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Co-ordination and conformational isomerism in bis(tricyclohexylphosphine) gold(I) halides

Graham A. Bowmaker,[a] Christopher L. Brown,[b] Robert D. Hart,[c] Peter C. Healy,*[b] Clifton E. F. Rickard[a] and Allan H. White[c]

[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[b] *School of Science, Griffith University, Brisbane, 4111, Queensland, Australia. E-mail: P.Healy@sct.gu.edu.au*
[c] *Department of Chemistry, University of Western Australia, Nedlands, 6907, Western Australia, Australia*

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Solid state complexes of bis(tricyclohexylphosphine)gold(I) with halide counter ions, $Au(PCy_3)_2X$ (X = Cl, Br or I), have been crystallised from solutions of $[NBu_4][AuX_2]$ and PCy_3 in dimethylformamide and characterised by single crystal structure determinations, far-infrared spectroscopy and solid state ^{31}P CP MAS NMR spectroscopy. The results show the complexes crystallise as a unique array of co-ordination and conformational isomers which reflect the conformational flexibility of the tricyclohexylphosphine ligand and the relative preferences of the halide anions for $C–H\cdots X^-$ *versus* $Au^+\cdots X^-$ bonding interactions. The chloride crystallises as a single ionic complex, $[Au(PCy_3)_2]^+Cl^-$, with the gold two-co-ordinate and the cations and anions well separated in the crystal lattice. The bromide crystallises as three different polymorphs with four distinct molecular structures. The first (α) form crystallises as ionic $[Au(PCy_3)_2]^+Br^-$ with the bromide adjacent to but not co-ordinated to the gold. The second (β) form presents two crystallographically independent $[Au(PCy_3)_2Br]$ molecules with semi-co-ordinated bromide and significant differences in the conformational dispositions of the PCy_3 ligands. The third (γ) form crystallises as $[Au(PCy_3)_2Br]$ with fully co-ordinated bromide. The iodide crystallises with semi-co-ordinated and co-ordinated iodide in $[Au(PCy_3)_2I]\cdot PCy_3$ and $[Au(PCy_3)_2I]$ complexes respectively. The study provides an unusual series of molecular 'vignettes' in which the response of the $[Au(PCy_3)_2]^+$ cation to halide anion can be monitored as it passes through the ligand substituents and co-ordinates to the central gold atom.

Introduction

Structural and spectroscopic studies on monomeric bis(monodentate tertiary phosphine)gold(I) complexes with halide counter ions, $Au(PR_3)_2X$ (X = Cl, Br or I), show a noticeable dependence of the gold co-ordination geometry on the choice of phosphine ligand. Thus, for X = Cl, the complexes with tri-*tert*-butylphosphine (P^tBu_3) and tricyclohexylphosphine (PCy_3) crystallise as linear two-co-ordinate ionic salts, $[Au(PR_3)_2]^+Cl^-$ with isolated cations and anions,[1,2] while those with trimethylphosphine (PMe_3) and 1,3,5-triaza-7-phosphaadamantane (TPA) crystallise as "ion-pair" salts, $[Au(PR_3)_2^+\cdots Cl^-]$, which exhibit relatively short $Au\cdots Cl$ distances (<3.2 Å) but in which the P–Au–P angle remains close to 180°.[3,4] By contrast, the complexes of triphenylphosphine (PPh_3) for X = Cl, Br and I all form neutral three-co-ordinate molecules, $[Au(PPh_3)_2X]$, with strongly co-ordinated halide and the P–Au–P angles diminished to 132–136°.[5,6] Mössbauer studies on the triethylphosphine complexes $Au(PEt_3)_2X$ (X = Cl or I) and solid state ^{31}P CP MAS NMR as well as low frequency vibrational and Mössbauer spectroscopic studies on $Au(PMe_3)_2I$ provide further evidence that gold–halide bonding interactions are involved in the formation of these complexes.[7,8]

This diversity of structural form and co-ordination geometry for the chloride complexes and the relative lack of structural data for systems utilising bromide and iodide as counter ions, coupled with our interest in delineating the relative significance of the roles of $Au^+\cdots X^-$ and $C–H\cdots X^-$ bonding interactions in the formation and stabilisation of these complexes, suggested that further structural and spectroscopic studies on this system were warranted. Towards this end, we investigated the properties of complexes containing tricyclohexylphosphine as the co-ordinating ligand. These complexes were prepared by crystallisation of the product from stoichiometric solutions of $[NBu_4][AuX_2]$ and PCy_3 in dimethylformamide. Single crystal structure determinations, solid state ^{31}P CP MAS NMR and far infrared spectroscopic studies on the products obtained revealed the formation of a unique array of co-ordination and conformational isomers in which the chloride was obtained as an ionic $[Au(PCy_3)_2]^+Cl^-$ complex with two-co-ordinate gold, the iodide as $[Au(PCy_3)_2I]$ and $[Au(PCy_3)_2I]\cdot PCy_3$ complexes with three-co-ordinate gold and the bromide as a series of both two- and three-co-ordinate complexes. The results of this work are reported herein.

Experimental

Synthesis

The compounds were prepared in similar fashion by crystallisation from *ca.* 0.1 M solutions of the complex formed from the reaction of stoichiometric quantities of the appropriate tetrabutylammonium dihalogenoaurate(I) salt, $[NBu_4][AuX_2]$ (where X = Cl, Br or I) and PCy_3 in dimethylformamide (dmf). The $[NBu_4][AuX_2]$ salts were prepared as previously described.[9] The compound PCy_3 was obtained from Strem Chemicals and used as received.

$Au(PCy_3)_2Cl$. The salt $[NBu_4][AuCl_2]$ (0.10 g, 0.2 mmol) and PCy_3 (0.12 g, 0.43 mmol) were dissolved in 3 ml of warm (≈60 °C) dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate

(Found: C, 54.9; H, 8.6. $C_{36}H_{66}AuClP_2$ requires C, 54.5; H, 8.4%), mp 200–202 °C. Unit cell determinations and a low-temperature (203 K) single crystal structure determination showed the crystals formed to have the structure previously recorded for crystals obtained from the reaction in ethanol of PCy_3 and Au^I, the latter being obtained by reduction of $HAuCl_4$ with thiodiethanol.[2]

$Au(PCy_3)_2Br$. Far infrared and solid state CP MAS ^{31}P NMR spectra on products obtained show the formation of several different polymorphs; three of which (denoted α, β and γ) were characterised by single crystal X-ray structure determinations.

α Form. The salt $[NBu_4][AuBr_2]$ (0.147 g, 0.25 mmol) and PCy_3 (0.144 g, 0.51 mmol) were dissolved in 5 ml warm dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate (Found: C, 51.2; H, 8.0. $C_{36}H_{66}AuBrP_2$ requires C, 51.6; H, 7.9%), mp 194–197 °C. The product was shown by solid state ^{31}P NMR spectroscopy and unit cell dimension checks on several typical crystals to consist of predominantly the α form, together with cocrystallised β and γ forms plus possibly further, as yet unidentified, forms (see Discussion). Interestingly, repetition of the experiment under essentially identical reaction conditions resulted in crystallization of the γ form only.

β Form. The salt $[NBu_4][AuBr_2]$ (0.175 g, 0.29 mmol) and PCy_3 (0.180 g, 0.64 mmol) were dissolved in 3 ml warm dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate, mp 198–200 °C.

