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Cycloauration of 2-substituted pyridine derivatives. Synthesis, structure and reactivity of six-membered cycloaurated complexes of 2-anilino-, 2-phenoxy- and 2-(phenylsulfanyl)-pyridine

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At room temperature and in ethanol 2-anilinopyridine reacted with $H[AuCl_4]\cdot 4H_2O$ as well as $Na[AuCl_4]\cdot 2H_2O$ to give directly the six-membered cycloaurated complex [$AuCl_2$(pap-C^1, N)] **1a** [pap = 2-(2-pyridylamino)phenyl], whereas 2-phenoxypyridine (Hpop) and 2-(phenylsulfanyl)pyridine (Hptp) produced only the salts [H_2pop][$AuCl_4$] **2b** and [H_2ptp][$AuCl_4$] **2c**, respectively. The adducts [$AuCl_3$(Hpop)] **3b** and [$AuCl_3$(Hptp)] **3c** have separately been prepared by the reactions of $Na[AuCl_4]\cdot 2H_2O$ with Hpop and Hptp, respectively, in an acetonitrile–water mixed solvent. The salts **2b** and **2c** can be converted into the corresponding adducts **3b** and **3c** when they are stirred in acetonitrile–water at room temperature. The cycloaurated complexes [$AuCl_2$(pop-C^1, N)] [pop = 2-(2-pyridyloxy)-phenyl] **1b** and [$AuCl_2$(ptp-C^1, N)] [ptp = 2-(2-pyridylsulfanyl)phenyl] **1c** have been obtained by heating the salts or the adducts in acetonitrile–water. Moreover, complexes **1b** and **1c** have been synthesized directly by the reaction of $H[AuCl_4]\cdot 4H_2O$ with Hpop and Hptp in refluxing acetonitrile–water, ethanol–water and propan-2-ol–water. The reaction of **1a** with an equimolar amount of PPh_3 in the presence of $NaBF_4$ gave the cationic complex [AuCl-(pap-C^1, N)(PPh_3)]BF_4 **5a**, while two equivalents of PPh_3 or PEt_3 afforded [AuCl(pap-C^1)(PPh_3)$_2$]Cl **6a** or [AuCl-(pap-C^1)(PEt_3)$_2$]Cl **7a** where the pap ligand co-ordinates through only the carbon atom. On the other hand, the C–N chelates in **1b** and **1c** are easily cleaved with one equimolar amount of PPh_3 to give [$AuCl_2$(pop-C^1)(PPh_3)] **8b** and [$AuCl_2$(ptp-C^1)(PPh_3)] **8c**, respectively. The boat-form structures of the three six-membered auracycles have been confirmed by X-ray diffraction studies of **1b**, **1c** and **5a**. The crystal structure of **7a** has also been determined.

Cyclometallation is an elegant method used to activate C–H bonds in heterosubstituted molecules.[1] However, cycloauration is generally hard to achieve and until now examples have been in principle limited to 2-substituted pyridine derivatives, *i.e.* 2-phenylpyridine,[2] 2,9-diphenyl-1,10-phenanthroline,[3] 4-(4-methoxyphenyl)-6-phenyl-2,2′-bipyridine,[4] 2-benzylpyridine,[5,6] 6-benzyl-2,2′-bipyridine derivatives[7] and 6-*tert*-butyl-2,2′-bipyridine.[7] With other ligands such as azobenzene,[8] *N*,*N*-dimethylbenzylamine,[9,10] 4,4-dimethyl-2-phenyl-1,3-oxazoline,[10] 1-(dimethyl- or methyl-aminomethyl)naphthalene,[10] 1,3-bis(dimethylaminomethyl)benzene[10] and 4-butyl-*N*-(3,4,5-trimethoxybenzylidene)aniline,[11] stable cycloaurated complexes have been synthesized by transmetallation from the corresponding organomercury(II) compounds.

We have been challenging the development of new cycloaurations in recent years and have succeeded in the cycloauration of 2-benzoylpyridine.[6] As an extension of this work, we wish to report here the cycloauration of 2-anilino-, 2-phenoxy- and 2-(phenylsulfanyl)-pyridine by tetrachloroaurate ion and the X-ray crystallographic analysis of the resulting six-membered cycloaurated complexes. While the present work concerning the cycloauration of 2-anilinopyridine was nearly established, Nonoyama *et al.*[12] reported isolation of the cycloaurated complexes [$AuCl_2$(C–N)] derived from 2-anilino-, 2-(4-toluidino)- and 2-(*N*-methylanilino)-pyridine.

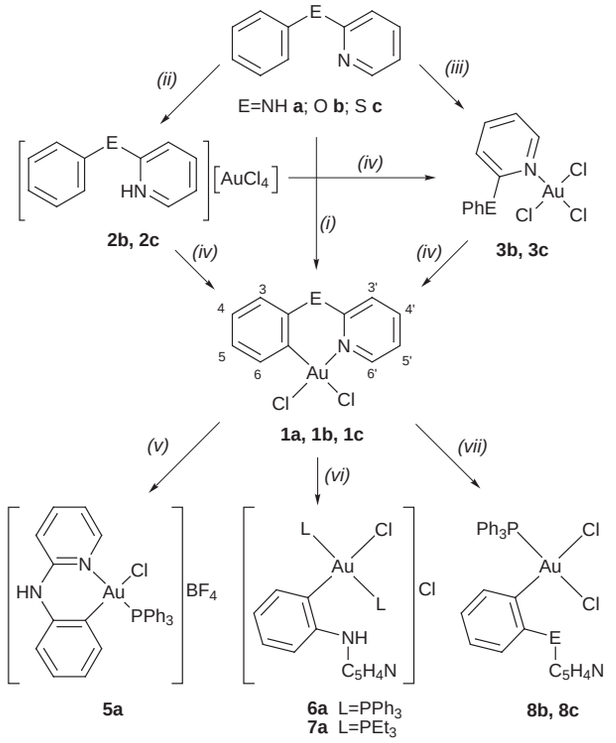
Results and discussion

The method of preparation of the six-membered cycloaurated complexes derived from 2-anilino- (Hpap), 2-phenoxy- (Hpop) and 2-(phenylsulfanyl)-pyridine (Hptp) is shown in Scheme 1. Assignment of the ^{1}H NMR spectra was performed with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY) and the data are summarized in Table 1.

