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Synthesis and characterization of gold(III) adducts and cyclometallated derivatives with 6-benzyl- and 6-alkyl-2,2′-bipyridines

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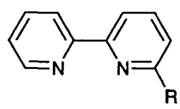
The reaction of a series of 6-substituted-2,2′-bipyridines HL ($N_2C_{10}H_7R$, R = CH_2Ph, CHMePh, CMe_2Ph, CH_2Me, CMe_3 or CH_2CMe_3) with $HAuCl_4$ or $Na[AuCl_4]$ has been investigated. Under different experimental conditions, salts $[H_2L][AuCl_4]$, adducts $[Au(HL)Cl_3]$ or cyclometallated derivatives $[Au(L)Cl][X]$ (X = $AuCl_4$, BF_4 or PF_6) have been isolated. The cyclometallated species arise from direct activation of a C–H bond either of a phenyl or a methyl substituent. The structures of an adduct $[Au\{N_2C_{10}H_7(CHMePh)\text{-}6\}Cl_3]$ and two metallated species $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl][AuCl_4]$ and $[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}Cl][BF_4]\cdot0.5H_2O$ have been determined by X-ray diffraction. In the adduct 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, Au ··· N 2.758(4) Å. In the two cyclometallated species the bipyridines act as tridentate N,N,C anions, giving a [5,6] and a [5,5]-fused ring system, respectively. In $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl]^+$ the hexaatomic N,C ring adopts a boat-like conformation: the structure reveals a rather short interaction between one hydrogen of the Me group in axial position and the gold atom, Au ··· H 2.62 Å. The pentaatomic N,C ring in $[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}Cl]^+$ is not planar: the co-ordination around the gold atom is essentially square planar. The new cyclometallated complexes $[Au(N,N,C)Cl]^+$ are compared with those derived from similarly substituted pyridines described previously.

In the field of the organic chemistry of gold(III), a topic of interest for many years,[1] cyclometallated derivatives having a Au^{III}–C bond supported by co-ordination of a nitrogen atom have been reported in the last fifteen years. Most involve ligands such as azobenzenes[2] and *N,N*-dimethylbenzylamines[3] and have been obtained through transmetallation reactions. More recently, examples of cycloaurated(III) complexes with 2-phenylpyridine[4] and 6-phenyl-2,2′-bipyridine[5] have been described. In addition, the species $[Au(L)Cl]^+$, where L is a carbanion of either 2,9-diphenyl-1,10-phenanthroline[6] or of 4′-(4-methoxyphenyl)-6′-phenyl-2,2′-bipyridine,[7] which act as terdentate N,N,C ligands, have been synthesized and found to be luminescent. Adducts and metallated derivatives with 2-substituted pyridines have been described previously by us;[8] the metallated species, arising from 2-benzylpyridines, contain a six-membered N,C ring, as unambiguously shown by X-ray diffraction in the case of $[Au\{NC_5H_4(CMe_2C_6H_4)\text{-}2\}Cl_2]$.[8] All the above cited examples of cyclometallated derivatives entail a $C(sp^2)$–Au^{III} bond: as far as we know no activation of $C(sp^3)$–H bonds has been reported.

In this paper we discuss the reactivity of 6-benzyl- and 6-alkyl-2,2′-bipyridines HL. Besides salts $[H_2L][AuCl_4]$ and adducts $[Au(HL)Cl_3]$, cyclometallated species $[Au(L)Cl][X]$ (X = $AuCl_4$, BF_4 or PF_6) have been obtained by direct activation of C–H bonds of both phenyl and methyl substituents. The structures of $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl][AuCl_4]$ and $[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}Cl][BF_4]\cdot0.5H_2O$, solved by X-ray diffraction, give evidence for a six-and a five-membered N,C ring in the two complexes, respectively. A brief report on part of this work has been given.[9]

Results and Discussion



	R
I	CH_2Ph
II	CHMePh
III	CMe_2Ph
IV	CH_2Me
V	CMe_3
VI	CH_2CMe_3

The 6-substituted-2,2′-bipyridines HL, **I**–**VI**, have been prepared from the corresponding 2-substituted pyridines, according to established methods.[10] Mostly the starting gold-containing compound was $HAuCl_4\cdot3H_2O$: in some cases $Na[AuCl_4]\cdot2H_2O$ was used.

The reaction of $HAuCl_4$ with HL (1 : 1 molar ratio), at room temperature, affords either the salts $[H_2L][AuCl_4]$ or the adducts $[Au(HL)Cl_3]$ depending on the experimental conditions such as the medium and the time (see Experimental section). In some cases a mixture of the salt and the adduct is obtained and this accounts for the low yield of some pure compounds. Pure salts have been isolated only with compounds **I** and **III**; they have been characterized by microanalyses, conductivity measurements, ^1H NMR and mass (FAB) spectra (positive and negative ions). In the IR spectra, besides the absorptions in the ranges 3200–3050 and 1635–1525 cm^{-1}, a strong band at *ca.* 355 cm^{-1} is consistent with an $[AuCl_4]^-$ anion.[11] No NH signal is observed in the ^1H NMR spectra.

Pure 1 : 1 adducts $[Au(HL)Cl_3]$ have been obtained with all compounds **I**–**VI**. This contrasts with the behaviour of the corresponding pyridines: indeed no adduct was obtained when the 2 substituent was an alkyl group.[8] In the IR spectra of the adducts strong absorptions in the range 365–355 cm^{-1} are typical for $AuCl_3$ adducts with substituted pyridines.[8,12] In the ^1H NMR spectra (Table 1) all the resonances are shifted

Table 1 Proton NMR data[a]

Compound	Solvent	H(6′)	Other aromatics	CH	CH_2	CH_3	Others
$N_2C_{10}H_7(CH_2Ph)$-6	$(CD_3)_2CO$	8.65 (dd)	8.53–7.17		4.22 (s)		
$[HN_2C_{10}H_7(CH_2Ph)$-6$][AuCl_4]$	$(CD_3)_2CO$	9.14 (dd)	8.95–7.25		4.43 (s)		
1a	$(CD_3)_2CO$	9.38 (dd)	8.65–7.18		4.57 (s)		
1m $AuCl_4^-$ salt	$(CD_3)_2CO$	9.43 (dd)	9.01–7.16		4.94 (s)		
PF_6^- salt	$(CD_3)_2CO$	9.42 (dd)	8.99–7.15		4.93 (s)		
1*m[b]	$(CD_3)_2CO$	9.39 (dd)	9.02–7.20				6.54 (d, H_A), 6.45 (d, H_X) [$J(H_AH_X)$ = 5, CHOH]
$N_2C_{10}H_7(CHMePh)$-6	$CDCl_3$	8.67 (dd)	8.58–7.10	4.35 (q, 7.0)		1.80 (d, 7)	
	$(CD_3)_2CO$	8.66 (dd)	8.60–7.15	4.39 (q, 7.0)		1.77 (d, 7.0)	
2a	$CDCl_3$	9.07 (dd)	8.22–7.20	4.97 (q, 7.1)		1.88 (d, 7.1)	
2m $AuCl_4^-$ salt	$(CD_3)_2CO$	9.46 (dd)	9.01–7.18	5.18 (q, 7.3)		1.88 (d, 7.3)	
BF_4^- salt	CD_2Cl_2	9.38 (dd)	8.82–7.15	4.79 (q, 7.2)		1.85 (d, 7.2)	
	$(CD_3)_2CO$	9.45 (dd)	9.00–7.17	5.18 (q, 7.1)		1.87 (d, 7.1)	
2p[c]	CD_2Cl_2	8.81 (d) [3]	8.31–6.58	4.90 (q, 7.2)		2.10 (d, 7.2)	
		8.71 (d) [1]		4.75 (m, br)		2.3 (d, br)	
2c	$CDCl_3$	9.22 (dd)	8.81–7.18	4.65 (q, 7.0)		1.81 (d, 7.0)	3.51 (s, CH_2), 2.29 (s, CH_3)
$N_2C_{10}H_7(CMe_2Ph)$-6	$CDCl_3$	8.65 (dd)	8.55–7.02			1.83 (s)	
	$(CD_3)_2CO$	8.66 (dd)	8.55–7.15			1.83 (s)	
$[HN_2C_{10}H_7(CMe_2Ph)$-6$][AuCl_4]$	$(CD_3)_2CO$	9.17 (dd)	9.04–7.21			1.88 (s)	
3a	$CDCl_3$	9.07 (dd)	8.25–7.14			1.97 (s)	
	$(CD_3)_2CO$	9.38 (dd)	8.58–7.19			1.95 (s)	
3m $AuCl_4^-$ salt	$(CD_3)_2CO$	9.42 (dd)	9.00–7.15			2.2 (s)	
BF_4^- salt	$(CD_3)_2CO$	9.40 (dd)	9.00–7.14			2.19 (s)	
3p	$(CD_3)_2CO$	9.05 (d, br)	8.54–6.57			2.59 (s), 2.26 (s)	
$N_2C_{10}H_7(CH_2Me)$-6	$CDCl_3$	8.67 (dd)	8.47–7.16		2.90 (q, 7.6)	1.38 (t, 7.6)	
4a	$CDCl_3$	9.04 (d)	8.20–7.47		3.27 (q, 7.5)	1.48 (t, 7.5)	
$N_2C_{10}H_7(CMe_3)$-6	$CDCl_3$	8.65 (dd)	8.55–7.21			1.43 (s)	
5a	$CDCl_3$	9.04 (dd)	8.23–7.65			1.57 (s)	
	$(CD_3)_2CO$	9.34 (dd)	8.54–7.78			1.55 (s)	
5m	$(CD_3)_2CO$	8.98 (dd)	8.91–8.06		3.51 (s)	1.73 (s)	
5p	$(CD_3)_2CO$	8.81 (d)	8.73–7.63		3.36 (d, 3.7)[d]	1.61 (s)	
$N_2C_{10}H_7(CH_2CMe_3)$-6	$CDCl_3$	8.66 (dd)	8.46–7.11		2.76 (s)	1.01 (s)	
	$(CD_3)_2CO$	8.66 (dd)	8.51–7.24		2.76 (s)	1.01 (s)	
6a	$CDCl_3$	9.05 (dd)	8.22–7.41		3.15 (s)	1.03 (s)	
	$(CD_3)_2CO$	9.34 (dd)	8.68–7.57		3.17 (s)	1.02 (s)	

