

μ -Oxo and alkoxo complexes of gold(III) with 6-alkyl-2,2'-bipyridines. Synthesis, characterization and X-ray structures

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The reactivity of a series of gold(III) adducts [Au(HL)Cl₃] **1a–4a** with 6-alkyl-2,2'-bipyridines HL (N₂C₁₀H₇R, R = CH₂Me **1**, CHMe₂ **2**, CMe₃ **3** and CH₂CMe₃ **4**) has been studied. The reactions of **1a–4a** with silver(I) ions or MeCO₂Na afford cationic complexes [Au₂(HL)₂(μ -O)₂]²⁺ **1b–4b** (as BF₄ or PF₆ salts) having the gold atom bonded to the nitrogen atoms of the bipyridine and to two oxygen atoms. The crystal structure of **4b**[PF₆]₂, solved by X-ray diffraction, shows that the cation is a centrosymmetric dimer with two oxo (O²⁻) groups bridging two [Au{N₂C₁₀H₇(CH₂CMe₃)-6}] moieties. In the case of **2a**, besides the oxo species, mononuclear ionic derivatives [Au(L*)Cl]⁺ **2*c** [HL* = N₂C₁₀H₇(CMe₂OH)-6; BF₄, PF₆ or AuCl₄ salts] have been isolated. The latter complexes contain an unexpected Au–O bond. The spectroscopic data and the crystal structure of **2*c**[AuCl₄] indicate a tridentate N,N,O behaviour of the ligand which forms a [5,5]-fused ring system.

Gold has always been considered as the most noble of all metals, and in tune with this it binds only weakly to oxygen. Therefore gold complexes in which oxygen is directly linked to the metal tend to have limited stability. Only one oxide of gold is known, Au₂O₃,¹ and even this is unstable decomposing to gold metal at moderately high temperatures (ca. 160 °C).² Several oxoaurates have been characterized and recently the synthesis and structure of a new aurate, CaAu₂O₄, has been reported.³ At least as far as we know, gold(III) oxo complexes are unknown, the only oxo complexes being the gold(I) species [(R₃P)Au]₃(μ -O)]⁴ (R = alkyl or Ph) and [(Ph₃P)Au]₄(μ -O)]²⁺.⁵

Oxo complexes⁶ are potential models for the activation of molecular oxygen on metal surfaces and are likely to be involved in reactions catalysed by second and third series Group 9–11 metal surfaces.⁷

In a recent paper⁸ we have reported the synthesis of a series of adducts [Au(HL)Cl₃] and cyclometallated derivatives [Au(L)Cl][X] (X = AuCl₄, BF₄ or PF₆) with 6-benzyl- and 6-alkyl-2,2'-bipyridines, HL. In the metallated species the 6-substituted-2,2'-bipyridines act as tridentate N,N,C ligands giving rise to [5,6]- or [5,5]-fused ring systems. Both sp² and sp³ C–H activation was achieved. The activation of the latter bond required removal of two chloride ligands from the adduct by means of silver ions. From the reaction of the complex [Au{N₂C₁₀H₇(CMe₃)-6}Cl₃] with AgBF₄, besides the cyclometallated derivative [Au{N₂C₁₀H₇(CMe₂CH₂)-6}Cl][BF₄], a second product was isolated which was tentatively formulated as the cationic dimer [Au₂(HL)₂(μ -O)]₂[BF₄]₂ on the basis of microanalytical, conductivity and spectroscopic data.

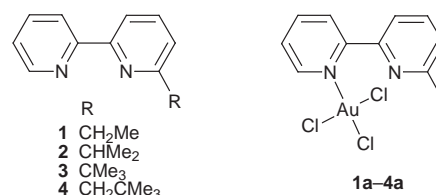
In this paper we discuss the reactions of a series of adducts [Au(HL)Cl₃] (HL = 6-alkyl-2,2'-bipyridine) with silver ions and with MeCO₂Na to give oxo-bridged adducts [Au₂(HL)₂(μ -O)]₂[X]₂ (X = BF₄ or PF₆). The crystal structure of [Au₂{N₂C₁₀H₇(CH₂CMe₃)-6}₂(μ -O)]₂[PF₆]₂, the first gold(III) oxo complex, gives evidence for an Au₂(μ -O)₂ core.

The reaction of N₂C₁₀H₇(CHMe₂)-6 with Na[AuCl₄] is also reported. Besides the adduct [Au(HL)Cl₃] and the oxo-bridged derivatives, a mononuclear cationic species [Au(L*)Cl]⁺ [HL* = N₂C₁₀H₇{CMe₂(OH)}-6] is obtained. According to

spectroscopic and X-ray data this compound contains an Au–O bond. The anionic ligand L* binds to the metal through a set of N,N,O donor atoms to form a [5,5]-fused ring system. A brief report on part of this work has been given.⁹

Results and Discussion

The adducts [Au(HL)Cl₃] **1a–4a** (HL = N₂C₁₀H₇R, R = CH₂Me **1**, CHMe₂ **2**, CMe₃ **3** and CH₂CMe₃ **4**) have been prepared according to established methods.⁸ As shown by the X-ray structure determination of complex [Au{N₂C₁₀H₇(CHMePh)-6}Cl₃],⁸ the gold atom is bonded to the nitrogen atom of the unsubstituted pyridine ring; a long-range interaction with the other nitrogen atom is observed.

