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Gold(III) derivatives with anionic oxygen ligands: mononuclear hydroxo, alkoxo and acetato complexes. Crystal structure of $[Au(bpy)(OMe)_2][PF_6]$

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A variety of gold(III) adducts having σ-ligated oxygen-donor ligands have been prepared from $[Au(bpy)Cl_2][PF_6]$ **1** (bpy = 2,2′-bipyridine) either by partial or total replacement of the chloride ions. The new species comprise hydroxo, $[Au(bpy)(OH)Cl][PF_6]$ **2** and $[Au(bpy)(OH)_2][PF_6]$ **3**, oxo, $[Au_2(bpy)_2(\mu\text{-}O)_2][PF_6]_2$ **4**, acetato, $[Au(bpy)(O_2CMe)_2][PF_6]$ **5**, and alkoxo complexes, $[Au(bpy)(OR)Cl][PF_6]$ **6**, **7** and $[Au(bpy)(OR)_2][PF_6]$ **8**–**10** (R = Me **6** and **8**; Et **7** and **9**; Pr^i **10**). The dihydroxo and the oxo complexes can be interconverted by refluxing the former in anhydrous THF and the latter in water. The hydroxides **2** and **3** and the acetato complex **5** undergo σ-ligand metathesis in ROH solution (R = Me, Et or Pr^i) to give the corresponding alkoxides. The crystal structure of **8**, the first of a gold(III) methoxo complex, has been determined by X-ray diffraction analysis.

Introduction

The chemistry of late transition metal complexes with oxygen-donor ligands has been a topic of interest for many years.[1] Particular endeavour has been devoted to the syntheses of hydroxo, alkoxo and oxo (O^{2-}) complexes due to their unique reactivity as well as for their implications in organic synthesis. Furthermore they are often postulated as intermediates in many important chemical and biochemical processes. Whereas a number of Group 8–10 metal–oxo complexes have been synthesized and their reactivity studied, analogous gold complexes are less common[2–6] and almost neglected in most of the reviews dealing with late transition metal–oxo complexes.

While all the gold(I)–oxygen bonded compounds have a phosphine co-ordinated to the metal ion, all of the very small number of gold(II) and most of the gold(III) derivatives are organometallic complexes and are dimeric species. Dimethylgold(III) hydroxide, for example, has a dimeric structure in aqueous solution, but in the solid state or in benzene solution it is a tetramer with bridging hydroxides.[3a] Very recently a monomeric gold(III) hydroxide, with the terdentate nitrogen donor ligand 2,2′:6′,2″-terpyridine, has been characterized structurally.[3f]

In some recent papers we have reported the synthesis and crystal structures of a series of oxo-bridged gold(III) adducts,[4n] $[Au_2(HL)_2(\mu\text{-}O)_2]^{2+}$ (HL = 6-alkyl-2,2′-bipyridine), oxo-bridged gold(III) cyclometallated complexes,[5k] $[Au_2(L)_2(\mu\text{-}O)]^{2+}$ (HL = 6-benzyl-2,2′-bipyridine) and more recently the synthesis and the reactivity of stable monomeric cyclometallated alkoxo complexes,[4o] $[Au(L)(OR)]^+$ (HL = 6-benzyl-2,2′-bipyridine; R = Me or Et).

In light of the interest towards complexes or intermediates having Au–O bonds because of their involvement in several stoichiometric[4c,f,i,j,o,5c,6i,7] reactions as well as in catalytic[4k,8] and in biochemical[6s,9] processes, we have extended our study on gold(III) complexes with oxygen donor ligands to the unsubstituted 2,2′-bipyridine. Herein we report the synthesis, characterization and some aspects of the reactivity of monomeric hydroxo, alkoxo and acetato complexes and a dimeric oxo complex obtained from $[Au(bpy)Cl_2][PF_6]$ (bpy = 2,2′-bipyridine) by partial or total replacement of the chloride ligands. To the best of our knowledge inorganic gold(III) complexes having OR ligands (R = alkyl) are unprecedented.

