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Gold(III) derivatives with C(4)-aurated 1-phenylpyrazole

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Abstract

The reaction of 1-phenylpyrazole (HL), with gold(III) chloride has been studied. Besides a 1:1 adduct $[Au(HL)Cl_3]$ **1**, where the ligand is bonded through the nitrogen atom, several C(4) aurated species have been isolated. Thus treatment of $[AuCl_3]_2$ with HL in dichloromethane solution affords a complex, $[Au(L)Cl_2HCl]_n$, **2**, where the gold atom is bonded to the 4-carbon atom of the pyrazole ligand. Deprotonation of complex **2** by means of the not coordinating base 1,8-bis(dimethylamino)naphthalene (proton sponge), B, affords the salt $[BH][Au(L)Cl_3]$, **3**, whereas reaction of **2** with 3,5-Me_2py and PPh_3 (molar ratio 1:2) gives the neutral species *trans*-$[Au(L)(3,5\text{-}Me_2py)Cl_2]$, **4**, and *cis*-$[Au(L)(PPh_3)Cl_2]$, **5**, respectively. The structure of compound **4** solved by X-ray diffraction, unambiguously shows the anionic ligand L bonded to the gold ion through the C4 atom. Alternatively, compounds **4** and **5** can be obtained in two steps, i.e. deprotonation of **2** with NaOH to give $[Au(L)Cl_2]_n$, **6**, and reaction of **6** with 3,5-Me_2py and PPh_3, respectively. The new species were characterized by elemental analyses, conductivity measurements, IR, NMR and FAB-MS spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gold(III); 1-Phenylpyrazole; Auration

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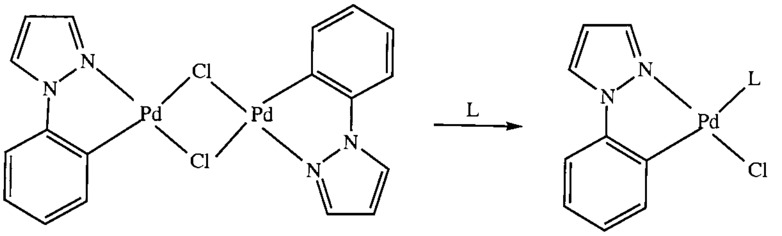
1. Introduction

Recently we have described gold(III) *ortho*-metallated derivatives arising from 2-benzyl pyridines [1] and 6-benzyl-2,2′-bipyridines [2] and observed some analogies in the behaviour of these ligands towards gold(III) and palladium(II). It was reported many years ago by Trofimenko that 1-phenylpyrazole reacts with palladium(II) to give *ortho*-metallated derivatives



(L = neutral ligand) [3]. At variance, at least as far as we know, the reactivity with gold(III) has not been studied. 1-Phenylpyrazole is known to undergo substiution at the C4 atom of the heterocyclic ring by electrophiles such as $HgCl_2$ and $Hg(OAc)_2$ [4] and we wondered whether gold(III) might give *ortho*-metallated derivatives or C(4) substituted species.

Here we report the synthesis of an adduct $[Au(HL)Cl_3]$, where the ligand is N-bonded, and several C(4) aurated derivatives, including an organometallic

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Table 1
Proton NMR data[a]

Compound	Solvent	H(3)+H(5)	H(4)	Phenyl H(4′) H(3′) H(2′)	Other
HL[b]	$CDCl_3$	7.72, 7.87	6.46	7.2–7.6	
HL[c]	$(CD_3)_2CO$	7.70, 8.32	6.51	7.31, 7.50, 7.86	
$[Au(HL)Cl_3]$ **1**	$CDCl_3$	8.02, 8.03	6.89	7.60–7.71	
$[Au(L)Cl_2HCl]_n$ **2**	$(CD_3)_2CO$	8.55, 8.60[d]		7.68–7.96	
$K[Au(L)Cl_3]$ **3a**	$(CD_3)_2CO$	7.69, 8.08		7.25, 7.46, 7.81	
$[BH][Au(L)Cl_3]$ **3b**[e]	$CDCl_3$	7.84, 8.04		7.23, 7.41, 7.80	BH: 3.33 (d, 12H, $^3J_{HH}$ 2.7, 4Me), 7.96 [d, 2H, H(2) and H(7)], 7.68 [t, 2H, H(3) and H(6)], 7.67 (d, 2H, H(4) and H(5)], 19.03 (s, 1H, NH)
$[Au(L)(3,5\text{-}Me_2py)Cl_2]$ **4**[f]	$CDCl_3$	7.86, 8.05		7.27 7.44 7.71	3,5-Me_2py: 2.45 (s, 6H, 2Me), 7.63 [s (broad), 1H, H(4)], 8.56 [s, 2H, H(2) and H(6)]
$[Au(L)(PPh_3)Cl_2]$ **5a**	$CDCl_3$	7.07, 7.08		g	PPh_3: g
$\{Au(L)[P(4\text{-}MeC_6H_4)_3]Cl_2\}$ **5b**	$CDCl_3$	6.90, 7.18		h	$P(4\text{-}MeC_6H_4)_3$: 2.33 (s, 9H, 3Me), h
$[Au(L)Cl_2]_n$ **6**	$CDCl_3$	7.99, 8.02		7.26–7.63	