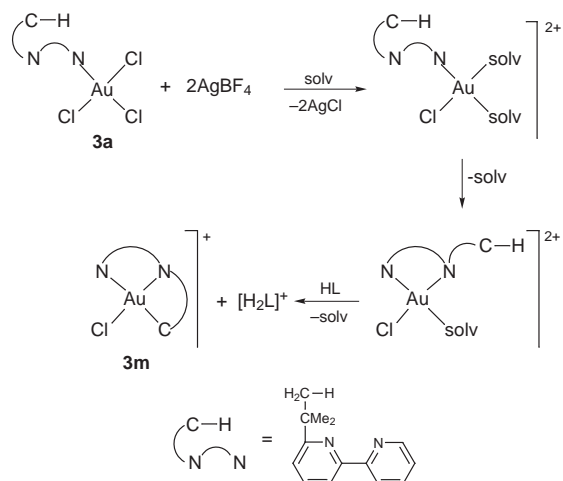


In a previous paper⁸ we have shown that the cyclometallated derivative [Au{N₂C₁₀H₇(CMe₂CH₂)-6}Cl][BF₄] **3m**[BF₄] can be obtained by reaction of complex **3a** with AgBF₄ in acetone solution according to Scheme 1.

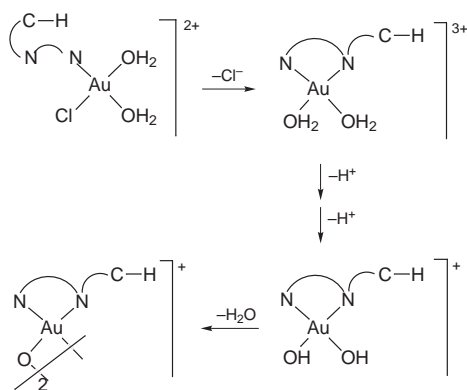
In spite of several attempts, cation **3m** is the only cyclometallated species we were able to obtain with the 6-alkyl-2,2'-bipyridines **1–4**. It is not simple to account for the behaviour of this series of ligands; however it is worth noting that (i) ligand **4**, i.e. the neopentyl-substituted bipyridine, should form by metallation a six-membered C,N cycle which is best known to be less favoured than a five-membered one¹⁰ and (ii) that on going from **1** to **3** the number of Me groups increases from one to three. Thus with ligand **3**, activation of a C–H bond might be favoured by statistical effects.

To achieve activation of the C(sp³)–H bond both removal of two chloride ligands with silver salts, likely to give bis(solvato) intermediate, and addition of HL are required. Cyclometallated **3m**[BF₄] is accompanied by a second species which can be separated due to its low solubility in acetone. On the basis of microanalytical data, conductivity measurements, IR, NMR

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Scheme 1 solv = Me₂CO or H₂O

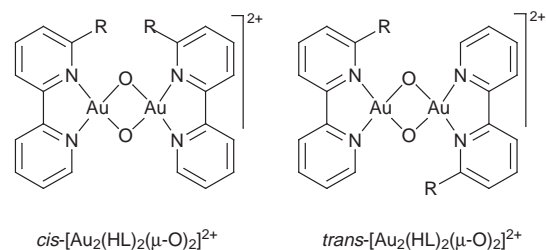


Scheme 2

and mass spectra the latter species was tentatively formulated as a cationic dimer $[\text{Au}_2(\text{HL})_2(\mu\text{-O})_2]^{2+}$ **3b**.⁸

Now we report that by reaction of the adducts **1a**, **2a** and **4a** with AgBF_4 , in the presence of equimolar amounts of the corresponding ligand the oxo-bridged adducts **1b**, **2b** and **4b**, analogous to **3b**, are isolated. The oxo species are likely to result from a diaqua complex $[\text{Au}(\text{HL})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$ postulated as an intermediate, through an alternative route (Scheme 2). The reaction was carried out in acetone, thus the aqua complexes are presumed to be due to adventitious water. The presence of excess ligand is necessary to prevent decomposition; the excess is recovered from the reaction mixture in the protonated form $[\text{H}_2\text{L}][\text{BF}_4]$. The same oxo derivatives can be obtained in better yields by reaction of **1a**, **2a** and **4a** with sodium acetate in $\text{MeCN-H}_2\text{O}$ in the presence of KPF_6 .

The compounds $[\text{Au}_2(\text{HL})_2(\mu\text{-O})_2][\text{X}]_2$ ($\text{X} = \text{BF}_4$ or PF_6) **1b**[X]₂–**4b**[X]₂ are light-sensitive pale yellow solids with relatively high melting points. They are readily soluble in acetonitrile, sparingly soluble in acetone and insoluble in water, alcohols and chlorinated solvents. The molar conductivity values of **1b**[X]₂–**4b**[X]₂ in acetonitrile, at room temperature, are typical of a 2 : 1 electrolyte.¹¹ In the infrared spectra, in addition to strong bands due to the anions, bands typical of a co-ordinated bipyridyl are observed at expected wavenumbers. Strong absorptions at 672–675 and 640–650 cm^{-1} are tentatively assigned to Au_2O_2 stretching modes by comparison with a number of di- μ -oxo bridged complexes of other metals.¹² In the ¹H NMR spectra (Table 1) of complexes **3b**[BF₄]₂ and **4b**[PF₆]₂ only one set of signals is observed suggesting that of the two possible geometrical isomers, *cis* and *trans*, one only is present in solution at room temperature. The resonances of the seven aromatic protons are shifted downfield with respect to free HL (Table 2). The resonances of the alkyl substituents are likewise



shifted: in complex **3b** the methyl protons resonate at δ 1.74 ($\Delta\delta$ +0.33 in CD_3CN), in complex **4b** the methylene protons are shifted 0.87 ppm downfield. These features on the whole support co-ordination of both nitrogen atoms.

