



# Gold(III) adducts of 2-vinyl- and 2-ethylpyridine and cyclometallated derivatives of 2-vinylpyridine: Crystal structure of the cyclometallated derivative $[\text{Au}(k^2\text{-C,N-CH}_2\text{CH(Cl)-C}_5\text{H}_4\text{N})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$

Maria Agostina Cinellu<sup>a,\*</sup>, Fabio Cocco<sup>a</sup>, Giovanni Minghetti<sup>a</sup>, Sergio Stoccoro<sup>a</sup>, Antonio Zucca<sup>a</sup>, Mario Manassero<sup>b</sup>

<sup>a</sup> Dipartimento di Chimica, Università degli Studi di Sassari, Via Vienna 2, I-07100 Sassari, Italy

<sup>b</sup> Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Centro CNR, I-20133 Milano, Italy

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## ABSTRACT

Reaction of  $\text{Na}[\text{AuCl}_4]$  with 2-vinylpyridine (vinpy) and 2-ethylpyridine (etpy) affords the N-bonded adducts  $\text{Au}(\text{Rpy})\text{Cl}_3$  ( $\text{R} = \text{CH}_2=\text{CH}$ , vinpy;  $\text{CH}_3\text{CH}_2$ , etpy). Cationic adducts,  $[\text{Au}(\text{vinpy})_2\text{Cl}][\text{X}]_2$  ( $\text{X} = \text{BF}_4$ ,  $\text{PF}_6$ ) and  $[\text{Au}(\text{etpy})_2\text{Cl}_2][\text{BF}_4]$ , were also obtained by reaction of  $\text{Au}(\text{Rpy})\text{Cl}_3$  with Rpy (1:1) and excess  $\text{NaBF}_4$  or  $\text{KPF}_6$ . Thermal activation of  $\text{Au}(\text{vinpy})\text{Cl}_3$  in water gives the five-membered cycloaurated derivative  $[\text{Au}(k^2\text{-C,N-CH}_2\text{CH(Cl)-C}_5\text{H}_4\text{N})\text{Cl}_2]$  formally resulting through a *trans* nucleophilic addition of a chloride onto the  $\text{C}=\text{C}$  bond. No cyclometallated derivatives are obtained by reactions of  $\text{Au}(\text{etpy})\text{Cl}_3$ . An X-ray crystal structure determination on the  $\text{PPh}_3$  derivative  $[\text{Au}(k^2\text{-C,N-CH}_2\text{CH(Cl)-C}_5\text{H}_4\text{N})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$  was carried out.

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## 1. Introduction

The chemistry of cyclometallated gold(III) complexes containing C,N backbones [1] continues to attract great interest due to the promising pharmacological activities manifested by a number of derivatives, mainly as anti tumour agents [2], and the great potential as homogeneous catalysts [3,4]. Actually, the enhanced stability of the gold(III) centre towards reduction granted by the cyclometallated C,N ligand [5] is an important requirement for biological studies, and the less acidic character of these organogold(III) compounds with respect to  $\text{AuCl}_3$ , the most employed gold(III) homogeneous catalyst, enables their use with acidic-sensitive substrates.

Following our interest in the synthesis and reactivity of cycloaurated derivatives of 2-substituted pyridines [6] and 6-substituted 2,2'-bipyridines [7], bearing a variety of alkyl, benzyl and aryl groups, we report herein on the reaction of gold(III) chlorides with 2-vinylpyridine.

2-Vinylpyridines are versatile ligands, which have been widely used to stabilize transition-metal-carbon bonds in a chelating coordination mode, this being deemed to play a key role in catalysis [8]. Cyclometallation reactions of 2-vinylpyridine, or its deriva-

tives, have been reported previously with metal complexes of Pd [9], Pt [9a,10], Co [11], Rh [12], Ir [13], Ru [14], Os [14d,e,15] and Re [16]. In most cases  $\text{C}(\text{sp}^2)\text{-H}$  activation of 2-vinylpyridine occurs with formation of the cyclometallated derivatives  $[\text{M}(k^2\text{-C,N-CH}=\text{CH-C}_5\text{H}_4\text{N})]$ . At variance, reaction with palladium(II) and platinum(II) chlorides in alcoholic media resulted in the formation of  $[\text{M}(k^2\text{-C,N-CH}_2\text{CH(OR)-C}_5\text{H}_4\text{N})\text{Cl}_2]$  ( $\text{M} = \text{Pd, Pt}$ ) [9a].

Surprisingly, the previously attempted auration of 2-vinylpyridine with gold(III) bromide failed to give any cyclometallated species [17].

## 2. Results and discussion

### 2.1. Adducts

As previously observed with various 2-substituted-pyridines [6], the reaction of  $\text{Na}[\text{AuCl}_4]$  with 1 equiv. of 2-vinylpyridine (vinpy) in  $\text{MeCN-H}_2\text{O}$  affords the N-bonded adduct  $\text{Au}(\text{vinpy})\text{Cl}_3$  (1). An adduct was also previously described as the outcome of the reaction of vinpy with  $\text{Au}_2\text{Br}_6$  [17]. The  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  shows the vinylic protons at lower field with respect to the free ligand, thus ruling out coordination of the vinyl group to gold, as an upfield shift is expected for a coordinated vinyl group. The large downfield shift displayed by the  $\text{H}_c$  proton (cfr. Fig. 1 for numbering scheme)

\* Corresponding author. Tel.: +39 079 229499; fax: +39 079 229559.

E-mail address: [cinellu@uniss.it](mailto:cinellu@uniss.it) (M.A. Cinellu).

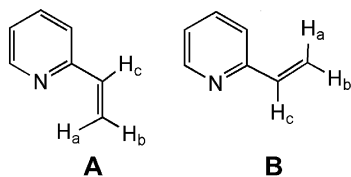


Fig. 1. Two possible conformations for vinpy.

on coordination,  $\Delta\delta$  0.71 ppm, with respect to the small shift of  $H_a$ ,  $\Delta\delta$  0.02 ppm, suggests some kind of interaction of  $H_c$  with the gold(III) centre,  $C-H \cdots Au$ , or with a chloride ligand,  $C-H \cdots Cl$ . Both  $C-H \cdots M$  ( $M = d^8$  metal) and  $C-H \cdots X$  ( $X = Cl, Br, I$ ) interactions are known to cause strong deshielding of the proton resonances [18] and have often been observed in various gold(III) complexes [6,7].