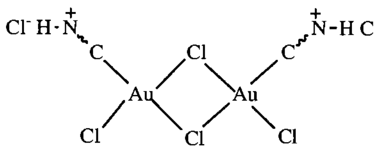
[a] Spectra recorded at room temperature, chemical shifts in ppm from internal $SiMe_4$.
[b] Data from Katritzky and Rees [6]; J_{3-4}, 1.9; J_{4-5}, 2.5; and J_{3-5}, 0.7 Hz.
[c] This work.
[d] J_{3-5} 0.7 Hz.
[e] B = 1,8-bis(dimethylamino)naphtalene
[f] Assignments based on NOE difference experiment.
[g] C_6H_5–N(1)+$P(C_6H_5)_3$ 7.06–7.64 [m, 22H].
[h] C_6H_5–N(1)+$P(4\text{-}MeC_6H_4)_3$ 7.21–7.49 [m, 19 H].

anion $[Au(L)Cl_3]^-$. No *ortho*-metallated species has been observed under various experimental conditions.

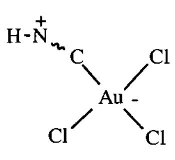
2. Results and discussion

Attempts to attain C,N cyclometallation of 1-phenylpyrazole (HL) from both $Na[AuCl_4]\cdot 2H_2O$ and $AuCl_3\cdot xH_2O$ failed, in spite of the different approaches which were tested. Likewise, unsuccessful were the attempts to promote cyclometallation on the adduct $[Au(HL)Cl_3]$, **1**, which can be isolated by reaction of $Na[AuCl_4]\cdot 2H_2O$ with HL in water at room temperature (yield ca. 75%). According to IR and conductivity data, compound **1** is likely to be a mononuclear neutral species, analogous to other adducts with nitrogen heterocycles previously reported [5]. Nevertheless a not negligible ionization occurs in acetone solution.

An unexpected result was obtained when anhydrous $AuCl_3$ (as obtained from $AuCl_3\cdot xH_2O$ and $SOCl_2$) was reacted with HL in dichloromethane. After prolonged stirring at room temperature (ca. 24 h) a cream solid was collected and recrystallized, compound **2**. The 'empirical' formula which best fits the analytical values (C,H,N,Cl; see Section 3) is $C_9H_8AuCl_3N_2$, i.e. an isomer of compound **1**. A striking evidence for the difference between **1** and **2**, is given by the ^{1}H-NMR spectrum (Table 1): in the spectrum of **2** the resonance assigned to H(4) of the pyrazole ring [6], at higher field with respect to H(3) and (5), is missing. Other significant differences between 1 and 2 are observed in the IR spectra: indeed, in complex **2**, four strong or very strong bands are observed in the range 365–270 cm^{-1}, where the stretching modes of the Au–Cl vibrations are usually observed. In addition, the spectrum of **2** exhibits a typical pattern in the range 3150–2760 cm^{-1} (Nujol mull) indicative of the presence of N–H bonds. Taken together, the ^{1}H-NMR and IR spectra suggest that electrophilic attack of gold at the 4-carbon atom and protonation of the nitrogen atom has occurred. Either dimeric (oligomeric), A, or monomeric, B, species can be considered.

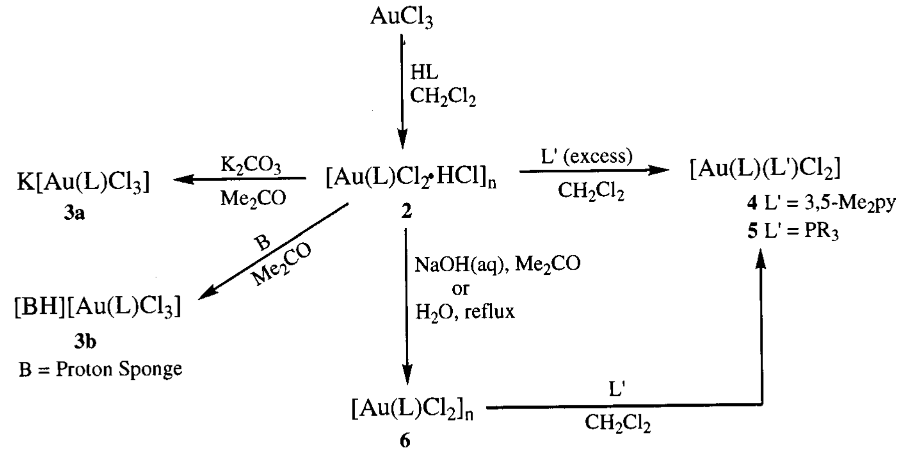


A



B

Although conductivity measurements, which show complex **2** to be partially dissociated, at least in acetone solution, point to A as the more probable species, the reactivity of compound **2** does not allow to rule out B completely. In the latter hypothesis the complex pattern exhibited in the ν(Au–Cl) region of the IR spectrum might be explained taking into account a lowering of symmetry due to intra- or intermolecular hydrogen bonds. In order to get an insight in the nature of

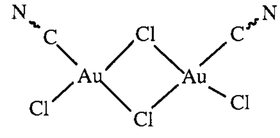


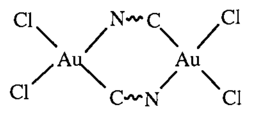
Scheme 1. Syntheses of the metallated species **2**–**6**.

compound **2**, the reactivity with different bases has been studied (Scheme 1).