γ Form. The salt $[NBu_4][AuBr_2]$ (0.300 g, 0.50 mmol) and PCy_3 (0.280 g, 1.00 mmol) were dissolved in 5 ml warm dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate, mp 195–204 °C.

$[Au(PCy_3)_2I]$. The salt $[NBu_4][AuI_2]$ (0.334 g, 0.46 mmol) and PCy_3 (0.276 g, 0.98 mmol) were dissolved in 20 ml warm dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate (Found: C, 48.5; H, 7.7. $C_{36}H_{66}AuIP_2$ requires C, 48.9; H, 7.5%), mp 206–208 °C.

$[Au(PCy_3)_2I]\cdot PCy_3$. The salt $[NBu_4][AuI_2]$ (0.284 g, 0.34 mmol) and PCy_3 (0.282 g, 1.01 mmol) were dissolved in 10 ml of warm dmf. The solution was cooled to room temperature and allowed to stand for 2–3 d to yield a crystalline precipitate (Found: C, 53.7; H, 8.5. $C_{54}H_{99}AuIP_3$ requires C, 55.7; H, 8.6%), mp 206–209 °C. The precipitate was shown by solid state ^{31}P NMR (see below) to also contain unsolvated complex and cocrystallised 'free' ligand.

Crystallography

X-Ray data collections were performed using Mo-Kα radiation on an Enraf-Nonius CAD-4 diffractometer with scintillation counter at 295 K for α-$[Au(PCy_3)_2Br]$ and $[Au(PCy_3)_2I]$, on a Siemens diffractometer with a SMART CCD area detector at 203 K for $[Au(PCy_3)_2Cl]$, β-$[Au(PCy_3)_2Br]$ and $[Au(PCy_3)_2I]\cdot PCy_3$, and on a Rigaku four circle diffractometer (rotating anode source) with scintillation counter at 295 K for γ-$[Au(PCy_3)_2Br]$. The structures were solved by direct methods and refined by full matrix least squares refinement on $|F|$ for observed data or F^2 (all data) after absorption corrections. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals at convergence, R, R', are quoted. Computation used XTAL 3.2,[10] SHELX 97[11] and TEXSAN[12] software. The carbon atoms of the PCy_3 ligands are labelled C(*lmn*) where *l* is the ligand number 1 or 2, *m* is the ring number 1, 2 or 3 and *n* is the atom number 1–6 with the carbon bound to the phosphorus labelled C(*lm*1).

Crystal/refinement data. $[Au(PCy_3)_2]Cl \equiv C_{36}H_{66}AuClP_2$, M = 793.2, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 9.4566(1), b = 17.3328(3), c = 11.5786(2) Å, β = 107.93(1)°, U = 1805.6 Å^3, Z = 2, D_c = 1.459 g cm^{-3}, $F(000)$ = 816, μ = 42.6 cm^{-1}, crystal size = 0.48 × 0.24 × 0.23 mm, $T_{max,min}$ = 0.441, 0.234, $2\theta_{max}$ = 56°, N = 4077, N_o [$I > 2\sigma(I)$] = 3188, R = 0.027, R' = 0.065.

α-$[Au(PCy_3)_2]Br \equiv C_{36}H_{66}AuBrP_2$, M = 837.7, orthorhombic, space group $Ccm2_1$ (C^{12}_{2v}, no. 36, variant), a = 11.600(4), b = 17.913(12), c = 18.000(16) Å, U = 3740 Å^3, Z = 4, D_c = 1.489 g cm^{-3}, $F(000)$ = 1704, μ = 51.1 cm^{-1}, crystal size = 0.23 × 0.27 × 0.70 mm, $T_{min,max}$ = 0.23, 0.39, $2\theta_{max}$ = 60°, N = 2901, N_o [$I > 3\sigma(I)$] = 2062, R = 0.041, R' = 0.041 (both chiralities).

β-$[Au(PCy_3)_2Br] \equiv C_{36}H_{66}AuBrP_2$, M = 837.7, orthorhombic, space group $Pca2_1$ (C^5_{2v}, no. 29), a = 17.1299(3), b = 17.5458(1), c = 24.7345(4) Å, U = 7434.2 Å^3, Z = 8, D_c = 1.497 g cm^{-3}, $F(000)$ = 3408, μ = 51.4 cm^{-1}, crystal size = 0.41 × 0.38 × 0.16 mm, $T_{min,max}$ = 0.23, 0.49, $2\theta_{max}$ = 52°, N = 12972, N_o [$I > 2\sigma(I)$] = 10052, R = 0.046, R' = 0.104.

γ-$[Au(PCy_3)_2Br] \equiv C_{36}H_{66}AuBrP_2$, M = 837.7, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), a = 18.01(1), b = 9.198(4), c = 22.485(7) Å, β = 95.63(3)°, U = 3707 Å^3, Z = 4, D_c = 1.50 g cm^{-3}, $F(000)$ = 1704, μ = 51.7 cm^{-1}; crystal size = 0.25 × 0.25 × 0.10 mm, $T_{min,max}$ = 0.42, 0.60, $2\theta_{max}$ = 50°, N = 3478, N_o [$I > 3\sigma(I)$] = 2309, R = 0.040, R' = 0.041.

$[Au(PCy_3)_2I]\cdot PCy_3 \equiv C_{54}H_{99}AuIP_3$, M = 1165.1, monoclinic, space group $P2_1/c$, a = 18.3435(3), b = 17.6264(3), c = 17.6136(2) Å, β = 100.838(1)°, U = 5593 Å^3, Z = 4, D_c = 1.38 g cm^{-3}, $F(000)$ = 2400, μ = 33.0 cm^{-1}, crystal size = 0.43 × 0.26 × 0.08 mm, $T_{min,max}$ = 0.33, 0.78, $2\theta_{max}$ = 50°, N = 9820, N_o [$I > 2\sigma(I)$] = 7393, R = 0.070, R' = 0.169.

$[Au(PCy_3)_2I] \equiv C_{36}H_{66}AuIP_2$, M = 884.2, triclinic, space group $P\bar{1}$ (C^2_i, no. 2), a = 9.211(6), b = 9.727(4), c = 23.216(3) Å, α = 94.01(2), β = 97.61(4), γ = 114.88(5)°, U = 1852 Å^3, Z = 2, D_c = 1.58 g cm^{-3}, $F(000)$ = 888, μ = 49.1 cm^{-1}, crystal size = 0.38 × 0.27 × 0.13 mm, $T_{min,max}$ = 0.32, 0.57, $2\theta_{max}$ = 55°, N = 6761, N_o = 5767, R [$I > 3\sigma(I)$] = 0.031, R' = 0.054.

Abnormal features. The cyclohexyl rings (2*mn*) in α-$[Au(PCy_3)_2Br]$ and (12*n*) in molecule 2 of β-$[Au(PCy_3)_2Br]$ show large thermal parameters at the periphery indicative of considerable disorder in the atom positions for these rings.

CCDC reference number 186/1327.

See http://www.rsc.org.suppdata/dt/1999/881/ for crystallographic files in .cif format.

Spectroscopy

Solid state cross-polarisation magic-angle spinning (CP MAS) ^{31}P NMR spectra were recorded at room temperature on a Varian Unity-400 spectrometer at 161.93 MHz. Single contact times of 1 ms were used with proton pulse width of 7.2 μs, proton decoupling field at 60 kHz, and a recycle time of 30 s. The samples were packed in Kel-F inserts within silicon nitride rotors and spun at 5 kHz. Chemical shifts were referenced to 85% H_3PO_4 *via* solid triphenylphosphine (δ −9.9).

