Synthesis and Characterization of Gold(III) Adducts and Cyclometallated Derivatives with 2-Substituted Pyridines. Crystal Structure of [Au{$NC_5H_4(CMe_2C_6H_4)$-2}Cl_2]†

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The 2-benzylpyridines HL [NC_5H_4-(CH_2Ph)-2, -(CHMePh)-2 and (CMe_2Ph)-2] reacted with $AuCl_3{\cdot}2H_2O$ or Na[$AuCl_4$] to give adducts [Au(HL)Cl_3] or cyclometallated derivatives [AuLCl_2]. The metallation reaction involves direct activation of a C–H bond of the phenyl substituent. With the 2-alkylpyridines $NC_5H_4(CMe_3)$-2 and $NC_5H_4(CH_2CMe_3)$-2 (HL) only the tetrachloroaurate(III) salts [H_2L][$AuCl_4$] were isolated. The structure of [Au{$NC_5H_4(CMe_2C_6H_4)$-2}Cl_2] has been determined by X-ray diffraction. It reveals a six-membered ring having a boat-like conformation: there is a rather short interaction between one hydrogen of the Me group in axial position and the gold atom, Au···H 2.56(5) Å. The cyclometallated species react with PPh_3 to give cationic complexes [AuL(PPh_3)Cl]$^+$ and with 1,2-bis(diphenylphosphino)ethane (dppe) to yield [AuL(dppe)Cl]$^+$. Under pressure (50 atm, 60 °C) of CO extrusion of the metal occurs. The organic products formed likely arise from insertion of CO into the Au–C bond. The reactivity of the cycloaurated species is compared with that of analogous palladium(II) derivatives described previously.

Most reviews which deal with cyclometallation reactions neglect gold chemistry, attention being focused on other d^8 ions, *e.g.* Pd^{II}, Pt^{II} and Rh^{I}.[1]

Nevertheless, a number of cycloaurated species involving nitrogen ligands has been described in previous years. Vicente *et al.*[2] have reported the synthesis, characterization and reactivity of many species arising from azobenzene and *N*,*N*-dimethylbenzylamines: all of them imply an aromatic C–H activation to give five-membered rings. The auration was not achieved directly: in most cases organomercury derivatives were used as arylating agents. Constable and co-workers[3] have described gold(III) cyclometallated species with 6-(2-thienyl)- or 6-phenyl-2,2′-bipyridine, *i.e.* with potentially terdentate ligands, as well as with likewise substituted pyridines: some of these species were obtained by direct activation of an aromatic C–H bond. Very recently, the complex [Au(dpphen)Cl]$^+$, where dpphen = 2,9-diphenyl-1,10-phenanthroline,[4] has been reported.

Previously we have reported cyclometallated species of platinum(II) and palladium(II) with substituted pyridines and 2,2′-bipyridines both with benzyl and alkyl substituents.[5] We have now extended our investigations to gold(III) and report the first results with 2-benzyl- and 2-alkyl-pyridines. The results for 2,2′-bipyridines will be described in a forthcoming paper.

With 2-benzylpyridines, activation of C(sp^2)–H bonds was achieved directly. The structure in the solid state of one of these cycloaurated species was solved by X-ray diffraction: this is the first structure of a gold(III) six-membered C,N derivative.

Finally we deemed it worthwhile to study the reactivity of the cycloaurated derivatives with carbon monoxide. To the best of our knowledge, the reaction of organogold(III) derivatives with CO has not been previously investigated. The behaviour of the gold species is compared with that of the palladium analogues.[5d,6] A brief report on part of this work has been given.[7]

Results and Discussion

The 2-benzylpyridines (HL = NC_5H_4-CH_2Ph-2, -CHMePh-2 or -CMe_2Ph-2), and the 2-alkylpyridines (HL = NC_5H_4-CMe_3-2 and -CH_2CMe_3-2) were prepared from the appropriate cyanides, according to literature methods.[8]

The reaction of either $AuCl_3{\cdot}2H_2O$ or Na[$AuCl_4$] with the 2-benzylpyridines was carried out in water at room temperature. With NC_5H_4-CH_2Ph-2 and -CHMePh-2 the reaction leads to the adducts [Au(HL)Cl_3] **1a** and **2a** in fairly good yields, *ca.* 75%. With $NC_5H_4(CMe_2Ph)$-2, under the same conditions, only the salt [H_2L][$AuCl_4$] **3s** was isolated (see Scheme 1). The formulation of **1a** and **2a** as [Au(HL)Cl_3] adducts is supported by microanalytical data, conductivity measurements, IR, NMR and mass spectra. In the IR spectra a strong absorption around 360 cm^{-1} is assignable to a Au–Cl stretching mode, at a value comparable to that observed for other 1:1 adducts of $AuCl_3$ with heterocyclic ligands.[9] In the ^1H NMR spectra all the resonances are shifted downfield upon co-ordination: in the aromatic region the spectra exhibit the expected nine resonances.

With NC_5H_4-CMe_3-2 and -CH_2CMe_3-2 only the salts [H_2L][$AuCl_4$] **4s** and **5s** were isolated: so far, in spite of several attempts carried out under various conditions, adducts were not obtained.

The adducts **1a** and **2a** as well as the salt **3s** can be converted into the cycloaurated species [AuLCl_2] **1m**–**3m** by warming their suspensions in aqueous acetonitrile (*ca.* 4:1). It is noteworthy that the metallated species can be obtained also from $AuCl_3{\cdot}2H_2O$ and the pyridines under reflux in water, *i.e.*

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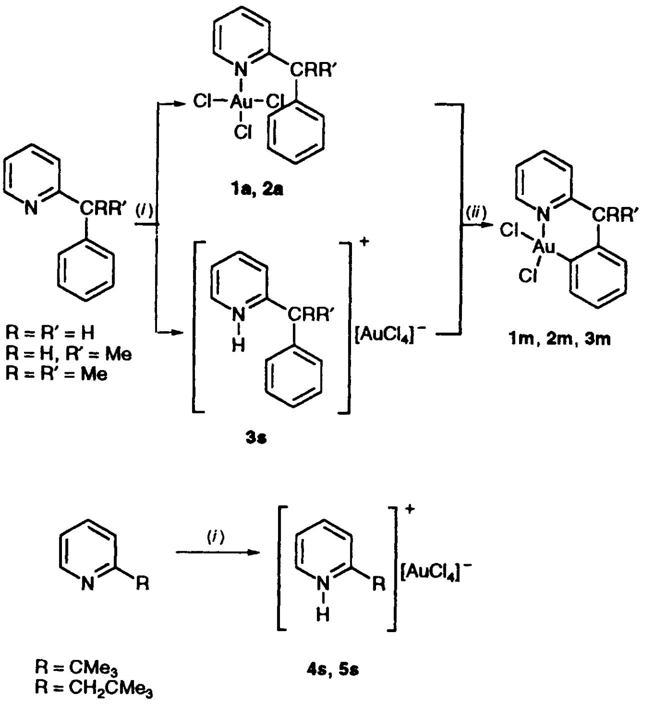
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: atm = 101 325 Pa.



