Solid and solution structures of ternary gold(I) complexes with triphenylphosphine and nitrogen-containing ligands

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A series of gold(I) complexes $[Au(PPh_3)L]ClO_4$ (L = pyridine 1a, 2,6-dimethylpyridine 1b, 2,6-di-*tert*-butylpyridine 1c, quinoline 1d, acridine 1e, benzo[h]quinoline 1f, naphthyridine 2a, 1,10-phenanthroline 2b, 2,2'-biquinoline 2c, di-2-pyridyl ketone 2d, di-2-pyridylamine 3a or 2-(2-pyridyl)benzimidazole 3b) were prepared by reaction of L with $[Au(PPh_3)(ClO_4)]$ which was synthesized *in situ*. All complexes were characterized by IR, UV/VIS and ¹H NMR spectroscopy. The crystal and molecular structures of 1b, 2a and 3b were investigated by single-crystal X-ray diffraction techniques. The gold(I) is co-ordinated to one nitrogen atom and one phosphine atom. Detailed ¹H NMR studies suggested that linear two-co-ordinated structures persist in solution and further that all the complexes $[Au(PPh_3)L]ClO_4$, (2a–2d), are fluxional species in which the co-ordination site of gold(I) rapidly exchanges between two nitrogen atoms of the ligand.

A number of neutral gold(I) complexes with N-donor ligands have been reported,1-5 whereas complexes [Au(PPh3)L]+ with N-heterocyclic ligands L are rather rare.^{6,7} To the best of our knowledge, only one such complex, [Au(PPh₃)(qncd)]BF₄ (qncd = quinuclidine) has been characterized by X-ray diffraction.⁸ By contrast to the trialkylphosphinegold(I) halides, the stability constant of the [Au(PR₃)L]⁺ complexes is generally not as large and is dependent on the properties of the nitrogen ligand. In this paper a series of triphenylphosphinegold(I) complexes with nitrogen-containing ligands is prepared and characterized to shed further light on the general principles governing the bonding properties, Scheme 1. First, the preparation of complexes 1 with pyridine and derivatives was undertaken to understand the steric effects. Complexes 2 with bidentate ligands containing two pyridine groups were prepared to explore the ligand function of site opening and closing, and 3 with ligands containing pyridine and benzimidazole or amine to study the selective co-ordination of Au^I to nitrogen atoms of a multinitrogen ligand.

Results and Discussion

Solid-state studies

(a) Infrared spectroscopy. The complexes were all prepared by cleavage reaction of the chloride in $[Au(PPh_3)Cl]$ with $AgClO_4$ and replacement of ClO_4 in the resulting complex $[Au(PPh_3)-ClO_4]$ by ligand, equations (1) and (2). Preliminary character-

$$\begin{split} & [\operatorname{Au}(\operatorname{PPh}_3)\operatorname{Cl}] + \operatorname{AgClO}_4 \longrightarrow & [\operatorname{Au}(\operatorname{PPh}_3)(\operatorname{ClO}_4)] + \\ & \operatorname{AgCl}(\downarrow) \quad (1) \end{split}$$

$$[Au(PPh_3)(ClO_4)] + L \longrightarrow [Au(PPh_3)L]ClO_4 \quad (2)$$

ization was done by elemental analysis. In all cases satisfactory results for C, H and N were obtained. Infrared spectra of all complexes showed the expected ligand and anion (ClO_4^-) absorptions. The absorption of C=N of the N-ligands did not show significant changes upon complexation indicating that the interaction between gold(I) and the nitrogen ligand is not strong. The C=N absorption of **2a** showed two peaks at 1602



and 1587 cm^{-1} ; this means that only one nitrogen is coordinated to Au^I, as indicated by the single-crystal X-ray analysis.

(b) Crystal structures of complexes 1b, 2a and 3b. Single crystals suitable for single-crystal X-ray analysis were obtained for complexes 1b, 2a and 3b. The structure of 1b is shown in Fig. 1 and consists of the cation $[Au(PPh_3)(dmpy)]^+$ and a per-chlorate anion. Selected interatomic distances and bond angles are listed in Table 1. In the cation the gold atom is linearly coordinated by PPh₃ and dmpy, the P-Au-N angle being 178.8(3)°. The bond distances Au-N [2.091(13) Å] and Au-P [2.233(4) Å] are similar to those in the complexes [Au-(PPh₃)(NMe₃)]ClO₄⁷ [2.108(7) and 2.231(2) Å] and [Au-(PPh₃)(qncd)]BF₄⁸ [2.11(1) and 2.240(4) Å], respectively.

