Structural, Far-infrared and ^{31}P Nuclear Magnetic Resonance Studies of Two-co-ordinate Complexes of Tris(2,4,6-trimethoxyphenyl)phosphine with Gold(I) Halides†

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The complexes [AuX(tmpp)] [X = Cl, Br or I; tmpp = tris(2,4,6-trimethoxyphenyl)phosphine] were prepared by reaction of tmpp with [AuX(Me$_2$S)] or [AuX$_2$]$^-$. The crystalline compounds are isomorphous with the corresponding complexes of Cu and Ag, with Au–P 2.253(5), 2.255(4), 2.239(7), Au–X 2.303(6), 2.413(2), 2.586(2) Å and P–Au–X 176.0(2), 175.9(1), 177.7(2)°. The Au···O contacts involving the nearest *o*-methoxy oxygen atoms on the three phenyl groups in the ligand are: 3.15(1), 3.08(1), 2.92(2) (chloride); 3.13(2), 3.11(1), 2.96(1) (bromide); 3.01(2), 3.10(1), 3.09(2) Å (iodide). The complexes [AuX(tmpp)] were characterized by far-IR spectroscopy [ν(Au–X) 313, 218, 183 cm^{-1}; X = Cl, Br, I] and by ^{31}P NMR spectroscopy in acetonitrile [δ(^{31}P) −35.9, −31.8, −23.9]. All members of the series [MX(tmpp)] (M = Cu, Ag or Au; X = Cl, Br or I) are now known (although the AgI complex has so far only been detected in solution). The M–X bond properties in this series show trends which reveal the presence of relativistic effects in the M = Au case. Reaction of [AuX(tmpp)] with tmpp in a 1:1 mole ratio in solution results in displacement of X$^-$ to yield [Au(tmpp)$_2$]$^+$ [δ(^{31}P) −24.9]. Unlike the corresponding PPh$_3$ complexes, [AuX(tmpp)] show no evidence of $^1J(^{197}\mathrm{Au}^{31}\mathrm{P})$ spin–spin splitting in their solid-state ^{31}P cross polarization magic angle spinning NMR spectra. A simple one-pot synthesis of the known gold(I) complex [NBu$_4$][AuI$_2$] from metallic gold was achieved.

There is a considerable variation in co-ordination behaviour between the different members of the Group 11, or coinage metals, in their monovalent (d^{10} configuration) state. Thus, for Au$^{\mathrm{I}}$, linear two-co-ordination is by far the most common situation,[1] whereas for Cu$^{\mathrm{I}}$ and Ag$^{\mathrm{I}}$, tetrahedral four-co-ordination is more frequently encountered[2–4] and two-co-ordination can only be achieved by using more sterically demanding ligands.[5–9]

Tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) is both a very basic and a sterically very hindered phosphine,[10,11] and a number of co-ordination complexes of it have recently been reported which have unusual geometries.[7–9,12–14] We have previously shown that it forms mononuclear adducts [MX(tmpp)] (M = Cu, X = Cl, Br or I; M = Ag, X = Cl or Br) which contain almost linear two-co-ordinate copper(I) or silver(I), a slight deviation from linearity (P–M–X angles in the range 171–175°) being associated with a weak interaction with one of the *o*-methoxy oxygens in the ligand.[7–9] The aim of the present study was to prepare the corresponding gold(I) complexes [AuX(tmpp)] (X = Cl, Br or I) in order to allow a comparison of their properties with those of the corresponding copper(I) and silver(I) species, and also with those of the corresponding PPh$_3$ complexes. In particular, it is important to compare the ^{31}P cross polarization magic angle spinning (CP MAS) NMR spectra of [AuX(tmpp)] with those of [AuX(PPh$_3$)] in order to analyse the occurrence of the unusual $^1J(^{197}\mathrm{Au}^{31}\mathrm{P})$ spin–spin splitting patterns previously observed in the PPh$_3$ complexes.[15,16]

Experimental

Preparation of Compounds.—Tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) was prepared by the reaction of P(OPh)$_3$ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization of the solid product from ethanol.[10] Chloro(dimethyl sulfide)gold(I), [AuCl(Me$_2$S)], and bromo(dimethyl sulfide)gold(I), [AuBr(Me$_2$S)], were prepared by modifications of the literature methods.[17]

Tetra-n-butylammonium diiodoaurate(I), [NBu$_4$][AuI$_2$]. Granular gold metal (10 g, 51 mmol), diiodine (7.3 g, 29 mmol) and tetra-*n*-butylammonium iodide (20.5 g, 56 mmol) were suspended in absolute ethanol (150 cm^3) and the mixture refluxed for 7 d. At the end of this time 9.1 g of the gold metal had dissolved. The clear solution was decanted from the remaining metal and allowed to cool to room temperature to yield yellow-orange needle-like crystals of the compound. Yield 31 g (97%), m.p. 79–82 °C (lit.,[18] 79 °C) (Found: C, 27.5; H, 5.3; N, 1.7. Calc. for $C_{16}H_{36}AuI_2N$: C, 27.7; H, 5.2; N, 2.0%).

