

# Replacement of the chloride ligand in $[\text{Au}(\text{C},\text{N},\text{N})\text{Cl}][\text{PF}_6]$ cyclometallated complexes by C, N, O and S donor anionic ligands

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Replacement of the chloride ligand in the cyclometallated complexes  $[\text{Au}(\text{C},\text{N},\text{N})\text{Cl}][\text{PF}_6]$  ( $\text{C},\text{N},\text{N} = \text{N}_2\text{C}_{10}\text{H}_7(\text{CH}_2\text{C}_6\text{H}_4)-6$  **1**,  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)-6$  **2**, or  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)-6$  **3**, where  $\text{N}_2\text{C}_{10}\text{H}_8 = 2,2'$ -bipy) by C, N, O and S donor anionic ligands Y was accomplished through different routes depending both on the nature of HY or the C,N,N ligand. Stable alkoxo  $[\text{Au}(\text{C},\text{N},\text{N})(\text{OR})][\text{PF}_6]$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) and amido  $[\text{Au}(\text{C},\text{N},\text{N})(\text{NHAr})][\text{PF}_6]$  ( $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2-4$ ) complexes were obtained in fairly good yields. The molecular structure of the thiolato complex  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)-6\}(\text{SPh})][\text{PF}_6]$  has been determined by X-ray crystallography. The diorgano-gold(III) complex  $[\text{Au}(\text{C},\text{N},\text{N})(\text{C}_2\text{Ph})][\text{PF}_6]$  on addition of  $\text{PPh}_3$  (1 : 2) undergoes reductive elimination to give  $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$  and an unsymmetric diarylacetylene.

## Introduction

Substitution reactions play an important role in organo-transition metal chemistry being an essential first step, and sometimes the rate-controlling step, in stoichiometric and catalytic reactions.<sup>1</sup>

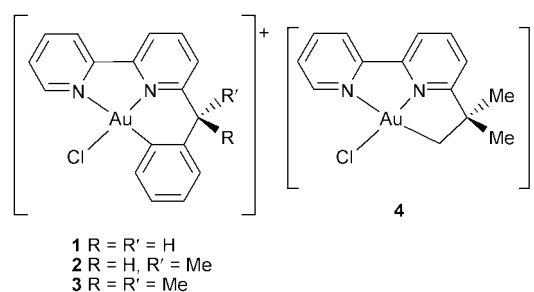
Organogold chemistry has been recently reviewed<sup>2</sup> in light of the applications of some new derivatives in various fields including homogeneous catalysis.<sup>3</sup> Both gold(I) and -(III) organic derivatives are reported in the review and in more recent papers: among them, gold(III) cyclometallated complexes,<sup>4</sup> a recent topic of interest, are described and their potential applications in organic synthesis,<sup>5</sup> photochemistry<sup>4c,i,6</sup> or chemotherapy<sup>4e,i,7</sup> pointed out as well. Replacement of halide ions by suitable ligands is the general procedure to obtain most of these cycloaurated complexes.

In a previous paper<sup>8</sup> we have described the synthesis and the crystal structures of a series of gold(III) cyclometallated complexes  $[\text{Au}(\text{C},\text{N},\text{N})\text{Cl}][\text{X}]$  ( $\text{X} = \text{BF}_4$  or  $\text{PF}_6$ ) with three 6-benzyl-2,2'-bipyridines and one 6-alkyl-2,2'-bipyridine. Few other gold(III) cyclometallated complexes with C,N,N tridentate ligands, all bearing a chloride as fourth ligand, are reported<sup>6</sup> and in no case substitution reaction derivatives.

In the present paper we describe the synthesis, characterization and reactivity of a number of new gold(III) cyclometallated derivatives  $[\text{Au}(\text{C},\text{N},\text{N})(\text{Y})][\text{PF}_6]$  ( $\text{C},\text{N},\text{N} = 6$ -benzyl-2,2'-bipyridine;  $\text{Y} = \text{C}-$ ,  $\text{N}-$ ,  $\text{O}-$  or  $\text{S}-$ donor anionic ligand) obtained by replacement of a chloride ligand. Among these, stable methoxo and ethoxo complexes  $[\text{Au}(\text{C},\text{N},\text{N})(\text{OR})][\text{PF}_6]$  are obtained in fairly good yields by means of different approaches; these compounds are versatile intermediates in the synthesis of other derivatives such as, for example the amido complexes  $[\text{Au}(\text{C},\text{N},\text{N})(\text{NHAr})][\text{PF}_6]$ . Gold alkoxides are an attractive topic of interest in the light of the recent discovery of the catalytic activity displayed by some gold(I) and -(III) fluoro-alkoxides.<sup>3a</sup> To the best of our knowledge simple alkoxo complexes ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) are unprecedented in gold(III) chemistry, whereas a few examples of amido species<sup>9</sup> have been reported. Further investigations will be devoted to ascertain the potential of the new derivatives.

## Results and discussion

In a previous paper<sup>8</sup> concerning the synthesis and the crystal structures of a series of gold(III) cyclometallated complexes  $[\text{Au}(\text{C},\text{N},\text{N})\text{Cl}]^+$  **1–4** with 6-benzyl- and 6-alkyl-2,2'-bipyridines we reported that displacement of the chloride by a neutral ligand such as  $\text{PPh}_3$  occurs only in complex **4** $[\text{BF}_4]$  to give the dicationic derivative  $[\text{Au}(\text{C},\text{N},\text{N})(\text{PPh}_3)]^{2+}$ . Under the same reaction conditions, complexes **2** $[\text{BF}_4]$  and **3** $[\text{BF}_4]$  undergo displacement of the nitrogen *trans* to the carbon atom to yield  $[\text{Au}(\text{C},\text{N},\text{N})(\text{PPh}_3)\text{Cl}]^+$  ( $\text{C},\text{N},\text{N} = \text{C},\text{N}$ -ligated 6-benzyl-2,2'-bipyridine). In the latter cases spectroscopic evidence suggested that isomerization also occurs to give the more thermodynamically stable complex, *i.e.* that with the C and P ligands in mutually *cis* position.

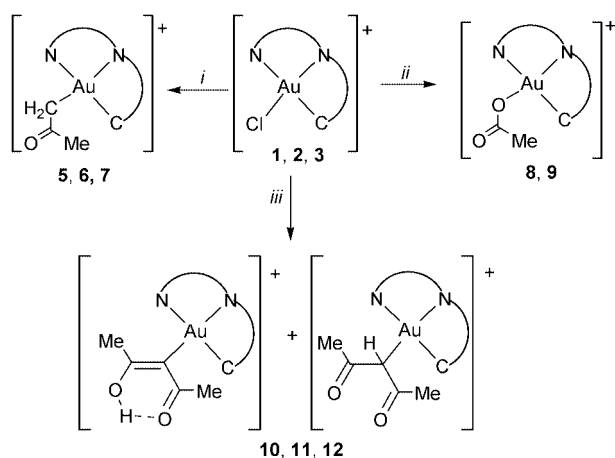


The forced displacement of the chloride from compound **2** $[\text{BF}_4]$  by means of  $\text{AgBF}_4$  was also reported; the outcome of the reaction, carried out in refluxing acetone, was an acetonil derivative  $[\text{Au}(\text{C},\text{N},\text{N})\{\text{CH}_2\text{C}(\text{O})\text{Me}\}][\text{BF}_4]$ , similar to those described by Vicente *et al.*<sup>5c</sup> for C,N cycloaurated complexes and reported to be efficient starting materials for the synthesis of ketones *via* C–C coupling.

Successively we have observed that in the reaction of compounds **2** $[\text{BF}_4]$  and **3** $[\text{BF}_4]$  with  $\text{AgBF}_4$  in acetone at room temperature, besides acetonil derivatives, dinuclear oxo-bridged complexes  $[\text{Au}_2(\text{C},\text{N},\text{N})_2(\mu\text{-O})][\text{BF}_4]_2$  are formed.<sup>10</sup> The latter compounds are the first examples of gold(III) oxo-bridged

cyclometallated derivatives. The reactivity of these species is currently under investigation.

Surprisingly when complexes **1** [ $\text{PF}_6$ ]-**3** [ $\text{PF}_6$ ] are treated with  $\text{AgPF}_6$  in acetone solution the acetonyl derivatives  $[\text{Au}(\text{C},\text{N},\text{N})\text{-}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}][\text{PF}_6]$  **5**-**7** are solely obtained in high yields (*ca.* 80%). When silver or thallium salts of co-ordinating anions are employed replacement of the chloride by the anionic ligands occurs:  $[\text{Au}(\text{C},\text{N},\text{N})(\text{O}_2\text{CMe})]^+$  **8** and **9** and  $[\text{Au}(\text{C},\text{N},\text{N})(\text{acac})]^+$  **10**-**12** [ $\text{C},\text{N},\text{N} = \text{N}_2\text{C}_{10}\text{H}_7(\text{CH}_2\text{C}_6\text{H}_4)$ -**6** **10**,  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)$ -**6** **8** and **11**,  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)$ -**6** **9** and **12**;  $\text{Hacac} = \text{CH}_2\{\text{C}(\text{O})\text{Me}\}_2$ ] are obtained in good yields from the reaction at room temperature of complexes **1**-**3** with  $\text{AgO}_2\text{CMe}$  in acetone solution and with  $\text{Tl}(\text{acac})$  in  $\text{CH}_2\text{Cl}_2$ , respectively (Scheme 1).