Scheme 1 (*i*) $AuCl_3{\cdot}2H_2O$, water, room temperature (r.t.); (*ii*) MeCN–water, reflux

by direct activation of the C–H bond. Complexes **1m**–**3m** are isolated in good yields as white solids: they are not electrolytes and are slightly soluble in the most common solvents. The solubility in chlorinated solvents is sufficient to allow well resolved ^1H NMR spectra to be obtained which unambiguously show the activation of an aromatic C–H bond. The strong deshielding of the H(6) proton, usually observed when a chlorine is in the proximity of the pyridine ring,[10] is consistent with co-ordination of the nitrogen atom. The spectra indicate a boat conformation of the six-membered ring, as in the previously reported palladium derivatives.[5d] No rapid inversion of the boat occurs on the NMR time-scale up to room temperature, as shown by the AB pattern displayed by the CH_2 resonance of complex **1m**, as well as by the two distinct resonances for the Me substituents in **3m**. The latter resonances are both at low field (δ 2.06 and 2.35, CD_2Cl_2) with respect to the free pyridine (δ 1.75, $CDCl_3$). The more deshielded one is likely to be associated with the methyl group pointing toward the metal, *i.e.* in a pseudo-axial position. In agreement with a boat conformation, two diastereomers are formed in the case of complex **2m** (*a* and *b*).

The structure of complex **3m** in the solid state has been solved by X-ray diffraction. It consists of the packing of $[AuLCl_2]$ molecules separated by normal van der Waals interactions. An ORTEP[11] view of the molecule is shown in Fig. 1. Crystal data, selected bond distances and angles, and atomic coordinates are listed in Tables 1, 2 and 3, respectively. The gold atom displays an almost regular square-planar co-ordination, with a distortion in the N–Au–C(9) angle, 85.7(1)°. The bite of the six-membered cyclometallated ring is comparable with that observed in $[PtL(PPh_3)Cl]$ [HL = $NC_5H_4(CHMePh)$-2][5f] [C–Pt–N 85.1(1)°], as well as in a number of six-membered N–Au–N rings [range 84.7(3)–86.8(2)°].[12] The bond lengths involving the gold atom are all normal. The Au–Cl(2) bond [2.390(1) Å] is much longer than Au–Cl(1) [2.282(1) Å] as expected owing to the great *trans* influence of the aryl carbon atom. The Au–C(9) bond length [2.021(3) Å] is identical with the Au–C(sp^2) distance found in $[Au\{C_6H_3(N{=}NC_6H_4Me\text{-}4)\text{-}2\text{-}Me\text{-}5\}Cl_2]$, 2.021(5) Å,[2m] and the Au–N bond length, 2.041(3) Å, is statistically coincident with Au–N(sp^2), 2.031(6) Å, found in

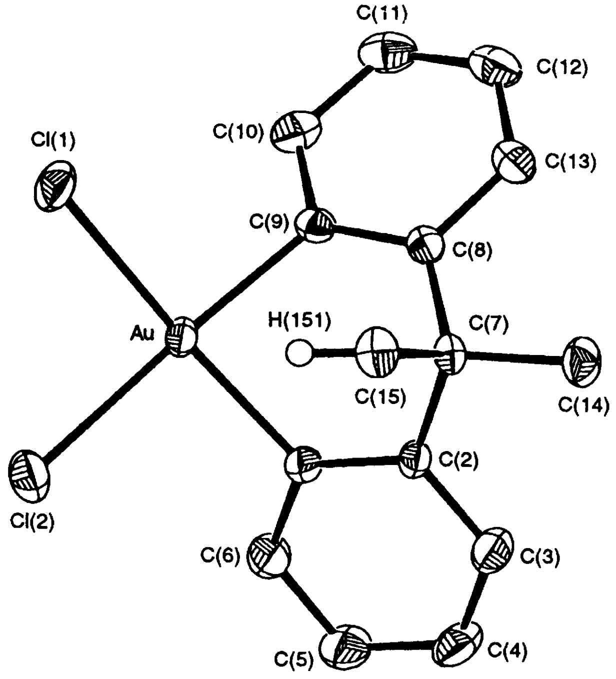


Fig. 1 An ORTEP view of compound $[Au\{NC_5H_4(CMe_2C_6H_4)\text{-}2\}Cl_2]$ **3m**

Table 1 Crystallographic data for complex **3m**

Formula	$C_{14}H_{14}AuCl_2N$
M	464.2
Colour	Colourless
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.379(1)
b/Å	8.712(2)
c/Å	11.533(2)
α/°	72.05(2)
β/°	79.18(1)
γ/°	62.09(2)
U/Å³	706.8(3)
Z	2
F(000)	436
D_c/g cm⁻³	2.181
Crystal dimensions/mm	0.17 × 0.23 × 0.48
μ(Mo-Kα)/cm⁻¹	107.5
Minimum, maximum transmission factors	0.68, 1.00
Scan mode	ω
ω-Scan width/°	1.2 + 0.35 tan θ
θ Range/°	3–27
Reciprocal space explored	+*h*, ±*k*, ±*l*
Measured reflections	3087
Unique observed reflections [*I* > 3σ(*I*)]	2829
Final *R* and *R′*[a]	0.025, 0.032
No. of variables	176
Goodness of fit[b]	1.41

[a] $R = [\Sigma(|F_o - k|F_c||)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/2F_oL_p$, N_o is the number of observations and N_v the number of variables.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **3m**

Au–Cl(1)	2.282(1)	Au–Cl(2)	2.390(1)
Au–N	2.041(3)	Au–C(9)	2.021(3)
Cl(1)–Au–Cl(2)	91.6(4)	Cl(1)–Au–N	176.2(8)
Cl(1)–Au–C(9)	90.8(1)	Cl(2)–Au–N	91.9(9)
Cl(2)–Au–C(9)	177.4(1)	N–Au–C(9)	85.7(1)

Table 3 Fractional atomic coordinates with e.s.d.s in parentheses for the refined atoms of complex **3m**