Deprotonation of **2** was tried first with strong bases such as aqueous NaOH or KOH solutions. Compound **6** obtained in these conditions analyses for [Au(L)Cl_2]. At variance with **2**, the pattern associated with N–H stretching vibrations is absent in the IR spectrum of **6** confirming deprotonation. The ^{1}H-NMR spectrum gives evidence for a C(4) aurated ligand.

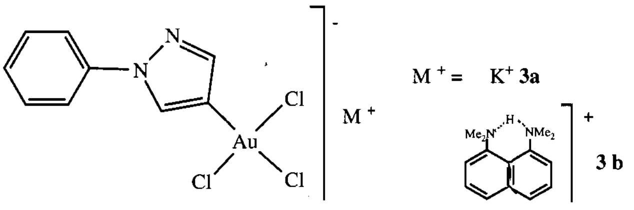
Dimers (or oligomers), with bridging chlorides or bridging C,N bonded pyrazoles can be envisaged.





Afterwards it was found that compound **6** can be obtained also in the absence of an added base, by refluxing an aqueous suspension of complex **2**. A quantitative determination of chlorine on a sample obtained in this way, identical with that obtained by reaction with NaOH, confirms that no substitution of hydroxide for chloride occurs.

In the presence of solid K_2CO_3 or of a not coordinating base such as 1,8-bis(dimethylamino)naphthalene (proton sponge) the deprotonation of **2** goes a different way to give salts of the complex anion **3**.



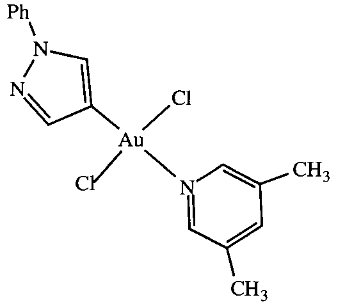
3

Complexes **3a** and **3b** are air and moisture stable, both in the solid state and in solution; they behave as 1:1 electrolytes in acetone solution. The FAB-MS spectra (negative ion) confirm the anionic nature of the gold complexes. In the IR spectra both **3a** and **3b** show two absorptions in the region 370–360 and 300–295 cm^{-1}, respectively, in agreement with a structure having chloride ions *trans* to ligands with different *trans*-influence. In the ^{1}H-NMR spectra of **3b** a signal at very low field, δ 19.03, is assignable to the NH resonance of the protonated proton sponge; the CH_3 signal is split into a doublet ($^3J_{HH} = 2.7$ Hz).

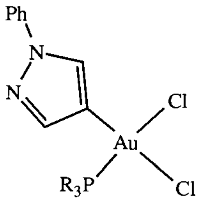
The reaction of compound **6** with two electron donors such as 3,5-Me_2py and PR_3 (R = C_6H_5, 4-MeC_6H_4) was found to give the neutral adducts **4** and **5** (**a**, R = C_6H_5; **b**, R = 4-MeC_6H_4), respectively. The same species **4** and **5** can be obtained from the protonated complex **2** provided an excess of ligand (molar ratio Au:L = 1:2) is used.

A *trans*- and *cis*- geometry is assigned to compounds **4** and **5**, respectively, on the basis of the IR spectra which show one (complex **4**) and two (complex **5**) Au–Cl bands in the region 370–300 cm^{-1}.

The *cis* arrangement in complex **5** is likely to be dictated by the need to avoid an arrangement with two ligands having high *trans*-influence, *trans* to each other.



4



5 a R = Ph
5 b R = 4-MeC_6H_4

The structure of complex **4** in the solid state has been solved by X-ray diffraction. It consists of the packing of

Table 2
Selected bond distances (Å) and angles (°) with estimated S.D.'s in parentheses for [Au(3,5-Me_2py)(L)Cl_2], compound 4