In this case, such interactions are possible if the vinyl group is oriented like in conformer **B** (Fig. 1). A  $^1H$  NOE difference spectrum shows contacts between the methylenic  $H_a$  and the H-3 proton of the pyridine (Fig. 2) thus supporting this structure.

As according to calculations [19] and NMR studies [20] the preferred conformation of free 2-vinylpyridine is **A** rather than **B**, steric repulsion between the vinyl group and the  $AuCl_3$  moiety of the complex is likely responsible of the change in the conformation upon coordination.

Downfield shift of similarly positioned H in (L) $AuCl_3$  adducts of 2-benzyl- and 2-methylbenzyl-pyridine have been previously observed by us [6], and also found in the 2-ethylpyridine (etpy) adduct,  $Au(etpy)Cl_3$  (**2**), synthesized for comparison. In this case the methylenic protons shift downfield by 0.63 ppm, while the methyl protons move downfield by only 0.22 ppm.

Two different kinds of cationic adducts have been obtained by reaction in acetone of  $Au(Rpy)Cl_3$  (**1** and **2**) [ $R = CH=CH_2$ , vinpy (**1**);  $CH_2CH_3$ , etpy (**2**)] with an equimolar amount of the respective Rpy and excess  $NaBF_4$ , or  $KPF_6$ , namely  $[Au(vinpy)_2Cl][X]_2$  ( $X = BF_4, PF_6$ ), (**3-BF\_4**) and (**3-PF\_6**), and  $[Au(etpy)_2Cl_2][BF_4]$  (**4-BF\_4**). In the case of complex **2** the expected substitution of ethylpyridine for one chloride ligand gave the monocationic complex **4** as a 1:4 mixture of the *cis* and *trans* isomers, as indicated by the two sets of signals, partially overlapping, in the  $^1H$  NMR spectrum (in  $CD_3COCD_3$ ). In the case of complex **1**, analytical data of **3-BF\_4** and **3-PF\_6** (C,H,N analyses and conductivity measurements) suggested that replacement of two chloride ligands by one 2-vinylpyridine had occurred to give a dicationic complex, where one of the two vinylpyridines acts as a bidentate ligand through the nitrogen atom and the  $C=C$  moiety of the vinyl group. In the  $^1H$  NMR spectra of **3-BF\_4** and **3-PF\_6** in  $CD_3COCD_3$  broad unresolved clusters of signals indicate a very complex situation likely arising from: (i) the presence of *cis*- and *trans*-N-Au-N isomers, (ii) rapid chemical exchange between coordinated and non-coordinated vinyl groups, and (iii) different conformations of the uncoordinated vinyl group. Averaged signals are also observed even at low temperature.

## 2.2. Cyclometallated derivatives

Heating of a suspension of  $Au(vinpy)Cl_3$  (**1**) in  $MeCN/H_2O$  to 60–80 °C resulted in the formation of a new species (**5**) that according

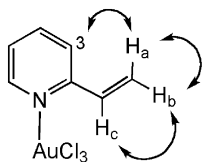


Fig. 2. NOE contacts in  $Au(vinpy)Cl_3$ .

to CHN analyses is a not ionic ( $\Lambda_M$  in acetone solution  $16 \Omega^{-1} cm^2 mol^{-1}$ ) isomer of **1**: no C–H activation occurred to give a cyclometallated species,  $Au(vinpy-H)Cl_2$ . At variance, under comparable conditions, N-coordinated 2-substituted pyridines, such as 2-benzyl- [6] and 2-aryl-pyridines [21] undergo  $C(sp^2)$ –H bond activation to give cycloaurated derivatives  $Au(C,N)Cl_2$ .

The same product **5** was obtained by reaction of  $NaAuCl_4$  with 2 equiv. of vinpy in  $MeCN/H_2O$  at reflux, but under these reaction conditions also  $Au(vinpy)Cl_3$  as well as unidentified species are obtained. Large decomposition with formation of metallic gold was observed in both cases.

The  $^1H$  NMR spectrum of **5** shows the disappearance of the vinyl protons and appearance of a new set of signals (in  $CD_2Cl_2$ ) at  $\delta$  3.22, 3.53 and 5.51 ppm with integral ratio 1:1:1; moreover a large downfield shift ( $\Delta\delta = 1.04$  ppm) of the pyridinic H-6 proton is observed. NOE effects were observed between the proton at  $\delta$  3.53 and those at  $\delta$  5.51 and 3.22, when this signal was irradiated. In the far-IR spectrum Au–Cl stretching vibrations are observed at 358 and 294  $cm^{-1}$ , consistent, respectively, with Au–Cl *trans* to N and *trans* to C [6].

On the whole, spectroscopic data suggest that **5** is the cycloaurated species  $[Au(k^2-C,N-CH_2CH(Cl)-C_5H_4N)Cl_2]$  containing a  $C(sp^3)$ –Au bond (Fig. 3). An analogous bromurated derivative was suggested by Monaghan and Puddephatt as the probable intermediate in the formation of  $CH_2=CH(Br)C_5H_4N$  by thermolysis of  $Au(vinpy)Br_3$  at 200 °C [17]. Similar palladium(II) and platinum(II) derivatives (cfr. Fig. 3) were isolated by reaction of 2-vinylpyridine with  $[MCl_4]^{2-}$  ( $M = Pd, Pt$ ) in ROH ( $R = Me, Et$ ) [9a].

Three plausible mechanisms can be proposed for the formation of these cyclometallated derivatives, all implying the formation of the M–N bond as the first step (in Scheme 1 the three mechanisms are illustrated for the gold complexes). The first mechanism involves the intramolecular insertion of the double bond into the M–X bond ( $M = Au$ ). In the second, it is assumed that the reaction occurs via an external nucleophilic addition of  $X^-$  ( $M = Au, X = Cl, Br$ ) or ROH ( $M = Pd, Pt$ ) onto the metal-coordinated double bond. In the third case, the electrophilic attack of the metal on the double bond generates a secondary carbocation, unstable for the presence of the electron-withdrawing pyridine, which undergoes nucleophilic attack by  $X^-$  ( $M = Au$ ) or ROH ( $M = Pd, Pt$ ). In the latter case deprotonation at the  $\beta$ -position of the carbocation to give the cyclometallated derivatives  $[M](k^2-C,N-CR'=CR''C_5H_4N)$  ( $R', R'' = H, alkyl$ ) was observed for  $M = Pd$  [9b] and  $Rh$  [12b,22]. Whatever the mechanism, the vinyl group in the adduct must be oriented toward the metal centre in order to be prone to the successive steps.

