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# Synthesis, structure and reactivity of a new six-membered cycloaurated complex of 2-benzoylpyridine [AuCl$_2$(pcp-$C^1$,$N$)] [pcp = 2-(2-pyridylcarbonyl)phenyl]. Comparison with the cycloaurated complex derived from 2-benzylpyridine

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A six-membered cycloaurated complex [AuCl$_2$(pcp-$C^1$,$N$)] [pcp = 2-(2-pyridylcarbonyl)phenyl] has been prepared by the reaction between the adduct [AuCl$_3$(Hpcp)] (Hpcp = 2-benzoylpyridine) and AgO$_2$CCF$_3$, and its structure determined by X-ray diffraction. The boat-like conformation of the six-membered pcp–Au ring has been compared to that of the pmp–Au ring in [AuCl(pmp-$C^1$,$N$)(PPh$_3$)]BF$_4$ [pmp = 2-(2-pyridylmethyl)phenyl] the structure of which has also been established by X-ray diffraction. The complex [AuCl$_2$(pcp-$C^1$,$N$)] reacts with PPh$_3$ in a 1 : 1 molar ratio to give a neutral complex [AuCl$_2$(pcp)(PPh$_3$)]. This is further converted into *trans*-[AuCl(pcp)(PPh$_3$)$_2$]BF$_4$ and [Au(pcp-$C^1$,$N$)$_2$]BF$_4$ by treating with PPh$_3$ in the presence of NaBF$_4$ and excess of AgBF$_4$, respectively. This reactivity towards triphenylphosphine has been compared with that of the known cycloaurated complex [AuCl$_2$(pmp-$C^1$,$N$)]. Temperature-dependent $^1$H NMR spectra attributable to inversion of the six-membered pmp–Au ring have been observed and the rates of inversion measured by line shape analysis of the methylene protons in [AuCl(pmp-$C^1$,$N$)(PPh$_3$)]BF$_4$.

In contrast to the rich chemistry of cyclometallation involving Pd$^{II}$ and Pt$^{II}$,[1] examples of cycloaurated complexes are limited. Two types of synthetic methods for cycloaurated compounds have been reported so far. One is by transmetallation from the corresponding organomercury(II) compounds and thereby cycloaurated complexes of azobenzene,[2] *N*,*N*-dimethylbenzylamine,[3,4] 4,4-dimethyl-2-phenyl-1,3-oxazoline,[4] 1-(dimethyl- or methyl-aminomethyl)naphthalene,[4] 1,3-bis(dimethylaminomethyl)benzene[4] and 4-butyl-*N*-(3,4,5-trimethoxybenzylidene)aniline[5] have been prepared. The other is by direct C–H bond activation. Thereby cycloaurated complexes of 2-phenylpyridine,[6] 2-benzylpyridine,[7] 6-benzyl-2,2′-bipyridine derivatives[8] and 6-*tert*-butyl-2,2′-bipyridine[8] have been synthesized on heating the corresponding adducts [AuCl$_3$L], while those of 2,9-diphenyl-1,10-phenanthroline[9] and 4-(4-methoxyphenyl)-6-phenyl-2,2′-bipyridine[10] were obtained by reaction with the [AuCl$_4$]$^-$–Ag$^I$ system.

Concerning the synthesis of six-membered cycloaurated complexes, examples are very rare and limited to benzylpyridine derivatives.[7,8] Here we describe the synthesis and characterization of a new type of six-membered cycloaurated complexes derived from 2-benzoylpyridine. Comparison of the reactivity towards triphenylphosphine between [AuCl$_2$(pcp-$C^1$,$N$)] [pcp = 2-(2-pyridylcarbonyl)phenyl] and previously reported [AuCl$_2$(pmp-$C^1$,$N$)] [pmp = 2-(2-pyridylmethyl)phenyl],[7] and a line shape analysis of the temperature-dependent $^1$H NMR spectra attributable to the inversion of the six-membered pmp–Au ring are also described.

## Results and Discussion

The method of preparation of the complexes and selected $^1$H NMR spectral data are summarized in Scheme 1 and Table 1, respectively.

### Synthesis of [AuCl$_2$(pcp-$C^1$,$N$)] and comparison of the six-membered pcp–Au and pmp–Au ring structures

2-Benzoylpyridine (Hpcp) reacted with H[AuCl$_4$]·4H$_2$O in EtOH to give the adduct [AuCl$_3$(Hpcp)] **1a**. When complex **1a** was refluxed in propionitrile in the presence of silver(I) trifluoroacetate a new six-membered cycloaurated complex of 2-benzoylpyridine, [AuCl$_2$(pcp-$C^1$,$N$)] **2a** [pcp = 2-(2-pyridylcarbonyl)phenyl], was obtained in 12% yield (Scheme 1). It is interesting that no reaction occurred when **1a** was refluxed in acetonitrile or in an acetonitrile–water mixed solvent, while a similar six-membered cycloaurated complex of 2-benzylpyridine, [AuCl$_2$(pmp-$C^1$,$N$)] **2b** [pmp = 2-(2-pyridylmethyl)phenyl], was formed just by heating the adduct [AuCl$_3$(Hpmp)] in an acetonitrile–water mixed solvent.[7] Prolonged heating decreased the recovery of the starting compound **1a** but promoted decomposition of the product **2a**. Other silver(I) salts such as AgBF$_4$ and AgO$_2$CMe did not work well for the formation of **2a**. The $^1$H NMR spectrum of **2a** exhibited only eight and well separated aromatic protons due to the cycloaurated moiety and the spectral assignment was performed with the aid of $^1$H–$^1$H correlation spectroscopy (COSY) (Table 1). In the IR spectrum **2a** showed two bands at 362 and 300 cm$^{-1}$ assignable to ν(Au–Cl) *trans* to a nitrogen-donor ligand and ν(Au–Cl) *trans* to carbon atoms, respectively.[5] On the basis of these results, elemental analysis and its reactivity (see below), **2a** was assigned to a six-membered cycloaurated complex.