Reactions of the 2-substituted pyridines, Hpap, Hpop and Hptp, with $[AuCl_4]^-$, resulting in the formation of salts, adducts and six-membered cycloaurated complexes

2-Anilinopyridine reacted at room temperature in ethanol with an equimolar amount of $H[AuCl_4]\cdot 4H_2O$ or $Na[AuCl_4]\cdot 2H_2O$ to give directly the six-membered cycloaurated complex [$AuCl_2$(pap-C^1, N)] **1a** [pap = 2-(2-pyridylamino)phenyl] in 27 or 62% yield, respectively. It should be noted that the cycloauration proceeds under very mild conditions at room temperature, while Nonoyama *et al.*[12] reported previously that **1a** was obtained only when an aqueous mixture containing equimolar amounts of Hpap and $Na[AuCl_4]\cdot 2H_2O$ was heated under reflux. It was found that the yields of **1a** depend upon the molar ratio between Hpap and $[AuCl_4]^-$, and the highest yields, 88 and 93%, were obtained when the ratio was 3 : 1 for $H[AuCl_4]\cdot 4H_2O$ and 2 : 1 for $Na[AuCl_4]\cdot 2H_2O$, respectively. These facts indicated that an excess of Hpap accelerates the cycloauration probably by trapping hydrogen chloride generated during the course of the reaction.

On the contrary, in ethanol 2-phenoxypyridine and 2-(phenylsulfanyl)pyridine did not cyclometallate by $H[AuCl_4]\cdot 4H_2O$ at room temperature and even at refluxing temperature,



Scheme 1 (*i*) $H[AuCl_4]\cdot 4H_2O$ or $Na[AuCl_4]\cdot 2H_2O$; (*ii*) $H[AuCl_4]\cdot 4H_2O$ in ethanol; (*iii*) $Na[AuCl_4]\cdot 2H_2O$ in CH_3CN–water (1 : 5); (*iv*) CH_3CN–water (1 : 5); (*v*) PPh_3, $NaBF_4$; (*vi*) $2PPh_3$ or $2PEt_3$; (*vii*) PPh_3.

only producing the tetrachloroaurate salts, $[H_2pop][AuCl_4]$ **2b** and $[H_2ptp][AuCl_4]$ **2c**, respectively. Interestingly, in an acetonitrile–water (1 : 5) mixed solvent the same reaction carried out at room temperature afforded the adducts $[AuCl_3(Hpop)]$ **3b** and $[AuCl_3(Hptp)]$ **3c**. It was also found that the salts could be converted into the corresponding adducts almost quantitatively at room temperature in acetonitrile–water (1 : 5). Although Nonoyama *et al.*[12] demonstrated that both 2-(*p*-tolyloxy)- and 2-(*p*-tolylsulfanyl)-pyridine do not cyclometallate, novel six-membered cycloaurated complexes $[AuCl_2(pop\text{-}C^1, N)]$ **1b** [pop = 2-(2-pyridyloxy)phenyl] and $[AuCl_2(ptp\text{-}C^1, N)]$ **1c** [ptp = 2-(2-pyridylsulfanyl)phenyl] could be obtained in about 70 and 20% yields respectively by heating the salts or the adducts at 105 °C in acetonitrile–water (1 : 5). It seems reasonable that the cycloauration from the salts proceeds *via* the formation of the adducts. Moreover, it was also found that cycloaurations of Hpop and Hptp by $H[AuCl_4]\cdot 4H_2O$ occur in refluxing alcohol (ethanol or propan-2-ol) in the presence of water. In addition to this fact, the result that the salts and the adducts did not produce the cycloaurated complexes by refluxing in water-free acetonitrile clearly showed the necessity of water for the cycloauration of Hpop and Hptp. However, the role of water is not clear at the moment. It is also noted that a yellow complex **4c** was always obtained in the course of the isolating procedures for **1c**. The yield of **4c** was about two thirds by weight of that of **1c**. However, in spite of the simple ^{1}H NMR and far-IR spectra (see Experimental section), the structure could not be assigned.

The far-IR spectra of the cycloaurated complexes **1a**, **1b** and **1c** showed two bands characteristic of ν(Au–Cl) frequencies *trans* to pyridyl nitrogen atom [356 (**1a**),[12] 361 (**1b**) and 360 (**1c**)] and phenylene carbon atom [284 (**1a**),[12] 303 (**1b**) and 295 (**1c**)].[11] Each ^{1}H NMR spectrum of **1a**, **1b** and **1c** exhibited only eight well separated aromatic protons due to the cycloaurated moiety, and a significant feature of all is the lower field shifts of $\delta(H^{6'})$ (numbering scheme in Scheme 1) compared with those of the 'free' ligands [Hpap (δ 8.14), Hpop (8.15) and Hptp (8.40)], the salts (**2b** and **2c**) and the adducts (**3b** and **3c**). Such lower field shifts of $\delta(H^{6'})$ have been reported for other cycloaurated complexes containing pyridine ligands[2,5–7] and usually observed when a chlorine is in the proximity of the pyridine ring.[13]

Reactivity of the cycloaurated complexes 1a, 1b and 1c towards triphenylphosphine

