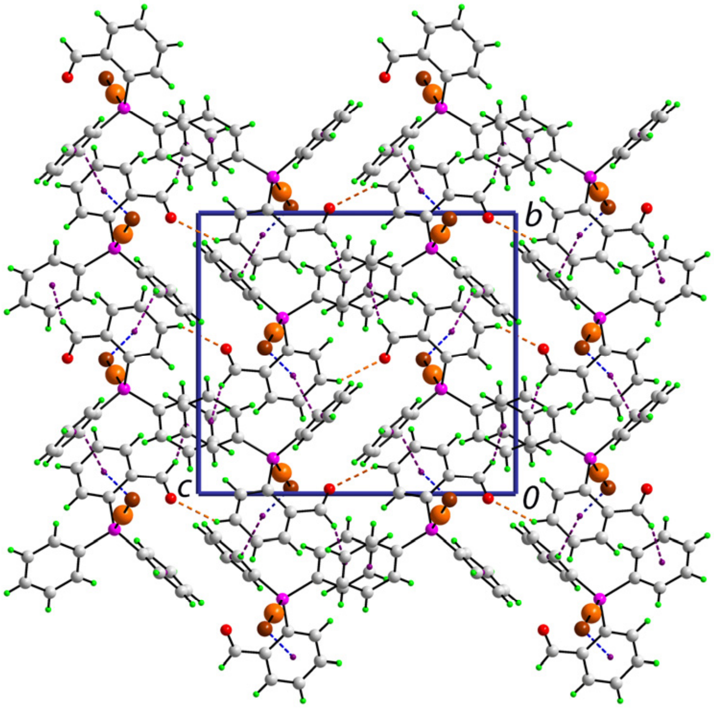


Fig. 4. View of the crystal packing down the *a*-axis for [Ph_2(Ph-CHO)PAuBr] with C-H...O, C-H...π and Br...π interactions shown as orange, purple and blue dashed lines, respectively.

For the centrosymmetric chloride complex, [Ph_2(Ph-CHO)PAuCl], Fig. 5, the values of τ_m are found to be similar for the two independent molecules in the asymmetric unit, with values of -60.2(4), -42.4(4), -3.1(4)° for molecule 1 and -65.1(4), -41.4(4) and 0.5(4)° for molecule 2. The major difference in these angles with respect to the α structures is the rotation of ring 3 by ~ 30°.

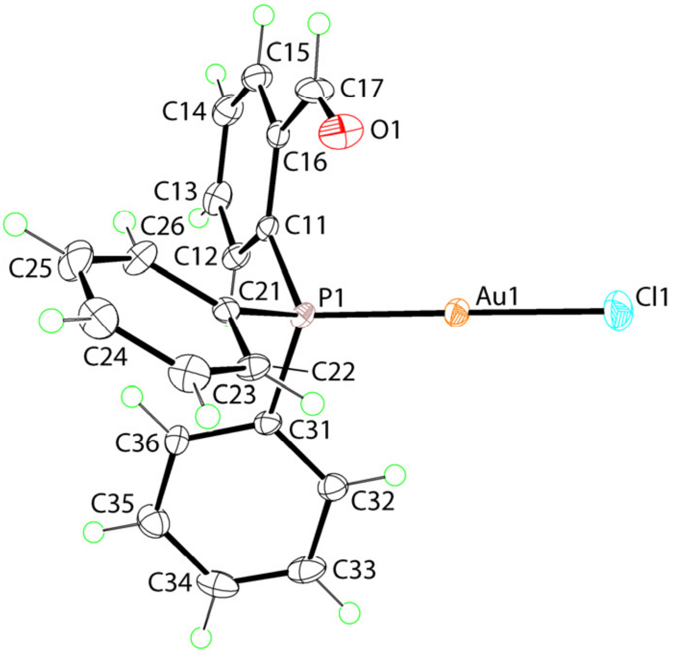
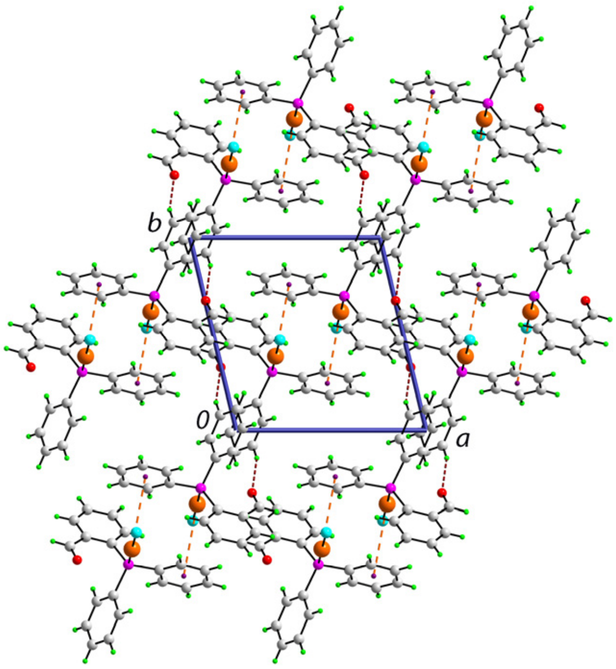
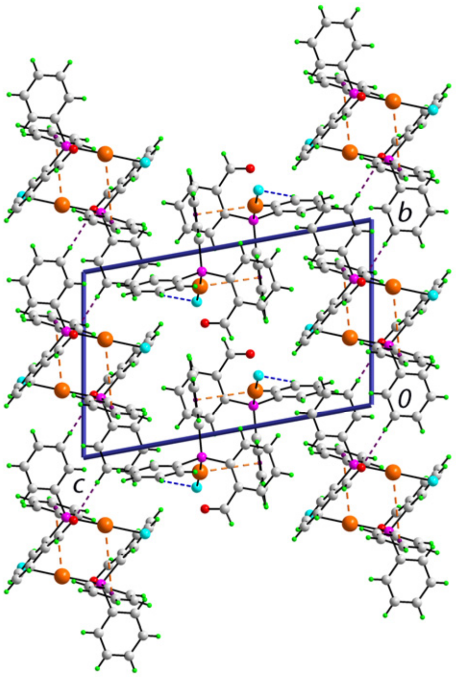