The structures of complex **2a** and [AuCl(pmp-$C^1$,$N$)(PPh$_3$)]BF$_4$ **7b** (see below) were established by X-ray diffraction and ORTEP[11] views of the molecules are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are summarized in Tables 2 (for **2a**) and 3 (for **7b**). The co-ordinations

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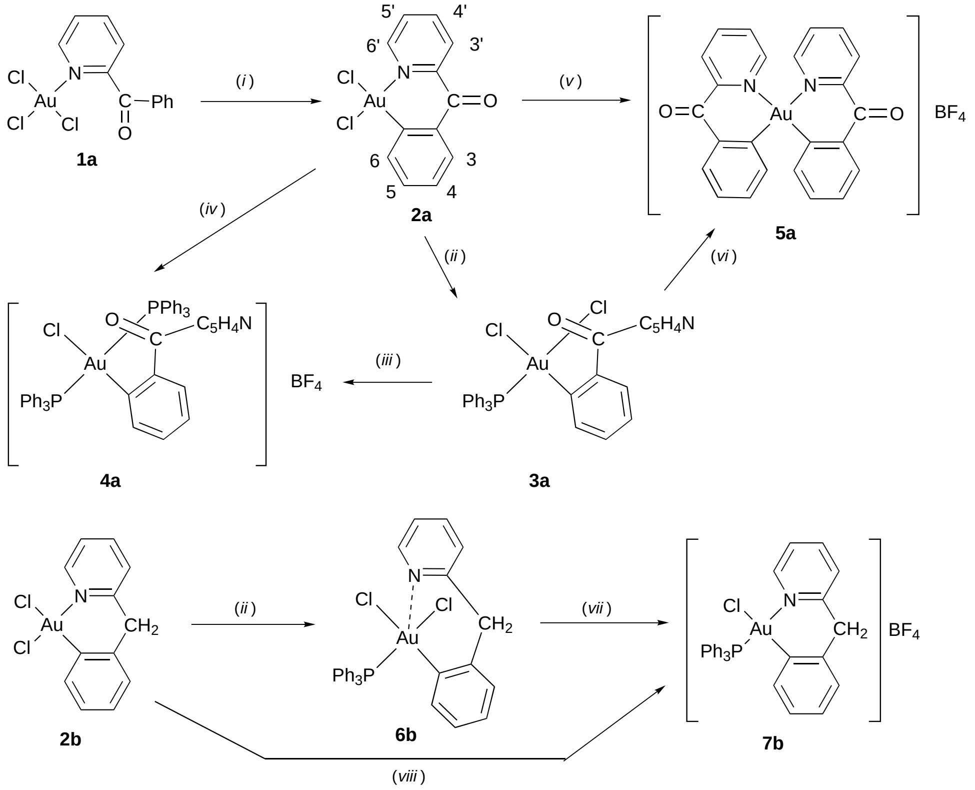
**Table 1** Proton NMR spectra of the new cycloaurated complexes$^{a}$

