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Mercury(II) and gold(III) derivatives of 2-phenyl pyridines and 2-phenyl-4-(methylcarboxylato)quinoline

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Abstract

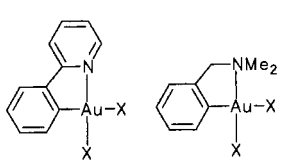
ortho-Mercurated derivatives of several substituted 2-phenylpyridines and of 2-phenyl-4-(methylcarboxylato)quinoline have been prepared and characterised. C,N-chelated gold(III) derivatives, $[AuCl_2(C_6H_4C_5H_3RN)]$ (R = H, 3-Me, 3,5-Me_2, 4-Pr^n, 4-Bu^t) are prepared more efficiently by *trans*-metallation reactions than by direct reaction of $AuCl_4^-$ with the phenylpyridines. The new gold complexes were characterised spectroscopically and a variety of substitution reactions have been effected. As is usual with unsymmetrical bidentate ligands, the softer donor atom is found *trans* to the N-donor of the pyridine unit. Crystal-structure determinations are reported for $[Au(OAc)(pmpy)(py)]ClO_4$, $[Au(ppy)(dpbt)]BPh_4$, $[Au(ppy)(S_2CNMe_2)]BPh_4$ and $AuCl(pqcm)_2$ [Hppy = 2-phenylpyridine, Hpmpy = 2-phenyl-3-methylpyridine, Hpqcm = 2-phenyl-4-(methylcarboxylato)quinoline]. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Mercury(II); Gold(III); *ortho*-Metallation; 2-Phenylpyridines

1. Introduction

Direct auration of aromatic ligands was first achieved in 1931 by Kharasch [1], but it was not for a further 50 years that other concrete examples were obtained. In 1989, Constable and co-workers reported the *ortho*-metallation of 2-phenyl-pyridine [2] and related materials [3], giving stable five-membered C,N-chelates. More recently various substituted pyridines have been shown to undergo similar reactions, forming five- or six-membered chelates [4–6]. However, the yields in reactions of this type can be low, and it is frequently better to employ a transmetallation reaction from the *ortho*-mercurated derivative, a method well exploited by Vicente and co-workers for the preparation of derivatives of azobenzene [7] and dimethylbenzylamine [8].

There is developing interest in the use of gold compounds in chemotherapy [9], and we have shown that Constable's original compound $[AuCl_2(ppy)]$ (**I**) showed toxicity to and some discrimination between a variety of cell lines [10]. Our observation that other C,N-chelates of gold(III) (**II**, X = Cl, OAc) have more interesting pharmacological properties [10,11] stimulated the preparation of a wide range of analogues, of which those derived from various 2-phenylpyridines and 2-phenyl-4-(methylcarboxylato)quinoline are reported here, together with some of their ligand-substitution reactions.



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2. Results and discussion

Although it was possible to obtain the desired *ortho*-metallated products by direct reaction between the ligand and $[AuCl_4]^-$, transmetallation from the mercury derivatives was much more efficient, giving cleaner and quicker reactions. It was therefore necessary to prepare both the phenylpyridines and their *ortho*-mercurated derivatives.

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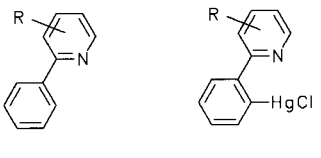
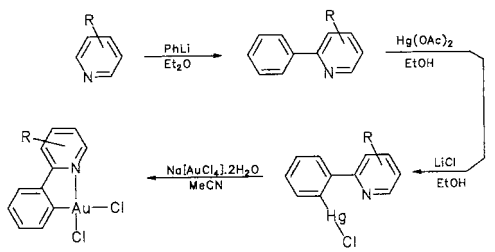


R							
H	Hppy	III	HgCl(ppy)	VIII	$AuCl_2$(ppy)	I
3-Me	Hpmpy	IV	HgCl(pmpy)	IX	$AuCl_2$(pmpy)	XIII
3,5-Me_2	Hpmmpy	V	HgCl(pmmpy)	X	$AuCl_2$(pmmpy)	XIV
4-Pr-n	Hpppy	VI	HgCl(ppy)	XI	$AuCl_2$(pppy)	XV
4-Bu-t	Hpbpy	VII	HgCl(pbpy)	XII	$AuCl_2$(pbpy)	XVI

2.1. Preparation of ligand precursors

The 2-phenylpyridines **IV**–**VII** were prepared by the established method [12] of reaction of the substituted pyridine with phenyllithium (Scheme 1). 2-Phenylquinoline 4-carboxylic acid (**XVII**) was prepared from benzaldehyde and pyruvic acid (Scheme 2) [13]. These materials were characterised by NMR (Tables 1 and 2) and used immediately.



Scheme 1.

2.2. Preparation and characterisation of organomercurials

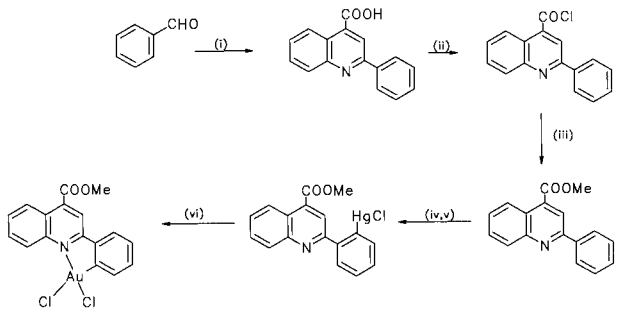
Mercuration was achieved by direct reaction of the 2-phenylpyridines with mercury(II) acetate in ethanol [14,15] followed by replacement of the acetate by chloride (Schemes 1 and 2). Yields were modest (30–40%), and considerable quantities of insoluble by-products were always formed. This has been observed previously during the reaction of 2-phenylpyridine[12] and attributed to the formation of bis-mercurated derivatives [16].

The organomercury compounds **VIII**–**XII** were characterised by chemical analysis, IR and NMR (Tables 1 and 2). In the far infrared, all showed bands in the regions 413–422 cm^{-1} [ν(Hg–C)] and 332–337 cm^{-1} [ν(Hg–Cl)]. The latter are consistent with linear two-coordination [13]. The pyridine C–N deformation bands (ca. 1600 cm^{-1}) were at frequencies very similar to those of the parent phenylpyridines, indicating lack of coordination of the pyridine nitrogen atom.

