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(TERTIARY PHOSPHINE)GOLD(I) DERIVATIVES OF 2-PYRIDONES *

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Summary

Reaction of $(R_3P)AuCl$ with some 1-unsubstituted 2-pyridones and alkali in homogeneous or heterogeneous medium has given $(R_3P)AuQ$ compounds (QH is 2-pyridone, 3-nitro-, 5-chloro-, or 6-methyl-pyridone; R is t-Bu, cyclo-hexyl, phenyl, or 1-naphthyl). Combined infrared and NMR evidence indicates that the compounds are derived from the 2-pyridone tautomer, the metal being in the 1-position. An X-ray crystal structure determination carried out on $Ph_3PAu(6\text{-methylpyridonato-}N)\cdot H_2O\cdot 0.5C_6H_6$, the first structural analysis on a derivative in which the Q ligand is monodentate, reveals that the pyridonato-*N* ligand is derived from the keto-tautomer, the C=O distance being 1.23(2) Å, and that the coordination around the gold atom is approximately linear (P–Au–N 173.4(3)°), with Au–N 2.077(9), Au–P 2.236(3) Å and no metal–metal interaction.

Introduction

We previously described organogold compounds obtained from the reaction of various pyrazolones with (tertiary phosphine)chlorogold(I) species in the presence of alkali [1]. The pyrazolones-5 investigated are known [2] to be a mixture of three tautomers, **a**, **b**, and **c** (M = H) and the gold compounds were found to be derived from the last tautomer, **c**, and to be represented by the formula **c** ($M = AuPPh_3$).

Several other azolones are known to exist as similar tautomeric mixtures [3]; one of the most interesting of them is 2-pyridone, a nucleobase analogue related to uracyl. In the case of 2-pyridone possible structures are **d**, **e**, **f**, and **f′**, and the predominance of the lactame tautomer, **d**, was suggested as early as 1891 [4]. There is less of the lactim tautomer, **e**, but its presence is well established [5]; moreover, this

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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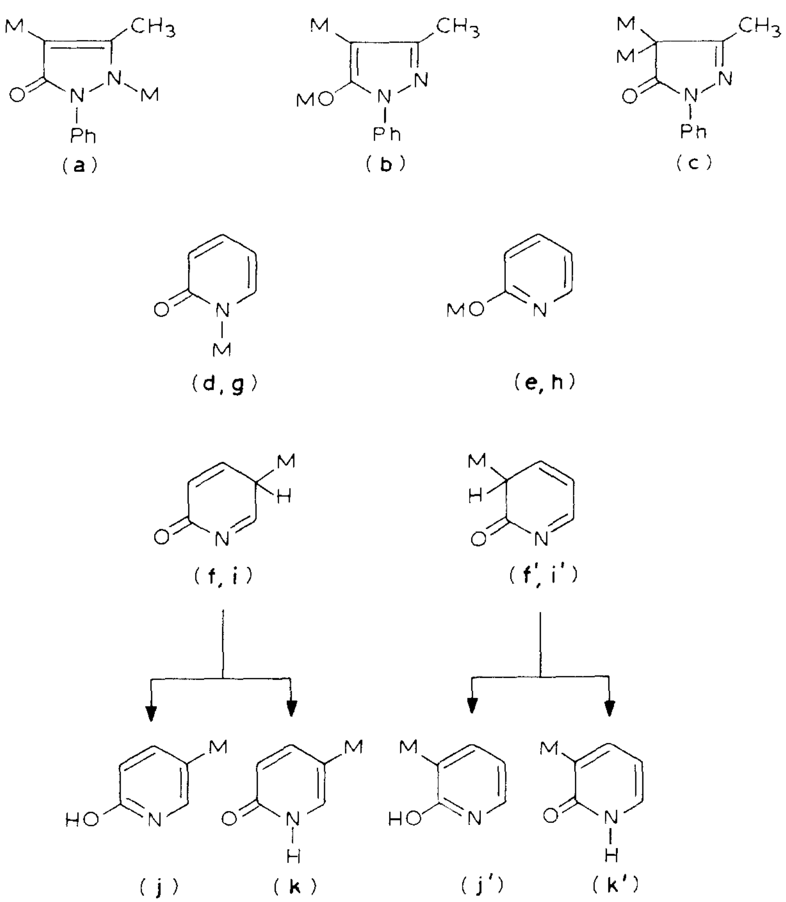


Fig. 1. Tautomers and their metal derivatives. M indicates either hydrogen (**a**–**f**) or trialkylphosphinegold(I) (**a**, **b**, **c** and **g**–**k′**).

is the species present in the crystal in the case of at least one substituted pyridone, namely 6-chloro-2-hydroxypyridine [6]. The tautomers **f** or **f′** have never been detected, but the available methods for investigating tautomeric equilibria would not usually reveal a species present in only small amounts.

This investigation was begun in the (unrealized) hope of isolating an organogold(I) compound deriving from a tautomer such as **f**, or **f′**: indeed, a preliminary reaction with 2-pyridone had given a compound, I, for which the available data would fit formulae such as **j**, **j′**, **k**, or **k′**, although **g** or **h** plus water of crystallization could not be ruled out. By comparison, *C*-metallated 2-pyridones are known, for example 1-methyl-6-[bis(tertiary phosphine)chloroplatinum]-2-pyridone [8].