In our case, cyclometallation of the N-bonded 2-vinylpyridine requires thermal activation. In order to get insight into the possible mechanism, a  $CD_3CN$  solution of  $Au(vinpy)Cl_3$  (**1**) in an NMR tube was gradually heated and the reaction monitored by  $^1H$  NMR. Signals of **5** start to be recognizable after 30 min at 60 °C, together with those of a new species **1'**; both species grow gradually and become appreciable after 1 h at 78 °C. After this time the integral ratio of the species is: **1**:**1'**:**5** = 22.5:2.5:1. Species **1'** features a

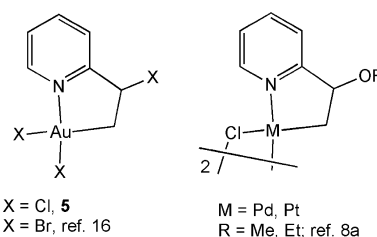
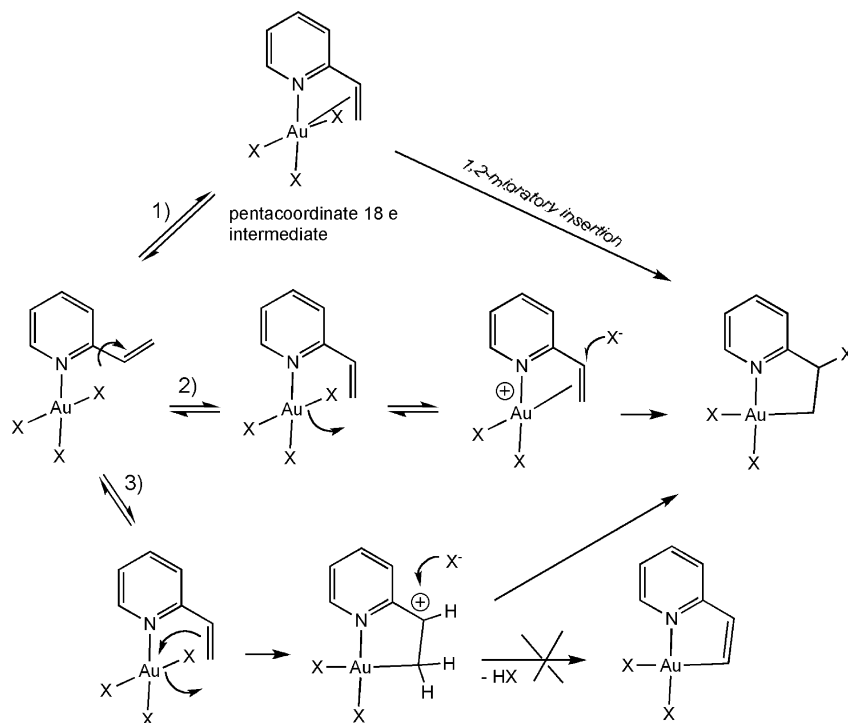


Fig. 3. Cyclometallated derivatives of 2-vinylpyridine.



**Scheme 1.** Plausible mechanisms for the cycloauration of 2-vinylpyridine (X = Cl, Br).

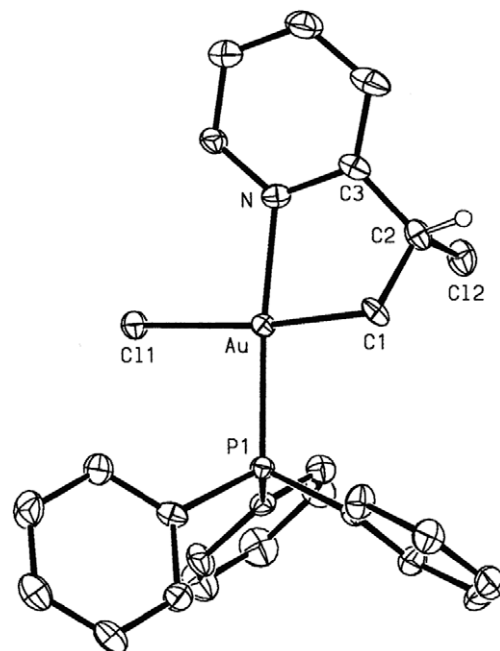
pattern of signals similar to that of **1**, with resonances shifted with respect to the corresponding in **1**. Notably, the methynic proton,  $\text{H}_c$ , is upfield shifted by 0.61 ppm with respect to that of **1**, at variance  $\text{H}_a$  is downfield shifted by 0.11 ppm, while  $\text{H}_b$  moves upfield by only 0.07 ppm; the pyridine 6-H proton is also shifted upfield by 0.29 ppm. These data suggest that the new species **1'** could be either an adduct with the vinyl group oriented toward the gold centre, i.e. in a more favourable position to undergo successive reactions, or the cationic isomer  $[\text{Au}(\text{vinpy})\text{Cl}_2]\text{Cl}$  featuring a coordinated vinyl group.

In the attempt to obtain the cyclometallated derivative  $\text{Au}(\text{CH}=\text{CHC}_5\text{H}_4\text{N})\text{Cl}_2$ , thermal activation of **1** was carried out in the presence of bases such as  $\text{NEt}_3$  and 2,6-lutidine, but complex mixtures of unidentified products were obtained in both cases, and, in the case of  $\text{NEt}_3$ , large decomposition to metallic gold was observed. Unreacted **1** was quantitatively recovered from a dichloromethane solution when treated with  $\text{K}_2\text{CO}_3$  at reflux.

As previously observed for platinum(II) [10], no metallacyclic derivatives were obtained from the 2-ethylpyridine adduct **2**.

Compound **5** is one of the few cycloaurated derivatives featuring a  $\text{N}^+\text{C}(\text{sp}^3)$  auracycle [7a,23]: indeed reaction of gold(III) chlorides with 2-vinyl substituted heterocycles could be a general method to obtain this kind of compounds.