Fig. 5 Molecular projection of one of the two independent molecules of [Ph_2(Ph-CHO)PAuCl] also representative of the second which incorporates an additional 'a' in the atomic labels.

Both molecules in this lattice crystallize in close association with an inversion related image to form loose dimer pairs in which the Au...Au distances of 5.48 Å (molecule 1) and 5.62 Å (molecule 2) are shorter than those observed for the α structures, but are still too long to indicate the presence of significant Au...Au aurophilic interactions. Centrosymmetrically related molecules associate via weak Au...π(ring 3) interactions of 3.71 Å (molecule 1) and 3.90 Å (molecule 2), and other pairs via C-H...O contacts to form a supramolecular layer in the *ab*-plane (Fig. 6a). These are connected in a three-dimensional architecture by a combination of C-H...Cl interactions, whereby molecules of 1 are linked into a linear supramolecular chain (H...Cl = 2.82 Å), and C-H...π(ring 2) interactions (Fig. 6b).



(a)



(b)

Fig. 6. (a) View of the supramolecular layer in the *ab*-plane in the crystal structure of [Ph_2(Ph-CHO)PAuCl] sustained by Au...π and C-H...O interactions, and (b) view of the unit cell contents in projection down the a-axis. The Au...π, C-H...O, C-H...Cl and C-H...π interactions are shown as orange, brown, blue and purple dashed lines, respectively.

3.3 General features of the $P2_12_12_1$ α series of complexes.

While this present paper has focused on the similarities and differences in homomolecular structure and crystal packing of the [Ph_3PAuX] and [Ph_2(Ph-CHO)PAuX] series of complexes for X = Cl, Br, I, there are a number of interesting features of the α series of compounds that warrant mention:

- The range of anions for these isomorphous / isostructural complexes extends from simple halides and pseudo halides to acetate and trifluoroacetate.
- The range of phosphine and arsine ligands include Ph_3P, Ph_3As, Ph_2(2X-Ph)P, Ph_2(Me-imidazoly)P, *m*-tolyl$_3$P, *m*-tolyl$_3$As, *m*-FPh_3P. i.e. *ortho* and *meta* H atoms and the presence of either P or As atoms are not critical in the determination of the crystal lattice.
- The substitution of Au by halide in Ph_3PX_2 and Ph_3AsX_2 structures – suggesting that

the weak Au...π interactions in these complexes are similar to X....π interactions [6].