Chloro[tris(2,4,6-trimethoxyphenyl)phosphine]gold(I), [AuCl(tmpp)]. Tris(2,4,6-trimethoxyphenyl)phosphine (0.173 g, 0.325 mmol) and [AuCl(Me$_2$S)] (0.096 g, 0.326 mmol) were added to absolute ethanol (2 cm^3) and the mixture was stirred while heating on a water-bath until the evolution of Me$_2$S ceased. The white microcrystalline product which formed on cooling the mixture was collected and recrystallized once from acetonitrile. Yield 63%. M.p. 254–255 °C (decomp.) (Found: C, 42.3; H, 4.3. Calc. for $C_{27}H_{33}AuClO_9P$: C, 42.4; H, 4.4%). This complex was also prepared *via* an electrochemical method. A gold anode and a platinum-wire cathode were placed in a solution of HPLC-grade acetonitrile (25 cm^3) containing a 10% aqueous solution of NMe$_4$OH (1 cm^3) and a 35% aqueous solution of HCl (0.5 cm^3) under an atmosphere of argon. A

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

constant potential of 3.0 V was applied to the cell for 90 min, resulting in dissolution of 0.06 g (0.3 mmol) of gold, most probably as the $[AuCl_2]^-$ ion in association with the $[NMe_4]^+$ counter ion.[19] On completion of electrolysis, tmpp (0.16 g, 0.3 mmol) was then dissolved in the solution. On filtration and standing the solution yielded crystalline [AuCl(tmpp)]. Crystals suitable for X-ray diffraction studies were obtained by recrystallization of this product from dimethylformamide (dmf).

Bromo[*tris*(2,4,6-*trimethoxyphenyl*)*phosphine*]*gold*(I), [AuBr(tmpp)]. This compound was prepared by a method analogous to the first of the methods given above for the chloride, but using acetonitrile instead of ethanol as solvent. The product was obtained from the reaction mixture as a pale mauve microcrystalline powder. Yield 74%. M.p. 246–247 °C (Found: C, 40.5; H, 4.1. Calc. for $C_{27}H_{33}AuBrO_9P$: C, 40.1; H, 4.1%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization from dimethylformamide.

Iodo[*tris*(2,4,6-*trimethoxyphenyl*)*phosphine*]*gold*(I), [AuI(tmpp)]. Tris(2,4,6-trimethoxyphenyl)phosphine (0.26 g, 0.49 mmol) and potassium iodide (0.08 g, 0.48 mmol) were dissolved in dmf (20 cm^3). Gold(I) iodide (Strem Chemicals; 0.16 g, 0.49 mmol) was slowly added to the warmed, stirred solution. Most of the AuI dissolved with some decomposition to metallic gold. The solution was filtered and left to stand overnight to give well formed, colourless needles of the complex. Yield 0.18 g. M.p. 244–245 °C (Found: C, 37.9; H, 3.9. Calc. for $C_{27}H_{33}AuIO_9P$: C, 37.9; H, 3.9%). An alternative, more direct method is as follows: Tris(2,4,6-trimethoxyphenyl)phosphine (0.10 g, 0.18 mmol) and $[NBu_4][AuI_2]$ (0.11 g, 0.16 mmol) were dissolved in dmf (10 cm^3) to give a clear, colourless solution. This was left overnight to yield well formed needles of the complex. M.p. 244–246 °C. The far-IR spectrum of this product was identical to that of the compound prepared by the first method given above.

Structure Determinations.—Unique data sets were measured at ≈295 K within the specified $2\theta_{max}$ limit using an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; scan mode 2θ–θ) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$ at convergence R, R' are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed; computation used the XTAL 3.0 program system implemented by Hall.[20] Pertinent results are quoted in Fig. 1 and in Table 1; atom labelling and setting (as $P4_1$ or its enantiomer $P4_3$) is in conformity with that established previously for the copper(I) chloride and bromide analogues.[7]

Crystal/refinement data. [AuCl(tmpp)], $C_{27}H_{33}AuClO_9P$, $M = 765.0$, tetragonal, space group $P4_3$ (C_4^4, no. 78), $a = 15.317(5)$, $c = 12.366(1)$ Å, $U = 2901$ Å^3, D_c ($Z = 4$) = 1.75 g cm^{-3}, $F(000) = 1512$, $\mu_{Mo} = 52.7$ cm^{-1}, specimen 0.16 × 0.15 × 0.52 mm, $A^*_{min,max} = 2.00, 2.34$, $2\theta_{max} = 65°$, $N = 4649$, $N_o = 2533$, $R = 0.054$, $R' = 0.052$.

[AuBr(tmpp)], $C_{27}H_{33}AuBrO_9P$, $M = 809.4$, tetragonal, space group $P4_3$, $a = 15.349(7)$, $c = 12.397(7)$ Å, $U = 2921$ Å^3, D_c ($Z = 4$) = 1.84 g cm^{-3}, $F(000) = 1584$, $\mu_{Mo} = 65.1$ cm^{-1}, specimen 0.31 × 0.33 × 0.38 mm, $A^*_{min,max} = 4.50, 6.39$, $2\theta_{max} = 60°$, $N = 4053$, $N_o = 3182$, $R = 0.056$, $R' = 0.063$.

[AuI(tmpp)], $C_{27}H_{33}AuIO_9P$, $M = 856.4$, tetragonal, space group $P4_1$ (C_4^2, no.76), $a = 15.207(6)$, $c = 12.888(7)$ Å, $U = 2980$ Å^3, D_c ($Z = 4$) = 1.91 g cm^{-3}, $F(000) = 1656$, $\mu_{Mo} = 60.7$ cm^{-1}, specimen 0.08 × 0.09 × 0.18 mm, $A^*_{min,max} = 1.61, 1.77$, $2\theta_{max} = 50°$, $N = 2757$, $N_o = 1806$, $R = 0.052$, $R' = 0.044$.