The molecular structure of complex 2a is shown in Fig. 2 and the bond parameters are listed in Table 2. The distances Au-N(1) [2.093(13) Å] and Au-P [2.230(4) Å] are comparable



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 Table 1
 Selected bond distances (Å) and angles ($^{\circ}$) for complex 1b with estimated standard deviations (e.s.d.s) in parentheses

Au–P P–C(7) P–C(13) N–C(23) C(23)–C(25)	2.233(4) 1.813(14) 1.809(13) 1.323(22) 1.475(29)	Au–N P–C(1) N–C(19) C(19)–C(24)	2.091(3) 1.803(15) 1.328(20) 1.511(27)
P-Au-N	178.8(3)	Au-N-C(19)	119.6(11)
Au-N-C(23)	120.3(11)	N-C(19)-C(24)	119.5(19)
N-C(23)-C(25)	118.3(16)	C(19)-N-C(23)	120.1(14)
Au-P-C(1)	111.5(5)	Au-P-C(7)	113.2(5)
Au-P-C(13)	110.1(5)	C(1)-P-C(7)	107.2(6)
C(1)-P-C(13)	107.6(7)	C(7)-P-C(13)	107.0(7)

Table 2 Selected bond distances (Å) and angles (\circ) for complex 2a with e.s.d.s in parentheses

Au-P	2.230(4)	Au-N(1)	2.093(13)
P-C(11)	1.807(11)	P-C(21)	1.794(18)
P-C(31)	1.786(14)	C(1) - N(1)	1.297(19)
C(8) - N(2)	1.338(18)	C(8) - N(1)	1.373(26)
P-Au-N(1)	174.3(4)	Au-P-C(11)	113.9(5)
Au-P-C(21)	112.2(5)	Au-P-C(31)	112.7(6)
C(11)-P-C(21)	105.1(9)	C(11)-P-C(31)	106.2(7)
C(21)-P-C(31)	106.2(7)	N(1)-C(8)-N(2)	116.6(14)
Au-N(1)-C(1)	120.3(14)	Au-N(1)-C(8)	119.1(8)
C(1)-N(1)-C(8)	119.1(8)	C(7)-N(2)-C(8)	117.2(15)



Fig. 1 Structure of the cation $[Au(PPh_3)(dmpy)]^+$ in complex 1b with hydrogen atoms omitted. The thermal ellipsoids correspond to 50% probability

with those of **1b**. However, the Au \cdots N(2) distance of 3.06 Å indicates no co-ordination bond and the napy ligand behaves as a monodentate ligand in **2a**.

In complex **3b** the most important feature is the coordination of the imidazole group to Au^I rather than the pyridine group (Fig. 3). The Au–N (imidazole) bond distance of 2.075(4) Å (Table 3) is slightly shorter than the Au–N (pyridine) distances in **1b** and **2a**. Thus gold(1) is more strongly coordinated to imidazole than to pyridine. The P–Au–N angles in the two-co-ordinate gold complexes **1b**, **2a** and **3b** are not equal and deviate from linearity in the order **3b** [172.4(1)] < **2a** [174.3(4)] < **1a** [178.8(3)°]. This is obviously related to the steric effect of the N-ligand. In fact the P–Au–N angle [179.3(2)°] in [Au(PPh₃)(NMe₃)]⁺ having a NMe₃ ligand of small steric hindrance is almost linear.