Au–Cl1	2.283(1)	Au–Cl2	2.278(1)
Au–N3	2.124(3)	Au–C4	2.006(4)
N1–N2	1.350(5)	N2–C3	1.344(7)
C3–C4	1.397(7)	C4–C5	1.345(6)
C5–N1	1.357(5)	N1–C6	1.432(5)
Cl1–Au–Cl2	178.9(1)	Cl1–Au–N3	89.7(1)
Cl1–Au–C4	89.4(1)	Cl2–Au–N3	91.0(1)
Cl2–Au–C4	89.9(1)	N3–Au–C4	178.7(1)
Au–C4–C3	123.8(3)	Au–C4–C5	131.3(3)
N2–N1–C5	111.5(3)	N1–N2–C3	104.0(4)
N2–C3–C4	111.6(4)	C3–C4–C5	104.9(4)
C4–C5–N1	108.0(4)	N2–N1–C6	118.7(3)
C5–N1–C6	129.7(4)		

trans-[Au(L)(3,5-Me_2py)Cl_2] molecules with no unusual van der Waals contacts. Principal bond lengths and angles are reported in Table 2. An ORTEP view of the molecule is shown in Fig. 1. The coordination around the gold atom is square planar, with a very slight pyramidal distortion: thus, atoms Cl(1), Cl(2), N(3) and C(4) are strictly coplanar, with the gold atom lying 0.016(1) Å above their best plane. The Au–Cl(1) and Au–Cl(2) bond lengths, 2.283(1) and 2.278(1) Å, respectively, are normal and can be compared with the average Au–Cl distance, 2.275 Å, found in [Au{$N_2C_{10}H_7$(CHMePh)-6}Cl_3] [2], and with the Au–Cl(1) distance, 2.282(1) Å, found in [Au{NC_5H_4($CMe_2C_6H_4$)-2}Cl_2] [1]. The Au–C(4) bond length, 2.006(4) Å, is also normal, and can be compared with the Au–C distance, 2.009(4) Å, found in cation [Au{$N_2C_{10}H_7$($CMe_2C_6H_4$)-6}Cl]$^+$ (**7**) [2]. The Au–N(3) bond length, 2.124(3) Å, is long but typical for an Au–N bond *trans* to an atom having high *trans*-influence: compare for instance Au–N(1), 2.121(5) Å, in cation **7**, where the Au–N(1) bond is *trans* to a phenyl carbon atom.

Bond lengths and angles within the pyrazole moiety compare well with the corresponding average values reported by F. Bonati in 1989 for a series of substituted pyrazoles [7]: the only large difference is in the C(4)–C(5) distance, 1.345(6) Å here, and 1.379 Å in Bonati's paper. (The values reported by Bonati are the averages of a large number of crystal structure determinations and estimated S.D. are not given). Bonati found out various trends in the internal and external angles of pyrazoles and pyrazole derivatives. In particular, he observed that in N(1)-substituted pyrazoles the N(2)–N(1)–R angle (119.1° in Bonati's paper, 118.7(3)° here) is always much smaller than the C(5)–N(1)–R one (129.0 and 129.7(4)°, respectively), and explained this trend with a higher amount of p character in the N(1) sp^2 hybrid orbital pointing towards the more electronegative N(2) atom with respect to the N(1) sp^2 orbital pointing towards C(5). He also found out that in C(4)-substituted pyrazoles the C(3)–C(4)–R and

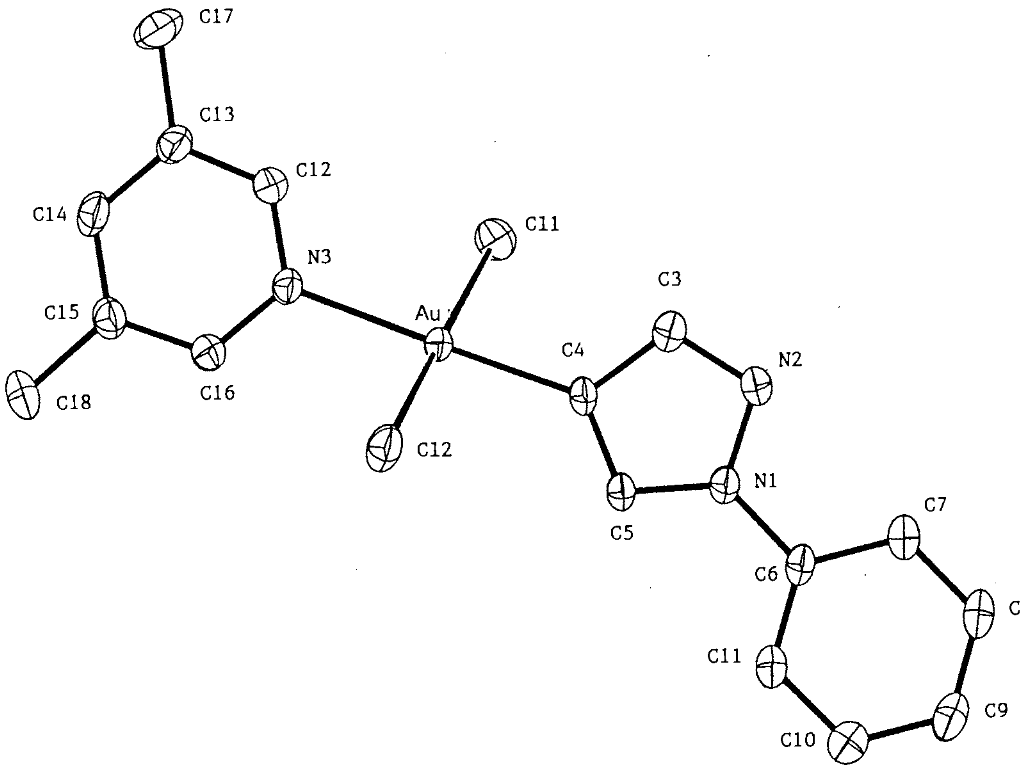


Fig. 1. A perspective view of compound **4**. Thermal ellipsoids are drawn at the 30% probability level.