Abnormal features/variations in procedure. The absolute configurations of the specimens employed for the crystallographic work are as given; in the iodide the methoxy C(34) methyl group was modelled as disordered over two sites with equal populations constrained after trial refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Spectroscopy.—Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed Polythene discs on a Digilab FTS-60 Fourier-transform spectrometer employing an FTS-60V vacuum optical bench with a 6.25 µm mylar-film beam splitter, a mercury-lamp source and a pyroelectric triglycine sulfate detector. Solution $^{31}P-\{^1H\}$ NMR spectra were obtained at room temperature on a Bruker AM-400 spectrometer at a frequency of 161.98 MHz. Chemical shifts were referenced to 85% H_3PO_4 *via* trimethyl phosphite (δ 139.2). Solid-state CP MAS $^{31}P-\{^1H\}$ NMR spectra were obtained at ambient temperature on a Varian Unity-400 spectrometer at 161.92 MHz. Single contact times of 2 ms were used with a proton pulse width of 6.5 µs, a proton decoupling field of 60 kHz and a recycle delay time of 45 s. The samples were packed in Kel-F inserts within silicon nitride rotors and spun at a speed of 5 kHz at the magic angle. A total of 32 free induction decays were collected and transformed with an experimental line broadening of 10 Hz. Chemical shift data are referenced to 85% H_3PO_4 *via* an external sample of solid PPh_3 (δ −9.9 ppm).

Ab-initio Calculations.—In the current study we have used a relativistic one-component (spin-orbit averaged) pseudopotential for gold[21] within a coupled-cluster procedure [QCISD(T)[22]] to obtain the spectroscopic constants for the $^1\Sigma^+$ ground state of AuCl. The basis set used for gold is a (9s, 7p,6d,3f) set contracted to (8s,4p,5d,3f).[21] For chlorine we used a Sadlej–MacLean-Chandler basis set,[23] *i.e.* a 14s,10p,4d,1f set contracted to 7s,6p,2d,1f. Both basis sets produce atomic energies of near Hartree-Fock limit quality. We calculated five points of the AuCl potential-energy curve, each point taking approximately 100 h on an IBM 530H RISC6000 workstation. The dissociation energy was calculated using the separate atoms. The following spectroscopic constants were obtained: bond distance $r_e = 2.248$ Å, dissociation energy $D_e{}^0 = 275$ kJ mol^{-1}, force constant $k_e = 239$ N m^{-1}; $^{197}Au^{35}Cl$ harmonic vibrational frequency $\omega_e = 369.5$ cm^{-1}, anharmonicity constant $\omega_e x_e = 1.32$ cm^{-1}, rotational constant $B_e = 0.1123$ cm^{-1}; $^{197}Au^{37}Cl$, $\omega_e = 360.9$ cm^{-1}, $\omega_e x_e = 1.26$ cm^{-1}, $B_e = 0.1072$ cm^{-1}.

Results and Discussion

Syntheses.—The gold(I) complexes [AuX(tmpp)] (X = Cl, Br or I) were prepared either by the displacement of Me_2S from $[AuX(Me_2S)]$ or by displacement of X^- from $[AuX_2]^-$ (see Experimental section). Attempts to prepare them by displacement of PPh_3 from $[AuX(PPh_3)]$ were unsuccessful, as this reaction resulted in the displacement of X^- rather than PPh_3 (see below).

During the course of this study we made the observation that metallic gold dissolved readily in a solution of elemental iodine and tetrabutylammonium iodide in absolute ethanol to give an essentially quantitative yield of the known gold(I) complex $[NBu_4][AuI_2]$[18] according to reaction (1). This method is

$$2Au + I_2 + 2I^- \longrightarrow 2[AuI_2]^- \qquad (1)$$

analogous to a procedure which has been used previously to prepare iodocuprate(I) species from copper metal, iodine and iodide salts.[24] However, the relative ease with which the reaction occurs in the case of gold was somewhat unexpected.

Table 1 Non-hydrogen atom coordinates for [AuX(tmpp)]