Results

Hydroxo $[Au(bpy)(OH)X][PF_6]$ (X = Cl 2 or OH 3) and oxo complexes $[\{Au(bpy)(\mu\text{-}O)\}_2][PF_6]_2$ 4

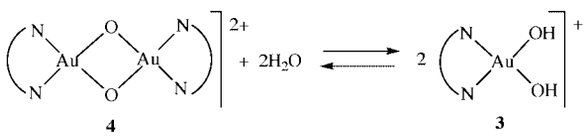
The starting compound, $[Au(bpy)Cl_2][PF_6]$ **1**, has been prepared by a modification of the method described forty years ago by Harris and Lockyer for the perchlorate salt.[10] The crystal structure of the complex, as the tetrafluoroborate salt, was determined only a few years ago.[11] Complex **1** undergoes facile hydrolysis in aqueous solution in the presence of $MeCO_2Na$ to give the mono(hydroxo) complex **2**. Complete hydrolysis of complex **1** to give the bis(hydroxide) **3** requires more severe conditions. Small amounts of complex **3** are obtained by reaction of **1** with KOH in water at reflux. Best results have been obtained from the reaction of **1** with Ag_2O in water.

Complexes **2** and **3** gave satisfactory analyses and their molecular ions M^+ have been detected by FAB mass spectrometry (see Experimental Section). The IR spectrum of complex **2** displays a very strong sharp band at 3528 cm^{-1} for the AuO–H stretch, which for **3** appears as a medium broad band at 3499 cm^{-1}; in addition, **2** shows a strong band at 373 cm^{-1} assignable to the Au–Cl stretch and **3** a weak to medium broad band at 2375 cm^{-1}. The latter absorption is likely to be due to a hydrogen bonded OH group. The ^1H NMR spectra in $(CD_3)_2CO$ of complexes **2** and **3** are characterized by sharp singlets for the OH protons at δ 5.91 (1 H) and 4.15 (2 H), respectively, which disappear upon addition of D_2O. The chemical shift of the OH protons of both complexes is not dependent on concentration $[(CD_3)_2CO]$ but displays a strong dependence on solvent. In CD_3CN solution this resonance is shifted upfield (δ = 4.84 **2**; 3.31 **3**). The aromatic region of complex **2** shows two sets of resonances for the H^6, H^5, and H^4 protons: assignment of the CH protons can be achieved by comparison with

the spectra of complexes **1** and **3** in $(CD_3)_2CO$. It is found that the resonances of the CH protons of the pyridine ring *cis* to the chloride are shifted downfield with respect to those *cis* to the hydroxide.

When the reaction of complex **1** with KOH is carried out at room temperature the main product is the oxo-bridged adduct **4**, similar to those previously reported with a series of 6-alkyl-2,2′-bipyridines.[4n] The IR spectrum is characterized by two strong absorptions at 682 and 662 cm^{-1}, peculiar to the Au_2O_2 stretching modes.[4n]

Complex **4** can be quantitatively converted into **3** by refluxing a water suspension of **4**, eqn. (1). Reaction (1) can be reversed



4 3

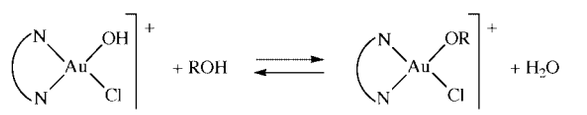
by treating **3** with anhydrous THF at reflux. Nevertheless, from the latter reaction, besides **4**, an unidentified product is obtained which analyses as **4** but shows quite different spectroscopic and conductivity data.

Bis(acetato) complex [Au(bpy){OC(O)Me}$_2$][PF$_6$] 5

Complex **5** is obtained in good yields by reaction of **1** with AgO_2CMe. The monodentate O-bonded acetato ligands are characterized by strong absorptions at 1696 $\{\nu_{asym}(CO_2)\}$ and 1258 cm^{-1} $\{\nu_{sym}(CO_2)\}$. The methyl protons give rise to a singlet at δ 2.20 (6 H). Complex **5** undergoes hydrolysis reaction in aqueous solution to give the hydroxo complex **3** and small amounts of **4**.

Alkoxo complexes [Au(bpy)(OR)Cl][PF$_6$] 6, 7 and [Au(bpy)-(OR)$_2$][PF$_6$] 8–10

The hydroxo complexes **2** and **3** as well as the acetato complex **5** undergo σ-ligand metathesis in ROH solution to give the alkoxides [Au(bpy)(OR)Cl][PF_6] (R = Me **6** or Et **7**) (Scheme 1)



2 **6** R = Me
7 R = Et

Scheme 1

and [Au(bpy)$(OR)_2$][PF_6] (R = Me **8**, Et **9** or Pr^i **10**), respectively. Complex **10** has been obtained only by metathesis of **5**. In the case of **3** the equilibrium reaction was driven toward the alkoxides by addition of a drying agent, such as neutral Al_2O_3, to remove the water formed in the reaction.