Solution studies

(a) ¹H NMR spectroscopy. Binary gold(I) complexes with N-ligands are generally unstable and become stable only when a soft ligand such as PPh_3 is also co-ordinated. For example,

Table 3 Selected bond distances (Å) and angles (°) for complex 3b with e.s.d.s in parentheses

Au–P	2.238(1)	Au-N(1)	2.075(4)
P-C(19)	1.804(6)	P-C(13)	1.817(6)
C(1) - N(1)	1.333(7)	P-C(25)	1.828(6)
C(2) - N(1)	1.388(7)	C(1)-N(2)	1.331(7)
P-Au-N(1)	172.4(1)	Au-P-C(13)	113.0(2)
Au-P-C(19)	113.1(2)	Au-P-C(25)	111.7(2)
C(13) - P - C(19)	106.1(3)	Au-N(1)-C(1)	128.7(4)
C(19)–P–C(25)	106.1(3)	C(1)-N(1)-C(2)	106.3(5)
Au-N(1)-C(2)	124.9(4)	C(1)-N(2)-C(7)	108.9(5)



Fig. 2 Structure of the cation $[{\rm Au}({\rm PPh}_3)({\rm napy})]^+$ 2a. Details as in Fig. 1



Fig. 3 Structure of the cation $[Au(PPh_3)(pbzim)]^+$ in complex 3b. Details as in Fig. 1

the tertiary phosphine complexes $[Au(PR_3)(N-ligand)]^+$ (N-ligand = bipyridyl,⁹ pyrimidines,¹⁰ or imidazole¹¹) are stable, whereas chloro(piperidine)gold(I) is stable only at -20 °C and rapidly disproportionates in air.¹²

The stability of these complexes is thus a reflection of the donor properties of the N-ligand both from steric and electronic effects. The ¹H NMR spectra of **1a**, **1b** and **1c** were



measured at 23 and -90 °C, respectively; the ligand structures with atom numbering are shown in Scheme 2. The resonances of both the phenyl and N-ligand protons of 1a and 1b were shifted downfield with no significant difference between 23 and -90 °C. On the other hand the complex [Au(PPh₃)(dbpy)]ClO₄ 1c at -60 °C in CDCl₃-(CD₃)₂CO (8:12 v/v) exhibits ¹H NMR resonances of both free and co-ordinated dbpy. The intensity ratio of the proton resonances indicates ca. 80% dissociation of 1c in solution. For comparison, the spectra of 1d, 1e and 1f were obtained at 23, -60 and -90 °C respectively. The ¹H NMR resonances of the *p*-protons of the nitrogen ligands in 1d, 1e and 1f shift downfield, and the co-ordination shifts ($\delta_{complex}$ – δ_{free}) are 0.63 (H⁴), 0.80 (H⁹) and 0.05 ppm (H⁴) at 23 °C. Large co-ordination shifts were also observed for H^8 of 1d (0.68), $H^{4,5}$ of 1e (0.96) and H^{10} of 1f (0.48 ppm) because of the hydrogen-gold interaction.

Interestingly, the ¹H NMR resonances of quinoline in complex **1d** become broader as the temperature decreases, indicating that the ligand exchange takes place in solution, equation (3). However in the case of acridine, in which the electron pair

$$[Au(PPh_3)(quin)]ClO_4 = [Au(PPh_3)(ClO_4)] + quin \quad (3)$$

of the nitrogen can be delocalized, no broadening of resonances for complex 1e was observed due to the related strong interaction of Au^I with acridine. For 1f a rapid ligand exchange was observed since the proton resonances of benzo[*h*]quinoline broadened at -60 °C, and the co-ordination shift of the *p*hydrogen is much less than that of 1e, indicating that the second benzene ring in the 7,8 position has a great steric effect on the co-ordination of Au^I to the nitrogen of quinoline. From the ¹H NMR studies the co-ordination shifts of 1a–1f were largest at the *para* position to the nitrogen of the ligand system. The stability decreases in the order 1a > 1b > 1c for the monocyclic nitrogen ligand owing to the steric hindrance in these complexes and 1e > 1d \gg 1f for the multiring ligands.