The ¹H NMR spectra of **1b**[X]₂, **2b**[X]₂ ($\text{X} = \text{BF}_4$ or PF_6) and **4b**[BF₄]₂ in various solvents show the presence of two isomers in molar ratios that depend on the bulkiness of the alkyl substituent as well as on the method of preparation. In the ¹H NMR spectra of the mixtures the resonances of some protons in the *cis* and *trans* isomers are quite distinct from one another, whereas others are partially overlapping. In the case of complex **4b**[BF₄]₂ assignment of the resonances to the *cis* and *trans* isomer respectively can be achieved by comparison with the spectrum of **4b**[PF₆]₂ (*trans* isomer) whose structure in the solid state has been solved by an X-ray determination (see below). In particular, the resonance of the H⁶ proton of the *cis* isomer is shifted downfield with respect to that of the *trans* isomer [$\Delta\delta$ +0.14 in $(\text{CD}_3)_2\text{CO}$] whereas that of the H⁵ proton is shifted upfield ($\Delta\delta$ –0.05). Similarly the resonance of the methylene protons of the *cis* isomer is shifted downfield ($\Delta\delta$ +0.06) and that of the methyl protons upfield ($\Delta\delta$ –0.02). The ¹H NMR spectrum of *trans*-**4b**[PF₆]₂ at variable temperature (20–70 °C, CD_3CN) shows that, on increasing temperature, *trans*→*cis* isomerization occurs; at ca. 70 °C the molar ratio *cis*:*trans* is 1 : 5. The spectra of the other oxo complexes are comparable to that of **4b**[BF₄]₂.

The dinuclear nature of these dicationic complexes is supported by their FAB mass spectra (positive ions). In each case (see Experimental section) the more intense peaks are observed at mass values that correspond to $([M + \text{X}]^+)$ ($\text{X} = \text{BF}_4$ or PF_6) and to $(\frac{1}{2}M^+)$; in addition, fragments corresponding to $(M - \text{H})$ are found in some cases. Surprisingly, in all the mass spectra a weak peak is found corresponding to the species $[\text{Au}(\text{HL})(\text{OH})_2]^+$, *i.e.* a reasonable precursor of the dimeric oxo complex (see Scheme 2).

The structure in the solid state of the oxo-bridged dimer *trans*- $[\text{Au}_2\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CH}_2\text{CMe}_3)_6\}_2(\mu\text{-O})_2][\text{PF}_6]_2$ **4b**[PF₆]₂ has been solved by X-ray diffraction. It consists of the packing of $[\text{Au}_2\{\text{N}_2\text{C}_{10}\text{H}_7(\text{CH}_2\text{CMe}_3)_6\}_2(\mu\text{-O})_2]^{2+}$ cations and $[\text{PF}_6]^-$ anions in the molar ratio 1 : 2 with no unusual van der Waals contacts. An ORTEP¹³ view of the cation is reported in Fig. 1. Principal bond parameters are reported in Table 3. The dinuclear cation displays crystallographic inversion symmetry and the central Au_2O_2 ring is thus exactly planar; the transannular $\text{Au}\cdots\text{Au}$ distance, 3.017(1) Å, is rather short.‡ The co-ordination at gold is substantially planar, with a minor deviation towards square pyramidal [maximum deviations from the best plane being $\text{Au} +0.0251(4)$ Å and $\text{O}' -0.0195(35)$ Å]. The dihedral angle between this best plane and the Au_2O_2 core is 1.4(3.1)°. The $\text{Au-N}(1)\text{-C}(5)\text{-C}(6)\text{-N}(2)$ pentaatomic ring is quasiplanar [maximum deviations from the best plane being $\text{N}(1) +0.0421(37)$ Å and $\text{C}(5) -0.0289(45)$ Å] and forms, with the gold best plane, a dihedral angle of 3.6(1.4)°. The two Au-O and $\text{Au-O}'$ bond lengths, 1.976(3) and 1.961(3) Å, respectively,

‡ For a comparison the $\text{Au}\cdots\text{Au}$ distances in the dinuclear species $[\text{Au}(\text{C}_6\text{H}_4\text{NO}_2)_2(\mu\text{-OH})_2]\cdot 2\text{Et}_2\text{O}$ ¹⁴ and 1-hydroxy-2,3,4,5-tetra-phenylauracyclopentadiene¹⁵ are 3.150(1) and 3.428 Å (average of two independent molecules), respectively.

