Journal of Organometallic Chemistry, 344 (1988) 119–135
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reactions of (tertiary phosphine)gold(I) substituted imidazoles or pyrazolones with acidic reagents: protonation, azole displacement, and adduct formation. Crystal structure determination of the adduct 1-methyl-2-(cyclohexylphosphinegoldthiolato)imidazole • 2benzimidazole

Flavio Bonati, Alfredo Burini, Bianca Rosa Pietroni, Elisabetta Giorgini
Dipartimento di Scienze Chimiche, Università, 62032 Camerino (Italy)

and Bruna Bovio
Dipartimento di Chimica Generale, Università, Viale Taramelli 12, 27100 Pavia (Italy)

(Received September, 21st, 1987)

Abstract

Imidazole (QH) or pyrazolone ($Q'H_2$) in QAuL or $(LAu)_2Q'$ (where L is a tertiary phosphine) is displaced by some acidic reagents HZ, where HZ = terminal acetylene, imide, thiol, dithio acid, or HI, to give ZAuL. If Z^- is not a soft ligand an adduct between the reagents is obtained, and this is formulated as a protonated species, e.g. $[LAuQH]^+Z^-$ (HZ = picric acid). In other cases the adduct is LAuZ · HQ (rather than LAuQ · HZ or a protonated species), in which the displaced QH is hydrogen-bonded to the product, as shown by the crystal structure of the adduct 1-methyl-2(cyclohexylphosphinegoldthiolato)imidazole · 2benzimidazole. In this species gold(I) is two-coordinated (P–Au–S 172.0(1)), with Au–P and Au–S 2.292(3) and 2.331(3) Å, respectively; the first benzimidazole is hydrogen-bonded to N(3) of the imidazole, and the second benzimidazole to the N(3) of the first, the inter-diazole N · · · H–N distance being 2.81 and 2.86(1) Å, respectively.

Introduction

During our investigations of derivatives of gold(I), we isolated compounds of the general formula LAuQ and $(L–Au)_2Q'$, where L is a tertiary phosphine or arsine, QH is an heterocycle, such as imidazole [1], and $Q'H_2$ is a pyrazolone, such as 1-phenyl-3-methyl-pyrazol-5-one [2]. The availability of these air- and moisture-stable compounds in which N–Au or C–Au bonds are present prompted us to study their reactions.

0022-328X/88/$03.50

For several metal alkyls or amides, R′–M(ligand), it is known that the displacement reaction

$$R'M(ligand) + ZH = R'H + ZM(ligand)$$

(R′H is a hydrocarbon or an amine)

takes places readily when ZH is more acidic than R′H. The same process with LAuQ or $(LAu)_2Q'$ compounds was expected to give LAuZ species smoothly in the absence of added alkali. Thus the possibility of displacement of QH and of $Q'H_2$ by several acidic reagents was examined, and the results are reported below, together with details of an X-ray structural determination needed to interpret otherwise ambiguous data.

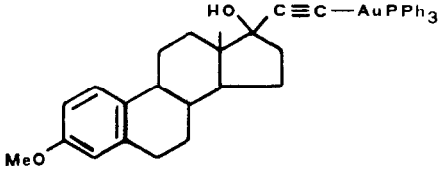
Results and discussion

The possible displacement of QH and $Q'H_2$:

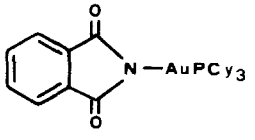
$$LAuQ + ZH = LAuZ + QH$$

$$(LAu)_2Q' + 2\ ZH = 2\ LAuZ + Q'H_2$$

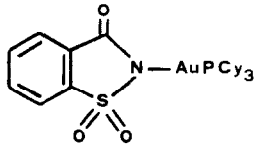
was examined for several ZH compounds. Displacement is observed only when the ZH is more acidic than QH or $Q'H_2$ and also the resulting anion is a good nucleophile: this is the case for the compounds **1–13** which were identified from their analytical and spectral data (see Scheme 1; Tables 1–3). In these complexes the



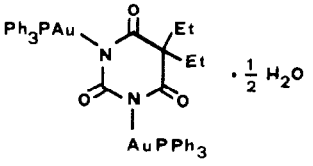
3



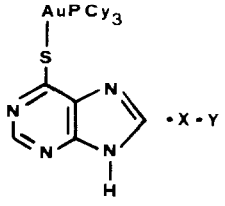
4



5

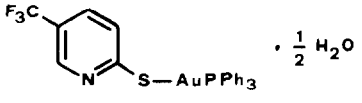


6

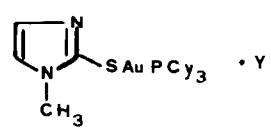


7a X = Benzimidazole ; Y = O

7b X = O ; Y = H_2O



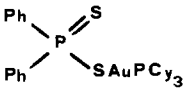
8



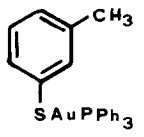
9a Y = 2 Benzimidazole

9b Y = O

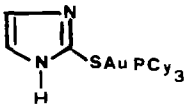
9c Y = Imidazole



11

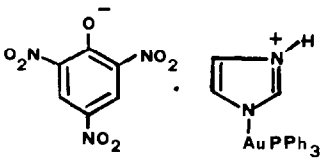


10



12

13



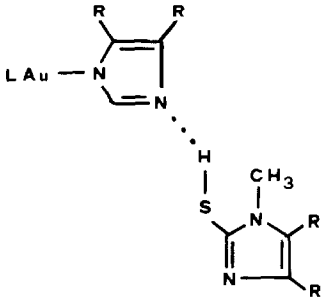
14

Scheme 1

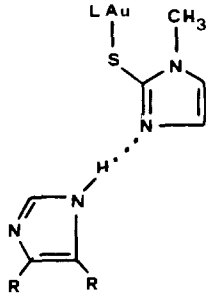
gold atom is bonded to an element of group IV, V, VI, or VII of the periodic system. The group IV reagents include terminal acetylenes, group V imides, such as succinimide, saccharine or 5,5′-diethylpyrimidin-2,4,6-trione (veronal), group VI thiols, diphenyldithiophosphinic acid, 6-thiopurine, 2-thiopyridone, and group VII hydriodic acid. Although the same products could often be isolated from the reaction of LAuCl, ZH and alkali, the displacement reaction is likely to be more useful than the latter since no alkali is required in order to generate the anion Z^-, a feature which may be of value in the preparation of gold derivatives of natural products. Furthermore, when Z–H can exist as tautomers (e.g. 2-thiopyridone or 6-thiopurine), it might be possible to obtain a complex different from that formed by reaction of LAuCl, ZH and alkali. Unfortunately, apart from the often confusing presence of clathrated or solvated molecules, in the case of the Z^- ligands used in the present study the same complex was obtained in both cases, suggesting that the choice of product is thermodynamically rather than kinetically controlled.