The co-ordination chemistry of 1,8-naphthyridine and its 2,7-methyl derivative has been extensively studied in relation to a variety of metal centers. These heterocycles are of considerable interest as ligands because they can act in bi- and mono-dentate manners. For example, a monodentate behavior of



Fig. 4 Proton NMR spectra for complexes **2a**, **2b** and **2c** at 270 MHz and 23, -60 and -90 °C (× represents the signal of CHCl₃ contained as an impurity in CDCl₃)



napy was observed in [Hg2(napy)2][ClO4]213 (Hg-N 2.03 Å, non-bonding distance 2.78 Å), but the phen in [Hg2- $(\text{phen})(\text{NO}_3)_2]^{14}$ is clearly bidentate with Hg–N 2.30 and 2.48 Å. The properties of site exchange (or fluxional behavior) of Nligands in square-planar and octahedral complexes in solution have been well studied. For example, [Cr(CO)₅(napy)],¹⁵ [Mn- $(\eta^{1}-\text{napy})(\eta^{2}-\text{napy})(\text{CO})_{3}]\text{ClO}_{4}^{16}$ cis-[PtCl(PPh_{3})_{2}(\text{napy})]BF_{4}^{17} and [AuMe_3(napy)]Cl¹⁸ exhibit site exchange in solution. However, no site exchange of a linear complex has been found so far. The ¹H NMR spectrum of **2a** exhibits a downfield shift compared with free napy and basically is similar to that of complexes 1c, but the narrow resonances of H^2 and H^7 at 23 °C broaden at low temperature (-90 °C) as shown is Fig. 4(a)and 4(b), indicating that the co-ordination site of napy rapidly exchanges in solution. The site-exchange mode is represented in Scheme 3. As reported by Kang et al.,¹⁹ the intermediate **B** is very unstable due to the unfavorable orientation of the nitrogen lone pairs of napy, when compared with that in 2,2'-bipyridine and 1,10-phenanthroline. The larger angle of Au-N(1)-C(8) for 2a also indicates that intermediate B is higher in energy, because the co-ordination of the lone-pair electron of the second nitrogen in napy to Au requires the bending of the Au-N(1)-C(8) angle (Table 2).

As for complex 2d with one carbonyl group between the two pyridines, the ¹H NMR resonances show a downfield shift. It would be of interest to see whether the gold(1) of 2d is coordinated to one nitrogen of dpk in a linear geometry or to two nitrogens in a trigonal geometry, since the intermediate is six membered and the C=N solid-state IR absorption showed only one peak at 1584 cm⁻¹. Unfortunately we have no single-crystal structure data to support it.

The ¹H NMR spectrum of complex **3a** was obtained in $(CD_3)_2CO-CDCl_3$ (1:1) at 23 °C and showed a downfield shift. The signal of the NH proton became very weak, indicating that a bond from Au^I to NH is formed. In this case gold(I) is probably bonded only to this nitrogen atom. A slight broadening of the ¹H NMR resonances of **3b** at -90 °C in $(CD_3)_2CO$ indicating site exchange. The resonances of all the protons of the 2-(2-pyridyl)benzimidazole show a downfield shift except that of proton H⁶ which is far from the center of co-ordination and has a 0.1 ppm upfield shift. It is worth noting that almost all of the ¹H NMR spectra discussed above show downfield shifts. This is of interest for the co-ordination chemistry of gold(I) since it was previously reported that the bonding of Au^I to nitrogen resulted in upfield shifts.²⁰

In summary, the co-ordination of gold(I) to nitrogen donor atoms in complexes 1a-1f is affected by the steric effect of substituted groups in the N ligand; the stability is in the order 1a > 1b > 1c for monoring ligands and 1e > 1d > 1f for tworing ligands. In the solid state the favored co-ordination geometry of gold(I) complexes with PPh₃ and a N-ligand is two-coordinate linear. Exchange of gold(I) at nitrogen co-ordination sites in 2a-2d was found in solution. For 2b and 2c an unstrained five-membered ring transition state results in more rapid exchange of gold(I) between the two ligating nitrogens than that of the strained four-membered ring of 2a.

Experimental

Preparations were carried out using standard Schlenk techniques under an argon atmosphere. All solvents were dried by standard methods before use. The HAuCl₄·H₂O was obtained from Aldrich Chemicals and used to prepare the [Au(PPh₃)Cl] by the literature procedure.²¹ All nitrogen ligands (Wako Pure Chemical Co., Japan) were used without further purification, except for the bis(imidazol-2-yl)methane which was synthesized according to the literature.²² Infrared spectra were measured as KBr discs on a JASCO FT/IR-8000 spectrometer, and ¹H NMR spectra on JEOL FX 200 FT and GSX 270 FT spectrometers respectively. **CAUTION**: AgClO₄·H₂O is potentially explosive.

