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

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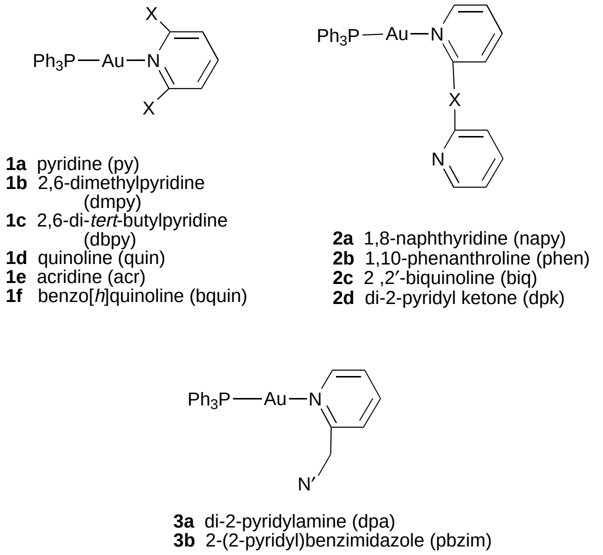
A series of gold(I) complexes $[Au(PPh_3)L]ClO_4$ (L = pyridine **1a**, 2,6-dimethylpyridine **1b**, 2,6-di-*tert*-butylpyridine **1c**, quinoline **1d**, acridine **1e**, benzo[*h*]quinoline **1f**, naphthyridine **2a**, 1,10-phenanthroline **2b**, 2,2′-biquinoline **2c**, di-2-pyridyl ketone **2d**, 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 $[Au(PPh_3)L]^+$ with N-heterocyclic ligands L are rather rare.[6,7] To the best of our knowledge, only one such complex, $[Au(PPh_3)(qncd)]BF_4$ (qncd = quinuclidine) has been characterized by X-ray diffraction.[8] By contrast to the trialkylphosphinegold(I) halides, the stability constant of the $[Au(PR_3)L]^+$ 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.



Scheme 1

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 characterization 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 co-ordinated to Au^I, as indicated by the single-crystal X-ray analysis.

$$[Au(PPh_3)Cl] + AgClO_4 \longrightarrow [Au(PPh_3)(ClO_4)] + AgCl\,(\downarrow) \quad (1)$$

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

(*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 perchlorate anion. Selected interatomic distances and bond angles are listed in Table 1. In the cation the gold atom is linearly co-ordinated by PPh_3 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 $[Au(PPh_3)(NMe_3)]ClO_4$[7] [2.108(7) and 2.231(2) Å] and $[Au(PPh_3)(qncd)]BF_4$[8] [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

Table 1 Selected bond distances (Å) and angles (°) for complex **1b** with estimated standard deviations (e.s.d.s) in parentheses

Au–P	2.233(4)	Au–N	2.091(3)
P–C(7)	1.813(14)	P–C(1)	1.803(15)
P–C(13)	1.809(13)	N–C(19)	1.328(20)
N–C(23)	1.323(22)	C(19)–C(24)	1.511(27)
C(23)–C(25)	1.475(29)		
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 (°) 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)

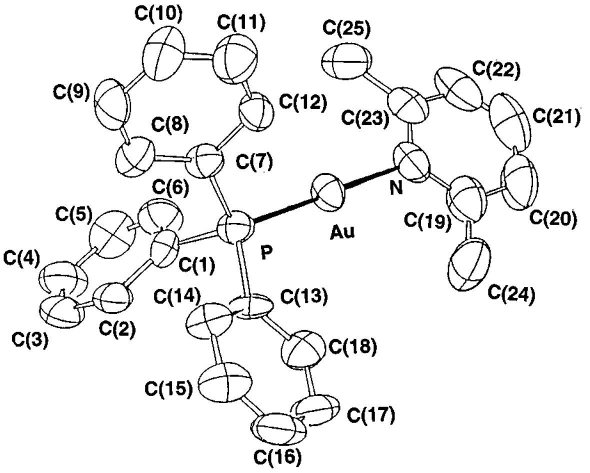


Fig. 1 Structure of the cation [Au(PPh$_3$)(dmpy)]$^+$ in complex **1b** with hydrogen atoms omitted. The thermal ellipsoids correspond to 50% probability

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 co-ordination of the imidazole group to Au$^{\text{I}}$ 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(I) is more strongly co-ordinated 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(PPh$_3$)(NMe$_3$)]$^+$ having a NMe$_3$ ligand of small steric hindrance is almost linear.