- The lack of polymorphism in the gold(I) members of the series - with the only exception to date being observed for [$Ph_3AsAuCl$] [10a] which crystallizes simultaneously as needles (α series) and as prisms (β series), and, potentially, for [$Ph_3PAuSCN$] [7b, 8a] (see below).

3.4 The $P2_12_12_1$ structure of [$Ph_3PAuSCN$]

Since the original determination of the structure of [Ph_3PAu*S*CN] in space group $P2_12_12_1$ [8a], a further determination [7c] has proved to be that of a new monoclinic $P2_1/c$ form, one molecule devoid of crystallographic symmetry comprising the asymmetric unit of the structure, indicating polymorphism for this complex. The refinement of the $P2_1/c$ structure was straightforward, resulting in Au-P, S bond lengths of 2.2542(13), 2.3312(15) Å and P-Au-S, Au-S-C angles of 177.88(5), 85.4(3)º. In this form, unlike the $P2_12_12_1$ complex, the Au-X (= *S*CN) component lies in close proximity to an inversion image, forming a loose dimer (Au...S' 3.495(1) Å), impacting only weakly on the P-Au-S angle. As noted in the Experimental section, our original structure determination of '[Ph_3PAu*S*CN]' in space group $P2_12_12_1$ was of inferior quality with limited data supporting only isotropic displacement parameter refinement for the light atoms. With stable crystals of the original sample of [$Ph_3PAuSCN$] associated with this determination still in hand, the acquisition of greatly improved low-temperature data supported a superior model, with incorporation of bromide as a minor impurity component, consistent with the earlier solid-state ^{31}P CPMAS NMR data [8a] and refinement behaviour, to the extent of *ca.* 9%. With that model, Au-P, S, Br are 2.2552(8), 2.3242(10), 2.407(5) Å, with P-Au-S, Br 174.70(4), 167.42(11)º and Au-S-C 102.7(12)º, the distances being very similar to those of related compounds although the angular deviations are considerable, probably beyond what might be expected as consequent upon the disorder. Crystals of the monoclinic form were reported as being obtained from dichloromethane/pentane solution, a system not unlike that which yielded our $P2_12_12_1$ α complex, suggesting that crystallization with bromide may impose constraints consequent on solubilities/solvent interactions which favour the formation of the complex as a member of the α series.

Conclusion

In the structures of the [Ph_3PAuX] and [$Ph_2(Ph\text{-}CHO)PAuX$] halide complexes, introduction of the -CHO group results in only very minor differences in the conformational structures of the phosphine ligands and the corresponding Au-P, Au-X and P-Au-X bond lengths and angles. There is also remarkable homogeneity in the symmetry of crystal packing exhibited by a range of related/similar phosphine gold(I) species, in that they uniformly adopt the non-centrosymmetric orthorhombic space group $P2_12_12_1$. As shown by an examination of the crystal packing of [Ph_3PAuX], X = Cl, Br, I, and [Ph_2(Ph-CHO)P)AuX], X = Br, I, while these are isomorphous, different supramolecular synthons may be present, suggesting that global crystal packing considerations, i.e. the packing of quasi-spherical aggregates, are all important - rather than specific supramolecular interactions. This is borne out by the different packing found for the centrosymmetric [Ph_2(Ph-CHO)P)AuCl] complex. The isolation of [$Ph_3PAuSCN$] as a member of the α-series when crystallized in the presence of bromide as a minor impurity suggests that further co-crystallization experimentation may expand the range of complexes found for this polymorph.

Acknowledgements

We thank the University of Western Australia and Griffith University for support of this work, and Dr Bradley Loughrey and Dr Ben Cunning for helpful assistance with the project. The Ministry of Higher Education (Malaysia) and the University of Malaya is also thanked for funding through the High-Impact Research scheme (UM.C/HIR-MOHE/SC/03).

References

[1] (a) L. Maini, D. Braga, P.P. Mazzeo, B.Ventura, Dalton Trans. 41 (2012) 531;
(b) P.F. Barron, J.C. Dyason, L.M. Engelhardt, P.C. Healy, A.H. White, Inorg. Chem. 23 (1984) 3766;
(c) J.C. Dyason, P.C. Healy, L.M. Engelhardt, C. Pakawatchai, V.A. Patrick, C.L. Raston, A.H. White, J. Chem. Soc., Dalton Trans. (1985) 831;
(d) G.A. Bowmaker, Effendy, R.D. Hart, J.D. Kildea, A.H. White, Aust. J. Chem. 50 (1997) 653;
(e) G.J.S. Venter, A. Roodt, R. Meijboom, Inorg. Chim. Acta 362 (2009) 2475.