**Scheme 1** (i)  $+\text{AgPF}_6$ ,  $\text{Me}_2\text{CO}$ ,  $-\text{AgCl}$ ; (ii)  $+\text{AgO}_2\text{CMe}$ ,  $\text{Me}_2\text{CO}$ ,  $-\text{AgCl}$ ; (iii)  $+\text{Tl}(\text{acac})$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-\text{TlCl}$ ,  $\text{C},\text{N},\text{N} = \text{N}_2\text{C}_{10}\text{H}_7(\text{CH}_2\text{C}_6\text{H}_4)$ -**6** **1**, **5**, **10**;  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)$ -**6** **2**, **6**, **8**, **11**; or  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)$ -**6** **3**, **7**, **9**, **12**.

The reaction of complex **1** with  $\text{AgO}_2\text{CMe}$  failed to give the acetato derivative. The IR and  $^1\text{H}$  NMR spectra of a whitish product, isolated in small amounts, are complex; the undoubted fact is that activation of a benzylic C-H bond has occurred. Complexes **8**-**12** gave satisfactory analyses and their molecular ions  $M^+$  have been detected by FAB mass spectrometry (see Experimental section).

Complexes **8** and **9** show strong bands at  $1666$  ( $\nu_{\text{asym}}(\text{CO}_2)$ ) and  $1270$   $\text{cm}^{-1}$  ( $\nu_{\text{sym}}(\text{CO}_2)$ ) and  $1669$  and  $1264$   $\text{cm}^{-1}$ , respectively, typical of monodentate O-bonded acetato ligands.<sup>11</sup> The IR spectra of the acetylacetonate derivatives **10**-**12** show one medium absorption at  $1675$   $\text{cm}^{-1}$ , sometimes flanked by a shoulder at *ca.*  $1700$   $\text{cm}^{-1}$ , *i.e.* in a region characteristic of the C=O stretching modes of a C-bonded acac ligand.<sup>11</sup> Nevertheless, the profile appears more complex than expected for such a co-ordination mode, and other bands overlapped by those of the bipyridine ligand in the region  $1600$ - $1575$   $\text{cm}^{-1}$  cannot be excluded. The  $^1\text{H}$  NMR spectra in various solvents show the presence of two isomers in molar ratios that depend on the solvent. Complex **11** is a *ca.* 3:1 mixture of isomers: the major species is characterized by the presence in the  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; room temperature) of a sharp singlet at  $\delta$  16.30 (16.46 for **12**) which disappears upon addition of  $\text{D}_2\text{O}$  (Table 1). We feel confident to assign this resonance to a hydrogen-bonded OH of a C-bonded acac ligand in the enol form. The second isomer shows a resonance at  $\delta$  5.31 (5.30 for **12**), which exchanges with  $\text{D}_2\text{O}$ , assigned to the  $\alpha$ -methine proton of a C-bonded acac ligand in the keto form. For complex **11** the molar ratio of the two tautomers is slightly temperature dependent in the range  $-80$  to  $+54$   $^\circ\text{C}$ : on going from  $-80$  to  $+20$   $^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  solution a *ca.* seven per cent increase of the keto tautomer is observed, whereas a comparable decrease is observed on going from  $+20$  to  $+54$   $^\circ\text{C}$  in  $\text{CDCl}_3$  solution. In complex **11** the methyl protons of the acac ligand in both tautomers are not

equivalent likely owing to hindered rotation of the acac ligand about the Au-C bond, as suggested by inspection of molecular models.

The  $^1\text{H}$  NMR spectrum of complex **10** in various solvents features a more complicated situation; in  $\text{CDCl}_3$  singlets at  $\delta$  16.36 and 16.30 (integral ratio 0.4:1) (which disappear by addition of  $\text{D}_2\text{O}$ ) and two singlets at  $\delta$  5.31 and 5.29 (*ca.* 1:2) (which do not exchange with  $\text{D}_2\text{O}$ ) are found for the two tautomers, respectively. Besides these, several other minor signals are present.

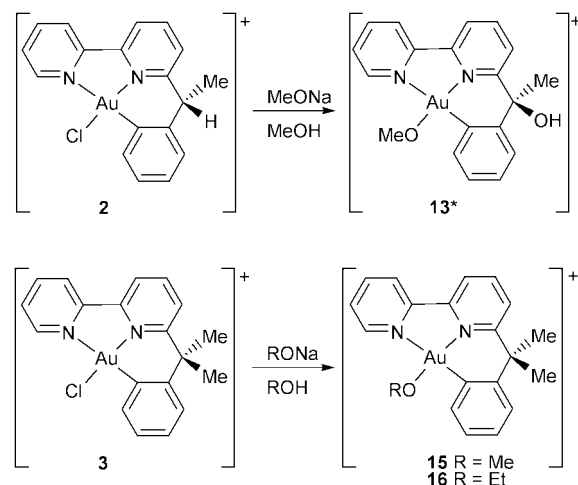
The C(3) bonding of the acetylacetonate anion in the keto form to several metals including gold(III)<sup>12</sup> is well established. At variance such bonding in the enol form has been proposed in some cases including gold(III).<sup>12a</sup> In our complexes, the  $\{\text{Au}(\text{C},\text{N},\text{N})\}$  fragment with formal charge +2 can account for the stabilization of the enol form: it is known that electron-withdrawing substituents favour the enol tautomer of  $\beta$ -diketones.<sup>13</sup>

In contrast to C,N cyclometallated gold(III) acetylacetonate complexes, **10**-**12** do not activate acetone to give the corresponding acetonyl derivatives.<sup>12b-e</sup> Treatment of **11** with acetone for one day at room temperature results in a *ca.* ten per cent increase of the enol tautomer ( $^1\text{H}$  NMR criterion).

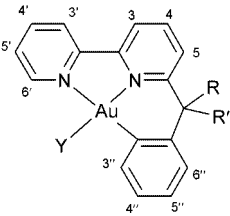
As it will be shown, the acetato derivatives **8** and **9** are useful intermediates, therefore we tried to synthesize them by metathesis reaction with sodium acetate. The reaction was carried out in various solvents giving different results for the chloro complexes **2** and **3**. From the reaction of **2** in acetone a new species  $[\text{Au}(\text{C},\text{N},\text{N}^*)\text{Cl}]^+$  **2\*** was isolated which contains the cyclometallated anion  $\text{N}_2\text{C}_{10}\text{H}_7\{\text{C}(\text{OH})\text{MeC}_6\text{H}_4\}$ -**6**, C,N,N\*, resulting from the activation of the benzylic C-H bond; no displacement of the chloride was observed. Complex **3** reacts only in part to give **9** and the acetonyl derivative. Unchanged **2** or **3** is recovered almost quantitatively when the reaction is carried out in refluxing acetonitrile-water.

Activation of the solvent was also observed when complex **2** was treated with an equimolar amount of KOH in acetone or in methanol. In acetone, a mixture of unchanged **2**, acetonyl derivative **6** and a unidentified product is obtained ( $^1\text{H}$  NMR criterion). Unchanged **2**, dinuclear oxo  $[\text{Au}_2(\text{C},\text{N},\text{N})_2(\mu\text{-O})]^{2+}$  and methoxo  $[\text{Au}(\text{C},\text{N},\text{N})(\text{OMe})]^+$  **13** complexes were formed in methanol; under these conditions no activation of the benzylic C-H was observed. Unfortunately pure products cannot be separated from these mixtures either by chromatography or crystallization.