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)

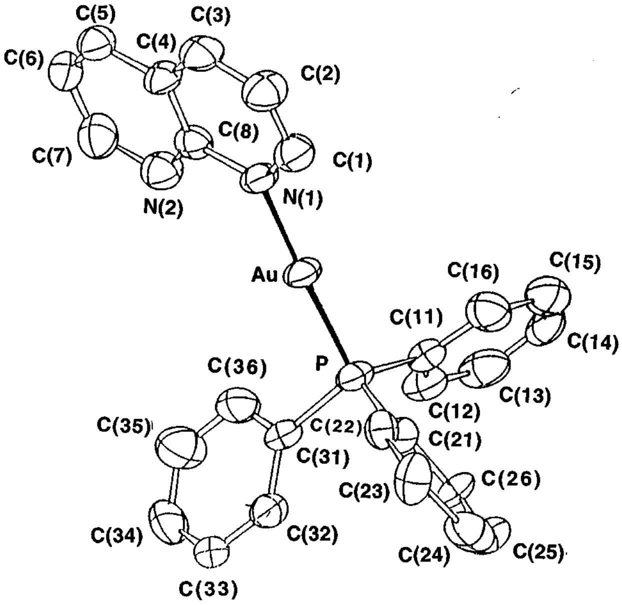


Fig. 2 Structure of the cation [Au(PPh$_3$)(napy)]$^+$ **2a**. Details as in Fig. 1

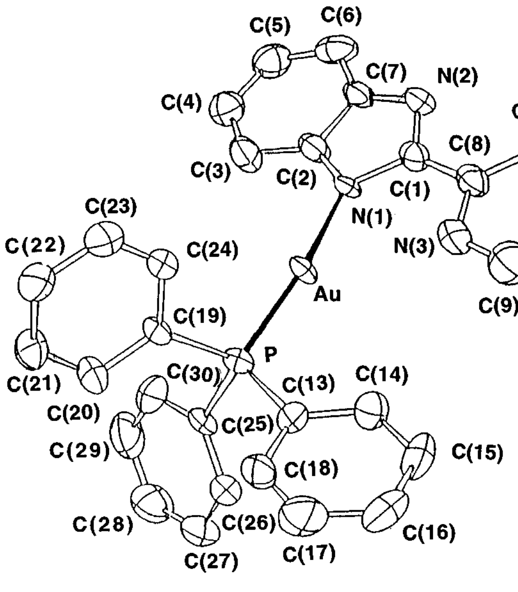
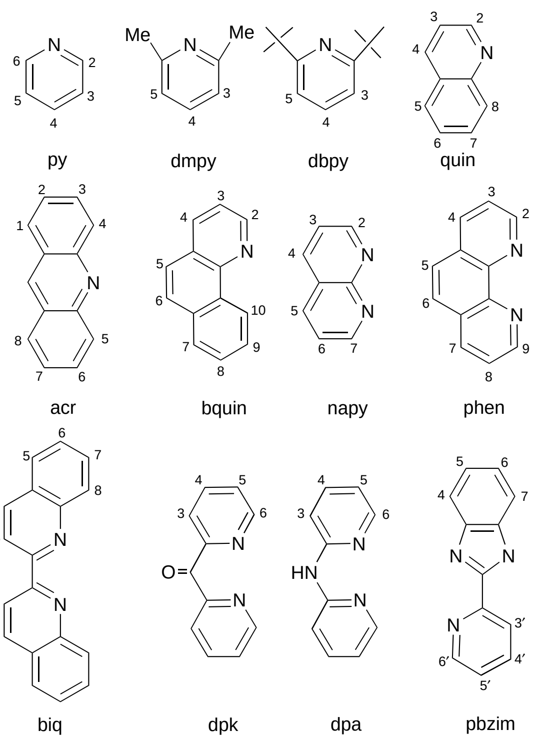


Fig. 3 Structure of the cation [Au(PPh$_3$)(pbzim)]$^+$ in complex **3b**. Details as in Fig. 1

Solution studies

(*a*) **^{1}H 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, the tertiary phosphine complexes [Au(PR$_3$)(N-ligand)]$^+$ (N-ligand = bipyridyl,[9] pyrimidines,[10] or imidazole[11]) 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 ^{1}H NMR spectra of **1a**, **1b** and **1c** were