[2] (a) E.C. Alyea, G. Ferguson, J. Malito, B.L. Ruhl, Inorg. Chem. 24 (1985) 3719;
(b) G.A. Bowmaker, J.D. Cotton, P.C. Healy, J.D. Kildea, S. bin Silong, B.W. Skelton, A.H. White, Inorg. Chem. 28 (1989) 1462;
(c) L.-J. Baker, G.A. Bowmaker, R.D. Hart, P.J. Harvey, P.C. Healy, A.H. White,

Inorg. Chem. 33 (1994) 3925;

(d) L.-J. Baker, G.A. Bowmaker, D. Camp, Effendy, P.C. Healy, H. Schmidbaur, O. Steigelmann, A.H. White, Inorg. Chem. 31 (1992) 3656.

[3] (a) P.G. Jones, A.F. Williams, J. Chem. Soc., Dalton Trans. (1977) 1430;

(b) R.C. Bott, G.A. Bowmaker, R.W. Buckley, P.C. Healy, M.C. Senake Perera, Aust. J. Chem. 52 (1999) 271.

[4] A.O. Borissova, A.A. Korlyukov, M.Y. Antipin, K.A. Lyssenko, J. Phys. Chem. A 112 (2008) 11519.

[5] B.T. Loughrey, B.V. Cunning, P.C. Healy, C.L. Brown, P.G. Parsons, M.L. Williams, Chem. Asian J. 7 (2012) 112.

[6] (a) N.A. Barnes, K.R. Flower, S.M. Godfrey, P.A. Hurst, R.Z. Khan, R.G. Pritchard, CrystEngComm 12 (2010) 4240;

(b) I. Dance, M. Scudder, CrystEngComm 11 (2009) 2233.

[7] (a) N.A. Barnes, K.R. Flower, S.A. Fyyaz, S.M. Godfrey, A.T. McGown, P.J. Miles, R.G. Pritchard, J.E. Warren, CrystEngComm 12 (2010) 784;

(b) H.W. Chen, E.R.T. Tiekink, Acta Crystallogr., Sect. E 59 (2003) m50;

(c) D. Schneider, S. Nogai, A. Schier, H. Schmidbaur, Inorg. Chim. Acta 352 (2003) 179;

(d) R.C. Bott, P.C. Healy, G. Smith, Aust. J. Chem. 57 (2004) 213;

(e) K. Nunokawa, S. Onaka, T. Tatematsu, M. Ito, J. Sakai, Inorg. Chim. Acta 322 (2001) 56;

(f) E.R.T. Tiekink, J. Zukerman-Schpector, CrystEngComm 11 (2009) 1176;

(g) I. Caracelli, J. Zukerman-Schpector, E.R.T. Tiekink, Gold Bull. 46 (2013) 81.

(h) D.V. Partyka, T.J. Robilotto, M. Zeller, A.D. Hunter, T.G. Gray, Organometallics 27 (2008) 28;

(i) P.C. Healy, Acta Crystallogr., Sect. E 59 (2003) m1112;

(j) R.C. Bott, P.C. Healy, G. Smith, Polyhedron 26 (2007) 2803;

(k) P. Politzerm, P. Lane, M.C. Concha, Y. Ma, J.S. Murray, J. Mol. Model. 13 (2007) 305.

[8] (a) P.F. Barron, L.M. Engelhardt, P.C. Healy, J. Oddy, A. H. White, Aust. J. Chem. 40 (1987) 1545;

(b) S. Arland, K. Dreisch, B. Noren, A. Oskarsson, Acta Chem. Scand. A 41 (1987) 173;

(c) P.L. Bellon, M. Manassero, M. Sansoni, Ric. Sci. 39 (1989) 173;

(d) P.G. Jones, J. Lautner, Acta Crystallogr., Sect. C 44 (1988) 2091;

(e) W.P. Bosman, W. Bos, J.M.M. Smits, P.T. Beurskens, J.J. Bour, J.J. Steggerda, Inorg. Chem. 25 (1986) 2093;

(f) P.G. Jones, Acta Crystallogr., Sect. C 40 (1984) 1320;

(g) Z.-Y. Zhang, E. Szlyk, G.J. Palenik, S.O. Colgate, Acta Crystallogr., Sect. C 44 (1988) 2197.