As well as leading to the isolation and characterization of a series of (tertiary phosphine)(pyridonato)gold compounds the present investigation has provided evidence for a difference in behaviour between pyrazolones-5, which give compounds with Au–C bonds, and 2-pyridones, which do not. Furthermore it has led to determination of the X-ray crystal structure of $(Ph_3P)Au(6\text{-Me-pyridonato}) \cdot H_2O \cdot 0.5C_6H_6$, the first determined structural analysis in which the ligand is monodentate,

TABLE 1

ANALYTICAL AND OTHER DATA FOR COMPOUNDS I–VIII

Compound	Method [a]	Yield (%)	M.p. (°C)	Elemental analyses [b]		
				C	H	N
I [c]	A	79	155–156	48.30	3.65	2.89
				(48.35)	(3.70)	(2.45)
II	A	57	149–151	41.29	6.56	2.79
				(41.38)	(6.33)	(2.84)
III	A	76	205–207	48.15	6.37	2.62
				(48.34)	(6.52)	(2.45)
IV	B	57	262–265	58.22	3.47	1.74
			(dec.)	(58.99)	(3.68)	(1.96)
V	A	67	133–135	46.22	3.32	2.93
				(46.29)	(3.21)	(2.35)
VI	A	81	209–211	45.53	3.16	4.47
			(dec.)	(45.48)	(3.15)	(4.16)
VII	B	70	96–97	51.97	4.41	2.47
				(51.93)	(4.20)	(2.24)
VIII	B	64	250–252	59.81	3.90	1.56
			(dec.)	(59.51)	(3.88)	(1.93)

[a] Methods A and B are described in the Experimental part. [b] Calculated values in brackets. [c] Additional value: oxygen 5.49% (5.60%).

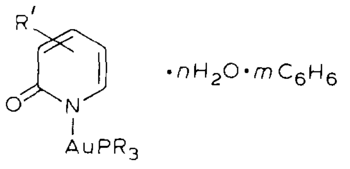
and this structure is compared with that of several other metal pyridonates in which this ligand has always been found to be either chelating or exobidentate (i.e. bidentate and bridging). While the only mononuclear compound, *trans*-$(Ph_3P)_2Ru(Q')_2$ contains two chelating pyridonato-*O,N* ligands [9], all the other complexes contain exobidentate pyridonato-*O,N* ligands (QH = 2-pyridone, Q'H = 6-methyl-2-pyridone, and Q''H = 6-chloro-2-pyridone); $M_2Q'_4 \cdot CH_2Cl_2$ where M is chromium, molybdenum or tungsten [10], Tc_2Q_4Cl [11], $Re_2Q_4Cl_2$ [12], $Ru_2Q'_4 \cdot CH_2Cl_2$ [13], $Rh_2Q'_4Q'H \cdot 0.5$(toluene) or $(Rh_2Q'_4)_2 \cdot CH_2Cl_2$ [14], $Rh_2Q'_4 \cdot CH_2Cl_2$ [15], $Rh_2Q'_4 \cdot L$ where L may be water, acetonitrile, or imidazole plus 0.5 acetonitrile, $Rh_2Q'_2(OAc)_2 \cdot L$ where L may be either imidazole or imidazole plus $2CH_2Cl_2$, $Rh_2Q''_4$, $Rh_2Q''_4 \cdot$ imidazole $\cdot 3H_2O$ [16], $Os_2Q_4Cl_2 \cdot L$ where L may be diethyl ether or 2(acetonitrile) [17], and, finally, several binuclear and tetranuclear platinum derivatives, some of which contain metal atoms in a non-integer oxidation number [18].

Results and discussion

The compounds listed in Table 1 were obtained in good yields as air-stable, colourless solids (except VI, pale yellow) from 2-pyridones (QH) according to the reaction:

$$QH + R_3PAuCl + OH^- \rightarrow R_3PAuQ + Cl^- + H_2O$$

which was carried out either in methanol solution or in dichloromethane with phase transfer catalysis. Some of the phosphines involved, such as tricyclohexyl-, or tri-t-butyl- or tri-1-naphthyl phosphine have a very big cone angle [19], but in all the cases the expected compound was obtained smoothly, even when 6-methyl-2-pyri-



Compound	R	R'	*n*	*m*
I	phenyl		1	0
II	t-butyl		0	0
III	cyclohexyl		0	0
IV	1-naphthyl		0.5	0
V	phenyl	5-chloro	0.5	0
VI	phenyl	3-nitro	0.5	0
VII	phenyl	6-methyl	1	0.5
VIII	1-naphthyl	6-methyl	0.5	0

Fig. 2. Formulae of the various compounds obtained.

done was employed. This is another [20] example of the ability of gold(I) to accommodate bulky ligands readily because of its tendency towards two-coordination.

All the compounds were characterized by analytical and spectral data (shown in the Tables 1–3), which in all the cases except II and III suggested the presence of water and, sometimes, solvent molecules, a complicating feature typical of most metal derivatives of 2-pyridones [10,13–17].

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA FOR COMPOUNDS I–VIII [a]

Compound	Aryl ring + pyridone 4- and 6-protons	Pyridone ring		Other protons
		3-H [b]	5-H [b]	
I [c]	8.1–7.0 m [17]	6.58d (9)	6.17t (6)	2.38s [2] [d]
II	7.5–7.1 m [2]	6.50d (9)	6.13t (6)	1.57d [27], *J* 14 Hz
III	7.45–7.1 m[2]	6.50d (9)	6.12t (6)	2.6–0.8 m, br [33]
IV	9.05–7.0 m [23]	6.48d (9)	6.00t (6)	2.05s [1] [d]
V	7.7–7.0 m [17]	6.50d (9)		2.10s [1] [d]
VI	8.4–8.2 m [2] 8.05–7.50 m [16]		6.45dd (6; 8)	3.46s [1] [d]
VII	7.8–7.1 m [19]	6.41d (9)	6.05d (6)	2.38s [3]; 2.1s [2] [d]
VIII	9.0–7.0 m [22]	6.35d (9)	5.90d (9)	2.11s [3]; 1.94s [2] [d]

[a] The data were recorded on a Varian instrument operating at 90 MHz in $CDCl_3$ solution except for VI which was in $(CD_3)_2SO$, with TMS as reference; they are in δ units. Coupling constants in Hz: s, singlet; d, doublet; dd, double doublet; m, multiplet. [b] Equivalent to one proton in all cases; the coupling constant is shown in brackets. [c] $\delta(P)$ 29.2 from external 85% H_3PO_4, singlet, $CDCl_3$ solution, Bruker instrument operating at 24 MHz. [d] This signal disappears on deuteration.

