Bis[2-(phenylazo)phenyl-C^1N']gold(III) Complexes. Crystal and Molecular Structure of Bis[2-(phenylazo)phenyl-C^1N']gold(III) Tetrachloroaurate †

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The reaction between $[NMe_4][AuCl_4]$ and $[Hg(pap)_2]$ [pap = 2-(phenylazo)phenyl] gave the gold(III) complex $[Au(pap)_2Cl]$ which reacts with $AgClO_4$ to form $[Au(pap)_2]ClO_4$. Addition of $[PPh_3(CH_2Ph)]X$ (X = Cl), NaX (X = Br), or KX (X = I, CN, or O_2CMe), to the cationic complex leads to the corresponding neutral complexes $[Au(pap)_2X]$. Reaction of $[Au(pap)_2]ClO_4$ with $[NMe_4][AuCl_4]$, leads to $[Au(pap)_2][AuCl_4]$. By reacting the neutral acetato-complex with $[Hpy]ClO_4$ (Hpy = pyridinium), $[Au(pap)_2(py)]ClO_4$ is prepared. The crystal structure of $[Au(pap)_2][AuCl_4]$ has been determined and shows that the cation has a square-planar co-ordination with two *cis*-nitrogen [Au–N = 2.17(2) Å (av.)] and two *cis*-carbon [Au–C = 2.00(2) Å (av.)] atoms bonded to gold.

Most 2-(phenylazo)phenyl complexes have been prepared by *ortho*-metallation reactions of azobenzene.[1] However, auration reactions of arenes are inhibited by the presence of a co-ordinating substituent in the aromatic ring.[2] In fact, reactions between azobenzene and gold(III) halides hopefully to form *ortho*-metallated complexes have been carried out by several authors,[2a] only to result in the isolation of adducts with azobenzene.

Transmetallation reactions using organomercurials are a well established synthetic route to organometallic compounds.[3–18] In particular, [2-(phenylazo)phenyl]mercury(II) compounds have been used in the synthesis of some palladium(II), platinum(II), nickel(II), manganese(I),[7,8] and tellurium(IV),[14] 2-(phenylazo)phenyl complexes. In this context we have recently reported the synthesis of organogold(III) complexes [19] including dichloro[2-(phenylazo)phenyl]gold(III) and some neutral, anionic, and cationic derivatives.[19a] We have also reported the synthesis, and crystal and molecular structure of dichlorobis[2-(phenylazo)phenyl]tin(IV) [20] using metallic tin and chloro[2-(phenylazo)phenyl]mercury(II).

The only reported bis[2-(phenylazo)phenyl] complexes having a 'spirane' metal atom, $[M(L)_2]$ [M = Pd or Pt; L = 2-(phenylazo)phenyl or *para*-disubstituted CH_3^- or CH_3O^- derivatives [9,21]] have been prepared in good yields through redox transmetallation reactions *e.g.* $2[Hg(L)_2] + [M_2(dba)_3] \longrightarrow 2Hg + 2[M(L)_2] + 3dba$, where dba is $(PhCH{=}CH)_2CO$. Although there is no known crystal structure of such complexes they are thought to be *trans*.

In this paper we report the synthesis of several bis[2-(phenylazo)phenyl]gold(III) complexes through a non-redox transmetallation reaction using organomercurials and the first crystal structure of a 'spirane' type complex $[Au(pap)_2]^+$ [pap = 2-(phenylazo)phenyl].

Results and Discussion

When equimolar amounts of $[NMe_4][AuCl_4]$ and $[Hg(pap)_2]$ are reacted in dichloromethane at room temperature for 24 h a precipitate of $[NMe_4]_2[Hg_2Cl_6]$ and a red solution of $[Au(pap)_2Cl]$ (1) are obtained. The reaction between (1) and $AgClO_4$ (1 : 1) in benzene leads to $[Au(pap)_2]ClO_4$ (2). This complex reacts: (*i*) with $[PPh_3(CH_2Ph)]Cl$, NaBr, or KX (X = I, CN, or O_2CMe) to give the neutral complexes $[Au(pap)_2X]$ [X = Cl (1), Br (3), I (4), CN (5), or O_2CMe (6)]; and (*ii*) with $[NMe_4][AuCl_4]$ to give $[Au(pap)_2][AuCl_4]$ (7). Reaction between the acetato-complex (6) and $[Hpy]ClO_4$ (Hpy = pyridinium) allows the synthesis of $[Au(pap)_2(py)]ClO_4$ (8). All these reactions are summarized in Scheme 1. Analytical data and physical properties of the complexes are listed in Table 1.