No reaction was observed with acetic acid, even though the expected product, $Ph_3PAuOAc$, is known to be stable [3]. Acetate ion is not as good a nucleophile as the anions considered above, and, in addition, gold(I), a soft acceptor, interacts more readily with soft donors, such as those listed above, than with a ligand which is to be attached through a hard oxygen atom. Likewise, no reaction was observed with other acidic species such as ethyl acetoacetate, nitromethane, *p*-tosylmethyl isocyanide, phenothiazine, and cyclohexanone *p*-tosylhydrazone.

As an unforeseen complication, in some cases from reactions under seemingly identical conditions, a product was isolated which gave analytical and spectral data consistent with the formation of an "adduct"; thus thiopurine gave **7a**, 1-methyl-2-mercaptoimidazole gave **9a** or **9c** (but not **9b**, the expected product), and picric acid gave **14**. Two isomeric formulae are possible for such "adducts", both involving hydrogen bonding, as shown for **9c**:



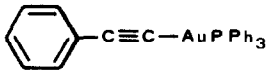
L–Au–Q · HZ



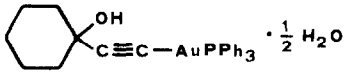
L–Au–Z · HQ

For the species LAuQ · HZ (or, in solution, $[LAuQH]^+Z^-$) the "adduct" is formed between the reagents with ZH hydrogen-bonded to the basic nitrogen available on the Q moiety. For the species LAuZ · HQ, the "adduct" is formed between the product, i.e. the displaced Q–H is hydrogen-bonded to the expected products LAuZ. In both cases, when the ZH content is above that for a 1 : 1 adduct, the additional ZH may be either hydrogen-bonded or clathrated.

The first type of formulation, LAuQ · HZ (QH = imidazole), can be suggested for the picrate, **14**, for two reasons. First, in the ^{31}P NMR spectrum the signal due to a given R_3P–Au–X arrangement is a fairly sensitive function of the donor atom opposite to phosphorus (Table 4); for **14** it appeared at 31.0 ppm, a typical position for a P–Au–N but not for a P–Au–O arrangement (P = triphenylphosphine). Secondly, the compound is an electrolyte in acetone solution, and so must be able to ionize in this solvent; e.g. where HZ is picric acid:



1



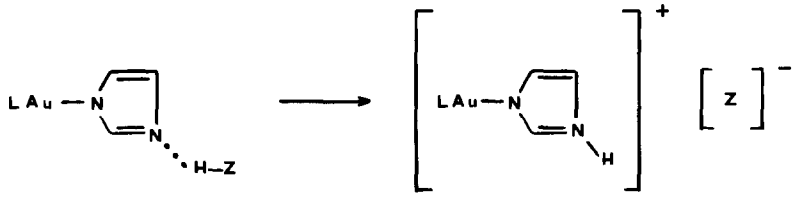
2

Table 1

Analytical and other data [a]

Compound	M.p. (°C)	Analyses (Found (calc) (%))				Λ (ohm^{-1} cm^2 mol^{-1})
		C	H	N	S	
1	158–160	55.52	3.60			
		(55.73)	(3.60)			
2	145–147	52.58	4.76			
		(52.80)	(4.60)			
3	155–157 [b]	60.55	5.32			
		(60.94)	(5.24)			
4	238–240	50.21	5.93	2.21		
		(50.08)	(5.98)	(2.24)		
5	236–238	45.95	5.82	2.11	4.67	
		(45.52)	(5.65)	(2.12)	(4.89)	
6	> 280 [b]	47.45	3.62	2.51		
		(47.62)	(3.72)	(2.52)		
7a	194–196	47.89	5.71	11.50	4.24	1.13
		(48.26)	(5.67)	(11.25)	(4.29)	
7b	153–155 [b]	42.34	5.83	8.61	4.82	
		(42.72)	(5.92)	(8.66)	(4.96)	
8	160–162	44.79	2.81	2.08	4.93	
		(44.55)	(2.96)	(2.17)	(4.95)	
9a	115–118	51.95	6.11	10.14	4.03	
		(52.29)	(6.09)	(10.16)	(3.87)	
9b	176–178	44.59	6.71	4.37	5.24	
		(44.74)	(6.48)	(4.74)	(5.43)	
9c	130–135	45.26	6.39	8.14	5.29	
		(45.59)	(6.43)	(8.51)	(4.87)	
10	164–166	51.76	3.83		5.42	
		(51.55)	(3.80)		(5.49)	
11	186–188	49.39	5.93		9.03	
		(49.58)	(5.96)		(8.82)	
12	218–221	43.63	6.09	5.13	5.33	
		(43.75)	(6.29)	(4.86)	(5.56)	
13	230–231	37.06	2.55			
		(36.88)	(2.58)			
14	179–181	42.95	2.74	9.30		153.53
		(42.93)	(2.80)	(9.27)		

[a] Elemental analyses were performed in our Microanalytical Laboratory (Carlo Erba 1106 elemental microanalyzer). Conductivity measurements were carried out at 25 °C using a Philips GM 4249 bridge; the solvent was acetone that had a specific conductivity of 3.03×10^{-7} Ω^{-1}. The solutions were ca. 10^{-3} *M*. [b] With decomposition.



Such ionization is possible for LAuQ · HZ (HZ = picric acid), the "adduct" between the reagents, but is unlikely to take place for LAuZ · HQ (HQ = imidazole), the

Table 2

Reaction conditions

Compound	Method	Reagent [a]	Temperature	Time (h)	Crystallized from	Yield (%)
1	A	ImL	r.t. [b]	5	benzene/hexane	90
1	A	PzL_2	r.t.	5	benzene/hexane	61
2	A	ImL	r.t.	5	benzene/hexane	86
3	A	ImL	reflux	2	CH_2Cl_2/hexane	53
4	A	BzimL′	r.t.	15	CH_2Cl_2/hexane	82
5	A	BzimL′	r.t.	15	benzene/hexane	80
6	A	ImL	r.t.	1	CH_2Cl_2/hexane	75
7a	A	BzimL′	r.t.	5	CH_2Cl_2/hexane	76
7b	A	ImL′	reflux	15		83
8	A	ImL	r.t.	2	benzene/hexane	77
8	B	LCl	r.t.	2	CH_2Cl_2/hexane	81
9a	A	BzimL′	r.t.	5	CH_2Cl_2/hexane	74
9b	B	L′Cl	r.t.	5	CH_2Cl_2/hexane	86
9b	A	ImL′	reflux	5	CH_2Cl_2/hexane	80
9c	A	ImL′	r.t.	5	CH_2Cl_2/hexane	94
10	A	ImL	r.t.	1		95
10	A	PzL_2	r.t.	2		87
11	A	BzimL′	r.t.	5		88
12	A	ImL′	reflux	7	CH_2Cl_2/hexane	59
12	B	L′Cl	r.t.	15	CH_2Cl_2/hexane	65
13	A	ImL	r.t.	1		93
14	A	ImL	reflux	5	CH_2Cl_2/hexane	76