Scheme 2

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 $[Au(PPh_3)(dbpy)]ClO_4$ **1c** at −60 °C in $CDCl_3$–$(CD_3)_2CO$ (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 ($\delta_{complex} - \delta_{free}$) are 0.63 ($H^4$), 0.80 ($H^9$) and 0.05 ppm ($H^4$) 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

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

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** ≫ **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 monodentate manners. For example, a monodentate behavior of napy was observed in $[Hg_2(napy)_2][ClO_4]_2$[13] (Hg–N 2.03 Å, non-bonding distance 2.78 Å), but the phen in $[Hg_2(phen)(NO_3)_2]$[14] is clearly bidentate with Hg–N 2.30 and 2.48 Å. The properties of site exchange (or fluxional behavior) of N-ligands in square-planar and octahedral complexes in solution have been well studied. For example, $[Cr(CO)_5(napy)]$,[15] $[Mn(\eta^1\text{-napy})(\eta^2\text{-napy})(CO)_3]ClO_4$,[16] *cis*-$[PtCl(PPh_3)_2(napy)]BF_4$[17] and $[AuMe_3(napy)]Cl$[18] 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).

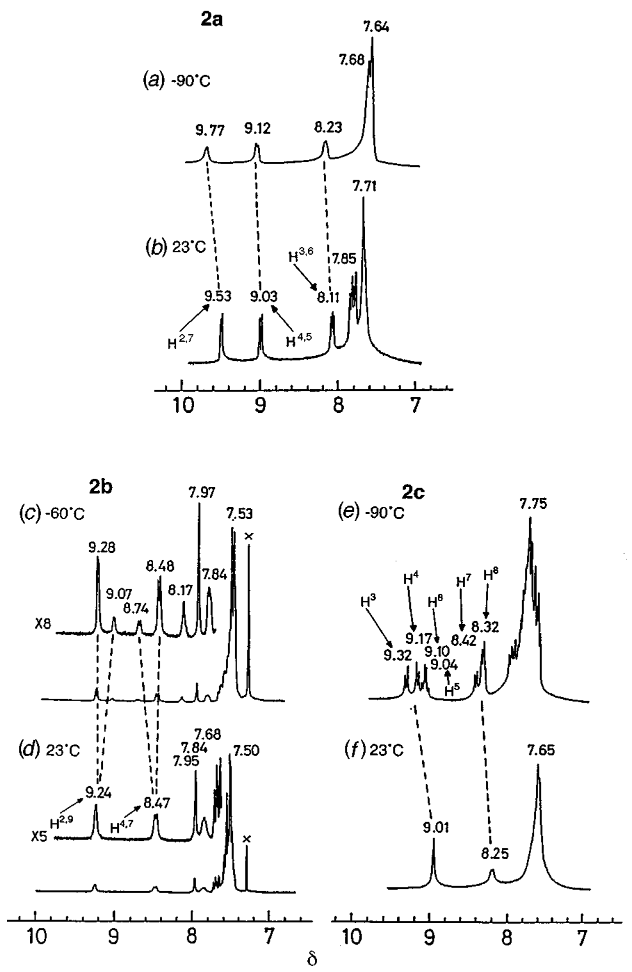
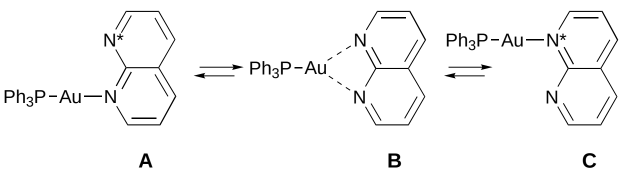


Fig. 4 Proton NMR spectra for complexes **2a**, **2b** and **2c** at 270 MHz and 23, −60 and −90 °C (× represents the signal of $CHCl_3$ contained as an impurity in $CDCl_3$)



Scheme 3

The H^2 and H^9 NMR signals of $[Au(PPh_3)(phen)]^+$ **2b** at 23 °C in $CDCl_3$–$(CD_3)_2CO$ appeared at δ 9.24 as a single resonance. Interestingly, as the temperature was decreased to −60 °C this single resonance split into two at δ 9.28 and 9.07 [Fig. 4(*c*) and 4(*d*)]. This means the site-exchange reaction also occurs in solution for **2b** through the transition state **B**. As indicated in Fig. 4(*e*) and 4(*f*), a splitting of the resonances of **2c** was also observed at −90 °C. This means that site exchange is taking place in solution and the intermediate **B** may be favorable due to the greater flexibility of the ligand biq.