Atom	X = Cl			X = Br			X = I		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Au	0.640 54(4)	0.774 49(4)	1.0	0.639 20(4)	0.776 14(4)	1.0	0.370 51(6)	0.210 71(7)	0.0(–)
X	0.512 0(3)	0.800 5(4)	1.091 0(5)	0.503 9(1)	0.804 0(1)	1.092 9(2)	0.513 8(1)	0.181 0(1)	−0.102 1(2)
P	0.760 9(3)	0.743 3(3)	0.902 7(4)	0.760 2(3)	0.744 8(3)	0.904 3(4)	0.249 1(4)	0.241 0(5)	0.091 6(6)
C(11)	0.794(1)	0.838(1)	0.819(1)	0.792(1)	0.839 5(9)	0.827(1)	0.222(1)	0.147(1)	0.166(2)
C(12)	0.728(1)	0.880(1)	0.761(2)	0.728(1)	0.883(1)	0.766(2)	0.291(2)	0.108(2)	0.228(2)
O(12)	0.651 1(8)	0.841 3(7)	0.760(1)	0.649 9(7)	0.839 9(7)	0.761(1)	0.369(1)	0.150(1)	0.222(1)
C(121)	0.578(1)	0.882(1)	0.721(2)	0.578(1)	0.883(1)	0.720(2)	0.446(2)	0.110(2)	0.257(3)
C(13)	0.743(1)	0.957(1)	0.709(1)	0.742(1)	0.957(1)	0.710(2)	0.279(2)	0.032(2)	0.283(2)
C(14)	0.828(1)	0.994(1)	0.712(1)	0.824(1)	0.995(1)	0.712(2)	0.200(2)	−0.007(2)	0.293(2)
O(14)	0.836(1)	1.070 3(9)	0.657(1)	0.833 4(9)	1.069 8(9)	0.655(1)	0.189(1)	−0.079(1)	0.353(2)
C(141)	0.915(2)	1.116(2)	0.666(2)	0.913(2)	1.116(2)	0.667(3)	0.105(3)	−0.119(2)	0.357(3)
C(15)	0.892(1)	0.953(1)	0.767(1)	0.890(1)	0.954(1)	0.767(2)	0.129(2)	0.030(2)	0.237(3)
C(16)	0.876(1)	0.877(1)	0.823(1)	0.876(1)	0.877(1)	0.824(1)	0.140(2)	0.105(2)	0.177(2)
O(16)	0.939 5(8)	0.841 2(9)	0.882(1)	0.939 6(8)	0.841 1(9)	0.883(1)	0.073(1)	0.139(1)	0.124(1)
C(161)	1.024(2)	0.850(2)	0.852(2)	1.027(1)	0.847(1)	0.850(3)	−0.013(2)	0.133(2)	0.153(3)
C(21)	0.732(1)	0.651(1)	0.820(2)	0.731 8(8)	0.652 3(9)	0.821(1)	0.274(1)	0.336(2)	0.165(2)
C(22)	0.700(1)	0.577(1)	0.871(1)	0.698 9(9)	0.581(1)	0.879(1)	0.305(2)	0.411(2)	0.118(2)
O(22)	0.702 6(7)	0.583 8(7)	0.984 0(9)	0.701 3(7)	0.583 5(7)	0.983 8(9)	0.304(1)	0.403 0(9)	0.008(2)
C(221)	0.662(1)	0.517(1)	1.047(1)	0.665(1)	0.516(1)	1.044(2)	0.346(2)	0.470(2)	−0.051(2)
C(23)	0.668(1)	0.507(1)	0.817(1)	0.667(1)	0.508(1)	0.821(1)	0.333(2)	0.483(1)	0.168(2)
C(24)	0.667(1)	0.506(1)	0.706(1)	0.667(1)	0.506(1)	0.711(1)	0.331(2)	0.489(2)	0.272(2)
O(24)	0.633 0(9)	0.432 9(8)	0.662(1)	0.631 0(9)	0.433 9(8)	0.663(1)	0.359(1)	0.565(1)	0.316(2)
C(241)	0.615(2)	0.430(1)	0.548(2)	0.613(1)	0.432(1)	0.550(2)	0.375(3)	0.566(2)	0.421(4)
C(25)	0.702(1)	0.574(1)	0.650(1)	0.702(1)	0.575(1)	0.651(1)	0.300(2)	0.421(2)	0.326(2)
C(26)	0.735(1)	0.645(1)	0.702(1)	0.736(1)	0.644 9(9)	0.713(1)	0.274(2)	0.344(2)	0.277(2)
O(26)	0.772 8(8)	0.713 2(8)	0.653(1)	0.773 1(9)	0.714 0(8)	0.656(1)	0.237(1)	0.274(1)	0.330(2)
C(261)	0.771(2)	0.715(2)	0.539(2)	0.768(2)	0.717(2)	0.545(2)	0.239(4)	0.271(3)	0.441(3)
C(31)	0.854(1)	0.706(1)	0.977(1)	0.853(1)	0.705(1)	0.985(2)	0.152(2)	0.278(2)	0.028(3)
C(32)	0.858(1)	0.712(1)	1.094(2)	0.855(1)	0.716(1)	1.097(1)	0.143(2)	0.263(2)	−0.085(3)
O(32)	0.792(1)	0.756(1)	1.142(1)	0.791 0(9)	0.763 3(9)	1.146(1)	0.204(1)	0.218(1)	−0.136(1)
C(321)	0.775(2)	0.738(2)	1.247(3)	0.768(1)	0.744(2)	1.247(2)	0.245(2)	0.257(2)	−0.222(2)
C(33)	0.926(1)	0.678(2)	1.149(2)	0.926(1)	0.684(1)	1.153(2)	0.073(2)	0.297(2)	−0.139(3)
C(34)	0.992(1)	0.638(1)	1.096(2)	0.992(1)	0.639(1)	1.102(1)	0.008(3)	0.338(2)	−0.092(4)
O(34)	1.057(1)	0.608(1)	1.166(1)	1.055(1)	0.608(1)	1.172(1)	−0.064(2)	0.370(2)	−0.145(3)
C(341)*	1.123(2)	0.565(2)	1.123(2)	1.122(1)	0.562(2)	1.127(2)	−0.085(6)	0.394(5)	−0.217(6)
							−0.113(4)	0.419(4)	−0.130(6)
C(35)	0.992(1)	0.627(1)	0.986(2)	0.992(1)	0.630(1)	0.994(2)	0.012(2)	0.349(2)	0.017(4)
C(36)	0.923(1)	0.663(1)	0.932(2)	0.922(1)	0.662(1)	0.931(1)	0.083(2)	0.319(2)	0.070(3)
O(36)	0.916 8(8)	0.661(1)	0.819(1)	0.916 9(7)	0.660 6(8)	0.825 0(9)	0.092(1)	0.321(1)	0.180(2)
C(361)	0.984(1)	0.624(2)	0.757(2)	0.985(1)	0.621(1)	0.759(2)	0.028(2)	0.362(2)	0.237(3)

* Modelled as disordered over two sites of equal occupancy for X = I.