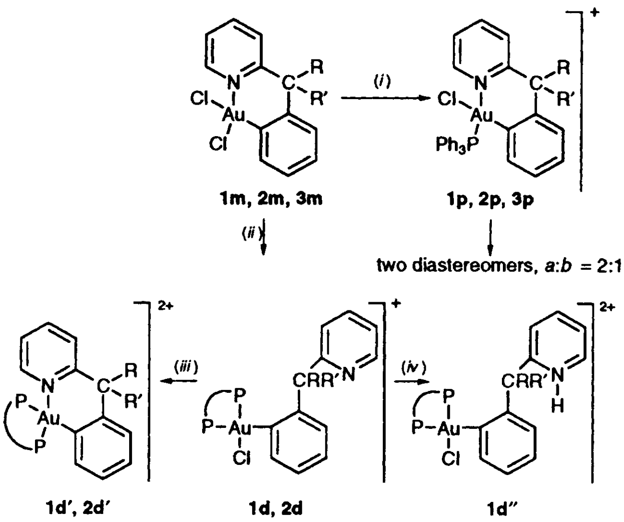
Atom	*x*	*y*	*z*
Au	0.032 43(2)	−0.044 97(1)	0.308 93(1)
Cl(1)	−0.117 9(2)	0.253 5(1)	0.217 0(1)
Cl(2)	0.218 4(1)	0.009 6(1)	0.409 5(1)
N	0.161 8(4)	−0.315 3(4)	0.382 2(3)
C(2)	0.216 1(4)	−0.434 0(4)	0.313 4(3)
C(3)	0.300 9(6)	−0.616 1(5)	0.370 7(4)
C(4)	0.329 4(7)	−0.673 6(6)	0.493 8(5)
C(5)	0.272 7(7)	−0.551 5(7)	0.561 0(4)
C(6)	0.188 5(6)	−0.371 4(6)	0.502 7(4)
C(7)	0.179 1(4)	−0.363 9(4)	0.177 3(3)
C(8)	−0.025 9(4)	−0.243 5(4)	0.168 1(3)
C(9)	−0.115 6(5)	−0.102 6(5)	0.224 2(3)
C(10)	−0.302 4(6)	−0.004 2(6)	0.226 3(4)
C(11)	−0.403 8(5)	−0.042 5(7)	0.166 7(5)
C(12)	−0.317 2(5)	−0.174 1(6)	0.104 5(4)
C(13)	−0.132 1(5)	−0.273 8(5)	0.105 8(4)
C(14)	0.240 8(6)	−0.520 5(5)	0.119 2(4)
C(15)	0.287 3(5)	−0.257 0(5)	0.109 4(4)
H(151)	0.263(6)	−0.168(6)	0.142(5)
H(152)	0.256(6)	−0.189(7)	0.032(5)
H(153)	0.415(6)	−0.321(6)	0.122(5)

the cation $[Au(dmp)(NC_9H_6O)]^+$ [dmp = 2-(dimethylaminomethyl)phenyl].[2h] The six-membered metallacycle is in a boat conformation, with atoms N, C(2), C(8) and C(9) essentially coplanar [maximum deviations from their best plane −0.016(4) Å for C(2) and +0.015(4) Å for C(8)]. This best plane forms dihedral angles with planes C(2)–C(7)–C(8) and N–Au–C(9) of 44.6(3) and 38.2(2)°, respectively. The three hydrogen atoms bonded to C(15) are in a staggered conformation with respect to the C(7)–C(2), C(7)–C(8), and C(7)–C(14) bonds. As a consequence atom H(151) is in a pseudo-axial position with respect to the metal co-ordination plane. The Au $\cdots$ H(151) distance, 2.56(5) Å, is rather short, well below the value reported as upper limit for long-range metal–hydrogen interactions in platinum(II) chemistry.[13] Bond lengths and angles within the bidentate ligand are normal, with the two aromatic rings strictly planar and forming a dihedral angle of 63.2(2)° with each other.

Reactivity of Cyclometallated Derivatives **1m**–**3m**.—To evaluate the stability of the cycloaurated ring, we investigated first the reaction of compounds **1m**–**3m** with triphenylphosphine. The reaction (molar ratio PPh_3:Au = 1:1 or 2:1) carried out in the presence of $NaBF_4$ gives the cationic species $[AuL(PPh_3)Cl][BF_4]$ **1p**–**3p**. The spectroscopic data are consistent with **1p**–**3p** being-cyclometallated species. In particular, the ^1H NMR spectra suggest that the rigid boat-like conformation of the ring is maintained: in agreement, diastereomers (*a* and *b*) are observed in the case of complex **2p**. Of the two possible geometrical isomers, *trans*-P–Au–N or *trans*-P–Au–C, the IR and NMR spectra, taken together, support a *trans*-P–Au–N arrangement. Indeed in the IR spectra the Au–Cl stretching vibrations are observed at values consistent with a chlorine *trans* to a carbon atom[2c] (see Experimental section) and in the ^1H NMR spectra the H(6) protons are strongly deshielded (Table 4).

No further reaction occurs on addition of an excess of PPh_3 to complex **1p** (^{31}P NMR criterion): thus it seems that these gold(III) derivatives are rather stable towards both ring opening and reduction to gold(I) species.

At variance, the nitrogen atom can be displaced from the metal by reaction with the potentially chelating diphosphine $(Ph_2PCH_2)_2$ (dppe) (see Scheme 2). Reaction of complexes **1m** and **2m** with dppe leads to the cationic derivatives $[AuL(dppe)Cl][BF_4]$ **1d** and **2d**. The two sharp resonances observed in the $^{31}P-\{^1H\}$ NMR spectra at room temperature are consistent with square-planar species: the difference between their chemical shifts suggests that the phosphorus atoms are *trans* to ligands having markedly different *trans* influence, such as Cl and C. In the ^1H NMR spectra, the single resonances observed for the protons of the substituents at the benzylic carbon atom indicate a non-co-ordinated nitrogen atom (see Table 4). In agreement, complex **1d** was easily protonated by reaction with HBF_4. The co-ordination of the pyridine ring can be restored and the chloride ligand removed by means of silver tetrafluoroborate to give complexes **1d′** and **2d′**.



Scheme 2 (*i*) PPh_3, BF_4^-; (*ii*) dppe, BF_4^-; (*iii*) $AgBF_4$; (*iv*) $HBF_4{\cdot}Et_2O$

Although the chemistry of gold with carbon monoxide is rather sparse,[14] we deemed it worth investigating the reaction of the cyclometallated species **1m**–**3m** with CO in order to compare their behaviour with that of homologous palladium(II) and platinum(II) derivatives.[5d,f,6] Under mild conditions, *e.g.* bubbling CO at room temperature through a solution of **1m** in CH_2Cl_2 or in CH_2Cl_2–EtOH, no reaction occurs: the starting complex is almost quantitatively recovered, only trace amounts of gold being formed. Under more vigorous conditions, 50 atm of CO, 60 °C in CH_2Cl_2–EtOH solution (*ca.* 4:1), a mirror of gold and bright-yellow organic molecules are formed (see Scheme 3). The organic derivatives were separated by chromatography on silica gel and fully characterized by mass and NMR (^1H, $^{13}C-\{^1H\}$) spectra (see Table 5). From **1m**, three carbonylated species were obtained, **I**–**III**. Compound **II**, identical to that obtained as the only product from $[\{Pd(L)Cl\}_2]$ [HL = $NC_5H_4(CH_2Ph)$-2] and CO under comparable conditions,[6] is likely to be the first product of the reaction. Its oxidative chlorination, brought about by gold(III) chloride, can easily explain the formation of compound **I**. Indeed, in a separate experiment **II** was converted into **I** upon treatment with $AuCl_3$. The C–C coupling, involved in the formation of compound **III**, may arise from the activation of a C–Cl bond. It is worth noting that both chlorination and C–C coupling of the ligand have previously been observed in the reaction of $Na[AuCl_4]$ with 2-(2-thienyl)pyridine.[15] When the benzylic carbon atom bears a substituent, as in complex **2m**, one only product, 11-methylbenzo[*b*]quinolizin-6-one **IV** is obtained, as in the case of the palladium analogue.[5d]