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(I) of **2d** is co-ordinated 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 H^6 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 two-ring ligands. In the solid state the favored co-ordination geometry of gold(I) complexes with PPh_3 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 $HAuCl_4 \cdot H_2O$ was obtained from Aldrich Chemicals and used to prepare the $[Au(PPh_3)Cl]$ 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**: $AgClO_4 \cdot H_2O$ is potentially explosive.

Syntheses

$[Au(PPh_3)(py)]ClO_4$ 1a. Chloro(triphenylphosphine)gold(I) (69.3 mg, 0.14 mmol) was dissolved in dry tetrahydrofuran (2 cm^3) at 0 °C and a tetrahydrofuran (1 cm^3) solution of $AgClO_4$ (29.0 mg, 0.14 mmol) was added. After filtration, a tetrahydrofuran (1 cm^3) solution of pyridine (0.36 cm^3, 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_{Cl-O}). ^1H NMR [23 °C $(CD_3)_2CO$, 200 MHz]: δ 7.40–7.71 (overlapping, Ph), 8.11 (2 × 1 H, $H^{3,5}$), 8.49 (1 H, H^4) and 9.17 (2 × 1 H, $H^{2,6}$) (Found: C, 43.21; H, 3.09; N, 2.10. Calc. for $C_{23}H_{20}AuClNO_4P$: C, 43.31; H, 3.16; N, 2.20%).

$[Au(PPh_3)(dmpy)]ClO_4$ 1b. A acetone solution (1 cm^3) of $AgClO_4$ (24.9 mg, 0.12 mmol) was added dropwise to a stirred, cooled (0 °C) chloroform solution (3 cm^3) of $[Au(PPh_3)Cl]$ (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 cm^3, 0.12 mmol) in chloroform (3 cm^3) and stirred for 30 min at room temperature. The colorless solution of $[Au(PPh_3)(ClO_4)]$ 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 ($\nu_{C=N}$), 1444s, 1437s (ν_{P-Ph}), 1145vs, 1119vs, 1105vs and 1094vs (ν_{Cl-O}). ^1H NMR [23 °C, $(CD_3)_2CO$, 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, H^4) (Found: C, 45.02; H, 3.58; N, 2.08. Calc. for $C_{25}H_{24}AuClNO_4P$: C, 45.10; H, 3.63; N, 2.10%).

$[Au(PPh_3)(dbpy)]ClO_4$ 1c. Colorless crystals (10%) of complex **1c** were obtained in a similar procedure to that for **1b**, using $[Au(PPh_3)(ClO_4)]$ (44.67 mg, 0.08 mmol), and 2,6-di-*tert*-butylpyridine (0.18 cm^3, 0.08 mmol). IR, $\tilde{\nu}$/cm^{-1}: 1587w ($\nu_{C=N}$), 1447s, 1440s (ν_{P-Ph}), 1146vs, 1120vs, 1105vs and 1095vs (ν_{Cl-O}). ^1H NMR [−60 °C, $CDCl_3$–$(CD_3)_2CO$ (80 : 1, v/v), 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, H^4) (Found: C, 48.86; H, 4.68; N, 1.84. Calc. for $C_{31}H_{36}AuClNO_4P$: C, 49.64; H, 4.84; N, 1.87%).

$[Au(PPh_3)(quin)]ClO_4$ 1d. Colorless crystals (21%) of complex **1d** were obtained in a similar procedure to that for **1b**, using $[Au(PPh_3)(ClO_4)]$ (44.67 mg, 0.08 mmol) and quinoline (0.095 cm^3, 0.8 mmol). IR, $\tilde{\nu}$/cm^{-1}: 1586w ($\nu_{C=N}$), 1444s, 1440s (ν_{P-Ph}), 1145vs and 1091vs (ν_{Cl-O}). ^1H NMR [23 °C, $(CD_3)_2CO$, 270 MHz]: δ 7.70–7.75 (overlapping, Ph), 7.82 (1 H, t, H^3), 7.94 (1 H, t, H^6), 8.04 (1 H, t, H^7), 8.27 (1 H, d, H^5), 8.73 (1 H, d, H^8), 8.87 (1 H, d, H^4) and 9.34 (1 H, d, H^2) (Found: C, 46.89; H, 3.11; N, 2.06. Calc. for $C_{27}H_{22}AuClNO_4P$: C, 47.14; H, 3.22; N, 2.04%).