The bis(alkoxides) **8** and **9** can be synthesized one pot by metathesis of **1** with the sodium alkoxides in the corresponding alcohols (Scheme 2). The gold(III) methoxides **6** and **8** are thermally stable at room temperature in the solid state and in solution. The ethoxide **9** is less stable: some decompositon is observed even in the solid state. As a consequence the elemental analyses of **9** are sometimes affected by the presence of metallic gold. Nevertheless acceptable analytical data could be obtained on a freshly prepared sample.

The IR spectra of the alkoxo complexes **6**–**10** show strong absorptions in the region 1000–1100 cm^{-1}, which can be ascribed to the stretching vibration $\{\nu$(C–O)$\}$ of the alkoxide unit.[12] The MeO protons of the methoxide complexes resonate at δ 3.33 (3 H) {**6**, $(CD_3)_2CO$} and 3.58 (6 H) (**8**, CD_2Cl_2). In the ethoxide complexes the methylene protons are equivalent giving rise to a quartet at δ 3.61 (2 H) {**7**, $(CD_3)_2CO$} and 3.79 (4 H) (**9**, CD_2Cl_2) with ^3J = 6.8 Hz; the methyl protons appear as a triplet

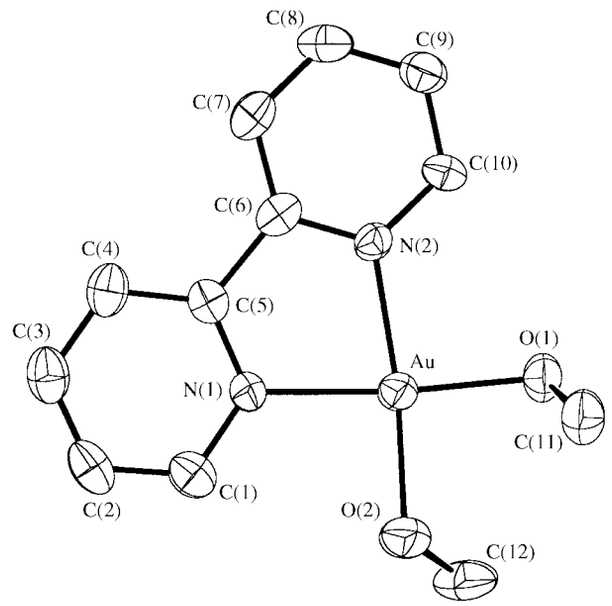
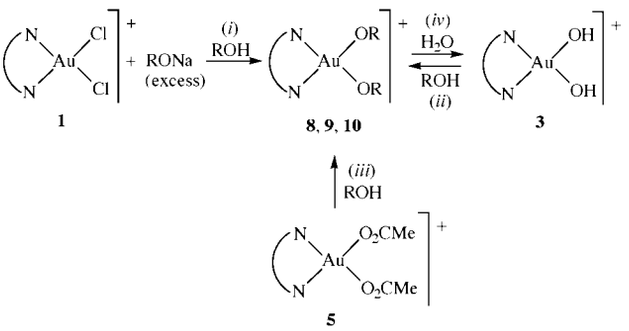


Fig. 1 An ORTEP view of the [Au(bpy)$(OMe)_2$]$^+$ cation in compound **8**. Thermal ellipsoids are drawn at the 30% probability level.



1 **8**, **9**, **10** 3

5

Scheme 2 (*i*) R = Me or Et; (*ii*) R = Me or Et; (*iii*) R = Me, Et or Pr^i. R = Me **8**; Et **9** or Pr^i **10**.

at δ 1.38 (3 H) (**7**) and 1.45 (6 H) (**9**). In the isopropoxide the methine proton resonates as septuplet at δ 4.18 (2 H) (CD_2Cl_2) with ^3J = 6.1 Hz; the methyl protons appear as a doublet at 1.43 (12 H).

Treatment of the alkoxides **6** and **8** with water at room temperature resulted in the formation of the hydroxo complexes **2** and **3**, respectively.