Reaction of **5** with an equimolar amount of  $\text{PPh}_3$  and excess  $\text{KPF}_6$  in acetone solution caused replacement of a chloride ligand to give  $[\text{Au}\{\kappa^2\text{-C,N-CH}_2\text{CH}(\text{Cl})\text{-C}_5\text{H}_4\text{N}\}(\text{PPh}_3)\text{Cl}][\text{PF}_6]$  (**6**). Crystals of **6** were obtained by slow evaporation of an acetone solution. The structure consists of the packing of  $[\text{Au}\{\kappa^2\text{-C,N-CH}_2\text{CH}(\text{Cl})\text{-C}_5\text{H}_4\text{N}\}(\text{PPh}_3)\text{Cl}]^+$  cations and  $[\text{PF}_6]^-$  anions in the molar ratio 1:1, with no unusual van der Waals contacts, in the non-centrosymmetric space group  $\text{Pna}2_1$ . An ORTEP [24] view of the cation is shown in Fig. 4 and selected bond parameters of the cation are listed in Table 1. The gold atom displays a square-planar coordination with a slight square-pyramidal distortion, maximum displacements from the best plane being +0.025(1) and -0.013(5) Å for atoms Au and N, respectively. Bond parameters



**Fig. 4.** ORTEP view of the cation of **6**. Ellipsoids are drawn at the 30% probability level.

**Table 1**

Selected bond distances (Å) and angles (°) for the cation of **6** with estimated standard deviations (esd's) on the last figure in parentheses.

Au–Cl(1)	2.370(1)	Au–P(1)	2.279(1)
Au–N	2.071(5)	Au–C(1)	2.032(5)
N–C(3)	1.364(8)	C(1)–C(2)	1.513(8)
C(2)–C(3)	1.484(8)	C(2)–Cl(2)	1.819(6)
Cl(1)–Au–P(1)	91.7(1)	Cl(1)–Au–N	93.3(1)
Cl(1)–Au–C(1)	173.6(2)	P(1)–Au–N	174.6(1)
P(1)–Au–C(1)	94.6(2)	N–Au–C(1)	80.3(2)

involving gold can be compared with those found in  $[\text{AuCl}(\text{epi-C}^1\text{N})(\text{PPh}_3)][\text{PF}_6]$  (**7**) (epi = 2-(1-ethyl-2-imidazolyl)phenyl) [25], which shows the same atomic arrangement for the moiety involving Au,  $\text{PPh}_3$ , Cl, the five-membered metallacycle and the heterocyclic ring. In **7** there are two crystallographically independent molecules, with very similar bond parameters, so we will refer to the mean values. Thus, Au–Cl(1) 2.370(1) Å here and 2.365 Å in **7**. Similarly, Au–P(1) 2.279(1) and 2.303 Å, Au–N 2.071(5) and 2.046 Å, Au–C(1) 2.032(5) and 2.052 Å, respectively. As can be seen in Table 1, the C(1)–C(2) and C(2)–C(3) bond lengths are typical of  $sp^3$ – $sp^3$  and  $sp^2$ – $sp^3$  single bonds. The C(2)–Cl(2) bond length is normal. At difference with compound **7**, the five-membered metallacycle is definitely non-planar, with maximum displacements from the best plane of +0.262(6) and –0.271(6) Å for atoms C(1) and C(2), respectively. The distance of atom Cl(2) from this plane is –0.084(2) Å. The dihedral angle between this plane and the metal coordination plane is 13.4(3) Å. The pyridine ring is strictly planar and forms a dihedral angle with the metal coordination best plane of 17.2(3)°. C(2) is an asymmetric carbon atom, but as the space group contains mirror planes both the enantiomers are present in the crystals. Bond lengths and angles in the anion are normal.

The spectroscopic data of **6** are consistent with the structure in Fig. 4, showing that only this isomer, the thermodynamic product, is formed as a result of the strong *trans* influence of the  $\text{PPh}_3$  ligand. The far-IR spectrum shows the Au–Cl stretching vibration at  $304\text{ cm}^{-1}$ , a value typical of a chlorine *trans* to a carbon atom [6]. In accordance with a *trans*-P–Au–N arrangement, the phosphorus resonance is found at  $\delta$  29.2 ppm. The downfield resonance of the H-6 pyridine proton ( $\delta$  9.46 ppm) indicates its proximity to the chlorine atom. The  $-\text{CH}(\text{Cl})\text{CH}_2-$  fragment gives rise (in  $\text{CD}_2\text{Cl}_2$ ) to a well resolved ABCX ( $X = {}^{31}\text{P}$ ) spin system, with  $\delta_A$  2.52,  $\delta_B$  3.17,  $\delta_C$  5.51,  $J_{A-C} = 5.1$ ,  $J_{A-X} = 4.0$ ,  $J_{B-C} = 4.8$ ,  $J_{B-X} = 1.8\text{ Hz}$ , and  $J_{A-B} = 10.5\text{ Hz}$ . The resonances of the methylenic protons are both shifted upfield with respect to the starting compound ( $\Delta\delta_A$  0.70 and  $\Delta\delta_B$  0.36 ppm) likely due to the anisotropic shielding of one phenyl ring of the *cis*  $\text{PPh}_3$  ligand. Comparable NOE effects were observed between these protons and the phenyl protons of  $\text{PPh}_3$  centered at  $\delta$  7.80. NOE effects were also observed between the  $\text{H}_C$  proton and the H-3 of the pyridine when this signal was irradiated, and between  $\text{H}_C$  and both  $\text{H}_A$  and  $\text{H}_B$ , when the  $\text{H}_C$  signal was irradiated; the larger effect observed with  $\text{H}_A$  indicates that these protons are on the same side of the metallacycle plane.

At variance, reaction of **5** with 1 equiv. of vinpy and excess  $\text{KPF}_6$  failed to give the cationic derivative  $[\text{Au}\{k^2\text{-C}_5\text{H}_4\text{N}-\text{CH}_2\text{CH}(\text{Cl})-\text{C}_5\text{H}_4\text{N}\}(\text{CH}_2=\text{CH}-\text{C}_5\text{H}_4\text{N})\text{Cl}][\text{PF}_6]$  (**8-PF**<sub>6</sub>), analogous to **6-PF**<sub>6</sub>. Nevertheless, **8-PF**<sub>6</sub> could be obtained by using an equivalent of  $\text{AgPF}_6$  to abstract a chloride ligand. According to its  ${}^1\text{H}$  NMR spectrum, complex **8-PF**<sub>6</sub> is a mixture of the two possible isomers: that with the N-bonded vinpy ligand *trans* to the pyridine nitrogen or to the  $\text{CH}_2$  group in a 1:2 molar ratio. This is in accordance with the comparable *trans* influences of the pyridine and the chloride ligands.