$[Au(PPh_3)(acr)]ClO_4$ 1e. Colorless crystals (50%) of complex **1e** were obtained in a similar manner to that for **1b**, using $[Au(PPh_3)(ClO_4)]$ (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_{Cl-O}). ^1H NMR [23 °C, $(CD_3)_2CO$, 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, H^9) (Found: C, 50.06; H, 3.17; N, 1.86. Calc. for $C_{31}H_{24}AuClNO_4P$: C, 50.46; H, 3.28; N, 1.90%).

$[Au(PPh_3)(bquin)]ClO_4$ 1f. Colorless crystals (50%) of complex **1f** were obtained in a similar procedure to that for **1b**, using $[Au(PPh_3)(ClO_4)]$ (33.51 mg, 0.06 mmol) and benzo[*h*]quinoline (10.8 mg, 0.06 mmol). IR, $\tilde{\nu}$/cm^{-1}: 1590w ($\nu_{C=N}$), 1437s (ν_{P-Ph}), 1144vs and 1090vs (ν_{Cl-O}). ^1H NMR [−60 °C, $CDCl_3$–$(CD_3)_2CO$ (80 : 1, v/v), 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, H^5), 9.10 (1 H, s, H^4) and 9.29 (1 H, s, H^2) (Found: C, 50.12; H, 3.36; N, 1.78. Calc. for $C_{31}H_{24}AuClNO_4P$: C, 50.46; H, 3.28; N, 1.90%).

$[Au(PPh_3)(napy)]ClO_4$ 2a. A solution of $AgClO_4$ (12.5 mg, 0.06 mmol) in thf (1 cm^3) was added dropwise to a solution of $[Au(PPh_3)Cl]$ (29.7 mg, 0.06 mmol) in thf (2 cm^3), stirred at 0 °C for 10 min, and then the resulting solution of $[Au(PPh_3)(ClO_4)]$ was filtered. The filtrate was added to a solution of 1,8-naphthyridine (7.8 mg, 0.06 mmol) in thf (1 cm^3), 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 cm^3) 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**

	1b	**2a**	**3b**
Formula	$C_{25}H_{24}AuClNO_4P$	$C_{26}H_{21}AuClN_2O_4P$	$C_{30}H_{23}AuClN_3O_4P$
M	665.87	688.87	752.92
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P1$	$P2_1/a$
a/Å	11.431(2)	11.587(5)	10.788(4)
b/Å	19.984(8)	12.805(5)	8.373(3)
c/Å	10.845(4)	9.590(4)	31.205(3)
α/°		93.52(5)	
β/°		108.3(8)	98.24(2)
γ/°		67.69(4)	
U/Å^3	2477.4	1246.5	2789(1)
Z	4	2	4
μ/cm^{-1}	61.10	60.77	118.66
F(000)	1300.0	666.0	1472.0
D_c/g cm^{-3}	1.790	1.840	1.795
Radiation (λ/Å)	Mo-Kα (0.710 73)	Mo-Kα (0.739 30)	Cu-Kα (1.541 78)
Crystal dimensions/mm	0.40 × 0.20 × 0.20	0.15 × 0.20 × 0.35	0.35 × 0.40 × 0.40
Scan speed/° min^{-1}	8	8	8
Scan mode (2 θ_{max}/°)	2θ (45)	2θ (45)	2θ (120)
Reflections used	2639	4939	3776
R^a	0.062	0.078	0.032
R'^b	0.066	0.090	0.045

^{a} $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $[\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$.

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_{Cl-O}). ^{1}H NMR [23 °C, $(CD_3)_2CO$, 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 $C_{26}H_{21}AuClN_2O_4P$: C, 45.33; H, 3.07; N, 4.07%).

[Au(PPh$_3$)(phen)]ClO$_4$ 2b. Crystals of complex **2c** were obtained by pouring a solution (1 cm^3) of [Au(PPh$_3$)(ClO$_4$)] (1.6 × 10^{-5} 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 cm^3). Then a dilute solution (1 cm^3) 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_{Cl-O}). ^{1}H NMR [23 °C, $CDCl_3$–$(CD_3)_2CO$ (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, $H^{5,6}$), 8.47 (2 × 1 H, br, $H^{4,7}$) and 9.24 (2 × 1 H, br, $H^{2,9}$) (Found: C, 48.23; H, 3.08; N, 3.63. Calc. for $C_{30}H_{23}AuClN_2O_4P$: C, 48.76; H, 3.14; N, 3.79%).