Structure determination of complex 8

Crystals suitable for a diffraction study were grown from a cooled methanol solution. Complex **8** is the first gold(III) methoxide stucturally characterized and, to the best of our knowledge, the second structurally characterized late transition metal bis(methoxide).[13] The structure consists of [Au(bpy)-$(OMe)_2$]$^+$ cations and PF_6^- anions with normal van der Waals contacts. An ORTEP[14] view of the cation with the atom labelling scheme is shown in Fig. 1. Selected bond distances and angles are reported in Table 1. The gold atom displays a square-planar co-ordination, maximum deviations from the best plane being +0.011(5) and −0.013(5) Å for atoms N(2) and N(1), respectively. The Au–N(1), 2.039(5), and Au–N(2), 2.032(5) Å, distances are statistically coincident and very similar to the Au–N bond lengths *trans* to oxygen in the two crystallographically independent cations of [Au{$N_2C_{10}H_7(CMe_2O)$-6}Cl][$AuCl_4$] **11**,[4n] 2.028(10) and 2.053(9) Å, respectively. The Au–O(1) and Au–O(2) bond lengths, 1.971(4) and 1.960(6) Å, respectively, are equal within two esds and compare well with the two Au–O distances, 1.974(9) and 1.958(9) Å, found in the two independ-

Table 1 Selected bond distances (Å) and angles (°) with esds in parentheses for compound **8**

Au–O(1)	1.971(4)	Au–O(2)	1.960(6)
Au–N(1)	2.039(5)	Au–N(2)	2.032(5)
O(1)–C(11)	1.403(8)	O(2)–C(12)	1.376(10)
O(1)–Au–O(2)	92.5(2)	O(1)–Au–N(1)	174.6(2)
O(1)–Au–N(2)	94.1(2)	O(2)–Au–N(1)	92.9(2)
O(2)–Au–N(2)	173.4(2)	N(1)–Au–N(2)	80.6(2)
Au–O(1)–C(11)	111.7(4)	Au–O(2)–C(12)	116.8(5)

ent cations of **11**. The Au–O distance observed in the cation $[Au(terpy)(OH)]^{2+}$,[3f] 2.000(4) Å, is only slightly longer.

The O(1)–C(11) and O(2)–C(12) bond lengths, 1.403(8) and 1.376(10) Å, respectively, are equal within three esds and can be compared with the two O–C distances found in [Pt(DPPE)(OMe)$_2$], 1.369(14) and 1.370(13) Å.[13] The two pyridine rings are strictly planar and form a dihedral angle of 5.1(1.9)° with each other.

Further aspects of the reactivity of the monomeric complexes are currently under investigation.

Experimental

General procedures

All starting materials were used as received from commercial sources; the solvents were purified and dried according to standard methods. The solvents were purchased from Fluka Chemika, Celite (filter aid) and 2,2′-bipyridine from Aldrich Chemical Co., neutral Al_2O_3 (activity I) from Merck and $HAuCl_4 \cdot 3H_2O$ from Chimet; $NaAuCl_4$ was prepared by neutralization of an aqueous solution of $HAuCl_4$ with $NaHCO_3$. 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, ^{1}H NMR spectra with a Varian VXR 300 spectrometer operating at 299.9 MHz and mass spectra on a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol (NBA) as supporting matrix.

Preparations

[Au(bpy)Cl$_2$][PF$_6$] 1. To a solution of 2,2′-bipyridine (0.781 g, 5 mmol) in acetonitrile (5 cm^3) were added an aqueous solution of $NaAuCl_4$ (5 mmol) (50 cm^3) and solid KPF_6 (2.761 g, 15 mmol, excess). The resulting yellow suspension was refluxed for 15 h, cooled at room temperature, and filtered off. Recrystallization from acetone–diethyl ether afforded the analytical sample: yield 2.760 g (97%), mp 253 °C {Found: C, 21.14; H, 1.54; N, 4.55%; M^+ *m*/*z* 423. $C_{10}H_8AuCl_2F_6N_2P$ requires: C, 21.11; H, 1.42; N, 4.92%; *M* 423 [Au(bpy)Cl$_2^+$]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 172 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 377vs (Au–Cl); δ_H\{$(CD_3)_2CO$\} 9.65 (dd, 2 H, H^6), 9.03 (dd, 2 H, H^3), 8.88 (td, 2 H, H^4) and 8.32 (td, 2 H, H^5); FAB mass spectrum *m*/*z* 423 (M^+), 388 (M − Cl) and 353 (M − 2Cl).