| | Cycloaurated moiety$^{b}$ | | | | |
|---|---|---|---|---|---|
| Complex | $H^{6'}$ | Other protons | | | Others |
| **2a** [$AuCl_2$(pcp-$C^1$,$N$)] | 9.48 (1 H, d)$^{c}$ | 7.4–7.55 (2 H, m) | 7.65–7.73 (2 H, m) | 8.09 (1 H, dt, $H^{5'}$)$^{d}$ | |
| | | 8.37 (1 H, dd, $H^{3'}$)$^{d}$ | 8.56 (1 H, dt, $H^{4'}$)$^{d}$ | | |
| **3a** [$AuCl_2$(pcp-$C^1$)($PPh_3$)] | 8.67 (1 H, d)$^{c}$ | 7.00 (1 H, dt)$^{d}$ | 7.11 (1 H, t)$^{e}$ | 7.40 (2 H, m) | 7.7–7.45 (15 H, m, $PPh_3$)$^{f}$ |
| | | 7.7–7.45 (1 H, m)$^{f}$ | 7.80 (1 H, d, $H^{3'}$)$^{e}$ | 8.04 (1 H, dt, $H^{4'}$)$^{d}$ | |
| **4a** [AuCl(pcp-$C^1$)($PPh_3$)$_2$]$BF_4$ | 8.55 (1 H, d)$^{c}$ | 6.93 (1 H, t)$^{e}$ | 6.97 (1 H, t)$^{e}$ | 7.31 (1 H, d)$^{e}$ | 7.45–7.7 (30 H, m, $PPh_3$)$^{f}$ |
| | | 7.45–7.7 (3 H, m)$^{f}$ | 7.98 (1 H, t, $H^{4'}$)$^{e}$ | | |
| **5a** [Au(pcp-$C^1$,$N$)$_2$]$BF_4$ | 8.44 (2 H, d)$^{c}$ | 6.83 (2 H, d, $H^{6}$)$^{e}$ | 7.40 (2 H, dt, $H^{5}$)$^{d}$ | 7.50 (2 H, dt, $H^{4}$)$^{d}$ | |
| | | 7.79 (2 H, dd, $H^{3}$)$^{d}$ | 7.91 (2 H, dt, $H^{3'}$)$^{d}$ | 8.29 (2 H, d, $H^{4'}$)$^{e}$ | |
| | | 8.52 (2 H, dt, $H^{5'}$)$^{d}$ | | | |
| **6b** [$AuCl_2$(pmp-$C^1$,$N$)($PPh_3$)] | 9.14 (1 H, d)$^{c}$ | 6.44 (1 H, dt, $H^{5}$)$^{d}$ | 6.74 (1 H, d, $H^{3}$)$^{e}$ | 6.93 (1 H, t, $H^{4}$)$^{e}$ | 4.33 (1 H, d, $CH_2$)$^{g}$ |
| | | 7.17 (1 H, dd, $H^{6}$)$^{d}$ | 7.5–7.9 (16 H, m)$^{f}$ | 7.94 (1 H, d, $H^{3'}$)$^{e}$ | 4.94 (1 H, d, $CH_2$)$^{g}$ |
| | | 8.22 (1 H, dt, $H^{4'}$)$^{d}$ | | | |
| **7b** [AuCl(pmp-$C^1$,$N$)($PPh_3$)]$BF_4$ | 9.17 (d)$^{c}$ | 6.43 (1 H, dt, $H^{5}$)$^{d}$ | 6.72 (1 H, dd, $H^{3}$)$^{d}$ | 6.95 (1 H, t, $H^{4}$)$^{e}$ | 4.34 (1 H, d, $CH_2$)$^{g}$ |
| | | 7.22 (1 H, dd, $H^{6}$)$^{d}$ | 7.5–7.9 (16 H, m)$^{f}$ | 7.99 (1 H, d, $H^{3'}$)$^{e}$ | 5.05 (1 H, d, $CH_2$)$^{g}$ |
| | | 8.26 (1 H, dt, $H^{4'}$)$^{d}$ | | | |

[a] Measured in $(CD_3)_2SO$ 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) = 5.4 Hz. [d] $^3J$(HH) = 7.8, $^4J$(HH) = 1.5 Hz. [e] $^3J$(HH) = 7.8 Hz. [f] Overlapping each other with signals due to $PPh_3$ or cycloaurated moiety. [g] $^2J$(HH) = 15.1 Hz.



**Scheme 1** (*i*) $AgO_2CCF_3$; (*ii*) $PPh_3$; (*iii*) $PPh_3$, $NaBF_4$; (*iv*) 2$PPh_3$, $NaBF_4$; (*v*) $PPh_3$, 3$AgBF_4$; (*vi*) 3$AgBF_4$; (*vii*) $NaBF_4$; (*viii*) $PPh_3$, $AgBF_4$

around the gold atoms of both **2a** and **7b** are essentially planar and the maximum deviations are 0.062 and 0.037 Å of the N atoms from the mean planes composed of Au–Cl(1)–Cl(2)–N–C(1) (for **2a**) and Au–Cl–N–P–C(1) (for **7b**), respectively. In complex **2a** the Au–Cl(1) bond [2.381(2) Å] is longer than Au–Cl(2) [2.276(2) Å] owing to the greater *trans* influence of the aryl carbon atom than the nitrogen atom. The bond angle C(1)–Au–N is 89.5(3)°, which is wider than those in five-membered auracycles derived from *N*,*N*-dimethylbenzylamine [82.2(4)°],[12] 4,4-dimethyl-2-phenyl-1,3-oxazoline [81.7(3)°],[4] 4-butyl-*N*-(3,4,5-trimethoxybenzylidene)aniline [81.41(14)°][5] and 4,4′-dimethylazobenzene [80.1(2)°][13] and is the widest in six-membered auracycles ever reported {**7b**, 85.8(4)°; [$AuCl_2$($C_6H_4CMe_2C_5H_4N$-$C^1$,$N$)], 85.7(1)°[7]}.

Both the pcp–Au and the pmp–Au six-membered auracycles have boat-like conformations, with atoms N, C(1), C(6) and C(8) essentially coplanar [mean deviations from their best planes are 0.024 Å for **2a** and 0.012 Å for **7b**]. In complex **7b** this best plane forms dihedral angles with planes C(6)–C(7)–C(8) and N–Au–C(1) of 46.3 and 42.0°, respectively. On the other hand in complex **2a** corresponding dihedral angles have smaller values of 19.0 and 33.9° for planes C(6)–C(7)–C(8)–O and N–Au–C(1), respectively. Concerning the dihedral angles between the benzene and pyridine rings, the value of 140.5° in **2a** is much wider than that of 114.0° in **7b**. These results demonstrate that the planarity of the pcp–Au ring is higher than that of the pmp–Au ring, which is probably due to the different hybridization of the carbon atom between the benzene

