

Dinuclear gold(I) and silver(I) derivatives with bridging phosphines containing an imidazole ring; X-ray crystal structure of (1-benzyl-2-imidazolyl)diphenylphosphinegold(I)chloride [☆]

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Abstract

(1-Benzyl-2-imidazolyl)diphenylphosphine [(BzIm)Ph₂P] can act as a monodentate or bidentate ligand to afford mononuclear (BzIm)Ph₂PAuCl (**I**) or dinuclear [μ -(BzIm)Ph₂PAu]₂²⁺2X[−] (X = PF₆[−], BF₄[−] or NO₃[−]) (**IIa,b,c**) derivatives of gold(I). Analogous dinuclear silver(I) derivatives were obtained reacting the ligand [(BzIm)Ph₂P] with AgX salts (X = NO₃[−], BF₄[−]) (**IIIa,b**). In solution the silver complexes show a fluxional behaviour, and two conformers were observed by ³¹P NMR spectroscopy. The structure of compound **I** was established by X-ray crystallography (monoclinic, space group C2/c, *a* = 18.068(2), *b* = 16.576(2), *c* = 15.391(2) Å, β = 117.2(2)°, *Z* = 8). The short intermolecular Au...Au distance of 3.03(2) Å indicates a metal–metal interaction. The ¹⁹⁷Au Mössbauer parameters of compounds **I** and **IIa** are consistent with IR, NMR and crystallographic data.

Keywords: Gold complexes; Imidazole complexes; Silver complexes; Crystal structures

1. Introduction

Imidazoles are both interesting ligands and important biochemical molecules, and their coordination chemistry has been widely studied [1].

We previously reported the synthesis and characterization of mononuclear, trinuclear and polynuclear derivatives containing imidazole rings with N–Au or C–Au bonds [2–4]. Some of the gold(I) derivatives with imidazoles have shown promising anticancer activity in vitro [5].

Another exciting topic in gold chemistry is the synthesis and reactivity of dinuclear gold derivatives containing bridging ligands [6]. Much work has been done in this field using bidentate ligands, especially bisphosphines [7] or phosphorus ylides [8]. In contrast, little is known about dimeric gold derivatives with phosphines containing heterocycles [9].

In view of this we decided to use a phosphine containing an imidazole ring to obtain cationic, dimeric derivatives of gold(I) and silver(I).

2. Experimental

Elemental analyses were carried out on a Carlo Erba 1106 elemental microanalyzer. ¹H and ³¹P{H} NMR spectra were recorded (unless specified otherwise) in deuterated DMSO solution on a Varian VXR-300 instrument at 300 MHz or a Varian Gemini 200 instrument at 200 MHz, using SiMe₄ or H₃PO₄ 85% as the internal standard. Chemical shifts are reported as δ in units of parts per million (ppm); coupling constants are reported in hertz (Hz). The following abbreviations are used: s, singlet; t, triplet; d, doublet; dd, double doublet; m, multiplet; br, broad. Infrared spectra were recorded in the range 4000–200 cm^{−1} (reporting only bands in the range 600–200 cm^{−1}) on a Perkin-Elmer 1310 spectrophotometer using Nujol mulls in sodium chloride or polyethylene windows (vs, very strong; s, strong; m, medium; w, weak). Conductivities were mea-

[☆] This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Dinitrogen atmosphere was always used. The products I-III (Fig. 1) were obtained by carrying out the reactions in the dark. THF was dried using sodium/benzophenone and freshly distilled under dinitrogen prior to use.

To a stirred THF solution (10 ml) of 1-benzylimidazole (0.31 g, 1.97 mmol) cooled at $-40\text{ }^{\circ}\text{C}$, a 2.5 M hexane solution of butyllithium (0.8 ml, 1.97 mmol) was added. After 1.5 h, Ph_2PCl (0.4 ml, 1.97 mmol) was introduced. The mixture was stirred at room temperature until the colour of the solution turned from orange to yellow (about half an hour); then it was adsorbed, under dinitrogen, on silica gel (8 g) and evaporated to dryness (*attention*: until the reaction mixture is adsorbed on silica gel, the phosphine ligand is easily oxidized to the phosphine oxide, reducing the yield greatly). The powder obtained was loaded on a silica gel (50 g) chromatography column, washed with cyclohexane (300 ml) and eluted with a cyclohexane/acetoacetate (50:50) mixture,