Far-infrared spectra were recorded at 2 cm^{-1} resolution as Polythene discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 lines mm^{-1} wire mesh beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector. All measurements were carried out at room temperature.

Results and discussion

Structural data

The single crystal structure determinations of $Au(PCy_3)_2X$ arrays for X = Cl, Br or I are consistent with the formulation of the structures as either ionic two-co-ordinate $[Au(PCy_3)_2]^+X^-$ or neutral three-co-ordinate $[Au(PCy_3)_2X]$ monomeric species. Representative views of the molecules projected onto their P_2AuX planes are shown in Figs. 1–3. Relevant geometric

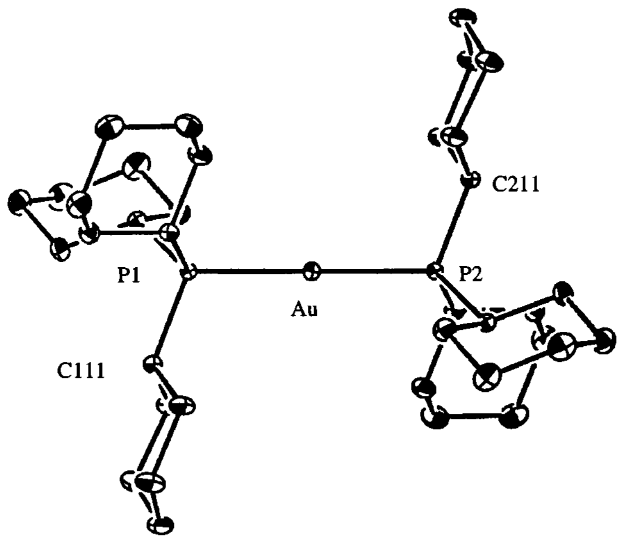
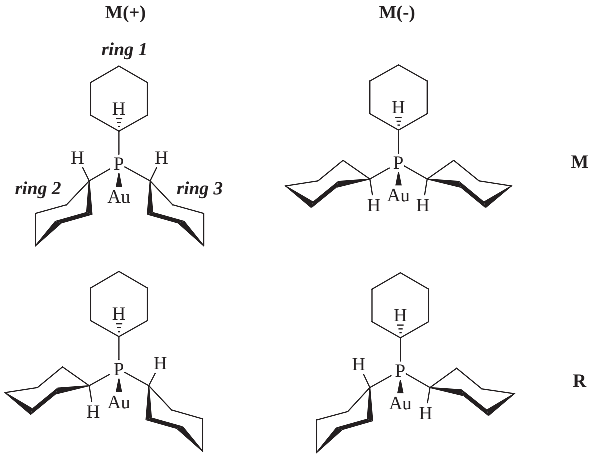


Fig. 1 Representative view of the cation of $[Au(PCy_3)_2]Cl$; 30% ellipsoids are shown. Hydrogen atoms are omitted for clarity.

parameters are listed in Tables 1 and 2, with comparative data for the analogous $[Au(PPh_3)_2X]$ complexes included in Table 1. All the cyclohexyl rings adopt chair conformations with equatorial C′–P bonds. For all ligands the plane of one cyclohexyl ring (ring 1) lies approximately orthogonal to the Au–P–C(11) plane with the associated P–Au and C(11)–H(11) bonds antiperiplanar. Rings 2 and 3 are disposed either above or below the Au–P–C(11) plane with the associated P–Au and C(n1)–H(n1) bonds ($n = 2$ or 3) variously (+,−) synclinal, (+,−) anticlinal or orthogonal. The overall conformational disposition of the ligands falls into one of two basic types depending on the relative orientations of rings 2 and 3 (Scheme 1). In the first (labelled M) the C(21)–H(21) and C(31)–H(31) bonds point in the same direction [either towards (M+) or away (M−) from ring 1] such that the symmetry of the ligand is approximately m; in the second (labelled R) the two C–H bonds point in opposite directions such that the ligand is chiral by virtue of a stereogenic phosphorus centre.



Scheme 1

The present low temperature structure determination of the chloride complex is essentially the same as the previously determined room temperature structure,[2] crystallising in the monoclinic space group $P2_1/c$ as discrete $[Au(PCy_3)_2]^+$ cations with two-co-ordinate gold (Fig. 1). The lattice structure for this complex forms a well packed array of alternating cations and anions with multiple C–H · · · Cl interactions with H · · · Cl distances ranging from 2.7 to 3.0 Å. These results, unlike those for the bromide and iodide complexes (see below), indicate a strong preference by the chloride anion for the formation of C–H · · · Cl hydrogen bonds with respect to co-ordinating to the gold centre. In the cation the gold is located on a crystallographic inversion centre such that the P–Au–P geometry is linear while the symmetrically equivalent ligands are perfectly staggered, adopting R dispositions of opposite chirality. The Au–P bond lengths of 2.321(2) Å (room temperature[2]) and 2.318(1) Å (203 K) are the same within experimental error and are the same also as the analogous bond lengths reported for other two-co-ordinate ionic $[Au(PCy_3)_2]^+X^-$ complexes: 2.325(6), 2.324(6) Å for $X = PF_6$,[13] and 2.295(11), 2.316(13) Å for X = SCN.[14] It is interesting that the PCy_3 ligands in these latter two complexes are eclipsed rather than staggered, indicating that steric interactions between the PCy_3 ligands may be small enough to allow free rotation of the ligands with respect to each other without affecting the Au–P bond lengths.

The α form of $Au(PCy_3)_2Br$ crystallises in the orthorhombic space group $Ccm2_1$ as an ionic species $[Au(PCy_3)_2]^+Br^-$ with two-co-ordinate gold [Fig. 2(a)]. The crystallographic mirror plane contains the phosphorus, gold and bromide atoms and bisects ring 1 of both ligands. The ligands are staggered and adopt M dispositions (Scheme 1) in conformity with the associated crystallographic symmetry. The bromide anion is located in the region between the ligand substituents and adjacent to the gold centre. The very long Au · · · Br distance of 3.764(4) Å and the P–Au–P angle of 178.4(1)° indicate an absence of any substantial $Au^+ \cdots Br^-$ bonding interactions in this complex (see discussion below). Instead, the bromide is displaced towards rings 2 and 3 of ligand 1 and engages in C–H · · · Br hydrogen bonding interactions with these rings. This interaction results in an M(−) disposition of this ligand rather than the M(+) found for all the other 'M' type ligands in the series. This 'capture' of the bromide anion by the cyclohexyl rings can, in the light of the results described below for the β and γ forms, be considered unusual but clearly demonstrates the comparability in the strength of the C–H · · · Br and Au · · · Br bonding interactions in these complexes.

The β form crystallises in the orthorhombic space group $Pca2_1$ with two crystallographically independent $Au(PCy_3)_2Br$ molecules (β_1 and β_2) in the unit cell [Fig. 2(b) and 2(c)]. In contrast to the α form, the bromide anions in these molecules are semi-co-ordinated to the gold atoms with Au–Br bond lengths of 2.894(1) and 2.842(1) Å and P–Au–P angles of 162.06(9) and 157.7(1)° respectively. The P_2AuBr array is both planar and symmetric with P–Au–Br angles of 99.56(7) and 97.69(7)° for β_1 and 101.65(8) and 100.51(8)° for β_2. The ligand conformations for both molecules are midway between staggered and eclipsed with the ring 1 planes orthogonal to each other. In β_1 both ligands adopt R dispositions, but, unlike the chloride complex, of the same chirality, whereas in β_2 the two ligands adopt R and M(+) dispositions respectively.