Table 2 Core geometries (distances in Å, angles in °) for [AuX(tmpp)]

	X		
	Cl	Br	I
Au–X	2.303(6)	2.413(2)	2.586(2)
Au–P	2.253(5)	2.255(4)	2.239(7)
P–C(11)	1.85(2)	1.81(2)	1.78(2)
P–C(21)	1.80(2)	1.81(1)	1.77(3)
P–C(31)	1.79(2)	1.85(2)	1.78(3)
Au···O(12)	3.15(1)	3.13(2)	3.01(2)
Au···O(22)	3.08(1)	3.11(1)	3.10(1)
Au···O(32)	2.92(2)	2.96(1)	3.09(2)
P–Au–X	176.0(2)	175.9(1)	177.7(2)
Au–P–C(11)	110.8(6)	109.3(5)	108.0(8)
Au–P–C(21)	105.6(6)	105.6(5)	105.8(8)
Au–P–C(31)	116.3(6)	114.9(7)	120(1)
C(11)–P–C(21)	111.3(8)	112.9(7)	115(1)
C(11)–P–C(31)	108.9(8)	110.1(8)	108(1)
C(21)–P–C(31)	103.6(8)	103.9(7)	100(1)

While AuI dissolves in water in the presence of iodide to give $[AuI_2]^-$ anions,[25] and in the present study, we observed the ready dissolution of AuI in a solution of potassium iodide in dimethylformamide, the direct reaction between elemental gold and iodine to produce AuI has been reported to be extremely slow.[26] This present method provides a direct and cost-effective route to the synthesis of an air-stable gold(I) compound and we are presently undertaking a more detailed study of this and related reactions.

Crystal Structures.—Crystalline [AuX(tmpp)] (X = Cl, Br or I) are isomorphous/enantiomorphous (crystallizing in space groups $P4_1/P4_3$) with [MX(tmpp)] (M = Cu, X = Cl, Br or I; M = Ag, X = Cl or Br).[7–9] They are monomeric, with the gold atom in a nearly linear two-co-ordinate environment (Fig. 1). The core geometry parameters are given in Table 2. The Au–X and Au–P bond lengths are compared with those for other $[AuX(PR_3)]$ complexes in Table 3, and with the M–X and M–P bond lengths in [MX(tmpp)] (M = Cu or Ag) in Table 4. The Au–X bond lengths in the tmpp complexes are longer than those in the corresponding complexes of PPh_3 or the other triarylphosphines in Table 3, and are similar to those in the complexes of the more basic PMe_3 and PEt_3 ligands. This is consistent with the description of tmpp as a strongly basic ligand.[10] These changes are relatively small, however, and are less significant in the X = Br than in the X = Cl series. The Au–P bond lengths in the tmpp complexes are longer than those in the other complexes in Table 3. This is consistent with an overall trend of increasing Au–P bond length with increasing cone angle of the phosphine ligand which is evident in Table 3.

Table 3 Distances (in Å) Au–P and Au–X for [AuX(PR$_3$)] complexes

PR$_3$	Au–P	Au–Cl	Ref.	Au–P	Au–Br	Ref.	Au–P	Au–I	Ref.
PMe$_3$	2.233(3) 2.234(4) 2.234(4)	2.306(4) 2.310(4) 2.310(4)	27	2.242(7) 2.235(5) 2.228(6)	2.419(3) 2.415(3) 2.415(3)	28	2.256(3)	2.583(1)	29
PEt$_3$	2.232(9)	2.305(8)	30						
PPh$_3$	2.235(3)	2.279(3)	31	2.252(6)	2.407(2)	15	2.249(2)	2.553(1)	29
P(C$_6$H$_4$Me-*o*)$_3$	2.243(2)	2.281(3)	32						
P(C$_6$H$_{11}$)$_3$	2.242(4)	2.279(5)	33						
tmpp	2.253(5)	2.303(6)	*	2.255(4)	2.413(2)	*	2.239(7)	2.586(2)	*

* This work.

Table 4 Distances (in Å) M–X and M–P for [MX(tmpp)] complexes

	M–X			M–P			
M	Cl	Br	I	Cl	Br	I	Ref.
Cu	2.118(2)	2.259(2)	2.417(2)	2.177(1)	2.197(3)	2.118(4)	7, 9
Ag	2.342(1)	2.448(1)		2.379(1)	2.374(2)		8
Au	2.303(6)	2.413(2)	2.586(2)	2.253(5)	2.255(4)	2.239(7)	*

* This work.