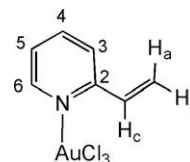
### 3. Conclusions

Neutral and cationic gold(III) adducts of 2-ethyl- and 2-vinylpyridine have been synthesized and characterized by IR and NMR spectroscopies. A new cycloaurated derivative featuring a Au–C( $sp^3$ ) bond,  $[\text{Au}\{k^2\text{-C}_5\text{H}_4\text{N}-\text{CH}_2\text{CH}(\text{Cl})\text{C}_5\text{H}_4\text{N}\}\text{Cl}_2]$ , was also obtained from the neutral adduct  $\text{Au}(\text{vinpy})\text{Cl}_3$  by thermal activation. Plausible mechanisms are proposed for its formation. Reaction of the cyclometallated derivative with  $\text{PPh}_3$  resulted in the displacement of one chloride ligand with formation of the thermodynamic product only, i.e. that with a *trans*-P–Au–N arrangement.

### 4. Experimental

2-Vinylpyridine and 2-ethylpyridine were purchased from commercial sources (AlfaAesar) and were used as received.  $\text{H}[\text{AuCl}_4]\cdot 3\text{H}_2\text{O}$  was obtained from Johnson Matthey;  $\text{Na}[\text{AuCl}_4]$  was prepared from  $\text{HAuCl}_4$  and  $\text{NaHCO}_3$  in a 1/1 molar ratio. All the solvents were purified before use according to standard procedures. All the reactions were performed in air. Elemental analyses were performed with a Perkin–Elmer elemental analyzer 240B by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Italy). Infrared spectra were recorded with a FT-IR Jasco 480P using nujol mulls.  ${}^1\text{H}$ ,  ${}^{13}\text{C}\{{}^1\text{H}\}$  and  ${}^{31}\text{P}\{{}^1\text{H}\}$  NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0, 75.4 and 121.4 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS for  ${}^1\text{H}$ ,  ${}^{13}\text{C}\{{}^1\text{H}\}$  and external  $\text{H}_3\text{PO}_4$  (85%) for  ${}^{31}\text{P}\{{}^1\text{H}\}$ .  $J$  values are given in Hz. NOE difference experiments were performed by means of standard pulse sequences. Conductivities were measured with a Philips PW 9505 conductimeter. Mass spectra were recorded on a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol operating as supporting matrix.

#### 4.1. $[\text{Au}(\text{vinpy})\text{Cl}_3]$ (**1**)



To a solution of 2-vinylpyridine (126.2 mg, 1.2 mmol) in acetonitrile (2 mL) and water (30 mL) was added an aqueous solution of  $\text{Na}[\text{AuCl}_4]$  (477.6 mg, 1.2 mmol). The resulting yellow suspension was stirred for 2 days at room temperature, then filtered, washed with water, ethanol and diethyl ether, and dried in vacuo. The crude product was recrystallized from dichloromethane/diethyl ether to give the analytical sample. Yield: 67%. M.p.:  $126^\circ\text{C}$ . Anal. Calc. for  $\text{C}_7\text{H}_7\text{AuCl}_3\text{N}$ : C, 20.58; H, 1.73; N, 3.43. Found: C, 20.72; H, 1.96; N, 3.43%. IR ( $\nu/\text{cm}^{-1}$ , nujol): 1602 m, 1560 m, 1165 m, 963 w, 939 s, 780 vs, 759 s, 722 m, 365 vs (Au–Cl).  ${}^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta$  6.08 (d,  $J_{bc} = 11.1\text{ Hz}$ , 1H,  $\text{H}_b$ ), 6.27 (d,  $J_{ac} = 17.5\text{ Hz}$ , 1H,  $\text{H}_a$ ), 7.55 (dd,  $J_{cb} = 11.1$ ,  $J_{ca} = 17.5\text{ Hz}$ , 1H,  $\text{H}_c$ ), 7.65 (td,  ${}^3J_{HH} = 6.5$ ,  ${}^4J_{HH} = 1.5\text{ Hz}$ , 1H, H-5), 7.97 (dd,  ${}^3J_{HH} = 8.1$ ,  ${}^4J_{HH} = 1.3\text{ Hz}$ , 1H, H-3), 8.14 (td,  ${}^3J_{HH} = 7.5$ ,  ${}^4J_{HH} = 1.4\text{ Hz}$ ; 1H, H-4), 8.69 (d;  ${}^3J_{HH} = 6.0\text{ Hz}$ ; 1H, H-6); ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  6.15 (d,  $J_{bc} = 11.3\text{ Hz}$ , 1H,  $\text{H}_b$ ), 6.47 (d,  $J_{ac} = 17.1\text{ Hz}$ , 1H,  $\text{H}_a$ ), 7.58 (dd,  $J_{cb} = 11.3$ ,  $J_{ca} = 17.1\text{ Hz}$ , 1H,  $\text{H}_c$ ), 7.91 (t,  ${}^2J_{HH} = 6.7\text{ Hz}$ , 1H, H-5), 8.31 (d,  ${}^3J_{HH} = 8.1\text{ Hz}$ , 1H, H-3), 8.39 (t,  ${}^3J_{HH} = 7.7\text{ Hz}$ , 1H, H-4), 9.23 (d,  ${}^3J_{HH} = 6.1\text{ Hz}$ , 1H, H-6).  ${}^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  127.0 ( $=\text{CH}_2$ ), 127.2 (C-5), 128.0 (C-3), 133.9 ( $=\text{CH}$ ), 143.6 (C-4), 150.7 (C-6), 156.1 (C-2).

#### 4.2. $[\text{Au}(\text{etpy})\text{Cl}_3]$ (**2**)

To a solution of 2-ethylpyridine (107.2 mg, 1.0 mmol) in acetonitrile (2 mL) and water (30 mL) was added an aqueous solution of  $\text{Na}[\text{AuCl}_4]$  (397.9 mg, 1.0 mmol). The resulting yellow suspension was stirred for 2 days at room temperature, then filtered, washed with water, ethanol and diethyl ether, and dried in vacuo. The crude product was recrystallized from dichloromethane/diethyl ether to give the analytical sample. Yield: 78%. M.p.:  $195^\circ\text{C}$ . Anal. Calc. for  $\text{C}_7\text{H}_9\text{AuCl}_3\text{N}$ : C, 20.48; H, 2.21; N, 3.41.