Alkoxo complexes  $[\text{Au}(\text{C},\text{N},\text{N})(\text{OR})]^+$  ( $\text{R} = \text{Me}$  **15** or  $\text{Et}$  **16**) have been synthesized by metathesis reaction on **3** using sodium alkoxide in the corresponding alcohol (Scheme 2). Under the same conditions, **2** gave the methoxide  $[\text{Au}(\text{C},\text{N},\text{N}^*)(\text{OMe})]^+$  **13\***; whereas with  $\text{EtONa}$  a mixture of unchanged **2**, **2\*** and



**Scheme 2**

**Table 1** Proton NMR data<sup>a</sup>


Compound	Solvent	H <sup>6'</sup>	Other aromatics	CH	CH <sub>2</sub>	Me	Others (Y)
<b>1</b>	(CD <sub>3</sub> ) <sub>2</sub> CO	9.42 (dd)	8.99–7.15		4.93 (s)		
<b>2</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.38 (dd)	8.82–7.15	4.79 (q, 7.2)		1.85 (d, 7.2)	
	(CD <sub>3</sub> ) <sub>2</sub> CO	9.45 (dd)	9.00–7.17	5.18 (q, 7.1)		1.87 (d, 7.1)	
<b>3</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.35 (dd)	8.68–7.13			2.14 (s)	
	(CD <sub>3</sub> ) <sub>2</sub> CO	9.40 (dd)	9.00–7.14			2.19 (s)	
<b>5</b>	CDCl <sub>3</sub>	9.24 (dd)	8.66–7.16		4.53 (s)		3.50 (s) CH <sub>2</sub> ; 2.33 (s) Me
<b>6</b>	(CD <sub>3</sub> ) <sub>2</sub> CO	9.41 (d)	8.95–7.25	4.99 (q, 7.3)		1.89 (d, 7.3)	3.62 (s) CH <sub>2</sub> ; 2.29 (s) Me
<b>7</b>	CDCl <sub>3</sub>	9.25 (d)	8.72–7.18			2.10 (s)	3.50 (s) CH <sub>2</sub> ; 2.31 (s) Me
<b>8</b>	CD <sub>2</sub> Cl <sub>2</sub>	8.78 (dd)	8.66–7.21	4.82 (q, 7.2)		1.85 (d, 7.2)	2.35 (s) Me
<b>9</b>	CD <sub>2</sub> Cl <sub>2</sub>	8.77 (dd)	8.68–7.19			2.14 (s)	2.35 (s) Me
<b>10<sup>b</sup></b>	CDCl <sub>3</sub>	[1.5] [1] [2.6] [1] [1.3] [1]	8.69 (dd) 8.84 (dd) <i>d</i> 8.83 (dd) <i>d</i> 8.86 (dd)	8.65–7.00 <sup>c</sup>  8.74–7.03 <sup>c</sup>  8.76–7.08 <sup>c</sup>	4.63 (s) 4.57 (s)  4.65 <sup>c</sup> (q, 7.3)		16.36 (s), 16.30 (s) OH; 2.25 (s) Me 5.31 (s), 5.29 (s) CH; 2.48 (s) Me 16.30 (s) OH; 2.30 (s), 2.22 (s) Me 5.31 (s) CH; 2.49 (s), 2.46 (s) Me 16.46 (s) OH; 2.25 (s) Me 5.30 (s) CH; 2.47 (s) Me 3.86 (s) MeO; 3.43 (s, br) OH
<b>11<sup>b</sup></b>	CDCl <sub>3</sub>					1.81 (d, 7.3) 1.92 (d, 7.3) 2.11 (s) 2.15 (s) 2.04 (s)	3.91 (s) MeO 4.05 (m, <sup>2</sup> J = 10.5; <sup>3</sup> J = 6.8) CH <sub>2</sub> ; 1.50 (t, 6.8) Me 3.94 (s) MeO 4.06 (q, 6.8) CH <sub>2</sub> , 1.51 (t, 6.8) Me
<b>12<sup>b</sup></b>	CDCl <sub>3</sub>					1.80 (d, 7.1) 1.81 (d, 7.3)	
<b>13<sup>*</sup></b>	CD <sub>2</sub> Cl <sub>2</sub>	9.10 (dd)	8.64–7.25			2.04 (s)	
<b>13</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.18 (dd)	8.64–7.34	4.79 (q, 7.1)		1.80 (d, 7.1)	
<b>14</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.19 (dd)	8.63–7.34	4.78 (q, 7.3)		1.81 (d, 7.3)	
<b>15</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.14 (dd)	8.63–7.31			2.11 (s)	
<b>16</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.15 (dd)	8.62–7.27			2.10 (s)	
<b>17</b>	CDCl <sub>3</sub>	9.31 (d)	8.74–7.08 <sup>e</sup>	4.61 (q, 7.1)		1.74 (d, 7.1)	
<b>18</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.38 (dd)	8.67–7.09 <sup>e</sup>			2.07 (s)	
<b>19</b>	(CD <sub>3</sub> ) <sub>2</sub> CO	9.17 (d)	8.99–7.09	5.12 (q, 7.1)		1.90 (d, 7.1)	7.95 (d, 9.0, 2H) H <sup>meta</sup> ; 7.12 (d, 9.0, 2H) H <sup>ortho</sup> ; 6.90 (s) NH
<b>20</b>	(CD <sub>3</sub> ) <sub>2</sub> CO	9.13 (dd)	9.00–7.05			2.21 (s)	7.94 (d, 9.3, 2H) H <sup>meta</sup> ; 7.07 (d, 9.3, 2H) H <sup>ortho</sup> ; 6.92 (s) NH
<b>21</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.54 (d)	8.69–7.21 <sup>f</sup>	4.77 (q, 7.2)		1.84 (d, 7.2)	
<b>22</b>	CD <sub>2</sub> Cl <sub>2</sub>	9.46 (dd)	8.67–7.15 <sup>f</sup>			2.11 (s)	

<sup>a</sup> Spectra recorded at room temperature; chemical shifts in ppm from internal SiMe<sub>4</sub>, coupling constants (in parentheses) in Hz. <sup>b</sup> Enol and keto isomers, integral ratios are in square brackets; the first line refers to the enol unless otherwise stated. <sup>c</sup> Enol + keto. <sup>d</sup> Overlapped. <sup>e</sup> C,N,N + PhS. <sup>f</sup> C,N,N + PhC<sub>2</sub>.

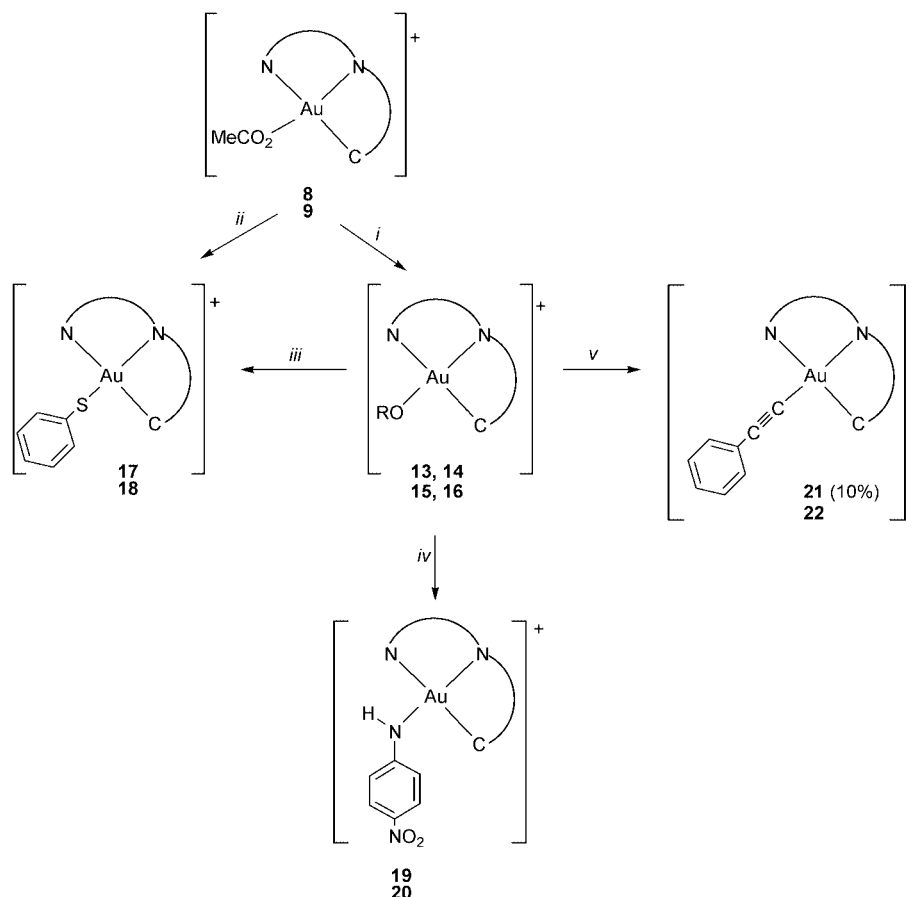
trace amounts of the ethoxide [Au(C,N,N)(OEt)]<sup>+</sup> **14** are formed.