Syntheses

[Au(PPh₃)(py)]ClO₄ 1a. Chloro(triphenylphosphine)gold(I) (69.3 mg, 0.14 mmol) was dissolved in dry tetrahydrofuran (2 cm³) at 0 °C and a tetrahydrofuran (1 cm³) solution of AgClO₄ (29.0 mg, 0.14 mmol) was added. After filtration, a tetrahydrofuran (1 cm³) solution of pyridine (0.36 cm³, 4.2 mmol) was added, stirred for 30 min at 0 °C, and then transferred to a glass tube (10 mm diameter) and sealed. After standing for 2 d at 0 °C a colorless crystal was obtained (20%). IR, $\tilde{\nu}/cm^{-1}$: 1609w ($\nu_{C=N}$), 1444s, 1439s (ν_{P-Ph}), 1145vs, 1114vs and 1091vs (ν_{CI-O}). ¹H NMR [23 °C (CD₃)₂CO, 200 MHz]: δ 7.40–7.71 (overlap-

ping, Ph), 8.11 (2 × 1 H, H^{3,5}), 8.49 (1 H, H⁴) and 9.17 (2 × 1 H, H^{2,6}) (Found: C, 43.21; H, 3.09; N, 2.10. Calc. for $C_{23}H_{20}Au-CINO_4P$: C, 43.31; H, 3.16; N, 2.20%).

[Au(PPh₃)(dmpy)]ClO₄ 1b. A acetone solution (1 cm³) of AgClO₄ (24.9 mg, 0.12 mmol) was added dropwise to a stirred, cooled (0 °C) chloroform solution (3 cm³) of [Au(PPh₃)Cl] (59.4 mg, 0.12 mmol) under an argon atmosphere. The AgCl precipitated was filtered off and the colorless solution was added to 2,6-dimethylpyridine (0.14 cm³, 0.12 mmol) in chloroform (3 cm³) and stirred for 30 min at room temperature. The colorless solution of [Au(PPh₃)(ClO₄)] was sealed in a glass tube under an argon atmosphere. After standing for 3 d at 5 °C colorless crystals were obtained (60%). IR, $\tilde{\nu}$ /cm⁻¹: 1580w (ν_{C=N}), 1444s, 1437s (ν_{P-Ph}), 1145vs, 1119vs, 1105vs and 1094vs (ν_{Cl-O}). ¹H NMR [23 °C, (CD₃)₂CO, 200 MHz]: δ 3.08 (2 × 3 H, for 2,6-Me), 7.70–7.73 (overlapping, Ph), 7.76 (2 × 1 H, H^{3,5}) and 8.14 (1 H, H⁴) (Found: C, 45.02; H, 3.58; N, 2.08. Calc. for C₂₅H₂₄AuClNO₄P: C, 45.10; H, 3.63; N, 2.10%).

[Au(PPh₃)(dbpy)]ClO₄ 1c. Colorless crystals (10%) of complex 1c were obtained in a similar procedure to that for 1b, using [Au(PPh₃)(ClO₄)] (44.67 mg, 0.08 mmol), and 2,6-di-*tert*-butylpyridine (0.18 cm³, 0.08 mmol). IR, $\tilde{\nu}/cm^{-1}$: 1587w ($\nu_{C=N}$), 1447s, 1440s (ν_{P-Ph}), 1146vs, 1120vs, 1105vs and 1095vs (ν_{C-O}). ¹H NMR [-60 °C, CDCl₃-(CD₃)₂CO (80:1, ν/ν), 270 MHz]: δ 1.64 (6 × 3 H, for 2,6-Bu^t), 7.50–7.54 (overlapping, Ph), 7.87 (2 × 1 H, H^{3,5}) and 8.50 (1 H, H⁴) (Found: C, 48.86; H, 4.68; N, 1.84. Calc. for C₃₁H₃₆AuClNO₄P: C, 49.64; H, 4.84; N, 1.87%).