Found: C, 20.23; H, 2.05; N, 3.38%. IR ( $\nu/\text{cm}^{-1}$ , nujol): 1604 s, 1565 m, 1455 vs, 1167 m, 1060 m, 893 m, 807 vs, 768 vs, 365 vs and 341 sh (Au–Cl).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  1.53 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 3H,  $\text{CH}_3$ ), 3.46 (q,  $^3J_{\text{HH}} = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 7.57 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 1H, H-5), 7.66 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 1H, H-3), 8.08 (td,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.4$  Hz; 1H, H-4), 8.63 (dd;  $^3J_{\text{HH}} = 5.7$ ,  $^4J_{\text{HH}} = 1.2$  Hz; 1H, H-6); ( $\text{CD}_3\text{COCD}_3$ , 293 K): 1.53 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1H,  $\text{CH}_3$ ), 3.44 (q,  $^3J_{\text{HH}} = 7.6$  Hz, 1H,  $\text{CH}_2$ ), 7.85 (td,  $^3J_{\text{HH}} = 6.8$ ,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, H-5), 7.98 (dd,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.3$  Hz, 1H, H-3), 8.36 (td,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.5$  Hz; 1H, H-4), 9.19 (dd;  $^3J_{\text{HH}} = 5.8$ ,  $^4J_{\text{HH}} = 1.0$  Hz; 1H, H-6). FAB mass spectrum  $m/z$ : 410  $[\text{M}+\text{H}]^+$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 293 K): 12.3 ( $\text{CH}_3$ ), 32.4 ( $\text{CH}_2$ ), 125.4 (C-5), 127.6 (C-3), 141.9 (C-4), 149.2 (C-6),  $\delta$  163.4 C-2).

#### 4.3. $[\text{Au}(\text{vinpy})_2\text{Cl}][\text{PF}_6]_2$ (**3-PF<sub>6</sub>**)

To a solution of **1** (150.0 mg, 0.37 mmol) in acetonitrile (50.0 mL) were added  $\text{KPF}_6$  (204.3 mg, 1.11 mmol) and vinpy (38.9 mg, 0.37 mmol). The resulting mixture was stirred for 1 day at room temperature and then evaporated to dryness. The residue was extracted with chloroform to remove unreacted **1**, washed with water and recrystallized from acetone/diethyl ether to give the analytical sample as a whitish powder. Yield 55%. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{AuClF}_{12}\text{N}_2\text{P}_2$ : C, 22.95; H, 1.93; N, 3.82. Found: C, 22.97; H, 2.03; N, 3.71%.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone)  $210 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR ( $\nu/\text{cm}^{-1}$ , nujol): 1623 s, 1574 w, 1509 m, 1173 w, 844 vs ( $\text{PF}_6$ ), 779 s, 558 s, 357 w (Au–Cl).

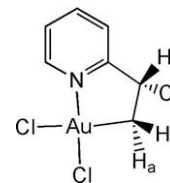
#### 4.4. $[\text{Au}(\text{vinpy})_2\text{Cl}][\text{BF}_4]_2$ (**3-BF<sub>4</sub>**)

To a solution of **1** (150.0 mg, 0.37 mmol) in acetonitrile (50.0 mL) were added  $\text{NaBF}_4$  (162.5 mg, 1.48 mmol) and vinpy (38.9 mg, 0.37 mmol). The resulting mixture was stirred for 1 day at room temperature and then evaporated to dryness. The residue was extracted with chloroform to remove unreacted **1**, washed with water and recrystallized from acetone/diethyl ether to give the analytical sample as a whitish powder. Yield 50%. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{AuB}_2\text{ClF}_8\text{N}_2$ : C, 27.28; H, 2.29; N, 4.55. Found: C, 27.68; H, 2.25; N, 4.63%.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone)  $200 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR ( $\nu/\text{cm}^{-1}$ , nujol): 1625 s, 1511 m, 1061 vs-broad ( $\text{BF}_4$ ), 781 s, 552 w, 522 w, 358 m (Au–Cl).

#### 4.5. $[\text{Au}(\text{etpy})_2\text{Cl}_2][\text{BF}_4]$ (**4-BF<sub>4</sub>**)

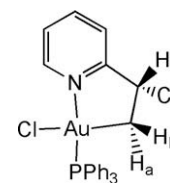
To a solution of **2** (410.5 mg, 1.0 mmol) in acetonitrile (100 mL) were added  $\text{NaBF}_4$  (548.9 mg, 5.0 mmol) and etpy (107.2 mg, 1.0 mmol). The resulting mixture was stirred for 2 days at room temperature and, then evaporated to dryness. The residue was extracted with chloroform to remove unreacted **2**, washed with water and recrystallized from acetone/diethyl ether to give the analytical sample as a whitish powder. Yield: 38%. M.p.: 157 °C. Anal. Calc. for  $\text{C}_{14}\text{H}_{18}\text{AuBCl}_2\text{F}_4\text{N}_2$ : C, 29.55; H, 3.19; N, 4.92. Found: C, 29.33; H, 3.07; N, 4.85%.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone)  $160 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR ( $\nu/\text{cm}^{-1}$ , nujol): 1608 vs, 1568 m, 1217 m, 1167 m, 1096 vs(sh), 1056 vs(broad) ( $\text{BF}_4$ ), 805 s, 762 vs, 520 s, 477 w, 446 m, 376 vs (Au–Cl), 284 w, 255 w.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  1.61 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 3H,  $\text{CH}_3$  B), 1.63 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 3H,  $\text{CH}_3$  A), 3.63 (q,  $^3J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{CH}_2$  A), 3.69 (q,  $^3J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{CH}_2$  B), 7.96 (t + t, overlapping,  $^3J_{\text{HH}} = 7.6$  Hz, 1H A + 1H B, H-5), 8.09 (d + d, overlapping,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.4$  Hz, 1H A + 1H B, H-3), 8.47 (td,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.5$  Hz, 1H, H-4 A), 8.49 (td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.5$  Hz, 1H, H-4 B), 9.26 (dd,  $^3J_{\text{HH}} = 6.2$ ,  $^4J_{\text{HH}} = 1.1$  Hz, 1H, H-6 B), 9.28 (dd,  $^3J_{\text{HH}} = 6.2$ ,  $^4J_{\text{HH}} = 1.1$  Hz, 1H, H-6 A), A:B = 4:1. FAB mass spectrum  $m/z$ : 480  $[\text{M}-\text{H}]^+$ , 444  $[\text{M}-2\text{H}-\text{Cl}]$ , 410  $[\text{M}-\text{H}-2\text{Cl}]$ .

