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GOLD-CONTAINING PYRAZOLONES

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Summary

Reaction of LAuCl with various pyrazol-5-ones and alkali in homogeneous or heterogeneous medium has given several 1-R-3-R′-4$(LAu)_2$-pyrazol-5-one derivatives (R = H, phenyl, *p*-bromophenyl, tosyl, methyl; R′ = methyl, trifluoromethyl; L = Ph_3P or Et_3P). In the case of 1-aryl-5-methylpyrazol-3-one 1-aryl-2-triphenylphosphinegold-5-methylpyrazol-3-one, a compound with an Au–N bond is formed. The scope, limitation, and characteristic of the auration reaction are discussed.

Introduction

During our previous investigations in the field of azoles several types of gold(I) derivatives were obtained [1]. In the case of pyrazole (pzH) or imidazole (imH) ligands, mono-, bi-, tri-, or poly-nuclear derivatives were prepared, such as: $(pzH)_nAuCl$ [1a], $(imH)_nAuCl$ [1b], $Ph_3PAu(pz\text{-}N)$ [1c], $Ph_3PAu(im\text{-}N)$ [1d], $[Ph_3PAu(\mu\text{-}3,5\text{-}R_2pz\text{-}N,N')AuPPh_3]^+$, [1a,1e], $[Au_3(\mu\text{-}pz\text{-}N,N')_3]$ [1f,1g] or $[Au\{\mu\text{-}(2\text{-phenylimidazolato-}N,N')\}]_n$ [1b]. All these compounds contain gold–nitrogen bonds, and, in particular, when the diazole ring loses a proton this comes from the 1-nitrogen, the so-called "pyrrole-type nitrogen". Such a proton is available in one of the possible tautomers of a pyrazol-5-one [2,3].

In the case where R = phenyl, R′ = methyl, and R″ = H it was found [1h] that a compound was formed having two Au–C bonds, as in **a′**, rather than a species with a Au–N bond as in the azole derivatives listed above [1]. In view of the current interest in gold chemistry, it was decided to investigate the reaction of R_3PAuCl with various pyrazolones. We wished to ascertain whether the reaction is general or not, and to find an explanation for the different behaviour of pyrazolones compared with other diazoles.

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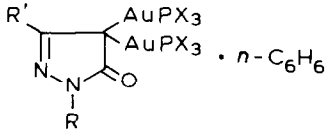
Results and discussion

The reaction leading to molecules containing two gold atoms is general, and can be represented as follows:

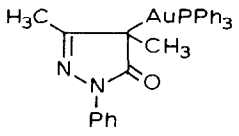
$$2X_3PAuCl + 2OH^- + C_3H_2RR'N_2O \rightarrow C_3RR'N_2O(AuPX_3)_2 + 2H_2O + 2Cl^-$$

The organic molecule is 1-R-3-R'-pyrazol-5-one, where the groups R or R' may be electron-donating or -withdrawing, and the phosphine may be aliphatic or aromatic, as shown in Fig. 1. All the compounds **1–8** (as well as **9**, which is considered later) are air-stable colourless solids, soluble in organic solvents. They were indentified through analytical, and spectral data (Tables 1 and 2). As found for related compounds [1d,1h], these molecules containing bulky and/or hardly flexible ligands have a tendency to clathrate the solvent used for crystallization, evidence for this

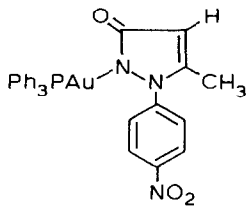


(1-8)

	R	R'	X	n
1	C_6H_5	CH_3	C_6H_5	0
2	C_6H_5	CH_3	C_2H_5	1/3
3	p-CH_3–C_6H_4–SO_2	CH_3	C_6H_5	1
4	p-Br–C_6H_4	CH_3	C_6H_5	1
5	H	CH_3	C_6H_5	1/2
6	H	CH_3	C_2H_5	0
7	CH_3	CH_3	C_6H_5	1
8	C_6H_5	CF_3	C_6H_5	0



(9)



(10)