TABLE 3

SELECTED INFRARED DATA[a]

No.	ν(OH)	ν(CH)	1500–1650 cm^{-1} region
I	3460m, br; 3350m, br; 3240m, br	3070w; 3060w	1610s; 1535w; 1500s
II	–	3090w; 3060w 3040w	1620s; 1610s, sh; 1582s; 1548s; 1516s
III	–	not resolved	1620s; 1612s, sh; 1588w; 1543a; 1516s
IV	not detected	3080w; 3050w; 3040w	1620s, 1611s, sh; 1589m; 1538s; 1515s; 1501s
V	3240w, m; 3160w, br	3086w; 3050w	1603w, sh; 1618s; 1610s, sh; 1532s; 1507s
VI	3530w, br; 3440w, br	–	1630s; 1558m; 1523s
VII	3550–3110m	3090w; 3080w; 3050w	1621s; 1585w; 1510s (all asymmetric)
VIII	not detected	3085w; 3050w	1612s; 1610w, sh; 1588m; 1562w; 1540w; 1520s; 1500s

[a] Recorded as Nujol mull in the NaCl region on a Perkin–Elmer 297 instrument.

Several types of structures must be considered for the compounds here described, namely: **g** derived from the *N*-tautomer (**d**), **h** derived from the *O*-tautomer (**e**), **i** or **i′** from the *C*-tautomer (**f** or **f′**). In addition a proton shift on **i** or **i′** might yield other structures, such as **j** and **k** or **j′** and **k′**, respectively, a few palladium(II), or platinum(II) *C*-derivatives of *N*-methyl-2-pyridone were in fact, recently prepared by another route [8].

In the case of II and of III the assignment of structure g was rather straightforward; they are related to the *N*-tautomer, the one which dominates in all but the gaseous phase [21]. Indeed, in II or in III the proton NMR spectrum showed all the four protons of the pyridonato ring and the chemical shifts were very near to those of 2-pyridone or 1-methyl-2-pyridone. Thus, the observed signals could be assigned to –CH= groups rather than to saturated carbon atoms as in a –CH(metal) structure, for which, in addition, a displacement of the chemical shifts would be expected, as previously observed for *C*-metallation of a pyridine ring [7,8]. From this evidence structures **i**, **i′**, **j**, **j′**, **k** and **k′** were ruled out. The strong infrared band at 1620 cm^{-1}, with a weak shoulder at 1610 cm^{-1}, was assigned to the carbonyl stretching vibration, thus ruling out structure **e**. By comparison, only an absorption at 1574 cm^{-1}, was reported for the *O*-trityl derivative of 2-pyridone, compared with two strong bands at 1595 and 1665 cm^{-1} observed in the *N*-isomer and assigned to C=C plus C=O stretching vibration [22]. A lowering of ca. 40 cm^{-1} is consistent with a lower C=O bond order in II or III than in an *N*-alkylated 2-pyridone. For the same reason there is a carbonyl stretching vibration at 1620 cm^{-1}, together with a shoulder at 1630 cm^{-1}, in 1-methyl-6-[*trans*-$(Ph_3P)_2ClPt$]-2-pyridone [8].

Although for the remaining compounds, I and IV–VIII, the same structure as for II or III might have been assumed by analogy, additional discussion of the available evidence is needed since all the compounds for which an X-ray crystal structure has been reported have bidentate ligands [9–18] and the two groups of compounds (II and III on the one hand, I and IV–VIII on the other) might come each from a different tautomer, especially since in the crystal 2-pyridone is in the lactam form, **d**, while the related 6-chloro-2-pyridone has the lactim form, **e** [6]. Indeed, II and III contain an aliphatic phosphine and are anhydrous, while the remaining compounds contain an aromatic phosphine and are hydrated. Because of hydration a *C*-derivative, such as **j** or **k**, might escape detection, since the expected O–H or N–H stretching vibrations might be masked by those of water, and in proton NMR spectrum the extensive aromatic absorptions might hide the displacement or even the disappearance of a pyridone ring proton.

In the NMR spectra of the compounds (Table 2) the doublet at ca. 6.5 could be due to either 3- or 6-proton of the Q ligand, but it must be assigned to the former since it was found in VII and VIII which have a 6-methyl substituent. Similarly, the signal at 6.0–6.2 is a triplet in the compounds I–IV and a doublet in VII and VIII, and is absent in V and so it must be due to the 5-proton. Consequently structures having gold in the 3- or 5-position (that is: **i**, **i′**, **j**, **j′**, **k** and **k′**) must be discarded; of the remaining two, **g** and **h**, only the first is consistent with both the proton NMR spectra of all the compounds, I–VIII, and the presence of a carbonyl stretching vibration. It thus seems that no O–H or N–H vibration is hidden by the absorption due to clathrated water.