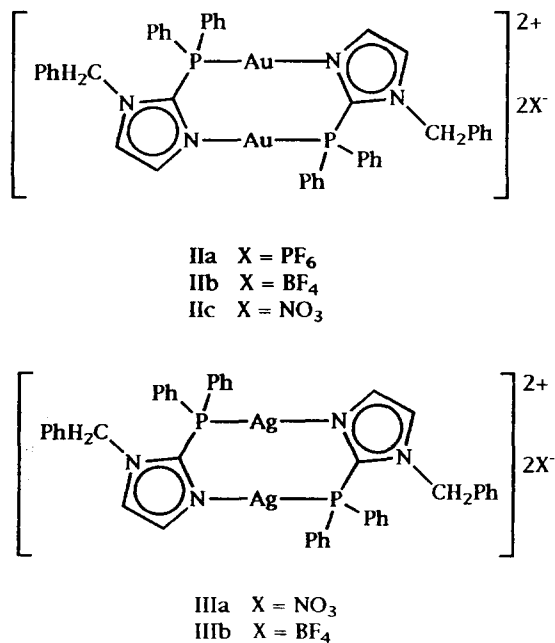


Fig. 1. Scheme of the compounds studied.

Anal. Calc. for $C_{22}H_{19}N_2P$: C, 77.18; H, 5.59; N, 8.18. Found: C, 77.05; H, 5.88; N, 8.11%. 1H NMR: δ 5.48 (d, 2H, $^4J(H-P)=2.34$ Hz), 7.08–7.65 (m, 17H). ^{31}P NMR ($CDCl_3$): δ -32.63 (s). IR: 618 s, 574 w, 552 w, 542 w, 510 s, 508 s, 465 m, 458 m, 420 w, 285 s.

To a stirred THF solution (15 ml) of the ligand [(BzIm)Ph₂P] (0.40 g, 1.18 mmol) cooled at 0 °C chloro(triphenylarsine)gold(I) (0.637 g, 1.18 mmol) was added. After half an hour the solution obtained was evaporated to dryness to give an oily crude compound. This was washed with hexane, and the solid obtained was crystallized at 4 °C from dichloromethane (5 ml)/hexane (3 ml) to give the analytical sample as a colourless crystalline solid (m.p. 165–67 °C). Yield 79%.

Anal. Calc. for $C_{22}H_{19}N_2PAuCl$: C, 45.97; H, 3.33; N, 4.87. Found: C, 46.23; H, 3.38; N, 4.76%. 1H NMR (δ 5.70 (s, 2H), 6.91–6.80 (m, 2H), 7.08–7.16 (m, 3H), 7.31 (t, 1H, $^3J(H-H) = ^4J(H-P) = 1.2$ Hz), 7.44–7.60 (m, 10H), 7.73 (dd, 1H, $^3J(H-H) = 1.2$ Hz, $^4J(H-P) = 2.2$ Hz). ^{31}P NMR ($CDCl_3$): δ 10.67 (s). IR: 616 s, 577 w, 547 vs, 524 s, 479 m, 459 m, 448 w, 315 m, 308 m, 285, s. Conductivity: $\lambda(DMSO) = 20 \Omega^{-1} cm^2 mol^{-1}$; does not conduct in CH_3CN solution.

To a stirred THF solution (10 ml) of the gold complex **I** (0.324 g, 0.56 mmol) cooled at 0 °C, a solution of AgPF₆ (0.171 g, 0.56 mmol) in the same solvent (4 ml) was added dropwise. Immediately, a white precipitate containing AgCl and the product was formed. After half an hour the reaction mixture was evaporated to dryness. The residue was extracted with CH₃CN (20 ml) and crystallized by slow diffusion of ethyl ether to give the analytical sample as a white microcrystalline solid (m.p. > 260 dec.). Yield 75%.

Anal. Calc. for $C_{44}H_{38}N_4Au_2P_4F_{12}$: C, 38.61; H, 2.80; N, 4.09. Found: C, 38.85; H, 2.99; N, 4.25%. 1H NMR: δ 5.22 (s, 2H), 6.44 (d, 2H), 7.20 (t, 2H), 7.32 (t, 1H), 7.53–7.69 (m, 6H), 7.80 (dd, 4H), 8.07 (s, 2H). ^{31}P NMR: δ 19.03 (s). IR: 618 s, 588 w, 557 vs, 547 s, 517 w, 478 w, 458 w, 285 s. Conductivity: $\lambda = 310 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Compound **IIb** was synthesized in a way similar to that reported for **IIa**, using AgBF_4 as the silver salt (m.p. 250–52 °C dec.). Yield 70%.