Fig. 1

TABLE 1

ANALYTICAL AND OTHER DATA FOR COMPOUNDS **1–10**

Compound	Method	Yield(%)	M.p. (°C)	Elemental analyses (Found (calcd.)(%))		
				C	H	N
1 [12]	B	53	202–203	50.01	3.45	2.77
				(50.66)	(3.51)	(2.57)
2	B	62	174–178	34.40	4.90	3.38
				(34.74)	(4.82)	(3.37)
3	B	49	208–211	50.55	3.71	2.40
				(51.05)	(3.72)	(2.25)
4	B	61	159–162	50.32	3.53	2.21
				(50.06)	(3.47)	(2.25)
5	A	64	157–160	48.76	3.87	2.57
				(48.99)	(3.54)	(2.66)
6	A	62	166–171	25.76	4.69	3.81
				(26.44)	(4.72)	(3.85)
7	A	79	207–210	51.01	3.93	2.59
				(51.01)	(3.82)	(2.53)
8	B	64	218–220	48.56	3.31	2.45
				(48.26)	(3.08)	(2.45)
9	A	40	123–126	55.33	4.56	4.15
				(56.07)	(4.26)	(4.09)
10	A	59	189–192	49.93	3.65	5.90
				(49.64)	(3.42)	(6.20)

TABLE 2

NUCLEAR MAGNETIC RESONANCE AND INFRARED DATA FOR COMPOUNDS **1–10** [a]

Compound	$\delta(^1H)$		$\delta(^{31}P)$ (ppm)	IR data [d] (cm^{-1})
	Aryl ring protons	Other protons		
1	7.2–8.3 m (35H)	2.34 s (3H)	35.58	1620
2	6.8–8.3 m (7H)	1.05 t (9H) *J* 7.5 Hz;1.25 t (9H) *J* 7.0 Hz;1.72 q (6H) *J* 7.5 Hz; 1.80 q (6H) *J* 7.0 Hz;2.20 s (3H)	33.67	1605
3	7.0–8.2 m (40H)	2.18 s (3H);2.27 s (3H)	34.88	1640
4	7.1–8.3 m (40H)	2.32 s (3H)	34.58	1610
5 [b]	7.1–7.7 m (33H)	2.17 s (3H)	30.26	1530
6		1.08 t (9H) *J* 7.0 Hz;1.28 t (9H) *J* 7.0;1.5–2.1 2q (12 H) [c]; 2.20 s (3H)		1525
7	7.1–7.7 m (36H)	2.28 s (3H);3.48 s (3H)	34.58	1590
8 [b]	7.1–8.25m (35H)			1630
9	7.1–8.0 m (23H)	1.95 s (3H);2.28 s (3H)		1620
10:	7.2–8.25m (19H)	2.2 s (3H);5.6 s (1H)		1580

[a] NMR data were recorded on a Varian or a Bruker instrument operating at 90 MHz for H and 24 MHz for ^{31}P, respectively. Solvent was $CDCl_3$ (DMSO for **3** and **10**) and reference Me_4Si or external 85% H_3PO_4; s, singlet; t, triplet; q, quadruplet; m, multiplet. Phosphorus signals are singlets. [b] N–H or O–H proton not observed. [c] Not resolved. [d] Most relevant absorption in the 1500–2000 cm^{-1} region; Nujol mull.

comes from the analytical data, from integration in proton NMR spectra and, in the case of 1-$(C_6H_{11})_3$PAu-2-isopropylimidazole · C_6H_6, also from an X-ray crystal structure determination [1i].

Since pyrazol-5-ones are known to give three tautomers (**a**,**b**,**c**) if R ≠ H, then in the cases of **1**–**4**, **7** and **8**, the corresponding di-gold derivatives **a'**, **b'**, and **c'** have to be considered. For these compounds only structure **a'** agrees with the available data, which include a singlet in the $^{31}P\{^1H\}$ NMR spectra and a carbonyl stretching vibration in the 1590–1640 cm^{-1} region, the highest values being observed in the presence of strongly electronegative substituents on the heterocyclic ring.

The observed ^{31}P chemical shifts are in the range 33–35 ppm relative to 85% H_3PO_4, which compares with a range of 28–32 ppm for several Ph_3PAuY compounds when Y is an *N*-bonded diazolyl or triazolyl group [1d,1h]. Nevertheless, no generalization is possible linking the ^{31}P shift to either a R_3PAuC or a R_3PAuN arrangement, because there is almost an overlap of the two ranges mentioned above even for the limited number of compounds investigated.

In the case of the reaction with 1-phenyl-3,4-dimethylpyrazol-5-one only monosubstitution is possible, yielding a compound formulated as **9** on the proton NMR evidence and by analogy with the others. No reaction was observed with antipyrine, 1-phenyl-2,3-dimethylpyrazol-5-one.