[a] Spectra recorded at room temperature, chemical shifts in ppm from internal $SiMe_4$, coupling constants (in parentheses) in Hz. [b] At +50 °C, δ 6.43 (s, 2 H, CHOH); $+D_2O$, δ 6.30 (s, 1 H). [c] Compound **2p** is present in solution as diastereomers, a and b, integrals are in square brackets. [d] Due to coupling with phosphorus, $^3J(H–P)$.

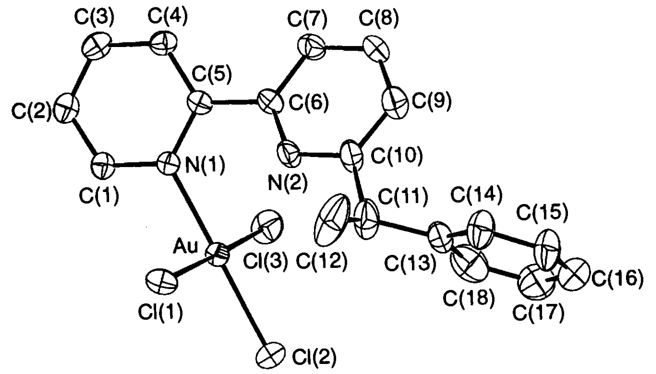


Fig. 1 An ORTEP view of compound **2a**. Ellipsoids are drawn at the 30% probability level

downfield with respect to free HL: besides the strong deshielding of the H(6′) proton [*ca.* 0.4 ppm in $CDCl_3$ and *ca.* 0.7 ppm in $(CD_3)_2CO$], even the resonances of the protons on the substituent at C(6) move somewhat downfield. Conductivity measurements rule out ionic species such as $[Au(HL)Cl_2]Cl$, whereas the IR and ^1H NMR data on the whole do not allow a choice to be made between a five-co-ordinated species with both the nitrogen atoms bonded to the gold atom or a square-planar complex with the bipyridine acting as a monodentate ligand.

The crystal structure of the adduct **2a** was solved by X-ray diffraction. It consists of the packing of discrete $[Au\{N_2C_{10}H_7(CHMePh)\text{-}6\}Cl_3]$ molecules with normal van der Waals contacts. An ORTEP[13] view of the molecule 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 square-planar co-ordination with a very slight pyramidal distortion: thus atoms Cl(1), Cl(2), Cl(3) and N(1) are strictly coplanar, with the gold atom lying 0.0509(2) Å above their best plane. Both the Au–N(1) [2.047(4) Å] and the three Au–Cl bond lengths (average 2.275 Å) are normal and can be compared for instance with the Au–N [2.041(3) Å] and Au–Cl(1) [2.282(1) Å] found in $[Au\{NC_5H_4(CMe_2C_6H_4)\text{-}2\}Cl_2]$.[8] The relative rigidity of the bipyridyl ligand automatically brings atom N(2) to a distance from the gold atom, 2.758(4) Å, which is well below the sum of the van der Waals radii of Au and N (2.2 + 1.5 = 3.7 Å)[14] but much longer than the usual Au^{III}–N single bonds [see for instance 1.976(5) and 2.151(5) Å in cation **5m**]. Similar Au–N interactions have been previously observed in a number of cases.[15] They have generally been considered fairly weakly bonding; however it has been pointed out that they take place only when sterically enforced by the presence of relatively rigid multidentate ligands.[15a] The two pyridine rings

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

Au–Cl(1)	2.288(1)	Au–Cl(2)	2.264(1)
Au–Cl(3)	2.274(2)	Au–N(1)	2.047(4)
Au···N(2)	2.758(4)		
Cl(1)–Au–Cl(2)	91.01(6)	Cl(1)–Au–Cl(3)	176.60(6)
Cl(1)–Au–N(1)	90.6(1)	Cl(2)–Au–Cl(3)	90.49(6)
Cl(2)–Au–N(1)	177.2(1)	Cl(3)–Au–N(1)	87.8(1)
Au–N(1)–C(1)	116.4(3)	Au–N(1)–C(5)	122.5(3)

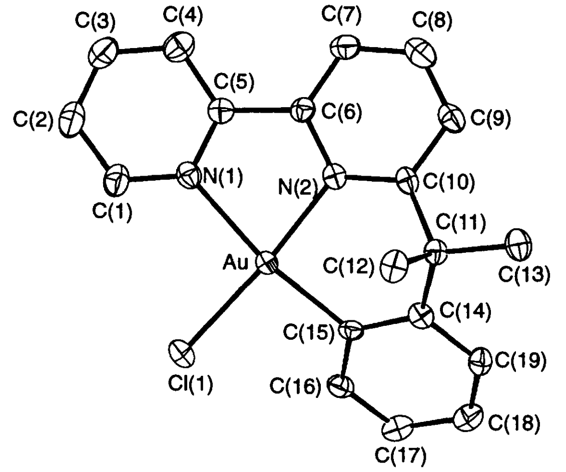
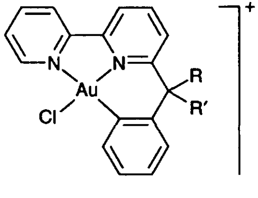


Fig. 2 An ORTEP view of cation **3m**. Ellipsoids as in Fig. 1



1m R = R′ = H
2m R = H, R′ = Me
3m R = R′ = Me

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

Au–Cl(1)	2.263(2)	Au–N(1)	2.121(5)
Au–N(2)	2.009(4)	Au–C(15)	2.009(6)
Cl(1)–Au–N(1)	95.6(1)	Cl(1)–Au–N(2)	174.9(1)
Cl(1)–Au–C(15)	93.8(2)	N(1)–Au–N(2)	79.5(2)
N(1)–Au–C(15)	165.7(2)	N(2)–Au–C(15)	91.3(2)

are strictly planar and are twisted by 29.0(3)° with respect to each other. The dihedral angle between the metal co-ordination plane and the N(1) ⋯ C(5) ring is 72.1(1)°. It is worthy of note that in the solid state the phenyl group points away from the metal: in spite of this, under certain experimental conditions, orthometallation occurs.

The cationic cyclometallated derivatives **1m**–**3m** and **5m**, which involve a N,N,C donor atom set, have been obtained with the 6-benzylbipyridines **I**–**III**, as well as with the *tert*-butyl-substituted ligand **V**, according to the reactions (1)–(5) (Scheme 1). Reactions (1) and (2) give the tetrachloroaurate(III) salts of the cations **1m**–**3m** in fairly good yields from both $HAuCl_4$ and $Na[AuCl_4]$. Attempts to exchange $AuCl_4^-$ with other anions were unsuccessful: nevertheless the cyclometallated cations **2m** and **3m** can be isolated as the BF_4^- salts from the preformed adducts **2a** and **3a** [equation (3)] by prolonged heating of their suspension in water at *ca.* 80 °C. Isolation of the pure $[Au(L)Cl][BF_4]$ complexes requires some work-up of the crude products which are often contaminated by the corresponding tetrachloroaurates.