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

| | | | |
|---|---|---|---|
| Au–C(1) | 2.033(7) | Au–N | 2.035(5) |
| Au–Cl(1) | 2.381(2) | Au–Cl(2) | 2.276(2) |
| C(1)–C(6) | 1.395(9) | C(6)–C(7) | 1.486(10) |
| C(7)–O | 1.213(8) | C(7)–C(8) | 1.501(10) |
| C(8)–N | 1.355(8) | | |
| C(1)–Au–N | 89.5(3) | C(1)–Au–Cl(2) | 90.3(2) |
| C(1)–Au–Cl(1) | 177.4(2) | N–Au–Cl(1) | 92.0(2) |
| N–Au–Cl(2) | 176.2(2) | Cl(1)–Au–Cl(2) | 88.29(7) |

**Table 3** Selected bond distances (Å) and angles (°) with e.s.d.s. in parentheses for complex **7b**

| | | | |
|---|---|---|---|
| Au–C(1) | 2.03(1) | Au–N | 2.079(10) |
| Au–Cl | 2.362(3) | Au–P | 2.311(3) |
| C(1)–C(6) | 1.38(2) | C(6)–C(7) | 1.50(2) |
| C(7)–C(8) | 1.47(2) | C(8)–N | 1.33(1) |
| C(1)–Au–N | 85.8(4) | C(1)–Au–P | 94.8(3) |
| C(1)–Au–Cl | 175.2(3) | N–Au–Cl | 89.4(3) |
| N–Au–P | 176.4(3) | Cl–Au–P | 89.9(1) |

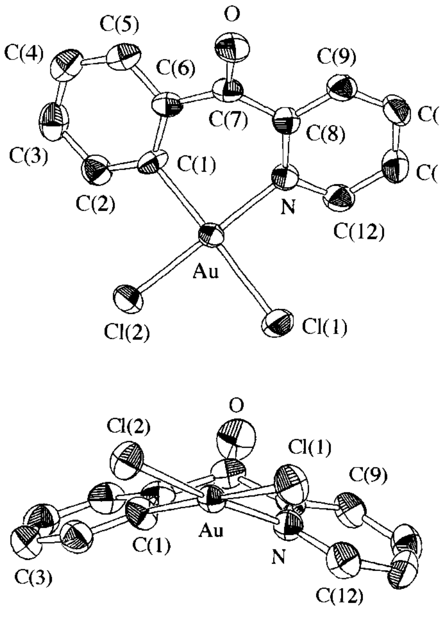


**Fig. 1** An ORTEP view of complex $[AuCl_2(pcp\text{-}C^1,N)]$ **2a**

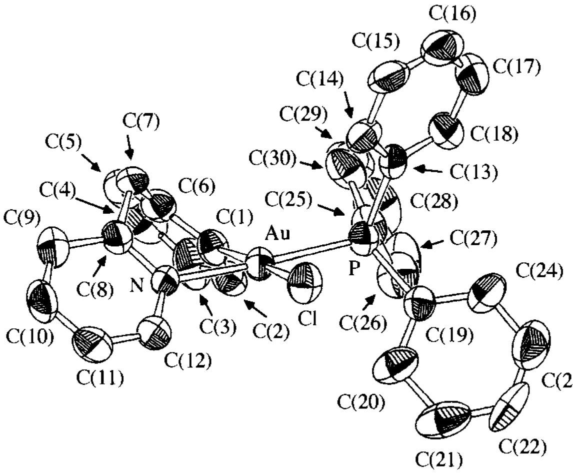


**Fig. 2** An ORTEP view of complex $[AuCl(pmp\text{-}C^1,N)(PPh_3)]BF_4$ **7b**

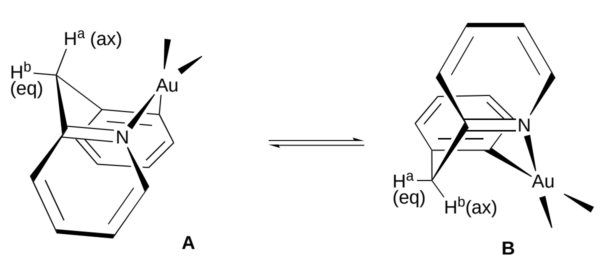
and pyridine rings ($sp^2$ in pcp–Au and $sp^3$ in pmp–Au). Considering the fact that all the atoms constructing 2-benzoylpyridine have $sp^2$ hybridization, it is reasonable to think that the pcp–Au ring has a strong tendency to have a planar conformation. From this standpoint, in the ideal planar six-membered pcp–Au ring the bond angle C(1)–Au–N in **2a** should be 120°. The actual value [89.5(3)°] is ideal for the square-planar configuration, but much smaller for the planar six-membered pcp–Au ring indicating the presence of strain in it.