Once again, treatment of complex **2** with strong bases resulted in activation of the co-ordinated ligand. Since in the presence of benzylic C–H bonds this approach for the substitution of the chloride ligand is not straightforward a different route for the preparation of alkoxides was developed, at least for **2**. In a typical reaction, the acetato derivative [Au(C,N,N)(O<sub>2</sub>CMe)]<sup>+</sup> **8** was dissolved in methanol and the resulting solution stirred at room temperature until a white precipitate of the methoxide **13** was separated in fairly good yield. The analogous reaction of **8** in ethanol to give the ethoxide **14** required a slightly modified procedure (see Experimental section). σ-Ligand metathesis reaction is a very useful synthetic method to prepare late transition metal alkoxides by addition of alcohols to other metal alkoxides, amides or hydroxides;<sup>14</sup> less common is the metathesis of an acetato complex. Complexes **13–16** are the first isolated methoxo- and ethoxo-gold complexes: actually, gold alkoxides are rare and unstable unless bulky alkoxides, fluoro-substituted alkoxides or aryl oxides are employed.<sup>15</sup> Recently a series of gold-(I) and -(III) fluoro-alkoxides displaying catalytic activity has been reported.<sup>3a</sup>

Complexes **13–16** are air stable white solids with relatively high melting points; they gave satisfactory analyses and their molecular ions M<sup>+</sup> have been detected by FAB mass spectrometry. The IR spectra of **13** and **15** are characterized by

strong ν(C–O) absorptions at 1016 and 1024 cm<sup>−1</sup> respectively; the MeO protons resonate at δ 3.91 (complex **13**) and 3.94 (**15**) in CD<sub>2</sub>Cl<sub>2</sub>. For complex **14** the ethoxide protons appear as an AA'B<sub>3</sub> pattern: the diastereotopic methylene protons give rise to two doublets of quartets at δ 4.05 (CD<sub>2</sub>Cl<sub>2</sub>) with <sup>2</sup>J = 10.5 and <sup>3</sup>J = 6.8 Hz; the methyl protons appear as a triplet at δ 1.50 with J = 6.8 Hz. At variance with **14**, the methylene protons in complex **16** are equivalent giving rise to a quartet at δ 4.06 (CD<sub>2</sub>Cl<sub>2</sub>) with <sup>3</sup>J = 6.8 Hz; the methyl protons appear as a triplet at δ 1.51.

The acetato complexes do not react with the more bulky and less acidic *t*-BuOH under various reaction conditions. As expected, the reaction with the more acidic PhSH proceeds smoothly to yield the thiolato complexes [Au(C,N,N)(SPh)]<sup>+</sup> (C,N,N = N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6 **17**, or N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6 **18**) (Scheme 3). They are air stable bright yellow solids soluble in the common organic solvents. The crystal structure of **18**[PF<sub>6</sub>]<sub>2</sub> has been determined by single crystal X-ray diffraction (see below). Complexes **17** and **18** are likewise easily obtained from the reaction of the methoxides **13** and **15** with PhSH. The methoxo complexes [Au(C,N,N)(OMe)]<sup>+</sup> are intermediates more versatile than the acetato derivatives being able to abstract a proton from weak acids such as PhC<sub>2</sub>H or NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4 to give the σ-ligand metathesis products. The monomeric amido complexes [Au(C,N,N)(NHAr)]<sup>+</sup> (C,N,N = N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6 **19** or N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6 **20**) are formed in high

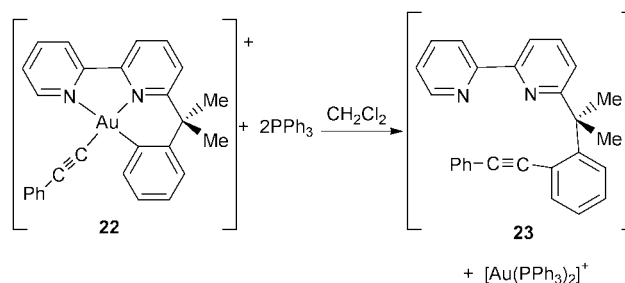


**Scheme 3** (i) + ROH,  $-\text{MeCO}_2\text{H}$ ; (ii) + PhSH,  $-\text{MeCO}_2\text{H}$ ; (iii) + PhSH,  $-\text{MeOH}$ ; (iv) +  $\text{H}_2\text{NC}_6\text{H}_4\text{NO}_2$ -4,  $-\text{MeOH}$ ; (v) +  $\text{PhC}_2\text{H}$ ,  $-\text{MeOH}$ . C,N,N =  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)$ -6 **13**, **14**, **17**, **19**, **21** or  $\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)$ -6 **15**, **16**, **18**, **20**, **22**; R = Me **13**, **15** or Et **14**, **16**.

yields by treatment of **13** and **15**, respectively, with the amine in dichloromethane solution. The reaction is most likely reversible;<sup>14</sup> it is driven to completion by the addition of an excess of reagent as well as by the low solubility of the product in the reaction solvent. The amido complexes **19** and **20** are orange-yellow air stable compounds both in the solid state and in solution at room temperature. The IR spectra are characterized by a sharp strong  $\nu(\text{N-H})$  absorption at  $3350\text{ cm}^{-1}$  and by very strong absorptions at *ca.*  $1580$  and *ca.*  $1280\text{ cm}^{-1}$  due to the asymmetric and symmetric stretching vibrations of the  $\text{NO}_2$  group. The  $^1\text{H}$  NMR spectra in  $(\text{CD}_3)_2\text{CO}$  of **19** and **20** reveal a medium broad singlet at  $\delta$  6.90 and 6.92, respectively, for the N-H proton which disappears upon addition of  $\text{D}_2\text{O}$ . The aromatic region shows, for both complexes, well separated resonances for the fifteen protons. For **19** broadening of the  $\text{H}^6$  and  $\text{H}^{3'}$  resonances is observed at room temperature likely due to coupling to the  $^{14}\text{N}$  quadrupole nucleus of the  $\text{NHC}_6\text{H}_4\text{NO}_2$ -4 ligand.

The methoxo complex  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)\text{-6}\}(\text{OMe})]^+$  **15** undergoes facile exchange reaction with  $\text{PhC}_2\text{H}$  to give the alkynyl derivative  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)\text{-6}\}(\text{C}_2\text{Ph})]^+$  **22**; only small amounts of the analogous complex  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)\text{-6}\}(\text{C}_2\text{Ph})]^+$  **21** are obtained from **13**. In the latter case the outcome of the reaction is the oxo complex  $[\text{Au}_2\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CHMeC}_6\text{H}_4)\text{-6}\}_2(\mu\text{-O})]^{2+}$ . Similar results were found even when the ethoxide **14** was employed in place of **13**. In the IR spectra of the alkynyl derivatives no absorption due to the  $\text{C}\equiv\text{C}$  stretching mode was observed, nevertheless a medium intensity band at *ca.*  $700\text{ cm}^{-1}$  indicates the presence of a mono-substituted phenyl ring. In the  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  of **21** and **22** the resonance of the  $\text{H}^6$  proton is strongly deshielded due to anisotropy effects originated by the alkynyl ligand; the aromatic protons are in the correct integral ratios.

The diorganogold derivative  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)\text{-6}\}(\text{C}_2\text{Ph})][\text{PF}_6]$  **22**, on addition of  $\text{PPh}_3$  (molar ratio



**Scheme 4**

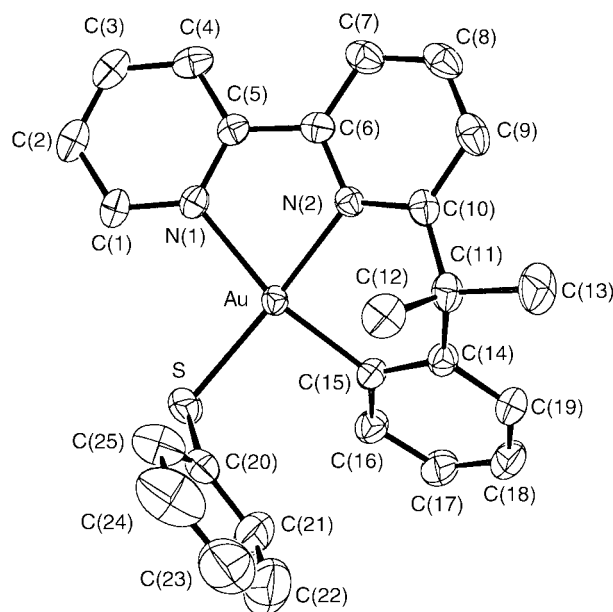
$\text{Au}:\text{PPh}_3 = 1:2$ ), at room temperature, undergoes reductive elimination to give  $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$  and the C-C coupling product  $\text{N}_2\text{C}_{10}\text{H}_7\{\text{CMe}_2\text{C}_6\text{H}_4(\text{C}_2\text{Ph})\text{-2''}\}$ -6 **23** in quantitative yields (Scheme 4). Various C-C coupling products have been obtained by thermolysis of alkyl-,<sup>16</sup> alkylaryl-,<sup>16e,17</sup> alkyl(alkoxy-carbonyl)-<sup>18</sup> and vinyl-gold(III)<sup>16e,19</sup> complexes. Symmetrical and unsymmetrical biaryls as well as benzyl alkyl and benzyl aryl ketones have been synthesized under mild conditions *via* C-C coupling by addition of  $\text{PPh}_3$  to *cis*-diaryl-<sup>5a,d</sup> and arylketonyl-gold(III)<sup>5c</sup> complexes, respectively. As far as we know, **23** is the first unsymmetrical diarylacetylene obtained *via* C-C coupling from an organogold compound.