The auration reaction was extended to an *N*-unsubstituted pyrazolone, namely 3-methylpyrazol-5-one, for which several tautomers are possible [4], e.g. those depicted in Fig. 2. The compounds **5** and **6** were obtained upon reaction with triphenyl-or triethyl-phosphinechlorogold(1), respectively, and were found to contain two gold atoms per molecule. For these species structures such as **a'** and **d'** are conceivable, but the absence in their proton NMR spectra of any signal correspond-

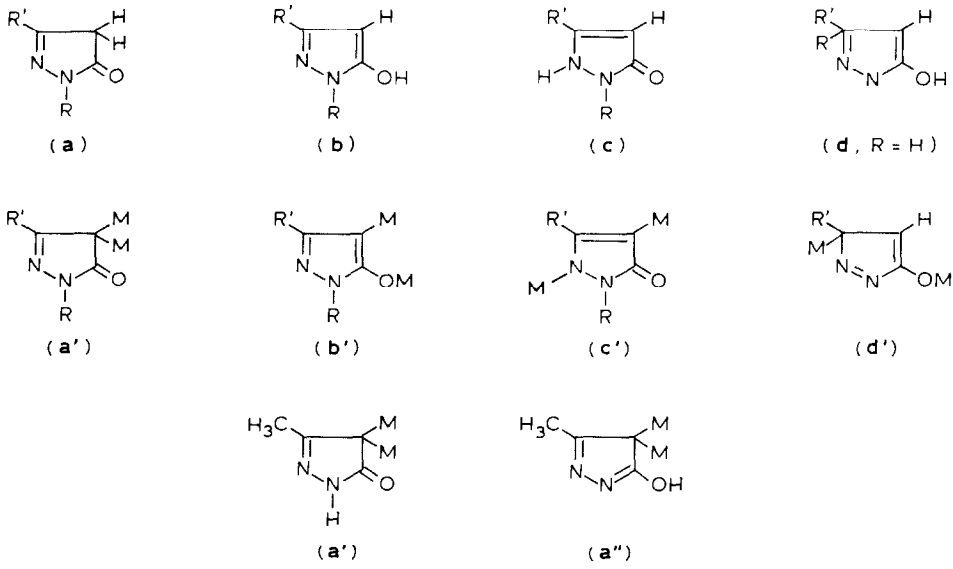


Fig. 2

ing to a 4-CH or to a 3-CH of the pyrazolone ring rules out structures such as **d'**. Although the same NMR spectra do not show any NH or OH protons, an OH function is likely to be present because the infrared spectra (Nujol mull) show a broad absorption ranging from ca. 2500 to 3500 cm^{-1}. Of the remaining structures (**a'**, **b'**, **c'**) the one having equivalent phosphorus nuclei is favoured, since the $^{31}P\{^1H\}$ NMR spectrum of **5** shows a singlet. Therefore **a'** must be considered, or, better, the structure **a''** derived from **a'** by a proton shift. Structure **a'** would be comparable with a secondary amide: this requires both a CO absorption in the 1680–1630 cm^{-1} region and a N–H stretching above 3000 cm^{-1}, whereas in **5** or **6** no such ν(CO) is observed and the broad band going from 2500 to 3500 cm^{-1} is likely to be due to hydrogen-bonded OH stretching vibrations.

To complete our investigation the reaction of one 1-aryl-5-methylpyrazol-3-one [5] was examined. Although this is an isomer of the other employed above, it can give only two tautomeric forms, **e** and **f**, (Fig. 3), and correspondingly the compound obtained, **10**, which contains only one gold atom in the molecule, may be either **g** or **h**. Other structures having a C–Au bond are excluded by the presence in the proton NMR spectrum of all the signals required for the CH protons. Structure **h** involves an O–Au bond, which is generally considered to be weak although this bond was found in the very stable compound $Me_3PAuOSiMe_3$ [6]. However, a structure resonating between **g** and **g'** is more likely because of an infrared absorption at 1575 cm^{-1}: this band may be due to C=O, corresponding to a bond order intermediate between 1 and 2.

It is known that pyrazol-5-ones and -3-ones are weak acids [3]. The pyrazolones with substituents in the 4-position undergo two aurations at carbon, and, correspondingly, that having a 4-CH_3 substituent is only singly-aurated at carbon. This behaviour is parallel to that toward proton exchange of the hydrogen(s) in the 4-position of various pyrazol-5-ones: this position is deuterated easily, e.g. when the $CDCl_3$ solution is shaken with heavy water. On the other hand the pyrazol-3-one employed undergoes neither *C*-auration nor deuteration. In view of this, it is