Anal. Calc. for $C_{44}H_{38}N_4Au_2P_2B_2F_8$: C, 42.20; H, 3.06; N, 4.47. Found: C, 42.12; H, 3.20; N, 4.36%. 1H NMR:

δ 5.22 (s, 2H), 6.44 (d, 2H), 7.20 (t, 2H), 7.32 (t, 1H), 7.53–7.69 (m, 6H), 7.80 (dd, 4H), 8.07 (s, 2H). ^{31}P NMR: δ 19.02 (s). IR: 618 s, 594 w, 582 w, 551 vs, 520 m, 472 m, 462 w, 453 w, 285 s. Conductivity: $\lambda = 320 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.5. Preparation of compound **IIc**

Compound **IIc** was synthesized as reported for **IIa**, using AgNO_3 as the silver salt and crystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ (m.p. 202–4 °C dec.). Yield 58%.

Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{N}_6\text{Au}_2\text{P}_2\text{O}_6$: C, 43.94; H, 3.18; N, 6.99. Found: C, 43.67; H, 3.31; N, 6.80%. ^1H NMR: δ 5.22 (s, 2H), 6.44 (d, 2H), 7.20 (t, 2H), 7.32 (t, 1H), 7.53–7.69 (m, 6H), 7.80 (dd, 4H), 8.07 (s, 2H). ^{31}P NMR: δ 19.03 (s). IR: 549 s, 521 s, 505 m, 486 m, 456 m, 283 s. Conductivity: $\lambda = 305 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.6. Preparation of compound **IIIa**

To a stirred THF (6 ml) and MeOH (4 ml) solution of the ligand $[(\text{BzIm})\text{Ph}_2\text{P}]$ (0.20 g, 0.58 mmol), AgNO_3 (0.10 g, 0.58 mmol) at room temperature was added. After half an hour the solution was evaporated to dryness; the yellow oil obtained was washed with hexane until the crude solid compound was formed. This was dissolved in CH_3CN (8 ml) and crystallized by slow diffusion of ethyl ether to give the analytical sample as a colourless crystalline solid (m.p. 244–46 °C dec.). Yield 63%.

Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{N}_6\text{Ag}_2\text{P}_2\text{O}_6$: C, 51.58; H, 3.74; N, 8.22. Found: C, 50.38; H, 3.78; N, 7.89%. ^1H NMR: δ 5.18 (s, br, 2H), 6.60 (s, br, 2H), 7.08–7.25 (m, 3H), 7.25–7.61 (m, 11H), 7.67 (s, 1H). ^{31}P NMR: δ -6.6 (m, br). IR: 618 s, 573 w, 550 w, 537 s, 509 m, 470 w, 455 w, 283 s. Conductivity: $\lambda = 302 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

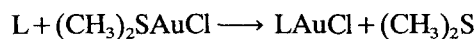
2.7. Preparation of compound **IIIb**

Compound **IIIb** was synthesized in a way similar to that reported above for **IIIa**, using THF as solvent and AgBF_4 as silver salt (m.p. 250–52 °C dec.). Yield 70%.

Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{N}_6\text{Ag}_2\text{P}_2\text{B}_2\text{F}_8$: C, 53.97; H, 4.34; N, 5.24. Found: C, 54.27; H, 4.44; N, 5.22%. ^1H NMR: δ 5.18 (s, br, 2H), 6.60 (s, br, 2H), 7.08–7.25 (m, 3H), 7.25–7.61 (m, 11H), 7.67 (s, 1H). ^{31}P NMR: δ -7.7 (m, br). IR: 552 s, 541 vs, 510 m, 458 m, 385 w, 376 w. Conductivity: $\lambda = 320 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

3. Results and discussion

A general method for obtaining the gold(I) derivatives LAuCl , where L is a tertiary phosphine, consists of the use of $(\text{CH}_3)_2\text{SAuCl}$ as the starting material [10]:



When this procedure was employed to form compound **I** (see Section 2) using (1-benzyl-2-imidazolyl)-diphenylphosphine $[(\text{BzIm})\text{Ph}_2\text{P}]$ as the ligand L, low yields and an impure product containing colloidal gold were obtained. This could be explained by considering that the ligand in $(\text{CH}_3)_2\text{SAuCl}$ can also be displaced by the N donor atom of the bihapto ligand $(\text{BzIm})\text{Ph}_2\text{P}$ to give an unstable N–Au derivative. This trouble was overcome when Ph_3AsAuCl was employed instead of $(\text{CH}_3)_2\text{SAuCl}$.

From the reaction of compound **I** with AgX , where X is a weakly coordinating anion such as PF_6^- , BF_4^- or NO_3^- , the respective dinuclear cationic gold(I) complexes **IIa**, **IIb** and **IIc** were obtained:



The analogous silver(I) derivatives **IIIa** and **IIIb** were prepared by reacting the ligand $(\text{BzIm})\text{Ph}_2\text{P}$ with the AgNO_3 and AgBF_4 salts directly. The different anions X were used in order to obtain crystals of the dimeric gold and silver compounds suitable for X-ray analysis.