[a] L = Ph_3PAu; L′ = Cy_3PAu; ImH = imidazole; BzimH = benzimidazole; PzH_2 = 1-phenyl-3-methylpyrazol-5-one. [b] r.t. denotes room temperature.

"adduct" between the products. These findings are in line with the hard character of the picrate ligand, an oxygen donor.

In the case of **9**, however, the spectral evidence did not permit a choice between the two formulae, and so a single crystal X-ray structure determination (see below) was carried out on **9a**, and this showed that the compound is of the second type, LAuZ · HQ, and is 1-methyl-2-(cyclohexylphosphinegoldthiolato)imidazole · 2benzimidazole. This result is consistent with the soft character of thiolato ligands. By analogy, similar conclusion can be drawn for **7a**; here additional support comes from the isolation of **7b**, which differs from **7a** because it contains no hydrogen-bonded imidazole. It seems, then, that in these cases displacement does occur, and then may or may be not followed by hydrogen bonding, depending on the conditions encountered during the isolation of the solid compound.

X-Ray crystal structure determination

The crystal structure of the compound, [tri(cyclohexyl)phosphine](1-methylimidazole-2-thiolato)gold · 2benzimidazole, involves discrete molecules, with no Au · · · Au interactions.

An ORTEP [4] view of the molecule, with the numbering scheme, is shown in Fig. 1. The molecule consists of a two-coordinated gold(I) complex together with an appendage of two molecules of benzimidazole. The interatomic distances and bond angles are listed in Table 5. The shortest intermolecular approaches between the

Table 3

^{1}H and ^{31}P NMR spectral data [a]

Compound	^{1}H NMR		^{31}P NMR
	Aryl protons	Other protons	
1	7.1–7.9 m		42.34 s
2	7.1–7.9 m [15]	3.48 s [2] [b]; 1.0–2.2 m [10]	42.41 s
3	7.8–7.0 m [16]; 6.55–6.85 m [2]	3.78 s [3]; 3.0–1.0 m [15] [c]; 0.88 s [3]	
4	7.8–7.5 m [4]	2.6–0.8 m [33]	50.56 s
5	8.0–7.6 m [4]	2.6–1.0 m [33]	52.12 s
6	7.8–7.3 m [30]	3.48 s [1] [b]; 2.03 q [4] $J = 7.0$; 0.90 t [6] $J = 7.4$	32.84 s
7a	8.71 s [1]; 8.29 s [1]; 8.25 s [1]; 7.88–7.55 m [2]; 7.40–7.10 m [2]	9.47 s [2] [b]; 2.5–1.0 m [33]	56.24 s
7b	8.97 s [1]; 8.22 s [1]	13.07 s [1] [b]; 3.3 s [2] [b]; 2.6–1.0 m [33]	
8	8.6 s [1]; 7.85–7.45 m [17]	3.3 s [1] [b]	38.26 s
9a	8.21 s [2]; 7.9–7.6 m [4]; 7.4–7.1 m [4]; 7–6.75 m [2]	12.5 s,br [2] [b]; 3.69 s [3]; 2.3–0.8 m [33]	
9b	6.9–6.75 m [2]	3.61 s [3]; 2.3–0.9 m [33]	56.39 s
9c	7.85 s [1]; 7.13 s [2]; 6.90–6.75 m [2]	3.65 s [3]; 2.3–0.9 m [33]	
10	8.0–7.35 m [15]; 7.2–6.73 m [4]	2.22 s [3]	38.93 s
11	8.38–7.95 m [4]; 7.60–7.10 m [6]	2.5–0.9 m [33]	62.29 d, $J = 7.06$; 56.98 d, $J = 7.76$
12	6.90 s [2]	6.6–5.4 s, br [1] [b]; 2.65–0.9 m [33]	56.62 s
13	7.8–7.35 m		39.12 s
14	8.82 s [2]; 8.15 s [1]; 7.9–7.35 m [15]; 7.35–7.25 m [2]	[d]	30.98 s

[a] NMR spectra were recorded on a Varian or Bruker instrument operated at 90 MHz for ^{1}H and 80 MHz for ^{31}P. The solvent was DMSO for **7b** and **8**, but for all the others $CDCl_3$ was used. The reference was Me_4Si or external 85% H_3PO_4; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad. Coupling constants in Hz. [b] The signal disappears on deuteration. [c] OH not observed. [d] NH not observed.

molecule (x,y,z) and the equivalent ones, $x,1+y,z$; $1/2-x,1/2+y,1/2-z$; $-1/2-x,1/2+y,1/2-z$; $-x,-y,-z$; and $-x,-y,1-z$, are normal Van der Waals contacts.

The molecules of benzimidazole are hydrogen-bonded, the first to the 3-nitrogen of the 1-methylimidazole-2-thiolato ligand, the second to the other nitrogen of the first. The values of the N ··· H distances in the two N ··· H bonds, 1.92(5) and 1.64(6) Å, respectively, and the intermolecular N ··· N separations, 2.81(1) and 2.86(1) Å, respectively, show that hydrogen bonding in our molecule is strong, even stronger than that in the crystal of free benzimidazole, for which the N ··· H and N ··· N distances are 2.00(4) and 2.856(5) Å, respectively [5]. The type of hydrogen bonding found here, between an *N*-unsubstituted azole and an *N*-aurated azole, was previously suggested to be present in another gold(I) complex, namely $Ph_3PAu(Im\text{-}N)(ImH)$ [1]. The present X-ray crystal structure determination is not only con-

Table 4

^{31}P NMR shifts of $(R_3P)Au(ligand)$ compounds used for comparisons [a]