Furthermore in the case of compound **I**, $N_2C_{10}H_7(CH_2Ph)$-6, the cyclometallated complex isolated under these conditions, **1*m**, does not contain **I** but the hydroxy-substituted ligand $N_2C_{10}H_7[CH(OH)Ph]$-6 **I***, as shown by ^1H NMR and FAB mass spectra. The latter (positive ions) exhibits the molecular ion M^+ at m/z 493 as well as a peak at m/z 261 due to the deprotonated ligand **I***. The substitution at the benzylic carbon is confirmed in the ^{13}C NMR spectra by an APT (attached proton test) experiment.

$$2\,HAuCl_4 + HL \xrightarrow{(i)} \underset{\mathbf{1m,2m}}{[Au(L)Cl][AuCl_4]} + 3\,HCl \qquad (1)$$

$$2\,Na[AuCl_4] + HL \xrightarrow{(i)} \underset{\mathbf{3m}}{[Au(L)Cl][AuCl_4]} + 2\,NaCl + HCl \qquad (2)$$

$$\underset{\mathbf{2a,3a}}{[Au(HL)Cl_3]} + NaBF_4 \xrightarrow{(ii)} \underset{\mathbf{2m,3m}}{[Au(L)Cl][BF_4]} + NaCl + HCl \qquad (3)$$

$$\underset{\mathbf{1a}}{[Au(HL)Cl_3]} + KPF_6 \xrightarrow{(iii)} \underset{\mathbf{1m}}{[Au(L)Cl][PF_6]} + KCl + HCl \qquad (4)$$

$$\underset{\mathbf{5a}}{[Au(HL)Cl_3]} + 2AgBF_4 + HL \xrightarrow{(iv)} \underset{\mathbf{5m}}{[Au(L)Cl][BF_4]} + 2\,AgCl + [H_2L][BF_4] \qquad (5)$$

Scheme 1 (*i*) MeCN–water, room temperature (r.t.); (*ii*) water, heat; (*iii*) water, r.t.; (*iv*) Me_2CO, r.t.

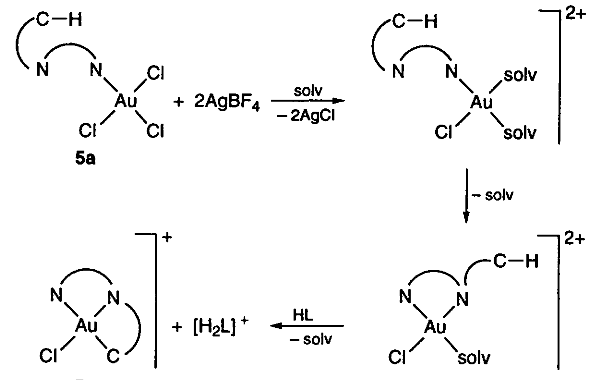
The cationic complex **1m** was obtained from the adduct **1a** in the presence of KPF_6 [equation (4)]: in this case metallation occurs at room temperature.

In the IR spectra of compounds **1m**–**3m** the disappearance of a band at *ca.* 700 cm^{-1}, assigned in the ligands to an out-of-plane skeletal mode typical of a monosubstituted phenyl ring, can be assumed as diagnostic of metallation involving a C–H aromatic bond. A sharp absorption at 700 ± 3 cm^{-1} is observed for the adducts **1a**–**3a**, as well as for the salts. $[H_2L][AuCl_4]$ (HL = **I** or **III**).

As observed previously for analogous palladium(II) N,N,C metallated derivatives,[16] even in the gold(III) species, the six-membered C,N ring is fluxional on the NMR time-scale. Indeed in the ^1H NMR spectra one resonance alone is observed for the protons of the substituents on the benzylic carbon atom, suggesting a fast inversion of the ring. This dynamic behaviour contrasts with that of the N,C six-membered rings in the corresponding gold(III) metallated species derived from 2-benzylpyridines.[8]

The structure in the solid state of the cyclometallated derivative $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl][AuCl_4]$ **3m** $[AuCl_4]$ has been solved by X-ray diffraction. It consists of the packing of $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl]^+$ cations and $[AuCl_4]^-$ anions with normal van der Waals contacts. An ORTEP view of the cation with the atom labelling scheme is shown in Fig. 2. Selected bond distances and angles are reported in Table 3.

The gold atom in the cation displays a distorted square-planar co-ordination, with atoms Au, Cl(1), N(1) and N(2) essentially coplanar [maximum deviations from their best plane being +0.018(1) and −0.010(5) Å for Au and N(2), respectively], whereas atom C(15) is displaced 0.417(6) Å out of this plane. The dihedral angle between the Au–N(1)–N(2) and Au–Cl(1)–C(15) planes is 11.2(6)°. The distortion from the ideal square-planar geometry is probably due to the limited flexibility of the N,N,C ligand. A similar distortion has been previously found in [Pd(L)Cl] [HL = $N_2C_{10}H_7(CHMePh)$-6], where the dihedral angle between the Pd–N–N and Pd–Cl–C planes is 16°.[16] The similarity of the present tridentate ligand with that in [Pd(L)Cl] (the only difference is the substitution of a benzylic hydrogen atom with a methyl group), and the similarity of the covalent radii of Pd^{II} and Au^{III}, allow a comparison between the metal–ligand distances in the present compound and in [Pd(L)Cl]. Thus, the Au–N(1), Au–N(2) and Au–C(15) bond lengths [2.121(5), 2.009(4) and 2.009(6) Å, respectively] are very similar to the Pd–N(1), Pd–N(2) and Pd–C distances in [Pd(L)Cl] [2.119(4), 2.008(4) and 1.980(6) Å, respectively]. The elongation of the Au–N(1) bond is obviously due to the *trans* influence of atom C(15). The two bites of the tridentate ligand in the present compound [N(1)–Au–N(2) and N(2)–Au–C(15),



Scheme 2 solv = Solvent

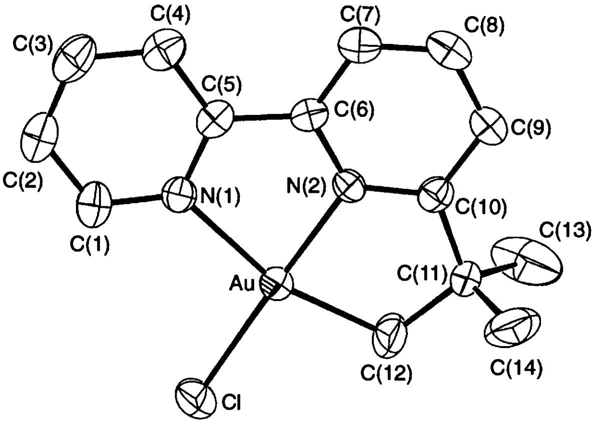


Fig. 3 An ORTEP view of cation **5m**. Ellipsoids as in Fig. 1

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for cation **5m**

Au–Cl	2.259(2)	Au–N(1)	2.151(5)
Au–N(2)	1.976(5)	Au–C(12)	2.028(7)
Cl–Au–N(1)	101.8(1)	Cl–Au–N(2)	178.5(2)
Cl–Au–C(12)	94.9(2)	N(1)–Au–N(2)	79.4(2)
N(1)–Au–C(12)	163.0(3)	N(2)–Au–C(12)	84.0(3)

79.5(2) and 91.3(2)°, respectively] are also very similar to the corresponding angles in [Pd(L)Cl], 79.5(2) and 91.9(2)°. The Au–Cl(1) bond length, 2.263(2) Å, is normal. The six-membered metallacycle is in a boat conformation, with atoms N(2), C(10), C(14) and C(15) essentially coplanar [maximum deviations from their best plane being +0.038(6) and −0.038(6) Å for C(10) and C(14), respectively], whereas atoms Au and C(11) lie 0.550(1) and 0.657(6) Å, respectively, above their best plane. The dihedral angles of this best plane with the N(2)–Au–C(15) and C(10)–C(11)–C(14) planes are 23.1(5) and 48.1(4)°, respectively. One of the hydrogen atoms (not refined) bonded to C(12) lies 2.62 Å from the gold atom, a distance comparable to that found in [Au{$NC_5H_4(CMe_2C_6H_4)$-2}Cl_2], 2.56(5) Å,[8] and well below the value reported for long-range metal–hydrogen interactions in platinum(II) chemistry.[17] The N(1) ··· C(5) and C(14) ··· C(19) rings are strictly planar, whereas the planarity of ring N(2) ··· C(10) is less rigorous, with maximum deviations from the best plane of +0.042(5) and −0.026(6) Å for atoms N(2) and C(10), respectively. The dihedral angle between the best planes of the two pyridine rings is 9.6(9)°; that between the best planes of rings N(2) ··· C(10) and C(14) ··· C(19) is 55.4(2)°.