X-ray crystal structure determination of VII

The X-ray crystal structure of $Ph_3PAu(6\text{-methylpyridonato-}N)\cdot H_2O\cdot 0.5C_6H_6$ consists of discrete monomeric molecules without any Au...Au interaction. An

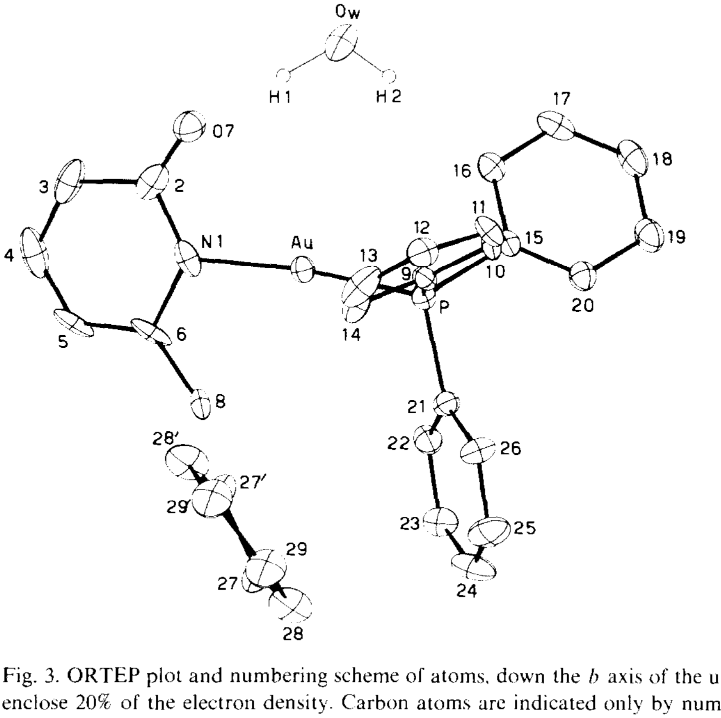


Fig. 3. ORTEP plot and numbering scheme of atoms, down the *b* axis of the unit cell. Thermal ellipsoids enclose 20% of the electron density. Carbon atoms are indicated only by numbers. Hydrogen atoms are omitted for clarity, except those of the clathrated water molecule.

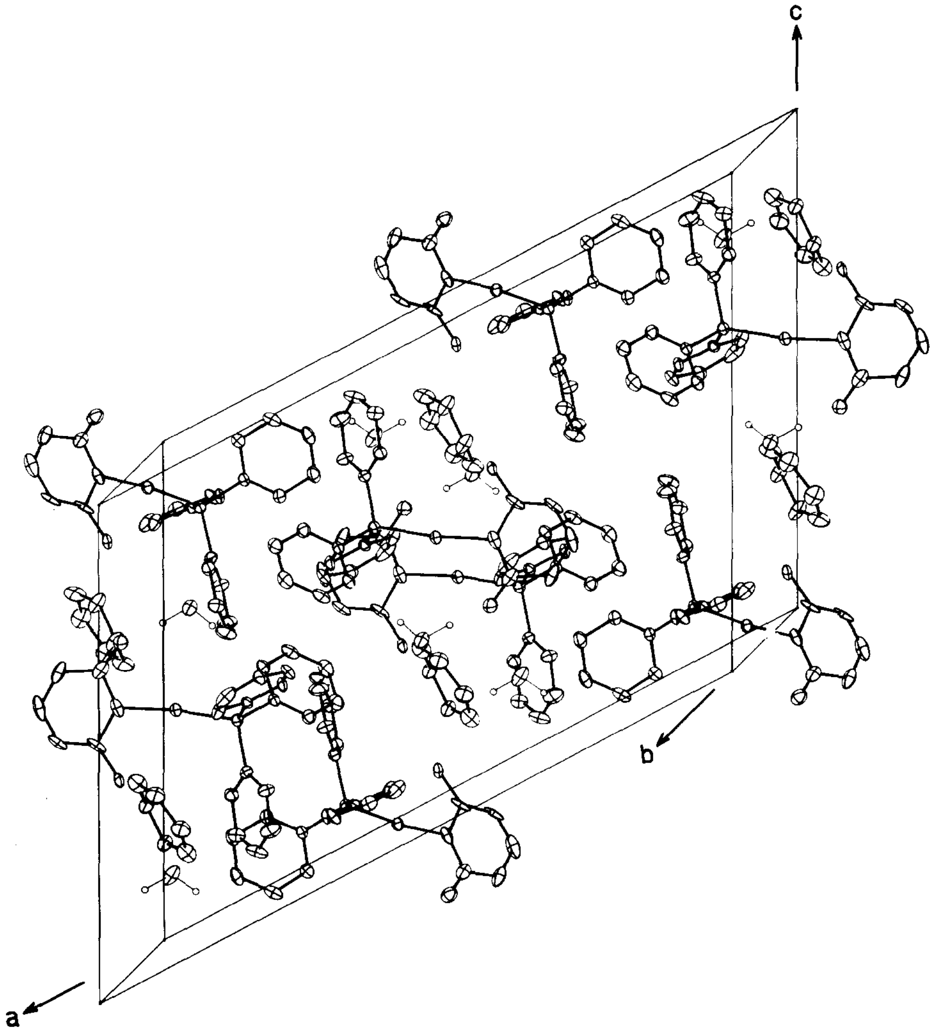


Fig. 4. Molecular packing in the unit cell viewed along the *b* axis.

ORTEP [23] representation of the molecule with the numbering scheme is shown in Fig. 3. The bond distances and angles are given in Table 4. The packing of the molecules in the crystal (Fig. 4) allows space for clathrated molecules of water and benzene (O(7)... O(w) 2.79 Å).

The coordination around the gold atom is approximately linear (P–Au–N 173.4(3)°). The Au–P and Au–N distances, 2.236(3) and 2.077(9) Å respectively, are in line with other values found for monovalent and two-coordinated gold compounds; comparable values are 2.255(2) and 2.019(5) Å, respectively, for tris(cyclohexyl)phosphine(2-isopropylimidazolato-*N*)gold(I) [20].