Table 1
^{1}H-NMR data for substituted pyridines (HL), [HgCl(L)] and [$AuCl_2$(L)] ($CDCl_3$ solutions)

Compound	Phenyl				Pyridine/quinoline				Other
	H_3	H_4	H_5	H_6	H_8	H_9	H_{10}	H_{11}	
Hppy (**III**)	7.93	7.29	7.29	7.29	7.49	7.49	7.01	8.58	H_1 7.93
Hpmpy (**IV**)	7.43	7.28	7.28	7.28	–	7.43	7.02	8.41	H_1 7.43, CH_3 2.21
Hpmmpy (**V**)	7.32	7.19	7.19	7.19	7.41	7.12	–	8.16	H_1 7.32, CH_3 2.30
Hpppy (**VI**)	7.92	7.30	7.30	7.30	7.51	–	6.89	8.48	H_1 7.92, CH_3 0.85, CH_2 1.57
Hpbpy (**VII**)	7.84	7.22	7.22	7.22	–	–	6.96	8.40	H_1 7.84
Hpcqm (**XVII**)	8.05	7.31	7.31	7.31	8.20	–	8.05	7.41	H_{12} 7.56. H_{13} 8.37, CH_3 3.81
HgCl(ppy) (**VIII**)	8.60	7.92	7.81	8.60	8.00	7.44	7.42	7.51 [a]	
HgCl(pmpy) (**IX**) [b]	8.56	–	7.86	8.56	7.74	7.47	7.47	7.74 [c]	CH_3 2.48
HgCl(pmmpy) (**X**)	8.35	–	7.42	8.35	7.66	7.39	7.39	7.50 [d]	CH_3 2.35, 2.48
HgCl(pppy) (**XI**)	8.24	7.53	-	8.24	7.80	7.28	7.28	7.28 [e]	CH_3 0.88, CH_2 1.59, 2.48
HgCl(pbpy) (**XII**)	8.53	7.80		8.53	8.04	7.43	7.43	7.55 [f]	CH_3 1.26
HgCl(pcqm) (**XVIII**)	8.01	7.39	7.39	7.39	8.59	–	7.54	7.06	H_{12} 8.43, H_{13} 8.37, CH_3 4.01
$AuCl_2$(ppy) (**I**) [b]	9.52	8.40	8.40	9.52	7.97	7.48	7.38	7.81	
$AuCl_2$(pppy) (**XV**) [b]	9.61	–	7.89	9.61	8.24	7.72	7.62	8.14	CH_3 1.21, CH_2, 2.00, 3.08
$AuCl_2$(pqcm) (**XIX**)	8.44	7.80	7.50	7.19	8.60	–	8.15	8.15	H_{12} 8.00, H_{13} 8.86, CH_3 4.35

[a] J_{Hg} 211 Hz.
[b] In $(CD_3)_2SO$.
[c] J_{Hg} 218 Hz.
[d] J_{Hg} 207 Hz.
[e] J_{Hg} 211 Hz.
[f] J_{Hg} 211 Hz.



Scheme 2.

The NMR assignments shown in Tables 1 and 2 were made from consideration of the values of the ^{199}Hg coupling constants and ^{13}C DEPT(135°) of all the compounds, and from complete ($^1H-^1H$) and ($^1H-^{13}C$) COSY studies of the *t*-butyl-substituted compound **XII** [17]. As observed previously [12,18], mercuration gives a strong (ca. 22 ppm) downfield shift for C_1, and the coupling constants appear in the expected order [19]. For **X**, **XI** and **XVIII**, the FAB mass spectra show parent ions with the correct isotopic patterns. Peaks corresponding to the phenylpyridines and, in two cases, to the loss of a chlorine atom are also seen. The bis-aryl disproportionation products are also observed.

2.3. Preparation and characterisation of gold complexes

Our efforts to prepare the unsubstituted $[AuCl_2(ppy)]$ on a relatively large scale by the direct auration route always gave low yields (ca. 20%) and considerable quantities of metallic gold. Similar problems have been found by other workers for 2-benzoylpyridine [5] and 6-phenyl-2,2′-bypyridine [20], even when silver ion was used to facilitate removal of chloride ligands from the intermediate $[AuCl_3(pyridine)]$ complexes. Comparable difficulty was met here with the substituted phenylpyridines. However, the transmetallation reaction of the mercury derivatives with $[AuCl_4]^-$ in acetonitrile worked cleanly and rapidly, and gave good yields (60–80%).

The new compounds **XIII**–**XVI**, **XIX** were characterised by chemical and spectroscopic analysis (Tables 1 and 2). In the infrared (IR) spectrum, an increase in ν(C–N) of the pyridine rings indicates that the pyridine is coordinated, and Au–Cl stretching modes at 360–380 and 300–310 cm^{-1} are consistent with chloride ligands *trans* to nitrogen and to carbon, respectively.

Several of the compounds exhibited rather low solubility, and NMR spectra were obtained only for the *n*-propylpyridinyl and quinolyl complexes, **XV** and **XIX**. Downfield shifts of all the pyridine ring carbon signals confirm that the nitrogen is coordinated. The FAB mass spectra did not give strong parent-ion peaks, but signals corresponding to the loss of one and both chlorine atoms were seen, as well as those of the free phenylpyridines. Strong peaks corresponding to the bis-aryl compounds are also seen.

There is thus no doubt that these compounds have the now-conventional C,N-chelated structures shown in the Schemes.

2.4. Substitution chemistry of the gold complexes

The chloride ligands are readily substituted by a range of other, softer, ligands and we have used a variety of anionic sulfur-based materials. Substitution by a hard ligand requires assistance from silver ion. These reactions are summarised in Scheme 3.

Complexes **XIII**, **XIV** and **XVI** reacted readily with silver acetate, provided light was excluded. The products, **XX**–**XXII**, were the expected di-acetato complexes, obtained as white, air- and moisture-stable, light-sensitive crystalline solids, with good solubility in common solvents. NMR data for these complexes are given in Tables 3 and 4 (COSY and NOE data are given in Ref. [17]). The two sets of ^{13}C signals for the acetato groups have not only different chemical shifts but different intensities: the higher-shifted signals are broadened considerably. We first observed this effect for $[Au(OAc)_2(damp)]$ [damp = 2-(dimethylaminomethyl)phenyl] [21], and showed that it was due to rapid exchange of the group *trans* to carbon with small amounts of adventitious water in the solvent.