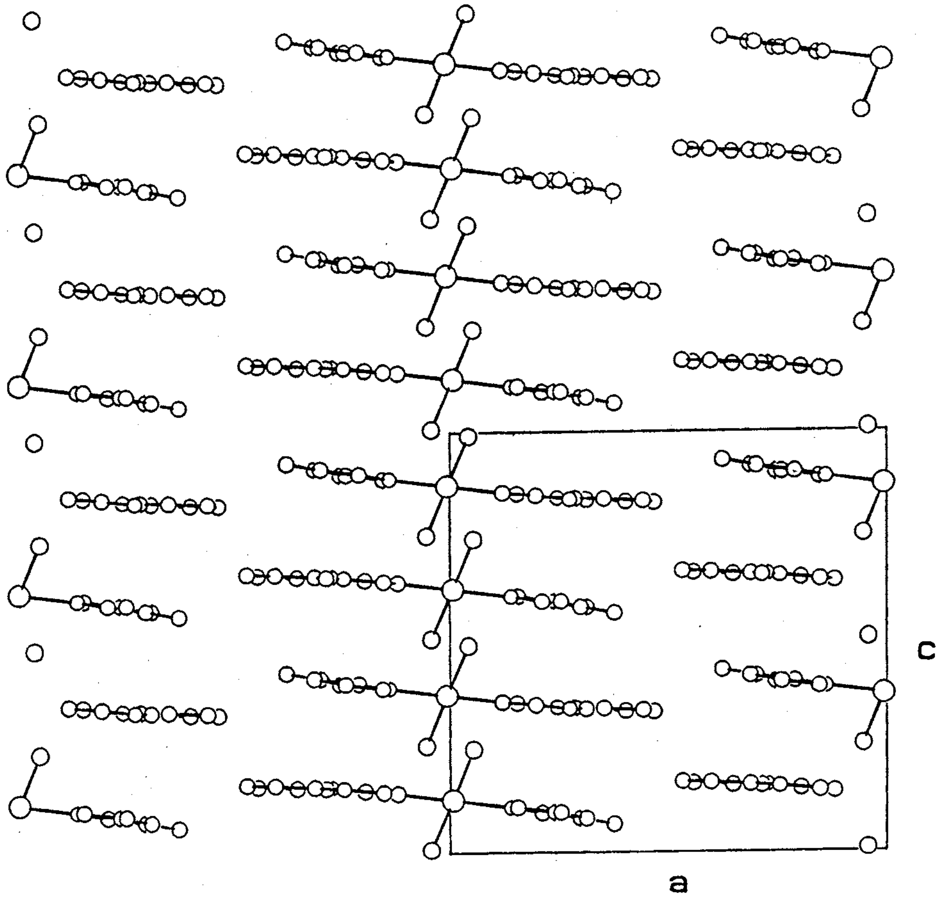


Fig. 2. A projection down the *b*-axis of the packing in compound **4**, showing the quasi-parallel stacking of phenylpirazole and 3,5-lutidine moieties.

C(5)–C(4)–R angles are usually very similar (126.9 and 127.2°, respectively). At variance, in the present C(4)-metallated phenylpyrazole the C(3)–C(4)–Au angle, 123.8(3)°, is much smaller than the C(5)–C(4)–Au one, 131.3(3)°, and in the absence of more evidence on other C(4)-metallated pyrazoles, we believe that it can be ascribed to packing forces. Actually, the crystal packing is dictated by the quasi-parallel stacking of alternating 3,5-lutidine (3,5-Me_2py) and phenylpyrazole moieties belonging to different molecules, as shown in Fig. 2. Because the stacking planes are not exactly parallel, we cannot refer to their distance. Instead, we report the shortest intermolecular contacts, which are C(12)···C(5′) 3.502(6) Å, and C(14)···C(6″) 3.473(6) Å, where primed and double primed atoms are obtained through the symmetry operations $-x$, $1/2+y$, $1/2-z$, and $-x$, $-y$, $-z$, respectively.

Within a single molecule, each of the three (hetero)aromatic rings is strictly planar, and the dihedral angles between their best planes are: pyrazole-phenyl 3.5(4)°, pyrazole-lutidine 3.3(5)°, phenyl-lutidine 6.2(3)°. The dihedral angles of the metal coordination best plane with the three (hetero)aromatic rings are 50.4(2), 50.6(1), and 52.9(1)° for pyrazole, phenyl, and lutidine, respectively.