[Au(bpy)(OH)Cl][PF$_6$] 2. To a solution of complex **1** (0.569 g, 1 mmol) in acetonitrile (5 cm^3) was added an aqueous solution of $MeCO_2Na$ (0.164 g, 2 mmol) (25 cm^3). The resulting yellow suspension was refluxed for 1 h to give a pale yellow solution. The pale yellow precipitate which separated after cooling to room temperature was filtered off. Recrystallization from acetone–diethyl ether afforded the analytical sample: yield 0.495 g (90%), mp 183 °C (decomp.) {Found: C, 22.07; H, 1.62; N, 4.97%; M^+ *m*/*z* 405. $C_{10}H_9AuClF_6N_2OP$ requires: C, 21.81; H, 1.65; N, 5.09%; *M* 405 [Au(bpy)(OH)Cl$^+$]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 170 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3528vs (O–H) and 373s (Au–Cl); δ_H\{$(CD_3)_2CO$\} 9.40 (dd, 1 H, H^6), 9.31 (dd, 1 H, H$^{6'}$), 8.98 (dd, 2 H, H^3 and H$^{3'}$), 8.84 (td, 1 H, H^4), 8.78 (td, 1 H, H$^{4'}$), 8.35 (td, 1 H, H^5), 8.24 (td, 1 H, H$^{5'}$) and 5.91 (s, 1 H, OH); δ_H(CD_3CN) 9.23 (dd, 1 H, H^6), 9.10 (dd, 1 H, H$^{6'}$), 8.63–8.51 (m, 4 H, H^3, H$^{3'}$, H^4 and H$^{4'}$), 8.10 (td, 1 H, H^5), 8.00 (m, 1 H, H$^{5'}$) and 4.84 (s, 1 H, OH); FAB mass spectrum *m*/*z* 405 (M^+), 388 (M − OH) and 353 (M − OH − Cl).

[Au(bpy)(OH)$_2$][PF$_6$] 3. To a solution of complex **1** (0.569 g, 1 mmol) in acetone (20 cm^3) was added an aqueous suspension of Ag_2O (0.232 g, 1 mmol). The mixture was stirred for 24 h at room temperature, AgCl was removed by filtration and the solution evaporated to dryness under reduced pressure. The residue was extracted with acetonitrile and filtered over Celite. The pale yellow filtrate was concentrated to a small volume (*ca.* 10 cm^3) and diethyl ether added to give a white precipitate of **3**: yield 0.426 g (80%), mp 192 °C {Found: C, 22.65; H, 1.78; N, 5.03%; M^+ *m*/*z* 387. $C_{10}H_{10}AuF_6N_2O_2P$ requires: C, 22.57; H, 1.89; N, 5.26%; *M* 387 [Au(bpy)(OH)$_2^+$]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 158 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3499m (broad) (O–H) and 2375w (broad) (O–H $\cdots$ O); δ_H\{$(CD_3)_2CO$\} 9.14 (dd, 2 H, H^6), 8.92 (dd, 2 H, H^3), 8.76 (td, 2 H, H^4), 8.25 (td, 2 H, H^5) and 4.15 (s, 2 H, OH); δ_H(CD_3CN) 8.98 (d, 2 H, H^6), 8.56–8.49 (m, 4 H, H^3 and H^4), 8.03 (m, 2 H, H^5) and 3.31 (s, 2 H, OH); FAB mass spectrum *m*/*z* 387 (M^+), 370 (M − OH) and 353 (M − 2OH).

[{Au(bpy)(μ-O)}$_2$][PF$_6$]$_2$ 4. To a solution of complex **1** (0.569 g, 1 mmol) in acetonitrile (5 cm^3) were added 30 cm^3 of an aqueous solution of KOH (0.168 g, 3 mmol). The resulting pale yellow suspension was stirred for 72 h at room temperature and then filtered off. Recrystallization from acetonitrile–diethyl ether gave a creamy product: yield 0.230 g (45%), mp 186 °C {Found: C, 23.11; H, 1.30; N, 5.38%; M^+ *m*/*z* 739. $C_{10}H_8AuF_6N_2OP$ requires: C, 23.36; H, 1.57; N, 5.45%; *M* 738 [{Au(bpy)(μ-O)}$_2^{2+}$]}; Λ_M(5×10^{-4} mol dm^{-3}, MeCN) 240 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 682vs and 662vs (Au_2O_2); δ_H(CD_3CN) 8.66 (dt, 2 H, H^6), 8.56–8.49 (m, 4 H, H^3 and H^4) and 8.08 (td, 2 H, H^5); FAB mass spectrum *m*/*z* 739 ([M + H]$^+$), 509 ([Au(bpy)$_2$]$^+$), 506 ([Au(bpy)(NBA)]$^+$), 388 ([Au(bpy)(OH)(OH$_2$)]$^+$) and 353 (M/2 − O).