The formation of the species **I**–**IV** implies insertion of CO into the metal–carbon bond, followed by nucleophilic intramolecular attack of the nitrogen atom on an acyl intermediate. Consistent with the existence of this intermediate, in the case of **3m** the expected ester **V** is obtained. As far as we know, insertion of CO into gold(III)–carbon bonds is unprecedented. The analogies observed in the behaviour of

Table 4 Proton NMR data[a]

Compound	Solvent		H(6)	Other aromatics	CH	CH_2	CH_3	Other
NC_5H_4-(CH_2Ph)-2	$CDCl_3$		8.55 (d)	7.6–7.05		4.16 (s)		
1a	$CDCl_3$		8.69 (d)	8.0–7.25		4.73 (s)		
1m	CD_2Cl_2		9.27 (d)	8.1–7.1		H(A) 4.56 (d); H(B) 4.08 (d) [*J*(AB) = 15]		
1p	$CDCl_3$		8.95 (d)	8.0–6.4		4.37 (br s)		
	CD_2Cl_2		9.10 (d)	8.1–6.5		H(A) 4.58 (d); H(B) 4.29 (d) [*J*(AB) = 15]		
1d	$CDCl_3$		8.15 (d)	7.9–6.75		3.94 (s)		3.45 (m), 2.95 (m) CH_2 of dppe
1d″	CD_2Cl_2		8.33 (d)	8.25–7.3		4.36 (s)		3.38 (m), 2.87 (m) CH_2 of dppe
1d′[b]	CD_2Cl_2		8.70 (d)	8.3–6.8		4.10 (br)		2.2 (br m, 1 H), 3.4–4.5 (br m, 3 H) CH_2 of dppe
NC_5H_4-(CHMePh)-2	$CDCl_3$		8.58 (d)	7.6–7.0	4.28 (q, 7.0)		1.70 (d, 7.0)	
	Me_2SO		8.48 (d)	7.7–7.1	4.24 (q, 7.0)		1.58 (d, 7.0)	
2a	$CDCl_3$		8.66 (d)	8.0–7.3	5.30 (q, 7.2)		1.86 (d, 7.2)	
2m[c]	$CDCl_3$	*a* [2]	9.40 (d)	8.1–7.1	4.43 (q, 7.2)		2.16 (d, 7.2)	
		b [1]	9.30 (d)		4.68 (q, 7.2)		1.94 (d, 7.2)	
	Me_2SO	*a* [3]	9.21 (d)	8.3–7.0	4.84 (q, 7.5)		1.98 (d, 7.5)	
		b [1]	9.16 (d)		4.73 (q, 7.0)		1.86 (d, 7.0)	
2p[c]	$CDCl_3$	*a* [2]	9.15 (t)[d]	8.0–6.4	4.80 (q, 7.4)		2.14 (d, 7.4)	
		b [1]	9.11 (t)[d]		4.67 (q, 6.9)		1.99 (d, 6.9)	
2d	CD_2Cl_2		8.18 (d)	7.9–6.9	4.04 (q, 6.9)		1.21 (d, 6.9)	3.60 (m), 2.86 (m) CH_2 of dppe
2d′	CD_2Cl_2		8.68 (d)	8.3–6.8	1.11 (d, 7.2)		4.46 (q, 7.2)	2.57 (m, 1 H), 4.2–3.7 (m, 3H) CH_2 of dppe
NC_5H_4-(CMe_2Ph)-2	$CDCl_3$		8.57 (d)	7.6–7.1			1.75 (s)	
3s	$(CD_3)_2CO$		8.94 (d)	8.9–7.3			1.99 (s)	
3m	CD_2Cl_2		9.39 (d)	8.1–7.0			2.35 (s), 2.06 (s)	
3p	$CDCl_3$		9.32 (t)[d]	8.15–6.45			2.36 (s), 2.11 (s)	
NC_5H_4-(CMe_3)-2	$CDCl_3$		8.55 (d)	7.6–7.05			1.36 (s)	
4s	$CDCl_3$		8.86 (d)	8.7–8.1			1.62 (s)	
	$(CD_3)_2CO$		8.96 (d)	8.8–8.1			1.63 (s)	
NC_5H_4-(CH_2CMe_3)-2	$CDCl_3$		8.53 (d)	7.6–7.1		2.68 (s)	0.94 (s)	
5s	$CDCl_3$		8.93 (br m)	8.5–7.8		3.10 (s)	1.08 (s)	

[a] Spectra recorded at room temperature, chemical shifts in ppm from internal $SiMe_4$, coupling constants in Hz. [b] At −40 °C, CH_2 (pyridine) AB system, δ 3.91 (d, 1 H) and 4.04 (d, 1 H), *J*(AB) = 17.0 Hz; CH_2 (dppe), δ 2.11 (m, 1 H), 3.39 (m, 1 H), 4.05 (m, 1 H) and 4.47 (m, 1 H). [c] Compounds **2m** and **2p** are present in solution as diastereomers, *a* and *b* (see text), integral ratios are in square brackets. [d] Due to coupling with phosphorus.

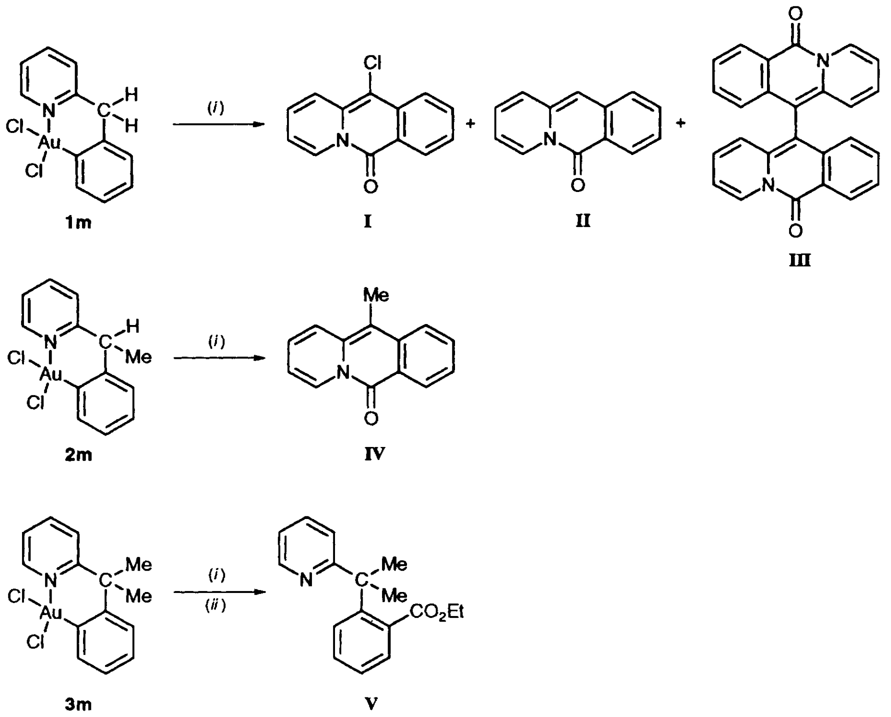
palladium(II) and gold(III) cyclometallated derivatives suggests the potential reactivity of the latter species, which is still largely unexplored.