Complex **1a** reacted with an equimolar amount of PPh_3 in the presence of $NaBF_4$ to give a cationic complex **5a** (Λ_M 169 S cm^2 mol^{-1} in acetone). The IR spectrum exhibited a strong band due to BF_4^- at 1060 cm^{-1} and only one band at 313 cm^{-1} assignable to the ν(Au–Cl) frequency *trans* to the phenylene group.[11] Moreover, in the ^{1}H NMR spectrum the $H^{6'}$ proton in the pyridine moiety resonated at δ 8.79 which is essentially the same chemical shift as that of **1a** (δ 8.82), indicating that the six-membered pap–Au ring remains unchanged. On the basis of these data and elemental analysis **5a** was assigned as a cationic four-co-ordinate complex $[AuCl(pap\text{-}C^1, N)(PPh_3)]BF_4$. The similar complex $[AuCl(pap\text{-}C^1, N)\{P(C_6H_4CH_3\text{-}4)_3\}]Cl$ has been prepared by Nonoyama *et al.*[12] On the other hand, when a two-fold excess of PPh_3 was treated with **1a** another cationic complex $[AuCl(pap\text{-}C^1)(PPh_3)_2]Cl$ **6a** (Λ_M 123 S cm^2 mol^{-1} in MeOH) was obtained. A ν(Au–Cl) band at 295 cm^{-1} in the far-IR spectrum was characteristic of a frequency *trans* to carbon, supporting the presence of a Au–C bond. The $H^{6'}$ proton resonance observed significantly upfield (δ 8.20) compared to δ 8.82 for **1a** and δ 8.79 for **5a** confirmed that the second incoming PPh_3 cleaved the C–N chelate by dissociating the pyridine–nitrogen co-ordination. Such an upfield shift of $\delta(H^{6'})$ caused by C–N bond cleavage was also observed for cycloaurated complexes of 2-benzoylpyridine.[6] A triethylphosphine analogue $[AuCl(pap\text{-}C^1)(PEt_3)_2]Cl$ **7a** was also prepared for the X-ray diffraction study (see below).

In contrast to the C–N chelate in complex **1a**, those in the cycloaurated complexes **1b** and **1c** were easily cleaved by only one equimolar amount of PPh_3 giving neutral complexes $[AuCl_2(pop\text{-}C^1)(PPh_3)]$ **8b** (Λ_M 1.4 S cm^2 mol^{-1} in acetone) and $[AuCl_2(ptp\text{-}C^1)(PPh_3)]$ **8c** (Λ_M 7.3 S cm^2 mol^{-1} in acetone), respectively. Two ν(Au–Cl) frequencies of **8b** [301 and 325 cm^{-1}] and **8c** [301 and 316 cm^{-1}] lacked the characteristic bands due to chlorine *trans* to pyridine nitrogen.[11] The $H^{6'}$ protons of **8b** and **8c** appeared significantly upfield δ 7.99 and 8.30, respectively, compared with those for **1b** (δ 9.06) and for **1c** (δ 9.17). Such different reactivity towards PPh_3 of the three cycloaurated complexes **1a**, **1b** and **1c** is probably associated with the stability of the Au–N bonds judging from the basicity of the nitrogen donors in the pyridyl moiety [pK_a values:[14] 2-$MeNHC_5H_4N$ (7.30), 2-$MeOC_5H_4N$ (3.55) and 2-$MeSC_5H_4N$ (4.36)].

Crystal structures of complexes 1b, 1c, 5a and 7a

The structures of complexes **1b**, **1c**, **5a** and **7a** were established by X-ray diffraction and ORTEP[15] views of the molecules are shown in Figs. 1–4. Selected bond distances and angles are summarized in Tables 2–5. In complexes **1b**, **1c** and **5a** the gold atoms have essentially square-planar $AuCNCl_2$ and AuCNClP co-ordination with the mean deviation from the best planes of 0.017, 0.017, 0.019 Å, respectively, whereas in **7a** the gold atom displays a square-planar $AuCClP_2$ co-ordination with a very slight pyramidal distortion with deviations from the best plane of −0.089, +0.033 and +0.038 Å at Au, Cl(1) and C(1), respectively. The Au–C, Au–N, Au–Cl and Au–P bond distances are very similar to those reported for other gold(III) complexes.[3,5,7,10,11,16]

In complexes of **1b**, **1c** and **5a** the pop–Au, ptp–Au and pap–Au six-membered auracycles have boat conformations, with atoms N, C(1), C(6) and C(8) essentially coplanar [mean deviations from their best planes of 0.012, 0.020 0.009 Å, respectively]. These best planes form dihedral angles with planes C(6)–O–C(7) and N–Au–C(1) of 47.2 and 34.8° for **1b**, with planes C(6)–S–C(7) and N–Au–C(1) of 42.5 and 43.4° for **1c**

Table 1 Proton NMR spectral data of the gold(III) complexes[a]