#### Structural data for $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)\text{-6}\}(\text{SPh})][\text{PF}_6]$ **18** $[\text{PF}_6]$

The structure in the solid state of complex **18** $[\text{PF}_6]$  has been solved by X-ray diffraction. It consists of the packing of  $[\text{Au}\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CMe}_2\text{C}_6\text{H}_4)\text{-6}\}(\text{SPh})]^+$  cations and  $\text{PF}_6^-$  anions with normal van der Waals contacts. An ORTEP<sup>20</sup> view of the cation with the atom labelling scheme is shown in Fig. 1. Selected bond distances and angles are reported in Table 2. The gold atom displays a tetrahedrally distorted square-planar co-

**Table 2** Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for cation **18**

Au–S	2.292(1)	Au–N(1)	2.121(3)
Au–N(2)	2.063(2)	Au–C(15)	2.014(4)
S–C(20)	1.792(5)		
S–Au–N(1)	99.0(1)	N(1)–Au–N(2)	78.6(1)
S–Au–C(15)	93.0(1)	N(2)–Au–C(15)	91.2(1)
N(1)–Au–C(15)	162.6(1)	S–Au–N(2)	171.8(1)
Au–S–C(20)	100.9(1)		



**Fig. 1** An ORTEP view of the cation in complex **18**[PF<sub>6</sub>]. Thermal ellipsoids are drawn at the 30% probability level.

ordination, with maximum deviations from the best plane of +0.208(3) Å for N(2) and –0.200(3) Å for N(1). The dihedral angle between the Au–N(1)–N(2) and Au–S–C(15) planes is 16.0(2)°. The Au–S distance, 2.292(1) Å, is statistically coincident with that found in [Au(C,N,C)(Spy-2)], 2.296(2) Å (HC,N,CH = 2,6-diphenylpyridine).<sup>4c</sup> Bond parameters involving the present C,N,N terdentate ligand can be compared with those found in cation [Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}Cl]<sup>+</sup> **3**,<sup>8</sup> which differs from the present one only in the replacement of the thiolate with a chloride ligand. The Au–N(1) and Au–C(15) bond lengths observed here, 2.121(3) and 2.014(4) Å, respectively, compare well with those found in **3**, 2.121(5) and 2.009(6) Å, respectively. The present Au–N(2) distance, 2.063(2) Å, is longer than that found in **3**, 2.009(4) Å, probably due to the higher *trans* influence of the thiolate ligand with respect to that of the chloride. The bites of the terdentate ligand are also very similar (N(1)–Au–N(2) 78.6(1)° here and 79.5(2)° in **3**, N(2)–Au–C(15) 91.2(1)° here and 91.3(2)° in **3**). The six-membered metallacycle is in a boat conformation, with atoms N(2), C(10), C(14) and C(15) nearly coplanar [maximum deviations from their best plane being +0.012(3) Å for C(14) and –0.013(3) Å for C(10)], whereas atoms Au and C(11) lie 0.635(1) and 0.646(4) Å above their best plane, respectively. One of the hydrogen atoms (not refined) bonded to C(12) lies 2.54 Å from the gold atom, a distance comparable to that found in **3**, 2.62 Å, and in [Au{NC<sub>5</sub>H<sub>4</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-2}Cl<sub>2</sub>], 2.56 Å.<sup>5b</sup> These short metal–hydrogen interactions have been described by Crabtree and co-workers<sup>21</sup> as weak hydrogen bonds. The dihedral angle between the best planes of the two pyridine rings is 14.0(1)°, that between the best planes of rings N(2)–C(10) and C(14)–C(19) is 54.7(1)°, and that between the metal co-ordination and C(20)–C(25) best planes is 85.7(1)°.

## Conclusion

Replacement of the chloride ligand in a series of C,N,N cyclaurated complexes, although not straightforward in all cases, may be carried out by means of different strategies depending both on the nature of the C,N,N cyclometallated ligand or of the incoming ligand Y<sup>–</sup>.

Unprecedented gold(III) alkoxo complexes have been obtained either from the chlorides by metathesis with sodium alkoxides or by reaction of alcohols on acetato complexes. The acetato and the alkoxo complexes can cleave the E–H (E = C, N or S) bonds of moderately to weakly acidic compounds to give thiolato, alkynyl and amido complexes under mild conditions. Although exchange reactions of late transition metal complexes have been extensively studied due to their involvement in various stoichiometric and catalytic processes, up to now, investigations on analogous gold(III) complexes have almost been neglected. Further investigations will be devoted to ascertain the potential of the new species reported.

## Experimental

### General procedures

All starting materials were used as received from commercial sources; the solvents were purified and dried according to standard methods. Complexes **1**[PF<sub>6</sub>]**–3**[PF<sub>6</sub>] were prepared as reported previously;<sup>8</sup> **5–22** have been obtained as PF<sub>6</sub><sup>–</sup> salts. Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer using Nujol mulls, <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra with a Varian VXR 300 spectrometer operating at 299.9 and 75.4 MHz, respectively; the 2-D experiments were performed by means of COSY-90. Chemical shifts are given in ppm relative to internal tetramethylsilane. Mass spectra were obtained with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol as supporting matrix unless otherwise stated.

### Substitution reaction products

[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}{CH<sub>2</sub>C(O)Me}][PF<sub>6</sub>] **5**. To a stirred solution of complex **1**[PF<sub>6</sub>] (0.093 g, 0.149 mmol) in acetone (20 cm<sup>3</sup>) was added solid AgPF<sub>6</sub> (0.040 g, 0.159 mmol); the resulting suspension was stirred for 3 d at room temperature and then filtered through Celite. Removal of solvent under reduced pressure was followed by extraction with chloroform (20 cm<sup>3</sup>) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a pale green solid product. Recrystallization from dichloromethane–diethyl ether yielded the analytical sample (0.068 g, 70%), mp 133–134 °C {Found: C, 36.87; H, 2.65; N, 4.48%; *M*<sup>+</sup> *m/z* 499. C<sub>20</sub>H<sub>18</sub>AuF<sub>6</sub>N<sub>2</sub>OP requires C, 37.28; H, 2.82; N, 4.35%; *M* 499 [Au(C,N,N){CH<sub>2</sub>C(O)Me}<sup>+</sup>]; *A*<sub>M</sub> (5 × 10<sup>–4</sup> mol dm<sup>–3</sup>, Me<sub>2</sub>CO) 130 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>; *ν*<sub>max</sub>/cm<sup>–1</sup> 1681 (C=O), 1604, 1227, 843 and 778.

[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}{CH<sub>2</sub>C(O)Me}][PF<sub>6</sub>] **6**. The procedure was similar to that for complex **5**. Yield 80%, mp 122–124 °C {Found: C, 37.90; H, 2.93; N, 4.25%; *M*<sup>+</sup> *m/z* 513. C<sub>21</sub>H<sub>20</sub>AuF<sub>6</sub>N<sub>2</sub>OP requires C, 38.31; H, 3.06; N, 4.26%; *M* 513 [Au(C,N,N){CH<sub>2</sub>C(O)Me}<sup>+</sup>]; *A*<sub>M</sub> (5 × 10<sup>–4</sup> mol dm<sup>–3</sup>, Me<sub>2</sub>CO) 120 Ω<sup>–1</sup> cm<sup>2</sup> mol<sup>–1</sup>; *ν*<sub>max</sub>/cm<sup>–1</sup> 1678 (C=O), 1603, 1224, 841 and 780.

[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}{CH<sub>2</sub>C(O)Me}][PF<sub>6</sub>] **7**. The procedure was similar to that for **5**. Yield 85%, mp 141–142 °C {Found: C, 39.29; H, 3.30; N, 4.15%; *M*<sup>+</sup> *m/z* 527. C<sub>22</sub>H<sub>22</sub>AuF<sub>6</sub>N<sub>2</sub>OP requires C, 39.30; H, 3.30; N, 4.17%; *M* 527 [Au(C,N,N){CH<sub>2</sub>C(O)Me}<sup>+</sup>]; *A*<sub>M</sub> (5 × 10<sup>–4</sup> mol dm<sup>–3</sup>,