With the 6-alkyl-substituted compounds **IV**–**VI** (R = CH_2Me **IV**, CMe_3 **V** or CH_2CMe_3 **VI**), 1 : 1 $AuCl_3$: HL adducts have been isolated and characterized as neutral species [Au(HL)Cl_3] **4a**–**6a**. It is worth noting that we failed to obtain adducts with the corresponding 2-alkylpyridines.[8] Thus it is likely that in **4a**–**6a** co-ordination occurs through the nitrogen atom of the unsubstituted pyridine as shown in the case of 6-benzyl-2,2′-bipyridines. In agreement, in the ^1H NMR spectra the resonances of the H(6′) protons are strongly deshielded with respect to those of the free HL. The resonances of the alkyl protons are likewise shifted downfield, suggesting that some kind of interaction between the gold atom and the nitrogen of the substituted ring persists even in solution.

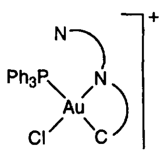
Attempts to achieve metallation with compounds **IV** and **VI** were unsuccessful, whereas a cyclometallated species was isolated in the case of 6-*tert*-butyl-2,2′-bipyridine **V** [Scheme 1, equation (5)]. Activation of the C(sp^3)–H bond requires removal of two chloride ligands with silver salts, likely to give a bis(solvated bond) intermediate (Scheme 2).

The structure of complex [Au{$N_2C_{10}H_7(CMe_2CH_2)$-6}Cl][BF_4]·0.5H_2O **5m**[BF_4]·0.5H_2O consists of the packing of [Au{$N_2C_{10}H_7(CMe_2CH_2)$-6}Cl]$^+$ cations, BF_4^- anions and water molecules in the molar ratio 2 : 2 : 1. The van der Waals contacts are normal (but see Experimental section for a possible fluorine–water hydrogen bond). An ORTEP view of the cation with the atom labelling scheme is shown in Fig. 3. Selected bond distances and angles are reported in Table 4. The gold atom displays an essentially square-planar co-ordination, with maximum deviations from the best plane of +0.042(5) Å for N(2) and of −0.044(9) Å for C(12). The molecular parameters of the cation can be compared with those found in the analogous neutral platinum complex [Pt(L)Cl] (HL = 6-*tert*-butyl-2,2′-bipyridine)[18] where the N,N,C ligand is the same as in the present cation. Thus, the Au–N(1), Au–N(2) and Au–C(12) distances [2.151(5), 1.976(5) and 2.028(7) Å, respectively] are similar to the corresponding distances in the platinum complex [2.117(7), 1.959(7) and 2.000(11) Å]. The Au–Cl bond length, 2.259(2) Å, is slightly shorter than the Pt–Cl one, 2.303(3) Å. The two bites of the tridentate ligand are also very similar in the two compounds {N(1)–Au–N(2) 79.4(2) and N(2)–Au–C(12) 84.0(3)° here, N–Pt–N 79.9(3) and N–Pt–C 83.8(4)° in [Pt(L)Cl]}. The pentaatomic ring Au–N(1)–C(5)–C(6)–N(2) is essentially planar [maximum deviations from their best plane being +0.028(5) and −0.026(6) Å for N(1) and C(5), respectively], whereas in the pentaatomic metallacycle atoms Au, N(2), C(10) and C(11) are strictly planar, with C(12) lying 0.161(9) Å above their best plane. The two pyridine rings are each strictly planar, and are twisted by 4.2(9)° with respect to each other.

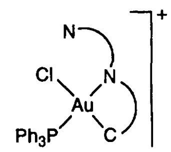
Even the five-membered cyclometallated complex **5m** is fluxional in solution, as shown by the ^1H NMR spectrum: no significant variation is observed on lowering the temperature from 20 to −90 °C.

From the reaction of complex **5a** with $AgBF_4$, besides **5m**, a second product was isolated and characterized (see Experimental Section). On the basis of microanalytical data, conductivity measurements, IR, NMR and mass spectra, we suggest the formulation as a cationic dimer (or polymer) [$Au_2(HL)_2(\mu\text{-}O)_2$][$BF_4$]$_2$. Accordingly in the infrared spectrum no band assignable to a Au–Cl stretching mode is observed. The ^1H NMR spectrum exhibits seven aromatic resonances and a singlet at δ 1.74 (9 H, CH_3) strongly deshielded with respect to that of free HL (Δδ +0.33 in CD_3CN), supporting co-ordination of both nitrogen atoms.

The reaction of PPh_3 with the cyclometallated species **2m**, **3m** and **5m** as their BF_4^- salts (molar ratio 1 : 1) has been investigated. In the presence of an excess of $NaBF_4$ the compounds [Au{$N_2C_{10}H_7(CHMeC_6H_4)$-6}(PPh_3)Cl]BF_4 **2p**, [Au{$N_2C_{10}H_7(CMe_2C_6H_4)$-6}($PPh_3$)Cl]$BF_4$ **3p** and [Au{$N_2C_{10}H_7(CMe_2CH_2)$-6}(PPh_3)][BF_4]$_2$ **5p**, respectively, were isolated as white solids. Analytical data and conductivity



A



B

measurements show that **2p** and **3p** are univalent cations formed by addition of PPh_3 to **2m** and **3m**, respectively. According to spectroscopic evidence (IR and NMR) in **2p** and **3p** the nitrogen atom of the external ring is displaced from the metal atom. The strong absorption at *ca.* 313 cm^{-1} observed in the IR spectra, assigned to the Au–Cl stretching vibration, is consistent with a chlorine *trans* to a donor atom having a high *trans* influence.[3a,c,8] Therefore, of the two possible geometrical isomers **A** and **B**, the latter, which has a chlorine *trans* to the C atom, is the preferred one. The isolation of isomer **B** is likely to be due to the bulkiness of the phosphine: inspection of molecular models shows that the inflexible bipy ligand hampers the accommodation of PPh_3 *cis* to the nitrogen atom.

In the absence of an excess of BF_4^-, the reactivity of $[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl]BF_4$ **3m** with PPh_3 has been monitored by NMR spectroscopy. In the ^1H and $^{31}P\text{-}\{^1H\}$ spectra of a 1 : 1 mixture in $(CD_3)_2CO$ two species are observed (integral ratio 3 : 1). The major component is the cation **3p** (isomer **B**) isolated in the presence of BF_4^- {δ_H 9.05 [d, 1 H, H(6′)]; δ_P 28.1}; the less-abundant species, δ_P 31.17, not revealed in the ^1H spectrum, has not been identified. A PPh_3 adduct of a metallated gold(III) species having a similar ^{31}P chemical shift (δ 30.34) has been described as a five-coordinated complex.[19]

At variance with the behaviour of **2m** and **3m**, the reaction of compound **5m** with PPh_3 occurs with displacement of the chloride ion to give **5p** as the bis(tetrafluoroborate) salt (Scheme 3). It is worth noting that, even in analogous platinum(II) complexes, removal of the chloride has been observed to be easier when the N,N,C ligand arises from activation of a $C(sp^3)$–H[18] rather than a $C(sp^2)$–H bond.[20]

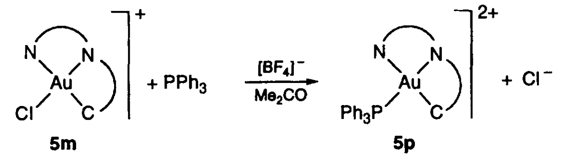
Displacement of the chloride from compound **2m** can be achieved by means of silver salts. When the reaction of $[Au\{N_2C_{10}H_7(CHMeC_6H_4)\text{-}6\}Cl][BF_4]$ was carried out in refluxing acetone (Scheme 4) compound **2c** was isolated as its BF_4^- salt and identified as having two *cis* gold–carbon bonds. Activation of acetone in similar gold(III) cyclometallated complexes with nitrogen ligands has been reported by Vicente *et al.*[21]

The reactivity of the gold–carbon bonds in the new metallated species **1m**–**5m** is currently under investigation.