Complex	2-Substituted pyridine ligand[b]				Phosphine
	$H^{6'}$	Other protons			
1a [$AuCl_2$(pap-C^1, N)]	8.82 (1 H, d)[c]	7.02 (1 H, t, H^5)[d] 7.40 (1 H, d, $H^{3'}$)[d] 10.69 (1 H, s, NH)	7.1 (2 H, m, H^3, $H^{5'}$) 7.56 (1 H, d, H^6)[d]	7.26 (1 H, t, H^4)[d] 7.97 (1 H, t, $H^{4'}$)[d]	—
1b [$AuCl_2$(pop-C^1, N)]	9.06 (1 H, d)[c]	7.23 (1 H, t, H^5)[d] 7.69 (1 H, t, $H^{5'}$)[e]	7.35 (2 H, m, H^3, H^4) 7.86 (1 H, d, $H^{3'}$)[e]	7.59 (1 H, d, H^6)[e] 8.43 (1 H, t, $H^{4'}$)[e]	—
1c [$AuCl_2$(ptp-C^1, N)]	9.17 (1 H, d)[f]	7.25 (2 H, m, H^4, H^5) 7.78 (1 H, dt, $H^{5'}$)[g,h]	7.45 (1 H, d, H^3) 8.25 (2 H, m, $H^{3'}$, $H^{4'}$)[g]	7.58 (1 H, d, H^6)[c]	—
2b [H_2pop][$AuCl_4$]	8.15 (1 H, d)[i]	7.02 (1 H, d, $H^{3'}$)[e] 7.4 (2 H, m, Ph)	7.15 (3 H, m, Ph) 7.85 (1 H, t, $H^{4'}$)[e]	7.21 (1 H, dt, $H^{5'}$)[e,h]	—
2c [H_2ptp][$AuCl_4$]	8.41 (1 H, d)[i]	6.95 (1 H, d, $H^{3'}$)[e] 7.6 (2 H, m, Ph)[d]	7.16 (1 H, dt, $H^{5'}$)[h,i] 7.66 (1 H, dt, $H^{4'}$)[e,h]	7.5 (3 H, m, Ph)	—
3b [$AuCl_3$(Hpop)]	8.15 (1 H, dd)[h,i]	7.02 (1 H, d, $H^{3'}$)[d] 7.4 (2 H, m, Ph)	7.1 (3 H, m, Ph) 7.86 (1 H, dt, $H^{4'}$)[d,h]	7.21 (1 H, dt, $H^{5'}$)[d,h]	—
3c [$AuCl_3$(Hptp)]	8.42 (1 H, dd)[h,i]	6.97 (1 H, d, $H^{3'}$)[d] 7.6 (2 H, m, Ph)	7.19 (1 H, dt, $H^{5'}$)[d,h] 7.66 (1 H, dt, $H^{4'}$)[d,h]	7.5 (3 H, m, Ph)	—
5a [AuCl(pap-C^1, N)(PPh_3)]-BF_4	8.79 (1 H, d)[c]	6.22 (1 H, t, H^4)[e] 7.12 (1 H, d, H^6)[e] 7.99 (1 H, t, $H^{4'}$)[e]	6.71 (1 H, d, H^3)[e] 7.19 (1 H, t, $H^{5'}$)[e] 10.55 (1 H, s, NH)	6.99 (1 H, t, H^5)[e] 7.46 (1 H, d, $H^{3'}$)[e]	7.5–7.85 (15 H, m)
6a [AuCl(pap-C^1)(PPh_3)$_2$]Cl	8.20 (1 H, br)	6.12 (1 H, t, H^4)[e] 6.95 (1 H, t, $H^{5'}$)[d] 7.76 (1 H, t, $H^{4'}$)[d]	6.68 (1 H, d, H^3)[e] 7.12 (1 H, d, H^6)[e] 10.13 (1 H, s, NH)	6.86 (1 H, t, H^5)[e] 7.31 (1 H, d, $H^{3'}$)[d]	7.45–7.55 (30 H, m)
7a [AuCl(pap-C^1)(PEt_3)$_2$]Cl	8.08 (1 H, dd)[h,i]	6.85 (1 H, t, $H^{5'}$)[d] 7.23 (1 H, t, H^4)[e] 7.65 (1 H, d, $H^{4'}$)[d]	6.92 (1 H, t, H^5)[e] 7.36 (1 H, d, H^6)[e] 9.13 (1 H, s, NH)	7.06 (1 H, d, $H^{3'}$)[d] 7.48 (1 H, d, H^3)[e]	
8b [$AuCl_2$(pop-C^1)(PPh_3)]	7.99 (1 H, d)[i]	6.57 (1 H, dd, H^3)[d,h] 6.90 (1 H, t, H^4)[d] 7.81 (1 H, t, $H^{4'}$)[d]	6.63 (1 H, t, H^5)[d] 7.06 (1 H, t, $H^{5'}$)[d]	6.82 (1 H, d, $H^{3'}$)[d] 7.17 (1 H, d, H^6)[d]	7.4–7.7 (15 H, m)
8c [$AuCl_2$(ptp-C^1)(PPh_3)]	8.30 (1 H, dd)[h,j]	6.9 (2 H, m, H^5, $H^{3'}$) 7.17 (1 H, d, H^6)[e]	6.99 (1 H, dt, H^4)[e,h] 7.45–7.65 (1 H, $H^{4'}$)[j]	7.1 (2 H, m, H^3, $H^{5'}$)	7.45–7.65 (15 H, m)[j]

[a] Measured in DMSO-d_6 at 270 MHz and at 23 °C; δ in ppm with respect to $SiMe_4$; s = singlet, d = doublet, t = triplet, br = broad, m = multiplet. [b] For numbering see Scheme 1. [c] ^3J(HH) = 6.4 Hz. [d] ^3J(HH) = 7.5 Hz. [e] ^3J(HH) = 7.8 Hz. [f] ^3J(HH) = 5.9 Hz. [g] ^3J(HH) = 6.8 Hz. [h] ^4J(HH) = 1.0 Hz. [i] ^3J(HH) = 4.9 Hz. [j] Overlapping signals.

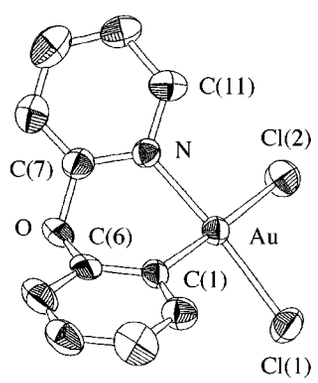


Fig. 1 An ORTEP view of complex [$AuCl_2$(pop-C^1, N)] **1b**. Hydrogen atoms are omitted for clarity.