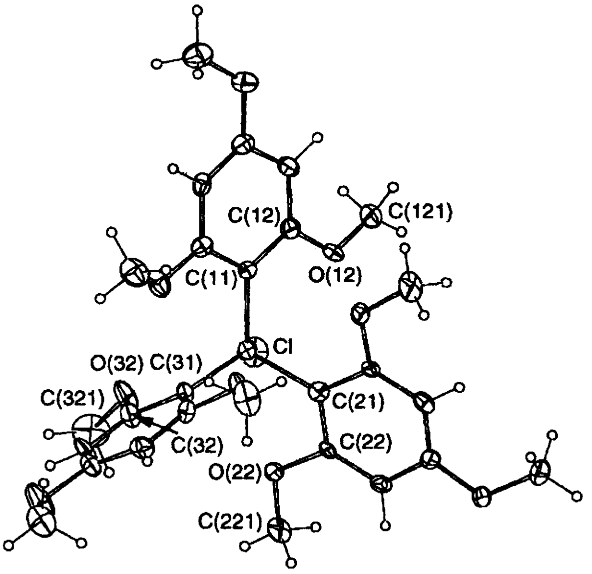

Fig. 1 The complex [AuCl(tmpp)] projected down the P–Au bond; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å

While the phosphorus and halogen atoms play a dominant role in the co-ordination environment of the [MX(tmpp)] complexes, the methoxy oxygen atoms on the ligand may play a significant role as well. An investigation of this point was one of the reasons for studying the gold complexes, since gold(I) shows a much stronger preference for linear two-co-ordination than does copper(I) or silver(I), so any effects on the structure which are a consequence of secondary M $\cdots$ O interactions should be evident as differences between the structures of the gold and the corresponding copper or silver complexes. The results show, however, that differences of this kind are quite small. The conformation of the ligand is such that one of the *o*-methoxy oxygen atoms O(*n*2) is closer to the metal atom than the other two. In the gold complexes the closest O(*n*2) contact is less than the furthest by only 0.2 (X = Cl or Br) or 0.1 Å (I), while for the copper compounds the corresponding differences are 0.5 and 0.4 Å.[7,9] This suggests that copper has a slightly greater tendency to increase its co-ordination number by interaction with one of the *o*-methoxy oxygen atoms, and this seems to correlate well with the slightly greater departure from linear two-co-ordination in the case of the copper complexes (P–Cu–X 171–173°)[7,9] compared to the gold complexes (P–Au–X 176–178°). The difference is quite small, however, supporting the view that these complexes essentially involve linear P–M–X co-ordination, with only a slight perturbation by the other atoms in the ligand.

Far-IR Spectra.—The far-IR spectra of the [AuX(tmpp)] complexes are shown in Fig. 2. The ν(Au–X) bands appear as sharp peaks at 313, 218 and 183 cm^{-1} for X = Cl, Br and I respectively. These wavenumbers are compared with those of a number of related complexes in Table 5. Also given in this table are the M–X bond force constants, calculated in the case of the [MXL$_n$] species by considering the diatomic MX unit only.[37] These force constants normally show a progressive decrease along the series X = Cl, Br, I but, for the [AuX(tmpp)] series, the decrease in the Au–X force constant from X = Br to I is somewhat less than that in other [AuXL] species (Table 5). Similar behaviour has been observed previously for [CuX(tmpp)][9] and for [AgX(tmpp)] (X = Cl or Br).[8]

A plot of ν(Au–Cl) *vs.* the bond length *d*(Au–Cl) for the series of [AuClL$_n$] (*n* = 0–3) complexes in Table 5 is shown in Fig. 3. This shows that the changes in the Au–Cl bond parameters in [AuCl(PPh$_3$)] upon replacing PPh$_3$ with tmpp are smaller but otherwise consistent with those which occur upon adding one or two further PPh$_3$ ligands. The point corresponding to the isolated diatomic AuCl molecule in Fig. 3 requires further comment. While an experimental vibrational frequency is available for this species,[34] there is no reported value for the bond length. This contrasts with the case of the diatomic CuX molecules, for which accurate bond-length data have been obtained from microwave spectroscopy.[38] We have therefore calculated the bond length in diatomic AuCl using large basis sets within a coupled-cluster procedure.[22] The value thus obtained (2.248 Å) is not much less than those in the two-co-ordinate complexes [AuCl(PPh$_3$)] (2.279 Å) and [AuCl(tmpp)] (2.303 Å), and this results in a rapid drop in the ν *vs.* *d* curve in this region which appears to have no counterpart in the corresponding curves for the CuX complexes.[9] In order to investigate this point further, we have included data for the complex [AuCl(CO)] in Fig. 3. The solid complex contains discrete linear [AuCl(CO)] molecules with *d*(Au–Cl) = 2.261

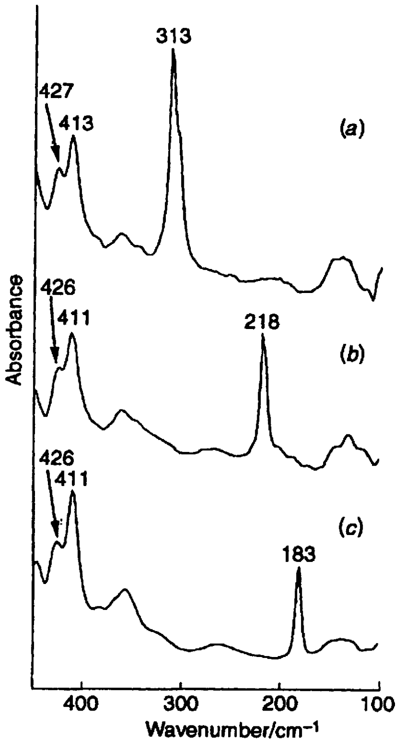

Fig. 2 Far-IR spectra of [AuX(tmpp)], X = Cl (*a*), Br (*b*) or I (*c*)