Me<sub>2</sub>CO) 120 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  1679 (C=O), 1599, 1226, 843 and 778.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}(O<sub>2</sub>CMe)][PF<sub>6</sub>] 8.** To a stirred solution of complex **2**[PF<sub>6</sub>] (0.339 g, 0.532 mmol) in acetone (25 cm<sup>3</sup>) was added solid AgO<sub>2</sub>CMe (0.098 g, 0.587 mmol); the resulting suspension was stirred for 3 h at room temperature and then filtered through Celite. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (20 cm<sup>3</sup>) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a pale yellow solid product. Recrystallization from dichloromethane–diethyl ether yielded the analytical sample (0.281 g, 80%), mp 173–174 °C {Found: C, 36.18; H, 2.80; N, 4.21%; *M*<sup>+</sup> *m/z* 515. C<sub>20</sub>H<sub>18</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 36.38; H, 2.75; N, 4.24%; *M* 515 [Au(C,N,N)(O<sub>2</sub>CMe)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 138 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  1666 (CO<sub>2</sub>), 1602, 1564, 1270 (CO<sub>2</sub>), 840 and 779.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}(O<sub>2</sub>CMe)][PF<sub>6</sub>] 9.** The procedure was similar to that for complex **8**. Yield 82%, mp 201–202 °C {Found: C, 37.20; H, 3.11; N, 4.08%; *M*<sup>+</sup> *m/z* 529. C<sub>21</sub>H<sub>20</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 37.40; H, 2.99; N, 4.15%; *M* 529 [Au(C,N,N)(O<sub>2</sub>CMe)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 148 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  1669 (C=O), 1601, 1562, 1264 (C–O), 835 and 783.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}(acac)][PF<sub>6</sub>] 10.** To a stirred suspension of complex **1**[PF<sub>6</sub>] (0.176 g, 0.282 mmol) in dichloromethane (20 cm<sup>3</sup>) was added a solution of Ti(acac) (0.092 g, 0.303 mmol) in the same solvent; the resulting suspension was stirred for 4 h at room temperature and then filtered through Celite. The filtered solution was concentrated to small volume; addition of diethyl ether gave a pale yellow solid product which was recrystallized from dichloromethane–diethyl ether. Yield 119 mg (61%), mp 178 °C (decomp.) {Found: C, 38.10; H, 2.31; N, 3.84%; *M*<sup>+</sup> *m/z* 541. C<sub>22</sub>H<sub>20</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 38.50; H, 2.94; N, 4.08%; *M* 541 [Au(C,N,N)(acac)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 140 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  3641 (O–H), 1674 (C=O), 1600, 1577, 840 and 777.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}(acac)][PF<sub>6</sub>] 11.** The procedure was similar to that for complex **10**. Yield 90%, mp 194–196 °C {Found: C, 39.08; H, 3.15; N, 3.94%; *M*<sup>+</sup> *m/z* 555. C<sub>23</sub>H<sub>22</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 39.44; H, 3.17; N, 4.00%; *M* 555 [Au(C,N,N)(acac)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 145 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  3646 (O–H), 1709 and 1676 (C=O), 1601, 1578, 841 and 776.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}(acac)][PF<sub>6</sub>] 12.** The procedure was similar to that for complex **10**. Yield 85%, mp 181 °C (decomp.) {Found: C, 39.90; H, 3.19; N, 3.63%; *M*<sup>+</sup> *m/z* 569. C<sub>24</sub>H<sub>24</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 40.35; H, 3.39; N, 3.92%; *M* 569 [Au(C,N,N)(acac)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 140 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  3646 (O–H); 1695, 1676 (C=O); 1598, 1578, 840 and 778.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(C(OH)MeC<sub>6</sub>H<sub>4</sub>)-6}(OMe)][PF<sub>6</sub>] 13\*.** To a stirred suspension of complex **2**[PF<sub>6</sub>] (0.096 g, 0.15 mmol) in methanol (20 cm<sup>3</sup>) was added a solution of MeONa (0.016 g, 0.3 mmol) in the same solvent; the resulting greenish solution was stirred for 1 h at room temperature. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (15 cm<sup>3</sup>) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a white product: yield 0.050 g (51%), mp 221–222 °C {Found: C, 35.25; H, 3.08; N, 4.20%; *M*<sup>+</sup> *m/z* 503. C<sub>19</sub>H<sub>18</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 35.20; H, 2.80; N, 4.32%; *M* 503 [Au(C,N,N\*)(OMe)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 135 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  3629 (O–H), 1600, 1576, 1558, 1025 (C–O), 845 and 781.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}(OMe)][PF<sub>6</sub>] 13.** A solution of complex **8** (0.219 g, 0.332 mmol) in methanol (25 cm<sup>3</sup>) was stirred for 24 h at room temperature. The white precipitate which was formed during this period was filtered off and washed with diethyl ether to give a first crop (0.091 g). The mother-liquor was concentrated to small volume and diethyl ether added to give a precipitate of a mixture of unchanged **8** and **13** (<sup>1</sup>H NMR criterion). The mixture was dissolved in methanol and stirred for 48 h and then worked up to give a second crop of **13** (0.061 g). Yield 72%, mp 193–195 °C {Found: C, 35.85; H, 3.08; N, 4.26%; *M*<sup>+</sup> *m/z* 487. C<sub>19</sub>H<sub>18</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 36.09; H, 2.87; N, 4.43%; *M* 487 [Au(C,N,N)(OMe)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 30 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  2798, 1601, 1578, 1568, 1028, 1016 (C–O), 845 and 787.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}(OEt)][PF<sub>6</sub>] 14.** A solution of complex **8** (0.100 g, 0.151 mmol) in dichloromethane (5 cm<sup>3</sup>) was added dropwise to 25 cm<sup>3</sup> of ethanol; the resulting solution was stirred for 48 h at room temperature and then concentrated to small volume. Addition of diethyl ether gave a white precipitate of the equilibrium mixture (<sup>1</sup>H NMR criterion). The mixture was subjected to the procedure described above until complete conversion of **8** had occurred. Yield 0.063 g (65%), mp 182 °C (decomp.) {Found: C, 36.83; H, 2.95; N, 4.42%; *M*<sup>+</sup> *m/z* 501. C<sub>20</sub>H<sub>20</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 37.17; H, 3.12; N, 4.33%; *M* 501 [Au(C,N,N)(OEt)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 36 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  1603, 1580, 1045, 1028 (C–O), 838 and 785.

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}(OMe)][PF<sub>6</sub>] 15.** To a stirred suspension of complex **3**[PF<sub>6</sub>] (0.207 g, 0.318 mmol) in methanol (30 cm<sup>3</sup>) was added a solution of MeONa (0.052 g, 0.954 mmol) in the same solvent; the resulting pale yellow solution was stirred for 1 h at room temperature. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (20 cm<sup>3</sup>) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a pink product: yield 0.145 g (70%), mp 205–206 °C {Found: C, 36.87; H, 3.23; N, 4.19%; *M*<sup>+</sup> *m/z* 501. C<sub>20</sub>H<sub>20</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 37.17; H, 3.12; N, 4.33%; *M* 501 [Au(C,N,N)(OMe)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 140 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  2798, 1599, 1576, 1024 (C–O), 843 and 782;  $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$  165.8, 156.0, 153.2, 139.9 and 138.2 (aromatic C), 147.2, 145.2, 144.3, 131.8, 129.3, 128.9, 128.8, 125.8, 125.7, 125.5 and 124.1 (aromatic CH), 62.9 (MeO), 50.7 (CMe<sub>2</sub>) and 32.6 (Me<sub>2</sub>C).

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-6}(OEt)][PF<sub>6</sub>] 16.** To a stirred suspension of complex **3**[PF<sub>6</sub>] (0.118 g, 0.181 mmol) in ethanol (20 cm<sup>3</sup>) was added a solution of EtONa (0.038 g, 0.558 mmol) in the same solvent; the resulting pale yellow solution was stirred for 90 min at room temperature. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (20 cm<sup>3</sup>) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a pale yellow product: yield 0.088 g (72%), mp 183 °C (decomp.) {Found: C, 37.91; H, 3.15; N, 4.18%; *M*<sup>+</sup> *m/z* 515. C<sub>21</sub>H<sub>22</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 38.20; H, 3.36; N, 4.24%; *M* 515 [Au(C,N,N)(OEt)<sup>+</sup>]; *A<sub>M</sub>* (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, Me<sub>2</sub>CO) 144 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>;  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  1601, 1578, 1046, 1027 (C–O), 836 and 784;  $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$  165.6, 156.0, 153.3, 139.9 and 138.3 (aromatic C), 147.1, 145.2, 144.3, 131.9, 129.3, 128.9, 128.8, 125.8, 125.7, 125.5 and 124.1 (aromatic CH), 69.3 (CH<sub>2</sub>O), 50.7 (CMe<sub>2</sub>), 32.5 (Me<sub>2</sub>C) and 21.5 (MeCH<sub>2</sub>O).

**[Au{N<sub>2</sub>C<sub>10</sub>H<sub>7</sub>(CHMeC<sub>6</sub>H<sub>4</sub>)-6}(SPh)][PF<sub>6</sub>] 17.** *Method (a).* To a stirred solution of complex **8** (0.102 g, 0.154 mmol) in dichloromethane (20 cm<sup>3</sup>) was added PhSH (0.051 g, 0.462 mmol); the solution changed immediately from pale yellow to orange. After stirring for 1 h at room temperature it was con-

centrated to small volume; addition of diethyl ether afforded an orange crystalline product: yield 0.98 g (89%).