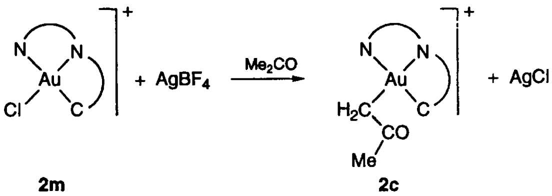
Conclusion

Palladium(II) and platinum(II) cyclometallated derivatives with terdentate anionic ligands having a N,N,C donor atom set have been widely investigated.[22] In contrast, monomeric derivatives of gold(III) with the same type of ligands are still very rare.[5–7] A number of new terdentate N,N,C bound benzyl- and alkyl-gold complexes have now been prepared by direct auration of 6-substituted 2,2′-bipyridines. Both six- and five-membered rings were formed and both sp^2 and sp^3 C–H activation was achieved: the latter activation is unprecedented.

Some preliminary studies on their reactivity have given evidence for a remarkable difference in behaviour regarding the lability of the fourth ligand. Subsequent studies will concern other aspects of their reactivity including that of the carbon–gold bond, a topic almost completely unexplored in the case of gold(III) cyclometallated species of this type. It is worth mentioning that the reactivity of gold(III) N,C cyclometallated species derived from 2-substituted pyridines,[8] in some cases, *e.g.* with carbon monoxide, is reminiscent of that of the analogous palladium(II) complexes.[23] The discovery of this peculiar feature prompted us to synthesize other gold derivatives and to investigate their behaviour.



Scheme 3



Scheme 4

Experimental

General

The bipyridines HL were prepared according to literature methods;[10] $HAuCl_4\cdot3H_2O$ and $Na[AuCl_4]\cdot2H_2O$ were obtained from Johnson Matthey. 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, ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra with a Varian VXR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz, respectively. The ^1H NMR data are collected in Table 1; chemical shifts are given in ppm relative to internal tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol as supporting matrix.

Preparations of 6-benzyl-2,2′-bipyridine derivatives

$[HN_2C_{10}H_7(CH_2Ph)\text{-}6][AuCl_4]$. To a solution of $N_2C_{10}H_7(CH_2Ph)\text{-}6$ (0.435 g, 1.77 mmol) in ethanol (5 cm^3) was added a solution of $HAuCl_4\cdot3H_2O$ (0.665 g, 1.77 mmol) in the same solvent (20 cm^3): a yellow precipitate was formed after few minutes. The suspension was stirred for 1 d at room temperature. The solid product was filtered off and dried under vacuum to give the required salt (0.947 g, 91%). Recrystallization from acetone–diethyl ether yielded an orange-yellow crystalline product, m.p. 135–136 °C [Found: C, 34.2; H, 2.7; N, 4.7%; *m/z* 247 (M^+, FAB+) and 337 (M^-, FAB−). $C_{17}H_{15}AuCl_4N_2$ requires C, 34.8; H, 2.6; N, 4.8%; *M* 247 (H_2L^+) and 337 ($AuCl_4^-$)]; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 122 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 3138vs, 3085vs, 3058vs, 1632w, 1619s, 1599s, 1588vs, 1563m, 1526vs, 1492w, 1261m, 1238m, 1215m, 1174m, 1149m, 1097m, 992m, 925m, 770vs, 735s, 717w, 698s and 360vs (Au–Cl).

$[Au\{N_2C_{10}H_7(CH_2Ph)\text{-}6\}Cl_3]$ 1a. To a solution of $N_2C_{10}H_7(CH_2Ph)\text{-}6$ (0.140 g, 0.57 mmol) in MeCN (5 cm^3) were added an aqueous solution (15 cm^3) of $HAuCl_4\cdot3H_2O$ (0.214 g, 0.57 mmol): the resulting yellow suspension was stirred for 12 h at room temperature. The solid product was filtered off and dried under vacuum to give $[Au(HL)Cl_3]$ (0.235 g, 75%). Recrystallization from dichloromethane–diethyl ether yielded an orange crystalline product, m.p. 150–151 °C [Found: C, 37.0; H, 2.6; N, 4.8%; *m/z* 548 (M^+). $C_{17}H_{14}AuCl_3N_2$ requires C, 37.1; H, 2.6; N, 5.1%; *M* 548]; $\tilde{\nu}_{max}/cm^{-1}$ 1600m, 1588s, 1568s, 1487s, 1250m, 997m, 925m, 769vs, 740s, 721m, 703s, 580s, 470m and 355vs and 266w (Au–Cl); *m/z* 830 $[Au(H_3L_2)Cl_4]$, 760 $[Au(H_3L_2)Cl_2]$, 548 (M^+), 512 ($M -$ HCl), 476 ($M -$ 2HCl) 442 (LAu) and 247 (H_2L).

$[Au\{N_2C_{10}H_7(CH_2C_6H_4)\text{-}6\}Cl]^+$ 1m. $AuCl_4^-$ *salt.* To a solution of $N_2C_{10}H_7(CH_2Ph)$-6 (0.246 g, 1 mmol) in MeCN (5 cm^3) was added an aqueous solution (30 cm^3) of $HAuCl_4\cdot3H_2O$ (0.752 g, 2 mmol): the resulting yellow suspension was stirred for 5 d at room temperature. The solid was filtered off and air dried to give 0.700 g of a crude product from which 0.110 g of complex **1a** was obtained by extraction with dichloromethane. The residue was dissolved in acetone, the filtered solution was concentrated to small volume and diethyl ether was added to yield **1m** as a yellow crystalline solid (0.570 g, 70%), m.p. 181–183 °C {Found: C, 25.0; H, 1.6; N, 3.3%; *m/z* 477 (M^+, FAB+) and 337 (M^-, FAB^-). $C_{17}H_{13}Au_2Cl_5N_2$ requires C, 25.0; H, 1.6; N, 3.4%; *M* 477 $[Au(L)Cl^+]$ and 337 ($AuCl_4^-$)}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 156 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1600s, 1576w, 1563m, 1490m, 1296m, 1041m, 1020s, 779vs, 753m, 746m and 355vs (Au–Cl); *m/z* 477 (M^+), 442 ($M -$ Cl) and 246 (HL).

PF_6^- *salt.* To a suspension of complex **1a** (0.227 g, 0.41 mmol) in MeCN (3 cm^3) was added an aqueous solution (25 cm^3) of KPF_6 (0.300 g, 2.07 mmol). The mixture was stirred at room temperature until the suspension became whitish (4 d). The solid product was filtered off and air dried to give **1m** (0.230 g, 90%). Recrystallization from acetone–diethyl ether yielded the analytical sample, m.p. 192–193 °C (Found: C, 32.6; H, 2.2; N, 4.5. $C_{17}H_{13}AuClF_6N_2P$ requires C, 32.8; H, 2.1; N, 4.5%); Λ_M(5×10^{-4} mol dm^{-3}, acetone) 157 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1602vs, 1581s, 1566s, 1494s, 1329m, 1297s, 1251m, 1181w, 1169w, 1129w, 1092m, 1056w, 1044s, 1020s, 837vs (br), 777vs, 759s, 750s, 720m, 646m, 557vs, 465m, 438w and 377m and 358w (Au–Cl).

$[Au\{N_2C_{10}H_7(CHOHC_6H_4)\text{-}6\}Cl]^+$ 1*m. *BF_4^- salt.* To a suspension of complex **1a** (0.549 g, 1 mmol) in MeCN (10 cm^3) was added an aqueous solution (20 cm^3) of $NaBF_4$ (0.440 g, 4 mmol). The mixture was refluxed at 80 °C for 1 h, during which the orange suspension became pink. After 12 h of stirring at room temperature the solid product was filtered off, air dried and extracted with acetone (3×20 cm^3). Addition of diethyl ether to the concentrated solution gave a whitish product (0.080 g). A second crop was obtained by treatment of the reaction mother-liquor with K_2CO_3 and extraction with dichloromethane: addition of diethyl ether to the solution gave 0.090 g of product. The combined crops were crystallized from acetone–diethyl ether to yield the analytical sample, m.p. 183–184 °C {Found: C, 34.9; H, 2.2; N, 4.5%; *m/z* 493 (M^+). $C_{17}H_{13}AuBClF_4N_2O$ requires C, 35.2; H, 2.2; N, 4.8%; *M* 493 $[Au(L^*)Cl^+]$}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 140 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 3497vs, 1674w, 1603vs, 1564m, 1492m, 1329m, 1307s, 1255m, 1184m, 1167m, 1063s (br), 783vs, 750s, 720m, 522s, 455s and 361m and 321w (Au–Cl); $\delta_C[(CD_3)_2CO]$ 159.7, 157.5, 154.9, 135.0 and 134 (5C, aromatic C), 148.9, 146.8, 144.8, 135.7, 130.0, 129.8, 129.5, 128.5, 127.2, 126.3 and 125.6 (11C, aromatic CH) and 79.2 (1C, CHOH); *m/z* 493 (M^+), 458 ($M -$ Cl) and 261 (L^{*+}).