Table 5 Metal–halide vibrational wavenumbers and force constants

	ν(M–X)/cm^{-1}			*k*/N m^{-1}			
Compound	Cl	Br	I	Cl	Br	I	Ref.
AuX	382			258			34
[AuCl(CO)]	358			227			35
$[AuX_2]^{-}$ [a]	350	254	210	204	191	171	4
$[AuX(PMe_3)]$	311	205	164	171	141	122	4
$[AuX(PMe_2Ph)]$	314	221		175	164		36
$[AuX(PMePh_2)]$	319	220		180	162		36
$[AuX(PPh_3)]$	330	229	187	193	176	159	4
$[AuX(PPh_3)_2]$	218	139	118	84	65	63	4
$[AuX(PPh_3)_3]$	163			47			4
[AuX(tmpp)]	313	218	183	172	159	152	*b*
[AgX(tmpp)]	282	215		125	125		8
[CuX(tmpp)]	355	262	236	169	143	139	7, 9

[a] The wavenumbers for the ν_3 mode are given. [b] This work.

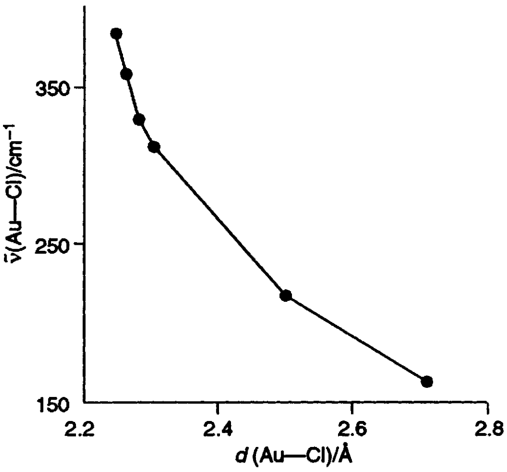

Fig. 3 Plot of the ν(Au–Cl) wavenumber *vs.* the Au–Cl bond length for [in ascending order of *d*(Au–Cl)] AuCl(vapour), [AuCl(CO)], $[AuCl(PPh_3)]$, [AuCl(tmpp)], $[AuCl(PPh_3)_2]$ and $[AuCl(PPh_3)_3]$

Å,[39] and ν(Au–Cl) 358 cm^{-1} has been measured from the Raman spectrum of the solid.[35] It is clear from Fig. 3 that these results fit very well with the other data reported therein, and this lends some support to the accuracy of the calculated bond length in AuCl.

It was expected that the ν(Au–X) results for [AuXL] in Table 5 would allow a comparison of the ligand donor properties of tmpp with those of the simpler ligands PPh_3 or PMe_3, since all of these complexes have the same linear two-co-ordinate structures, and ν(Au–X) should decrease with increasing ligand donor strength. However, the situation is clearly more complex than this. Thus ν(Au–Cl) for the tmpp complex is nearly the same as that for the PMe_3 complex and both of these are significantly lower than that for the PPh_3 complex. However, ν(Au–I) shows a different behaviour, the values for the tmpp complex being nearly the same as for the PPh_3 complex and both of these are higher than that for the PMe_3 complex. The situation for the bromo-complexes is intermediate between those of the chloro- and iodo-series. Another way of expressing this result is in terms of the decrease in ν(Au–X) which occurs upon replacing PPh_3 in $[AuX(PPh_3)]$ by PMe_3 or tmpp. In the case of PMe_3 this difference is fairly constant, whereas for tmpp it decreases progressively from X = Cl to I. This results in an unexpectedly high ν(Au–I) value for [AuI(tmpp)] compared with related complexes. Apparently the corresponding copper(I) complexes show similar behaviour, as ν(Cu–I) in [CuI(tmpp)] is also unexpectedly high.[9]

Members of the isostructural series [MX(tmpp)] (M = Cu, Ag or Au; X = Cl, Br or I) have now been characterized in the solid state for all except M = Ag, X = I.[7–9] Comparison of the M–X bond lengths *d* and force constants *k* in all cases where these data are available show that *d*(Ag–X) > *d*(Au–X) > *d*(Cu–X) and *k*(Ag–X) < *k*(Au–X) > *k*(Cu–X). The trend in the *k*(M–Cl) values in [MCl(tmpp)] (M = Cu, Ag or Au) is compared with that in the corresponding diatomic MCl molecules in Fig. 4. These trends have previously been shown to be due to relativistic effects which, for the gold compounds, decrease the Au–X bond lengths and increase the Au–X force constants.[21,40]

Solution ^{31}P NMR Studies.—The results of the solution ^{31}P NMR studies of [AuX(tmpp)] are given in Table 6. Like the corresponding silver(I) species, these show an increase in the co-ordination chemical shift from X = Cl to I, but this shift (*ca.* 40 ppm) is much greater than that observed for the silver complexes (*ca.* 5 ppm).[8] Addition of an excess of tmpp to the solutions of [AuX(tmpp)] resulted in the disappearance of the signal due to this species and the appearance of a new signal at δ −24.9 which is assigned to $[Au(tmpp)_2]^+X^-$. The ionic nature of this product is proven by the independence of the chemical shift on the nature of X. This demonstrates the facile displacement of X^- from [AuX(tmpp)] by an excess of tmpp. It contrasts with the situation for the corresponding three-co-ordinate PPh_3 complexes $[AuX(PPh_3)_2]$.[41] Addition of tmpp to [AuX(tmpp)] beyond a 1 : 1 mole ratio (*i.e.* above a 2 : 1 tmpp : AuX ratio) resulted only in the appearance of the signal due to uncomplexed tmpp.