δ(ppm)	Ligand	Ref.
	P = triphenylphosphine	
	P–Au–O arrangement	
24.5	ONO	24
24.6	OAc	24
25.0	ONO_2	24
27.0	O-t-Bu	24
	P–Au–N arrangement	
28.85	1,2,4-triazolato	25
29.05	benzimidazolato	25
29.15	benzotriazolato	25
29.2	2-pyridonato	26
29.25	5-nitroindazolato	25
29.65	4-phenylimidazolato	25
30.5	μ-(3,5-$(CF_3)_2$-pyrazolato-*N*,*N*′)	27
30.7	imidazolato	1
30.9	3,5-$(CF_3)_2$-pyrazolato	27
31.0	imidazole	this work
31.7	2-phenylimidazole	1
32.1	2-methylimidazole	1
32.7	phthalimidato	28
	P–Au–C (pzO = pyrazolone)	
34.6	1-(*p*-Br-phenyl)-3-Me-4,4′-$(LAu)_2$-pzO-5	2
34.6	1,3-Me_2-4,4′-$(LAu)_2$-pzO-5	2
34.9	1-(*p*-tosyl)-3-Me-4,4′-$(LAu)_2$-pzO-5	2
35.6	1-Ph-3-Me-4,4′$(LAu)_2$-pzO-5	2
35.8	*p*-tolyl	29
	P–Au–S	
38.3	2-thiolato-5-CF_3-pyridyl	this work
38.9	S(*m*-tolyl)	this work
	P–Au–C(*sp* hybrid)	
41.2	C≡C–CF_3	30
41.8	C≡C–Me	30
42.3	C≡C–Ph	this work
42.4	C≡C(OH)$(CH_2)_5$	this work
	P-tricyclohexylphosphine	
50.5	phthalidimato	this work
52.1	saccharinato	this work
57.0	S(S)PPh_2	this work

[a] $CDCl_3$ solution.

sistent with that suggestion, but also indicates that such bonding might be relevant in the interaction of gold containing drugs with NH groups belonging to purines or to proteins. The most important of these drugs are rather complicated gold(I) thiolates, $(RSAu)_x$ or $RSAuPR''_3$: in these RSH can be thioglucose (solganal) or disodium thiomalate (myocrysine), R′SH can be tetraacetylthioglucose and R″ ethyl (auranofin or ridaura) [6,7]. In all these species, there are plenty of sites available for

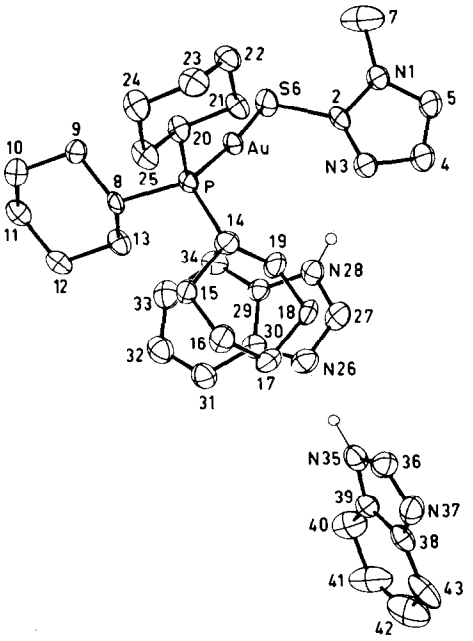


Fig. 1. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 30% of the electron density. Hydrogen atoms are omitted for clarity, except those involved in hydrogen bonds. Carbon atoms are indicated only by numbers.

hydrogen bonding, such as oxygen atoms, and it may thus be significant that some commercial samples of solganal or of myocrysine were found to contain water and, with the latter, also glycerol [8].

The slight distortion from linearity of the S–Au–P angle, 172.0(1)°, cannot be attributed to the effect of a gold–gold interaction, as often the case, because here the Au · · · Au separation is 6.3266(6) Å. Similar values were reported for all the available P–Au–S systems: 173.6(1)° for auranofin [9], values ranging from 171.9(3) to 176.9(3)° (av. 174.5(3)°) for the cation $[(Ph_3PAu)_3S]^+$ [10] or from 169.4(3) to 175.3(3)° (av. 171.5(3)°) for the cation $[\{(Ph_3Au)_2S)\}_2Au]^+$ [11], and 173.5° for $(Et_2PCH_2CH_2SAu)_2$ [12].

The gold–sulphur distance, 2.331(3) Å, is comparable with that in five other compounds containing the P–Au–S linkage (see Table 6); it is also one of the longest Au–S distances reported, in keeping with a strong *trans*-influence of the phosphine ligand, much stronger than that of a chloride or of a bromide. A significant, but weaker, *trans*-influence is also evident from the Au–P distance, 2.292(2) Å. This last value is comparable with those for other compounds having the P–Au–S arrangement (see Table 6); it is slightly smaller than those reported for the compounds having the P–Au–X arrangement when X = P, but is rather larger than those found when X is O, Cl, or N, where O represents acetate or benzoate, Cl terminal or bridging chloride, and N a pyrazole-*N*, a pyridonato-*N*, or an imidazolato-*N* ligand. The same order of *trans*-effects emerges from the available ^{31}P NMR spectra of several R_3PAuX complexes (Table 4).

While the Au–S and Au–P bond distances in our compound are normal, the corresponding parameters are smaller in auranofin [9], and for each of them the

Table 5. Selected interatomic distances (Å) and bond angles (°) (with e.s.d.'s in parentheses)