[9] (a) P. Papathanasiou, G. Salem, P. Waring, A.C. Willis, J. Chem. Soc., Dalton Trans. (1997) 3435;

(b) V.J. Catalano, S.J. Horner, Inorg. Chem. 42 (2003) 8430;

(c) C.S.W. Harker, E.R.T. Tiekink, Acta Crystallogr., Sect. C 47 (1991) 878;

(d) A.R. Al-Arfaj, J.H. Reibenspies, M.S. Hussain, A.A. Isab, Acta Crystallogr., Sect. C 54 (1998) 716;

(e) O. bin Shawkataly, A. Tariq, S.S. Ghani, C.S. Yeap, H.-K. Fun, Acta Crystallogr., Sect. E 66 (2010) m1217.

[10] (a) B. Weissbart, L.J. Larson, M.M. Olmstead, C.P. Nash, D.S. Tinti, Inorg. Chem. 34 (1995) 393;

(b) F.W.B. Einstein, R. Restivo, Acta Crystallogr., Sect. B 31 (1975) 624.

[11] (a) N. Bricklebank, S.M. Godfrey, A.G. Mackie, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc., Chem. Commun. (1992) 355;

(b) S.M. Godfrey, D.G. Kelly, C.A. McAuliffe, A.G. Mackie, R.G. Pritchard, S.M. Watson, J. Chem. Soc., Chem. Commun (1991) 1163.

[12] (a) W. Beck, T.M. Klapötke, P. Klüfers, G. Kramer, C.M. Rienäcker, Z. Anorg. Allg. Chem. 627 (2001) 1669;

(b) K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, J. Chem. Soc., Dalton Trans. (1998) 4101.

(c) N.A. Barnes, A.K. Brisdon, W.I. Cross, J.G. Fay, J.A. Greenall, R.G. Pritchard, J. Sherrington, J. Organomet. Chem. 616 (2000) 96.

(d) C.A. McAuliffe, B. Beagley, G.A. Gott, P.P MacRory, R.G. Pritchard, Angew. Chem., Int Ed., 26 (1987) 264.

[13] M.R.J. Elsegood, M.B. Smith, S.H. Dale, Acta Crystallogr., Sect. E 62 (2006) m1850.

[14] C. Kowala, J.M. Swan, Aust. J. Chem. 19 (1966) 547.

[15] A.D. Westland, Can. J. Chem. 47 (1969) 4135.

[16] (a) G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112;

(b) L.J. Farrugia, J. Appl. Cryst. 45 (2012) 849;

(c) A.L. Spek, J. Appl. Cryst. 36 (2003) 7.

[17] (a) A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 40 (2001) 6229;

(b) E.F. Landvatter, T.B. Rauchfuss, Organometallics 1 (1982) 506. Delaunay cell reduction shows the structures reported in these papers to have the same unit cell.

[18] B.J. Dunne, A.G. Orpen, Acta Crystallogr., Sect. C 47 (1991) 345.

[19] T. Schaefer, R. Sebastian, R.W. Schurko, F.E. Hruska, Can. J. Chem. 71 (1993) 1384.

[20] A.Y. Sokolov, O.V. Sizova, Russian J. Gen. Chem. 80 (2010) 1223.

[21] C. Hollatz, A. Schier, H. Schmidbaur, Z. Naturforsch. 54b (1999) 30.

[22] U. Monkowius, M. Zabel, Acta Crystallogr., Sect. E 64 (2008) m196.