**Method (b).** The procedure was similar to that in (a) except complex **13** (0.095 g, 0.15 mmol) was used in place of **8**. Yield 85%, mp 130–132 °C {Found: C, 39.95; H, 2.81; N, 3.55%;  $M^+$   $m/z$  565.  $C_{24}H_{20}AuF_6N_2PS$  requires C, 40.58; H, 2.84; N, 3.94%;  $M$  565 [Au(C,N,N)(SPh) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , CH $_2$ Cl $_2$ ) 32  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ,  $\tilde{\nu}_{max}/cm^{-1}$  1599, 1574, 842, 778, 746 and 692 (Ph).

**[Au{N $_2$ C $_{10}$ H $_7$ (CMe $_2$ C $_6$ H $_4$ )-6}(SPh)][PF $_6$ ] **18**.** The procedures were similar to those for complex **17**. Yield 80–85%, mp 176–178 °C {Found: C, 40.94; H, 2.97; N, 3.85%;  $M^+$   $m/z$  579.  $C_{25}H_{22}AuF_6N_2PS$ : C, 41.45; H, 3.06; N, 3.87%;  $M$  579 [Au(C,N,N)(SPh) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , CH $_2$ Cl $_2$ ) 34  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ;  $\tilde{\nu}_{max}/cm^{-1}$  1606, 1572, 836, 782, 749 and 689 (Ph). Crystals of **18**[PF $_6$ ] were obtained by slow diffusion of diethyl ether into a dichloromethane solution.

**[Au{N $_2$ C $_{10}$ H $_7$ (CHMeC $_6$ H $_4$ )-6}(NHC $_6$ H $_4$ NO $_2$ -4)][PF $_6$ ] **19**.** To a stirred solution of complex **13** (0.122 g, 0.193 mmol) in dichloromethane (20 cm $^3$ ) was added solid H $_2$ NC $_6$ H $_4$ NO $_2$ -4 (0.081 g, 0.586 mmol); the resulting yellow solution was stirred for 16 h. During this period an orange-yellow precipitate was formed, which was filtered off and washed with dichloromethane to give the analytical sample: yield 0.114 g (80%), mp 178–180 °C {Found: C, 36.25; H, 2.38; N, 6.65%;  $M^+$   $m/z$  593.  $C_{24}H_{20}AuF_6N_4O_2P \cdot CH_2Cl_2$  (the presence of CH $_2$ Cl $_2$  was confirmed by NMR spectroscopy) requires C, 36.47; H, 2.69; N, 6.81%;  $M$  593 [Au(C,N,N)(NHC $_6$ H $_4$ NO $_2$ -4) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , (CH $_3$ ) $_2$ CO) 138  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ;  $\tilde{\nu}_{max}/cm^{-1}$  3350 (N–H), 1601, 1581 (NO $_2$ ), 1277 (NO $_2$ ), 1109, 862 and 834.

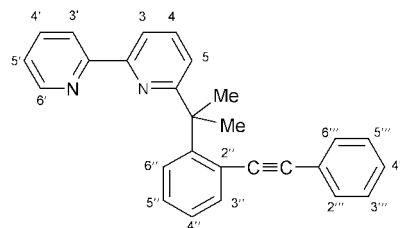
**[Au{N $_2$ C $_{10}$ H $_7$ (CMe $_2$ C $_6$ H $_4$ )-6}(NHC $_6$ H $_4$ NO $_2$ -4)][PF $_6$ ] **20**.** The procedure was similar to that for complex **19** except for the reaction time which was 2 d. Yield 75–80%, mp 178–179 °C (decomp.) {Found: C, 37.53; H, 2.58; N, 6.89%;  $M^+$   $m/z$  607.  $C_{25}H_{22}AuF_6N_4O_2P \cdot CH_2Cl_2$  (the presence of CH $_2$ Cl $_2$  was confirmed by NMR spectroscopy) requires C, 37.29; H, 2.89; N, 6.69%;  $M$  607 [Au(C,N,N)(NHC $_6$ H $_4$ NO $_2$ -4) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , (CH $_3$ ) $_2$ CO) 130  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ;  $\tilde{\nu}_{max}/cm^{-1}$  3352 (N–H), 1602, 1585 (NO $_2$ ), 1285 (NO $_2$ ), 1110, 857 and 846;  $\delta_C$ {(CD $_3$ ) $_2$ CO} 165.5, 160.8, 160.0, 157.9, 141.6 and 136.2 (aromatic C, C,N,N and NHC $_6$ H $_4$ NO $_2$ ), 148.8, 145.9, 144.8, 134.4, 129.6, 129.2, 128.9, 127.1, 126.2, 126.1 and 124.4 (aromatic CH, C,N,N), 126.8 and 117.2 (CH, NHC $_6$ H $_4$ NO $_2$ ), 51.1 (CMe $_2$ ) and 32.6 (Me $_2$ C).

**[Au{N $_2$ C $_{10}$ H $_7$ (CHMeC $_6$ H $_4$ )-6}(C $_2$ Ph)][PF $_6$ ] **21**.** To a stirred suspension of complex **13** (0.0843 g, 0.133 mmol) [or **14** (0.052 g, 0.08 mmol)] in benzene (20 cm $^3$ ) was added dichloromethane until a solution was obtained, and then PhC $_2$ H (0.045 cm $^3$ ,  $d$  = 0.930 g cm $^{-3}$ , 0.399 mmol). The resulting solution was stirred for 30 h at room temperature and then concentrated to small volume; addition of diethyl ether gave a white precipitate of [Au $_2$ {N $_2$ C $_{10}$ H $_7$ (CHMeC $_6$ H $_4$ )-6} $_2$ ( $\mu$ -O)][PF $_6$ ] $_2$  (0.050 g). The mother-liquor was evaporated to dryness and then extracted with *n*-hexane; the whitish residue insoluble in *n*-hexane was collected by filtration under vacuum to give the analytical sample: yield 0.010 g (10%), mp 213 °C (decomp.) (Found: C, 44.65; H, 2.98; N, 3.78.  $C_{26}H_{20}AuF_6N_2P$  requires C, 44.46; H, 2.87; N, 3.99%; IR (Nujol)  $\tilde{\nu}_{max}/cm^{-1}$  1600, 1563, 844, 778 and 689 (Ph).

**[Au{N $_2$ C $_{10}$ H $_7$ (CMe $_2$ C $_6$ H $_4$ )-6}(C $_2$ Ph)][PF $_6$ ] **22**.** To a stirred suspension of complex **15** (0.115 g, 0.178 mmol) in benzene (20 cm $^3$ ) was added dichloromethane until a solution was obtained, and then PhC $_2$ H (0.06 cm $^3$ ,  $d$  = 0.930 g cm $^{-3}$ , 0.534 mmol). The resulting solution was stirred for 20 h at room temperature and then concentrated to small volume; addition of diethyl

ether gave a pale yellow solid product. Recrystallization from dichloromethane–diethyl ether gave the analytical sample: yield 0.105 g (82%), mp 194–196 °C {Found: C, 44.95; H, 3.25; N, 3.81%;  $M^+$   $m/z$  571.  $C_{27}H_{22}AuF_6N_2P$  requires C, 45.27; H, 3.10; N, 3.91%;  $M$  571 [Au(C,N,N)(C $_2$ Ph) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , CH $_2$ Cl $_2$ ) 33  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ;  $\tilde{\nu}_{max}/cm^{-1}$  1599, 1563, 842, 812, 783 and 697 (Ph).