In the coordination sphere			
Au–P	2.292(2)	P–Au–S(6)	172.0(1)
Au–S(6)	2.331(3)		
In the 1-methyl-imidazolyl-2-thiolato ligand			
N(1)–C(2)	1.38(1)	C(2)–N(1)–C(7)	125.0(9)
N(1)–C(7)	1.50(2)	C(5)–N(1)–C(7)	129.5(8)
C(2)–N(3)	1.29(1)	N(1)–C(2)–N(3)	111.3(9)
C(2)–S(6)	1.75(1)	N(1)–C(2)–S(6)	121.0(8)
N(3)–C(4)	1.40(1)	N(3)–C(2)–S(6)	127.7(7)
C(4)–C(5)	1.33(2)	C(2)–N(3)–C(4)	106.2(8)
C(5)–N(1)	1.36(2)	N(3)–C(4)–C(5)	108.7(9)
Au–S(6)–C(2)	106.6(3)	C(4)–C(5)–N(1)	108.1(9)
C(2)–N(1)–C(5)	105.6(8)		
In the phosphine ligand			
P–C(8)	1.86(1)	C(14)–P–C(20)	106.0(5)
P–C(14)	1.85(1)	P–C(8)–C(9)	112.1(6)
P–C(20)	1.85(1)	P–C(8)–C(13)	109.0(6)
Au–P–C(8)	108.5(3)	P–C(14)–C(15)	114.5(7)
Au–P–C(14)	114.0(3)	P–C(14)–C(19)	114.1(7)
Au–P–C(20)	112.1(3)	P–C(20)–C(21)	110.6(7)
C(8)–P–C(14)	109.9(4)	P–C(20)–C(25)	111.4(6)
C(8)–P–C(20)	106.1(4)		
In the cyclohexyl rings			
Weighted average of bond distances and endocyclic angles:			
C(P)–C_{ortho}	1.541(10)	C_{ipso}	111.7(5)
C_{ortho}–C_{meta}	1.544(9)	C_{ortho}	109.9(8)
C_{meta}–C_{para}	1.534(15)	C_{meta}	112.4(1.3)
		C_{para}	109.8(7)
In the benzimidazole molecules			
N(26)–C(27)	1.32(1)	C(27)–N(28)–H(28)	111(3)
C(27)–N(28)	1.34(1)	C(29)–N(28)–H(28)	139(3)
N(28)–H(28)	0.93(5)	N(28)–C(29)–C(30)	105.3(9)
N(28)–C(29)	1.39(1)	C(29)–C(30)–N(26)	109.9(9)
C(29)–C(30)	1.40(1)	C(29)–C(30)–C(31)	119.1(1.0)
C(30)–N(26)	1.38(1)	C(30)–C(31)–C(32)	117.8(1.0)
C(30)–C(31)	1.40(2)	C(31)–C(32)–C(33)	121.5(1.1)
C(31)–C(32)	1.37(2)	C(32)–C(33)–C(34)	123.2(1.2)
C(32)–C(33)	1.38(2)	C(33)–C(34)–C(29)	115.5(1.0)
C(33)–C(34)	1.37(2)	C(34)–C(29)–C(30)	122.9(9)
C(34)–C(29)	1.39(2)	C(36)–N(35)–C(39)	104.9(9)
N(35)–H(35)	1.23(6)	C(39)–N(35)–H(35)	115(2)
N(35)–C(36)	1.34(2)	C(36)–N(35)–H(35)	138(3)
C(36)–N(37)	1.25(2)	N(35)–C(36)–N(37)	115.7(1.1)
N(37)–C(38)	1.35(2)	C(36)–N(37)–C(38)	104.0(1.1)
C(38)–C(39)	1.37(2)	N(37)–C(38)–C(39)	111.1(1.0)
C(39)–C(40)	1.38(2)	C(38)–C(39)–N(35)	104.2(9)
C(40)–C(41)	1.44(2)	C(38)–C(39)–C(40)	123.6(1.1)
C(41)–C(42)	1.40(3)	C(39)–C(40)–C(41)	114.9(1.3)
C(42)–C(43)	1.37(2)	C(40)–C(41)–C(42)	120.4(1.5)
C(43)–C(38)	1.39(2)	C(41)–C(42)–C(43)	122.4(1.7)
C(27)–N(26)–C(30)	104.1(9)	C(42)–C(43)–C(38)	117.0(1.6)
N(26)–C(27)–N(28)	114.5(1.0)	C(43)–C(38)–C(39)	121.7(1.1)
C(27)–N(28)–C(29)	106.2(8)		

Table 5 (continued)

The hydrogen bond			
H(28) · · · N(3)	1.92(5)	N(28)–H(28) · · · N(3)	161(5)
H(35) · · · N(26)	1.64(6)	N(35)–H(35) · · · N(26)	168(4)

shortening is nearly the same: 0.038 Å [= 2.331(2) − 2.293(3)] and 0.033 Å [= 2.292(2) − 2.259(3)]. No reason can be given at present for the substantial shortening of both bonds in this drug.

The value of the Au–S–C angle in our compounds, 106.6(3)°, is in line with most of the values reported, the lowest and the highest of which are likely to be associated with ring formation and/or Au · · · Au interaction: 103.8 and 113.7(8)° in $(Et_2PCH_2CH_2SAu)_2$ [12] and in $(MeCS_2Au)_4$ [13].

The least-squares planes of the imidazole ligand and of the benzimidazole rings and related data are given in Table 7. The probability that the ligand ring is non planar is $P = 76.1\%$, but the biggest displacement from the best plane is 0.010(12) Å in the case of the C(4); the 1-methyl carbon lies −0.009(18) Å below it and the

Table 6

Comparison of distances and angles in the coordination sphere

Compound	X–Au–S	Au–S (Å)	X–Au–S (°)	Au–X (Å)	Au–S–C (°)	Ref.
$BrAuS(CH_2Ph)_2$	Br–Au–S	2.275(4)	178.7(1)	2.387(2)	104.9(5) 107.6(5)	31
$ClAuS(CH_2Ph)_2$	Cl–Au–S	2.290(9)	172.3(3)	2.222(9)	105(1) 106(1)	31
$[ClAu(Ph)SCH_2]_2$	Cl–Au–S	2.258(11)	177.8(4)	2.329(8)	106.0(12) 105.9(11)	32
	Cl–Au–S	2.260(12)	173.5(4)	2.293(10)	104.7(15) 110.2(12)	32
$\{[(Ph_3PAu)_3S]\}_2(PF_6)_2$	P–Au–S	2.327(7) [a]	174.5(3) [a]			10
Auranofin	P–Au–S	2.293(3)	173.6(1)	2.259(3)	105.6(3)	9
$\{Au[S(AuPPh_3)_2]_2\}Me_3SnCl_2$	P–Au–S	2.322(6) [a]	171.5(3) [a]	2.257(6) [a]		11
	S–Au–S	2.319(7) 2.331(7)	179.0(3)			11
$(Cy_3P)Au(1\text{-}Me\text{-}2\text{-}S\text{-}im)\cdot 2LH$	P–Au–S	2.330(3)	172.0(1)	2.292(3)	106.4(4)	This work
$Ph_3PAuS(S)CNEt_2$	P–Au–S	2.338(3)	175.7(1)	2.251(3)		33
$(Et_2PCH_2CH_2SAu)_2$	P–Au–S	2.31	173.5	2.27	103.8	12
$Na_3[Au(S_2O_3)_2]\cdot 2H_2O$	S–Au–S	2.265(6) 2.279(6)	176.5(2)			34
	S–Au–S	2.280(3) 2.272(3)	176.5(2)			35
$(Au[S{=}C(NHCH_2)_2]_2\cdot H_2O)Cl$	S–Au–S	2.278(9) 2.279(8)	167.1(2)		109.8(8) 111.2(7)	36
$[Au(S_2CNPr_2)]_2$	S–Au–S	2.28(2)	180(1)		108(2)	37
$\{Au_2[S_2P(O\text{-}i\text{-}Pr)_2]_2\}_n$	S–Au–S	2.28(3) [a]	174(4) [a]			38
$\{(AuI_2)[Au(THT)_2]\}_n$	S–Au–S	2.306(7) 2.335(6)	172.4(2)		109(1) [a] 108(1) [a]	39
$(MeCS_2Au)_2$	S–Au–S	2.296(7) [a]	167.7(2) [a]		113.7(8) [a]	13

[a] Average values.