Table 1

Crystal data for [Ph_3PAuX] for X = Cl, Br, I, $(SCN)_{0.91}Br_{0.09}$ and [Ph_2(Ph-CHO)PAuX] for X = Cl, Br, I. All are space group $P2_12_12_1$ (orthorhombic, D_2^4, No. 19), $Z = 4$.*

Compound	[$C_{18}H_{15}PAuCl$]	[$C_{18}H_{15}PAuBr$]	[$C_{18}H_{15}PAuI$]	[$C_{18}H_{15}PAu$ $(SCN)_{0.91}Br_{0.09}$]	[$C_{19}H_{15}OPAuCl$]*	[$C_{19}H_{15}OPAuBr$]	[$C_{19}H_{15}OPAuI$]
M_r (Da)	494.7	539.2	586.1	519.3	522.7	567.2	614.1
a (Å)	10.116(2)	9.9916(8)	10.1325(8)	10.7673(9)	10.2723(6)	9.9223(8)	10.0367(5)
b (Å)	12.266(3)	12.338(1)	12.348(1)	11.9860(10)	10.5347(7)	12.5063(10)	12.6677(7)
c (Å)	13.002(3)	13.362(1)	13.794(1)	13.6240(10)	16.7150(11)	14.0493(11)	14.1504(8)
V (Å^3)	1613.3(6)	1647.2(2)	1725.9(2)	1758.3(2)	1696.4(2)	1743.4(2)	1799.1(2)
d_{calc} (g cm^{-3})	2.037	2.174	2.256	1.962	2.047	2.161	2.267
specimen (mm)	0.14x0.07x0.06	0.14x0.11x0.11	0.19x0.11x0.09	0.25x0.10x0.10	0.47x0.21x0.16	0.49x0.34x0.22	0.39x0.26x0.12
μ_{Mo} (mm^{-1})	9.4	11.4	10.4	8.8	8.9	10.8	10.0
$'T'_{min/max}$	0.59	0.81	0.53	0.46	0.26	0.182	0.169
$2\theta_{max}$ (°)	75	75	75	75	60	60	60
N_t	32325	32857	34521	35010	14249	14327	14934
N (R_{int})	8516 (0.053)	8649(0.047)	9079(0.026)	9244(0.041)	9730(0.024)	5081(0.034)	5220(0.031)
N_o	6725	7493	8448	7470	7970	4645	4716
$R1$	0.036	0.029	0.019	0.036	0.034	0.032	0.024
$wR2$ (a(,b))	0.068 (0.027, 0.24)	0.056 (0.021)	0.041 (0.021)	0.070 (0.033)	0.084 (0.042)	0.078 (0.037)	0.047 (0.010)
S	1.00	1.05	1.01	1.00	0.98	1.09	0.83
x_{abs}	-0.028(6)	-0.020(6)	-0.017(2)	-0.001(6)	n/a	0.013(10)	0.019(4)
T (K)	153	153	153	153	223	223	223

*Exception: [Ph_2(Ph-CHO)PAuCl] which is $P\bar{1}$, $Z = 4$ ($\alpha\,\beta\,\gamma$= 97.249(1), 103.535(1), 101.270(1)°).

Table 2

Au-P and Au-X bond lengths and P-Au-X bond angles for [Ph$_2$(Ph-CHO)PAuX] and [PPh$_3$AuX] for X = Cl, Br, I.

	Au-P (Å)			Au-X (Å)			P-Au-X(º)			Ref., T (K)
R$_3$P	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	
Ph$_2$(Ph-CHO) P	2.2315(12)	2.2398(14)	2.2515(10)	2.2810(13)	2.4050(7)	2.5539(4)	178.13(4)	179.89(4)	179.17(3)	This work, 223
	2.2304(11)			2.2807(11)			178.80(5)			
	2.2304(14)			2.2836(14)			178.12(5)			[13], 120
	2.2297(13)			2.2819(13)			178.79(5)			
Ph$_3$P	2.2280(11)	2.2366(8)	2.2533(5)	2.2883(12)	2.4059(4)	2.5633(3)	179.17(4)	179.74(2)	178.70(1)	This work, 153
	2.2308(4)			2.2915(4)			179.24(1)			[4], 100

Table 3

Interatomic distances (Å), bond angles (°) and torsion angles τ_m (= Au-P-C(m1)-C(m2)) (°) for [Ph_2(Ph-CHO)PAuX] and [Ph_3PAuX] complexes (present determinations) and for the free ligands Ph_2(Ph-CHO)P [16a] and Ph_3P [17].