The transition of the bromide anion from non- to semi- to fully co-ordinated to the gold centre is achieved with the γ form which crystallises as three-co-ordinate $[Au(PCy_3)_2Br]$ molecules [Fig. 2(d)] in the monoclinic space group $C2/c$ isomorphous with the analogous copper(I) nitrate and perchlorate adducts.[15,16] The molecule is disposed about the crystallographic two-fold axis which lies along the Au–Br bond. The two PCy_3 ligands are equivalent by symmetry and fully eclipsed with both adopting M(+) dispositions. The planes of rings 2 are coincident with the P_2AuBr array with the shortest C–H · · · Br contact distance of 3.3 Å significantly longer than the corresponding distances observed for the α and β forms and indicating a preference of the bromide for co-ordination to the gold(I) centre in this situation. The Au–Br bond length of 2.777(1) Å and the P–Au–P angle of 147.5(1)° are the smallest values of these parameters for the series but are still greater than the corresponding values of 2.625(2) Å and 132.45(8)° recorded for the analogous triphenylphosphine complex.[6]

The three-co-ordinate iodide complex has been obtained in

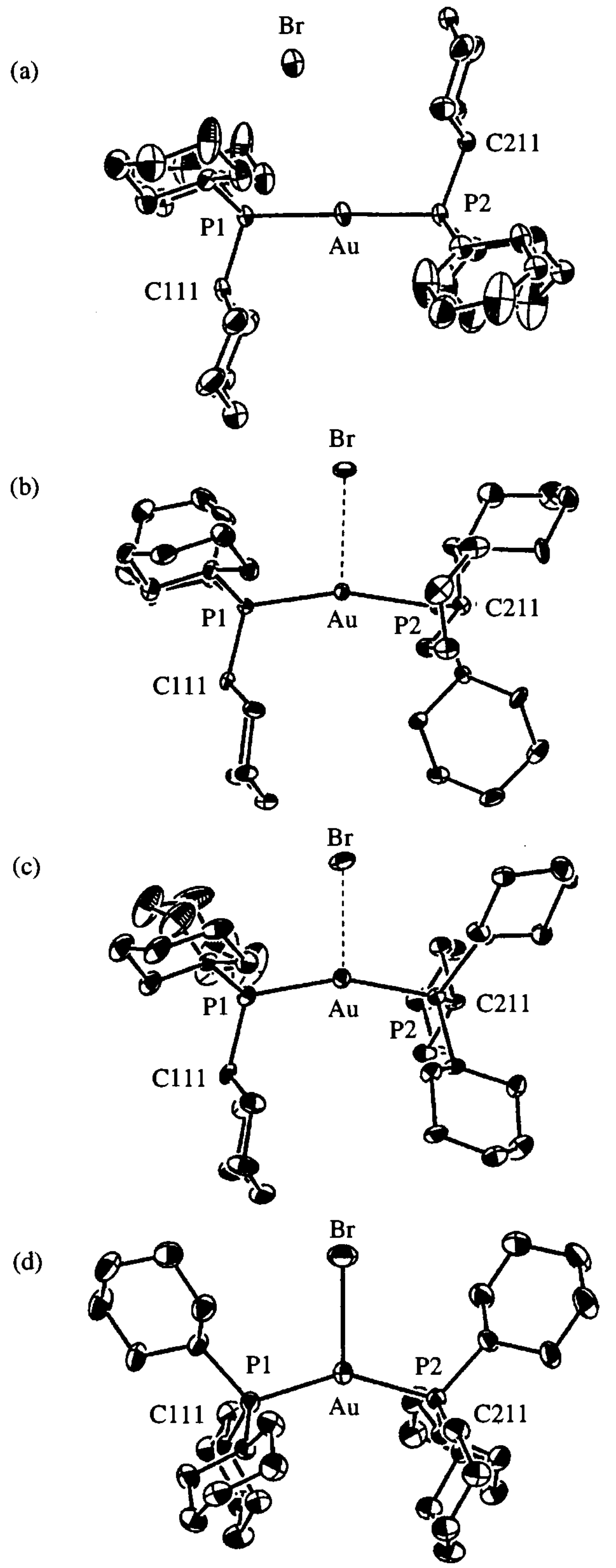


Fig. 2 Representative views of the molecular structures of (a) α-$Au(PCy_3)_2Br$, (b) β_1-$Au(PCy_3)_2Br$, (c) β_2-$Au(PCy_3)_2Br$ and (d) γ-$Au(PCy_3)_2Br$.

two forms: as $[Au(PCy_3)_2I]$ from 1 : 2 stoichiometric solutions of $[NBu_4][AuI_2]$ and PCy_3 in dmf and as a PCy_3 'solvated' complex, $[Au(PCy_3)_2I]\cdot PCy_3$, from 1 : 3 solutions of $[NBu_4][AuI_2]$ and PCy_3. This latter complex crystallises in the monoclinic space group $P2_1/c$ in which the $[Au(PCy_3)_2I]$ and unco-ordinated PCy_3 molecules constitute the asymmetric unit of the crystal lattice. The structure of the $[Au(PCy_3)_2I]$ molecule [Fig. 3(a)] is similar to that of the β_2 bromide with the iodide semi-co-ordinated to the gold [Au–I 3.008(1) Å, P–Au–P 159.1(1)°]

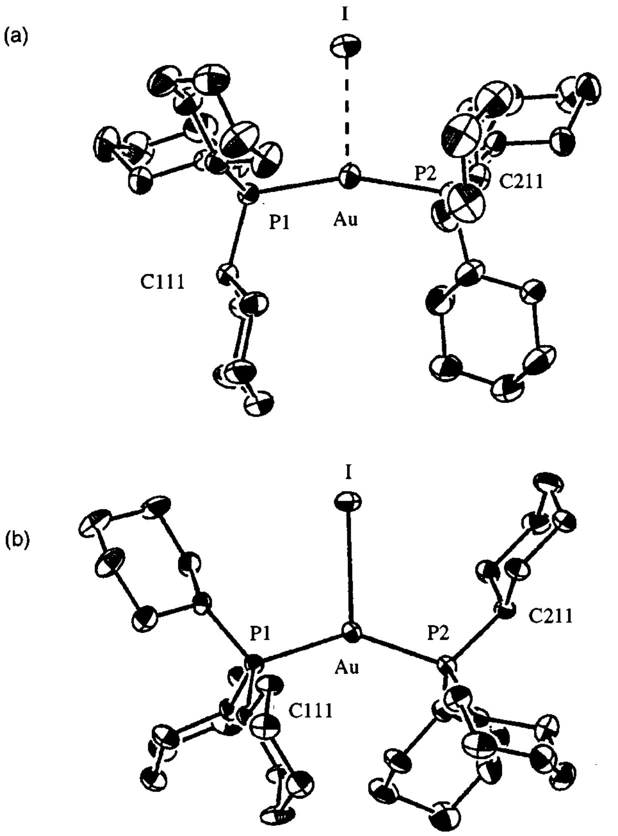


Fig. 3 Representative views of the molecular structures of (a) $[Au(PCy_3)_2I]\cdot PCy_3$ and (b) $[Au(PCy_3)_2I]$.

while the PCy_3 ligands adopt R and M(+) conformations respectively. The solvated PCy_3 molecule adopts an R disposition with X–P–C(11)–H(11) torsion angles of 176, 55 and 92° (the P–X vector being defined in the direction of the axis perpendicular to the base of the PC_3 pyramid). This conformation is essentially the same as that adopted for free PCy_3 which also crystallises in an R disposition[17] with X–P–C(11)–H(11) angles of 176, 62 and 90°.