Table 1 Proton NMR data^a

Compound	Solvent	H ^{6'}	Other aromatics	CH	CH ₂	CH ₃
1 N ₂ C ₁₀ H ₇ (CH ₂ Me)-6	CDCl ₃	8.67 (dd)	8.47–7.16		2.90 (q, 7.6)	1.38 (t, 7.6)
1a	CDCl ₃	9.04 (d)	8.20–7.47		3.27 (q, 7.5)	1.48 (t, 7.5)
1b^b BF ₄ ⁻ salt	DMSO	[1.2] 8.90 (dd)	8.85–7.90		3.48 (q, 7.5)	1.35 (t, 7.5)
		[1] <i>c</i>			3.42 (q, 7.2)	1.40 (t, 7.2)
PF ₆ ⁻ salt	CD ₃ CN	[1] 8.82 (d)	8.49–7.79		3.50 (q, 7.3)	1.41 (t, 7.3)
		[4] 8.67 (d)			3.45 (q, 7.5)	1.46 (t, 7.5)
2 N ₂ C ₁₀ H ₇ (CHMe ₂)-6	(CD ₃) ₂ CO	8.66 (dd)	8.56–7.26	3.13 (m, 6.8)		1.34 (d, 6.8)
	DMSO	8.85 (dd)	8.66–7.60	3.25 (m, 6.8)		1.34 (d, 6.8)
2a	(CD ₃) ₂ CO	9.36 (dd)	8.63–7.66	3.64 (m, 6.9)		1.45 (d, 6.9)
2b^b BF ₄ ⁻ salt	CD ₃ CN	[1] 8.88 (dd)	8.51–7.90	4.57 (m, 6.9)		1.43 (d, 6.9)
		[5] 8.63 (dd)		4.41 (m, 6.6)		1.46 (d, 6.6)
PF ₆ ⁻ salt	(CD ₃) ₂ CO ^d	[1] 9.11 (dd)	8.92–8.14	4.76 (m, 6.6)		1.53 (d, 6.6)
		[2] <i>c</i>		4.62 (m, 6.6)		1.54 (d, 6.6)
	CD ₃ CN	[3] 8.87 (dd)	8.52–7.91	4.57 (m, 6.8)		1.43 (d, 6.8)
		[2] 8.63 (dd)		4.41 (m, 6.8)		1.47 (d, 6.8)
	DMSO	[2] 8.93 (dd)	8.86–8.02	4.59 (m, 6.6)		1.37 (d, 6.6)
		[1] <i>c</i>		4.41 (m, 6.6)		1.42 (d, 6.6)
2*c AuCl ₄ ⁻ salt	(CD ₃) ₂ CO	9.22 (dd)	8.95–8.09			1.86 (s)
BF ₄ ⁻ salt	DMSO	9.04 (dd)	8.87–8.01			1.76 (s)
	CD ₃ CN	9.04 (dd)	8.59–7.72			1.78 (s)
PF ₆ ⁻ salt	(CD ₃) ₂ CO	9.22 (dd)	8.94–8.09			1.85 (s)
3 N ₂ C ₁₀ H ₇ (CMe ₃)-6	CD ₃ CN	8.63 (dd)	8.52–7.32			1.41 (s)
3a	(CD ₃) ₂ CO	9.34 (dd)	8.54–7.78			1.55 (s)
3b^e BF ₄ ⁻ salt	CD ₃ CN	8.83 (dd)	8.52–8.07			1.74 (s)
4 N ₂ C ₁₀ H ₇ (CH ₂ CMe ₃)-6	(CD ₃) ₂ CO	8.66 (dd)	8.51–7.24		2.76 (s)	1.01 (s)
4a	(CD ₃) ₂ CO	9.34 (dd)	8.68–7.57		3.17 (s)	1.02 (s)
4b^b BF ₄ ⁻ salt	(CD ₃) ₂ CO ^d	[2] 9.11 (dd)	8.91–7.95		3.84 (s)	1.18 (s)
		[1] 8.97 (dd)			3.78 (s)	1.20 (s)
	CD ₃ CN	[1] 8.84 (dd)	8.50–7.70		3.68 (s)	1.10 (s)
		[2] 8.71 (dd)			3.62 (s)	1.13 (s)
4b^e PF ₆ ⁻ salt	(CD ₃) ₂ CO	8.96 (dd)	8.91–7.97		3.78 (s)	1.19 (s)
	CD ₃ CN	8.73 (dd)	8.49–7.74		3.63 (s)	1.14 (s)

^a Spectra recorded at room temperature, chemical shifts in ppm from internal SiMe₄, coupling constants (in parentheses) in Hz. ^b *cis* and *trans* isomers, integral ratios are in square brackets. ^c Overlapped. ^d Filtered solution. ^e *trans* isomer.

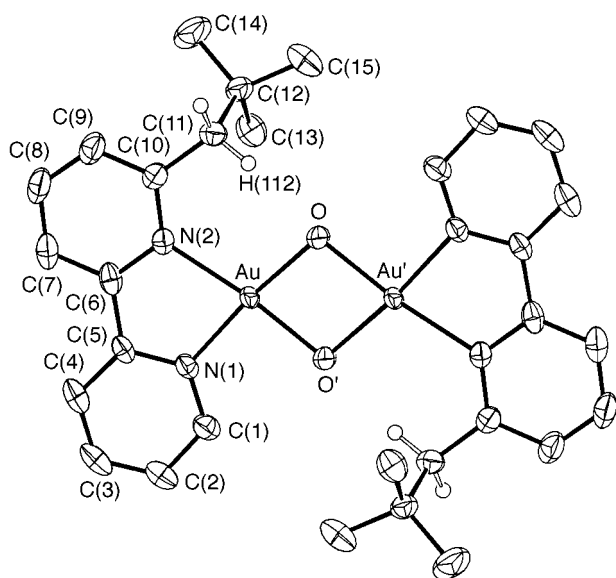


Fig. 1 An ORTEP view of the cation in **4b**[PF₆]₂. Thermal ellipsoids are drawn at the 30% probability level. Atom H(112), which displays a short contact with atom O (see text), is also shown

are very similar and can be compared with the 1.93(2) Å Au–O distance, observed in polymeric gold(III) oxide, involving the oxygen atom that bridges two gold atoms.¹ A much longer Au–OH distance, 2.074(4) Å, can be found in [Au(C₆H₄NO₂-2)₂-(μ-OH)]₂·2Et₂O,¹⁴ where the oxygen atom is *trans* to an elongating aryl group.

Surprisingly enough, the two Au–N bonds in **4b**[PF₆]₂ are very different: Au–N(1) 2.011(4), and Au–N(2) 2.100(3) Å. The former value is normal and can be compared, for instance,

Table 2 Aromatic protons^a of compounds **3**,^b **3b**[BF₄]₂,^b **4^c** and **4b**[PF₆]₂^c

	3	3b	Δδ	4	4b	Δδ
	δ	δ		δ	δ	
H ^{6'}	8.63	8.84	0.21	8.66	8.96	0.30
H ^{6'}	7.34	8.11	0.77	7.38	8.29	0.91
H ^{6'}	7.85	8.49	0.64	7.91	8.71	0.80
H ^{6'}	8.51	8.53	0.02	8.50	8.90	0.40
H ³	8.20	8.44	0.24	8.32	8.82	0.50
H ⁴	7.78	8.38	0.60	7.83	8.59	0.76
H ⁵	7.42	8.21	0.79	7.25	7.98	0.73

^a Assignments based on COSY experiments, room temperature, chemical shifts in ppm from internal SiMe₄. ^b In CD₃CN. ^c In (CD₃)₂CO.