The least-squares plane of the pyridone ligand and related data are given in Table 5. The probability that the hexaatomic ring is non planar is $P = 80.2\%$. In the 6-methylpyridonato ligand the biggest distance from the best plane passing through the nitrogen and the five carbon atoms is only 0.017(12) Å in the case of the C(4);

TABLE 4

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) (with e.s.d.'s in parentheses)

In the coordination sphere:			
Au–P	2.236(3)	P–Au–N(1)	173.4(3)
Au–N(1)	2.077(9)		
In the methylpyridone ligand:			
N(1)–C(2)	1.40(1)	C(2)–N(1)–C(6)	126.8(1.0)
C(2)–C(3)	1.49(2)	N(1)–C(2)–C(3)	111.1(1.0)
C(2)–O(7)	1.23(2)	N(1)–C(2)–O(7)	120.6(1.1)
C(3)–C(4)	1.41(2)	C(3)–C(2)–O(7)	128.4(1.0)
C(4)–C(5)	1.32(2)	C(2)–C(3)–C(4)	120.6(1.1)
C(5)–C(6)	1.36(2)	C(3)–C(4)–C(5)	123.5(1.5)
C(6)–N(1)	1.46(2)	C(4)–C(5)–C(6)	121.8(1.5)
C(6)–C(8)	1.46(2)	C(5)–C(6)–N(1)	116.1(1.3)
Au–N(1)–C(2)	115.0(7)	N(1)–C(6)–C(8)	116.6(1.4)
Au–N(1)–C(6)	118.2(8)	C(5)–C(6)–C(8)	127.2(1.5)
In the phosphine ligand:			
P–C(9)	1.827(7)	C(15)–P–C(21)	106.0(5)
C(9)–C(10)	1.38(1)	P–C(9)–C(10)	121.9(7)
C(10)–C(11)	1.39(1)	P–C(9)–C(14)	116.6(7)
C(11)–C(12)	1.37(2)	C(10)–C(9)–C(14)	121.4(7)
C(12)–C(13)	1.39(2)	C(9)–C(10)–C(11)	121.1(1.0)
C(13)–C(14)	1.41(1)	C(10)–C(11)–C(12)	118.4(1.1)
C(14)–C(9)	1.38(2)	C(11)–C(12)–C(13)	120.4(9)
P–C(15)	1.809(12)	C(12)–C(13)–C(14)	121.4(1.3)
C(15)–C(16)	1.42(1)	C(13)–C(14)–C(9)	117.1(1.1)
C(16)–C(17)	1.40(2)	P–C(15)–C(16)	115.6(8)
C(17)–C(18)	1.37(2)	P–C(15)–C(20)	122.9(8)
C(18)–C(19)	1.42(2)	C(16)–C(15)–C(20)	121.4(1.0)
C(19)–C(20)	1.40(2)	C(15)–C(16)–C(17)	115.9(1.0)
C(20)–C(15)	1.34(1)	C(16)–C(17)–C(18)	123.9(1.1)
P–C(21)	1.796(9)	C(17)–C(18)–C(19)	118.4(1.3)
C(21)–C(22)	1.43(1)	C(18)–C(19)–C(20)	117.8(1.2)
C(22)–C(23)	1.39(1)	C(19)–C(20)–C(15)	122.5(1.0)
C(23)–C(24)	1.32(1)	P–C(21)–C(22)	116.8(6)
C(24)–C(25)	1.39(2)	P–C(21)–C(26)	123.6(7)
C(25)–C(26)	1.40(2)	C(22)–C(21)–C(26)	119.7(8)
C(26)–C(21)	1.39(1)	C(21)–C(22)–C(23)	120.4(8)
Au–P–C(9)	113.2(3)	C(22)–C(23)–C(24)	119.0(9)
Au–P–C(15)	114.8(3)	C(23)–C(24)–C(25)	122.3(1.1)
Au–P–C(21)	109.6(4)	C(24)–C(25)–C(26)	121.1(1.0)
C(9)–P–C(15)	108.0(5)	C(25)–C(26)–C(21)	117.5(9)
C(9)–P–C(21)	104.5(4)		
In the clathrated benzene [a]:			
C(27)–C(28)	1.46(3)	C(28)–C(27)–C(27′)	119(2)
C(27)–C(27′)	1.46(4)	C(27)–C(28)–C(29)	118(2)
C(28)–C(29)	1.39(3)	C(28)–C(29)–C(29′)	122(2)
C(29)–C(29′)	1.44(3)		
In the water molecule:			
O–H(1)	1.10(13)	H(1)–O–H(2)	113(11)
O–H(2)	0.98(13)		

[a] In the benzene the atoms C(27′), C(28′), C(29′) are equivalent positions with coordinates: $1-x$, y, $1/2-z$.

TABLE 5

LEAST-SQUARES PLANE

Equation[a], χ^2, P	Atoms[b]	Displacements (Å)
$0.4631\ X' + 0.8862\ Y - 0.0172\ Z' - 5.5427 = 0$	N(1)*	0.004(7)
	C(2)*	−0.007(10)
$\chi^2 = 4.68$ ($n = 3$)	C(3)*	−0.002(10)
P 80.2%	C(4)*	0.017(12)
	C(5)*	−0.015(11)
	C(6)*	0.001(11)
	Au	0.0906(3)
	O(7)	0.012(7)
	C(8)	−0.071(16)
	H(3)	0.10(8)
	H(4)	0.00(9)
	H(5)	−0.02(8)

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[a] Transformation matrix from monoclinic X, Y, Z to orthogonal X', Y, Z' coordinates: $\begin{pmatrix} 1 & 0 & -\cos\beta^* \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta^* \end{pmatrix}$.