Experimental

General.—The pyridines HL were prepared according to literature methods;[7] $AuCl_3 \cdot 2H_2O$ and $Na[AuCl_4] \cdot 2H_2O$ were obtained from Aldrich and Johnson Matthey respectively. Elemental analyses were performed with a Perkin-Elmer Elemental Analyser 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-{^1H} and ^{31}P-{^1H} NMR spectra with a Varian VXR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz, respectively. The ^1H and ^{13}C-{^1H} NMR data are collected in Tables 4 and 5; 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, with 3-nitrobenzyl alcohol as supporting matrix, or electron-impact (EI) conditions.

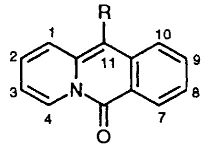
Preparations.—[Au{$NC_5H_4(CH_2Ph)$-2}Cl_3] **1a**. An aqueous solution (20 cm^3) of $AuCl_3 \cdot 2H_2O$ (1.55 mmol) was added to pure $NC_5H_4(CH_2Ph)$-2 (0.262 g, 1.55 mmol): the resulting yellow suspension was stirred for 3 d at room temperature. The solid product was filtered off and air dried to give complex **1a** (0.540 g, 74%). Recrystallization from acetone–diethyl ether yielded an orange crystalline product: m.p. 149–150 °C [Found: C, 30.8; H, 2.3; N, 2.9%; M^+ 471 (EI). $C_{12}H_{11}AuCl_3N$ requires C, 30.5; H, 2.3; N, 2.9%; *M* 471]; $\tilde{\nu}_{max}/cm^{-1}$ 1601s, 1563m, 1485s, 1477s, 1441vs, 1160m, 1105m, 766vs, 740vs, 731vs, 695s, 474s, 458s and (Au–Cl) 362vs; *m/z* 471 (M^+) and 435 (*M* − HCl) (EI).

[Au{$NC_5H_4(CH_2C_6H_4)$-2}Cl_2] **1m**. *Method* (*a*). A suspension of complex **1a** (0.471 g, 1 mmol) in MeCN (5 cm^3) and water (20 cm^3) was refluxed until the precipitate became white (*ca.* 8 h). The solid product was filtered off and air dried to give **1m** (0.400 g, 92%). Recrystallization from dichloromethane–diethyl ether yielded the analytical sample: m.p. 244–245 °C [Found: C, 33.2; H, 2.3; N, 3.1%; M^+ 435 (EI). $C_{12}H_{10}AuCl_2N$ requires C, 33.0; H, 2.3, N, 3.2%; *M* 435]; $\tilde{\nu}_{max}/cm^{-1}$ 1607m, 1563m, 1479s, 1025s, 779m, 751vs, (Au–Cl) 358vs and 294vs.



Scheme 3 (*i*) 50 atm CO, 60 °C, CH_2Cl_2–EtOH; (*ii*) K_2CO_3, CH_2Cl_2

Table 5 Proton and $^{13}C\text{-}\{^1H\}$ NMR data for compounds I–IV[a]



Compound	I[b] (R = Cl)	II[b] (R = H)	III[c]	IV[c,d] (R = Me)
H^1	7.88 (m)	7.19 (d)	6.89 (d)	7.57 (d)
H^2	7.16 (dd)	6.90 (dd)	6.89 (d)	6.99 (dd)
H^3	6.70 (dd)	6.56 (dd)	6.73 (m)	6.60 (dd)
H^4	8.89 (d)	8.77 (d)	9.02 (d)	8.89 (d)
H^7	8.66 (d)	8.57 (d)	8.73 (m)	8.69 (d)
H^8	7.58 (dd)	7.45 (dd)	7.53 (m)	7.53 (dd)
H^9	7.86 (m)	7.67 (dd)	7.56 (m)	7.79 (dd)
H^{10}	8.15 (d)	7.60 (d)	7.15 (m)	7.91 (d)
CH_3				2.57 (s)
H^{11}		6.76 (s)		
C^1			123.8	122.3
C^2			127.8	125.5
C^3			112.4	111.2
C^4			127.1	126.6
C^7			128.8	128.5
C^8			125.7	124.8
C^9			133.1	132.1
C^{10}			124.5	122.7
C^{11}		101.0		
CH_3				12.1

[a] Room temperature, $CDCl_3$, chemical shifts in ppm from internal $SiMe_4$. [b] ^{13}C NMR, aromatics: I, δ 111.9, 122.3, 123.0, 125.8, 126.7, 128.0, 128.5 and 133.2; II, δ 111.9, 125.1, 125.6, 125.6, 125.9, 126.1, 128.2 and 132.3. [c] Assignments based on correlation (COSY) and heteronuclear correlation (HETCOR) experiments. [d] Data taken from ref. 5(*d*).

Method (*b*). An aqueous solution (20 cm^3) of $AuCl_3·2H_2O$ (1 mmol) was added to pure $NC_5H_4(CH_2Ph)\text{-}2$ (0.169 g, 1 mmol): the resulting yellow suspension was refluxed until the precipitate became white (*ca.* 8 h). The solid product was filtered off and air dried to give complex **1m** (0.350 g, 80%).

$[Au\{NC_5H_4(CHMePh)\text{-}2\}Cl_3]$ **2a**. An aqueous solution (20 cm^3) of $AuCl_3·2H_2O$ (1.55 mmol) was added to pure $NC_5H_4(CHMePh)\text{-}2$ (0.283 g, 1.55 mmol): the resulting yellow suspension was stirred for 3 d at room temperature. The solid product was filtered off and air dried to give complex **2a** (0.564

g, 75%). Recrystallization from acetone–diethyl ether yielded an orange crystalline product: m.p. 169–170 °C [Found: C, 32.3; H, 2.7; N, 2.8%; M^+ 485 (EI). $C_{13}H_{13}AuCl_3N$ requires C, 32.1; H, 2.7; N, 2.9%; M 485]; $\tilde{\nu}_{max}$/cm^{-1} 1605vs, 1565m, 1482vs, 1432vs, 1161vs, 1124m, 1053m, 792m, 760vs, 700vs, 585s, 545vs and (Au–Cl) 359vs; m/z 485 (M^+) and 449 (M − HCl).

$[Au\{NC_5H_4(CHMeC_6H_4)\text{-}2\}Cl_2]$ **2m**. A suspension of complex **2a** (0.200 g, 0.41 mmol) in MeCN (3 cm^3) and water (15 cm^3) was refluxed until the precipitate became white (*ca.* 7 h). The solid product was filtered off and air dried to give the analytical sample (0.165 g, 90%), m.p. 277–278 °C [Found: C, 34.9; H, 2.7; N, 3.0%; M^+ 449 (EI). $C_{13}H_{12}AuCl_2N$ requires C, 34.7; H, 2.7; N, 3.1%; M 449]; $\tilde{\nu}_{max}$/cm^{-1} 1603vs, 1557m, 1477s, 1449vs, 1164w, 1025s, 797s, 764vs, 756vs and (Au–Cl) 352vs and 294vs.