### Reactivity of $[AuCl_2(pcp\text{-}C^1,N)]$ 2a and $[AuCl_2(pmp\text{-}C^1,N)]$ 2b towards triphenylphosphine

Complex **2a** reacted with an equimolar amount of $PPh_3$ to give a neutral complex **3a** ($\Lambda_M$ 3.9 S cm$^2$ mol$^{-1}$). In the far-IR spectrum of **3a** two bands characteristic of ν(Au–Cl) frequencies *trans* to $PPh_3$ and phenylene were observed at 325 and 301 cm$^{-1}$, respectively.[5] Moreover, the resonance of the $H^{6'}$ proton in the pyridine moiety of **3a** (see Scheme 1) significantly shifted to upfield at δ 8.67 compared to δ 9.48 for **2a**. These data together with elemental analysis clearly showed that $PPh_3$ cleaved the C–N chelate by dissociating the pyridine-nitrogen co-ordination. Concerning the ν(CO) band, this appeared at 1638 cm$^{-1}$ for **3a** which is lower than 1674 cm$^{-1}$ for **2a** and 1669 cm$^{-1}$ for the free 2-benzoylpyridine. So, there may be some possibility that **3a** is a five-co-ordinate complex, but reported five-co-ordinate species of $Au^{III}$, such as $[AuCl_3L]$ (L = 2,2′-biquinolyl),[14] $[AuX_3L]$ [L = 2,9-dimethyl-1,10-phenanthroline or 2-(2-pyridyl)quinoline];[16] X = Cl, Br and $\{Au(2\text{-}Me_2NCH_2\text{-}C_6H_4\text{-}C^1,N)(phen)(PPh_3)[BF_4]_2\}$,[17] usually contain rigid bidentate ligands. Considering that the pcp ligand has more degrees of freedom, **3a** was tentatively assigned to the normal four-co-ordinate complex $[AuCl_2(pcp\text{-}C^1)(PPh_3)]$. Further treatment of $PPh_3$ with **3a** in the presence of $NaBF_4$ gave a cationic complex **4a**. This complex resembled **3a** in IR [ν(CO) 1635 cm$^{-1}$] and $^1H$ NMR ($H^{6'}$, δ 8.55) spectra except for incorporation of 2 molecules of $PPh_3$ confirmed to be mutually *trans* on the basis of the observation of only one signal at δ 35.43 in the $^{31}P\text{-}\{^1H\}$ NMR spectrum. Moreover, the far-IR spectrum exhibited only one ν(Au–Cl) at 317 cm$^{-1}$ and the electric conductivity showed a typical value for a 1:1 electrolyte ($\Lambda_M$ 108 S cm$^2$ mol$^{-1}$ in acetone). Similarly to **3a**, a four-co-ordinate structure, *trans*-$[AuCl(pcp\text{-}C^1)(PPh_3)_2]BF_4$, was tentatively assigned for **4a**. Unfortunately, we have not succeeded in getting crystals suitable for X-ray crystal analysis.

On the other hand, complex **2b** reacted with an equimolar amount of $PPh_3$ to give **6b**. In the $^1H$ NMR spectrum the methylene protons appeared as an AB quartet and the $H^{6'}$ proton in the pyridine moiety resonated at δ 9.14 which is essentially the same chemical shift as that of **2b** (δ 9.17). The data strongly indicated that the six-membered pmp–Au chelate remains unchanged. Concerning the far-IR spectrum, medium and strong bands due to ν(Au–Cl) were observed at 316 and 295 cm$^{-1}$, respectively, suggesting the co-ordination of the two chloride ions. On the basis of these spectroscopic data, **6b** was assigned as a five-co-ordinate complex $[AuCl_2(pmp\text{-}C^1,N)(PPh_3)]$. As for the molar conductivity, a slightly higher value than for a non-electrolyte was obtained (16 S cm$^2$ mol$^{-1}$), which threw doubt on the five-co-ordination, but similar values have been reported for other five-co-ordinate complexes $[AuCl_2(C_6H_4N{=}NPh\text{-}C^1)(phen)]$ ($\Lambda_M$ 17 S cm$^2$ mol$^{-1}$)[18] and $[AuCl(C_4Ph_4)(phen)]$ ($\Lambda_M$ 13 S cm$^2$ mol$^{-1}$).[19] Unlike **4a**, in the presence of $NaBF_4$ **6b** did not react further with $PPh_3$, but afforded a cationic four-co-ordinate complex $[AuCl(pmp\text{-}C^1,N)(PPh_3)]BF_4$ **7b**. Its molar conductivity showed a typical value for a 1:1 electrolyte ($\Lambda_M$ 139 S cm$^2$ mol$^{-1}$ in acetone). Complex **7b** could be also prepared by the reaction between **2b**, $PPh_3$ and $AgBF_4$ in a molar ratio of 1:1:1.

In order to get $[AuCl(pcp\text{-}C^1,N)(PPh_3)]BF_4$, a pcp analogue of **7b**, the reaction of **2a** with an equimolar amount of $PPh_3$ was investigated in the presence of $AgBF_4$. When equimolar $AgBF_4$ was used the reaction products were complicated and