[b] The atoms denoted by * were included in the calculation of the plane.

although the ligand deviates slightly from planarity, the pseudo aromatic character of pyridone is maintained also in the monodentate pyridonato ligand.

From Table 6 it can be seen that in the heterocyclic anion the C=O bond distance of VII is comparable with that of 2-pyridone, but that it is shorter than the C–O distance found in 6-chloro-2-pyridol, or in several other metal derivatives where a pyridonato ligand is either exo- or endo-bidentate [9–17] (values for two representative compounds, both involving ruthenium(II), are in Table 6. By comparison, for an aromatic alcohol a C–O distance of about 1.36 Å is typical. All these data indicate that our gold complex must be regarded as a derivative of the keto form of 2-pyridone, **g**, while a derivative of the enol form, **e**, can be observed in the only mononuclear ruthenium(II) derivative investigated [9], and intermediate cases in the dinuclear ruthenium(II) complex [13] reported in Table 6 as well as in the group VI derivatives studied by Cotton [10]. In addition, also the NCO and CCO angles in VII are similar to the corresponding angles in 2-pyridone and each pair of values is not comparable with those for 6-chloro-2-pyridol or the other representative metal derivatives reported in Table 6.

TABLE 6

COMPARISON OF STRUCTURAL DATA[a]

Compound	C=O (Å)	NCO (deg)	CCO (deg)	Ref.
Ph_3PAuQ	1.23(2)	120.6(1.1)	128.4(1.0)	this work
QH	1.262(4)	118.8(3)	125.9(3)	[6]
Q″H	1.330(5)	117.7(3)	119.1(3)	[6]
$Ru_2Q'_4 \cdot CH_2Cl_2$	1.296(8)	119.4(4)	121.0(4)	[13]
$RuQ'_2(PPh_3)_2$	1.354(9)	108.4(5)	123.5(7)	[9]

[a] QH is 2-pyridone, Q′H is 6-methyl-2-pyridone and Q″H is 6-chloro-2-pyridone.

Tolman's ligand cone angle θ gives information about steric effects of the phosphorus ligand [19]. It is of interest to calculate effective cone angles of symmetrical ligands in X-ray crystal structures, because symmetrical ligands show cone angles of reduced symmetry. The effective cone angle for the $P(C_6H_5)_3$ ligand in our compound is similar to that for an unsymmetrical ligand. The cone apex, centered on the gold atom, was located 2.236 Å from the P atom; the apex angle of the cone, which lies at the Van der Waals radii of the outermost atoms (r 1.17 Å for H) turned out to be 149.6, 154.6 and 159.9° with respect to H(13), H(17) and H(23), respectively. The effective cone angle is the average θ of the outermost H atoms of the three phenyl groups: 154.7°, which is to be compared with the model based value of 145° [19]. A remarkable flexibility of the $P(C_6H_5)_3$ ligand is therefore evident.

Conclusion

All the gold(I) derivatives of the 2-pyridones used here are *N*-derivatives, **g**, and may be described as derivatives of the keto form. The behaviour of this azolone ring is similar to that of various imidazoles [20,24,25], or pyrazoles [26], of 1-aryl-5-alkyl-pyrazol-3-one [1] but is different from that of the isomer 1-aryl-3-alkyl-pyrazol-5-one, which yields compounds having two R_3PAu substituents on the same carbon atom. It seems that with 1-unsubstituted pyrazoles and imidazoles as well as with the three types of azolones considered here and elsewhere [1] the R_3PAu group replaces the hydrogen atom or atoms which undergo exchange with heavy water in solution.

Experimental

Elemental analyses were performed in our microanalytical laboratory or by Mr. A. Canu (University of Sassari). The starting (tertiary phosphine)chlorogold compounds were prepared by a standard method [24]; nitrogen atmosphere was used when tris-t-butylphosphine was employed.

Method A. To a methanol solution (20 ml) of 2-pyridone (0.15 g; 1.58 mmol) were added 1% sodium hydroxide in methanol (6.3 ml; 1.58 mmol) and (triphenylphosphine)chlorogold(I) (0.859 g; 1.73 mmol). After 6 h stirring at room temperature the solution was evaporated to dryness, and the residue was crystallized from benzene/hexane, to give the analytical sample I. Compounds II, III, and V were prepared similarly; in the case of VI the reaction time was 24 h and the crude product was crystallized from dichloromethane/hexane.

Method B. A dichloromethane solution (20 ml) of 2-pyridone (0.15 g; 1.58 mmol) and tris(1-naphthyl)phosphine (1.189 g; 1.73 mmol) was added to an ice-cold suspension of tetra-n-butylammonium hydrogen sulphate (0.533 g; 1.58 mmol) in 2*N* aqueous sodium hydroxide (1.57 ml). After 4 h stirring at room temperature the organic layer was separated, washed with water untill neutral, dried over sodium sulphate, and evaporated to dryness. The residue was crystallized from dichloromethane/hexane to yield the analytical sample, IV.

The compounds VII and VIII were obtained similarly. The former was crystallized from benzene/hexane, and the latter was washed several times with benzene and then crystallized from dichloromethane/hexane.