3. Experimental

All reactions were carried out in the dark. The solvents were dried and distilled before use. ^1H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 (^1H), 121.4 (^{31}P) and 75.4 MHz (^{13}C), respectively. Chemical shifts are given in ppm relative to internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). IR spectra were recorded with Perkin Elmer spectrophotometers 983 and 1310 using Nujol mulls. Mass spectra were obtained with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol as supporting matrix. Conductivity measurements were obtained using a Philips PW 9505 conductimeter at 25°C. Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240 B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari) [C,H,N] and Mikroanalytisches Labor Pascher (Germany) [Cl].

3.1. Synthesis of compounds ***1–6***

3.1.1. [Au(HL)Cl$_3$] ***(1)***

To an aqueous solution of Na[AuCl$_4$]·2H$_2$O, (397.8 mg, 1.49 mmol) were added 0.20 cm^3 of HL (d = 1.091 g·cm^{-3}, 97%, 1.47 mmol), the resulting yellow-green suspension was stirred for 5 days at room temperature. The solid product was filtered off and then extracted with benzene. The filtered solution was concentrated under vacuum to give the analytical sample. Yield 75%, m.p. 225°C (dec.). Anal. found: C, 24.34; H, 2.01; N, 6.01%. Anal. calc. for C$_9$H$_8$AuCl$_3$N$_2$: C, 24.16; H, 1.80; N, 6.26%. Λ_m (5×10^{-4} M, acetone): 46 Ω^{-1} cm^2 mol^{-1}, (5×10^{-4} M, dichloromethane): 1.4 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1591 m, 693 s, 380 m, 366 s. FAB mass spectrum (*m*/*z*): 341 [(HL)Au$^+$].

3.1.2. [Au(L)Cl$_2$HCl]$_n$ (n = 2) ***(2)***

To a solution of [AuCl$_3$]$_2$ (352 mg, 0.58 mmol) in dichloromethane were added 0.16 cm^3 of HL (d = 1.091 g·cm^{-3}, 97%, 1.17 mmol), the resulting yellow solution was stirred for 24 h at room temperature. During this period a pale yellow precipitate was formed. It was filtered off and recrystallyzed from acetone/diethyl ether to give the analytical sample (380 mg) as a cream solid. Yield 73%, m.p. 198°C (dec.). Anal. found: C, 24.27; H, 1.93; N, 6.02; Cl, 23.3%. Anal. calc. for C$_{18}$H$_{16}$Au$_2$Cl$_6$N$_4$: C, 24.16; H, 1.80; N, 6.26; Cl, 23.77%. Λ_m (5×10^{-4} M, acetone): 85 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 3150 s, 3080 s, 3040 s, 2800 s, 2760 s, 1590 m, 1530 m, 690 s, 365 vs, 335 s, 300 vs, 270 s. FAB mass spectrum (*m*/*z*): 822 [*M*–2Cl], 375 [LAuCl], 341 [(HL)Au].

3.1.3. [Au(L)Cl$_3$]K ***(3a)***

To a solution of complex **2** (47 mg, 0.052 mmol) in acetone, solid K$_2$CO$_3$ was added. The mixture was stirred for 15 h at room temperature. The filtered solution was concentrated to a small volume and diethyl ether was added to give a yellow precipitate of **3a**. Recrystallization from acetone/diethyl ether gave the analytical sample. Yield 78%, m.p. 172°C. Anal. found: C, 23.09; H, 1.87; N, 5.80%. Anal. calc. for C$_9$H$_7$AuCl$_3$KN$_2$: C, 22.26; H, 1.45; N, 5.77%. Λ_m (5×10^{-4} M, acetone): 84.6 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1593 m, 690 m, 370 m, 300 m. FAB mass spectrum (*m*/*z*): 445 [*M*$^-$], 375 [*M*–2Cl].

3.1.4. [Au(L)Cl$_3$][BH] ***(3b)***

To a solution of complex **2** (172 mg, 0.19 mmol) in acetone, 83.7 mg (0.39 mmol) of proton sponge (B) was added and the resulting solution was stirred for 5 h at room temperature and then concentrated to a small volume. Addition of diethyl ether gave the analytical sample as a yellow solid (203 mg), yield 80%, m.p. 102°C (dec.). Anal. found: C, 41.70; H, 3.87; N, 8.10%. Anal. calc. for C$_{23}$H$_{26}$AuCl$_3$N$_4$: C, 41.74; H, 3.96; N, 8.47%. Λ_m (5.4×10^{-4} M, acetone): 119.5 Ω^{-1} cm^2 mol^{-1}, Λ_m (5×10^{-4} M, dichloromethane): 29 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1593 m, 691 m, 363 s, 295 s. FAB mass spectrum (*m*/*z*): 215 [*M*$^+$], 445 [*M*$^-$], 375 [*M*–2Cl].