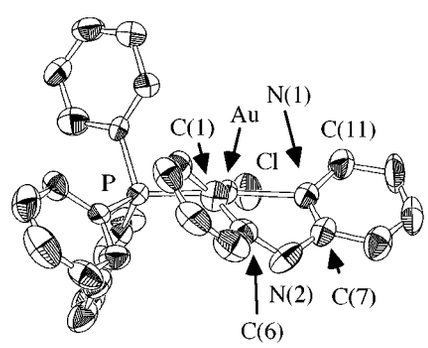


Fig. 3 An ORTEP view of complex [AuCl(pap-C^1, N)(PPh_3)]BF_4 **5a**. Hydrogen atoms and tetrafluoroborate anion are omitted for clarity.

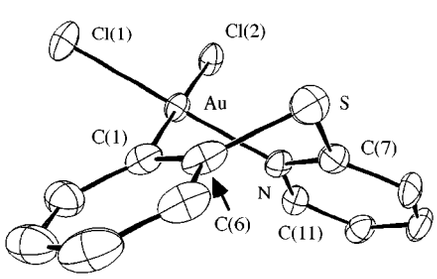


Fig. 2 An ORTEP view of complex [$AuCl_2$(ptp-C^1, N)] **1c**. Hydrogen atoms are omitted for clarity.

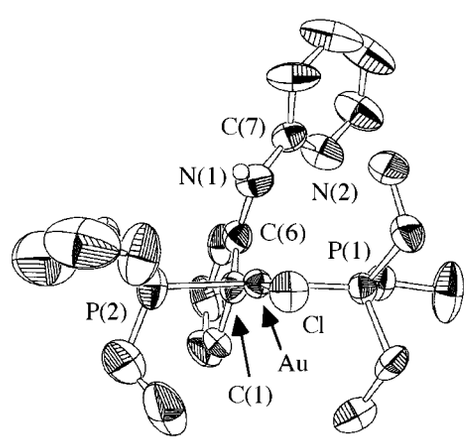


Fig. 4 An ORTEP view of complex [AuCl(pap-C^1)(PEt_3)$_2$]Cl **7a**. Hydrogen atoms and chloride anion are omitted for clarity.

and with planes C(6)–N(2)–C(7) and N(1)–Au–C(1) of 35.9 and 43.2° for **5a**. The dihedral angles between benzene and pyridine rings are 130.0 (**1b**), 118.8 (**1c**) and 133.1° (**5a**). The bite angles of the cycloaurated ligands are 86.6 (**1b**), 88.3 (**1c**) and 85.2° (**5a**), whose values are wider than those in five-

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1b**

Au–C(1)	2.03(2)	Au–N	2.02(1)
Au–Cl(1)	2.275(4)	Au–Cl(2)	2.369(5)
C(1)–C(6)	1.37(2)	C(6)–O	1.41(2)
C(7)–O	1.41(2)	C(7)–N	1.35(2)
C(1)–Au–N	86.6(6)	C(1)–Au–Cl(1)	89.5(4)
C(1)–Au–Cl(2)	177.7(4)	N–Au–Cl(2)	91.7(4)
N–Au–Cl(1)	175.2(3)	Cl(1)–Au–Cl(2)	92.1(2)

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **1c**

Au–C(1)	2.04(2)	Au–N	2.07(1)
Au–Cl(1)	2.277(4)	Au–Cl(2)	2.384(4)
C(1)–C(6)	1.41(3)	C(6)–S	1.77(2)
C(7)–S	1.76(2)	C(7)–N	1.36(2)
C(1)–Au–N	88.3(6)	C(1)–Au–Cl(1)	89.6(5)
C(1)–Au–Cl(2)	178.4(5)	N–Au–Cl(2)	90.2(4)
N–Au–Cl(1)	176.8(5)	Cl(1)–Au–Cl(2)	91.9(1)

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **5a**

Au–C(1)	2.06(1)	Au–N(1)	2.09(1)
Au–Cl	2.347(4)	Au–P	2.319(3)
C(1)–C(6)	1.37(2)	C(6)–N(2)	1.42(2)
C(7)–N(2)	1.40(2)	C(7)–N(1)	1.33(2)
C(1)–Au–N(1)	85.2(5)	C(1)–Au–P	94.5(4)
C(1)–Au–Cl	174.9(4)	N–Au–Cl	90.3(3)
N–Au–P	176.5(3)	Cl(1)–Au–P	89.8(1)

Table 5 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **7a**

Au–C(1)	2.039(8)	Au–P(1)	2.365(3)
Au–P(2)	2.361(3)	Au–Cl	2.371(3)
C(1)–C(6)	1.40(1)	C(6)–N(2)	1.40(1)
C(7)–N(2)	1.37(1)	C(7)–N(1)	1.32(1)
C(1)–Au–P(1)	89.9(2)	C(1)–Au–P(2)	88.9(3)
C(1)–Au–Cl	173.1(3)	P(1)–Au–Cl	87.45(9)
P(1)–Au–P(2)	175.2(1)	Cl–Au–P(2)	93.2(1)

membered auracycles derived from *N*,*N*-dimethylbenzylamine [82.2(4)°],[17] 4,4-dimethyl-2-phenyl-1,3-oxazoline [81.7(3)°],[10] 4-butyl-*N*-(3,4,5-trimethoxybenzylidene)aniline [81.41(14)°][11] and 4,4′-dimethylazobenzene [80.1(2)°][18] and are comparable to the values in the six-membered auracycles [AuCl($C_6H_4CH_2C_5H_4N$-C^1, N)(PPh_3)]BF_4 [85.8(4)°],[6] [$AuCl_2$($C_6H_4CMe_2C_5H_4N$-C^1, N)] [85.7(1)°],[7] [$AuCl_2$($C_6H_4COC_5H_4N$-C^1, N)] [89.5(3)°][6] and [$AuCl_2$(pap-C^1, N)] [87.3(9)°].[12] The pap–Au ring structure in **5a** was quite similar to that of [$AuCl_2$(pap-C^1, N)].[12] In complexes **1b** and **1c** the Au–Cl(2) bond [2.369(5) (**1b**) and 2.384(4) Å (**1c**)] is longer than Au–Cl(1) [2.275(4) (**1b**) and 2.277(4) Å (**1c**)] owing to the greater *trans* influence of the aryl carbon atom than the nitrogen atom.