[Au(PPh₃)(quin)]ClO₄ 1d. Colorless crystals (21%) of complex 1d were obtained in a similar procedure to that for 1b, using [Au(PPh₃)(ClO₄)] (44.67 mg, 0.08 mmol) and quinoline (0.095 cm³, 0.8 mmol). IR, $\tilde{\nu}$ /cm⁻¹: 1586w ($\nu_{c=N}$), 1444s, 1440s (ν_{P-Ph}), 1145vs and 1091vs (ν_{c1-O}). ¹H NMR [23 °C, (CD₃)₂CO, 270 MHz]: δ 7.70–7.75 (overlapping, Ph), 7.82 (1 H, t, H³), 7.94 (1 H, t, H⁶), 8.04 (1 H, t, H⁷), 8.27 (1 H, d, H⁵), 8.73 (1 H, d, H⁸), 8.87 (1 H, d, H⁴) and 9.34 (1 H, d, H²) (Found: C, 46.89; H, 3.11; N, 2.06. Calc. for C₂₇H₂₂AuClNO₄P: C, 47.14; H, 3.22; N, 2.04%).

[Au(PPh₃)(acr)]ClO₄ 1e. Colorless crystals (50%) of complex 1e were obtained in a similar manner to that for 1b, using [Au(PPh₃)(ClO₄)] (33.51 mg, 0.06 mmol) and acridine (10.8 mg, 0.06 mmol). IR, $\tilde{\nu}$ /cm⁻¹: 1620w ($\nu_{C=N}$), 1444s, 1437s (ν_{P-Ph}), 1125vs, 1115vs, 1105vs and 1094vs (ν_{CI-O}). ¹H NMR [23 °C, (CD₃)₂CO, 270 MHz]: δ 7.73–7.76 (overlapping, Ph), 7.90 (1 H, t, H^{2,7}), 8.26 (1 H, t, H^{3,6}), 8.54 (1 H, d, H^{1,8}), 9.14 (1 H, d, H^{4,5}) and 9.83 (1 H, d, H⁹) (Found: C, 50.06; H, 3.17; N, 1.86. Calc. for C₃₁H₂₄AuCINO₄P: C, 50.46; H, 3.28; N, 1.90%).

[Au(PPh₃)(bquin)]ClO₄ 1f. Colorless crystals (50%) of complex 1f were obtained in a similar procedure to that for 1b, using [Au(PPh₃)(ClO₄)] (33.51 mg, 0.06 mmol) and benzo[*h*]quino-line (10.8 mg, 0.06 mmol). IR, $\tilde{\nu}$ /cm⁻¹: 1590w ($\nu_{C=N}$), 1437s (ν_{P-Ph}), 1144vs and 1090vs (ν_{CI-O}). ¹H NMR [-60 °C, CDCl₃-(CD₃)₂CO (80:1, ν/ν), 270 MHz]: δ 7.52–7.58 (overlapping, Ph), 7.92–8.10 (6 × 1 H, overlapping, H^{3,6,7,8,9,10}), 8.76 (1 H, d, H⁵), 9.10 (1 H, s, H⁴) and 9.29 (1 H, s, H²) (Found: C, 50.12; H, 3.36; N, 1.78. Calc. for C₃₁H₂₄AuClNO₄P: C, 50.46; H, 3.28; N, 1.90%).

[Au(PPh₃)(napy)]ClO₄ 2a. A solution of $AgClO_4$ (12.5 mg, 0.06 mmol) in thf (1 cm³) was added dropwise to a solution of [Au(PPh₃)Cl] (29.7 mg, 0.06 mmol) in thf (2 cm³), stirred at 0 °C for 10 min, and then the resulting solution of [Au(PPh₃)-(ClO₄)] was filtered. The filtrate was added to a solution of 1,8-naphthyridine (7.8 mg, 0.06 mmol) in thf (1 cm³), stirred for 30 min, and filtered. The colorless filtrate was transferred to a glass tube (10 mm diameter) and layered with diethyl ether (1.0 cm³) as a diffusion solvent. After standing for 5 d at 5 °C colorless

Table 4 Crystal data and structure determination parameters for complexes 1b, 2a and 3b