[Au(bpy)(O$_2$CMe)$_2$][PF$_6$] 5. To a solution of complex **1** (0.150 g, 0.26 mmol) in acetonitrile (25 cm^3) was added solid AgO_2CMe. The resulting suspension was stirred for 4 h at room temperature and then filtered through Celite. Addition of diethyl ether to the concentrated solution afforded a creamy solid product. Recrystallization from acetone–diethyl ether gave the analytical sample: yield 0.150 g (95%), mp 180 °C (decomp.) {Found: C, 27.06; H, 2.07; N, 4.39%; M^+ *m*/*z* 471. $C_{14}H_{14}AuF_6N_2O_4P$ requires: C, 27.29; H, 2.29; N, 4.55%; *M* 471 [Au(bpy)(O$_2$CMe)$_2$]$^+$}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 153 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1696vs (C=O) and 1258vs (C–O); δ_H\{$(CD_3)_2CO$\} 8.98 (d, 2 H, H^6), 8.95 (d, 2 H, H^3), 8.85 (td, 2 H, H^4), 8.22 (td, 2 H, H^5) and 2.20 (s, 6 H, Me); FAB mass spectrum *m*/*z* 471 (M^+), 429 (M − CH_2CO), 412 (M − $MeCO_2$) and 353 (M − 2$MeCO_2$).

[Au(bpy)(OMe)Cl][PF$_6$] 6. A methanol suspension of complex **2** (0.125 g, 0.23 mmol) was refluxed until an orange solution was obtained. Concentration of the solution to half the initial volume and addition of diethyl ether gave **6** as an orange solid: yield 0.082 g (63%), mp 115 °C (decomp.) {Found: C, 23.15; H, 1.71; N, 4.85%; M^+ *m*/*z* 419. $C_{11}H_{11}AuClF_6N_2OP$ requires: C, 23.40; H, 1.96; N, 4.96%; *M* 419 [Au(bpy)(OMe)Cl$^+$]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 130 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1020s (C–O) and 379s (Au–Cl); δ_H\{$(CD_3)_2CO$\} 9.48 (dd, 1 H, H^6), 9.30 (dd, 1 H, H$^{6'}$), 8.97 (dd, 2 H, H^3 and H$^{3'}$), 8.82 (td, 1 H, H^4), 8.77 (td, 1 H, H$^{4'}$), 8.37 (td, 1 H, H^5), 8.24 (td,

1 H, $H^{5'}$) and 3.33 (s, 3 H, Me); FAB mass spectrum *m*/*z* 419 (M^+), 388 (M − MeO) and 353 (M − MeO − Cl).

[Au(bpy)(OEt)Cl][PF_6] 7. The preparation of this complex was carried out using the procedure described above for **6**, employing ethanol as solvent and **2** (0.27 mmol). In this case large decomposition to metallic gold was observed. The analytical sample was obtained after recrystallization from dichloromethane–diethyl ether: yield 35%, mp 174 °C {Found: C, 25.18; H, 2.16; N, 4.80%; M^+ *m*/*z* 433. $C_{12}H_{13}AuClF_6N_2OP$ requires: C, 24.91; H, 2.26; N, 4.84%; M 433 [Au(bpy)(OEt)Cl^+]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 125 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1046s and 1028s (C–O) and 374m (Au–Cl); δ_H{$(CD_3)_2CO$} 9.48 (dd, 1 H, H^6), 9.39 (dd, 1 H, $H^{6'}$), 8.98 (dd, 2 H, H^3 and $H^{3'}$), 8.82 (td, 1 H, H^4), 8.76 (td, 1 H, $H^{4'}$), 8.38 (td, 1 H, H^5), 8.24 (td, 1 H, $H^{5'}$), 3.61 (q, ^3J = 6.8 Hz, 2 H, CH_2) and 1.38 (t, ^3J = 6.8 Hz, 3 H, Me); FAB mass spectrum *m*/*z* 433 (M^+), 388 (M − EtO) and 353 (M − EtO − Cl).