Concerning the structure of complex **7a**, as expected from spectroscopic data it was confirmed that two PEt_3 ligands are located *trans* to each other and the 2-(2-pyridylamino)phenyl ligand is co-ordinated to Au only through the C(1) atom, forming a neutral complex. The phenyl ring in the 2-(2-pyridylamino)phenyl moiety is located nearly perpendicular to the gold(III) square plane (dihedral angle between two planes is 78.8°). There are no gold–nitrogen bonding interactions [N(1), 3.218(8); N(2), 5.109(9) Å], excluding a five-co-ordinate gold(III) configuration.

Experimental

General

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, ^{1}H NMR spectra on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. Conductivity measurements were carried out at 25 °C on a Toa Electronics CM-20E conductometer. 2-Phenoxypyridine[19] and 2-(phenylsulfanyl)pyridine[20] were prepared according to the literature. Other reagents were obtained commercially and used without purification.

Syntheses

[$AuCl_2$(pap-C^1, N)] 1a. An ethanol (5 cm^3) solution of 2-anilinopyridine (0.128 g, 0.752 mmol) was added to a solution of H[$AuCl_4$]·4H_2O (0.104 g, 0.251 mmol) in the same solvent (5 cm^3) and the resulting solution stirred at room temperature. After 15 h, the yellow precipitates obtained were filtered off and washed with diethyl ether to give complex **1a** (0.096 g, 88%), mp 253 °C (decomp.) (Found: C, 30.1; H, 2.1; N, 6.35. $C_{11}H_9AuCl_2N_2$ requires C, 30.25; H, 2.1; N, 6.4%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 356, 284 (Au–Cl).

Complex **1a** was also prepared in a similar way using Na[$AuCl_4$]·2H_2O (0.100 g, 0.252 mmol) and 2-anilinopyridine (0.091 g, 0.535 mmol) (yield of **1a**: 0.107 g, 93%).

[$AuCl_2$(pop-C^1, N)] 1b. *Method (a).* An ethanol solution (5 cm^3) of 2-phenoxypyridine (0.045 g, 0.264 mmol) was added to a solution of H[$AuCl_4$]·4H_2O (0.102 g, 0.248 mmol) in water (25 cm^3), whereupon yellow precipitates appeared. When the resulting suspension was heated at 105 °C for 14 h the precipitates turned to white. They were collected and recrystallized from dichloromethane and hexane to give complex **1b** (0.077 g, 71%) as white microcrystals, mp 240 °C (decomp.) (Found: C, 30.15; H, 1.85; N, 3.15. $C_{11}H_8AuCl_2NO$ requires C, 30.15; H, 1.85; N, 3.2%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 361, 303 (Au–Cl). Complex **1b** was also prepared similarly in 81% yield in propan-2-ol–water (1 : 5).

Method (b). An acetonitrile–water suspension (1 : 5, 24 cm^3) containing the salt [H_2pop][$AuCl_4$] **2b** (0.199 g, 0.389 mmol) was heated at 105 °C for 40 h. The resulting precipitates were collected and extracted with hot acetone (20 cm^3). The extract was concentrated to give white microcrystals of complex **1b** (yield 0.112 g, 66%).

Method (c). A yellow suspension of [$AuCl_3$(Hpop)] **3b** (0.077 g, 0.163 mmol) in acetonitrile–water (1 : 5, 24 cm^3) was heated at 105 °C for 18 h. The resulting white precipitates were collected and recrystallized from dichloromethane and hexane to give complex **1b** (0.055 g, 78%).

[$AuCl_2$(ptp-C^1, N)] 1c. *Method (a).* An ethanol solution (5 cm^3) of 2-(phenylsulfanyl)pyridine (0.048 g, 0.256 mmol) was added to a solution of H[$AuCl_4$]·4H_2O (0.102 g, 0.248 mmol) in water (25 cm^3), and the resulting mixture heated at 105 °C for 14 h. The resulting yellow suspension was filtered while hot. From the filtrate yellow microcrystals of complex **4c** (0.010 g) were precipitated on standing at room temperature. The filter cake was extracted with dichloromethane and the extract concentrated and diluted with hexane to give **1c** (0.014 g, 12%). Complex **4c** (Found: C, 25.2; H, 1.55; N, 2.65%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 357 (Au–Cl); δ_H(DMSO-d_6) 7.95 (2 H), 8.16 [1 H, t, $^3J_{HH}$ = 6.8], 8.53 (2 H, m), 8.91 (2 H, m), 10.10 [1 H, d, $^3J_{HH}$ = 6.4 Hz]. Complex **1c**: mp 239 °C (decomp.) (Found: C, 29.1; H, 1.8; N, 3.1. $C_{11}H_8AuCl_2NS$ requires C, 29.0; H, 1.85; N, 3.05%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 360, 295 (Au–Cl). Complex **1c** was also prepared similarly in 13% yield in propan-2-ol–water (1 : 5).