[Au(PPh$_3$)(biq)]ClO$_4$ 2c. 2,2′-Biquinoline (20.5 mg, 10^{-5} mol) in thf (5 cm^3) was added to a solution of [Au(PPh$_3$)(ClO$_4$)] (8.0 × 10^{-5} mol) prepared as for **2a** in thf (3 cm^3) and stirred for 30 min. A yellow crystal of **2d** was obtained by slowly evaporating the reaction mixture. IR, $\tilde{\nu}$/cm^{-1}: 1612w ($\nu_{C=N}$), 1434m, 1431m (ν_{P-Ph}), 1095vs, 1085vs and 1082vs (ν_{Cl-O}). ^{1}H NMR [−90 °C, $(CD_3)_2CO$, 270 MHz]: δ 7.70–7.75 (overlapping, Ph), 8.32 (2 × 1 H, d, H^6), 8.42 (2 × 1 H, t, H^7), 9.04–9.10 (2 × 1 H, overlapping of H^5 and H^8), 9.17 (2 × 1 H, d, H^4) and 9.75 (2 × 1 H, d, H^3) (Found: C, 53.26; H, 3.15; N, 3.38. Calc. for $C_{36}H_{27}AuClN_2O_4P$: C, 53.05; H, 3.34; N, 3.44%).

[Au(PPh$_3$)(dpk)]ClO$_4$ 2d. White solids (36%) of complex **2d** were obtained in a similar procedure to that for **2a**, using [Au(PPh$_3$)(ClO$_4$)] (67.02 mg, 0.12 mmol) and di-2-pyridyl ketone (22.1 mg, 0.12 mmol). IR, $\tilde{\nu}$/cm^{-1}: 1689m ($\nu_{C=O}$), 1584w ($\nu_{C=N}$), 1445s, 1439s (ν_{P-Ph}), 1114vs, 1105vs and 1094vs (ν_{Cl-O}). ^{1}H NMR [23 °C, $(CD_3)_2CO$, 270 MHz]: δ 7.60–7.64 (overlapping, Ph), 7.96 (1 H, br, H^5), 8.34–8.41 (2 × 1 H, m, $H^{3,4}$) and 9.01 (1 H, br, H^6) (Found: C, 46.59; H, 3.39; N, 3.29. Calc. for $C_{29}H_{23}AuClN_2O_5P$: C, 46.89; H, 3.12; N, 3.77%).

[Au(PPh$_3$)(dpa)]ClO$_4$ 3a. Di-2-pyridylamine (27.4 mg, 1.6 × 10^{-4} mol) in thf (5 cm^3) was added to a solution of [Au(PPh$_3$)ClO$_4$)] (1.6 × 10^{-4} mol) prepared as for **1a** in thf (4 cm^3). 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 (ν_{H-N}), 1610vs, 1599m ($\nu_{C=N}$), 1441m, 1431m (ν_{P-Ph}), 1105vs and 1093vs (ν_{Cl-O}). ^{1}H NMR [23 °C, $(CD_3)_2CO$–$CDCl_3$ (1 : 1, v/v), 270 MHz]: δ 7.09 (2 × 1 H, br, H^5), 7.58–7.60 (overlapping of Ph with H^3), 7.88 (2 × 1 H, t, H^4), 8.34 (2 × 1 H, br, H^6) and 9.67 (1 H, very weak, N–H) (Found: C, 46.10; H, 3.25; N, 5.68. Calc. for $C_{28}H_{24}AuClN_3O_4P$: C, 46.07; H, 3.31; N, 5.76%).

[Au(PPh$_3$)(pbzim)]ClO$_4$ 3b. 2-(2-Pyridyl)benzimidazole (15.6 mg, 8.0 × 10^{-5} mol) in chloroform (5 cm^3) was added to a solution of [Au(PPh$_3$)(ClO$_4$)] (8.0 × 10^{-5} mol) prepared as for **1a** in chloroform–acetone (1 : 1 v/v, 5 cm^3) 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_{Cl-O}). ^{1}H NMR [−90 °C, $(CD_3)_2CO$, 270 MHz]: δ 7.63 (1 H, $H^{4,7}$), 7.83 (Ph), 7.89 (1 H, $H^{5'}$), 7.91 (1 H, H^5), 7.94 (1 H, H^6), 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 $C_{30}H_{23}AuClN_3O_4P$: 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 Fourier-difference 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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