[Au(bpy)(OMe)$_2$][PF_6] 8. *Method (a)*. To a stirred methanol (20 cm^3) suspension of complex **1** (0.200 g, 0.35 mmol) was added dropwise a methanol solution (10 cm^3) of MeONa (0.076 g, 1.4 mmol). The resulting yellow solution was stirred for 1 h at room temperature. After filtration over Celite of a small amount of gold, the solution was evaporated to dryness and the residue extracted with dichloromethane (3 × 10 cm^3). The filtered solution was concentrated to small volume (*ca.* 5 cm^3) and diethyl ether added to give a yellow microcrystalline product: yield 0.100 g (51%), mp 124 °C (decomp.) {Found: C, 25.31; H, 2.48; N, 4.90%; M^+ *m*/*z* 415. $C_{12}H_{14}AuF_6N_2O_2P$ requires: C, 25.73; H, 2.52; N, 5.00%; M 415 [Au(bpy)(OMe)$_2^+$]}; Λ_M (5×10^{-4} mol dm^{-3}, Me_2CO) 135 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1016vs (C–O); $\delta_H(CD_2Cl_2)$ 9.13 (d, 2 H, H^6), 8.61–8.56 (m, 4 H, H^3 and H^4), 8.06 (td, 2 H, H^5) and 3.58 (s, 6 H, Me); (CD_3CN) 9.03 (dd, 2 H, H^6), 8.53–8.50 (m, 4 H, H^3 and H^4), 8.05 (m, 2 H, H^5) and 3.51 (s, 6 H, Me); FAB mass spectrum *m*/*z* 415 (M^+), 384 (M − MeO), 369 (M − Me_2O) and 353 (M − 2MeO). Yellow crystals of **8** were obtained by cooling of a methanol solution to −20 °C. They changed to amber within a few days after they were collected from the mother liquor.

Method (b). A methanol (30 cm^3) suspension of complex **3** (0.106 g, 0.2 mmol) was stirred for 15 h at room temperature. After filtration of a purple insoluble product, the pale yellow solution was treated with neutral Al_2O_3 (activity I) for 5 min, filtered off and concentrated to small volume (*ca.* 5 cm^3). Addition of diethyl ether afforded **8**. Recrystallization from dichloromethane–diethyl ether gave the analytical sample (0.064 g, 57%). The insoluble product (0.015 g) was a mixture of metallic gold and complex **4**.

Method (c). A methanol (30 cm^3) suspension of complex **5** (0.123 g, 0.2 mmol) was stirred for 3 h at room temperature until a pale yellow solution, impure of metallic gold, was formed. After filtration over Celite, the solution was concentrated to small volume (*ca.* 15 cm^3) and diethyl ether added to give **8**. Recrystallization from dichloromethane–diethyl ether gave the analytical sample (0.083 g, 74%).

[Au(bpy)(OEt)$_2$][PF_6] 9. The preparation of this complex was carried out using the procedures described above for **8**.

Method (a). An ethanol (25 cm^3) suspension of complex **1** (0.200 g, 0.35 mmol) was treated with 15 cm^3 of an ethanol solution of EtONa (0.095 g, 1.4 mmol). The crude product was recrystallized from dichloromethane–diethyl ether to give the analytical sample: yield 0.047 g (40%), mp 120 °C (decomp.) {Found: C, 28.38; H, 2.98; N, 4.86%; M^+ *m*/*z* 443. $C_{14}H_{18}AuF_6N_2O_2P$ requires: C, 28.58; H, 3.08; N, 4.76%; M 443 [Au(bpy)(OEt)$_2^+$]}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2CO) 120 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1113s, 1096s, 1047vs and 1029vs; $\delta_H(CD_2Cl_2)$ 9.16 (dd, 2 H, H^6), 8.62 (dd, 2 H, H^3), 8.54 (td, 2 H, H^4), 8.05 (td, 2 H, H^5), 3.79 (q, ^3J = 6.8, 4 H, CH_2) and 1.45 (t, ^3J = 6.8 Hz, 6 H, Me); FAB mass spectrum *m*/*z* 443 (M^+), 415 (M − $2CH_2$), 399 (M − MeC(O)H), 369 (M − Et_2O) and 353 (M − MeC(O)H − EtOH).

Method (b). An ethanol (25 mL) suspension of complex **3** (0.075 g, 0.14 mmol) was stirred for 24 h at room temperature. Yield 0.030 g (36%).

Method (c). An ethanol (40 cm^3) suspension of complex **5** (0.123 g, 0.2 mmol) was stirred for 12 h at room temperature. Recrystallization from dichloromethane–diethyl ether gave the analytical sample. Yield 0.061 g (52%).