Table 7

Least-squares planes

Equation [a] χ^2, P	Atoms	Displacements (Å)
$-0.8512X' + 0.4403Y - 0.2856Z' + 1.1366 = 0$	N(1)*	−0.004(9)
	C(2)*	0.009(10)
	N(3)*	−0.008(9)
	C(4)*	0.010(12)
	C(5)*	−0.003(13)
$\chi^2 = 2.90$ ($n = 2$), $P = 76.1\%$		
$-0.8073X' + 0.0157Y - 0.5899Z' + 1.6958 = 0$	N(26)*	0.007(9)
	C(27)*	−0.007(12)
	N(28)*	−0.000(8)
	C(29)*	0.004(9)
	C(30)*	−0.008(10)
$\chi^2 = 1.78$ ($n = 2$), $P = 57.7\%$		
$-0.8131X' - 0.0027Y - 0.5821Z' + 1.7069 = 0$	C(29)*	0.008(15)
	C(30)*	0.007(10)
	C(31)*	−0.007(11)
	C(32)*	0.001(12)
	C(33)*	0.002(11)
	C(34)*	0.001(11)
$\chi^2 = 1.28$ ($n = 3$), $P = 26.6\%$		
$0.0761X' - 0.2475Y - 0.9659Z' + 4.8587 = 0$	N(35)*	−0.004(15)
	C(36)*	0.001(12)
	N(37)*	0.000(9)
	C(38)*	−0.001(9)
	C(39)*	0.001(9)
$\chi^2 = 0.03$ ($n = 2$), $P = 1.6\%$		
$0.0661X' - 0.2323Y - 0.9704Z' + 4.8924 = 0$	C(38)*	−0.012(9)
	C(39)*	0.011(9)
	C(40)*	−0.003(10)
	C(41)*	−0.013(13)
	C(42)*	0.014(15)
	C(43)*	0.005(11)
$\chi^2 = 5.58$ ($n = 3$), $P = 85.8\%$		

[a] Transformation matrix from monoclinic X,Y,Z to orthogonal X',Y,Z' coordinates:

$$\begin{pmatrix} 1 & 0 & -\cos\beta^* \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta^* \end{pmatrix}$$

Starred atoms are included in the calculation of the plane.

sulphur atom 0.062(3) Å above it. The distances and angles in some compounds are affected by a rather big e.s.d.; nevertheless some relationships are evident when this and some other imidazoles are considered, namely imidazole [14], 4,5-di-t-butylimidazole [15], 1-(Cy_3PAu)-2-iso-propyl-imidazole [16], or bis(imidazol-1-yl)cobalt(II) [17] (see Table 8). These are: (1) N(1)–C(2) (1.38(1) Å) or C(5)–N(1) (1.36(2) Å), or N(3)–C(4) (1.40(1) Å) is longer than C(2)–N(3) (1.29(1) Å), which is written as a double bond in the classical formula of imidazole; (2) C(5)–N(1)–C(2) (105.6(8)°) is smaller than N(1)–C(2)–N(3) (111.3(9)°).

Table 8

Comparison of the distances and angles within the imidazole ring

Compound	Distances (Å)					Internal angles (°)				
	N(1)–C(2)	C(5)–N(1)	C(2)–N(3)	N(3)–C(4)	C(4)–C(5)	N(1)	C(2)	N(3)	C(4)	C(5)
[a]	1.38(1)	1.36(2)	1.29(1)	1.40(1)	1.33(2)	105.6(8)	111.3(9)	106.2(8)	108.7(9)	108.1(9)
[b]	1.349	1.369	1.326	1.378	1.358	107.2	111.3	105.4	109.8	106.3
[c]	1.350	1.387	1.318	1.396	1.401	108.37	111.72	106.18	108.97	104.73
	1.347	1.388	1.321	1.393	1.398	108.04	112.01	105.89	109.15	104.91
[d]	1.398(7)	1.362(9)	1.318(9)	1.370(10)	1.350(10)	104.1(5)	113.0(6)	103.7(6)	111.5(7)	107.6(6)
[e]	1.329(7)	1.368(9)	1.318(8)	1.358(8)	1.345(10)	103.0(5)	115.2(5)	103.7(5)	109.1(6)	109.0(6)

[a] (Cy_3P)Au(i-Me-2-thiolatoimidazole)·2benzimidazole (this work). [b] Imidazole [14]. [c] 4,5-Di-t-butylimidazole [15]. [d] 1-(Tri-cyclohexylphosphinegold)-2-(iso-propyl)imidazole [16]. [e] Bis(imidazol-1-yl)cobalt(II) [17].

Table 9

Final coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses) for the non-hydrogen atoms