Compounds **I–III** were characterized by elemental analysis, conductivity measurements, IR, ^1H and ^{31}P NMR spectroscopy; in addition, Mössbauer investigations (compounds **I**, **IIa**) and an X-ray crystal structure determination (compound **I**) were carried out. The infrared spectra of compounds **I–III** recorded in the range 600–200 cm^{-1} show bands that can be assigned to the bendings of the imidazole ring. Compound **I** also shows peaks at 315 and 308 cm^{-1} , assigned to the symmetric and asymmetric Au–Cl stretching, respectively; these peaks disappear in the infrared spectrum of compound **IIa**, where a strong peak arises at 557 cm^{-1} due to P–F bendings of the anion PF_6^- .

In CH_3CN solution, all the metal derivatives, except **I**, gave conductivity values in the range 302–320 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; these values are within the range expected for 1:2 electrolytes. Compound **I** was only partially dissociated in DMSO solution (see Experimental).

In the ^1H NMR spectra the benzylic CH_2 signal is a doublet ($J = 2.34 \text{ Hz}$) at δ 5.48 in the free ligand, while it is a singlet in the mononuclear (**I**) and dinuclear (**II**) gold derivatives situated at δ 5.70 and δ 5.22, respectively. The ^1H NMR spectra of the dinuclear derivatives **IIa**, **IIb** and **IIc** are exactly alike, indicating that they are not influenced by the different associated anions.

Particular attention was paid to the assignment of the aromatic protons of the ligand moiety. In the ^1H NMR spectrum of compound **IIa** the two protons of the imidazole moieties seem to become isochronous, as in the free ligand and in compound **I** they are always

well separated (e.g., δ 7.31 and δ 7.73 in compound **I**); this observation had to be confirmed. Saturation of benzylic protons at δ 5.22 produced a positive NOE on the doublet at δ 6.44 (*ortho* protons of the benzylic rings); they, in turn, are spin–spin coupled with the two triplets at δ 7.20 and δ 7.32 (*meta* and *para* protons of the same rings). The double doublet at δ 7.80 can be attributed to the *ortho* protons of the benzene rings (coupled with the neighbouring phosphorus atom), while the multiplet at δ 7.61 can be attributed to the *meta* and *para* protons of the same ring. What is left in the spectrum is a singlet at δ 8.07 (2H), which unambiguously must be due to the imidazole protons.

In the ^{31}P NMR spectra of the gold compounds only one singlet is observed; the signal undergoes a downfield shift on going from the free ligand $(\text{BzIm})\text{Ph}_2\text{P}$ (δ –32.63) to the monomeric compound **I** (δ 10.67) to the dimeric compounds **II** (δ 19.03). This behaviour can be attributed to the deshielding ability of the gold atom, which is increased in the cationic complex **II**. In compound **IIa** the expected septet due to the phosphorus atom of the anion PF_6^- was not observed, since it is known to fall at δ –145 [11]. As mentioned above, the family of **II** derivatives shows a singlet in the ^{31}P NMR spectra, which rules out the possibility of having the head-to-head isomers, in which a phosphorus–phosphorus coupling should be present, so only the head-to-tail isomers must be considered.

The silver(I) compounds **IIIa** and **IIIb** show ^1H NMR spectra similar to those of the gold(I) derivatives **IIa**, **IIb** and **IIc**, but the peaks at δ 5.18 and δ 6.60 are broad, suggesting a fluxional behaviour of the eight-membered ring; this hypothesis was confirmed by the ^{31}P NMR spectra, which show an unresolved broad multiplet. For compound **IIIa** a variable-temperature ^{31}P NMR spectrum, in CD_3CN solution, was recorded.

At 253 K the multiplet appears to be a doublet of doublets at δ –4.54 ppm ($J(^{31}\text{P}\text{--}^{107}\text{Ag})=462$ Hz) and at δ 1.68 ppm ($J(^{31}\text{P}\text{--}^{107}\text{Ag})=643$ Hz), revealing the presence of two conformers (Fig. 2). The different behaviour in solution between the gold(I) compounds **II** and the silver compounds **III** can be explained by supposing the presence of stronger intramolecular $\text{Au}\cdots\text{Au}$ interactions in the gold dimers. Interactions between closed-shell d^{10} gold(I) ions have been well established in the solid state as depending on the relativistic effects [12]. The strength of gold–gold interactions has been estimated to be of the same order of magnitude as that of hydrogen bonds (5–15 kcal mol^{-1}) [13]. It has been demonstrated that gold–gold interactions are present also in solution [14], and these forces could determine a preferential conformation of the eight-membered ring.