[Au(bpy)(OPr^i)$_2$][PF_6] 10. To an acetone solution (20 cm^3) of complex **5** (0.081 g, 0.13 mmol) were added 20 cm^3 of Pr^iOH. The resulting slightly opalescent solution was stirred for 15 h at room temperature. After filtration of a dark green (sometimes dark purple) insoluble product, the yellow solution was concentrated to small volume (15 cm^3) and diethyl ether added to give a yellow microcrystalline product: yield 0.050 g (62%), mp 110 °C (decomp.) (Found: C, 30.92; H, 3.37; N, 4.30. $C_{16}H_{22}AuF_6N_2O_2P$ requires: C, 31.18; H, 3.60; N, 4.55%); Λ_M (5×10^{-4} mol dm^{-3}, Me_2CO) 125 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1128vs, 1112vs and 997vs; $\delta_H(CD_2Cl_2)$ 9.23 (dd, 2 H, H^6), 8.62 (dd, 2 H, H^3), 8.54 (td, 2 H, H^4), 8.06 (td, 2 H, H^5), 4.18 (sept, ^3J = 6.1, 2 H, CH) and 1.43 (d, ^3J = 6.1 Hz, 12 H, Me).

Reactions

Interconversion between complexes 3 and 4. *From **4** to **3***. An aqueous suspension of complex **4** (0.051 g, 0.05 mmol) was refluxed for 2 h. The resulting colourless solution was cooled to room temperature and then evaporated to dryness. The residue was dissolved in acetone and the solution concentrated to small volume (5 cm^3); addition of diethyl ether gave a white precipitate of **3**. Yield 98%.

*From **3** to **4***. A suspension of complex **3** (0.151 g, 0.28 mmol) in freshly distilled THF (25 cm^3) was refluxed for 3 h and then filtered off. The solid was treated with acetone to give a pale yellow solution and a greyish residue. The latter was collected by filtration, dissolved in MeCN, filtered and the solution concentrated to small volume; addition of diethyl ether gave a creamy precipitate of **4**. Yield 0.074 g (50%). The acetone solution was concentrated to small volume and diethyl ether added to give 0.060 g of a pale yellow precipitate which analysed as follows: C, 23.65; H, 1.33; N, 5.35%; Λ_M(0.017 g; Me_2CO, 25 cm^3) 3.3×10^{-4} S cm^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 682m and 662m; δ_H{$(CD_3)_2CO$} 9.59 (dd, 1 H, H^6), 8.93 (d, 1H, H^3), 8.74 (td, 1H, H^4) and 8.21 (td, 1H, H^5); (CD_3CN) 9.26 (d, 1H, H^6), 8.56–8.53 (m, 2 H, H^3 and H^4) and 8.03 (td, 1 H, H^5).

Hydrolysis of complex 5. An aqueous suspension of complex **5** (0.050 g, 0.08 mmol) was stirred at room temperature. After 15 min a colourless solution was obtained; 15 min later a whitish precipitate was formed in small amounts. The mixture was stirred for about 24 h and then filtered off. The insoluble product (0.007 g) was identified as complex **4** (^{1}H NMR criterion). The filtered solution was evaporated to dryness and the residue crystallized from acetone–diethyl ether to give 0.034 g (79%) of complex **3**.

Exchange reaction of complex 6 with water. An aqueous suspension of complex **6** (0.051 g, 0.09 mmol) was stirred for 12 h at room temperature. The resulting pale yellow solution, containing small amounts of a purple insoluble product, was filtered off and then evaporated to dryness. The residue was crystallized from acetone–diethyl ether to give 0.040 g (81%) of **2**.

Exchange reaction of complex 8 with water. An aqueous suspension of complex **8** (0.050 g, 0.09 mmol) was stirred for 12 h at room temperature. The resulting colourless solution, containing small amounts of a purple insoluble product, was filtered

Table 2 Crystallographic data for complex **8**

Formula	$C_{12}H_{14}AuF_6N_2O_2P$
M	560.19
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	7.166(1)
b/Å	14.991(2)
c/Å	15.170(2)
β/°	98.80(1)
U/Å^3	1610.5(4)
Z	4
T/K	298
μ(Mo-Kα)/cm^{-1}	92.9
Measured reflections (total; independent)	18452; 3914
R_{int}	0.048
Final R_2 and R_{2w} indices (F^2, all reflections)	0.069, 0.084
Conventional R_1 index ($I > 2\sigma(I)$, 2394 reflections)	0.038

off and then evaporated to dryness. The residue was crystallized from acetone–diethyl ether to give 0.038 g (78%) of **3**.

X-Ray crystallography

Crystal data and other experimental details are summarized in Table 2. The diffraction experiment was carried out on a Siemens SMART CCD area-detector diffractometer at room temperature. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2. Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions and not refined.

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