**Reaction of [Au{N $_2$ C $_{10}$ H $_7$ (CMe $_2$ C $_6$ H $_4$ )-6}(C $_2$ Ph)][PF $_6$ ] **22** with PPh $_3$ .** To a stirred solution of complex **22** (0.080 g, 0.112 mmol) in dichloromethane (20 cm $^3$ ) was added a solution of PPh $_3$  (0.059 g, 0.224 mmol) in the same solvent. The reaction was carried out under an argon atmosphere. The resulting solution was stirred for 24 h and then concentrated to small volume; addition of diethyl ether afforded a white precipitate which was identified as [Au(PPh $_3$ ) $_2$ ][PF $_6$ ] (0.078 g, 80%). The mother-liquor was evaporated to dryness and extracted with *n*-pentane. Removal of the solvent under reduced pressure gave a white solid which was purified by chromatography on a column (47  $\times$  2 cm) of silica gel (Merck, 70–230 mesh ASTM) using *n*-hexane–dichloromethane (1:5) as eluent. Removal of the solvent yielded the C–C coupling product N $_2$ C $_{10}$ H $_7$ {CMe $_2$ -C $_6$ H $_4$ (C $_2$ Ph)-2"}-6 **23** as a white solid: yield 80%, mp 169–170 °C (Found: C, 86.45; H, 6.01; N, 7.26%;  $M$  – H  $m/z$  373 (EI).  $C_{27}H_{22}N_2$  requires C, 86.60; H, 5.92; N, 7.48%  $M$  374);  $\tilde{\nu}_{max}/cm^{-1}$  1595, 1578, 1562, 1490, 1440, 1422, 1401, 1258, 1160, 1151, 1126, 1071, 1044, 1006, 989, 923, 828, 783, 754, 692, 662, 622 and 610 (Nujol);  $\delta_H$ (CDCl $_3$ ) 8.63 (ddd, 1 H, H $^6$ ), 8.50 (dt, 1 H, H $^3$ ), 8.15 (dd, 1 H, H $^3$ ), 7.77 (td, 1 H, H $^4$ ), 7.67 (dd, 1 H, H $^3$  or H $^6$ ), 7.59 (t, 1 H, H $^4$ ), 7.51 (dd, 1 H, H $^6$  or H $^3$ ), 7.41 (td, 1 H, H $^4$  or H $^5$ ), 7.27 (2td, 2 H, H $^5$  or H $^4$  and H $^5$ ), 7.03 (tt, 1 H, H $^4$ ), 6.99 (dd, 2 H, H $^{2'}$ , 6"), 6.93 (dd, 1 H, H $^5$ ), 6.88 (tt, 2 H, H $^3$ , 5") and 1.92 (s, 6 H, 2Me) (COSY);  $\delta_C$ (CDCl $_3$ ) 168.1, 156.8, 154.1, 150.4, 123.0 and 122.9 (aromatic C), 148.8, 136.8, 136.6, 134.4, 131.0, 128.2, 127.7, 127.6, 126.3, 126.2, 123.2, 121.6, 121.2 and 117.5 (aromatic CH), 95.3 and 89.3 (C=C), 47.0 (CMe $_2$ ) and 29.3 (Me $_2$ C);  $m/z$  (%) 373 (50,  $M$  – H), 359 (100,  $M$  – Me), 282 (7,  $M$  – Me – Ph), 179 (10, Ph $_2$ C $_2$  + H), 155 (8, bipy – H), 149 (50) and 78 (11) (EI).



**Reactions of [Au(C,N,N)Cl][PF $_6$ ] with MeCO $_2$ Na.** (a) To a stirred solution of complex **2** (0.096 g, 0.15 mmol) in acetone (20 cm $^3$ ) was added a solution of MeCO $_2$ Na (0.037 g, 0.45 mmol) in the same solvent; the resulting solution was stirred for 2 h at room temperature. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (20 cm $^3$ ) and filtration through Celite. Addition of diethyl ether to the concentrated solution afforded a creamy product which analysed for [Au{N $_2$ C $_{10}$ H $_7$ (C(OH)MeC $_6$ H $_4$ )-6}Cl][PF $_6$ ] **2\***: yield 0.098 g (70%), mp 172–173 °C {Found: C, 33.24; H, 2.56; N, 4.16%;  $M^+$   $m/z$  507.  $C_{18}H_{15}AuClF_6N_2O$  requires C, 33.12; H, 2.32; N, 4.29%;  $M$  507 [Au(C,N,N\*)(Cl) $^+$ ];  $A_M$  ( $5 \times 10^{-4}$  mol dm $^{-3}$ , (CH $_3$ ) $_2$ CO) 136  $\Omega^{-1}$  cm $^2$  mol $^{-1}$ ;  $\tilde{\nu}_{max}/cm^{-1}$  3633, 3564 (O–H), 1600, 1559, 1019, 843, 778 and 369 (Au–Cl).  $\delta_H$ (CD $_2$ Cl $_2$ ) 9.37 (dd, 1H, H $^6$ ), 8.63–7.17 (m, 10 H, aromatics), 3.88 [s (broad), 1 H, OH] and 2.18 (s, 3 H, Me);  $\delta_C$ (CD $_2$ Cl $_2$ ) 163.4, 155.8, 153.6, 137.2, 133.5 (aromatic C), 148.6, 146.3, 135.5, 130.1, 129.4, 129.3, 126.9, 126.5, 125.8, 125.2 (aromatic CH), 82.7 [C(OH)Me] and 36.4 (Me).

(b) Complex **3** (0.098 g, 0.15 mmol) was treated with

**Table 3** Crystallographic data for complex **18** [PF<sub>6</sub>]

Formula	C <sub>25</sub> H <sub>22</sub> AuF <sub>6</sub> N <sub>2</sub> PS
<i>M</i>	724.46
Colour	Yellow
Crystal system	Trigonal (hexagonal indexing)
Space group	<i>R</i> $\bar{3}$ (no. 148)
<i>a</i> /Å	41.018(4)
<i>c</i> /Å	8.215(1)
<i>U</i> /Å <sup>3</sup>	11970(2)
<i>Z</i>	18
<i>T</i> /K	298
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	57.1
Measured reflections (total; independent)	22847; 5912
<i>R</i> <sub>int</sub>	0.029
Final <i>R</i> <sub>2</sub> and <i>R</i> <sub>2w</sub> indices ( <i>F</i> <sup>2</sup> )	0.038, 0.057
Conventional <i>R</i> <sub>1</sub>	0.037

MeCO<sub>2</sub>Na (0.037 g, 0.45 mmol) by a procedure similar to (a) for 20 h. The isolated product was a 6:1:1 mixture of **3**, **7** and **9** (<sup>1</sup>H NMR criterion).

(c) To a stirred suspension of complex **2** (0.105 g, 0.165 mmol) in acetonitrile–water (25 cm<sup>3</sup>) was added solid MeCO<sub>2</sub>Na (0.041 g, 0.495 mmol). The resulting mixture was refluxed for 12 h during which a solution was obtained. After the solution was cooled to room temperature a white solid separated; it was filtered off, dried under vacuum and identified as unchanged **2** (0.040 g). The mother-liquor was evaporated to dryness and extracted with dichloromethane. The solution was filtered through 1PS Whatman® (silicone treated filter paper) to remove traces of water and concentrated to small volume; addition of diethyl ether afforded a pale yellow product (0.045 g). It was identified as a 2.5:1 mixture of **2** and [Au<sub>2</sub>(C,N,N)<sub>2</sub>(μ-O)][PF<sub>6</sub>]<sub>2</sub> (<sup>1</sup>H NMR criterion).

(d) Complex **3** (0.104 g, 0.160 mmol) was treated with MeCO<sub>2</sub>Na (0.039 g, 0.48 mmol) by a procedure similar to (c). Unchanged **3** (0.054 g) was recovered after the reaction mixture was cooled to room temperature. A 1:1:2 mixture of **3**, [Au<sub>2</sub>(C,N,N)<sub>2</sub>(μ-O)][PF<sub>6</sub>]<sub>2</sub> and an unidentified compound was isolated after working up the mother-liquor.

**Reactions of complex 2 with KOH.** (a) To a stirred solution of complex **2** (0.100 g, 0.157 mmol) in acetone (20 cm<sup>3</sup>) was added an aqueous solution of KOH (0.009 g, 0.160 mmol); the resulting solution was stirred for 4 h at room temperature. Removal of solvent under reduced pressure was followed by extraction with dichloromethane (20 cm<sup>3</sup>), filtration through 1PS Whatman® and then through Celite. Addition of diethyl ether to the concentrated solution afforded a beige product (0.040 g) which was identified as a 3:3.5:4 mixture of **2**, [Au<sub>2</sub>(C,N,N)<sub>2</sub>(μ-O)][PF<sub>6</sub>]<sub>2</sub> and **6** (<sup>1</sup>H NMR criterion).

(b) To a stirred suspension of complex **2** (0.100 g, 0.157 mmol) in methanol (20 cm<sup>3</sup>) was added an aqueous solution of KOH (0.009 g, 0.160 mmol); the resulting blue solution was stirred for 4 h at room temperature then treated as above. Addition of diethyl ether to the concentrated pale yellow solution afforded a whitish product (0.054 g) which was identified as a 3:8:1 mixture of **2**, [Au<sub>2</sub>(C,N,N)<sub>2</sub>(μ-O)][PF<sub>6</sub>]<sub>2</sub> and **13** (<sup>1</sup>H NMR criterion).

### X-Ray crystallography

Crystal data and other experimental details are summarized in Table 3. The diffraction experiment was carried out on a Siemens SMART CCD area-detector diffractometer. Cell parameters and orientation matrix for complex **18**[PF<sub>6</sub>] were obtained from the least-squares refinement of 101 reflections measured in three different sets of 15 frames each, in the range 3 < θ < 23°. At the end of data collection no crystal decay was observed. The collected frames were processed with the software SAINT,<sup>22a</sup> and an absorption correction was applied

(SADABS<sup>22b</sup>) to the 22847 collected reflections. The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package<sup>23</sup> and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref. 24. The structure was refined by full-matrix least squares using all reflections and minimizing the function Σw(*F*<sub>o</sub><sup>2</sup> – *kF*<sub>c</sub><sup>2</sup>)<sup>2</sup> (refinement on *F*<sup>2</sup>). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions (C–H 0.97 Å, *B* 1.15 times those of the carbon atoms to which they are attached) and not refined. In the final Fourier-difference map the maximum residual was 0.70(13) e Å<sup>-3</sup> at 1.36 Å from F(2).

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