**Scheme 2** Inversion of the six-membered pmp–Au ring

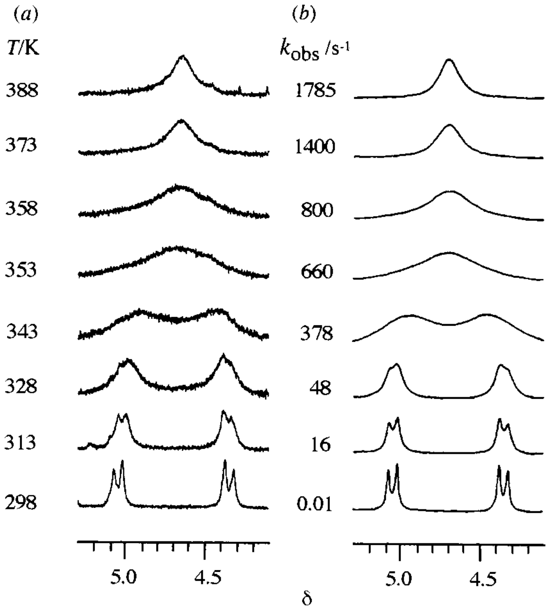


**Fig. 3** Methylene region of the $^1$H NMR spectra of complex **7b**. (*a*) Observed spectra, (*b*) simulated curves

no complexes could be isolated. However, when a three-fold excess of $AgBF_4$ was used the reaction proceeded cleanly and a bis-chelated complex [Au(pcp-$C^1$,$N$)$_2$]$BF_4$ **5a** was isolated. In this reaction $AgBF_4$ is considered to act as an abstracting reagent for $PPh_3$[20] as well as chloride ions. Separately, **5a** was also obtained by treating **3a** with a three-fold excess of $AgBF_4$, but the reaction of **2a** with only a two-fold excess of $AgBF_4$ (without $PPh_3$) again formed an intractable mixture. The $^1$H NMR spectrum of **5a** exhibited no signals due to $PPh_3$ but showed completely separated eight aromatic protons owing to the chelated pcp ring in the range δ 6.83–8.44. The FAB mass spectrum gave a parent peak at *m*/*z* 561 attributable to [Au(pcp-$C^1$,$N$)$_2$]$^+$. The conductivity in acetone revealed that **5a** was a 1 : 1 electrolyte ($\Lambda_M$ 137 S cm$^2$ mol$^{-1}$). These data together with elemental analysis confirmed the formation of **5a**. The mechanism is not clear at this stage. Similar bis-chelated gold(III) complexes have been reported for [Au($C_6H_4N$=NPh-$C^1$,$N$)$_2$]X (X = $ClO_4$ or $AuCl_4^-$)[21] and [Au($C_6H_4N$=NPh-$C^1$,$N$)($C_6H_4CH_2NMe_2$-$C^1$,$N$)]X (X = $ClO_4$ or $AuCl_4^-$),[22] the structures of which were determined by X-ray diffraction study to involve a *cis* geometry of the two chelated rings.

### Line shape analysis of [AuCl(pmp-$C^1$,$N$)($PPh_3$)]$BF_4$ 7b

Temperature-dependent $^1$H NMR spectra attributable to the inversion of the six-membered pmp–Au ring between the conformations A and B (Scheme 2) were observed for **7b**. In the low-temperature limiting spectrum of **7b** at 25 °C in $(CD_3)_2SO$ the methylene protons were observed as an AB quartet (Fig. 3). The signals began to broaden near 55 °C, reached coalescence point near 80 °C, and changed into a singlet at 115 °C. The rate of exchange of the two equally populated forms of complex **7b** was measured by line shape analysis of the AB quartet from the geminal $CH_2$ protons. Fig. 3 shows the experimental and simulated spectra together with the exchange rate $k_{obs}$. Activation parameters calculated from the Arrhenius and Eyring equations were $E_a = 78.2$ kJ mol$^{-1}$, $\Delta G^‡$ (300 K) = 70.5 kJ mol$^{-1}$, $\Delta H^‡ = 75.2$ kJ mol$^{-1}$ and $\Delta S^‡ = 15.8$ J K$^{-1}$ mol$^{-1}$. The comparatively small value of $\Delta S^‡$ indicates that the transition state for the inversion does not involve bond breaking.

## Experimental

### General

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, $^1$H and $^{31}$P-{$^1$H} NMR spectra on JEOL JNM GX-270 and GX-400 spectrometers using tetramethylsilane as an internal standard and trimethyl phosphite as an external standard, respectively. 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. The FAB mass spectrum was recorded on a JEOL-SX102A spectrometer. The complex [$AuCl_2$(pmp-$C^1$,$N$)] **2b** was prepared by a published procedure[7] or by the reaction of [$AuCl_3$(Hpmp)] with $AgBF_4$ in refluxing acetonitrile (yield 58%). Other reagents were obtained commercially and used without purification.

### Syntheses

**[$AuCl_3$(Hpcp)] 1a.** An ethanol (15 cm$^3$) solution of 2-benzoylpyridine (0.358 g, 1.95 mmol) was added to a solution of $HAuCl_4 \cdot 4H_2O$ (0.400 g, 0.971 mmol) in the same solvent (15 cm$^3$) and the resulting solution was stirred at room temperature. After 8 h the yellow precipitate was filtered off and washed with diethyl ether to give complex **1a** (0.297 g, 63%), m.p. 188 °C (decomp.) (Found: C, 29.0; H, 2.1; N, 2.8. $C_{12}H_9AuCl_3NO$ requires C, 29.6; H, 1.85; N, 2.9%); $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1671 (CO) and 353 (Au–Cl); $\delta_H[(CD_3)_2SO]$ 8.73 [1 H, d, $^3J$(HH) 7.8, H$^{6'}$], 8.15–7.95 (4 H, aromatic protons) and 7.75–7.5 (4 H, aromatic protons).