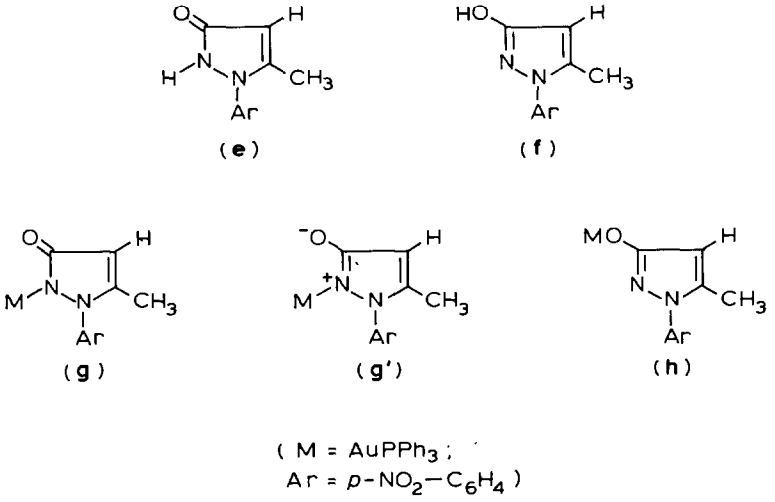


Fig. 3

suggested that auration of pyrazolones takes place by nucleophilic attack of the deprotonated ligand on Ph_3PAuCl. This may explain why antipyrine is not aurated at all, why a pyrazol-3-one is not *C*-aurated and is aurated only once, and finally, why 4-unsubstituted pyrazol-5-ones are doubly aurated at carbon. In addition to the general interest for gold chemistry [7], the double *C*-auration is important for the following reasons: (a) it readily affords compounds containing a $(ligand–Au)_2C$ moiety comparable to $[(\pi\text{-}C_5H_5)Fe\ \{\pi\text{-}C_5H_4(AuPPh_3)_2\}]BF_4$ [8] or to $(Ph_3PAu)_2C(CN)_2$ [9]; (b) it demonstrates that polymetallation, typical of mercury(II), occurs also with gold(I); and, (c) X-ray crystal data may prove to illustrate a principle valid in cluster chemistry, namely that a R_3PAu group can replace a hydrogen without significant change in the gross molecular structure [10].

Experimental

Elemental analyses were performed in our Microanalytical Laboratory (Perkin–Elmer 240 instrument). The preparations of 1-phenyl-3-trifluoromethyl-pyrazol-5-one [11] and of 1-(*p*-nitrophenyl)-5-methyl-pyrazol-3-one [5] was carried out by published methods.

Method a: Sodium hydroxide (320 mg; 8.0 mmol) in methanol (32 ml), and 1,3-dimethyl pyrazol-5-one (411 mg; 3.65 mmol) were added to a methanol suspension (50 ml) of Ph_3P AuCl (3.96 g; 8.0 mmol). After 5 h stirring the solution was evaporated to dryness, the residue was extracted with benzene, and the extract was concentrated to ca. 10 ml. A solid precipitated, and was washed several times with benzene to give **7**.

Compounds **5** and **6** were prepared in the same way using 3-methylpyrazol-5-one and Ph_3PAuCl or Et_3PAuCl as starting materials.

Compounds **9** and **10** were obtained similarly starting from 1-phenyl-3,4-dimethylpyrazol-5-one or 1-*p*-nitrophenyl-5-methylpyrazol-3-one and Ph_3PAuCl, respectively, in 1/1/1 molar ratio. After addition of hexane, a solid precipitated which was crystallized twice from benzene/hexane.

Method b: A dichloromethane solution (40 ml) of Ph_3PAuCl (3.96 g; 8.0 mmol) and 1-*p*-tosyl-3-methylpyrazol-5-one (926 mg; 3.67 mmol), and an ice-cold solution of tetra-n-butylammonium hydrogensulfate (2.492 g; 7.34 mmol) in 7.34 ml of 2 *N* aq. sodium hydroxide were mixed with stirring. After 2 h stirring at room temperature, the organic layer was separated, washed with water untill neutral, dried (sodium sulphate), and evaporated to dryness. The residue was extracted with benzene and the extract was concentrated; addition of hexane gave a solid precipitate, which was recrystallized to give the analytical sample of **3**.

Compounds **4** and **8** were obtained similarly using 1-*p*-bromophenyl-3-methyl-pyrazol-5-one and 1-phenyl-3-trifluoromethylpyrazol-5-one as starting materials. Compound **2** was prepared as above starting from 1-phenyl-3-methylpyrazol-5-one and Et_3PAuCl. The residue was extracted with benzene; concentration of the solvent gave a solid, which was purified by several washings with benzene.

The ^{13}C NMR spectrum in $CDCl_3$ solution was recorded for compound **3**: 19.4 Me, 21.5 Me, 127.9, 128.4, 128.7, 129.0, 129.5, 130.6, 131.4, 132.0, 133.7 and 134.6, aryl signals due to phosphine, tosyl and pyrazolone moieties. No signal due to CH_2 group was observed.

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