R_3P	X	m	P-C_{m1}	Au-P-C_{m1}	C_{m1}-P-$C_{(m+1)1}$	τ_m
R_3PAuX						
Ph_2(Ph-CHO)P	Cl	1	1.826(5)	113.4(2)	105.6(2)	–60.2(4)
		2	1.809(4)	114.3(2)	109.1(2)	–42.4(4)
		3	1.812(4)	111.9(2)	101.5(2)	–3.1(4)
	Cl	1	1.830(5)	112.9(2)	106.3(2)	–65.1(4)
		2	1.819(4)	117.0(2)	106.6(2)	–41.4(4)
		3	1.812(5)	110.9(2)	102.3(2)	0.5(4)
	Br	1	1.833(6)	112.3(2)	107.3(3)	59.6(5)
		2	1.828(6)	110.6(2)	104.7(3)	40.6(5)
		3	1.819(6)	116.4(2)	104.6(3)	28.1(6)
	I	1	1.837(4)	112.8(1)	107.0(2)	58.5(4)
		2	1.813(4)	110.4(1)	104.7(2)	39.1(4)
		3	1.811(4)	116.8(2)	104.1(2)	29.8(4)
Ph_3P	Cl	1	1.813(1)	112.8(1)	107.6(2)	–57.4(1)
		2	1.808(1)	111.9(1)	105.9(2)	–42.41)
		3	1.811(1)	114.2(1)	103.8(2)	–30.2(1)
	Br	1	1.812(3)	112.9(1)	107.8(1)	58.3(2)
		2	1.803(3)	111.9(1)	105.2(2)	42.8(3)
		3	1.813(3)	114.4(1)	103.9(1)	32.8(3)
	I	1	1.814(2)	113.7(1)	107.0(1)	–60.0(2)
		2	1.813(2)	111.3(1)	104.9(1)	–39.7(2)
		3	1.814(2)	114.7(1)	104.6(1)	–32.8(2)
Ligands						
Ph_2(Ph-CHO)P		1	1.839(2)		102.3(1)	–51.9
		2	1.833(2)		102.9(1)	–44.8
		3	1.838(3)		101.9(1)	–27.9
Ph_3P		1	1.832(2)		101.7(1)	55.9
		2	1.828(2)		103.3(1)	27.1
		3	1.834(2)		103.3(1)	24.7

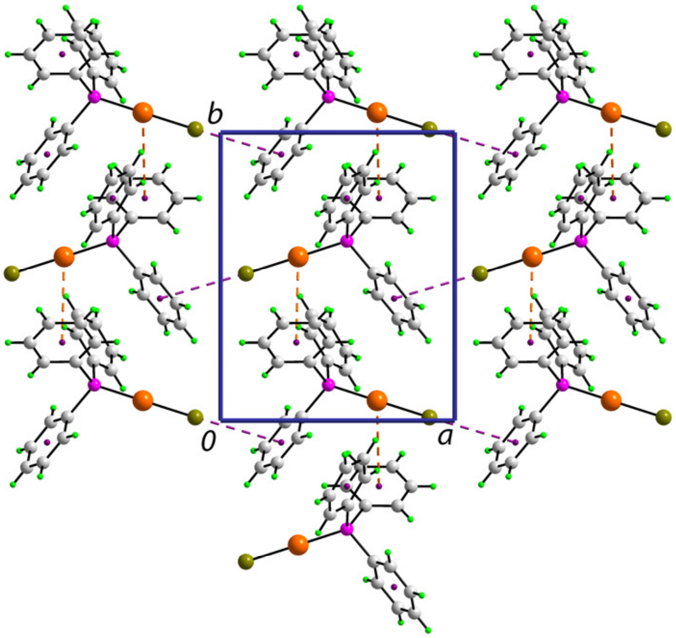
τ_m for the ligands Ph_2(Ph-CHO)P and Ph_3P are the torsion angles between the normal to the plane of the three *ipso* carbons and the C_{ipso} – C_{ortho} bonds.

Table 4

Unit cell dimensions and torsion angle data τ_n for α and β $P2_12_12_1$ R_3L-M-X complexes wher L = P,As; M = Au, Br, I, X= monovalent anion.