$[HNC_5H_4(CMe_2Ph)\text{-}2][AuCl_4]$ **3s**. *Method* (*a*). An aqueous solution (40 cm^3) of $AuCl_3{\cdot}2H_2O$ (2 mmol) was added to pure $NC_5H_4(CMe_2Ph)\text{-}2$ (0.394 g, 2 mmol): the resulting yellow suspension was stirred for 3 d at room temperature. The solid product was filtered off and air dried to give complex **3s** (0.628 g, 58%). Recrystallization from acetone–diethyl ether yielded an orange crystalline product: m.p. 134–135 °C [Found: C, 32.0; H, 3.0; N, 2.6%; M^+ 198 (FAB). $C_{14}H_{16}AuCl_4N$ requires C, 31.3; H, 3.0; N, 2.6%; M (H_2L^+) 198]; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3242vs, 3176vs, 3131vs, 1609vs, 1536s, 1494m, 1240m, 771vs, 759vs, 741s, 701vs, 566m, 541m and (Au–Cl) 357vs.

Method (*b*). To a chloroform solution (10 cm^3) of anhydrous $AuCl_3$ (0.080 g, 0.26 mmol) was added a chloroform solution (10 cm^3) of $NC_5H_4(CMe_2Ph)\text{-}2$: the resulting orange-yellow solution was stirred for 1 h at room temperature and then concentrated to small volume. Addition of diethyl ether gave complex **3s** (0.102 g, 73%).

Method (*c*). To a solution of $NC_5H_4(CMe_2Ph)\text{-}2$ (0.078 g, 0.39 mmol) in ethanol (5 cm^3) was added a solution of $Na[AuCl_4]{\cdot}2H_2O$ (0.156 g, 0.39 mmol) in the same solvent (15 cm^3): the resulting solution was stirred for 12 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 complex **3s** (0.130 g, 62%).

$[Au\{NC_5H_4(CMe_2C_6H_4)\text{-}2\}Cl_2]$ **3m**. A suspension of complex **3s** (0.462 g, 0.86 mmol) in MeCN (5 cm^3) and water (25 cm^3) was refluxed until the precipitate became white (*ca.* 8 h). The solid product was filtered off and air dried to give complex **3m** (0.334 g, 84%). Recrystallization from dichloromethane–diethyl ether yielded the analytical sample: m.p. 283–284 °C [Found: C, 35.7; H, 3.0; N, 3.1%; M^+ 463 (FAB). $C_{14}H_{14}AuCl_2N$ requires C, 36.2; H, 3.0; N, 3.0%; M 463]; $\tilde{\nu}_{max}$/cm^{-1} 1601s, 1579m, 1557m, 1479s, 1390m, 1368s, 1025vs, 771vs, 757s, 745vs, 720s, 569s and (Au–Cl) 353vs and 294vs.

$[HNC_5H_4(CMe_3)\text{-}2][AuCl_4]$ **4s**. An aqueous solution (20 cm^3) of $AuCl_3{\cdot}2H_2O$ (1.87 mmol) was added to pure $NC_5H_4(CMe_3)\text{-}2$ (0.253 g, 1.87 mmol): the resulting yellow suspension was stirred for 3 d at room temperature. The solid product was filtered off and air dried to give complex **4s** (0.563 g, 63%). Recrystallization from dichloromethane–diethyl ether yielded a bright yellow crystalline product: m.p. 201–202 °C [Found: C, 22.6; H, 2.9; N, 2.9%; M^+ 136 (FAB). $C_9H_{14}AuCl_4N$ requires C, 22.7; H, 2.9; N, 2.9%; M (H_2L^+) 136]; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 168 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3268vs, 3195vs, 1624s, 1610vs, 1532s, 1276s, 1243m, 1097m, 766vs, 739s, 541vs and (Au–Cl) 358vs.

The same product was obtained from $Na[AuCl_4]$ and $NC_5H_4(CMe_3)\text{-}2$ in aqueous or in ethanolic solution, at room temperature or at reflux.

$[HNC_5H_4(CH_2CMe_3)\text{-}2][AuCl_4]$ **5s**. An aqueous solution (20 cm^3) of $AuCl_3{\cdot}2H_2O$ (1.68 mmol) was added to pure $NC_5H_4(CH_2CMe_3)\text{-}2$ (0.251 g, 1.68 mmol): the resulting yellow suspension was stirred for 3 d at room temperature. The solid was filtered off and air dried to give a first crop of an orange-yellow product; a second crop was obtained by evaporation of the mother-liquor. The two crops were combined and crystallized from acetone–diethyl ether to give the analytical sample (0.370 g, 45%): m.p. 124–125 °C [Found: C, 24.0; H, 3.1; N, 2.9%; M^+ 150 (FAB). $C_{10}H_{16}AuCl_4N$ requires C, 24.5; H, 3.3; N, 2.9%; M (H_2L^+) 150]; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3245s, 3222s, 3173s, 3123s, 1625m, 1607s, 1529m, 1227w, 1169w, 782m, 755s and (Au–Cl) 359vs.

Reactions of the Cyclometallated Derivatives **1m–3m**.—*With* PPh_3. *General procedure.* To a suspension of $[AuLCl_2]$ (1 mmol) in acetone (20 cm^3) was added solid PPh_3 (1 or 2 mmol) and $NaBF_4$ (excess). After a few minutes a solution was obtained; this was stirred for 1–4 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 solid of $[AuL(PPh_3)Cl][BF_4]$ **1p–3p**, yield 80–90%. Recrystallization from dichloromethane–diethyl ether gave the analytical sample.

$[Au\{NC_5H_4(CH_2C_6H_4)\text{-}2\}(PPh_3)Cl][BF_4]$ **1p**: m.p. 142 °C (decomp.) {Found: C, 48.4; H, 3.7; N, 1.7%; M^+ 662 (FAB). $C_{30}H_{25}AuBClF_4NP$ requires C, 48.1; H, 3.3; N, 1.9%; M [$AuL(PPh_3)Cl^+$] 662}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1608m, 1558w, 1480s, 1059vs (br), 534vs, 515vs, 501vs and (Au–Cl) 305s; $\delta_P(CD_2Cl_2)$ 33.9.

$[Au\{NC_5H_4(CHMeC_6H_4)\text{-}2\}(PPh_3)Cl][BF_4]$ **2p**: m.p. 205–207 °C {Found: C, 48.9; H, 3.3; N, 1.9%; M^+ 676 (FAB). $C_{31}H_{28}AuBClF_4NP$ requires C, 48.7; H, 3.7; N, 1.8%; M [$AuL(PPh_3)Cl^+$] 676}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 164 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1610m, 1585w, 1565w, 1490s, 1055vs (br), 782w, 770m, 746vs, 721vs, 712s, 698s, 688s, 555s, 536vs, 513vs, 499vs and (Au–Cl) 313vs; $\delta_P(CDCl_3)$ 33.6 (s, P_a) and 32.8 (s, P_b) (a : b = 2 : 1).