Formula M Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $U/Å^{3}$ Z μ/cm^{-1} F(000) $D_{c}/g cm^{-3}$ Radiation $(\lambda/Å)$ Crystal dimensions/mm Scan speed/ $^{\circ}$ min ⁻¹ Scan mode $(2 \theta_{max}/^{\circ})$ Reflections used R^{a} R'^{b} $T = F ^{2} F - F ^{2} F ^{2}$	$C_{25}H_{24}AuClNO_4P$ 665.87 Orthorhombic $P_{2,2_{1}2_{1}}$ 11.431(2) 19.984(8) 10.845(4) 2477.4 4 61.10 1300.0 1.790 Mo-K α (0.710 73) 0.40 × 0.20 × 0.20 8 20 (45) 2639 0.062 0.066	$\begin{array}{c} C_{26}H_{21}AuClN_2O_4P\\ 688.87\\ Triclinic\\ P1\\ 11.587(5)\\ 12.805(5)\\ 9.590(4)\\ 93.52(5)\\ 108.3(8)\\ 67.69(4)\\ 1246.5\\ 2\\ 60.77\\ 666.0\\ 1.840\\ Mo-K\alpha\ (0.739\ 30)\\ 0.15\times 0.20\times 0.35\\ 8\\ 2\theta\ (45)\\ 4939\\ 0.078\\ 0.090\\ \end{array}$	$\begin{array}{c} C_{30}H_{23}AuClN_{3}O_{4}P\\ 752.92\\ Monoclinic\\ P2_{1}/a\\ 10.788(4)\\ 8.373(3)\\ 31.205(3)\\ 98.24(2)\\ 2789(1)\\ 4\\ 118.66\\ 1472.0\\ 1.795\\ Cu-K\alpha (1.541\ 78)\\ 0.35\times 0.40\times 0.40\\ 8\\ 2\theta (120)\\ 3776\\ 0.032\\ 0.045\\ \end{array}$
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brick crystals were isolated (12%). IR, $\tilde{\nu}$ /cm⁻¹: 1602w ($\nu_{C=N}$), 1587w, 1445s, 1439s (ν_{P-Ph}), 1148vs, 1120vs, 1105 and 1091vs (ν_{CI-O}). ¹H NMR [23 °C, (CD₃)₂CO, 270 MHz]: δ 7.71–7.85 (overlapping, Ph), 8.11 (2 × 1 H, t, H^{3,6}), 9.03 (2 × 1 H, d, H^{4,5}) and 9.53 (2 × 1 H, d, H^{2,7}) (Found: C, 45.28; H, 3.24; N, 4.17. Calc. for C₂₆H₂₁AuClN₂O₄P: C, 45.33; H, 3.07; N, 4.07%).

[Au(PPh₃)(phen)]ClO₄ 2b. Crystals of complex 2c were obtained by pouring a solution (1 cm³) of [Au(PPh₃)(ClO₄)] $(1.6 \times 10^{-5} \text{ mol})$, prepared following the procedure as for 2a in chloroform-acetone (50:1, v/v), into a glass tube (10 mm diameter) and adding on top of it benzene (5 cm³). Then a dilute solution (1 cm³) of 1,10-phenanthroline (2.88 mg, 1.6×10^{-5} mol) in acetone was added gently to avoid possible mixing. The glass tube was sealed and after standing at room temperature for 2 weeks yellow brick crystals (21%) grew in the buffer zone. IR, $\tilde{\nu}/cm^{-1}$: 1620w ($\nu_{C=N}$), 1439s, 1433s (ν_{P-Ph}), 1143vs, 1118vs, 1102vs and 1087vs (ν_{CI-O}). ¹H NMR [23 °C, CDCl₃-(CD₃)₂CO (50:1, v/v), 270 MHz]: δ 7.48-7.52 (overlapping, Ph), 7.68–7.84 (2 × 1 H, br, H^{3,8}), 7.95 (2 × 1 H, s, $\rm H^{5,6}$), 8.47 (2 × 1 H, br, $\rm H^{4,7}$) and 9.24 (2 × 1 H, br, $\rm H^{2,9}$) (Found: C, 48.23; H, 3.08; N, 3.63. Calc. for C₃₀H₂₃AuClN₂O₄P: C, 48.76; H, 3.14; N, 3.79%).