Atom	x	y	z	B (Å^2)
Au	0.19377(2)	0.30278(4)	0.20516(2)	3.56(1)
P	0.2234(1)	0.2639(2)	0.3398(1)	3.57(7)
N(1)	0.1597(4)	0.2389(8)	−0.0657(4)	4.9(3)
C(2)	0.1411(5)	0.2463(9)	0.0150(5)	3.7(3)
N(3)	0.1083(5)	0.1546(8)	0.0370(5)	4.7(3)
C(4)	0.1025(6)	0.0839(10)	−0.0322(6)	5.4(3)
C(5)	0.1345(7)	0.1352(11)	−0.0935(6)	6.0(4)
S(6)	0.1611(2)	0.3688(2)	0.0742(1)	4.81(8)
C(7)	0.1993(10)	0.3298(15)	−0.1101(6)	11.1(7)
C(8)	0.1890(5)	0.3815(9)	0.4042(5)	3.6(3)
C(9)	0.2282(5)	0.4951(9)	0.3937(6)	4.2(3)
C(10)	0.1957(6)	0.5889(9)	0.4469(7)	5.1(3)
C(11)	0.1177(6)	0.6066(10)	0.4306(6)	4.7(3)
C(12)	0.0808(5)	0.4895(10)	0.4399(6)	4.8(3)
C(13)	0.1111(5)	0.3975(9)	0.3825(6)	4.2(3)
C(14)	0.1921(6)	0.1224(10)	0.3759(6)	4.8(3)
C(15)	0.1674(6)	0.1225(9)	0.4658(6)	5.2(3)
C(16)	0.1409(9)	0.0049(12)	0.4897(7)	8.2(5)
C(17)	0.0932(6)	−0.0557(11)	0.4329(8)	6.5(4)
C(18)	0.1202(6)	−0.0562(9)	0.3450(6)	5.1(3)
C(19)	0.1410(7)	0.0642(11)	0.3173(6)	6.4(4)
C(20)	0.3185(5)	0.2632(9)	0.3597(6)	4.2(3)
C(21)	0.3528(5)	0.1756(10)	0.3048(6)	4.8(3)
C(22)	0.4330(5)	0.1822(11)	0.3179(6)	5.4(3)
C(23)	0.4539(5)	0.1616(12)	0.4112(8)	6.7(4)
C(24)	0.4191(6)	0.2518(12)	0.4643(7)	6.2(4)
C(25)	0.3377(5)	0.2425(10)	0.4532(5)	4.9(3)
N(26)	−0.0433(5)	0.0537(8)	0.2613(5)	5.1(3)
C(27)	−0.0047(6)	0.0444(10)	0.1963(7)	5.3(4)
N(28)	0.0146(4)	0.1457(8)	0.1645(5)	4.4(2)
C(29)	−0.0131(5)	0.2310(9)	0.2132(5)	3.7(3)
C(30)	−0.0484(5)	0.1713(9)	0.2739(6)	4.1(3)
C(31)	−0.0819(6)	0.2348(12)	0.3341(6)	5.5(4)
C(32)	−0.0799(6)	0.3529(13)	0.3293(7)	5.8(4)
C(33)	−0.0454(6)	0.4086(10)	0.2684(7)	5.3(3)
C(34)	−0.0110(5)	0.3510(11)	0.2086(6)	4.7(3)
N(35)	−0.0920(5)	−0.1583(9)	0.3280(5)	5.0(3)
C(36)	−0.0591(6)	−0.2570(13)	0.3488(7)	5.6(4)
N(37)	−0.0971(6)	−0.3420(9)	0.3608(6)	6.0(3)
C(38)	−0.1617(6)	−0.3007(12)	0.3473(5)	4.6(3)
C(39)	−0.1606(5)	−0.1857(10)	0.3265(5)	4.1(3)
C(40)	−0.2194(8)	−0.1205(12)	0.3116(6)	7.5(4)
C(41)	−0.2837(8)	−0.1826(20)	0.3175(8)	9.4(6)
C(42)	−0.2833(9)	−0.3013(23)	0.3360(9)	9.9(7)
C(43)	−0.2235(8)	−0.3617(14)	0.3515(6)	7.3(5)
Hydrogen atoms involved in hydrogen bonds				
H(28)	0.0507(27)	0.1360(47)	0.1293(32)	4.4
H(35)	−0.0783(26)	−0.0640(49)	0.2971(32)	5.0

To evaluate the steric effects of the tri(cyclohexyl)phosphine ligand, the effective cone angle θ as defined by Tolman [18] was calculated. The cone apex, centered on the gold atom, was located 2.292(2) Å from the P atom; the apex angle of the cone, which touches the Van der Waals radii of the outermost atoms ($r = 1.17$ Å for H) turned out to be 170.8, 160.4, 166.0° for H(11a), H(18a) and H(21a), respectively. An effective cone angle similar to that for an unsymmetrical ligand can be obtained by taking the average θ value of the outermost H atoms of the three cyclohexyl groups, viz. 165.7°, which compares with the model-based value of 179 ± 10°, and with the value of 170° based on the degree of substitution of CO by $P(c\text{-}C_6H_{11})_3$ from $Ni(CO)_4$ [19]; a similar cone angle of 163.9° was found in $1\text{-}(C_6H_{11})_3PAu\text{-}2i\text{-}Pr\text{-}imidazole \cdot C_6H_6$ [16]. All three cyclohexyl groups are in a chair conformation.

X-Ray analysis. A crystal of approximate dimensions 0.19, 0.18, 0.24 mm was used for data collection. Accurate unit-cell parameters were obtained by a least-squares fit of 2θ values for 25 reflections measured on a Philips PW1100 computer-controlled single-crystal diffractometer with graphite-monochromated Mo-K_α radiation at the Dipartimento di Chimica Organica, University of Padua (Italy). The intensities of 6619 independent reflections were collected at room temperature within the angular range $2 \leq \nu \leq 25°$, using the $\theta/2\theta$ scan technique (scan width = 1.0°, scan speed = 0.02° s^{-1}). The intensities of three standard reflections were monitored every 180 min and showed no significant variation. The intensities were corrected for Lorentz and polarization effects and for absorption (minimum and maximum absorption factors 0.9938 and 1.7707) [20]. An approximate absolute scale and a mean thermal factor were determined by Wilson's method [21]. A total of 3540 reflections having $I \geq 3\sigma(I)$ were considered to have observable intensity and used in the structure analysis.

Crystal data $C_{36}H_{50}N_6PSAu$; FW = 826.88; monoclinic; a 19.312(7), b 11.563(5), c 16.305(6) Å, β 92.27(2)°; V 3638(2) Å^3; $Z = 4$; D_c 1.51 g cm^{-3}; $F(000) = 1672$; λ(Mo-K_α) 0.7107 Å; μ(Mo − K_α) 43.1 cm^{-1}. Systematic absences: $(0k0)$, k odd; $(00l)$, l odd; $(h0l)$, $h + l$ odd. Space group $P2_1/n$.

Structure determination and refinement. The structure was solved by Patterson and Fourier methods. The positional and isotropic thermal parameters of the gold atom, derived from the three-dimensional Patterson map, were refined to $R = 0.259$ in three cycles of full-matrix least-squares refinement. All the remaining non-hydrogen atoms were located from a three-dimensional difference Fourier synthesis phased on the Au atom. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters reduced R to 0.074. The hydrogen atoms were located on a difference Fourier map and were not refined, except for H(28) and H(35) involved in hydrogen bonds; these were included in the calculations with same isotropic thermal parameters as their bonded atoms. Refinement was terminated as $R = 0.049$ ($R_w = 0.060$). The average shift/e.s.d. ratio in the final refinement cycle was 0.52 in the positional parameters and 0.32 in the thermal parameters of the non-hydrogen atoms. At all stages of the analysis the observed reflections were given unit weights, since the use of weights $\sigma^{-2}(|F_o|)$ led to the same results but also to some non-positive definite thermal factors.