**[$AuCl_2$(pcp-$C^1$,$N$)] 2a.** A propionitrile (5 cm$^3$) solution of $AgO_2CCF_3$ (0.232 g, 1.05 mmol) was added to a solution of complex **1a** (0.400 g, 0.971 mmol) in the same solvent (10 cm$^3$). After refluxing for 38 h the resulting mixture was filtered while hot. The yellow filtrate was concentrated to give white crystals, which were filtered off and washed with diethyl ether to yield **2a** (0.052 g, 12%), m.p. 248 °C (decomp.) (Found: C, 31.8; H, 1.75; N, 3.25. $C_{12}H_8AuCl_2NO$ requires C, 32.0; H, 1.8; N, 3.1%); $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1674 (CO), 362 (Au–Cl) and 300 (Au–Cl).

**[$AuCl_2$(pcp-$C^1$)($PPh_3$)] 3a.** An acetone (5 cm$^3$) solution of $PPh_3$ (0.029 g, 0.111 mmol) was added to an acetone (10 cm$^3$) suspension of complex **2a** (0.050 g, 0.111 mmol), and then the mixture was stirred at room temperature for 18 h. The resulting solution was filtered and the filtrate concentrated. Addition of diethyl ether afforded white microcrystals of **3a** (0.077 g, 98%), m.p. 176 °C (decomp.) (Found: C, 51.0; H, 3.45; N, 2.0. $C_{30}H_{23}AuCl_2NOP$ requires C, 50.6; H, 3.25; N, 1.95%); $\Lambda_M$(1 x 10$^{-3}$ mol dm$^{-3}$, acetone) 3.9 S cm$^2$ mol$^{-1}$; $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1638 (CO), 325 (Au–Cl) and 301 (Au–Cl); $^{31}$P-{$^1$H} NMR [161.9 MHz, 303 K, $(CD_3)_2SO$] δ 29.8 (s).

**[AuCl(pcp-$C^1$)($PPh_3$)$_2$]$BF_4$ 4a.** *Method* (*a*). To a methanol (10 cm$^3$) solution of complex **3a** (0.052 g, 0.073 mmol) was added successively a methanol (5 cm$^3$) solution of $PPh_3$ (0.021 g, 0.079 mmol) and $NaBF_4$ (0.041 g, 0.372 mmol). The resulting mixture was evaporated to dryness and the residue extracted with dichloromethane. The extract was concentrated and diluted with diethyl ether to give white microcrystals of **4a** (0.049 g, 66%), m.p. 165 °C (decomp.) (Found: C, 56.55; H, 3.85; N, 1.4. $C_{48}H_{38}AuBClF_4NOP_2$ requires C, 56.2; H, 3.75; N, 1.35%); $\Lambda_M(1 \times 10^{-3}$ mol dm$^{-3}$, acetone) 108 S cm$^2$ mol$^{-1}$; $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1635 (CO), 1060 ($[BF_4]^-$) and 317 (Au–Cl); $^{31}$P-{$^1$H} NMR [161.9 MHz, 303 K, $(CD_3)_2SO$] δ 35.4 (s).

*Method* (*b*). Triphenylphosphine (0.058 g, 0.222 mmol) was added to an acetone (10 cm$^3$) suspension of complex **2a** (0.051 g, 0.112 mmol). After the resulting mixture changed into a solution, $NaBF_4$ (0.062 g, 0.563 mmol) was added. The resulting mixture was stirred for 4 h at room temperature and then the volatile materials were evaporated. The residue was extracted with dichloromethane and the extract concentrated to yield **4a** (0.070 g, 61%).

**[Au(pcp-*C*$^1$,*N*)$_2$]BF$_4$ 5a.** *Method* (*a*). To an acetone (15 cm$^3$) suspension of complex **2a** (0.051 g, 0.112 mmol) was added $PPh_3$ (0.033 g, 0.126 mmol) and then $AgBF_4$ (0.074 g, 0.382 mmol). The resulting mixture was stirred for 7 h at room temperature and then filtered. The filtrate was concentrated to give crude product as white microcrystals (0.023 g, 32%). This crude product was recrystallized from MeCN–diethyl ether to yield **5a**·$H_2O$ (0.016 g, 22%), m.p. 242 °C (decomp.) (Found: C, 43.05; H, 2.6; N, 4.35. $C_{24}H_{18}AuBF_4N_2O_3$ requires C, 43.25; H, 2.7; N, 4.2%); $\Lambda_M(1.0 \times 10^{-3}$ mol dm$^{-3}$, acetone) 137 S cm$^2$ mol$^{-1}$; $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1671 (CO) and 1060 ($[BF_4]^-$).

*Method* (*b*). To an acetone (8 cm$^3$) solution of complex **3a** (0.079 g, 0.111 mmol) was added an acetone (8 cm$^3$) solution of $AgBF_4$ (0.065 g, 0.335 mmol). The resulting mixture was stirred overnight at ambient temperature. After the volatile materials were evaporated, the residue was extracted in propionitrile. Addition of diethyl ether gave 0.024 g (63%) of **5a**·$H_2O$.

**[AuCl$_2$(pmp-*C*$^1$,*N*)(PPh$_3$)] 6b.** Triphenylphosphine (0.030 g, 0.115 mmol) was added to an acetonitrile (10 cm$^3$) suspension of complex **2b** (0.050 g, 0.115 mmol). The resulting solution was stirred at room temperature for 18 h and then the volatile materials were removed *in vacuo*. The residue was extracted with acetone and the extract concentrated. Addition of diethyl ether gave **6b**·$H_2O$ (0.077 g, 94%), m.p. 123 °C (decomp.) (Found: C, 50.65; H, 3.95; N, 1.9. $C_{30}H_{27}AuCl_2NOP$ requires C, 50.3; H, 3.8; N, 1.95%); $\Lambda_M(1 \times 10^{-4}$ mol dm$^{-3}$, acetone) 16 S cm$^2$ mol$^{-1}$; $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 316 (Au–Cl) and 295 (Au–Cl).