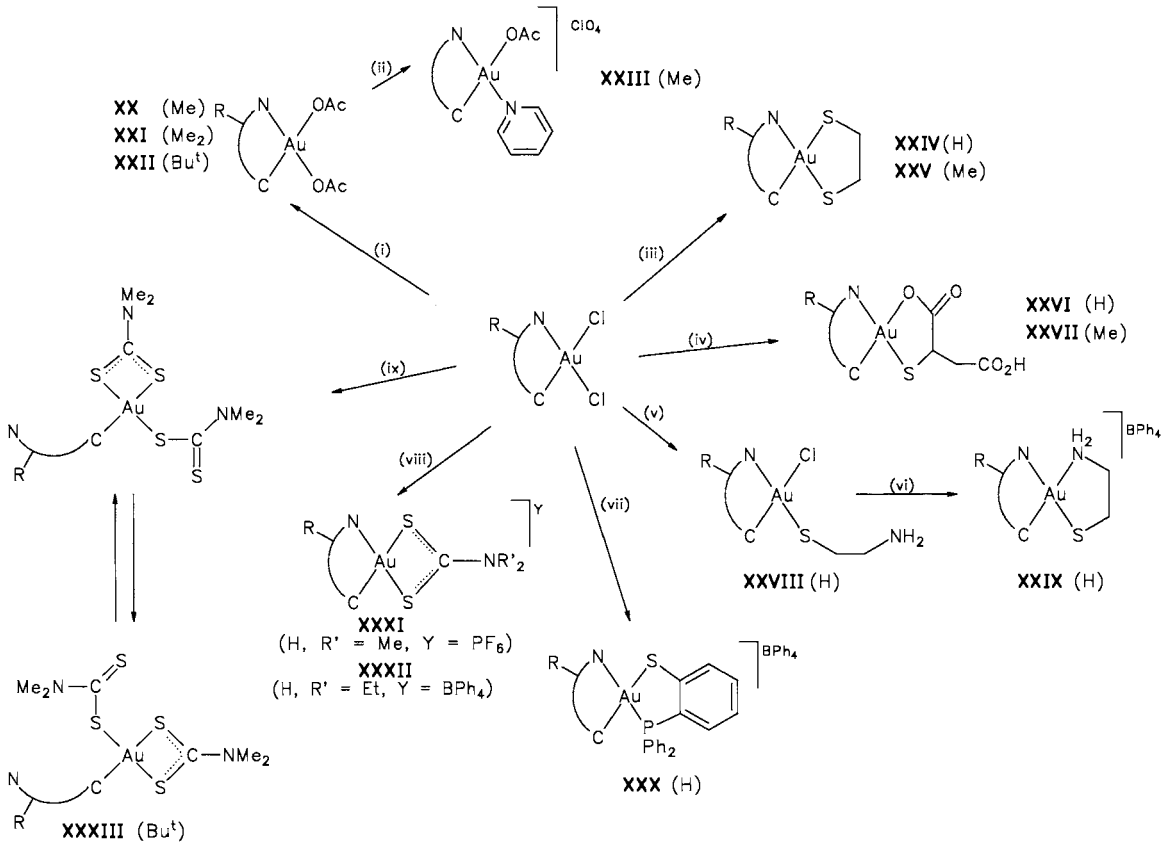
The IR spectra (Table 5) show two distinct sets of C–O stretching frequencies, both consistent with monodentate bonding of the acetate groups. As discussed previously [7,22] the lower frequencies correspond to the acetato group *trans* to the phenyl ligand.

Complex **XX** reacts with pyridinium perchlorate to give substitution of one acetato group by pyridine. The product is very light sensitive but stable to air and moisture. Similar compounds reported by Vicente et al. were thought, on the basis of IR data, to have structures analogous to **XXIII** (Scheme 3) [23,24]. This is now confirmed by X-ray diffraction for crystals of **XXIII**, the cation of which is shown in Fig. 1. Selected bond distances and angles are given in Table 6. The coordination of the gold atom is almost ideally planar, and the two different pyridine units are *trans* to each other. The Au–N(py) distance found here is rather shorter than those reported [22] for $[Au(py)_2(damp)](ClO_4)_2$ [2.016(7), 2.155(9) Å]. The carbonyl-group stretching frequencies of all these compounds are similar to those of the groups *trans* to carbon in the diacetato complexes (Table 5).

Table 2
$^{13}C\{^{1}H\}$-NMR data for substituted pyridines (HL), [HgCl(L)] and [$AuCl_2$(L)] (numbers in parentheses are J_{Hg} (Hz))

Compound	Phenyl						Pyridine					Other
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	
Hppy (**III**) [a,b,c]	127.1	139.6	127.1	128.7	129.0	128.7	156.7	119.9	136.2	121.5	149.1	
Hpmpy (**IV**) [c]	128.4	140.6	128.4	129.0	127.9	129.0	158.7	130.8	138.5	122.1	147.0	CH_3 20.1
Hpmmpy (**V**) [c]	127.9	140.4	127.9	128.8	126.9	128.8	155.7	129.9	138.5	131.2	147.2	CH_3 17.7, 19.7
Hpppy (**VI**) [c]	127.0	139.6	127.0	128.7	127.2	128.7	157.3	120.7	152.1	122.4	149.4	CH_3 13.7, CH_2 23.5, 37.4
Hpbpy (**VII**) [c]	127.1	140.0	127.1	128.4	128.5	128.4	160.6	117.4	157.4	119.7	149.6	CH_3 30.7, CMe_3 34.7
Hpqcm (**XVII**) [c]	127.5	138.8	127.5	129.2	129.0	129.2	156.6	120.3	124.1	125.5	130.8	C_{12} 130.1, C_{13} 130.2, C_{14} 135.5, C_{15} 149.3, CO_2 166.8, CH_3 52.7
HgCl(ppy) (**VIII**) [a,d,e]	147.9	141.3	127.1	129.2	128.2	137.8	155.9	120.9	138.3	123.4	149.1	
HgCl(pmpy) (**IX**) [e]	157.9	148.0	132.0 [181]	131.1 [30]	133.5 [151]	141.2 [113]	163.6	135.4	143.7	126.8	150.7	CH_3 24.3
HgCl(pmmpy) (**X**) [e]	152.1	143.7	127.6	130.1	128.5 [211]	137.0 [128]	155.6	131.1	141.1	132.7	147.3	CH_3 17.9, 20.9
HgCl(pppy) (**XI**) [c]	148.3	141.4	126.8 [151]	128.6 [24]	129.6 [211]	137.8 [132]	155.8	120.0	155.1	123.7	147.5	CH_3 13.7, CH_2 23.5, 37.6
HgCl(pbpy) (**XII**) [c]	148.5	142.3	127.0 [158]	128.6 [28]	129.7 [214]	137.9 [133]	162.4	117.5	155.7	120.8	147.9	CH_3 30.6, CMe_3 35.2
HgCl(pqcm) **XVIII** [c]	148.3	140.9	128.3	129.3	128.6	138.3	155.0	110.9	124.9	125.6	131.1	C_{12} 128.2, C_{13} 130.9, C_{14} 136.7, C_{15} 147.9, CO_2 166.5, CH_3 53.1
$AuCl_2$(ppy) (**I**) [a,e]	156.2	152.0	130.7	134.0	133.3	135.6	167.9	126.2	146.9	129.3	147.9	
$AuCl_2$(pppy) (**XV**) [e]	n.o.	146.8	130.5	133.9	135.2	135.4	164.3	125.9	156.0	129.0	151.1	CH_3 9.9
$AuCl_2$(pqcm) (**XIX**)	151.0	141.7	131.8	133.6	132.1	135.3	160.9	126.9	126.5	128.8	133.9	C_{12} 132.3, C_{13} 133.7, C_{14} 138.1, C_{15} 143.7, CO_2 169.2, CH_3 56.8

[a] ppy = 2-(2-pyridyl)phenyl.
[b] Ref. [38].
[c] In $CDCl_3$.
[d] Ref. [14].
[e] In $(CD_3)_2SO$.



Scheme 3. (i) AgOAc, CH_2Cl_2. (ii) $pyHClO_4$, CH_2Cl_2. (iii) $HSCH_2CH_2SH$, Et_3N, MeOH. (iv) $HSCH(CH_2CO_2H)CO_2H$, Me_2CO. (v, vi) $HSCH_2CH_2NH_2$, Et_3N, MeOH. (vii) $Ph_2PC_6H_4SH$, THF. (viii, ix) NaS_2CNR_2, Me_2CO; Au complex, MeCN.