$[Au\{NC_5H_4(CMe_2C_6H_4)\text{-}2\}(PPh_3)Cl][BF_4]$ **3p**: m.p. 184–185 °C {Found: C, 49.3; H, 3.7; N, 1.7%; M^+ 690 (FAB). $C_{32}H_{29}AuBClF_4NP$ requires C, 49.4; H, 3.7; N, 1.8%; M [$AuL(PPh_3)Cl^+$] 690}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1601s, 1570w, 1554w, 1480vs, 1051vs (br), 782s, 748vs, 731s, 719s, 691vs, 571m, 533vs, 510vs and (Au–Cl) 316s; $\delta_P(CDCl_3)$ 33.2.

With $Ph_2PCH_2CH_2PPh_2$ (dppe). *General procedure.* To a suspension of $[AuLCl_2]$ (0.5 mmol) in acetone (20 cm^3) was added solid dppe (0.5 mmol) and $NaBF_4$ (excess). After a few minutes a solution was obtained; this was stirred for 6 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 solid of $[AuL(dppe)Cl][BF_4]$ **1d** and **2d**.

$[Au\{NC_5H_4(CH_2C_6H_4)\text{-}2\}(dppe)Cl][BF_4]$ **1d**: yield 87%, m.p. 82–84 °C {Found: C, 51.4; H, 4.0; N, 1.7%; M^+ 798 (FAB). $C_{38}H_{34}AuBClF_4NP_2$ requires C, 51.5; H, 3.8; N, 1.6%; M [$AuL(dppe)Cl^+$] 798}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 164 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1587s, 1564w, 1103vs, 1057vs (br), 996vs, 734vs, 691vs, 529vs and (Au–Cl) 327w; $\delta_P(CDCl_3)$ 37.1 [1 P, d, *J*(PP) 54, P(A)] and 26.3 [1 P, d, *J*(PP) 54 Hz, P(X)].

$[Au\{NC_5H_4(CHMeC_6H_4)\text{-}2\}(dppe)Cl][BF_4]$ **2d**: yield 89%, m.p. 100–102 °C {Found: C, 52.2; H, 3.9; N, 1.6%; M^+ 812 (FAB). $C_{39}H_{36}AuBClF_4NP_2$ requires C, 52.6; H, 4.0; N, 1.6%; M [$AuL(dppe)Cl^+$] 812}; Λ_M(5×10^{-4} mol dm^{-3}, acetone) 160 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1585m, 1566w, 1104vs, 1058vs (br), 996s, 730vs, 692s, 530vs (br) and (Au–Cl) 328m; $\delta_P(CD_2Cl_2)$ 35.4 [1 P, d, *J*(PP) 57, P(A)] and 25.4 [1 P, d, *J*(PP) 57 Hz, P(X)].

Reactions of Complex **1d**.—*With* $HBF_4{\cdot}Et_2O$. To a solution of complex **1d** (0.075 g, 0.085 mmol) in dichloromethane (15 cm^3) was added $HBF_4{\cdot}Et_2O$ (5×10^{-2} cm^3, *ca.* 0.36 mmol) with stirring: the solution became slightly opalescent. It was stirred for 1 h at room temperature and then filtered and concentrated to small volume: addition of diethyl ether gave the white solid

[Au{$HNC_5H_4(CH_2C_6H_4)$-2}(dppe)Cl][BF_4]$_2$ **1d″** (0.070 g, 85%): m.p. 126–128 °C {Found: C, 46.0; H, 3.6; N, 1.4%; M^+ 797 (FAB). $C_{38}H_{35}AuB_2ClF_8NP_2$ requires C, 46.9; H, 3.6; N, 1.4%; M [Au(HL)(dppe)Cl^{2+}] 799}; Λ_M(5 × 10^{-4} mol dm^{-3}, acetone) 210 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3500vs (br), 1620s, 1585m, 1545m, 1060vs (br), 740vs, 700vs and (Au–Cl) 325w; δ_P(CD_2Cl_2) 35.0 [1 P, d, J(PP) 55, P(A)] and 24.3 [1 P, d, J(PP) 55 Hz, P(X)].

With $AgBF_4$. To a solution of complex **1d** (0.133 g, 0.15 mmol) in acetone (15 cm^3) was added a solution of $AgBF_4$ (0.030 g, 0.15 mmol) in acetone (10 cm^3), with stirring. Silver chloride was filtered off and the solution evaporated to dryness; the residue was taken up with dichloromethane, filtered and concentrated to small volume. Addition of diethyl ether gave a pale yellow product [Au{$NC_5H_4(CH_2C_6H_4)$-2}(dppe)][BF_4]$_2$ **1d′** (0.120 g, 85%): m.p. 175 °C (decomp.) {Found: C, 48.4; H, 3.7; N, 1.5%; M^+ 763 (FAB). $C_{38}H_{34}AuB_2F_8NP_2$ requires C, 48.7; H, 3.6; N, 1.5%; M [AuL(dppe)$^{2+}$] 763}; Λ_M(5 × 10^{-4} mol dm^{-3}, acetone) 210 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1609s, 1586m, 1568m, 1059vs (br), 996vs, 845m, 817m, 732vs and 692vs; δ_P(CD_2Cl_2): 36.6 [1 P, d, J(PP) 24, P(A)] and 26.7 [1 P, d, J(PP) 24 Hz, P(X)]; m/z 763 (M^+) and 850 ([M + BF_4]$^+$) (EI).

Reaction of [Au{$NC_5H_4(CHMeC_6H_4)$-2}(dppe)Cl][BF_4] **2d** *with* $AgBF_4$.—To a solution of complex **2d** (0.092 g, 0.102 mmol) in acetone (15 cm^3) was added a solution of $AgBF_4$ (0.020 g, 0.102 mmol) in acetone (10 cm^3), with stirring. Silver chloride was filtered off and the solution evaporated to dryness; the residue was taken up with dichloromethane, filtered and concentrated to small volume. Addition of diethyl ether gave a white product [Au{$NC_5H_4(CHMeC_6H_4)$-2}(dppe)][BF_4]$_2$ **2d′** (0.076 g, 78%): m.p. 190 °C (decomp.) {Found: C, 48.8; H, 3.8; N, 1.5%; M^+ 777 (FAB). $C_{39}H_{36}AuB_2F_8NP_2$ requires C, 49.2; H, 3.8; N, 1.5%; M [AuL(dppe)$^{2+}$] 777}; Λ_M(5 × 10^{-4} mol dm^{-3}, acetone) 210 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1606s, 1585m, 1568m, 1052vs (br), 823w, 729vs and 692vs; δ_P(CD_2Cl_2) 32.9 [1 P, d, J(PP) 12, P(A)] and 23.7 [1 P, d, J(PP) 12 Hz, P(X)]; m/z 777 (M$^+$) and 865 ([M + BF_4]$^+$) (FAB).

Reactions with Carbon Monoxide.—General procedure. A Pyrex bottle containing a suspension of [$AuLCl_2$] **1m–3m**, equipped with a magnetic stirrer bar, was placed in a stainless-steel autoclave. After removal of the air, the vessel was pressurized with CO (50 atm), heated at 60 °C and stirred for several hours. At the end of the reaction the CO was released and the mixture was worked up.