'Unsolvated' $Au(PCy_3)_2I$ crystallises in the triclinic space group $P\bar{1}$ as three-co-ordinate $[Au(PCy_3)_2I]$ molecules [Fig. 3(b)]. The unit cell is isomorphous with that of the analogous copper iodide and silver nitrate, perchlorate and cyanate adducts.[18,19] The two ligands are fully eclipsed and adopt M(+) and R dispositions respectively. Ring 1 of ligand 2 lies disposed across the P_2AuI array and on the same side of the molecule as the Au–I bond while ring 1 of ligand 1 is anticlinal to the Au–I bond. The Au–I bond length decreases to 2.895(2) Å with a corresponding decrease of the P–Au–P bond angle to 143.1(1)°, the smallest observed for all the cyclohexylphosphine/halide complexes in the series, but still greater than the values of 2.754(1) Å and 132.13(7)° found for the analogous triphenylphosphine complex.[6] It is interesting in this series of molecules that the transition from non-co-ordinated to co-ordinated halide is accompanied by changes in the conformational disposition of the ligands from staggered to eclipsed.

In previous work on both mercury(II) and silver(I) phosphine complexes it has been shown that the co-ordination of X^- to two-co-ordinate P_2M^+ cations and the consequent reduction of the P–M–P angle from 180° is often accompanied by an increase in the M–P bond length as the co-ordinating ability of the anion increases.[19–22] This correlation between the M–P distance and the P–M–P angle is rationalised in terms of competition for electron density between the M–P and M–X bonds. Similar correlation would be expected for the present series of complexes as a result of the decrease in Au–Br and Au–I bond lengths for the various isomers and with increasing co-

Table 1 P_2MX Core geometries for $[Au(PCy_3)_2X]$ and $[Au(PPh_3)_2X]$ molecules for X = Cl, Br or I

X	*T*/K	Au–P1/Å	Au–P2/Å	Au–X/Å	P–Au–P/°	P1–Au–X/°	P2–Au–X/°	Ref.
$[Au(PCy_3)_2X]$								
Cl	r.t.	2.321(2)	2.321(2)		180(−)			5
Cl	203	2.318(1)	2.318(1)		180(−)			[a]
Br α	295	2.328(3)	2.305(3)	3.764(4)	178.4(1)	72.52(9)	109.0(1)	[a]
Br β_1	203	2.317(3)	2.311(3)	2.894(1)	162.06(9)	99.56(7)	97.69(7)	[a]
Br β_2	203	2.292(3)	2.302(3)	2.842(1)	157.7(1)	100.51(8)	101.65(8)	[a]
Br γ	295	2.323(2)	2.323(2)	2.777(2)	147.5(1)	106.27(6)	106.27(6)	[a]
$I{\cdot}PCy_3$	203	2.315(3)	2.310(3)	3.008(1)	159.1(1)	98.69(7)	101.87(8)	[a]
I	295	2.344(2)	2.328(2)	2.895(2)	143.1(1)	106.26(7)	110.45(7)	[a]
$[Au(PPh_3)_2X]$								
Cl	295	2.336(4)	2.317(4)	2.533(4)	135.7(1)	109.1(1)	114.8(1)	6
$Cl{\cdot}C_6H_6$	r.t.	2.339(4)	2.323(4)	2.500(4)	132.1(1)	109.2(1)	118.7(1)	5
Br	295	2.323(2)	2.323(2)	2.625(2)	132.45(8)	113.78(5)	113.78(5)	6
I	295	2.333(2)	2.333(2)	2.754(1)	132.13(7)	113.93(7)	113.93(7)	6

[a] This work.

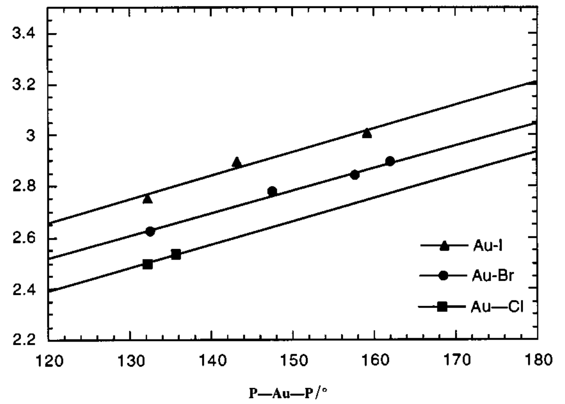


Fig. 4 Scatter plot of Au–Cl, Au–Br and Au–I bond lengths *versus* the P–Au–P angle for $[Au(PCy_3)_2X]$ and $[Au(PPh_3)_2X]$ complexes.

ordinating ability of the halides from chloride to iodide. The results in Table 1, however, show that while these changes significantly alter the P–Au–P angle, no corresponding trends are observed for the Au–P bond lengths which exhibit random values between 2.292(3) and 2.344(2) Å, with an average value of 2.32(1) Å that is essentially the same as for the chloride complex with no co-ordinated anion. This ability of the P–Au–P array to undergo significant deviations from linearity without seriously affecting the Au–P bond lengths is consistent with the view that the gold and phosphorus atoms in these complexes form single bonds only, and that these possess considerably more 6s than 6p character.[23]

Scatter plots of the Au–X bond lengths for X = Cl, Br and I against the P–Au–P angles for molecular $[Au(PCy_3)_2X]$ and $[Au(PPh_3)_2X]$ complexes are shown in Fig. 4, the data for X = Cl being derived from the two points available from the structures of the benzene solvated and unsolvated PPh_3 complexes.[5,6] The linear regression lines for each halide lie almost parallel with shifts for $\Delta[d(AuBr)–d(AuCl)]$ and $\Delta[d(AuI)–d(AuBr)]$ of 0.12 and 0.15 Å respectively. Interestingly, these differences are essentially the same as those found for the corresponding 1 : 1 $[Au(PCy_3)X]$ and $[Au(PPh_3)X]$ complexes.[24] Making the assumption that the radius of Au^+ does not change significantly, the differences can be ascribed to the differences in the radius of the chloride, bromide and iodide anions. Extrapolation of the three lines to 180° (at which point the halide can be assumed to just no longer be co-ordinated to the gold) yields Au–X distances of *ca.* 2.93 Å for X = Cl, 3.05 Å for X = Br and 3.20 Å for X = I. These distances represent an estimate of the non-bonded contact distance between Au^+ and X^- and show that the Au···Cl distances of 3.167(1) Å for the PMe_3 complex[3] and 3.224(4) Å for the TPA complex[4] place the chloride in these compounds just outside the gold co-ordination sphere while the Au···Br distance of 3.764(4) Å in the present α-bromide complex places the bromide anion well outside the gold co-ordination sphere.