3.1.5. [Au(L)(3,5-Me$_2$py)Cl$_2$] ***(4)***

(1) Addition of 3,5-Me$_2$py (0.04 cm^3, 0.34 mmol) to a suspension in dichloromethane of complex **2** (71 mg, 0.08 mmol) gave a yellow solution which was stirred for 2 h at room temperature. After this period it was concentrated to a small volume and diethyl ether was added to give a yellow solid. Recrystallization from dichloromethane/diethyl ether gave the analytical sample. Yield 72%.

(2) To a solution of **6** (44 mg, 0.053 mmol) in dichloromethane, 3,5-Me$_2$py (0.012 cm^3, 0.103 mmol) was added. The resulting yellow solution was stirred for 2 h and then concentrated to a small volume. Addition of diethyl ether gave a yellow precipitate of **4**. Yield 51%. m.p. 184°C. Anal. found: C, 37.14; H, 3.29; N, 7.77%. Anal. calc. for C$_{16}$H$_{16}$AuCl$_2$N$_3$: C, 37.08; H, 3.11; N, 8.11%. IR (Nujol, cm^{-1}) ν: 1593 s, 688 s, 368 s. FAB mass spectrum (*m*/*z*): 517 [*M*$^+$], 481 [*M*–HCl], 410 [*M*–L′] (L′ = 3,5-Me$_2$py). ^{13}C-NMR (CDCl$_3$) δ: 18.5 (CH$_3$), 119.0, 126.2, 126.4, 129.3, 141.6, 141.9 and 146.5 (10 C, aromatic CH), 97.9, 136.1, and 140.2 (4 C, aromatic C).

3.1.6. [Au(L)(PPh$_3$)Cl$_2$] ***(5a)***

(1) To a suspension of **2** (87.3 mg, 0.097 mmol) in dichloromethane, PPh$_3$ (51.7 mg, 0.197 mmol) was added. The resulting yellow solution was stirred for 1 h, concentrated to a small volume and added with diethyl ether to give a yellow precipitate of **5a** (104 mg), yield 80%.

(2) To a solution of **6** (61.5 mg, 0.075 mmol) in dichloromethane was added PPh$_3$ (39.8 mg, 0.150 mmol). The resulting solution was stirred for 1h, concentrated to a small volume and added with diethyl ether to give **5a** as a yellow solid. Yield 72%, m.p. 118°C. Anal. found: C, 48.88; H, 3.44; N, 4.35%. Anal. calc. for C$_{27}$H$_{22}$PAuCl$_2$N$_2$: C, 48.16; H, 3.29; N, 4.16%. Λ_m (6.2×10^{-4} M, dichloromethane): 6.45 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1598 m, 1100 s, 690 vs, 319 vs, 302 s. FAB mass spectrum (*m*/*z*): 673 [*M*$^+$], 637 [*M*–HCl], 602 [*M*–H–2Cl], 459 [AuPPh$_3$]. ^{31}P-NMR (CDCl$_3$) δ: 34.3.

3.1.7. [Au(L){P(4-MeC$_6$H$_4$)$_3$}Cl$_2$] ***(5b)***

To a suspension of **2** (59.3 mg, 0.07 mmol) in dichloromethane, P(4-MeC$_6$H$_4$)$_3$ (43 mg, 0.138 mmol) was added. The resulting yellow solution was stirred for 1 h and then concentrated to a small volume: addition of diethyl ether gave a yellow precipitate of **5b**. Yield

74%, m.p. 123°C. Anal. found: C, 50.63; H, 4.41; N,3.92%. Anal. calc. for $C_{30}H_{28}PAuCl_2N_2$: C, 50.37; H, 3.94; N, 3.92%. Λ_m (6.4×10^{-4} M, dichloromethane): 9.40 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1596 s, 1097 s, 693 m, 325 s, 304 vs. ^{31}P-NMR ($CDCl_3$) δ: 33.7.

3.1.8. [Au(L)Cl_2]$_2$ (**6**)

(1) To a solution of **2** (106 mg, 0.118 mmol) in acetone, an aqueous solution of NaOH (9.1 mg, 0.227 mmol) was added. The resulting solution was stirred for 6 h and then evaporated to dryness. The residue was taken up with dichlorometane, filtered and concentrated to a small volume: addition of diethyl ether gave a pale yellow compound. Yield 48%.

(2) An aqueous suspension of **2** (132 mg, 0.147 mmol) was refluxed for 16 h. During this period the precipitate darkened. It was filtered off and recrystallized from dichlorometane/diethyl ether to give 46 mg of a pale yellow product. Yield 38%, m.p. 183°C. Anal. found: C, 26.88; H, 1.56; N, 6.98; Cl, 15.9%. Anal. calc. for $C_{18}H_{14}Au_2Cl_4N_4$: C, 26.29; H, 1.72; N, 6.81; Cl, 17.25%. Λ_m (5×10^{-4} M, acetone): 12 Ω^{-1} cm^2 mol^{-1}, Λ_m (5×10^{-4} M, dichlorometane): 1 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}) ν: 1591 m, 691 s, 373 s (broad), 302 w and 249 w. FAB mass spectrum (m/z): 821 [MH^+], 750 [M–2Cl], 605 [M–L–2HCl], 340 [LAu].