[Au(PPh₃)(dpk)]ClO₄ 2d. White solids (36%) of complex 2d were obtained in a similar procedure to that for 2a, using [Au-(PPh₃)(ClO₄)] (67.02 mg, 0.12 mmol) and di-2-pyridyl ketone (22.1 mg, 0.12 mmol). IR, $\tilde{\nu}$ /cm⁻¹: 1689m ($\nu_{C=0}$), 1584w ($\nu_{C=N}$), 1445s, 1439s (ν_{P-Ph}), 1114vs, 1105vs and 1094vs (ν_{Cl-0}). ¹H NMR [23 °C, (CD₃)₂CO, 270 MHz]: δ 7.60–7.64 (overlapping, Ph), 7.96 (1 H, br, H⁵), 8.34–8.41 (2 × 1 H, m, H^{3,4}) and 9.01 (1 H, br, H⁶) (Found: C, 46.59; H, 3.39; N, 3.29. Calc. for C₂₉H₂₃-AuClN₂O₅P: C, 46.89; H, 3.12; N, 3.77%).

[Au(PPh₃)(dpa)]ClO₄ 3a. Di-2-pyridylamine (27.4 mg, 1.6×10^{-4} mol) in thf (5 cm³) was added to a solution of [Au-(PPh₃)ClO₄)] (1.6×10^{-4} mol) prepared as for 1a in thf (4 cm³). White precipitates were quickly formed and the colorless reaction mixture was stirred for 30 min at room temperature. The resulting yellow solution was filtered and yellow crystals (34%) were obtained by evaporating this filtrate. IR, $\tilde{\nu}$ /cm⁻¹: 3064w ($\nu_{\text{H-N}}$), 1610vs, 1599m ($\nu_{\text{C=N}}$), 1441m, 1431m ($\nu_{\text{P-Ph}}$), 1105vs and 1093vs ($\nu_{\text{CI-O}}$). ¹H NMR [23 °C, (CD₃)₂CO–CDCl₃ (1:1, ν/ν), 270 MHz]: δ 7.09 (2 × 1 H, br, H⁵), 7.58–7.60 (overlapping of Ph with H³), 7.88 (2 × 1 H, t, H⁴), 8.34 (2 × 1 H, br, H⁶) and 9.67 (1 H, very weak, N–H) (Found: C, 46.10; H, 3.25; N, 5.68. Calc. for C₂₈H₂₄AuClN₃O₄P: C, 46.07; H, 3.31; N, 5.76%).

[Au(PPh₃)(pbzim)]ClO₄ 3b. 2-(2-Pyridyl)benzimidazole (15.6 mg, 8.0×10^{-5} mol) in chloroform (5 cm³) was added to a solution of [Au(PPh₃)(ClO₄)] (8.0×10^{-5} mol) prepared as for **1a** in chloroform–acetone (1:1 v/v, 5 cm³) and stirred for 30 min at room temperature. The brown filtrate was transferred to a glass tube and layered with *n*-pentane as a diffusion solvent. After standing for 1 month at 5 °C brown crystals were isolated (26%). IR, $\tilde{\nu}$ /cm⁻¹: 1595w ($\nu_{C=N}$), 1441m, 1439m (ν_{P-Ph}), 1144vs, 1103vs (ν_{CI-O}). ¹H NMR [-90 °C, (CD₃)₂CO, 270 MHz]: δ 7.63 (1 H, H^{4,7}), 7.83 (Ph), 7.89 (1 H, H⁵), 7.91 (1 H, H⁵), 7.94 (1 H, H⁶), 8.32 (1 H, H^{4'}), 8.52 (1 H, H^{3'}), 8.68 (1 H, H^{6'}) and 14.68 (1 H, NH) (Found: C, 47.41; H, 3.11; N, 5.38. Calc. for C₃₀H₂₃AuClN₃O₄P: C, 47.86; H, 3.08; N, 5.58%).

Crystallography

Diffraction data for complexes **1b**, **2a** and **3b** were obtained on a Rigaku AFC-6B four-circle diffractometer at ambient temperature. Experimental details are included in Table 4. Their structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from ref. 23. Hydrogen atoms were included in the last cycle; their positions were obtained from Fourier-difference synthesis, and their thermal parameters were assumed to be isotropic. The final Fourierdifference maps were featureless. The calculations were carried out on the FACOM 780 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY.²⁴

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