Table 3
^{1}H-NMR data for substituted gold complexes [in $(CD_3)_2SO$]

Compound	Phenyl				Pyridine				Other diagnostic signals
	H_3	H_4	H_5	H_6	H_8	H_9	H_{10}	H_{11}	
$Au(OAc)_2(pmpy)$ [a] (**XXI**)	8.34	–	7.74	–	7.58	7.29	7.14	7.21	CH_3 2.21, 2.33; CH_3 (OAc) 2.11, 2.64
$Au(OAc)_2(bmpy)$ [a] (**XXII**)	8.33	7.75	–	7.30	7.58	7.21	7.01	7.01	CH_3 1.34; CH_3 (OAc) 2.09, 2.19
$Au(OAc)_2(bmpy)$ (**XXII**)	8.51	8.43	–	7.86	8.23	7.59	7.44	7.21	CH_3 1.55; CH_3 (OAc) 2.12, 2.28
$Au(pmpy)(edt_2)$ [a] (**XXIV**)	8.88	7.86	7.92	7.28	7.78	7.28	7.28	7.62	CH_2 2.86, 3.40
Au(pmmpy)(msa) (**XXVII**)	9.10	–	7.89	–	7.79	7.31	7.20	7.60	CH_3 2.30, 2.61; CH_2 2.81, CH 4.58
Au(ppy)(mea) (**XXIX**)	8.91	8.55	8.48	7.88	8.15	7.52	7.40	7.61	CH_2 2.91, 3.31, NH_2 6.24 b
Au(ppy)(ppbt) (**XXX**)	9.05	8.53	8.45	7.60	8.21	7.43	7.12	7.12	
$[Au(ppy)(S_2CNMe_2)]PF_6$ (**XXXI**)	8.60	8.38	8.38	7.60	7.98	7.42	7.23	6.90	CH_3 3.41, 3.42
$[Au(ppy)(S_2CNEt_2)]BPh_4$ (**XXXII**)	8.71	8.42	8.42	7.68	8.05	7.49	7.32	7.02	CH_3 1.42, 3.91
$Au(pbpy)(S_2CNMe_2)_2$ (**XXXIII**)	8.53	7.72	–	7.52	8.00	7.15	7.15	7.15	CH_3 1.25 (But), 3.21 (dtc)

[a] In $CDCl_3$.

Reactions of the parent dichloro complexes have been carried out with a range of bidentate thiols (Scheme 3). In the case of ethanedithiol, there is no ambiguity, and the products must have structures **XXIV**, **XXV**. The other thiols are all mixed-donor ligands. We presume that the derivatives from mercaptosuccinic acid (Hmsa), **XXVI** and **XXVII**, have the same configuration as that which we found for [Au(msa)(damp)] [10]. With $HS(CH_2)_2NH_2$, the intermediate mono-substitution product **XXVIII** was also isolated. The far-IR spectrum of this contains bands at 316 and 386 cm^{-1}, which presumably correspond to ν(Au–Cl) and ν(Au–S). On the grounds that (a) in all other monosubsituted derivatives of type [Au-Cl(Y)(C,N)] the incoming soft ligand Y is found *trans* to N rather than to C [25], and (b) the higher frequency

Table 4
$^{13}C\{^{1}H\}$-NMR data for substituted gold complexes [in $(CD_3)_2SO$]

Compound	Phenyl						Pyridine				Other diagnostic signals	
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	
$Au(Oac)_2(pmmpy)$ [a] (**XXI**)	143.1	141.4	127.8	128.7	129.2	145.9	159.4	133.3	129.8	133.5	147.1	H_3C 21.7, 22.2; H_3CO 26.1, 40.0; OOC 175.2, 176.9
$Au(Oac)_2(pbpy)$ [a] (**XXII**)	145.4	141.8	128.5	128.8	129.3	130.7	168.3	117.4	164.0	117.8	147.0	H_3C 30.0; Me_3C 36.0; H_3CO 22.2, 36.0; OOC 175.2, 177.0
$Au(Oac)_2(pbpy)$ (**XXII**)	144.3	145.0	130.2	133.0	133.1	135.1	172.7	123.1	167.1	126.3	151.4	H_3C 33.6; Me_3C 40.0; H_3CO 26.1, 28.4; OOC 177.6, 179.1
Au(ppty)(edt) [a] (**XXIV**)	162.8	143.5	125.6	127.3	132.6	141.2	165.4	120.8	132.9	124.4	149.8	CH_2 33.2, 44.5
Au(pmmpy)(msa) (**XXVII**)	153.8	148.4	131.5	132.5	133.1	149.0	160.5	137.3	133.9	138.0	150.8	CH_3 21.7, 26.1; CH_2 44.5, CH 46.0; CO_2 176.0, 177.3
Au(ppy)(mea) (**XXIX**)	150.8	148.0	130.8	132.5	135.8	147.1	165.5	125.6	136.7	129.5	152.7	CH_2 36.9, 53.9
$[Au(ppy)(S_2CNMe_2)]PF_6$ (**XXXI**)	155.4	148.9	131.3	132.1	133.3	147.9	167.3	126.6	136.4	130.3	153.8	CH_3 44.6, 46.1; NCS_2 196.9
$[Au(ppy)(S_2CNEt_2)]BPh_4$ (**XXXII**)	154.5	n.o.	130.6	131.3	132.5	147.1	166.4	125.8	135.6	129.5	153.0	CH_3 15.4, 15.8; CH_2 50.3, 51.8; NCS_2 196.1
$[Au(pqcm)(S_2CNMe_2)]PF_6$ (**XXXIV**)	156.0	148.2	133.7	133.3	130.9	137.5	168.9	123.3	128.7	129.2	138.0	C_{12} 146.7, C_{13} 149.6; CO_2 170.4, CH_3 57.8; CH_3 (dtc) 47.0, 45.2
$Au(pbpy)(S_2CNMe_2)_2$ (**XXXIII**) [a]	143.9	142.7	126.1	129.1	129.2	134.1	160.8	120.1	159.7	116.6	148.6	CH_3 (Bu^t) 36.0; CH_3 (dtc) 30.4, 45.4; NCS_2 201.9

[a] In $CDCl_3$.

Table 5
C–O stretching frequencies for acetato complexes

Compound	*trans* to C			*trans* to N		
	$\nu(C–O)_{asym}$	$\nu(C–O)_{sym}$	$\Delta\nu$	$\nu(C–O)_{asym}$	$\nu(C–O)_{sym}$	$\Delta\nu$
$Au(OAc)_2(pmpy)$ (**XX**)	1634	1308	326	1665	1366	299
$Au(OAc)_2(pmmpy)$ (**XXI**)	1631	1306	325	1665	1367	298
$Au(OAcO_2(pbpy)$ (**XIX**)	1620	1324	296	1667	1367	300
$[Au(OAc)_2(damp)]$ [a]	1620	1315	305	1670	1370	300
$[Au(OAc)_2(pap)]$ [b]	1629	1310	319	1665	1360	305
$[Au(OAc)(pmpy)(py)]ClO_4$ (**XX**)	1626	1308	318			
$[Au(OAc)(py)(damp)]ClO_4$ [a]	1610	–				
$[Au(OAc)(py)(pap)]ClO_4$ [b]	1620	1300	320			

[a] damp = 2-$C_6H_4CH_2NMe_2$ [8]
[b] pap = 2-C_6H_4N=NPh [23].

is too high for ν(Au–Cl) and must therefore be ν(Au–S), we assign structure **XXVIII** in which the incoming thiolate is bound *trans* to nitrogen. Unfortunately, the corresponding bands for the chelated product **XXIX** are obscured. The NMR spectra (Tables 3 and 4) are consistent with the suggested structures. We have recently found the analogous configuration for a C,P-chelated system, $[Au(Ph_2PC_6H_4CHCH_2OMe)(SCH_2CH_2NH_2)]$ [26].