These results also provide insight into the size of the gold and halide ions in these complexes. Recently, the radius of the Au^+ cation in linear two-co-ordinate complexes has been estimated to be 1.25 Å based on the Au–P bond length of 2.352(1) Å recorded for the trimesitylphosphine complex, $[Au\{P(mes)_3\}_2]BF_4$.[25] The average values of 2.32(1) Å for the Au–P bond length in the present PCy_3 and PPh_3 complexes suggest that the above estimate for the radius of Au^+ may, in fact, lie at the upper end of the range of possible values for this parameter. Using values of 1.22–1.25 Å, the radius of the halide anions can be estimated to be *ca.* 1.7 Å for X = Cl, 1.8 Å for X = Br and 2.0 Å for X = I. While these estimates are approximate only, it is interesting that they are consistently shorter than the quoted values[26] for the radii of the X^- anion of 1.81, 1.96 and 2.20 Å for X = Cl, Br and I respectively, and that the differences increase in the order Cl < Br < I. This trend is consistent with the increased co-ordinating ability of the halide and indicates that some residual level of covalent interaction between the gold and halide atoms such that, as further data become available, the lines in Fig. 4 may deviate from linearity and curve upwards by varying degrees as the P–Au–P angle approaches 180°.

Solid state ^{31}P CP MAS NMR spectroscopy

The solid state ^{31}P CP MAS NMR spectra recorded on these compounds are presented in Fig. 5, with chemical shift and coupling constant data listed in Table 3. Recently, we have shown that the analogous spectra of $[Au(PMe_3)_2]X$ for X = Cl and Br are split into doublets as a consequence of spin–spin interactions between the spin 1/2 phosphorus and spin 3/2 quadrupolar gold nuclei that were not averaged out by quadrupolar relaxation effects.[8] One aspect of this present work was to ascertain whether similar effects would be observable with the cyclohexylphosphine ligand which has similar σ-donor basicity to that of trimethylphosphine, and both ligands possess aliphatic substituent groups. In the event, the results showed no quadrupolar splitting of the peaks, indicating a dominance of relaxation effects on the spectra of these complexes.

In the spectrum of the chloride complex, shown in Fig. 5(a), the strong peak at δ 63.6 is assigned to the equivalent phosphorus nuclei of the $[Au(PCy_3)_2]^+$ cation and is comparable to the solution value of δ 63.8 recorded for the cation in $CDCl_3$ solution.[27] The minor peak at δ 55 arises from cocrystallised 1 : 1 complex.[24] The spectra recorded for the various samples of the

Table 2 $AuPC_3$ Geometric parameters (bond lengths in Å, angles in °) for $[Au(PCy_3)_2X]$ molecules (X = Cl, Br or I)

	Cl	Br α	Br β_1	Br β_2	Br γ	I·PCy_3	I
P1–C111	1.844(3)	1.83(2)	1.83(1)	1.86(1)	1.847(8)	1.86(1)	1.84(1)
P1–C121	1.850(3)	1.84(1)	1.87(1)	1.86(1)	1.847(8)	1.83(1)	1.84(1)
P1–C131	1.842(3)	1.84(1)	1.85(1)	1.87(1)	1.860(8)	1.86(1)	1.85(1)
P2–C211	1.844(3)	1.84(1)	1.85(1)	1.84(1)	1.847(8)	1.85(1)	1.84(1)
P2–C221	1.850(3)	1.84(2)	1.87(1)	1.83(1)	1.847(8)	1.85(1)	1.84(1)
P2–C231	1.842(3)	1.84(2)	1.86(1)	1.87(1)	1.860(8)	1.85(1)	1.85(1)
Au–P1–C111	111.2(1)	108.3(4)	112.0(3)	114.0(4)	111.4(3)	114.4(4)	114.3(3)
Au–P1–C121	113.8(1)	113.6(3)	113.4(3)	113.1(5)	114.9(3)	113.6(4)	108.1(3)
Au–P1–C131	109.2(1)	113.6(3)	110.9(4)	113.7(4)	109.4(3)	110.9(4)	114.3(3)
Au–P2–C211	111.2(1)	109.9(4)	111.8(4)	110.6(4)	111.4(3)	110.9(4)	117.8(3)
Au–P2–C221	113.8(1)	111.2(5)	110.4(4)	110.3(4)	114.9(3)	112.4(4)	108.8(3)
Au–P2–C231	109.2(1)	111.2(5)	114.8(4)	112.5(4)	109.4(3)	111.7(5)	111.7(3)
C111–P1–C121	108.5(1)	108.2(4)	104.7(5)	102.8(7)	103.5(4)	107.6(5)	103.7(4)
C121–P1–C131	108.0(1)	104.8(5)	107.1(5)	106.0(6)	111.5(4)	106.3(5)	112.3(4)
C131–P1–C111	105.8(1)	108.2(4)	108.5(5)	106.3(5)	105.6(4)	103.3(6)	103.6(4)
C211–P2–C221	108.5(1)	106.4(6)	104.2(5)	105.8(5)	103.5(4)	105.6(6)	104.1(4)
C221–P2–C231	108.0(1)	111.4(9)	108.3(5)	113.8(5)	111.5(4)	111.0(7)	106.0(4)
C231–P2–C211	105.8(1)	106.4(6)	106.8(5)	103.3(5)	105.6(4)	104.7(6)	107.6(4)
Torsion angles							
τ_{11}	−176	180	175	177	177	176	179
τ_{12}	−93	−92	58	138	44	54	68
τ_{13}	−59	92	80	78	−61	−65	−50
τ_{21}	176	180	174	177	177	−179	179
τ_{22}	93	60	54	64	44	−76	67
τ_{23}	59	−60	88	−44	−61	−143	81

τ_{nm} = Au–P*n*–C*nm*1–H*nm*1. Ring 1 is defined as the ring for which C1–H1 and P–Au are antiperiplanar, 2 and 3 as the rings to the left and right of 1 respectively when viewed down the Au–P bond (Scheme 1).

Table 3 ^{31}P CP-MAS NMR Chemical shift data for $[Au(PCy_3)_2X]$ molecules

X	δ_1	δ_2	^2J(P–P)/Hz
Cl	63.6		
Br α	58.0		
Br β_1	58.0	53.4	270
Br β_2	57.0	51.9	270
Br γ	49.8		
I·PCy_3	56.9	50.9	220
I	50.1		

bromide system reflect the crystallisation of the different forms of this complex. Considering the two simplest cases first, the spectrum of the γ form shown in Fig. 5(d) consists of a single sharp peak at δ 49.8, consistent with the structure determination in which the two ligands are equivalent by symmetry. The spectrum of the β form shown in Fig. 5(c) is considerably more complex and is built up of two overlapping AB quartets arising from $^2J(^{31}P–^{31}P)$ coupling interactions between the crystallographically independent phosphorus nuclei in molecules β_1 and β_2, the first so recorded in the solid state for bis(phosphine)gold(I) complexes. The chemical shifts for the two pairs of phosphorus nuclei are at δ 58.0, 53.4 and 57.0, 51.9 and are tentatively assigned to ligands 1, 2 of molecules β_1 and β_2 respectively. For both molecules, the value of $^2J(^{31}P–^{31}P)$ is 270 Hz which is comparable to the value of 300 Hz determined from the solution ^{31}P NMR spectra of annular $[Au_2\{Ph_2P(CH_2)_2PEt_2\}_2Cl_2]$.[28]

The spectrum recorded for the α form is shown in Fig. 5(b) with the strong peak at δ 58.0 assigned to the α form. Also evident in the spectrum are peaks assignable to cocrystallised β form, a small peak at δ 50 assignable to the γ form as a minor component of the mixture, and a broad peak centred at δ 63 which is assigned to yet a further form, possibly with a cationic structure similar to that of the chloride complex. Attempts to isolate this latter polymorph in crystalline form and/or a pure sample of the α form by repetition of the experiment resulted only in crystallisation of the γ form. This latter result reflects the range of factors that come into play in determining the products obtained by these experiments, including the diversity of compounds likely to be in equilibrium in the solution, the effects of variation in temperature and concentration on the relative solubilities of the various polymorphs, and the role played by the initial, chance formation of seed crystals in the determination of subsequent crystallisation pathways (*e.g.* see ref. 29).