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for **4b**[PF₆]₂

Au–O	1.976(3)	Au–O'	1.961(3)
Au–N(1)	2.011(4)	Au–N(2)	2.100(3)
Au···Au'	3.017(1)	O···H(112)	2.076
Au–O–Au'	100.0(1)	O–Au–O'	80.0(1)
O–Au–N(1)	174.1(1)	O–Au–N(2)	105.5(1)
O'–Au–N(1)	94.2(1)	O'–Au–N(2)	174.0(1)
N(1)–Au–N(2)	80.3(1)		

with the average Au–N distance (2.040 Å) found in the two crystallographically independent molecules of **2*c**[AuCl₄] (see later and references in the discussion of **2*c**[AuCl₄]), and shows that the oxygen atom has a low *trans* influence. The Au–N(2) bond is longer than Au–N(1) and the O–Au–N(2) angle,

At present we have no information on the mechanism of hydroxylation of ligand **2**.

Experimental

General

The bipyridines HL were prepared according to literature methods;²⁰ Na[AuCl₄] \cdot 2H₂O was obtained from Johnson Matthey and AgBF₄ from Aldrich Chimica. Elemental analyses were performed with a Perkin-Elmer 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, ¹H and ¹³C-¹H 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 a COSY-90. The ¹H NMR data are collected in Tables 1 and 2; 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.

Preparations of the adducts [Au(HL)Cl₃]

The adducts [Au(HL)Cl₃] **1a**, **3a** and **4a** were prepared as reported previously,⁸ **2a** was prepared likewise.

[Au{N₂C₁₀H₇(CHMe₂)-6}Cl₃] 2a. To a solution of N₂C₁₀H₇(CHMe₂)-**6**, **2** (0.495 g, 2.5 mmol) in MeCN (5 cm³) was added an aqueous solution (30 cm³) of Na[AuCl₄] \cdot 2H₂O (0.995 g, 2.5 mmol), the resulting yellow suspension was stirred for 30 h at room temperature. During this period the colour of the suspension turned to dark orange. The solid product was filtered off and air-dried under vacuum to give [Au(HL)Cl₃] **2a** (1.167 g, 93%). Recrystallization from chloroform–diethyl ether gave a dark orange crystalline product, m.p. 190–191 °C [Found: C, 30.43; H, 2.73; N, 5.47%; *m/z* 500 (*M*⁺). C₁₃H₁₄AuCl₃N₂ requires C, 31.13; H, 2.81; N, 5.58%; 500 (*M*); v_{\max}/cm^{-1} 1599m, 1589s, 1568s, 1485s, 1251s, 1165s, 1082m, 1037m, 1000s, 772vs and 358vs (Au–Cl); *m/z* 500 (*M*⁺), 464 (*M* – HCl), 429 (*M* – H – 2Cl), 394 (*M* – H – 3Cl) and 199 (H₂L⁺).

Reactions of the adducts 1a–4a

[Au₂{N₂C₁₀H₇(CH₂Me)-6}₂(μ-O)₂]²⁺ 1b. BF₄[–] Salt. To a solution of [Au{N₂C₁₀H₇(CH₂Me)-6}Cl₃] **1a** (0.487 g, 1 mmol) in acetone (25 cm³) were added compound **1** (0.184 g, 1 mol) and a solution of AgBF₄ (0.390 g, 2 mmol) in the same solvent (15 cm³), a precipitate of AgCl was formed immediately. The mixture was stirred for 12 h at room temperature. The solid product containing AgCl was filtered off and then extracted with Me₂SO. Addition of acetone to the filtered solution gave a pale yellow precipitate of [Au₂(HL)₂(μ-O)₂][BF₄]₂ **1b**[BF₄]₂ (0.134 g, 27%), m.p. 197–198 °C [Found: C, 28.96; H, 2.39; N, 5.79%; *m/z* 793 (*M*⁺). C₂₄H₂₄Au₂B₂F₈N₄O₂ \cdot H₂O requires C, 29.23; H, 2.66; N, 5.68%; 794 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); v_{\max}/cm^{-1} 3642m, 3560w, 1609m, 1601s, 1567m, 1498s, 1392s, 1294m, 1237m, 1172m, 1054vs (br), 829m, 791s, 672vs, 651m, 593m and 521s; *m/z* 881 ([*M* + BF₄]⁺), 793 (*M* – H), 593 (*M* – HL – OH), 415 ([Au(HL)(OH)]⁺), 397 ($\frac{1}{2}$ *M*⁺), 381 (HLAu) and 183 (L⁺).

PF₆[–] Salt. To a suspension of **1a** (0.212 g, 0.435 mmol) in MeCN (2 cm³) were added solid KPF₆ (0.240 g, 1.305 mmol) and an aqueous solution (15 cm³) of MeCO₂Na (0.0714 g, 0.87 mmol). The mixture was refluxed for 1 h and then filtered off and dried under vacuum to give **1b** as the PF₆[–] salt (0.208 g, 88%). Recrystallization from acetonitrile–diethyl ether gave the analytical sample as a pale yellow solid, m.p. 205–207 °C [Found: C, 26.41; H, 1.95; N, 5.14%; *m/z* 939 (*M*⁺). C₂₄H₂₄Au₂F₁₂N₄O₂P₂ requires C, 26.58; H, 2.23; N, 5.17%; 794 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); Λ_{M} (5 × 10^{–4} mol dm^{–3}, MeCN) 300 Ω^{–1} cm² mol^{–1}; v_{\max}/cm^{-1} 1605m, 1568m, 1498s, 1299s, 1261m,

1171w, 1106w, 1026w, 839vs, 786s, 674s, 663s, 652m, 592m and 566vs; *m/z* 939 ([*M* + PF₆]⁺) and 380 ($\frac{1}{2}$ *M* – OH).