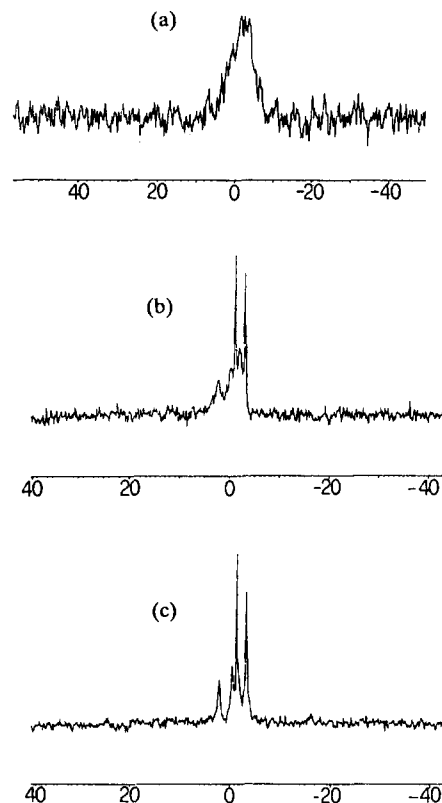


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compound **IIIa** at (a) 293 K, (b) 263 K and (c) 253 K.

4. X-ray crystal structure of [(1-benzyl-2-imidazolyl)diphenylphosphinegold(I)chloride] (**I**)

4.1. Crystal data

The following parameters were determined: $\text{C}_{22}\text{H}_{19}\text{N}_2\text{PAuCl}$, $M=574.8$, monoclinic $2/m$, space group no. 15, $C2/c$ C (centric), $a=18.068(2)$, $b=16.576(2)$, $c=15.391(2)$ Å, $\alpha=\gamma=90^\circ$, $\beta=117.2(2)^\circ$, $V=4100(7)$ Å³, $Z=8$, $D_c=1.86$ g cm^{-3} , $F(000)=2208.0$.

Intensity data were collected with a Philips PW 1100 diffractometer using $\text{Mo K}\alpha$ radiation in the range $4.9 < 2\theta < 56.0^\circ$. 3404 reflections were collected at room temperature. 2707 reflections having $F > 3\sigma(F)$ were considered observed and used in the structure analysis. The structure was solved by Fourier synthesis and refined by full-matrix least-squares technique, with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms were calculated but not refined. The final R value was 0.049 ($R_w=0.054$). Final atomic coordinates are listed in Table 1, bond distances and angles in Table 2.

The anisotropic thermal parameters, the positions of hydrogen atoms, the intermolecular contacts and the structural factors are available from the authors on request.

Table 1

Fractional atomic coordinates with equivalent isotropic thermal parameters ($\text{\AA}^2$)

Atom	x	y	z	$U_{\text{is/eq}}^a$
Au	0.09053(3)	0.17282(3)	0.77098(3)	0.0495(2)
P	0.0789(2)	0.2567(2)	0.6514(2)	0.046(1)
Cl	0.1144(3)	0.0858(2)	0.8977(3)	0.076(2)
N(1)	0.0812(6)	0.1298(6)	0.5291(7)	0.053(4)
N(2)	0.0183(7)	0.2401(6)	0.4528(7)	0.056(5)
C(1)	0.0583(7)	0.2047(7)	0.5389(8)	0.049(5)
C(2)	0.0167(9)	0.1856(9)	0.3868(9)	0.064(6)
C(3)	0.0531(8)	0.1174(8)	0.432(1)	0.060(6)
C(4)	0.1348(8)	0.0748(7)	0.608(1)	0.059(6)
C(5)	0.2242(4)	0.1032(5)	0.6579(6)	0.050(5)
C(6)	0.2610(4)	0.1432(5)	0.6078(6)	0.059(6)
C(7)	0.3450(4)	0.1643(5)	0.6564(6)	0.074(8)
C(8)	0.3921(4)	0.1455(5)	0.7550(6)	0.075(7)
C(9)	0.3552(4)	0.1055(5)	0.8051(6)	0.073(7)
C(10)	0.2713(4)	0.0844(5)	0.7566(6)	0.067(6)
C(11)	0.1737(4)	0.3121(5)	0.6830(5)	0.049(5)
C(12)	0.2360(4)	0.3111(5)	0.7789(5)	0.066(6)
C(13)	0.3101(4)	0.3545(5)	0.8038(5)	0.066(6)
C(14)	0.3198(4)	0.3989(5)	0.7326(5)	0.075(7)
C(15)	0.2565(4)	0.3998(5)	0.6367(5)	0.065(7)
C(16)	0.1834(4)	0.3564(5)	0.6119(5)	0.060(6)
C(17)	-0.0042(4)	0.3292(5)	0.6134(6)	0.053(5)
C(18)	-0.0863(4)	0.3027(5)	0.5622(6)	0.068(7)
C(19)	-0.1517(4)	0.3567(5)	0.5400(6)	0.080(7)
C(20)	-0.1351(4)	0.4371(5)	0.5689(6)	0.091(9)
C(21)	0.0530(4)	0.4637(5)	0.6200(6)	0.10(1)
C(22)	0.0125(4)	0.4097(5)	0.6423(6)	0.089(8)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.2. Description of the structure