The spectrum of the iodide complex, $[Au(PCy_3)_2I]·PCy_3$, is shown in Fig. 5(e) and consists of a broadened AB quartet with chemical shifts and line spacings similar to those found for the β bromide complex. This quartet is assigned to $^2J(^{31}P–^{31}P)$ coupling between the two crystallographically inequivalent phosphorus atoms in the molecule. The chemical shifts of the two phosphorus nuclei are estimated to be δ 56.9 and 50.9. The value of $^2J(^{31}P–^{31}P)$ of 220 Hz is *ca.* 20% smaller than for the bromide which is consistent with previous work on the effect of changes in the donor ligand X on $^2J(^{31}P–^{31}P)$ for a series of $[Hg(PPh_3)_2X_2]$ complexes which show correlation between the co-ordinating ability of X and decreasing $^2J(^{31}P–^{31}P)$.[30,31] The greater intensity of the doublet at δ 50.9 suggests that the presence of cocrystallised unsolvated or related complexes cannot be discounted. The single peaks at δ 6.7 and 3.4 are assignable to cocrystallised and 'solvated' free PCy_3 respectively. The difference of 3.3 ppm in the chemical shifts of these two molecules, despite the similarities in the structures of the two PCy_3 molecules, provides a good example of the sensitivity of ^{31}P chemical shifts to minor changes in chemical environment.

The spectrum of the 'unsolvated' iodide complex, $[Au(PCy_3)_2I]$, is shown in Fig. 5(f) and consists mainly of a broad single peak centred at δ 50.1 that is assigned to the 1 : 2 complex. As for the PCy_3 solvated complex, this complex has two crystallographically independent phosphorus nuclei bound to the gold atom. The absence of the expected AB multiplet suggests similar chemical shifts for the two nuclei together with a loss of resolution due to line broadening. The small peaks at *ca.* δ 56 are tentatively assigned to small quantities of cocrystallised 1 : 1 complexes[24] and/or the 'solvated' complex described above.

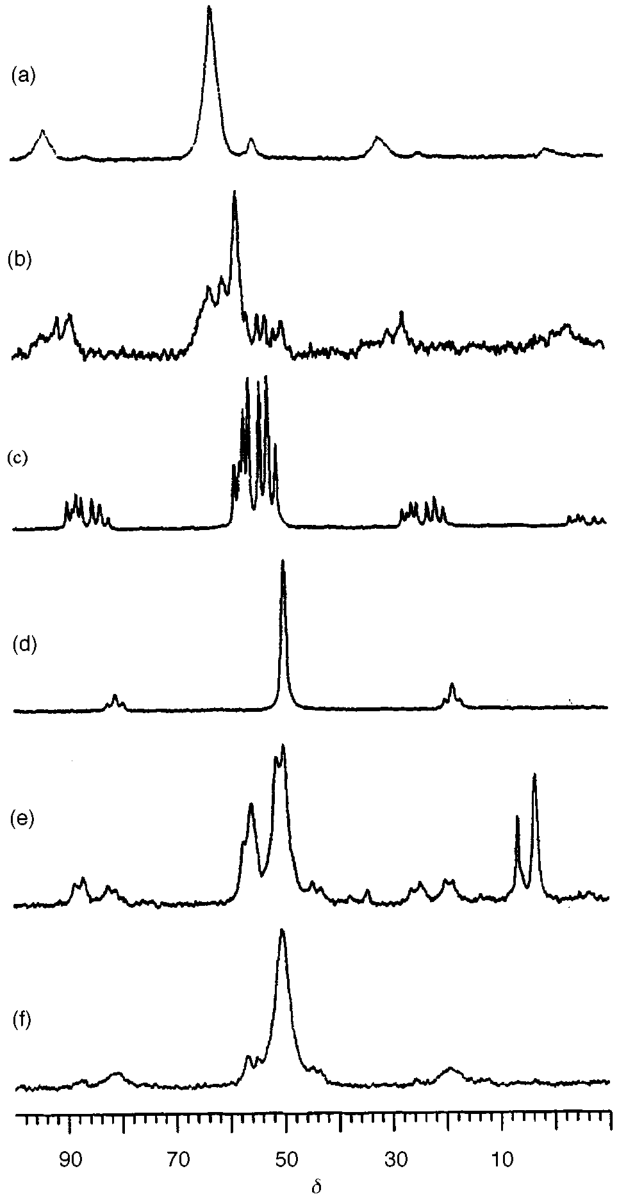


Fig. 5 Solid state ^{31}P CP MAS spectra of Au(PCy$_3$)$_2$X complexes for (a) X = Cl, (b) Br (α), (c) Br (β), (d) Br (γ), (e) I (PCy$_3$ solvate) and (f) I.

Further small, unassigned peaks are also apparent in the spectra of both the solvated and unsolvated complex in the region from δ 40 to 50, indicating, as for the bromide, the possible existence of further, as yet uncharacterised, polymorphs for this system.

Infrared spectroscopy

The far infrared spectra of the complexes are presented in Fig. 6, and the ν(AuX) assignments are compared with those for some related gold(I) complexes in Table 4.[32–39] The spectrum of the chloride complex, shown in Fig. 6(a), contains a strong band at 117 cm^{-1}, which is in the region expected for ν(AuCl) arising from a weak Au–Cl bond. Assignment of this band to ν(AuCl) (which was observed also in the spectrum recorded on handpicked crystals of identical habit and shape to the crystal used in the structure determination) is, however, inconsistent with both the structural and ^{31}P NMR results described and must therefore be due to a strong lattice mode. The presence of a small quantity of the 1 : 1 complex evident in the ^{31}P CP MAS NMR spectrum is also in evidence in the infrared spectrum with a weak band at 332 cm^{-1}.

The spectrum recorded on the samples from which the α-bromide was obtained is shown in Fig. 6(b). This contains only a weak, broad absorption below 100 cm^{-1}, consistent with the conclusion based on the solid state ^{31}P NMR that this sample consists mainly of the ionic α phase for which only lattice modes with frequencies significantly less than that observed in the chloride complex are expected. In contrast to this, the β and γ bromides show strong bands at 93 and 105 cm^{-1}, Fig. 6(c) and (d), which are assigned to ν(AuBr). Two such bands would be expected on the basis of the presence of two inequivalent molecules in the β complex, but these are apparently not resolved. The increase in ν(AuBr) from the β- to the γ-bromide is consistent with the observed decrease in the Au–Br bond length (Table 1), which reflects the presence of