For the phosphine-thiol $Ph_2PC_6H_4SH$, it is less easy to predict the structure of the chelated product **XXX**, since it is not obvious which donor atom is the softer or the better nucleophile. Fortunately, we were able to crystallise this product and to solve the X-ray diffraction pattern. There was some ambiguity (see Section 4) owing to the difficulty of distinguishing the phenyl and pyridine groups. The most satisfactory configuration is shown in Fig. 2 (bond lengths and distances are in Table 6), and has the phosphine group *trans* to N, suggesting that Ph_2P is softer than ArS^-.

Reaction of the parent dichloro complex with one molar equivalent of a dithiocarbamate gave displacement of both chlorides and formation of the cationic, di-chelated complexes **XXXI** and **XXXII**; $[AuCl_2(pqcm)]$ (**XIX**) reacts similarly to give $[Au(pqcm)S_2CNMe_2]PF_6$ (**XXXIV**). Chelation of the dithiocarbamates is confirmed by the C–N stretching frequencies (1557 and 1561 cm^{-1}, respectively), which are very similar to those of other chelated gold(III) derivatives [8,27,28] and by the non-equivalence in the NMR of the methyl and ethyl signals (Table 4). Final confirmation was obtained by X-ray analysis of **XXXI**, giving the structure shown in Fig. 3 (bond lengths and distances are in Table 6).

When two molar equivalents of dithiocarbamate are used, the disubstituted complex **XXXIII** is formed. This appears in all respects to be similar to the corresponding damp complex we reported earlier [10]: in the IR, the C–N and C–S stretching modes suggest the presence of both mono- and bidentate dithiocarbamate groups, and both the IR and NMR spectra indicate lack of coordination of the pyridine unit. On the other hand, only single sets of NMR signals (^1H and ^{13}C) are found for the dithiocarbamates: this is most probably due to a rapid equilibrium between the two forms as shown in Scheme 3. Such exchanges between mono- and bi-dentate dithiocarbamate have been observed previously for $[Au(damp)(S_2CNEt_2)_2]$ [10] and in the ylide complex $[Au(CH_2P(SPPh_2)(S_2CNEt_2)_2]$ [29].

Finally, $[AuCl_2(pqcm)]$ (**XIX**) reacts with a further molar equivalent of HgCl(pqcm) to give $[AuCl(pqcm)_2]$, **XXXVII**. X-ray crystal analysis (Fig. 4, Table 6) confirms that this material is analogous to similar di-aryl gold(III) complexes reported by Vicente et al. [22,30,31]: one of the aryl ligands is monodentate, the other is chelated, and the two Au–C bonds are mutually *cis*. This is a further example [10,30,32,33] where a fifth ligand is poised above the gold atom but at a relatively large distance [Au···N = 2.93(1) Å].

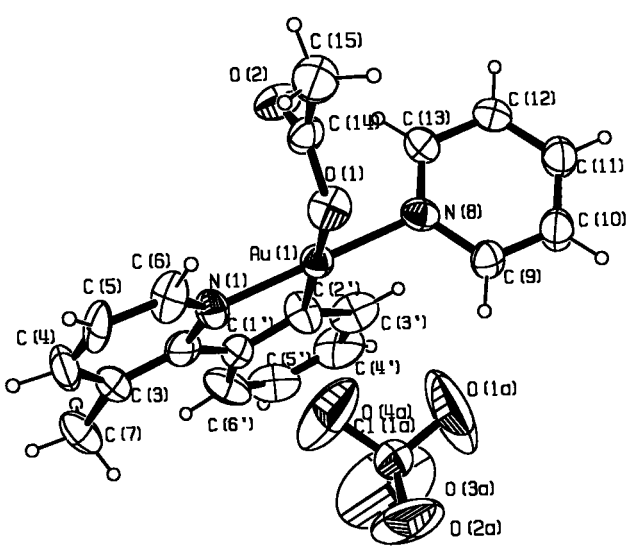


Fig. 1. Structure of the cation $[Au(OAc)(pmpy)(py)]^+$. Significant bond lengths and angles are given in Table 6.

Table 6
Selected bond lengths (Å) and angles (°)

Compound	$[Au(OAc)(pmpy)(py)]ClO_4$ (**XXIII**)	$[Au(ppy)(dpbt)]BPh_4$ (**XXX**) [a]	$[Au(ppy)(S_2CNEt_2)]BPh_4$ (**XXXI**)	$AuCl(pqcm)_2$ (**XXXV**)
Bond lengths				
Au–C	1.96(3)	1.88(1), 2.10(2)	2.036(17)	2.033(11)
Au–N [b]	2.02(5)	2.20(3), 2.02(3)	2.058(11)	2.223(9)
Au–L_1 [c]	1.93(5) (N)	2.24(1), 2.31(1)	2.291(4) (S)	2.007(10) (C)
Au–L_2 [d]	2.13(3) (O)	2.32(1), 2.31(1)	2.376(4) (S)	2.388(3) (Cl)
Bond angles				
C–Au–N	87.0	78.0(7), 84.0(8)	82.2(5)	81.0(4)
C–Au–L_1	92.0	106.3(2), 98.0(8)	99.0(4))	88.2(5)
L_2–Au–N	94.0	88.3(8), 90.8(7)	103.7(3)	105.2(3)
L_1–Au–L_2	87.0	87.4(4), 87.3(4)	75.19(14)	85.8(3)

[a] There are two independent cations in the crystal; data for both are given.
[b] N of phenylpyridine/quinoline.
[c] L_1 is the ligand *trans* to the N of the phenylpyridine/quinoline.
[d] L_2 is the ligand *trans* to the C of the phenylpyridine/quinoline.

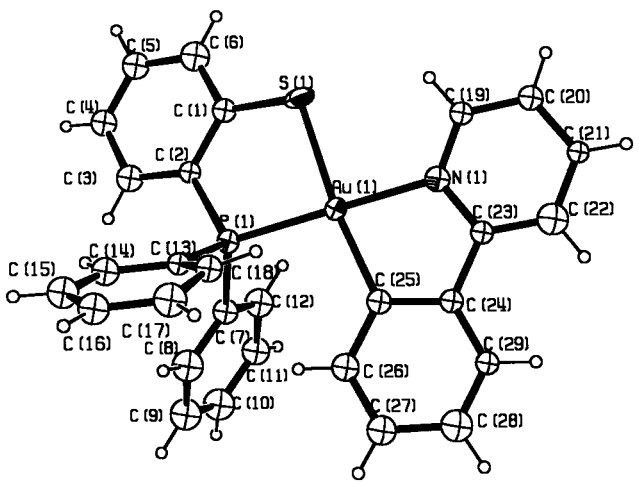


Fig. 2. Structure of the cation $[Au(ppy)(Ph_2PC_6H_4S)]^+$. Significant bond lengths and angles are given in Table 6.