The structure of [(1-benzyl-2-imidazolyl)diphenylphosphinegold(I)chloride] (**1**) is represented in the ORTEP plot of Fig. 3 [15], together with the numbering scheme. It consists of discrete units where the Au(I) atom is two-coordinate. The Au–Cl and Au–P bond lengths are 2.303(4) and 2.239(3) Å, respectively, and they are similar to those found in Ph_3PAuCl (cf. Au–Cl 2.279(3) Å and Au–P 2.235(3) Å) [16], indicating that the bond lengths are not influenced by the substitution of a phenyl with an imidazolyl ring. The imidazolyl and the three phenyl rings are planar.

The most significant parameter of the structure is the P–Au–Cl angle, which turns out to be 175.1(3)°. This value is distorted from the linearity found in most gold(I) derivatives (e.g., Ph_3PAuCl , 179.68(2)° [16]; $\text{Cy}_3\text{PAu}(2\text{-isopropylimidazolato-N, 177.0(1)° [4]; } \{[\text{CN}(\text{CH}_2\text{Ph})\text{CHCHN}(\text{COOEt})]\text{AuCl}\}$, 179.9(3)° [17]). This distortion can be justified considering the unit-cell packing given in Fig. 4.

The cell consists of eight units, which two by two give intermolecular Au···Au interactions at 3.03(2) Å; this distance is less than the van der Waals radius for gold (3.4 Å) [18] and is shorter than the intermolecular

Table 2

Bond lengths (Å) and angles (°)

Au–Cl	2.303(4)	Cl–Au–P	175.1(3)
Au–P	2.239(3)	Au–P–C(1)	113.0(4)
P–C(1)	1.81(1)	Au–P–C(11)	112.0(3)
P–C(11)	1.802(8)	Au–P–C(17)	115.6(4)
P–C(17)	1.800(9)	C(1)–P–C(11)	104.8(6)
C(1)–N(1)	1.34(2)	C(11)–P–C(17)	107.2(4)
C(3)–N(1)	1.35(2)	C(1)–N(1)–C(4)	127(1)
C(2)–C(3)	1.33(2)	C(1)–N(2)–C(2)	106(1)
C(2)–N(2)	1.35(2)	P–C(1)–N(2)	121.7(9)
C(1)–N(2)	1.32(1)	P–C(11)–C(12)	119.9(6)
C(4)–N(1)	1.47(1)	P–C(17)–C(18)	119.2(7)
C(4)–C(5)	1.51(1)	N(2)–C(2)–C(3)	110(1)
C(5)–C(6)	1.39(1)	N(1)–C(4)–C(5)	112.0(9)
C(6)–C(7)	1.395(9)	C(4)–C(5)–C(6)	122.3(8)
C(7)–C(8)	1.40(1)	C(5)–C(6)–C(7)	120.0(8)
C(8)–C(9)	1.40(1)	C(5)–C(10)–C(9)	120.0(8)
C(9)–C(10)	1.395(9)	C(7)–C(8)–C(9)	120.0(8)
C(5)–C(10)	1.40(1)	C(11)–C(12)–C(13)	120.0(7)
C(11)–C(12)	1.395(9)	C(13)–C(14)–C(15)	120.0(8)
C(12)–C(13)	1.40(1)	C(11)–C(16)–C(15)	120.0(7)
C(13)–C(14)	1.39(1)	C(17)–C(18)–C(19)	120.0(8)
C(14)–C(15)	1.395(9)	C(19)–C(20)–C(21)	120.0(8)
C(15)–C(16)	1.40(1)	C(17)–C(22)–C(21)	120.0(9)
C(11)–C(16)	1.39(1)	C(1)–P–C(17)	103.3(5)
C(17)–C(18)	1.40(1)	C(3)–N(1)–C(4)	126(1)
C(18)–C(19)	1.39(1)	C(1)–N(1)–C(3)	107(1)
C(19)–C(20)	1.40(1)	N(1)–C(1)–N(2)	111(1)
C(20)–C(21)	1.40(1)	P–C(1)–N(1)	127.6(8)
C(21)–C(22)	1.39(1)	N(1)–C(3)–C(2)	107(1)
C(17)–C(22)	1.40(1)	C(4)–C(5)–C(10)	117.6(9)
		C(6)–C(5)–C(10)	120.0(8)
		C(6)–C(7)–C(8)	120.0(8)
		C(8)–C(9)–C(10)	120.0(8)
		P–C(11)–C(16)	120.1(6)
		C(12)–C(11)–C(16)	120.0(8)
		C(12)–C(13)–C(14)	120.0(7)
		C(14)–C(15)–C(16)	120.0(7)
		P–C(17)–C(22)	120.6(8)
		C(18)–C(17)–C(22)	120.0(9)
		C(18)–C(19)–C(20)	120.0(9)
		C(20)–C(21)–C(22)	120.0(8)