[Au₂{N₂C₁₀H₇(CHMe₂)-6}₂(μ-O)₂]²⁺ 2b. BF₄[–] Salt. To a solution of [Au{N₂C₁₀H₇(CHMe₂)-6}Cl₃] **2a** (0.501 g, 1 mmol) in acetone (25 cm³) were added compound **2** (0.198 g, 1 mmol) and a solution of AgBF₄ (0.390 g, 2 mmol) in the same solvent (15 cm³), a precipitate of AgCl was formed immediately. The mixture was stirred for 12 h at room temperature. The solid product containing AgCl was filtered off and then extracted with MeCN. Addition of diethyl ether to the filtered solution gave a pale yellow precipitate of [Au₂(HL)₂(μ-O)₂][BF₄]₂ **2b**[BF₄]₂ (0.110 g, 22%), m.p. 195–196 °C [Found: C, 30.26; H, 2.63; N, 5.82. C₂₆H₂₈Au₂B₂F₈N₄O₂ \cdot H₂O requires C, 30.79; H, 2.98; N, 5.52%; Λ_{M} (5 × 10^{–4} mol dm^{–3}, MeCN) 280 Ω^{–1} cm² mol^{–1}; v_{\max}/cm^{-1} 3629w, 3558w, 1609m, 1600s, 1568m, 1495s, 1296m, 1257w, 1235m, 1172m, 1051vs (br), 825w, 788s, 722m, 673s and 520m.

PF₆[–] Salt. To a suspension of **2a** (0.502 g, 1 mmol) in MeCN (5 cm³) were added solid KPF₆ (0.552 g, 3 mmol) and an aqueous solution (20 cm³) of MeCO₂Na (0.164 g, 2 mmol). The mixture was stirred for 5 d at room temperature and then filtered off. Unreacted **2a** was extracted from the solid with CHCl₃. The residue was dissolved in acetone, the filtered solution was concentrated to small volume and diethyl ether was added to give a peach yellow precipitate of **2b** as the PF₆[–] salt (0.270 g, 48%), m.p. 186–187 °C [Found: C, 28.45; H, 2.50; N, 4.88%; *m/z* 821 (*M*⁺). C₂₆H₂₈Au₂F₁₂N₄O₂P₂ requires C, 28.07; H, 2.54; N, 5.04%; 822 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); Λ_{M} (5 × 10^{–4} mol dm^{–3}, MeCN) 300 Ω^{–1} cm² mol^{–1}; v_{\max}/cm^{-1} 1601vs, 1568s, 1495vs, 1296s, 1257m, 1236m, 1172s, 1087s, 1060vs, 1045w, 1021m, 840vs (br), 782vs, 740m, 723s, 672vs and 557s; *m/z* 967 ([*M* + PF₆]⁺), 821 (*M* – H), 805 (*M* – H – O), 607 (*M* – HL – OH), 591 (*M* – HL – 2O – H), 429 ([Au(HL)(OH)]⁺), 411 ($\frac{1}{2}$ *M*⁺), 395 (HLAu) and 198 (HL⁺).

[Au{N₂C₁₀H₇(CMe₂O)-6}Cl]⁺ 2*c. BF₄[–] Salt. To a solution of **2a** (0.501 g, 1 mmol) in MeCN (20 cm³) were added compound **2** (0.198 g, 1 mmol) and a solution of AgBF₄ (0.390 g, 2 mmol) in the same solvent (15 cm³), a precipitate of AgCl was formed immediately. The mixture was stirred for 4 h at room temperature and then filtered. The solution was evaporated to dryness and the residue treated first with dichloromethane, which extracted the salt [H₂L][BF₄], then with acetone, which extracted impure **2*c**, finally with MeCN. The filtered solution was concentrated to a small volume and diethyl ether was added to give **2*c** as a pale yellow solid (0.117 g, 22%), m.p. 215–216 °C [Found: C, 29.18; H, 2.44; N, 5.38%; *m/z* 445 (*M*⁺). C₁₃H₁₃AuBClF₄N₂O requires C, 29.32; H, 2.46; N, 5.26%; 445 (*M*, [Au(L*)Cl]⁺); Λ_{M} (5 × 10^{–4} mol dm^{–3}, MeCN) 140 Ω^{–1} cm² mol^{–1}; v_{\max}/cm^{-1} 1609m, 1601m, 1575w, 1493s, 1334w, 1307s, 1257s, 1205m, 1171w, 1105vs, 1056vs (br), 950w, 875m, 798m, 780vs, 684m, 669m, 521m, 390m, and 372m (Au–Cl); *m/z* 445 (*M*⁺), 429 (*M* – O), 410 (*M* – Cl), 395 (*MH* – O – Cl), 215 (H₂L*⁺) and 199 (H₂L* – O).

PF₆[–] Salt. To a suspension of complex **2a** (0.332 g, 0.66 mmol) in MeCN (10 cm³) was added an aqueous solution (15 cm³) of KPF₆ (0.488 g, 2.64 mmol). The resulting suspension was refluxed for 11 h and then filtered off and air dried. Some unreacted **2a** was extracted with chloroform from the solid product and the residue dissolved in acetone. The filtered solution was concentrated to a small volume and diethyl ether was added to give **2*c** as the PF₆[–] salt (0.055 g, 14%), m.p. 198–201 °C [Found: C, 26.23; H, 2.19; N, 4.61%; *m/z* 445 (*M*⁺). C₁₃H₁₃AuClF₆N₂OP requires C, 26.43; H, 2.22; N, 4.74%; 445 (*M*); v_{\max}/cm^{-1} 1601s, 1572m, 1492s, 1306m, 1256m, 1204w, 1167w, 1128m, 1103m, 1082w, 1060w, 875vs, 841vs (br), 796s, 776vs, 674m, 557vs, 389w and 357m (Au–Cl); *m/z* 590 ([*M* + PF₆]⁺), 445 (*M*⁺), 429 (*M* – O), 410 (*M* – Cl), 394 (*M* – O – Cl), 215 (H₂L*⁺) and 199 (H₂L* – O).