Method (b). An acetonitrile–water suspension (1 : 5, 30 cm^3)

containing the salt $[H_2ptp][AuCl_4]$ **2c** (0.200 g, 0.379 mmol) was heated at 105 °C for 20 h. The resulting mixture was filtered while hot. From the filtrate yellow microcrystals of complex **4c** (0.023 g) were precipitated, while from the filter cake after washing with hot water using a Soxhlet extraction apparatus yellow microcrystals of **1c** were obtained (0.035 g, 20%).

Method (c). An acetonitrile–water suspension (1 : 5, 30 cm^3) containing the adduct $[AuCl_3(Hptp)]$ **3c** (0.201 g, 0.409 mmol) was heated at 105 °C for 20 h and then the mixture was filtered while hot. From the filtrate yellow microcrystals of complex **4c** (0.022 g) were obtained. The filter cake was extracted with dichloromethane and the extract concentrated and diluted with hexane to give **1c** (0.034 g, 18%).

$[H_2pop][AuCl_4]$ 2b. An ethanol (5 cm^3) solution of 2-phenoxypyridine (0.171 g, 0.999 mmol) was added to a solution of $H[AuCl_4]\cdot 4H_2O$ (0.203 g, 0.493 mmol) in the same solvent (5 cm^3) and the resulting solution stirred at room temperature for 1 d. The resulting mixture was evaporated to dryness and the residue extracted with dichloromethane. The extract was concentrated and diluted with hexane to give yellow microcrystals of complex **2b** (0.233 g, 92%), mp 108 °C (decomp.) (Found: C, 26.05; H, 1.9; N, 2.7. $C_{11}H_{10}AuCl_4NO$ requires C, 25.85; H, 1.95; N, 2.75%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 360 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 157 S cm^2 mol^{-1}.

$[H_2ptp][AuCl_4]$ 2c. Complex **2c** was obtained as orange microcrystals in a similar way to that described above by the reaction between 2-(phenylsulfanyl)pyridine (0.185 g, 0.990 mmol) and $H[AuCl_4]\cdot 4H_2O$ (0.196 g, 0.475 mmol) in ethanol (10 cm^3), yield 0.182 g (73%), mp 149 °C (decomp.) (Found: C, 25.3; H, 1.95; N, 2.7. $C_{11}H_{10}AuCl_4NS$ requires C, 25.05; H, 1.9; N, 2.65%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 360 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 166 S cm^2 mol^{-1}.

$[AuCl_3(Hpop)]$ 3b. *Method (a).* An acetonitrile (5 cm^3) solution of 2-phenoxypyridine (0.023 g, 0.134 mmol) was added to a solution of $Na[AuCl_4]\cdot 2H_2O$ (0.051 g, 0.127 mmol) in water (25 cm^3), whereupon bright yellow microcrystals were precipitated. After the resulting suspension was stirred for 15 h at room temperature, the crystals were filtered off to give complex **3b** (0.060 g, 74%), mp 167 °C (decomp.) (Found: C, 27.95; H, 1.95; N, 2.95. $C_{11}H_9AuCl_3NO$ requires C, 27.85; H, 1.9; N, 2.95%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 365 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 1.3 S cm^2 mol^{-1}.

Method (b). Water (25 cm^3) was added to an acetonitrile solution of complex **2b** (0.125 g, 0.245 mmol) and the resulting suspension stirred for 16 h at 25 °C. Yellow precipitates were collected and washed with water to give **3b** (0.106 g, 91%).

$[AuCl_3(Hptp)]$ 3c. *Method (a).* Complex **3c** was obtained as bright orange microcrystals in a similar way to that described above by the reaction between 2-(phenylsulfanyl)pyridine (0.075 g, 0.402 mmol) and $Na[AuCl_4]\cdot 2H_2O$ (0.151 g, 0.380 mmol) in acetonitrile–water (1 : 5, 30 cm^3, yield 0.145 g (78%), mp 168 °C (decomp.) (Found: C, 27.0; H, 1.9; N, 2.85. $C_{11}H_9AuCl_3NS$ requires C, 26.95; H, 1.85; N, 2.85%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 362 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 0.8 S cm^2 mol^{-1}.

Method (b). Water (25 cm^3) was added to an acetonitrile solution of complex **2c** (0.103 g, 0.196 mmol) and the resulting suspension stirred for 13 h at 25 °C. Yellow precipitates were collected and washed with water to give **3c** (0.106 g, 92%).

$[AuCl(pap\text{-}C^1, N)(PPh_3)]BF_4$ 5a. Triphenylphosphine (0.063 g, 0.241 mmol) and then sodium tetrafluoroborate (0.028 g, 0.255 mmol) were added to an acetone solution (10 cm^3) of complex **1a** (0.100 g, 0.230 mmol). The resulting solution was stirred for 15 h and then the volatile materials were evaporated *in vacuo*. The residue was extracted with dichloromethane and the extract concentrated and diluted with diethyl ether to yield yellow microcrystals of **5a** (0.139 g, 80%), mp 153 °C (decomp.) (Found: C, 46.7; H, 3.35; N, 3.75. $C_{29}H_{24}AuBClF_4N_2P$ requires C, 46.4; H, 3.2; N, 3.65%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1060 (BF_4^-), 313 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 169 S cm^2 mol^{-1}.

$[AuCl(pap\text{-}C^1)(PPh_3)_2]Cl$ 6a. Triphenylphosphine (0.288 g, 1.10 mmol) was added to an acetone solution (10 cm^3) of complex **1a** (0.201 g, 0.460 mmol). After the mixture was stirred at room temperature for 1 d the volatile materials were evaporated *in vacuo*. The residue was extracted with dichloromethane and the extract concentrated and diluted with diethyl ether to afford yellowish white microcrystals of **6a**·H_2O (0.287 g, 90%), mp 131 °C (Found: C, 57.5; H, 4.25; N, 2.85. $C_{47}H_{41}AuCl_2N_2OP_2$ requires C, 57.6; H, 4.2; N, 2.85%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 295 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, MeOH) 123 S cm^2 mol^{-1}.