Au···Au distances found in other gold(I) derivatives containing no bridging ligands (e.g., $[\text{BrAuPh}_2(2\text{-MeC}_6\text{H}_4)]$, Au···Au = 3.097(1) Å [19]; $[\text{Au}_2(\text{tmb})_2\text{Cl}_2]$, Au···Au = 3.3063(3) Å [20]; $\{[\text{CN}(\text{CH}_2\text{Ph})\text{CHCHN}(\text{COPh})]\text{AuCl}\}$, Au···Au = 3.4308(4) Å [26]). The Au···Au distance we found in our compound falls within the range typical of Au(I) dimers (2.76–3.10 Å) [21–27].

5. ^{197}Au Mössbauer investigation

5.1. Experimental

The ^{197}Pt activity feeding the 77.3 keV Mössbauer transition was produced by neutron irradiation of enriched ^{196}Pt metal in the reaction $^{196}\text{Pt}(n,\gamma)^{197}\text{Pt}$. The

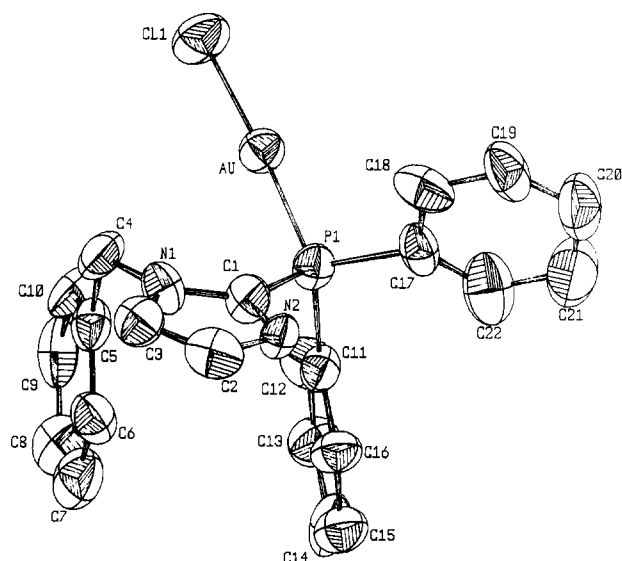


Fig. 3. ORTEP plot of compound **I** and the numbering scheme of the atoms. Hydrogen atoms are omitted for clarity.

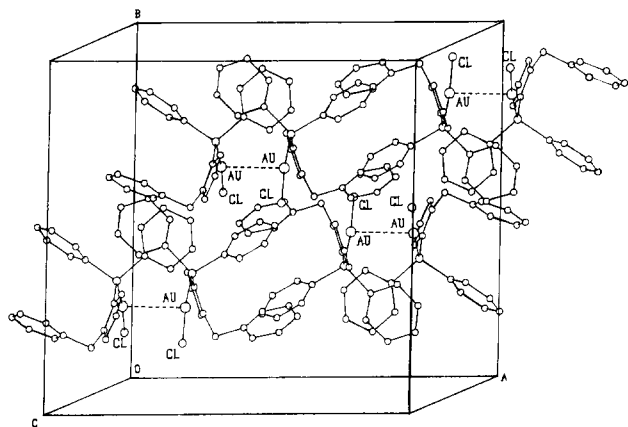


Fig. 4. ORTEP stereoscopic view of the packing in the lattice of $(\text{BzIm})\text{Ph}_2\text{PAuCl}$ (**I**) showing the $\text{Au}\cdots\text{Au}$ interactions.

half-life of ^{197}Pt is about 18 h. Both source and absorber were kept at 4.2 K. A sinusoidal velocity waveform and intrinsic Ge detector were used. The spectra reported in Fig. 5 have been fitted by the program MOS 90 with sets of equal Lorentzian lines. In both of the spectra the single line ($\text{IS} - 1.25 \text{ mm s}^{-1}$, percent area less than 3%) has been attributed to metallic gold produced on standing by decomposition processes. The shifts are relative to the source $\text{Au}(\text{Pt})$. In order to refer these shifts to metallic gold, the amount 1.25 mm s^{-1} has to be added.