AuCl₄⁻ Salt. An aqueous solution (20 cm³) of Na[AuCl₄]·2H₂O (0.796 g, 2 mmol) was added to a solution of compound **2** (0.198 g, 1 mmol) in MeCN (2 cm³), the resulting suspension was refluxed for 20 h and then filtered off. Treatment of the crude product with chloroform (3 × 10 cm³) gave a dark orange solution and a yellow residue. The filtered solution was concentrated to a small volume and diethyl ether was added to give complex **2a** (0.234 g, 47%). The residue was dissolved in acetone and filtered through Celite, addition of diethyl ether to the concentrated solution gave a yellow product which was crystallized from acetone–diethyl ether to yield **2*c** as the AuCl₄⁻ salt (0.220 g, 28%), m.p. 229–230 °C {Found: C, 19.87; H, 1.77; N, 3.55%; *m/z* 445 (*M*⁺, FAB⁺ MS) and 337 (*M*⁻, FAB⁻ MS). C₁₃H₁₃·Au₂Cl₅N₂O requires C, 19.90; H, 1.67; N, 3.57%; 445 (*M*, [Au(L*)Cl⁺]) and 337 (AuCl₄⁻); Λ_M (5 × 10⁻⁴ mol dm⁻³, acetone) 120 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ 1606m, 1596m, 1568w, 1488s, 1331w, 1302s, 1257m, 1200w, 1168w, 1126m, 1101m, 1079m, 1030m, 947m, 870m, 797m, 783s, 683m, 338m and 360vs (Au–Cl); δ_C[(CD₃)₂CO] 149.8, 146.0, 145.9, 131.3, 127.7, 126.5 and 125.2 (7C, aromatic CH), 176.2, 159.0 and 152.0 (3C, aromatic C), 98.75 (1C, CMeO) and 30.8 (2C, CH₃); *m/z* 445 (*M*⁺), 429 (*M* – O), 410 (*M* – Cl), 394 (*MH* – O – Cl), 215 (H₂L*⁺) and 199 (H₂L* – O). Crystals of complex **2*c**[AuCl₄] were obtained by slow diffusion of diethyl ether into an acetone solution.

[Au₂{N₂C₁₀H₇(CMe₃-6)₂(μ-O)₂}]²⁺ **3b. BF₄⁻ Salt. Complex **3b**[BF₄]₂ was obtained as a by-product of the synthesis of [Au{N₂C₁₀H₇(CMe₂CH₂-6)Cl}]⁺.⁸ Here are the reported analytical and spectroscopic data. Yield 24%, m.p. 160–162 °C {Found: C, 32.21; H, 3.42; N, 5.47; O, 3.0%; *m/z* 937 (*M*⁺). C₂₈H₃₂Au₂B₂F₈N₄O₂ requires C, 32.83; H, 3.15; N, 5.47; O, 3.1%; 850 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); Λ_M (5 × 10⁻⁴ mol dm⁻³, MeCN) 320 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ 1600s, 1566m, 1494s, 1329w, 1295m, 1282w, 1227m, 1050vs (br), 823w, 782vs, 707w, 669w, 672s, 654s, 641s, 589m and 520m; *m/z* 937 ([*M* + BF₄]⁺), 869 ([*M* + F]⁺), 637 (*M* – H₂L), 621 (*M* – HL – OH), 605 (*M* – HL – 2O – H), 443 [{Au(HL)(OH)₂}⁺], 425 ($\frac{1}{2}$ *M*⁺), 409 ($\frac{1}{2}$ *M* – O) and 213 (H₂L⁺).**

[Au₂{N₂C₁₀H₇(CH₂CMe₃-6)₂(μ-O)₂}]²⁺ **4b. BF₄⁻ Salt. To a solution of [Au{N₂C₁₀H₇(CH₂CMe₃-6)Cl₃] **4a** (0.529 g, 1 mmol) in acetone (25 cm³) were added compound **4** (0.226 g, 1 mmol) and a solution of AgBF₄ (0.390 g, 2 mmol) in the same solvent (15 cm³), a precipitate of AgCl was formed immediately. The mixture was stirred for 20 h at room temperature. The solid products were separated and the filtered solution was added to solid K₂CO₃ and stirred for 5 h. After filtration the solution was evaporated to dryness, the free ligand was extracted with diethyl ether from the solid, then the residue was crystallized from MeCN–diethyl ether to give a pale yellow solid of **4b** (0.110 g). A second crop (0.040 g) was extracted with MeCN from the solid residue containing AgCl, m.p. 223–225 °C {Found: C, 32.75; H, 3.36; N, 5.06%; *m/z* 877 (*M*⁺). C₃₀H₃₆Au₂B₂F₈N₄O₂·2H₂O requires C, 33.11; H, 3.70; N, 5.15%; 878 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); Λ_M (5 × 10⁻⁴ mol dm⁻³, MeCN) 300 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ 1601s, 1568s, 1496s, 1336m, 1307s, 1282m, 1222m, 1051vs (br), 825w, 785w, 743w, 719w, 677s and 663s; *m/z* 965 ([*M* + BF₄]⁺), 897 ([*M* + F]⁺), 877 (*M* – H), 663 (*M* – Au – H₂O), 649 (*M* – Au – 2O), 635 (*M* – HL – OH), 619 (*M* – HL – 2O – H), 457 ([Au(HL)(OH)₂]⁺), 439 ($\frac{1}{2}$ *M*⁺), 423 ($\frac{1}{2}$ *M* – O) and 227 (H₂L⁺).**

PF₆⁻ Salt. To a suspension of **4a** (0.767 g, 1.45 mmol) in MeCN (10 cm³) were added solid KPF₆ (0.800 g, 4.35 mmol) and an aqueous solution (15 cm³) of MeCO₂Na (0.238 g, 2.90 mmol). The mixture was refluxed for 8 h and then filtered off and dried under vacuum to give **4b** as the PF₆⁻ salt (0.793, 93.6%). Recrystallization from acetone–diethyl ether gave the analytical sample, m.p. 192–194 °C {Found: C, 30.59; H, 3.19; N, 4.65%; *m/z* 1023 (*M*⁺). C₃₀H₃₆Au₂F₁₂N₄O₂P₂ requires C,