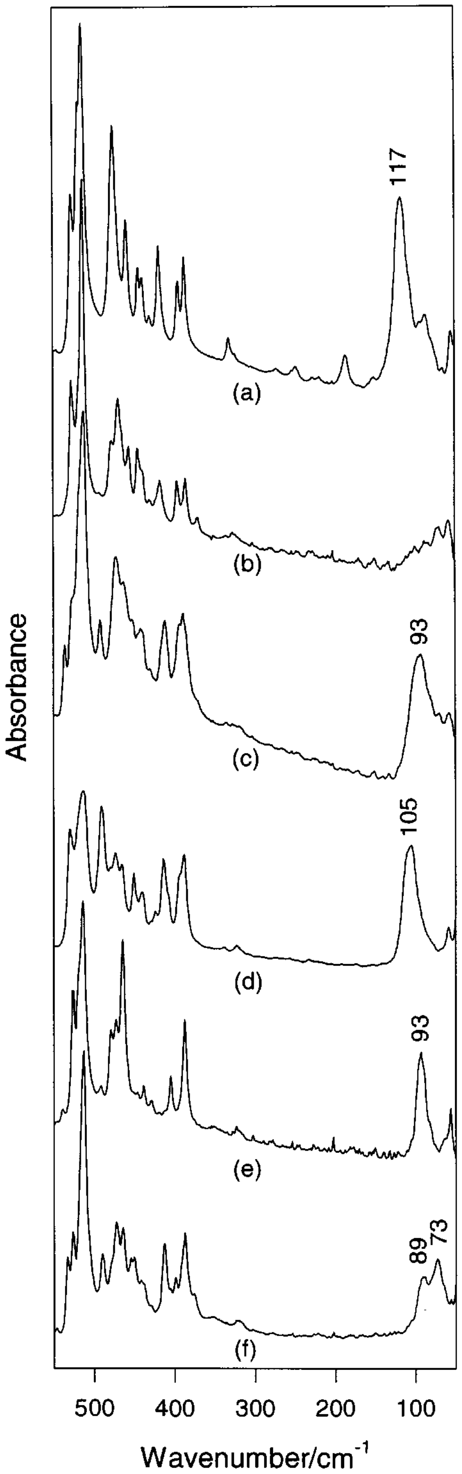


Fig. 6 Far-IR spectra of Au(PCy$_3$)$_2$X for (a) X = Cl, (b) Br (α), (c) Br (β), (d) Br (γ), (e) I and (f) I (PCy$_3$ solvate).

Table 4 Gold–halogen bond lengths r(AuX) and Au–X stretching vibrational wavenumbers ν(AuX) for some gold(I) halide complexes

	r(AuX)/Å				ν(AuX)/cm^{-1}			
Compound	Cl	Br	I	Ref.	Cl	Br	I	Ref.
AuX(calc.)	2.248			32	382			33
[AuX(CO)]	2.261			34	358			35
[AuX(PPh$_3$)]	2.279	2.407	2.553	36	330	229	187	38
[AuX(PCy$_3$)]	2.279	2.393	2.553	24	332	232	189	24
[AuX(tmpp)]	2.303	2.413	2.586	32	313	218	183	32
[AuX(PPh$_3$)$_2$]	2.500	2.625	2.754	6	218	139	118	39
[AuX(PPh$_3$)$_3$]	2.710			37	163			39
[AuX(PCy$_3$)$_2$]		2.868^a	2.895	^{b}		93^a	93	^{b}
		2.777^c	3.008^d	^{b}		105^c	73^d	^{b}

tmpp = Tris(2,4,6-trimethoxyphenyl)phosphine. ^{a} β Form. ^{b} This work. ^{c} γ Form. ^{d} The PCy$_3$ solvate.

slightly stronger Au–Br bonding in the γ complex. These frequencies are considerably lower than ν(AuBr) 139 cm^{-1} observed in the corresponding triphenylphosphine complex, [Au(PPh$_3$)$_2$Br],[39] consistent with the differences in the Au–Br bond lengths for the two complexes (Table 4).

The spectrum of the unsolvated iodide complex, shown in Fig. 6(e), contains a moderately strong band at 93 cm^{-1} which is assigned to the ν(AuI) vibration by analogy with the above results for the bromides. The spectrum of the PCy$_3$ solvated iodide complex shown in Fig. 6(f) contains two band at 73 and 89 cm^{-1}. These are also assigned as ν(AuI) modes. The more intense of these at 73 cm^{-1} is assigned to ν(AuI) of the solvated compound, the decrease in the frequency relative to the unsolvated complex being consistent with the observed increase in the Au–I bond length (Table 1). The weaker ν(AuI) band at 89 cm^{-1} occurs in a similar position to that in the unsolvated complex and is attributed to the presence of minor cocrystallised phases that are also evident in the solid state ^{31}P NMR spectrum (see above).

The ν(AuX) vibrational frequencies obtained in this study provided an opportunity further to investigate the relationship between ν(MX) and the corresponding bond lengths r(MX) in Group 11 metal halide complexes. We have previously shown that a relationship exists between the ν(CuX) wavenumber and the bond length r(CuX) for a wide range of copper(I) halide complexes containing a terminal Cu–X bond and from one to three phosphine or amine ligands.[40] This relationship has the form (1) with b = 13800, 18000, 32300; m = 4.9, 5.2, 5.6. Similar

$$\nu/\text{cm}^{-1} = b(r/\text{Å})^{-m} \qquad (1)$$

relationships have been established more recently for AgX complexes.[41] In order to investigate the situation for AuX compounds we have used the data in Table 4. These relationships are shown in Fig. 7, and the data are well fit by eqn. (1), with b = 12360, 20970, 44600; m = 4.37, 5.17, 5.82 for X = Cl, Br, I respectively. The results for the β- and γ-[Au(PCy$_3$)$_2$Br] complexes and for the two iodide complexes obtained in the present study show that the relationship seems to be valid even for the relatively long, semi-co-ordinated Au–X bonds found in these compounds. The fact that the ν(AuX) (X = Br or I) bands occur at such similar wavenumbers, when normally there is a considerable decrease from X = Br to I, is a further manifestation of the increase in bond strength that is also evident in the Au–X bond lengths.

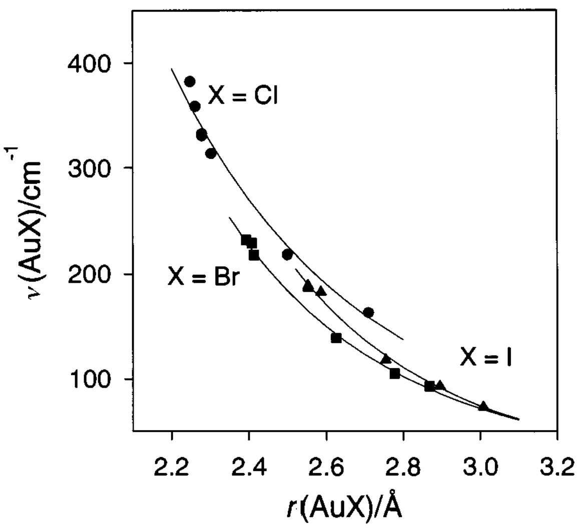


Fig. 7 Plots of ν(AuX) against the Au–X bond length [X = Cl (●), Br (■) or I (▲)]. The data are from Table 4, and the curves are the best fits using eqn. (1).

Conclusion

The compounds studied in this work show an unusually large number of polymorphs, involving a unique array of co-ordination and conformational isomers. This behaviour is attributed to the conformational flexibility of the tricyclohexylphosphine ligand, as well as to differences in the relative preferences of the halide anions for C–H···X$^-$ *versus* Au$^+$···X$^-$ bonding. The compounds that have been characterised provide an unusual series of molecular snapshots showing the response of the [Au(PCy$_3$)$_2$]$^+$ cation to the approach of the halide anion and reflect the significance of the role played by the substituent hydrogens in 'policing' access of the anions to the metal site. The results also provide some useful semi-quantitative insights into the location of the border between co-ordinated and non-co-ordinated anions in these complexes. Finally, the utility of solid state ^{31}P CP MAS NMR and vibrational spectroscopy in the study of these types of systems is clearly demonstrated with several of the compounds discovered in this work being first observed by means of these techniques.

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