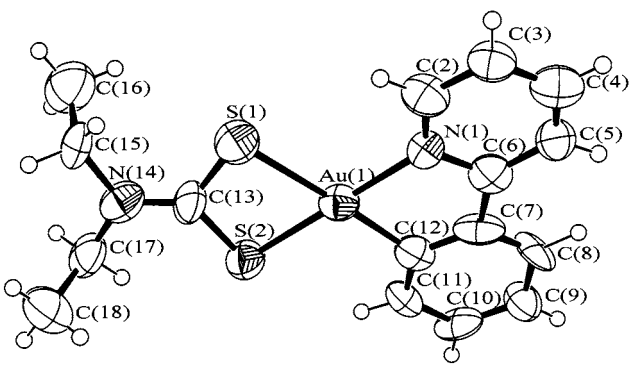


Fig. 3. Structure of the cation $[Au(ppy)(S_2CNEt_2)]^+$. Significant bond lengths and angles are given in Table 6.

3. Conclusions

The chemistry of 2-pheylpyridines orthometallated by gold(III) has been extended. It appears to be very similar to that of the corresponding aurated benzylamine, in that the C,N-coordination is tightly held during substitution. In other cases, such as the metallated azobenzene [6,7] and aromatic Schiff-base derivatives [34,35], the N-donor is displaced by for example, a tertiary phosphine.

4. Experimental

Elemental analyses were carried out by the UMIST Chemistry Department Microanalytical Service. IR spectra (4000–300 cm^{-1}) were recorded on a Nicolet 5PC Fourier transform IR spectrometer in Nujol mulls between KBr plates. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AC-300 spectrometer at respectively 200 and 50.3 MHz in $CDCl_3$ or $(CD_3)_2SO$ at 25°C using TMS as internal standard. $^{31}P\{^1H\}$-NMR spectra were obtained on a Bruker AC-200 spectrometer; chemical shifts are recorded relative to 85% aqueous H_3PO_4.

4.1. Substituted phenylpyridines (*IV–VII*)

The pyridine (0.10 mol) in ether (30 cm^3) was added dropwise to a refluxing solution of phenyl lithium (0.1 mol) in ether (30 cm^3). The solvent was removed under reduced pressure, being replaced by freshly distilled toluene (100 cm^3). Refluxing was continued for 8 h, after which the mixture was cooled and water (35 cm^3) was added cautiously and with continuous stirring. The aqueous layer was separated and extracted repeatedly with ether. The extracts were added to the toluene layer, the whole was dried (KOH) and

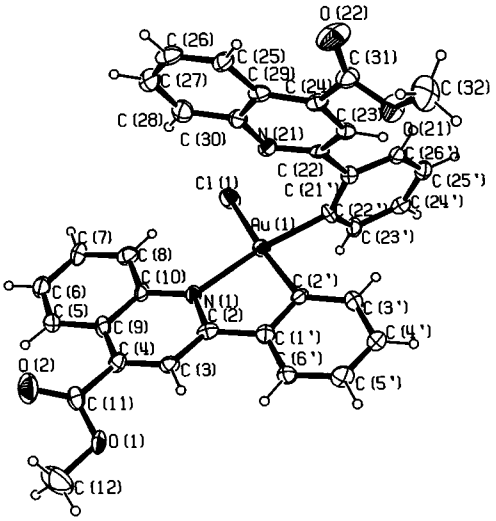


Fig. 4. Structure of $[AuCl(pqcm)_2]$. Significant bond lengths and angles are given in Table 6.

distilled; clear oils were obtained after two to three redistillations.

4.2. 2-Phenyl-4-(methylcarboxylate)quinoline (XVII)

2-Phenylquinoline-4-carboxylic acid was prepared by the method of Ref. [12]. This acid (32.7 g, 0.125 mol) was refluxed gently with thionyl chloride (14.6 cm^3, 0.2 mol) on a water bath for ca. 45 min. The excess thionyl chloride was removed under reduced pressure and the residue was washed with diethyl ether (30 cm^3). The crude 2-phenyl-4-benzoylquinoline was recrystallised from dichloromethane (20 cm^3). To the whole yield (27 g, 0.10 mol), kept at 0°C, methanol (15 cm^3) was added dropwise over 30 min. The resulting solution was refluxed for 2 h and then evaporated to dryness. The residue was extracted repeatedly with dichloromethane (portions of 30 cm^3) and the combined extracts were combined, dried ($MgSO_4$) and reduced to about 15 cm^3. White needles of **XVII** separated during the evaporation.

4.3. 2-(Substituted-2-pyridyl)phenyl]chloromercury (VIII–XII)

The phenylpyridine (0.1 mol) in ethanol (50 cm^3) was added slowly to a stirred solution of mercury(II) acetate (32.0 g, 0.1 mol) in ethanol (100 cm^3). The mixture was refluxed for 12 h and filtered (hot) into a solution of lithium chloride (6.0 g, 0.14 mol) in methanol (20 cm^3). This mixture was refluxed for a further hour and allowed to cool overnight. The precipitate was filtered off, washed with water (50 cm^3) and ethanol (50 cm^3, 0°C) and recrystallised from dichloromethane (30 cm^3).

The pqcm-derivative **XVIII** was obtained similarly. [Analytical and spectroscopic data (%C, %H, %N, %Cl, %Hg; ν(Hg–C) (cm^{-1}), ν(Hg–Cl) (cm^{-1}), $\delta(C-N)_{py}$ (cm^{-1})): **VIII**, 34.2 (33.9), 2.0 (2.1), 3.8 (3.6), 9.1 (9.1), n.o.; n.o., 320, 1586: **IX**, 35.7 (35.7), 2.4 (2.5), 3.7 (3.5), n.o., 49.6 (49.0); 419, 335, n.o.: **X**, 37.3 (37.4), 2.8 (2.9), 3.6 (3.4), 7.9 (8.5), 47.6 (47.9); 419, 336, n.o: **XI**, 37.1 (37.2), 3.3 (3.4), 3.5 (3.3), 8.3 (8.4), 46.3 (46.0); 417, 332, 1599: **XII**, 40.4 (40.4), 3.6 (3.5), 3.1 (3.1), 7.9 (8.0), 44.9 (45.3); 423, 337, 1599: **XVIII**, 40.8 (41.0), 2.1 (2.3), 2.5 (2.6), 13.7 (13.4), n.o; 428, 335b, n.o.]

4.4. 2-(Substituted-2-pyridyl)phenyl]dichlorogold(III) (XIII–XVI)

The chloromercury derivative (0.5 mmol) in dichloromethane 15 cm^3) was added to a solution of sodium tetrachloroaurate dihydrate (0.20 g, 0.5 mmol) in acetonitrile (15 cm^3), and the mixture was stirred for about 1 h. An off-white or yellow solid separated and was washed with acetonitrile (20 cm^3) and dried. Recrystallisation was effected from dichloromethane.