Table 3
Crystallographic data

Compound	4
Formula	$C_{16}H_{16}AuCl_2N_3$
M_r	518.20
Colour	Yellow
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	14.715(2)
b (Å)	8.142(1)
c (Å)	14.267(2)
β (°)	90.42(1)
U (Å^3)	1709.3(4)
Z	4
F(000)	984
$D_{calc.}$ (g cm^{-3})	2.014
Crystal dimensions (mm)	0.14 × 0.39 × 0.45
μ (Mo–K$_\alpha$) (cm^{-1})	89.1
Max/min transmission factors	0.49–1.00
Scan mode	ω
Frame width (°)	0.30
Time per frame (s)	20
No. of frames	2500
Detector-sample distance (cm)	5.50
θ-range (°)	2–25
Reciprocal space explored	$\pm h, \pm k, \pm l$
No. of reflections (total; independent)	15 457; 4144
Unique observed reflections with $I > 3\sigma(I)$	3182
Final R and R' indices[a]	0.024, 0.030
No. of variables	199
Goodness-of-fit[b]	1.17

[a] $R = [\Sigma(|F_o - k|F_c||)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$.

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

3.2. Crystallography

Crystal data and other experimental details are summarized in Table 3. The diffraction experiment was carried out on a Siemens SMART CCD area-detector diffractometer at room temperature using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam and the generator working at 50 kV and 35 mA. Cell parameters and orientation matrix were obtained from the least-squares refinement of 88 reflections measured in three different sets of 15 frames each, in the range $2 < \theta < 23°$. At the end of data collection the first 50 frames, containing 277 reflections, were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The 2500 collected frames were processed with the software SAINT [8], and an empirical absorption correction was applied (SADABS [9]) to the 15 457 collected reflections, 4144 of which are unique with $R_{int} = 0.050$ ($R_{int} = \Sigma|F_0^2 - F_{mean}^2|/\Sigma F_0^2$). The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package [10] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [11]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, mini-

Table 4
Fractional atomic coordinates with estimated S.D.'s in parentheses for the non-hydrogen atoms of [Au(3,5-Me_2py)(L)Cl_2], compound **4**.

Atom	x	y	z
Au	−0.00683(1)	0.09149(2)	0.12622(1)
Cl1	0.04283(8)	0.2578(1)	0.00839(8)
Cl2	−0.05414(8)	−0.0730(1)	0.24543(9)
N1	0.2450(2)	−0.1372(4)	0.1562(2)
N2	0.2735(3)	0.0203(5)	0.1598(4)
N3	−0.1403(2)	0.1862(4)	0.1080(2)
C3	0.1966(4)	0.1084(6)	0.1505(5)
C4	0.1203(3)	0.0072(5)	0.1433(3)
C5	0.1533(3)	−0.1467(5)	0.1463(3)
C6	0.3113(3)	−0.2657(5)	0.1606(3)
C7	0. 4022(3)	−0.2242(6)	0.1657(4)
C8	0.4673(4)	−0.3474(7)	0.1677(5)
C9	0.4421(3)	−0.5093(7)	0.1637(4)
C10	0.3522(4)	−0.5485(6)	0.1592(5)
C11	0.2854(3)	−0.4276(6)	0.1578(4)
C12	−0.1552(3)	0.3479(5)	0.1083(3)
C13	−0.2403(3)	0.4145(5)	0.0961(3)
C14	−0.3123(3)	0.3053(5)	0.0818(3)
C15	−0.2985(3)	0.1389(6)	0.0821(3)
C16	−0.2107(3)	0.0819(5)	0.0955(3)
C17	−0.2538(4)	0.5982(5)	0.0960(5)
C18	−0.3762(3)	0.0174(7)	0.0678(4)

mizing the function $\Sigma w(F_0 - k|F_c|)^2$. Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms of the two CH_3 groups were detected in the final Fourier maps and included in the calculations but not refined. All the other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å, B 1.15 times that of the carbon atom to which they are attached) and also not refined. The final difference Fourier map shows a maximum peak of 1.52(12) $e\text{Å}^{-3}$ at 1.20 Å from the gold atom. The atomic coordinates of the structure are listed in Table 4.

Molecular and packing drawings were produced with ORTEP [12] and SCHAKAL [13] programs.

4. Conclusions

The results of the above study show that 1-phenylpyrazole reacts with gold(III) chloride in protic solvents to give an adduct. At variance, anhydrous gold(III) chloride, in aprotic media, gives an aurated derivative. Of the two possible products, i.e. a five-membered cyclometallated derivative arising from activation of a C–H bond of the phenyl substituent, or a metallated species due to electrophilic substitution by gold(III) at the most electron-rich carbon atom of the pyrazole ring, only the latter is obtained. In addition, salts of the organometallic anion $[Au(L)Cl_3]^-$ have been isolated which are unusually air and moisture stable.

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