$AuCl_4^-$ *salt.* The insoluble residue, after extraction with acetone, was filtered off and dried under vacuum to give the analytical sample of **1*m** as its $[AuCl_4^-]$ salt (0.180 g), m.p. 220–221 °C {Found: C, 24.4; H, 1.4; N, 3.4%; *m/z* 493 (M^+, FAB+) and 337 (M^-, FAB−). $C_{17}H_{13}Au_2Cl_5N_2O$ requires C, 24.5; H, 1.6; N, 3.4%; *M* 493 $[Au(L^*)Cl^+]$ and 337 ($AuCl_4^-$)}; Λ_M(5×10^{-4} mol dm^{-3}, Me_2SO) 43 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1662s, 1600s, 1568s, 1489m, 1332s, 1296s, 1042m, 1021s, 778s, 750s, 458vs and 362vs (Au–Cl).

$[Au\{N_2C_{10}H_7(CHMePh)\text{-}6\}Cl_3]$ 2a. To a solution of $N_2C_{10}H_7(CHMePh)$-6 (0.468 g, 1.80 mmol) in MeCN (10 cm^3) was added an aqueous solution (20 cm^3) of $HAuCl_4\cdot3H_2O$ (0.676 g, 1.80 mmol): the resulting yellow suspension was stirred for 24 h at room temperature. The solid product was filtered off and air dried to give complex **2a** (0.810 g, 80%). Recrystallization from dichloromethane–diethyl ether yielded an orange crystalline product, m.p. 183–184 °C (Found: C, 38.6; H, 3.1; N, 4.7. $C_{18}H_{16}AuCl_3N_2$ requires C, 38.6; H, 2.8; N, 5.0%); $\tilde{\nu}_{max}/cm^{-1}$ 1600m, 1588m, 1564s, 1488vs, 1246m, 994w, 818w, 770vs, 746w, 715w, 703vs and 365vs and 332w (Au–Cl); *m/z* 490 ($M -$ 2HCl).

$[Au\{N_2C_{10}H_7(CHMeC_6H_4)\text{-}6\}Cl]^+$ 2m. $AuCl_4^-$ *salt.* To a solution of $N_2C_{10}H_7(CHMePh)$-6 (0.219 g, 0.84 mmol) in MeCN (5 cm^3) was added an aqueous solution (20 cm^3) of $HAuCl_4\cdot3H_2O$ (1.68 mmol): the resulting yellow suspension was stirred for 7 d at room temperature. The solid was filtered off and air dried. Treatment of the crude product with chloroform (3×15 cm^3) gave an orange solution and a pale yellow residue. The solution was concentrated to small volume and diethyl ether was added to give complex **2a** (0.217 g). The residue was dissolved in acetone: the filtered solution was concentrated to small volume and diethyl ether was added to give a pale yellow precipitate of **2m** (0.323 g, 46%), m.p. 222–224 °C {Found: C, 25.8; H, 1.8; N, 3.2%; *m/z* 491 (M^+, FAB+) and 337 (M^-, FAB−). $C_{18}H_{15}Au_2Cl_5N_2$ requires C, 26.0; H, 1.8; N, 3.4%; *M* 491 $[Au(L)Cl^+]$ and 337 ($AuCl_4^-$)}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1598s, 1579w, 1560m, 1489m, 1299s, 1019s, 781vs, 758s, 744m, 457m and 355vs (Au–Cl).

BF_4^- *salt.* To a suspension of complex **2a** (0.563 g, 1 mmol) in water (30 cm^3) was added solid $NaBF_4$ (0.220 g, 2 mmol). The mixture was refluxed until the precipitate became creamy (*ca.* 5 h). After cooling, the solid product was filtered off and dried under vacuum to give **2m** (0.530 g, 92%). Recrystallization from acetone–diethyl ether yielded the analytical sample, m.p. 239–240 {Found: C, 37.0; H, 2.7; N, 4.5%; *m/z* 491 (M^+). $C_{18}H_{15}AuBClF_4N_2$ requires C, 37.4; H, 2.6; N, 4.8%; *M* 491 $[Au(L)Cl^+]$}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 158 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1602m, 1563w, 1490m, 1301m, 1251m, 1104s, 1040s (br), 1019vs, 782s, 761m, 748w, 522m, 455m and 367s, 325m and 308w (Au–Cl).

$[HN_2C_{10}H_7(CMe_2Ph)\text{-}6][AuCl_4]$. To a solution of $N_2C_{10}H_7(CMe_2Ph)$-6 (0.493 g, 1.80 mmol) in MeCN (10 cm^3) was added an aqueous solution (20 cm^3) of $HAuCl_4\cdot3H_2O$ (0.676 g, 1.80 mmol): the resulting yellow suspension was stirred for 30 h at room temperature. The solid product was filtered off and air dried. The crude product was extracted with chloroform (3×20 cm^3) and the residue dissolved in acetone: the filtered solution was concentrated to small volume and diethyl ether was added to give a dark yellow precipitate (0.552 g, 50%), m.p. 168–170 °C (Found: C, 37.6; H, 3.3; N, 4.5. $C_{19}H_{19}AuCl_4N_2$ requires C, 37.2; H, 3.1; N, 4.6%); Λ_M(5×10^{-4} mol dm^{-3}, acetone) 142 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 3227vs, 3094s, 3056vs, 1635w, 1623s, 1606s, 1586s, 1565w, 1527s, 1442vs, 1308m, 772vs, 756m, 701s, 556s, 497m, 466w and 355vs (Au–Cl).

The chloroform extract was concentrated to small volume: addition of diethyl ether gave a pale yellow product; $[Au\{N_2C_{10}H_7(CMe_2Ph)\text{-}6\}Cl_3]$ **3a** (0.210 g, 20%), see below.

$[Au\{N_2C_{10}H_7(CMe_2Ph)\text{-}6\}Cl_3]$ 3a. *Method* (*a*). A solution of $[HN_2C_{10}H_7(CMe_2Ph\text{-}6)][AuCl_4]$ (0.230 g, 0.37 mmol) in acetone (15 cm^3) was treated with solid K_2CO_3 and stirred for 2 h. The filtered solution was evaporated to dryness: the residue was taken up with dichloromethane, filtered and concentrated to small volume. Addition of diethyl ether gave complex **3a** (0.163 g, 76%), m.p. 193–195 °C (Found: C, 39.8; H, 3.4; N, 4.8%. $C_{19}H_{18}AuCl_3N_2$ requires C, 39.5; H, 3.1; N, 4.8%); $\tilde{\nu}_{max}/cm^{-1}$ 1602m, 1587s, 1563s, 1487s, 1441vs, 1085m, 774vs, 765m, 740w, 698s, 561m and 365vs (Au–Cl).

Method (*b*). To a solution of $N_2C_{10}H_7(CMe_2Ph)$-6 (0.411 g, 1.5 mmol) in MeCN (5 cm^3) was added an aqueous solution (30 cm^3) of $Na[AuCl_4]\cdot 2H_2O$ (0.597 g, 1.5 mmol): the resulting yellow suspension was stirred for 2 d at room temperature. The solid product was filtered off and air dried to yield complex **3a** (0.838 g, 97%).

$[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl]^+$ 3m. $AuCl_4^-$ *salt*. To a solution of $N_2C_{10}H_7(CMe_2Ph)$-6 (0.274 g, 1.0 mmol) in MeCN (5 cm^3) was added an aqueous solution (25 cm^3) of $Na[AuCl_4]\cdot 2H_2O$ (0.796 g, 2.0 mmol): the resulting yellow suspension was refluxed for 6 h and then filtered off and dried under vacuum to yield complex **3m** (0.786 g, 93%). Recrystallization from acetone–diethyl ether gave the analytical sample m.p. 240–241 °C {Found: C, 27.1; H, 2.1; N, 3.2%; *m*/*z* 505 (M^+, FAB+) and 337 (M^-, FAB−). $C_{19}H_{17}Au_2Cl_5N_2$ requires C, 27.0; H, 2.0; N, 3.3%; *M* 505 $[Au(L)Cl^+]$ and 337 ($AuCl_4^-$)}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1596m, 1575w, 1557w, 1486w, 1019s, 776s, 769m, 758w and 358vs (Au–Cl).