Related to the above observations is the fact that [AuX(tmpp)] could not be prepared by displacement of PPh_3 from $[AuX(PPh_3)]$ by tmpp. This reaction was investigated by ^{31}P NMR spectroscopy in $CHCl_3$ solution. The resulting solution showed a broad signal at δ 33.5 and a sharper signal at δ −19.3. These are assigned to the PPh_3 and tmpp ligands respectively in $[Au(PPh_3)(tmpp)]^+$. There was also a weaker signal at δ −24.9 indicating the presence of some $[Au(tmpp)_2]^+$ which results from the displacement of PPh_3 from $[Au(PPh_3)(tmpp)]^+$. However, in agreement with the negative result of the attempted synthesis of [AuCl(tmpp)] by

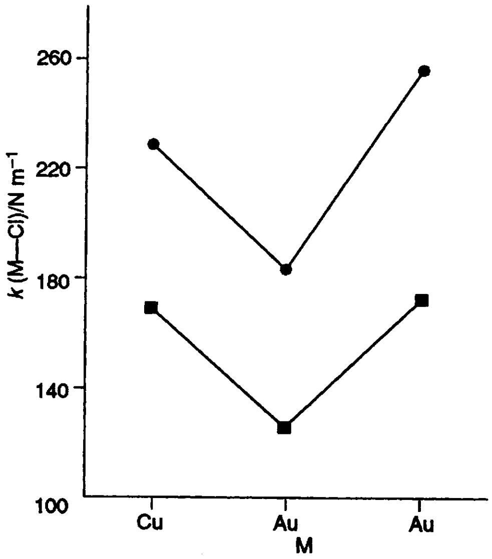

Fig. 4 Dependence of the M–Cl bond force constant k(M–Cl) on M (M = Cu, Ag or Au) in diatomic MCl (●) and [MCl(tmpp)] (■)

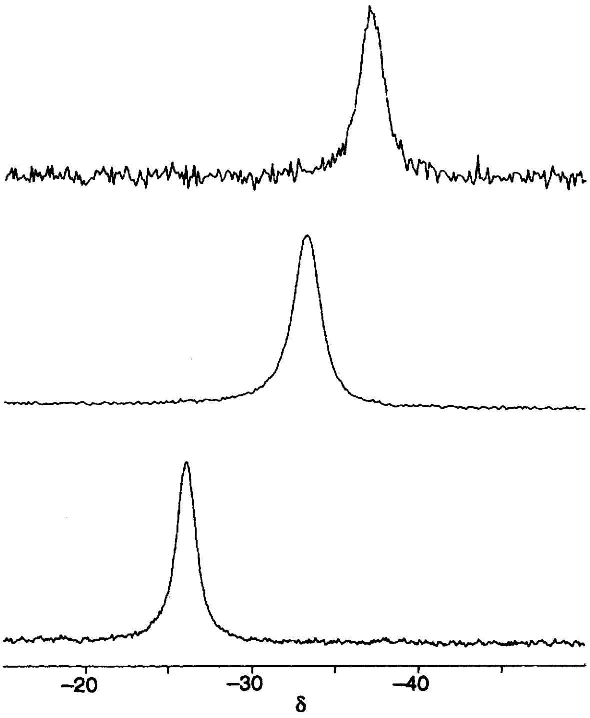

Fig. 5 The ^{31}P CP MAS NMR spectra of [AuX(tmpp)] X = Cl (top), Br (middle) and I (bottom)

this method, there was no evidence at all of a signal due to this species.

Table 6 Solution ^{31}P NMR parameters for [AuX(tmpp)] in $CHCl_3$

Compound	δ(^{31}P)	Δδ(^{31}P)*/ppm
[AuCl(PPh_3)]	31.4	37.4
[AuCl(tmpp)]	−35.9	35.7
[AuBr(tmpp)]	−31.8	39.8
[AuI(tmpp)]	−23.9	47.7
[Au$(tmpp)_2$]Cl	−24.9	46.7
[Au$(tmpp)_2$]Br	−24.9	46.7
[Au$(tmpp)_2$]I	−24.8	46.8

* Δδ = the co-ordination chemical shift = δ(complex) − δ(free phosphine).

Solid-state ^{31}P *CP MAS NMR Studies*.—Previous solid-state ^{31}P NMR studies of [AuX(L)] (L = PPh_3[15] or substituted phosphole ligands[42]) have revealed a line splitting which has been shown to be due to $^1J(^{197}Au^{31}P)$ spin–spin coupling.[16] Such a splitting has not been seen for gold complexes with three- and four-co-ordinate environments,[41] the one exception being the case of symmetrical tetrahedral four-co-ordination where the ^{197}Au quadrupole coupling constant is very small.[43] It is not clear why this coupling should be seen in the case of linear two-co-ordination, as this is expected to produce a larger ^{197}Au quadrupole coupling constant than any other co-ordination environment, and rapid quadrupolar relaxation is expected to result in an averaging of the ^{197}Au–^{31}P scalar coupling to zero. In order to investigate further the factors which result in the observation of such coupling, we recorded the ^{31}P CP MAS NMR spectra of solid [AuX(tmpp)], Fig. 5. These spectra consist of single peaks at δ −37, −33 and −26 with no evidence of $^1J(^{197}Au^{31}P)$ spin–spin coupling of the type which has been observed for the related complexes mentioned above. The reason for this is not yet known, but the present result shows that linear two-co-ordination is not the only condition required for the observation of this unusual effect.

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