The pqcm-derivative **XIX** was obtained analogously. [Analytical and spectroscopic data (%C, %H, %N, %Cl; ν(Au–C) (cm^{-1}), ν(Au–Cl) (cm^{-1}), $\delta(C-N)_{py}$ (cm^{-1})): **I**, 31.1 (31.3), 1.7 (1.9), 2.9 (3.3), 16.5 (16.8); 412, 363 and 310, 1607: **XIII**, 33.3 (33.1), 2.1 (2.3), 3.6 (3.2), 15.9 (16.3); 420, 366 and 302, n.o.: **XIV**, 34.9 (34.9), 2.4 (2.7), 3.2 (3.1), 15.5 (15.8); 415, 380, n.o.: **XV**, 35.9 (36.2), 2.7 (3.0), 3.1 (3.0), 15.4 (15.3); 414, 366 and 307, 1618: **XVI**, 37.7 (38.0), 3.4 (3.3), 2.9 (2.9), 14.8 (14.7); 415, 368 and 307, 1620: **XIX**, 33.1 (33.2), 2.4 (2.5), 4.1 (3.9), 9.1 (8.9).]

4.5. 2-(Substituted-2-pyridyl)phenyl]diacetatogold(III) (XX–XXII)

Solid silver acetate (0.17 g, 1.0 mmol) was stirred with a suspension of **XIII**, **XIV** or **XVI** (0.5 mmol) in dichloromethane (30 cm^3) for about 1 h in the absence of light. The solution was filtered and the residue extracted with dichloromethane (2 or 3×25 cm^3). The combined dichloromethane solutions were evaporated to dryness and the residue recrystallised from dichloromethane. [Analytical and spectroscopic data (%C, %H, %N, %X (X = S or Cl); ν(Au–C) (cm^{-1}): 39.5 (39.8), 3.2 (3.3), 2.9 (2.9); 415: **XXI**, 40.9 (41.1), 3.6 (3.7), 2.7 (2.8); 415: **XXII**, 42.9 (43.5), 3.6 (4.2), 2.7 (2.7); 414: **XXII** 42.9 (43.5), 3.6 (4.2), 2.7 (2.7); 414.]

4.6. Acetato(2-2-methylpyridylphenyl)(pyridine)gold(III) perchlorate (XXIII)

Solid pyridinium perchlorate (0.09 g, 0.5 mmol) was added to a solution of **XXI** (0.23 g, 0.5 mmol) in dichloromethane (20 cm^3). The mixture was stirred for 1 h and concentrated to 10 cm^3. Addition of ether (5 cm^3) gave a white solid, which was recrystallised from

dichloromethane–ether. [%C, %H, %N, ν(AuC) (cm^{-1}) = 35.0 (34.9), 2.5 (2.9), 4.2 (4.1), 414.]

4.7. 2-(Substituted-2-pyridyl)phenyl](1,2-ethanedithiolato)gold(III) (XXIV, XXV)

A solution of 1,2-ethanedithiol (42 μl, 0.5 mmol) in methanol (10cm^3) was treated with triethylamine (0.14 cm^3, 1.0 mmol) and added dropwise to a suspension of the dichlorogold complex **I** or **XIII** (0.5 mmol) in methanol (20 cm^3). The mixture was stirred for about 3 h and evaporated to dryness. The residue was recrystallised from dichloromethane. [Analytical and spectroscopic data (%C, %H, %N, %S, ν(Au–C) (cm^{-1}), ν(Au–S) (cm^{-1}): **XXIV**, 35.3 (35.2), 2.9 (2.7), 3.4 (3.2), 14.8 (14.5), 408, 327 and 373: **XXV**, 38.2 (37.9), 3.2 (3.4), 2.9 (3.0), 13.6 (13.6), n.o., 322 and 374.]

4.8. 2-(Substituted-2-pyridyl)phenyl]-(thiomalato)gold(III) (XXVI, XXVII)

Solid mercaptosuccinic acid (80 mg, 0.5 mmol) was added to a stirred solution of the dichlorogold complex **I** or **XIII** (0.5 mmol) in acetone (15 cm^3). The pale yellow precipitate which formed immediately was filtered off, washed with water, ethanol and ether, and dried. [For **XXVII**, %C, %H, %N, %S, ν(Au–C) (cm^{-1}): 36.3 (36.8), 2.9 (2.9), 2.6 (2.7), 6.2 (6.1), 419.]

4.9. (2-2-Pyridylphenyl)(2-aminoethylthiolato)-chlorogold(III) (XXVIII) and (2-2-pyridylphenyl)-(2-aminoethylthiolato)gold(III) tetraphenylboronate (XXIX)

2-Mercaptoethylamine hydrochloride (60 mg, 0.5 mmol) in methanol (10 cm^3) was treated with triethylamine (70 μl, 0.5 mmol), filtered, and added with stirring to a solution of dichlorogold complex **I** (0.21 g, 0.5 mmol) in methanol (20 cm^3). A yellow precipitate formed immediately, which was filtered off, washed with water, ethanol and ether, dried, and characterised as complex **XXVIII**. [%C, %H, %N, %S, ν(Au–C) (cm^{-1}), ν(Au–S) (cm^{-1}) = 33.8 (34.5), 3.1 (3.3), 6.1 (6.3), 6.9 (7.3), 411, 316 and 386.]

Dropwise addition of sodium tetraphenylboronate (0.19g, 0.55 mmol) in methanol (10 cm^3) to the above solution gave precipitation of a pale yellow solid, which was filtered off and washed with ethanol and ether. Recrystallisation from dimethylformamide–ether yielded dark yellow crystals of **XXIX**. [%C, %H, %N, %S, ν(Au–C) (cm^{-1}), ν(Au-S) (cm^{-1}) = 59.3 (59.6), 4.8 (4.6), 3.9 (3.8), 4.7 (4.3), 411, obsc.]

4.10. (2-2-Pyridylphenyl)(2-diphenylphosphino-phenylthiolato)gold(III) tetraphenylboronate (XXX)

A solution of 2-diphenylphosphinobenzenethiol (0.15 g, 0.5 mmol) in THF (20 cm^3) was added dropwise to a stirred suspension of dichlorogold complex **I** (0.21 g, 0.5 mmol) in THF (20 cm^3). The mixture was stirred for about 1 h, giving a clear solution that was then concentrated (15 cm^3). Addition of sodium tetraphenylboronate (0.19 g, 0.55 mmol) in methanol (20 cm^3) gave an immediate yellow precipitate of the product, which was washed with methanol (20 cm^3) and dichloromethane (20 cm^3) and recrystallised from dmf–ether. [%C, %H, %N, %S, ν(Au–C) (cm^{-1}), ν(Au–S) (cm^{-1}) = 65.8 (66.1), 3 (4.4), 3.9 (3.8), 3.7 (3.3), 413, 310.]