**[AuCl(pmp-*C*$^1$,*N*)(PPh$_3$)]BF$_4$ 7b.** *Method* (*a*). Sodium tetrafluoroborate (0.039 g, 0.354 mmol) was added to an acetone (10 cm$^3$) solution of complex **6b** (0.051 g, 0.071 mmol). The resulting suspension was stirred for 5 h and then evaporated to dryness. The residue was extracted with dichloromethane and the extract concentrated. Addition of hexane gave **7b** (0.049 g, 92%), m.p. 161 °C (decomp.) (Found: C, 47.6; H, 3.5; N, 1.95. $C_{30}H_{25}AuBClF_4NP$ requires C, 48.05; H, 3.35; N, 1.85%); $\Lambda_M(1 \times 10^{-3}$ mol dm$^{-3}$, acetone) 139 S cm$^2$ mol$^{-1}$; $\tilde{\nu}_{max}$/cm$^{-1}$ (KBr) 1060 ($[BF_4]^-$) and 310 (Au–Cl).

*Method* (*b*). To an acetonitrile (10 cm$^3$) suspension of complex **2b** (0.100 g, 0.230 mmol) was added $PPh_3$ (0.061 g, 0.232 mmol) and $AgBF_4$ (0.046 g, 0.237 mmol). The resulting mixture was stirred at room temperature and then evaporated to dryness. The residue was extracted with acetone and the extract concentrated. Addition of diethyl ether afforded **7b** (0.162 g, 94%). A similar procedure was reported by Cinellu *et al.*[7]

**Table 4** Crystallographic data for complexes **2a** and **7b**·$CH_2Cl_2$*

| | **2a** | **7b**·$CH_2Cl_2$ |
|---|---|---|
| Formula | $C_{12}H_8AuCl_2NO$ | $C_{31}H_{27}AuBCl_3F_4NP$ |
| $M$ | 450.07 | 834.66 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 8.594(5) | 13.382(7) |
| $b$/Å | 10.427(6) | 10.935(3) |
| $c$/Å | 7.635(6) | 22.611(3) |
| α/° | 109.86(5) | |
| β/° | 111.23(5) | 100.59(2) |
| γ/° | 88.79(5) | |
| $U$/Å$^3$ | 595.7(7) | 3252(1) |
| $Z$ | 2 | 4 |
| $F$(000) | 416 | 1642 |
| $D_c$/g cm$^{-3}$ | 2.510 | 1.705 |
| Crystal dimensions/mm | 0.20 × 0.30 × 0.40 | 0.15 × 0.35 × 0.55 |
| μ(Mo-Kα)/cm$^{-1}$ | 128.23 | 48.80 |
| Scan range/° | 1.84 + 0.30 tan θ | 1.52 + 0.30 tan θ |
| No. measured reflections | 2916 | 8196 |
| No. unique observed reflections [$I > 3\sigma(I)$] | 2379 | 4588 |
| $R, R'$ | 0.029, 0.030 | 0.053, 0.050 |

* Details in common: scan speed 16° min$^{-1}$; $2\theta_{max}$ 55°; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R^1 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$.

## X-Ray crystallography

Suitable crystals of [AuCl$_2$(pcp-*C*$^1$,*N*)] **2a** and [AuCl(pmp-*C*$^1$,*N*)(PPh$_3$)]BF$_4$ **7b** were grown from dichloromethane and dichloromethane–diethyl ether, respectively. Details of the crystal data, data collection and refinement are summarized in Table 4. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at 20 °C. Cell constants were obtained from a least-squares refinement of the setting angles of 23 reflections in the range 39.39 < 2θ < 40.39° for **2a** and 25 reflections in the range 35.98 < 2θ < 39.29° for **7b**. During the data collection the intensities of three representative reflections were measured after every 150 and an absorption correction based on azimuthal scans of several reflections was applied for **2a** (transmission range 0.70–1.00) and **7b** (transmission range 0.45–1.00). The observed data were corrected for Lorentz–polarization effects. All the calculations were performed using the TEXSAN software package.[23] Complex **7b** includes a $CH_2Cl_2$ molecule as solvent. The structures were solved by direct methods, expanded using Fourier techniques and refined by full-matrix least squares on $F^2$. The non-hydrogen atoms were refined anisotropically. While for **2a** hydrogen atoms were refined isotropically, for **7b** they were included but not refined.

CCDC reference number 186/839.

## Line shape analysis of [AuCl(pmp-*C*$^1$,*N*)(PPh$_3$)]BF$_4$ 7b

Experimental line shapes for the methylene proton signals of the pmp-*C*$^1$,*N* moiety were measured in the temperature range 298–388 K, and matched against those calculated for different exchange rate constants $k_{obs}$, using the modified Bloch equation[24] and Binsch's[25] computer program QUABEX. The Arrhenius and Eyring equations were used to evaluate $E_a$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ from $k_{obs}$.

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