R_3L-M-X	*a* (Å)	*b* (Å)	*c* (Å)	*V*(Å)	τ_1	τ_2	τ_3	M-L (Å)	Ref. CCDC
α form									
Ph_3P-Au-Cl	10.116(2)	12.266(3)	13.002(3)	1613.3	–58	–42	–30	2.228(1)	This work
Ph_3P-Au-Br	9.9916(1)	12.338(1)	13.362(1)	1647.2	58	43	33	2.237(1)	This work
Ph_3P-Au-I	10.1325(8)	12.348(1)	13.794(1)	1725.9	–60	–40	–33	2.253(1)	This work
Ph_3P-Au-CN	10.388(2)	12.420(2)	13.057(2)	1684.6	56	45	32	2.278(2)	[8d] CYTPAU01
Ph_3P-Au-CNO	10.891(1)	12.169(1)	12.871(1)	1705.8	–57	–39	–30	2.274(3)	[8e] DUCROI
Ph_3P-Au-NCO	10.782(1)	12.007(1)	13.077(1)	1692.9	–56	–36	–29	2.222(1)	[8e] DUCRIC
Ph_3P-AuSCN$_{0.91}$Br$_{0.09}$	10.7673(9)	11.986(1)	13.624(1)	1758.3	63	26	30	2.255(8)	This work
Ph_3P-Au-O_2CCH_3	11.088(3)	12.050(4)	13.839(5)	1849.0	–54	–30	–33	2.207(3)	[8f] CILYAX
Ph_3P-Au-O_2CCF_3	11.906(3)	11.771(2)	14.169(3)	1985.7	59	21	36	2.208(4)	[8g] GOJJOE
Ph_2Ph-CHOP-Au-Br	9.9223(8)	12.506(1)	14.049(1)	1743.2	60	41	28	2.240(1)	This work
Ph_2(Ph-CHO)P-Au-I	10.0367(5)	12.6677(7)	14.1504(8)	1799.1	58	39	30	2.252(1)	This work
Ph_2(Ph-NH_2)P-Au-I	10.220(2)	12.689(4)	14.112(4)	1830.1	56	41	29	2.269(4)	[9a] NOWJIS
(MeIm)Ph_2P-Au-Cl	9.804(1)	12.370(2)	13.267(2)	1608.9	62	50	36	2.227(6)	[9b] AVACIJ
m-tolyl$_3$P-Au-Cl	11.236(1)	12.994(4)	13.371(2)	1952.2	–68	–45	–27	2.288(2)	[9c] SIVCEF
m-tolyl$_3$P-Au-CN	11.312(2)	12.996(3)	13.308(3)	1956.4	–71	–46	–23	2.286(2)	[9d] NOZMAQ
m-FPh_3P-Au-Cl	10.4028(8)	12.328(1)	13.221(1)	1695.6	57	39	22	2.225(1)	[9e] XAKGOH
Ph_3As-Au-Cl	10.203(4)	12.186(4)	13.228(5)	1644.7	59	40	30	2.334(3)	[10a] YIKVIX
Ph_3As-Au-Br	10.191(1)	12.438(1)	13.637(1)	1728.6	–59	42	–31	2.342(5)	[10b] BTPASG
Ph_3P-Br-Br	10.030(5)	12.73(1)	13.312(5)	1699.7	58	49	43	2.181(3)	[11a] JOMSEJ
Ph_3P-I-I	10.461(6)	12.993(1)	13.673(3)	1858.4	57	45	38	2.481(4)	[11b] JITSIO
β form									
Ph_3As-Au-Cl	11.929(2)	12.622(2)	10.974(2)	1644.7	46	10	31	2.334(3)	[10a] YIKVIX01
Ph_3P-Au-NNN	11.5642(1)	13.0993(1)	10.9252(1)	1655.0	–43	–13	–36	2.237(1)	[12a] EBUXEE
Ph_3P-Au-N_3C_2	12.689(4)	13.660(7)	10.93(1)	1894	40	15	51	2.229(5)	[12b] FIKQIZ
Ph_3P-Au-$CFCF_2$	11.736(1)	13.433(2)	11.403(1)	1797.6	47	12	43	2.272(3)	[12c] GUKHUP
Ph_3As-I-I	12.056(4)	13.963(3)	10.990(4)	1850.0	49	8	50	2.64(1)	[12d] FESKAP

Graphical Abstract



Highlights

- [Ph_3PAuX] (X = Cl, Br and I) crystallize as members of an isomorphous series the chiral space group $P2_12_12_1$.
- [Ph_2(Ph-CHO)PAuX] (X = Br, I) belong to the same isomorphous series.
- [Ph_2(Ph-CHO)PAuCl] crystallizes in the centrosymmetric space group P-1.
- The -CHO group results in very minor differences in the conformational structures.
- The observation of different supramolecular synthons suggest global packing dominates while specific supra-molecular interactions comply with overall crystal packing.