The atomic scattering factors for non-hydrogen atoms were taken from the International Tables for X-ray Crystallography [22] and those for hydrogen atoms from Stewart et al. [23]. Anomalous dispersion effects were included in the scattering factors. The final atomic coordinates are given in Table 9. Thermal parameters,

hydrogen coordinates, bond lengths and angles for hydrogen atoms, and lists of structure factors can be obtained from B. Bovio.

Experimental

The compounds **1–14** were prepared by methods A or B, of which the following examples are typical.

Method A

To a stirred solution of *m*-thiocresol (0.048 g, 0.38 mmol) in (methanol) (20 ml) a solution of 1-(triphenylphosphinegold(I))imidazole (0.20 g, 0.38 mmol) in the same solvent (5 ml) was added dropwise. A white solid, that began to separate almost immediately, was filtered off after 1 h of additional stirring at room temperature, and then washed with hexane, to give **10**, which gave a satisfactory analysis.

Method B

To a methanol solution (20 ml) of *N*-methyl-2-mercaptoimidazole (0.15 g, 1.31 mmol) were added a solution of sodium hydroxide (0.052 g, 1.31 mmol) in the same solvent (5.25 ml) and Ph_3PAuCl (0.673 g, 1.31 mmol). After 5 h stirring at room temperature the solution was evaporated to dryness, and the residue crystallized from benzene/hexane to give **9b**, which gave a satisfactory analysis.

Acknowledgments

We thank Professor V. Busetti (Dipartimento di Chimica Organica, University of Padua, Italy) for the diffractometer data collection and Dr. W. Bos for sending us a copy of his doctoral thesis. Financial support was provided by "Ministero della Pubblica Istruzione" and by "Consiglio Nazionale delle ricerche".

References

1 F. Bonati, M. Felici, B.R. Pietroni and A. Burini, Gazz. Chim. Ital., 112 (1982) 5.
2 F. Bonati, A. Burini, B.R. Pietroni and M. Felici, J. Organomet. Chem., 273 (1984) 275.
3 P.G. Jones, Acta Crystallogr., C40 (1984) 1320.
4 C.K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, U.S.A. (1965).
5 C.J. Dik-Edixhoven, H. Schenk and H. van der Meer, Cryst. Struct. Comm., 2 (1973) 23.
6 R.V. Parish and S.M. Cottrill, Gold. Bull., 20 (1987) 3.
7 D.H. Brown and W.E. Smith, Chem. Soc. Rev., 8 (1980) 217.
8 D.T. Hill, B.M. Sutton, A.A. Isab, T. Razi, P.J. Sadler, J.M. Trooster and G.H.M. Calis, Inorg. Chem., 22 (1983) 2936.
9 D.T. Hill and B.M. Sutton, Cryst. Struct. Comm., 9 (1980) 679.
10 P.G. Jones, G.M. Sheldrick and E. Haedicke, Acta Crystallogr., B 36 (1980) 2777.
11 P.G. Jones, C. Lensch and G.M. Sheldrick, Z. Naturforsch. B, 37 (1982) 141.
12 W.S. Crane and H. Beall, Inorg. Chim. Acta, 31 (1978) L469.
13 B. Chiari, O. Piovesana, T. Tarantelli and P.F. Zanazzi, Inorg. Chem., 24 (1985) 366.
14 S. Martinez-Carrera, Acta Crystallogr., 20 (1966) 783.
15 G.J. Visser and A. Vos, Acta Crystallogr., B27 (1971) 1802.
16 B. Bovio, F. Bonati, A. Burini and B.R. Pietroni, Z. Naturforsch. B, 39 (1984) 1747.
17 M. Sturm, F. Brandl, D. Engel and W. Hoppe, Acta Crystallogr., B31 (1975) 2369.
18 C.A. Tolman, W.C. Seidel and L.W. Gosser, J. Am. Chem. Soc., 96 (1974) 53.

19 C.A. Tolman, Chem. Rev., 77 (1977) 313.
20 A.C.T. North, D.C. Phillips and F.C. Mathews, Acta Crystallogr., A24 (1968) 351.
21 A.J.C. Wilson, Nature (London), 150 (1942) 152.
22 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
23 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
24 W. Bos, Doctoral Thesis, Nijmegen (1987).
25 F. Bonati, A. Burini, M. Felici and B.R. Pietroni, Gazz. Chim. Ital., 113 (1983) 105.
26 F. Bonati, A. Burini, B.R. Pietroni and B. Bovio, J. Organomet. Chem., 296 (1985) 301.
27 G. Banditelli, A.L. Bandini, F. Bonati, R.G. Goel and G. Minghetti, Gazz. Chim. Ital., 112 (1982) 539.
28 S.J. Berners-Price, M.J. DiMartino, D.T. Hill, R. Kuroda, M.A. Mazid and P.J. Sadler, Inorg. Chem., (1985) 3425.
29 H. Schmidbaur and Y. Inoguchi, Chem. Ber., 113 (1980) 1646.
30 R.J. Cross and M.F. Davidson, J. Chem. Soc., Dalton Trans., (1986) 411; R.J. Cross, M.F. Davidson and A.J. McLennan, J. Organomet. Chem., 265 (1984) C37.
31 J. Straehle, W. Hiller and W. Conzelmann, Z. Naturforsch. B, 39 (1984) 538.
32 M.G.B. Drew and M.J. Riedl, J. Chem. Soc., Dalton Trans., (1973) 52.
33 J.G. Wijnhoven, W.P.J.H. Bosman and P.T. Beurskens, J. Cryst. Mol. Struct., 2 (1972) 7.
34 R.F. Baggio and S. Baggio, J. Inorg. Nucl. Chem., 35 (1973) 3191.
35 H. Ruben, A. Zalkin, M.O. Faltens and D.H. Templeton, Inorg. Chem., 13 (1974) 1836.
36 P.G. Jones, J.J. Guy and G.M. Sheldrick, Acta Crystallogr., B32 (1976) 3321.
37 R. Hesse and P. Jennische, Acta Chem. Scand., 26 (1972) 3855.
38 S.L. Lawton, W.J. Rohrbaugh and G.T. Kokotailo, Inorg. Chem., 11 (1972) 2227.
39 S. Ahrland, B. Noren and A. Oskarsson, Inorg. Chem., 24 (1984) 1330.