BF_4^- *salt*. To a suspension of complex **3a** (0.337 g 0.58 mmol) in water (20 cm^3) was added solid $NaBF_4$ (0.255 g, 2.32 mmol). The mixture was refluxed until the precipitate became pale yellow (*ca.* 8 h); after cooling, the solid product was filtered off and air dried. The product (0.221 g) was a mixture (IR spectrum and elemental analysis) of the $AuCl_4^-$ and BF_4^- salts (*ca.* 1 : 2): attempts to obtain pure products failed. The BF_4^- salt was obtained pure by working up the mother-liquor. After neutralization with solid K_2CO_3 and extraction with dichloromethane the extract was concentrated to small volume and diethyl ether was added to give a white crystalline product (0.050 g, 14.5%); m.p. 214–215 °C {Found: C, 38.7; H, 3.1; N, 4.6%; *m*/*z* 505 (M^+). $C_{19}H_{17}AuBClF_4N_2$ requires C, 38.5; H, 2.9; N, 4.7%; *M* 505 $[Au(L)Cl^+]$}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone) 156 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1601s, 1576w, 1567w, 1490m, 1067vs, 1044vs, 788vs, 769m, 761w, 747w, 519m and 367m (Au–Cl).

Preparation of 6-alkyl-2,2′-bipyridine derivatives

$[Au(HL)Cl_3]$ 4a–6a. *General procedure*. To a solution of compound HL (1 mmol) in MeCN (5 cm^3) was added an aqueous solution (20 cm^3) of $HAuCl_4\cdot 3H_2O$ (or $Na[AuCl_4]\cdot 2H_2O$) (1 mmol): the resulting yellow suspension was stirred for *ca.* 30 h at room temperature and then filtered off and air dried to give $[Au(HL)Cl_3]$ **4a–6a** in 80–90% yield. Recrystallization from chloroform–diethyl ether gave the analytical sample as a crystalline product.

$[Au\{N_2C_{10}H_7(CH_2Me)\text{-}6\}Cl_3]$ **4a**: peach, m.p. 169–170 °C (Found: C, 28.8; H, 2.5; N, 5.6%; *m*/*z* 486 (M^+). $C_{12}H_{12}AuCl_3N_2$ requires C, 29.6; H, 2.5; N, 5.7%; *M* 486); $\tilde{\nu}_{max}/cm^{-1}$ 1599s, 1587vs, 1560s, 1484vs, 1252m, 1158s, 1090m, 997m, 819s, 783vs, 764vs and 358vs (Au–Cl); *m*/*z* 486 (M^+), 450 (M − HCl), 415 (M − H − 2Cl), 380 (M − H − 3Cl) and 185 (H_2L^+).

$[Au\{N_2C_{10}H_7(CMe_3)\text{-}6\}Cl_3]$ **5a**: bright yellow, m.p. 210–211 °C (Found: C, 33.6; H, 3.3; N, 5.2%; *m*/*z* 514 (M^+). $C_{14}H_{16}AuCl_3N_2$ requires C, 32.6; H, 3.1; N, 5.4%; *M* 514); $\tilde{\nu}_{max}/cm^{-1}$ 1601s, 1589vs, 1563vs, 1476vs, 1240vs, 1216m, 1178m, 1168vs, 1086s, 990s, 818s, 768vs, 751m, 746m and 362vs, 336w and 324w (Au–Cl); *m*/*z* 514 (M^+), 478 (M − HCl), 443 (M − H − 2Cl), 408 (M − H − 3Cl) and 213 (H_2L^+).

$[Au\{N_2C_{10}H_7(CH_2CMe_3)\text{-}6\}Cl_3]$ **6a**: apricot, m.p. 208–209 °C (Found: C, 34.3; H, 3.4; N, 5.4%; *m*/*z* 528 (M^+). $C_{15}H_{18}AuCl_3N_2$ requires C, 34.0; H, 3.4; N, 5.3%; *M* 528); $\tilde{\nu}_{max}/cm^{-1}$ 1602s, 1589s, 1564s, 1488s, 1361s, 1244m, 1231s, 1167m, 1140m, 1089m, 994m, 822m, 772vs, 760vs and 358vs (Au–Cl) *m*/*z* 528 (M^+), 492 (M − HCl), 457 (M − H − 2Cl), 422 (M − H − 3Cl) and 227 (H_2L^+).

$[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}Cl][BF_4]$ 5m. To a solution of complex **5a** (0.515 g, 1 mmol) in acetone (25 cm^3) was added compound **V** (0.212 g, 1 mmol) and a solution of $AgBF_4$ (0.390 g, 2 mmol) in acetone (15 cm^3): a precipitate of AgCl was formed immediately. The mixture was stirred for 15 h at room temperature. The solid products were separated and the filtered solution was added to solid K_2CO_3 and stirred for 5 h. After filtration the solution was evaporated to dryness, free HL was extracted with diethyl ether from the solid, then the residue was crystallized from acetone–diethyl ether to give **5m** as a pale yellow crystalline solid (0.130 g, 24%), m.p. 158–160 °C {Found: C, 31.7; H, 3.2; N, 5.1%; *m*/*z* 443 (M^+). $C_{14}H_{15}AuBClF_4N_2$ requires C, 31.7; H, 2.8; N, 5.3%; *M* 443 $[Au(L)Cl^+]$}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone) 144 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 3615w, 3532w, 1668m, 1600vs, 1568m, 1490s, 1171w, 1153w, 1134m, 1054vs (br), 824m, 778vs, 650m, 521m, 391m and 367s, 320w and 303w (Au–Cl). Crystals of the $0.5H_2O$ adduct were obtained by slow evaporation of an acetone solution.

The insoluble residue containing AgCl was extracted with MeCN, filtered and concentrated to small volume. Addition of diethyl ether gave a pale yellow solid which analysed for $[Au_2(HL)_2(\mu\text{-}O)_2][BF_4]_2$ (0.123 g, 24%), m.p. 160–162 °C (Found: C, 32.1; H, 3.4; N, 5.5; O, 3.0. $C_{28}H_{32}Au_2B_2F_8N_4O_2$ requires C, 32.8; H, 3.1; N, 5.5; O, 3.1%); $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, MeCN) 320 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1600s, 1566m, 1494s, 1329w, 1295m, 1282w, 1227m, 1050vs (br), 823w, 782vs, 707w, 669w, 654s, 641s, 589m and 520m; $\delta_H(CD_3CN)$ 8.83 [1 H, dd, H(6′)], 8.52–8.07 (6 H, m, other aromatics), and 1.74 (9 H, s, 3 CH_3); *m*/*z* 937 ($[M + BF_4]^+$), 869 ($[M + F]^+$), 637 $[(HL)_2AuO]$, 621 $[(HL)_2Au]$, 513 ($\tfrac{1}{2}M + HBF_4$), 425 ($\tfrac{1}{2}M^+$), 409 ($\tfrac{1}{2}M$ − O) and 213 (H_2L^+).

Reactions of the cyclometallated derivatives 2m, 3m and 5m with PPh_3

General procedure. To a suspension of $[Au(L)Cl][BF_4]$ (**2m**, 0.096 g, 0.165 mmol; **3m** 0.111 g, 0.187 mmol; **5m**: 0.106 g, 0.2 mmol) in acetone (20 cm^3) were added solid $NaBF_4$ (excess) and PPh_3 (equimolar amount). The resulting solution was stirred for 4 h at room temperature and then evaporated to dryness. The residue was taken up with dichloromethane, filtered and concentrated to small volume: addition of diethyl ether gave a white precipitate of **2p**, **3p** and **5p**, respectively, yield 60–80%. Recrystallization from dichloromethane–diethyl ether gave the analytical sample.