#### 4.6. $[\text{Au}\{\text{CH}_2\text{CH}(\text{Cl})\text{C}_5\text{H}_4\text{N}\}\text{Cl}_2]$ (**5**)



A suspension of **1** (408.5 mg, 1.0 mmol) in acetonitrile (1.5 mL) and water (60 mL) was heated under reflux for 2 h, then filtered off, washed with water, ethanol and diethyl ether, and dried in vacuum to yield a yellow solid. Recrystallization from acetone/diethyl ether gave the analytical sample. Yield: 20%. M.p.: 173 °C. Anal. Calc. for  $\text{C}_7\text{H}_7\text{AuCl}_3\text{N}$ : C, 20.58; H, 1.73; N, 3.43. Found: C, 20.68; H, 1.63; N, 3.38%. IR ( $\nu/\text{cm}^{-1}$ , nujol): 1602 m, 1288 m, 1164 m, 939 m, 782 s, 719 m, 553 s, 365 s and 355 m-sh (Au–Cl), 281 m.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta$  3.22 (t,  $J_{\text{ab}} = J_{\text{ac}} = 9.3$  Hz, 1H,  $\text{H}_a$ ), 3.53 (dd,  $J_{\text{ba}} = 9.3$ ,  $J_{\text{bc}} = 6.4$  Hz, 1H,  $\text{H}_b$ ), 5.51 (dd,  $J_{\text{ca}} = 9.3$ ,  $J_{\text{cb}} = 6.4$  Hz, 1H,  $\text{H}_c$ ), 7.74 (t,  $^3J_{\text{HH}} = 6.7$  Hz, 1H, H-5), 7.94 (d,  $^3J_{\text{HH}} = 7.9$  Hz, 1H, H-3), 8.28 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 1H, H-4), 9.61 (d,  $^3J_{\text{HH}} = 5.8$  Hz, 1H, H-6); ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  3.23 (dd,  $J_{\text{ab}} = 9.1$ ,  $J_{\text{ac}} = 7.8$  Hz, 1H,  $\text{H}_a$ ), 3.50 (dd,  $J_{\text{ba}} = 9.1$ ,  $J_{\text{bc}} = 5.8$  Hz, 1H,  $\text{H}_b$ ), 5.87 (dd,  $J_{\text{ca}} = 7.8$ ,  $J_{\text{cb}} = 5.8$  Hz, 1H,  $\text{H}_c$ ), 7.97 (t,  $^3J_{\text{HH}} = 6.1$  Hz, 1H, H-5), 8.12 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 1H, H-3), 8.53 (td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.3$  Hz, 1H, H-4), 9.53 (d,  $^3J_{\text{HH}} = 5.2$  Hz, 1H, H-6); ( $\text{CD}_3\text{CN}$ , 293 K):  $\delta$  3.20 (dd,  $J_{\text{ab}} = 9.1$ ,  $J_{\text{ac}} = 8.0$  Hz, 1H,  $\text{H}_a$ ), 3.47 (dd,  $J_{\text{ba}} = 9.1$ ,  $J_{\text{bc}} = 6.0$  Hz, 1H,  $\text{H}_b$ ), 5.57 (dd,  $J_{\text{ca}} = 8.0$ ,  $J_{\text{cb}} = 6.0$  Hz, 1H,  $\text{H}_c$ ), 7.76 (t,  $^3J_{\text{HH}} = 6.8$  Hz, 1H, H-5), 7.94 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 1H, H-3), 8.32 (td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.5$  Hz, 1H, H-4), 9.47 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 1H, H-6).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  52.1 ( $\text{CH}_2\text{-Au}$ ), 62.9 ( $\text{CH-Cl}$ ), 126.3 (C-5), 127.7 (C-3), 144.6 (C-4), 149.3 (C-6).

#### 4.7. $[\text{Au}\{\text{CH}_2\text{CH}(\text{Cl})\text{C}_5\text{H}_4\text{N}\}(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ (**6-PF<sub>6</sub>**)



To a stirred solution of **5** (0.075 mmol) in acetone (25 mL) were added  $\text{PPh}_3$  (0.075 mmol) and  $\text{KPF}_6$  (0.225 mmol). The solution was stirred for 3 h, then concentrated to small volume and diethyl ether added to give a yellow precipitate which was filtered, washed with diethyl ether, and dried in vacuo. Recrystallization from dichloromethane/diethyl ether gave the analytical sample. Yield: 69%. M.p.: 191 °C. Anal. Calc. for  $\text{C}_{25}\text{H}_{22}\text{AuCl}_2\text{F}_6\text{NP}_2$ : C, 38.58; H, 2.85; N, 1.80. Found: C, 38.62; H, 2.24; N, 1.85%. IR ( $\nu/\text{cm}^{-1}$ , nujol): 1611 m, 1281 s, 1216 m, 1102 s ( $\text{PPh}_3$ ), 840 vs ( $\text{PF}_6$ ), 776 m, 748 s, 717 m, 691 s, 558 s, 537 s, 503 m, 304 m (Au–Cl).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta$  2.52 (ddd,  $J_{\text{ab}} = 10.5$ ,  $J_{\text{ac}} = 5.1$ ,  $J_{\text{H-P}} = 4.0$  Hz, 1H,  $\text{H}_a$ ), 3.17 (ddd,  $J_{\text{ba}} = 10.5$ ,  $J_{\text{bc}} = 4.8$ ,  $J_{\text{H-P}} = 1.8$  Hz, 1H,  $\text{H}_b$ ), 5.51 (broad t, 1H,  $\text{H}_c$ ), 7.65–7.85 (m, 16 H,  $\text{CH PPh}_3$  + H-5), 7.96 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 1H, H-3), 8.30 (td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.5$  Hz, 1H, H-4), 9.46 (pseudo-t,  $^3J_{\text{HH}} = 5.0$  Hz, 1H, H-6); ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  3.01–3.06 (m, 2H,  $\text{H}_a + \text{H}_b$ ), 6.03 (pseudo-t,  $J_{\text{ca}} = J_{\text{cb}} = 6.4$  Hz, 1H,  $\text{H}_c$ ), 7.71–8.03 (m, 15 H,  $\text{CH PPh}_3$ ), 8.06 (td,  $^3J_{\text{HH}} = 6.8$  Hz, 1H, H-5), 8.15 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 1H, H-3), 8.54 (td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, H-4),



9.47 (pseudo-t,  $^3J_{\text{HH}} = 5.1$ , 1H, H-6).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta$  29.2 (s,  $\text{PPh}_3$ ), -144.2 (sept,  $\text{PF}_6$ ). Crystals of X-ray quality were obtained by slow evaporation of an acetone solution.