Table 5 Crystallographic data

Compound	4b [PF ₆] ₂	2*c [AuCl ₄]
Formula	C ₃₀ H ₃₆ Au ₂ F ₁₂ N ₄ O ₂ P ₂	C ₁₃ H ₁₃ Au ₂ Cl ₅ N ₂ O
<i>M</i>	1168.51	784.46
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>Cc</i> (no. 9)
<i>a</i> /Å	8.287(1)	32.245(8)
<i>b</i> /Å	10.595(1)	8.162(2)
<i>c</i> /Å	10.947(1)	16.342(4)
α /°	73.27(1)	
β /°	76.65(1)	114.23(1)
γ /°	85.79(1)	
<i>U</i> /Å ³	895.6(2)	3922.1(2.0)
<i>Z</i>	1	8
<i>T</i> /K	298	298
μ (Mo-K α)/cm ⁻¹	83.5	156.1
No. of reflections (total, independent)	10 934, 3833	21 593, 8634
<i>R</i> _{int}	0.021	0.029
Final <i>R</i> ₂ and <i>R</i> _w indices (<i>F</i> ²)	0.038, 0.053	0.072, 0.086
Conventional <i>R</i> ₁ index	0.028	0.059

30.83; H, 3.10; N, 4.79%; 878 (*M*, [Au₂(HL)₂(μ-O)₂]²⁺); Λ_M (5 × 10⁻⁴ mol dm⁻³, MeCN) 288 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ 1600s, 1564s, 1495s, 1363s, 1333m, 1304s, 1282w, 1222s, 1173w, 1146w, 1114m, 1060m, 1020s, 832vs (br), 786vs, 744m, 719m, 675vs and 557vs; *m/z* 1023 ([*M* + PF₆]⁺), 664 (*M* – Au – OH), 648 (*M* – Au – OH – O), 456 (*M* – Au – L), 439 ($\frac{1}{2}$ *M*⁺), 422 ($\frac{1}{2}$ *M* – OH) and 227 (H₂L⁺).

Crystals of complex **4b**[PF₆]₂ were obtained by slow diffusion of diethyl ether into an acetonitrile solution.

Reactions of the μ-oxo derivatives with HX (X = BF₄⁻ or PF₆⁻)

To a solution of [Au₂{N₂C₁₀H₇(CMe₃-6)₂(μ-O)₂][BF₄]₂ **3b**[BF₄]₂ (0.102 g, 0.1 mmol) in MeCN (15 cm³) was added HBF₄·OEt₂ (0.2 mmol), some decomposition to metallic gold was observed. The solution was stirred for 1 h at room temperature, then filtered through Celite and concentrated to a small volume; addition of diethyl ether gave a pale yellow precipitate of the starting product (0.076 g).

To an aqueous suspension of [Au₂{N₂C₁₀H₇(CH₂CMe₃-6)₂(μ-O)₂][PF₆]₂ **4b** (0.117 g, 0.1 mmol) was added aqueous HPF₆ (2 mmol), the resulting mixture was stirred for 5 h at room temperature. The starting product was recovered almost quantitatively after filtration and crystallization from acetone–diethyl ether.

Crystallography

Crystal data and other experimental details for complexes **4b**[PF₆]₂ and **2*c**[AuCl₄] are summarized in Table 5. The diffraction experiments were carried out on a Siemens SMART CCD area-detector diffractometer at room temperature using Mo-K α radiation (λ = 0.710 73 Å) with a graphite crystal monochromator in the incident beam.

Crystals of **4b**[PF₆]₂ were of good quality, whereas crystals of **2*c**[AuCl₄] were thin and very weakly diffracting; one of the latter, giving the ‘best’ diffraction, was used for data collection. Cell parameters and orientation matrix were obtained from the least-squares refinement of 50 (for **4b**[PF₆]₂) and 57 (for **2*c**[AuCl₄]) reflections measured in three different sets of 15 frames each, in the range 2 < θ < 23°. At the end of data collections the first 50 frames, containing 379 reflections (for **4b**[PF₆]₂) and 400 reflections (for **2*c**[AuCl₄]), were recollected to monitor crystal decay, which was not observed, so no time-

§ Note added at proof: the crystal structure of compound *cis*-**2b**-[AuCl₄][PF₆]₂ has been solved (X-ray diffraction) by two of us (M. M. and M. S.).

decay correction was needed. The collected frames were processed with the software SAINT,^{21a} and an absorption correction was applied (SADABS^{21b}) to the 10 934 collected reflections of **4b**[PF₆]₂ (3833 of which are unique with $R_{\text{int}} = 0.0212$ ($R_{\text{int}} = \Sigma|F_o^2 - F_{\text{mean}}^2|/\Sigma F_o^2$) and to the 21 593 collected reflections of **2*c**[AuCl₄] (8634 of which are unique with $R_{\text{int}} = 0.0287$).

The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package²² and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref. 23. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares using all reflections and minimizing the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). 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 that of the carbon atom to which they are attached) and not refined. For non-centrosymmetric **2*c**[AuCl₄], full refinement of the reported structure model led to $R_2 = 0.072$ and $R_{2w} = 0.086$, full refinement of the inverted structure led to $R_2 = 0.081$ and $R_{2w} = 0.099$. The final Fourier-difference maps show for **4b**[PF₆]₂ a maximum residual of 1.29(4) e Å⁻³ at 0.89 Å from Au, a largest residual not close to the heavy atom of 1.16 e Å⁻³, and a maximum negative peak of -1.33 e Å⁻³; for **2*c**[AuCl₄] corresponding values are 2.84(6) e Å⁻³ at 0.72 Å from Au(1B), 1.40 e Å⁻³ and -2.92 e Å⁻³, respectively. The atomic coordinates of the structure models are deposited with the Cambridge Data File.

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