[Au{$NC_5H_4(CH_2C_6H_4)$-2}Cl_2] **1m** *in* CH_2Cl_2–EtOH. A suspension of complex **1m** (0.150 g, 0.345 mmol) in CH_2Cl_2–EtOH (4 : 1, 25 cm^3) was subjected to the general procedure described above for 24 h, after which the mixture consisted of a bright yellow solution and metallic gold. The solution was filtered and evaporated to dryness (0.067 g). The organic product was a mixture (TLC) from which three pure compounds were isolated by chromatography on a column (58 × 2 cm) of silica gel (Merck, 70–230 mesh ASTM), using dichloromethane (**I** and **II**) and acetone (**III**) as eluents. First band eluted (R_f 0.28 on silica gel plates): **I** (0.010 g, 0.042 mmol, 12%) [Found: M^+ 229 (FAB). $C_{13}H_8ClNO$ requires M 229]; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1675vs and 1630s, 1605s, 1563s, 1544w and 1522s; m/z 229 (100, M^+), 201 (M – CO), 166 (M – CO – Cl) and 139 (M – CO – Cl – HCN) (EI). Second band eluted (R_f 0.17): **II** (0.003 g, 0.015 mmol, 4.4%) [Found: M^+ 195 (FAB). $C_{13}H_9NO$ requires M 195]; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1665vs and 1628vs, 1610s, 1589w, 1569m and 1524m; m/z 195 (100, M^+) and 167 (M – CO) (EI). Third band eluted (R_f 0.09): **III** (0.054 g, 0.14 mmol, 81%), m.p. 130 °C (decomp.) [Found: M^+ 388 (FAB). $C_{26}H_{14}N_2O_2$ requires M 388]; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1652vs and 1628vs, 1603s, 1565m and 1520s; m/z 388 (100, M^+), 359 (M – HCO) and 195 ($\frac{1}{2}$ M + H) (EI).

[Au{$NC_5H_4(CHMeC_6H_4)$-2}Cl_2] **2m** *in* CH_2Cl_2–EtOH. A suspension of complex **2m** (0.112 g, 0.25 mmol) in CH_2Cl_2–EtOH (4 : 1, 25 cm^3) was subjected to the general procedure for 24 h, after which the mixture consisted of an intense yellow solution and metallic gold. The solution was filtered and evaporated to dryness, the residue was taken up with diethyl ether, filtered and evaporated to dryness to yield the analytical sample **IV** (0.0454 g, 87%), m.p. 198–200 °C [Found: M^+ 209 (EI). Calc. for $C_{14}H_{11}NO$: M 209]; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1652vs and 1632vs, 1606s, 1568s, 1548w and 1524s (CH_2Cl_2).

[Au{$NC_5H_4(CMe_2C_6H_4)$-2}Cl_2] **3m** *in* CH_2Cl_2–EtOH. A suspension of complex **3m** (0.180 g, 0.388 mmol) in CH_2Cl_2–EtOH (4 : 1, 25 cm^3) was subjected to the general procedure for 20 h, after which the mixture consisted of a pale yellow solution and metallic gold. The solution was filtered and evaporated to dryness, the residue was taken up with ethanol and filtered to separate a small amount of the starting material; the solution was evaporated to dryness, taken up with dichloromethane and neutralized with K_2CO_3. After filtration, the solution was evaporated to dryness to yield the analytical sample **V** (0.078 g, 74%) [Found: M + H$^+$ 270 (FAB). $C_{17}H_{19}NO_2$ requires M 269]; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1719s and 1658w, 1585m and 1563m (CH_2Cl_2); δ_H($CDCl_3$) 8.52 [1 H, ddd, J(H^3,H^6) 1.0, J(H^4,H^6) 2.0 and J(H^5,H^6) 4.8, H^6], 7.67 [1 H, dd, J($H^{4'}$,$H^{6'}$) 1.3 and J($H^{5'}$,$H^{6'}$) 8.0, $H^{6'}$], 7.55 [1 H, ddd, J(H^3,H^4) 8.1, J(H^4,H^5) 7.5 and J(H^4,H^6) 2.0, H^4], 7.47 [1 H, ddd, J($H^{3'}$,$H^{5'}$) 1.7, J($H^{4'}$,$H^{5'}$) 7.6 and J($H^{5'}$,$H^{6'}$) 8.0, $H^{5'}$], 7.42 [1 H, dd, J($H^{3'}$,$H^{4'}$) and J($H^{3'}$,$H^{5'}$) 1.7, $H^{3'}$], 7.27 [1 H, td, J($H^{3'}$,$H^{4'}$) 7.6, J($H^{4'}$,$H^{5'}$) 7.6 and J($H^{4'}$,$H^{6'}$) 1.3, $H^{4'}$], 7.13 [1 H, dt, J(H^3,H^4) 8.1, J(H^3,H^5) 1.0 and J(H^3,H^6) 1.0, H^3], 7.07 [1 H, ddd, J(H^4,H^5) 7.5, J(H^3,H^5) 1.0 and J(H^5,H^6) 4.8, H^5], 3.72 [2 H, q, J(HH) 7.2, OCH_2], 1.80 (6 H, s, 2 CH_3) and 1.07 [3 H, t, J(HH) 7.2 Hz, OCH_2CH_3) (COSY); δ_C($CDCl_3$) 169.8 (1 C, C^2 or CO), 168.4 (1 C, C^2 or CO), 148.4 (1 C, C^6), 147.1 (1 C, $C^{1'}$), 135.8 (1 C, C^4), 133.1 (1 C, $C^{2'}$), 130.4 (1 C, $C^{5'}$), 129.5 (1 C, $C^{3'}$), 127.2 (1 C, $C^{6'}$), 126.0 (1 C, $C^{4'}$), 121.2 (1 C, C^3), 120.5 (1 C, C^5), 60.7 (1 C, OCH_2), 46.6 [1 C, $C(CH_3)_2$], 30.7 (2 C, 2 CH_3) and 13.8 (1 C, CH_2CH_3) (HETCOR); m/z 268 (M – H), 224 (M – OCH_2CH_3) and 196 (100, M – $CO_2CH_2CH_3$) (EI).

X-Ray Data Collection and Structure Determination.—Crystal data and other experimental details are summarized in Table 1. The diffraction experiment was 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 package[16] and the physical constants tabulated therein. Periodic monitoring of three standard reflections revealed a crystal decay of about 4.9% (on intensities) at the end of data collection. The diffracted intensities were corrected for Lorentz, polarization, decay and absorption effects (empirically).[17] Scattering factors and anomalous dispersion corrections were taken from ref. 18. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. All the hydrogen atoms were detected on the Fourier maps; those bonded to atom C(15) were included in the least-squares refinement, whereas the remainder 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). In the final least-square cycles an extinction parameter, g, was included [according to the formula $|F_c|$(corrected) = $|F_c|/(1 + gI_c)$], which refined to the value 1.14(4) × 10^{-6}. The final Fourier map showed a maximum residual of 1.4(2) e Å^{-3} at 0.90 Å from the gold atom. The final atomic coordinates are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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