#### 4.8. $[\text{Au}\{\text{CH}_2\text{CH}(\text{Cl})\text{C}_5\text{H}_4\text{N}\}(\text{CH}_2=\text{CHC}_5\text{H}_4\text{N})\text{Cl}][\text{PF}_6]$ (**8**- $\text{PF}_6$ )

To an acetone solution of **5** (83.0 mg, 0.2 mmol) were added 2-vinylpyridine (21.3 mg, 0.2 mmol) and  $\text{AgPF}_6$  (51.3 mg, 0.2 mmol), with stirring. The resulting mixture was stirred for 6 h at room temperature, then silver chloride was filtered off and the solution evaporated to dryness. The residue was extracted with dichloromethane, filtered and concentrated to small volume; addition of diethyl ether gave a grey solid that was filtered off and dried in vacuo. Yield 77%. Mp: 99 °C. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{AuCl}_2\text{F}_6\text{N}_2\text{P}$  (623.11): C, 26.99; H, 2.26; N, 4.50. Found: C, 27.15; H, 2.36; N, 4.42%. IR ( $\nu/\text{cm}^{-1}$ , nujol): 1609 m, 1168 w, 970 w, 840 vs ( $\text{PF}_6$ ), 780 w, 721 m, 557 m, 375 m (Au–Cl), 305 w (Au–Cl).  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 293 K):  $\delta$  3.61 (dd,  $J_{\text{ab}} = 8.7$ ,  $J_{\text{ac}} = 5.2$  Hz, 1H, Au– $\text{CH}_a\text{H}_b$  A), 3.63 (dd,  $J_{\text{ab}} = 8.8$ ,  $J_{\text{ac}} = 4.2$  Hz, 1H, Au– $\text{CH}_a\text{H}_b$  B), 3.75 (dd,  $J_{\text{ba}} = 8.8$ ,  $J_{\text{bc}} = 6.3$  Hz, 1H, Au– $\text{CH}_a\text{H}_b$  B), 3.76 (dd,  $J_{\text{ba}} = 8.7$  Hz,  $J_{\text{bc}} = 5.9$  Hz, 1H, Au– $\text{CH}_a\text{H}_b$  A), 5.94–6.12 (m + d + d, 4H,  $\text{CHCl}$  A +  $\text{CHCl}$  B +  $=\text{CH}_a\text{H}_b$  A +  $=\text{CH}_a\text{H}_b$  B), 6.44 (d,  $J_{\text{ac}} = 17.3$  Hz, 1H,  $=\text{CH}_a\text{H}_b$  A), 6.52 (dd,  $J_{\text{ac}} = 17.0$ ,  $J_{\text{ab}} = 1.5$  Hz, 1H,  $=\text{CH}_a\text{H}_b$  B), 7.63–7.81 (ms, 2H,  $=\text{CH}_c$  A + B), 7.9–9.5 (ms, 16H, pyH A + B); A:B = 1:2.

### 5. X-ray data collection and structure determination

Crystal data are summarised in Table 2. The diffraction experiment was carried out on a Bruker APEX II CCD area-detector dif-

fractometer at 150 K, using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$ ) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT [26] and an empirical absorption correction was applied (SADABS) [27] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [28] and the physical constants tabulated therein [29]. The structure was solved by direct methods (SHELXS) [30] and refined by full-matrix least-squares using all reflections and minimising the function  $\sum w(F_o^2 - kF_c^2)^2$  (refinement on  $F^2$ ). All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms were placed in their ideal positions ( $\text{C}-\text{H} = 0.97$  Å), with the thermal parameter  $U$  1.10 times that of the carbon atom to which they are attached, and not refined. As the space group is non centrosymmetric, full refinement of the correct structure model led to  $R_2 = 0.046$  and  $R_{2w} = 0.083$ , full refinement of the inverted structure led to  $R_2 = 0.101$  and  $R_{2w} = 0.169$ . In the final Fourier map the maximum residual was  $2.34(31) \text{ e } \text{\AA}^{-3}$  at  $1.98$  Å from P1.

### Acknowledgement

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### Appendix A. Supplementary data

CCDC 725517 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.04.031](https://doi.org/10.1016/j.jorganchem.2009.04.031).

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**Table 2**

Crystallographic data and structure refinement details for **6**.

Compound formula	$\text{C}_{25}\text{H}_{22}\text{AuCl}_2\text{F}_6\text{N}_2\text{P}$
<i>M</i>	780.27
Colour	Colourless
Crystal system	Orthorhombic
Space group	$\text{Pna}2_1$
<i>a</i> (Å)	20.8361(12)
<i>b</i> (Å)	15.6902(9)
<i>c</i> (Å)	8.3264(5)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>U</i> (Å <sup>3</sup> )	2722.1(3)
<i>Z</i>	4
$F(000)$	1504
$D_c$ (g cm <sup>-3</sup> )	1.904
<i>T</i> (K)	150
Crystal dimensions (mm)	$0.15 \times 0.22 \times 0.31$
$\mu$ (Mo $\text{K}\alpha$ ) (cm <sup>-1</sup> )	57.65
Minimum and maximum transmission	
Factors	0.698–1.000
Scan mode	$\omega$
Frame width (°)	0.40
Time per frame (s)	15
No. of frames	2760
Detector-sample distance (cm)	6.00
$\theta$ -Range	3–28
Reciprocal space explored	Full sphere
No. of reflections	
(total; independent)	49 836, 7104
$R_{\text{int}}$	0.0381
Final $R_2$ and $R_{2w}$ indices <sup>a</sup>	
( $F^2$ , all reflections)	0.046, 0.083
Conventional $R_1$ index	
[ $I > 2\sigma(I)$ ]	0.031
Reflections with $I > 2\sigma(I)$	6040
No. of variables	334
Goodness of fit <sup>b</sup>	1.003

<sup>a</sup>  $R_2 = [\sum (|F_o^2 - kF_c^2| / \sum F_o^2)] / \sum F_o^2$ ,  $R_{2w} = [\sum w(F_o^2 - kF_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .  
<sup>b</sup>  $[\sum w(F_o^2 - kF_c^2)^2 / (N_o - N_v)]^{1/2}$ , where  $w = 4F_o^2 / \sigma(F_o^2)^2$ ,  $\sigma(F_o^2) = [\sigma^2(F_o)] / (0.05F_o^2)^{1/2}$ ,  $N_o$  is the number of observations and  $N_v$  the number of variables.

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