5.2. Results and discussion

The parameters of the quadrupole splitting doublets are typical of gold(I) sites that are linearly coordinated. Additional evidence, in the framework of the point-charge model, is provided (Table 3) by the substantial agreement between experimental splitting and that pre-

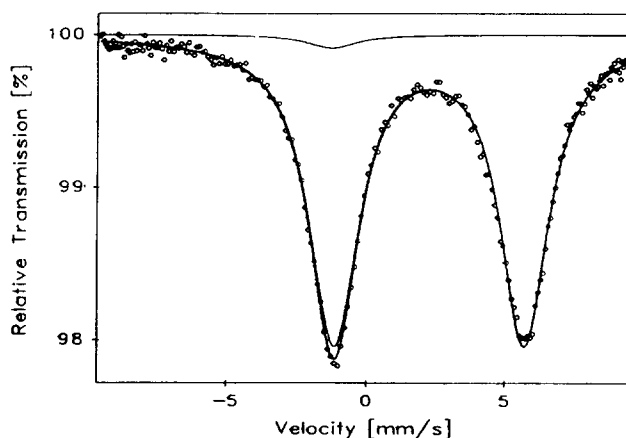
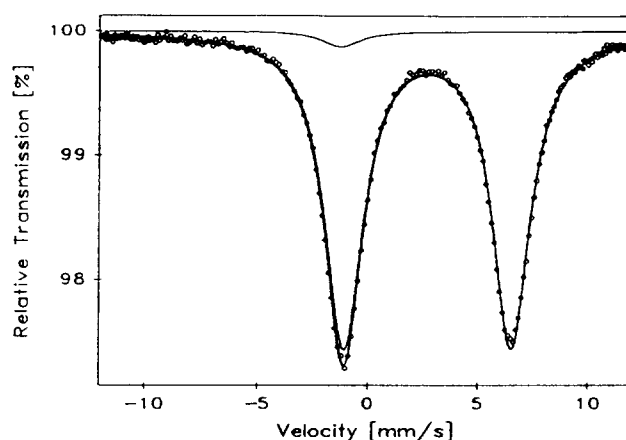


Fig. 5. Mössbauer spectra for samples **I** (top) and **IIa** (bottom) at 4.2 K (experimental points, small circles; envelope and subspectra, continuous lines).

Table 3
 ^{197}Au Mössbauer parameters at 4.2 K ^a

Sample	IS	LW	QS	QS ^b
I	2.29	2.14	6.87	−7.32
IIa	2.75	2.10	7.64	−8.48

^a Isomer shift IS, quadrupole splitting QS, and linewidth LW in mm s^{-1} .

^b Calculated assuming Cl -1.24 ; N (pyridine) -1.82 ; and PR_3 -2.42 mm s^{-1} .

dicted by using the literature partial quadrupole splitting values [28]. Consequently compound **I** contains the arrangement $\text{P}-\text{Au}-\text{Cl}$ and compound **IIa** the arrangement $\text{P}-\text{Au}-\text{N}$. For both compounds the average linewidth is close to the minimum observable width, 1.87 mm s^{-1} [28], showing that only one distinguishable gold site is present.

In comparison with the values expected for compounds containing the linear arrangement $\text{P}-\text{Au}-\text{Cl}$, compound **I** exhibits a smaller electric quadrupole interaction and a less positive shift. This is a consequence of the $\text{Au}\cdots\text{Au}$ interactions, evidenced for **I** by the

crystallographic data. In fact, for a coordination number greater than two, the s-electron density at the gold nucleus decreases together with the p-electron asymmetry of the gold centre.

The Mössbauer spectrum of **IIa** shows the presence of only one gold(I) site, in agreement with the dinuclear cationic scheme proposed in Fig. 1. The Mössbauer parameters for **IIa** are smaller than those reported for compounds containing the arrangement P–Au–N [29], showing again the presence of Au···Au interactions. On comparing the Mössbauer parameters for the mono- and dinuclear derivatives, weaker Au···Au interactions, and perhaps only those of the intramolecular type, are expected for the cationic complex **IIa**.

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