$[AuCl(pap\text{-}C^1)(PEt_3)_2]Cl$ 7a. Complex **7a** was obtained as beige microcrystals in a similar way to that described above by the reaction between **1a** (0.105 g, 0.239 mmol) and PEt_3 (0.118 g, 1.00 mmol) in acetone (10 cm^3), yield 0.128 g (80%), mp 139 °C (Found: C, 41.15; H, 5.9; N, 4.15. $C_{23}H_{39}AuCl_2N_2P_2$ requires C, 41.0; H, 5.85; N, 4.1%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 300 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 24 S cm^2 mol^{-1}.

$[AuCl_2(pop\text{-}C^1)(PPh_3)]$ 8b. Triphenylphosphine (0.031 g, 0.118 mmol) was added to a dichloromethane solution (10 cm^3) of complex **1b** (0.050 g, 0.114 mmol). The resulting solution was stirred at room temperature for 18 h and then filtered. The filtrate was concentrated and diluted with diethyl ether to give white microcrystals of **8b** (0.068g, 84%), mp 146 °C (Found: C, 49.75; H, 3.45; N, 2.15. $C_{29}H_{23}AuCl_2NOP$ requires C, 49.75; H, 3.3; N, 2.0%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 325, 301 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, MeOH) 1.4 S cm^2 mol^{-1}.

$[AuCl_2(ptp\text{-}C^1)(PPh_3)]$ 8c. Complex **8c** was obtained as white microcrystals in a similar way to that described above by the reaction between **1c** (0.062 g, 0.137 mmol) and PPh_3 (0.038 g, 0.144 mmol), yield 0.084 g (86%), mp 170 °C (Found: C, 48.8; H, 3.2; N, 1.9. $C_{29}H_{23}AuCl_2NPS$ requires C, 48.6; H, 3.25; N, 1.95%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 316, 301 (Au–Cl); $\Lambda_M(1.0 \times 10^{-3}$ mol dm^{-3}, acetone) 7.3 S cm^2 mol^{-1}.

X-Ray crystallography

Suitable crystals of $[AuCl_2(pop\text{-}C^1, N)]$ **1b**, $[AuCl_2(ptp\text{-}C^1, N)]$ **1c**, $[AuCl(pap\text{-}C^1, N)(PPh_3)]BF_4$ **5a** and $[AuCl(pap\text{-}C^1)(PEt_3)_2]Cl$ **7a** were grown from dichloromethane and hexane except for **1b** (dichloromethane and diethyl ether). Details of the crystal data, data collection and refinement are summarized in Table 6. Measurements were made on Rigaku AFC7S (for **1b**, **5a** and **7a**) and Enraf-Nonius CAD4 (for **1c**) diffractometers with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) at 23 °C except for **1c** (20 °C). Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $29.2 < 2\theta < 30.1°$ for **1b**, $20.0 < 2\theta < 30.0°$ for **1c**, $27.0 < 2\theta < 29.23°$ for **5a** and $33.7 < 2\theta < 34.8°$ for **7a**. Intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects and absorption. All the calculations for **1b**, **5a** and **7a** were performed using the TEXSAN software package,[21] whereas those for **1c** were carried out on a VAX station 4000 90A computer using a MO1EN program package.[22] The structures of **1b** and **1c** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms included but not refined. The structure of **5a** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms except for the tetrafluoroborate anion were refined anisotropically. The position of NH was freely

Table 6 Crystallographic data for complexes **1b**, **1c**, **5a** and **7a**

	1b	**1c**	**5a**	**7a**
Formula	$C_{11}H_8AuCl_2NO$	$C_{11}H_8AuCl_2NS$	$C_{29}H_{24}AuBClF_4N_2P$	$C_{23}H_{39}AuCl_2N_2P_2$
M	438.06	454.13	750.72	673.39
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	$Pbca$	$P2_12_12_1$
a/Å	8.22(2)	8.488(3)	20.899(3)	15.181(3)
b/Å	18.15(2)	14.363(3)	18.940(2)	15.873(1)
c/Å	7.76(1)	10.618(4)	14.319(2)	11.535(2)
β/°		103.74(2)		
U/Å^3	1157(2)	1257.3(7)	5667(2)	2779.6(7)
Z	4	4	8	4
D_c/g cm^{-3}	2.513	2.40	1.759	1.609
Crystal dimensions/mm	0.20 × 0.40 × 0.40	0.41 × 0.32 × 0.22	0.35 × 0.20 × 0.30	0.20 × 0.15 × 0.45
μ(Mo-Kα)/cm^{-1}	131.84	122.4	54.08	56.31
No. measured reflections	1577	2301	7169	3596
No. unique observed reflections [$I > 3\sigma(I)$]	1410	1617	3249	2708
R	0.039	0.036	0.046	0.028
R'	0.048	0.045	0.062	0.029

refined but its isotropic thermal parameter was fixed. The other hydrogen atoms were included but not refined. As for the refinement of the tetrafluoroborate anion, the atom B(1) was refined isotropically; F(1), F(2), F(3) and F(4) were treated as an idealized rigid group with a common isotropic atomic displacement parameter because the refinement of individual parameters of those atoms failed. The structure of **7a** was solved by direct methods and expanded using Fourier techniques. All the non-hydrogen atoms were refined anisotropically. The position of NH was freely refined but its isotropic parameters were fixed. The other hydrogen atoms were included but not refined.

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