$[Au\{N_2C_{10}H_7(CHMeC_6H_4)\text{-}6\}(PPh_3)Cl][BF_4]$ **2p**: m.p. 169–170 °C {Found: C, 50.2; H, 3.4; N, 3.4%; *m*/*z* 753 (M^+). $C_{36}H_{30}AuBClF_4N_2P$ requires C, 51.4; H, 3.6; N, 3.3%; *M* 753 $[AuL(PPh_3)Cl^+]$}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone), 156 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1597m, 1585m, 1557m, 1480s, 1187w, 1157w, 1096vs, 1053vs (br), 994s, 826w, 790s, 772m, 763m, 744s, 718s, 690vs, 534vs, 512vs, 499vs and 313s (Au–Cl); $\delta_P(CD_2Cl_2)$ 29.1 (s, P_a) and 28.2 (s, P_b) (a : b = 3 : 1); *m*/*z* 753 (M^+), 721 $[Au(PPh_3)_2]$, 718 (M − Cl), 491 (M − PPh_3) and 459 $[Au(PPh_3)]$.

$[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}(PPh_3)Cl][BF_4]$ **3p**: m.p. 185–186 °C {Found: C, 49.3; H, 3.6; N, 3.1%; *m*/*z* 767 (M^+). $C_{37}H_{32}AuBClF_4N_2P\cdot 0.5CH_2Cl_2$ requires C, 50.2; H, 3.7; N, 3.1%; *M* 767 $[AuL(PPh_3)Cl^+]$}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone) 154 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1594m, 1576s, 1557m, 1478vs, 1192s, 1159m, 1097vs, 1056vs (br), 992vs, 824w, 790vs, 770s, 746vs, 726vs, 690vs, 533vs, 510vs, 501vs and 312s (Au–Cl); $\delta_P[(CD_3)_2CO]$ 28.0; *m*/*z* 767 (M^+), 732 (M − Cl), 721 $[Au(PPh_3)_2]$, 505 (M − PPh_3) and 459 $[Au(PPh_3)]$.

$[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}(PPh_3)][BF_4]_2$ **5p**: m.p. 115–116 °C {Found: C, 45.6; H, 3.8; N, 3.2%; *m*/*z* 670 (M^+). $C_{32}H_{31}AuB_2F_8N_2P$ requires C, 45.5; H, 3.7; N, 3.3%; *M* 670 $[Au(L)PPh_3]$}; $\Lambda_M(5 \times 10^{-4}$ mol dm^{-3}, acetone) 240 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}/cm^{-1}$ 1601vs, 1569m, 1492s, 1331w, 1308m, 1284w, 1251s, 1058vs(br), 824w, 780vs, 753s, 714s, 693vs, 643m, 538vs, 511vs and 456w; $\delta_P[(CD_3)_2CO]$ 27.3; *m*/*z* 757 ($M + BF_4$), 721 $[Au(PPh_3)_2]$, 670 (M^+), 459 $[Au(PPh_3)]$ and 408 (M − PPh_3).

Table 5 Crystallographic data *

Compound	$[Au\{N_2C_{10}H_7(CHMePh)\text{-}6\}Cl_3]$ **2a**	$[Au\{N_2C_{10}H_7(CMe_2C_6H_4)\text{-}6\}Cl][AuCl_4]$ **3m**$[AuCl_4]$	$[Au\{N_2C_{10}H_7(CMe_2CH_2)\text{-}6\}Cl][BF_4]\cdot 0.5H_2O$ **5m**$[BF_4]\cdot 0.5H_2O$
Formula	$C_{18}H_{16}AuCl_3N_2$	$C_{19}H_{17}Au_2Cl_5N_2$	$C_{14}H_{16}AuBClF_4N_2O_{0.5}$
M	563.7	844.6	539.5
Colour	Orange	Yellow-orange	Pale yellow
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	*Pbcn*
a/Å	14.906(2)	8.197(2)	22.663(6)
b/Å	13.555(3)	31.392(8)	11.518(2)
c/Å	9.337(2)	9.154(3)	13.068(4)
β/°	92.04(2)	107.67(3)	
$U/Å^3$	1885.4(6)	2244.4(1.0)	3411.2(1.6)
Z	4	4	8
F(000)	1072	1552	2040
$D_c/g\ cm^{-3}$	1.99	2.50	2.10
Crystal dimensions/mm	0.19 × 0.45 × 0.50	0.23 × 0.34 × 0.46	0.25 × 0.39 × 0.51
μ(Mo-Kα)/cm^{-1}	82.2	136.5	88.1
Minimum transmission factor	0.66	0.64	0.68
ω-Scan width/°	$1.10 + 0.35 \tan\theta$	$1.10 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$
Reciprocal space explored	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
Measured reflections	4079	4873	3714
Unique observed reflections with $I > 3\sigma(I)$	2985	3340	2397
Final *R* and *R'*	0.028, 0.036	0.025, 0.029	0.030, 0.034
No. variables	217	253	249
Goodness of fit	1.36	1.25	1.19

* Details in common: ω scan mode; θ range 3–27°; $R = [\Sigma(|F_o - k|F_c||)/\Sigma F_o]$; $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$; goodness of fit $= [\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/2F_oL_p$, N_o is the number of observations, N_v the number of variables, and *p*, the ignorance factor, = 0.040 for complexes **2a** and **5m**$[BF_4]\cdot 0.5H_2O$ and 0.030 for **3m**$[AuCl_4]$.

Reaction of complex 2m with $AgBF_4$

To a suspension of complex **2m** as its BF_4^- salt (0.289 g, 0.5 mmol) in acetone (20 cm^3) was added a solution of $AgBF_4$ (0.097 g, 0.5 mmol) in acetone (10 cm^3). The resulting mixture was refluxed for 45 min with stirring, during which a dark blue solid and a pale blue solution were formed. The suspension was stirred for 4 h at room temperature and then filtered off. The solution was evaporated to dryness and the residue taken up with dichloromethane and filtered through Celite: addition of diethyl ether to the concentrated solution gave a pale grey product which was crystallized from dichloromethane–diethyl ether to yield $[Au\{N_2C_{10}H_7(CHMeC_6H_4)\text{-}6\}\{CH_2(CO)Me\}][BF_4]$ **2c** (0.116 g, 38%), m.p. 78–80 °C {Found: C, 41.7; H, 3.0; N, 4.7%; *m*/*z* 513 (M^+). $C_{21}H_{20}AuBF_4N_2O$ requires C, 42.0; H, 3.3; N, 4.7%; *M* 513 $[Au(L)\{CH_2(CO)CH_3\}^+]$}; $\Lambda_M(5 \times 10^{-4}\ mol\ dm^{-3}$, acetone) 162 $\Omega^{-1}\ cm^2\ mol^{-1}$; $\tilde{\nu}_{max}/cm^{-1}$ 1674vs, 1600vs, 1579m, 1563m, 1490s, 1251m, 1225m, 1050vs (br), 824s, 780vs, 749s, 734s, 724s and 646s; *m*/*z* 513 (M^+) and 456 ($M - CH_2COCH_3$).

Crystallography

Crystal data and other experimental details are summarized in Table 5. The diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo-Kα radiation (λ = 0.710 73 Å) with a graphite-crystal monochromator in the incident beam. The calculations were performed on a PDP 11/73 computer using the SDP Structure Determination Package[24] and the physical constants tabulated therein. A periodic monitoring of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated as about 1.4% for complex **2a**, 2.4% for **3m**$[AuCl_4]$ and 5.1% for **5m**$[BF_4]\cdot 0.5H_2O$ (on intensities) at the end of data collection. The diffracted intensities were corrected for Lorentz-polarization, decay and absorption effects (empirically).[25] Scattering factors and anomalous dispersion corrections were taken from ref. 26.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$ (refinement on *F*). In compound **5m**$[BF_4]\cdot 0.5H_2O$ the fluorine atoms are disordered; the ordered boron atom is surrounded by eight peaks of electron density, approximately defining two interpenetrating tetrahedra, which have been interpreted as eight fluorine atoms with occupancy factors of 0.50 each. Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms of the water molecule in **5m** were not detected in the final Fourier map and were ignored, however the observed F(4)···O distance, 2.824(13) Å, suggests the presence of a hydrogen bond. The other hydrogen atoms were placed in their ideal positions (C–H 0.97 Å, *B* 1.20 times that of the carbon atom to which they are attached) and not refined. The final Fourier maps showed maximum residuals of 0.91(12) e $Å^{-3}$ at 1.18 Å from Au in compound **2a**, 0.88(13) e $Å^{-3}$ at 0.78 Å from Au(2) in **3m**$[AuCl_4]$, and 0.90(12) e $Å^{-3}$ at 0.85 Å from Au in **5m**$[BF_4]\cdot 0.5H_2O$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/221.

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