X-ray analysis

A suitable crystal of compound VII, having approximate dimensions 0.77 × 0.64

× 0.48 mm, was used for data collection. Accurate unit cell parameters were determined by a least-squares fit of 2θ values for 25 reflections measured on a single-crystal Philips PW 1100 computer controlled diffractometer (using the graphite monochromated Mo-K_α radiation) of Centro di Studio per la Cristallografia Strutturale del C.N.R., Pavia, Italy. The intensities of 3000 independent reflections were collected at room temperature within the angular range $2 \leqslant \theta \leqslant 22°$. The $\omega/2\theta$ scan mode was used with a constant scan speed of 0.05° s^{-1} in ω. Three standard reflections monitored every 240 min showed only small random deviations about their mean intensities. 2625 reflections having $I \geqslant 3\sigma(I)$ were considered observed and used to solve and refine the structure. The intensities were corrected for Lorentz and polarization factors and for absorption as specified by North et al. [27]. The structure factors were then placed on an approximate absolute scale by Wilson's method [28] and a mean thermal parameter was thereby obtained.

Crystal data: $C_{27}H_{26}NO_2PAu$, F.W. 624.46; monoclinic, *a* 25.167(5), *b* 12.754(1), *c* 17.456(3) Å, β 119.14(2)°; *V* 4893.8 Å^3; $Z = 8$, D_c 1.69 g cm^{-3}; $F(000) = 2440$; λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 63.0 cm^{-1}. Systematic absences $h0l$, $l \neq 2n$ and hkl, $h + k \neq 2n$, defined the possible space groups $C2/c$ and Cc. The

TABLE 7

FINAL COORDINATES (with e.s.d.'s in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	0.45156(2)	0.20596(2)	0.46602(2)	C(28)	0.4620(10)	0.4724(22)	0.1551(14)
N(1)	0.5367(3)	0.1367(4)	0.5366(5)	C(29)	0.4803(10)	0.5647(11)	0.2030(13)
C(2)	0.5626(5)	0.1431(6)	0.6283(7)	O(wat.)	0.4221(4)	0.1416(6)	0.6614(5)
C(3)	0.6245(6)	0.0963(6)	0.6729(7)	H(3)	0.650(4)	0.103(5)	0.739(6)
C(4)	0.6501(6)	0.0533(8)	0.6236(11)	H(4)	0.689(5)	0.022(6)	0.654(6)
C(5)	0.6209(6)	0.0483(7)	0.5368(9)	H(5)	0.642(4)	0.015(6)	0.507(6)
C(6)	0.5642(7)	0.0899(5)	0.4876(10)	H(8-1)	0.551(4)	0.118(5)	0.363(6)
O(7)	0.5348(4)	0.1858(5)	0.6617(4)	H(8-2)	0.491(7)	0.128(9)	0.372(8)
C(8)	0.5266(8)	0.0869(11)	0.3923(8)	H(8-3)	0.518(4)	0.013(5)	0.372(5)
P	0.3618(1)	0.2803(1)	0.3768(1)	H(10)	0.275(3)	0.435(4)	0.372(4)
C(9)	0.3610(4)	0.4216(5)	0.3933(5)	H(11)	0.279(4)	0.615(4)	0.406(5)
C(10)	0.3115(4)	0.4714(6)	0.3908(6)	H(12)	0.363(4)	0.712(5)	0.427(5)
C(11)	0.3117(5)	0.5793(6)	0.4037(7)	H(13)	0.446(5)	0.626(6)	0.426(6)
C(12)	0.3623(6)	0.6355(7)	0.4183(7)	H(14)	0.438(4)	0.448(4)	0.378(5)
C(13)	0.4113(6)	0.5860(7)	0.4180(7)	H(16)	0.350(4)	0.180(4)	0.514(5)
C(14)	0.4113(5)	0.4769(5)	0.4048(6)	H(17)	0.269(4)	0.103(5)	0.530(5)
C(15)	0.2977(4)	0.2235(5)	0.3818(6)	H(18)	0.172(4)	0.093(5)	0.405(6)
C(16)	0.3107(5)	0.1801(5)	0.4638(6)	H(19)	0.151(4)	0.170(5)	0.265(6)
C(17)	0.2616(6)	0.1336(6)	0.4675(8)	H(20)	0.238(3)	0.235(4)	0.258(5)
C(18)	0.2039(6)	0.1281(7)	0.3976(8)	H(22)	0.378(4)	0.118(4)	0.283(4)
C(19)	0.1929(5)	0.1714(7)	0.3158(8)	H(23)	0.360(4)	0.082(5)	0.138(5)
C(20)	0.2419(5)	0.2173(6)	0.3118(6)	H(24)	0.315(5)	0.217(6)	0.033(6)
C(21)	0.3454(4)	0.2668(5)	0.2649(5)	H(25)	0.291(5)	0.387(6)	0.069(6)
C(22)	0.3594(5)	0.1681(6)	0.2403(6)	H(26)	0.311(4)	0.417(5)	0.219(5)
C(23)	0.3501(5)	0.1525(6)	0.1555(6)	H(27)	0.474(9)	0.310(6)	0.169(8)
C(24)	0.3278(6)	0.2301(8)	0.0982(7)	H(28)	0.437(5)	0.474(6)	0.092(6)
C(25)	0.3135(6)	0.3272(8)	0.1195(7)	H(29)	0.462(5)	0.630(6)	0.173(8)
C(26)	0.3215(5)	0.3470(6)	0.2033(6)	H(1)(wat.)	0.465(4)	0.138(6)	0.660(8)
C(27)	0.4857(9)	0.3740(11)	0.2020(19)	H(2)(wat.)	0.386(6)	0.128(7)	0.604(8)