4.11. (2-2-Pyridylphenyl)(dialkydithiocarbamato)-gold(III) salts (XXXI, XXXII)

A solution of sodium dialkyldithiocarbamate (0.5 mmol) in acetone (5 cm^3) was added dropwise to a solution of the dichloro complex **I** (0.5 mmol) in acetonitrile (20 cm^3), giving an orange coloration. After 30 min stirring, the mixture was filtered and a solution of sodium hexafluorophosphate or tetraphenylboronate (0.55 mmol) in methanol (5 cm^3) was added. The mixture was stirred for a further 30 min and the precipitated product was filtered off, washed with acetone (10 cm^3) and recrystallised from dmf–ether. The pqcm-derivative **XXXIV** was obtained similarly. [Analytical and spectroscopic data (%C, %H, %N, %S, ν(Au–C) (cm^{-1}, ν(Au–S) (cm^{-1}): **XXXI**, 25.8 (25.8), 1.9 (2.6), 4,1 (4.3), 9.8 (9.8), 413, 327 and 376: **XXXII**, 58.7 (58.4), 4.7 (5.0), 3.4 (3.3), 7.8 (8.4), 412, 354b and 375: **XXXIV**, 33.1 (33.2), 2.4 (2.5), 4.1 (3.9), 9.1 (8.9, n.o., n.o.]

4.12. [2-(t-Butyl-2-pyridyl)phenyl]bis(dimethyldithio-carbamato)-gold(III) (XXXIII)

A solution of sodium dimethyldithiocarbamate (1.0 mmol) in acetone (15 cm^3) was added dropwise to a solution of the dichloro complex **XVI** (0.5 mmol) in acetonitrile (20 cm^3), giving an intense orange coloration. The mixture was stirred for 1 h and filtered. The filtrate was evaporated to dryness, and the residue extracted with dichloromethane (10 cm^3). Slow evaporation of the extract gave the crystalline product. [%C, %H, %N, %S, ν(Au–C) (cm^{-1} = 38.8 (39.0), 4.3 (4.4), 6.4 (6.5), 20.6 (19.8), 414.]

4.13. Crystallography

Details of the crystal data, data-collection, and least-square parameters are summarised in Tables 7 and 8.

Table 7
Crystallographic details for **XXIII** and **XXX**

Compound	Au(OAc)(pmpy)-(py)ClO_4 (**XXIII**)	[Au(ppy)($Ph_2PC_6H_4S$)]-BPh_4 (**XXX**)
CCDC Reference No.	121694	121693
Empirical formula	$C_{20}H_{20}AuCl_3N_2O_6$	$C_{53}H_{42}AuBNPS$
Formula weight	687.70	963.68
Temperature (K)	293(2)	291(2)
Wavelength (Å)	0.71069	0.71069
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pna2_1$
Unit cell dimensions		
a	10.7054(10)	31.577(5)
b	13.163(2)	9.742(2)
c	16.958(2)	27.611(3)
β	91.40(2)	
Volume (Å^3)	2388.9(5)	8494(2)
Z, calculated density (Mg m^{-3})	4, 1.912	8, 1.507
Absorption coefficient (mm^{-1})	6.532	3.589
$F(000)$	1328	3856
Crystal size (mm)	$0.25\times0.25\times0.15$	$0.3\times0.25\times0.25$
θ range for data collection (°)	2.27–25.04	1.47–23.97
Index ranges	$-12\le h\le12$, $0\le k\le15$, $0\le l\le20$	$-36\le h\le-10$, $-11\le k\le0$, $-7\le l\le-31$
Reflections collected/ unique	4116/4116 [$R_{int}=0.0000$]	4216/4117 [$R_{int}=0.01211$]
Completeness to $2\theta=25.04$	92.8%	60.6%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4116/0/290	4117/165/490
Goodness-of-fit on F^2	1.038	1.015
Final R indices [$I>2\sigma(I)$]	$R_1=0.0787$, $wR_2=0.1576$	$R_1=0.0673$, $wR_2=0.1138$
R indices (all data)	$R_1=0.1606$, $wR_2=0.2080$	$R_1=0.0949$, $wR_2=0.1272$
Extinction coefficient	0.0005(2)	0.00004(3)
Largest difference peak and hole (e A^{-3})	1.007 and −2.324	0.760 and −0.704

Table 8
Crystallographic details for **XXXIII** and **XXXV**

Compound	[Au(ppy)(S_2CNEt_2)]-BPh_4 (**XXXIII**)	$AuCl(pqcm)_2$ (**XXXV**)
CCDC Reference No.	121692	121695
Empirical formula	$C_{40}H_{38}AuBN_2S_2$	$C_{34}H_{24}AuClN_2O_4$
Formula weight	818.62	756.97
Temperature (K)	293(2)	293(2)
Wavelength	0.71069	0.71069
Crystal system, space group	Monoclinic, Cc	Triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	11.499(2)	11.946(2)
b (Å)	33.114(4)	12.022(2)
c (Å)	9.439(2)	10.9394(10)
α (°)		96.46(2)
β (°)	102.06(2)	99.43(2)
γ (°)		62.28(2)
Volume (Å^3)	3514.6	1406.1(4)
Z, D_{calc} (Mg m^{-3})	4, 1.547	2, 1.788
Absorption coefficient (mm^{-1})	4.335	5.370
$F(000)$	1632	740
Crystal size (mm)	$0.30\times0.15\times0.15$	$0.30\times0.25\times0.20$
θ range for data collection (°)	1.23–24.96	2.50–25.00
Index ranges	$0\le h\le13$, $0\le k\le39$, $-11\le l\le10$	$-14\le h\le14$, $-14\le k\le14$, $0\le l\le12$
Reflections collected/ unique	3208/3208 [$R_{int}=0.0000$]	4791/4791 [$R_{int}=0.0000$]
Completeness to $2\theta=25.04$	49.4%	96.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	3208/2/415	4791/0/382
Goodness-of-fit on F^2	1.001	1.046
Final R indices [$I>2\sigma(I)$]	$R_1=0.0318$, $wR_2=0.0748$	$R_1=0.0482$, $wR_2=0.1210$
R indices (all data)	$R_1=0.00878$, $wR_2=0.0934$	$R_1=0.0870$, $wR_2=0.1348$
Extinction coefficient		0.0003(2)
Largest difference peak and hole (e Å^3)	0.590 and −1.069	1.816 and −1.405

Data were collected on a Rigaku/MSC AFC6S (for **XXIII**, **XXXV** and **XXXIII**) or an Enraf–Nonius CAD4 diffractometer (**XXX**), both with monochromated Mo–K_α radiation ($\lambda=0.71069$ Å). All structures were solved by direct methods [36] and refined versus F^2 (SHELXL-97) [37]. All non-hydrogen atoms were refined anisotropically. A riding model starting from calculated positions was employed for the hydrogen atoms. In structure **XXX** each asymmetric unit comprises two formula units. The chemically and conformationally identical ions were constrained so that their bond lengths and second-neighbour distances (angles) were equal within standard deviations of 0.02 Å. Two refinements were made, on the assumption that the pyridine was *trans* to the phosphine or to the thiol group. The former model was chosen since it gave slightly lower residuals and more consistent bond distances and vibrational parameters. The R-values were defined as $R_1=\Sigma\big||F_o|-|F_c|\big|^2/\Sigma|F_o|^2$ and $wR_2=[\Sigma(w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

5. Supplementary material

Further details of the crystal structure determinations may be obtained from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-

033) or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk, quoting the reference numbers in Tables 7 and 8.

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