statistical distribution of the normalized structure factors E indicated a centric distribution. The correct space group is therefore $C2/c$, as confirmed by the subsequent structure solution and refinement: the space group Cc did not lead to successful refinement.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods. The position of the unique gold atom was determined by a three-dimensional Patterson map. Three cycles of full-matrix least-squares refined the coordinates of the Au atom to give an R index 0.231. A subsequent three-dimensional difference Fourier synthesis phased on the Au atom revealed the remaining 27 non-hydrogen atoms of the complex molecule, whereas the O and C atoms of the clathrated water and benzene molecules were found in a subsequent difference Fourier map. Four cycles of least-squares refinement, including scale factor and individual isotropic thermal parameters for the 28 atoms of the complex molecule, reduced the R index to 0.117; three other refinement cycles with individual anisotropic thermal parameters gave $R = 0.065$. At this point a three-dimensional difference Fourier map revealed the positions of the remaining 4 unique non-hydrogen atoms and the 26 hydrogen atoms. The subsequent refinement, including the hydrogen atoms with the same isotropic thermal parameters as the atom to which they are attached, reduced the R index to 0.040 ($R_w = 0.031$) after four cycles. In the early stages of the structure analysis the observed reflections were given unit weights, in the last two cycles a weight $w = \sigma^{-2}(|F_0|)$ was used. The atomic scattering factors for the non-hydrogen atoms were taken from ref. 29 and those for hydrogen atoms from ref. 30. Anomalous dispersion effects were included in the scattering factors.

The final atomic coordinates are given in Table 7. Tables of thermal parameters and a list of structure factors can be obtained from one of the authors (B. Bovio) on request.

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References

1 F. Bonati, A. Burini, B.R. Pietroni and M. Felici, J. Organomet. Chem., 273 (1984) 275.

2 J. Elguero, R. Jacquier and G. Tarrago, Bull. Soc. Chim. France, (1967) 3772 and 3780; K. Schofield, M.R. Grimmett and B.R.T. Keene. The Azoles, Cambridge University Press, Cambridge, England, 1976, p. 11–13.

3 P. Beak, Acc. Chem. Res., 10 (1977) 186. and ref. therein.

4 H. von Pechmann and O. Balter, Ber. Dtsch. Chem. Ges., 24 (1891) 3144.

5 M.J. Scanlan and I.H. Hillier, J. Am. Chem. Soc., 106 (1984) 3737; M. Kuzuya, A. Noguchi and T. Okuda, J. Chem. Soc., Chem. Commun., (1984) 435.

6 J. Almlof, A. Kvick and I. Olovsson, Acta Crystallogr., B, 27 (1971) 1201 and ref. therein.

7 K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Mina, S. Kawaguchi, K. Kinoshita and K. Nakatsu, J. Am. Chem. Soc., 102 (1980) 2475; K. Isobe, Y. Nakamura and S. Kawaguchi, Bull. Chem. Soc. Japan, 53 (1980) 139.

8 B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 269 (1984) 295.
9 W. Clegg, M. Berry and C.D. Gardner, Acta Crystallogr., B 36 (1980) 3110.
10 F.A. Cotton, P.E. Fanwick, R.H. Niswander and J.C. Sekutowski, J. Am. Chem. Soc., 100 (1978) 4725.
11 F.A. Cotton, P.E. Fanwick and L.D. Gage, J. Am. Chem. Soc., 102 (1980) 1570.
12 F.A. Cotton and L.D. Gage, Inorg. Chem., 18 (1979) 1716.
13 W. Clegg, Acta Crystallogr., B, 36 (1980) 3112; M. Berry, C.D. Gardner, I.H. Hillier, A.A. McDowell and W. Clegg, Inorg. Chim. Acta, 53 (1981) L61.
14 M. Berry, C.D. Gardner, I.H. Hillier and W. Clegg, Inorg. Chim. Acta, 45 (1980) L209.
15 M. Berry, C.D. Gardner, I.H. Hillier, A.A. McDowell and W. Clegg, J. Chem. Soc. Chem. Commun., (1980) 494; W. Clegg, Acta Crystallogr., B, 36 (1980) 2437.
16 F.A. Cotton and T.R. Felthouse, Inorg. Chem., 20 (1981) 584.
17 F.A. Cotton and J.L. Thompson, J. Am. Chem. Soc., 102 (1980) 6437; idem, Inorg. Chim. Acta, 44 (1980) L247.
18 T.V. O'Halloran, M.M. Roberts and S.J. Lippard, J. Am. Chem. Soc., 106 (1984) 6427; A.P. Ginsberg, T.V. O'Halloran, P.E. Fanwick, L.S. Hollis and S.J. Lippard, J. Am. Chem. Soc., 106 (1984) 5430, and ref. therein.
19 C.A. Tolman, Chem. Rev., 77 (1977) 313.
20 B. Bovio, F. Bonati, A. Burini and B.R. Pietroni, Z. Naturforsch., B, 39 (1984) 1747.
21 H.B. Schlegel, P. Gund and E.M. Fluder, J. Am. Chem. Soc., 104 (1982) 5347 and ref. therein.
22 F. Effenberger, W. Brodt and J. Zinczuk, Chem. Ber., 116 (1983) 3011.
23 C.K. Johnson, ORTEP, Report ORNL-3793, Oak Ridge National Laboratory Tennessee, U.S.A., 1965.
24 F. Bonati, M. Felici, B.R. Pietroni and A. Burini, Gazz. Chim. Ital., 112 (1982) 5.
25 F. Bonati, A. Burini, M. Felici and B.R. Pietroni, Gazz. Chim. Ital., 113 (1983) 105.
26 B. Bovio, F. Bonati and G. Banditelli, Inorg. Chim. Acta, 87 (1984) 25 and ref. therein.
27 A.C.T. North, D.C. Phillips and F.C. Mathews, Acta Crystallogr., A 24 (1968) 351.
28 A.J.C. Wilson, Nature, 150 (1942) 152.
29 International Tables for X-Ray Crystallography Vol. IV. Kynoch Press, Birmingham 1974.
30 R.F. Stewart, F.R. Davidson and W.T. Simpson, J. Phys. Chem., 42 (1965) 3175.