If the reaction between $[NMe_4][AuCl_4]$ and $[Hg(pap)_2]$ is stopped after stirring for 6 h, a mixture of (1) and $[Au(pap)Cl_2]$ [19a] is obtained. The formation of the intermediate $[Au(pap)Cl_2]$ is likely to occur according to equation (i).

$$[AuCl_4]^- + [Hg(pap)_2] \longrightarrow [Au(pap)Cl_2] + [Hg(pap)Cl] + Cl^- \qquad \text{(i)}$$

A second process such as equation (ii) can be discarded as

$$[Au(pap)Cl_2] + [Hg(pap)Cl] \longrightarrow [Au(pap)_2Cl] + [HgCl_2] \qquad \text{(ii)}$$

a mixture of these compounds (1 : 1) was recovered unreacted after stirring for 24 h in dichloromethane. The complex [Hg(pap)Cl] neither reacts with $[PPh_3(CH_2Ph)][Au(pap)Cl_3]$ [19a] nor with $[NMe_4][AuCl_4]$ (dichloromethane, 1 : 1, 24 h). Therefore, the process leading to (1) could be the transmetallation reaction given by equation (iii), which we

$$[Au(pap)Cl_2] + [Hg(pap)_2] \longrightarrow [Au(pap)_2Cl] + [Hg(pap)Cl] \qquad \text{(iii)}$$

have verified by reacting both complexes in dichloromethane (1 : 1, 21 h, room temperature, 84% yield).

To account for the stoicheiometry of the reaction and the formation of the precipitate of $[NMe_4]_2[Hg_2Cl_6]$, the symmetrization reaction,[22] equation (iv), must be postulated.

$$2[Hg(pap)Cl] + Cl^- \longrightarrow [Hg(pap)_2] + \tfrac{1}{2}[Hg_2Cl_6]^{2-} \qquad \text{(iv)}$$

Such a type of reaction has been reported using PPh_3 [23] or NaI [8] as symmetrizing agents to give $[Hg(pap)_2]$ and $[HgCl_2(PPh_3)_2]$ or $[HgI_4]^{2-}$. We have observed that $[NMe_4]Cl$ can

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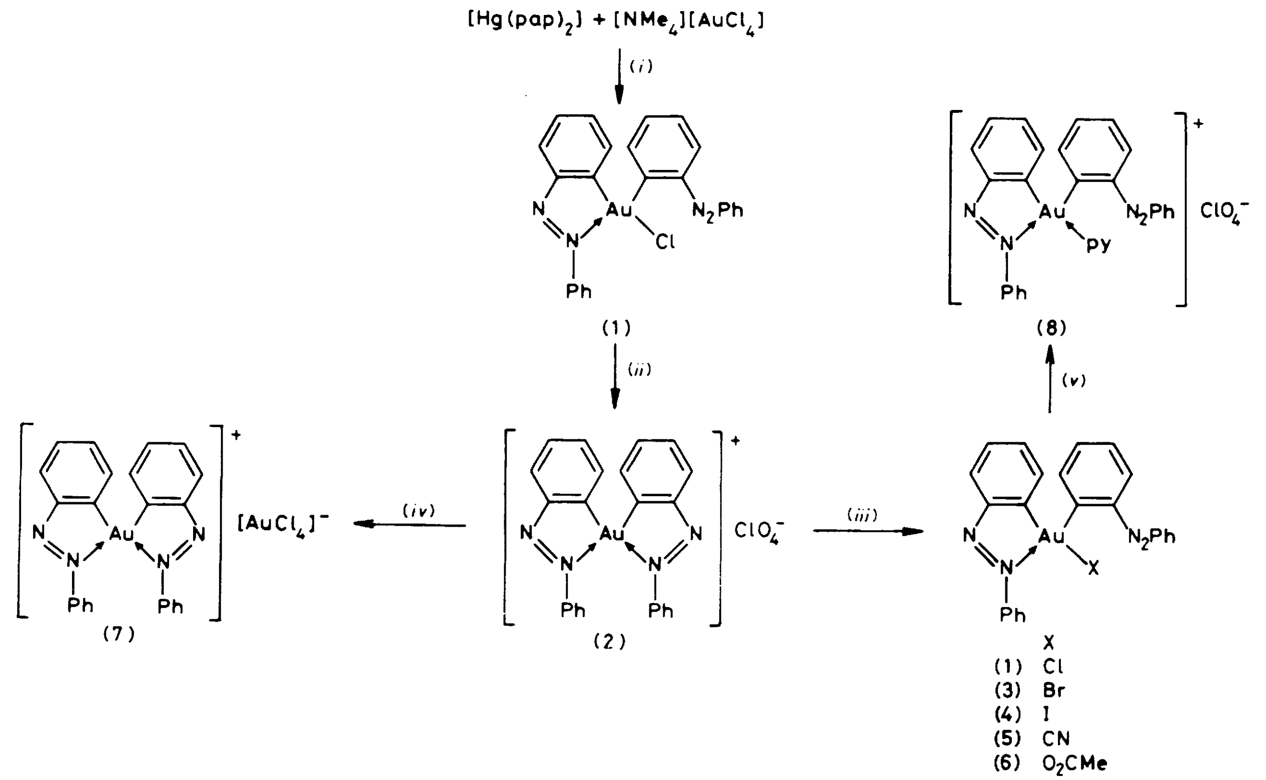
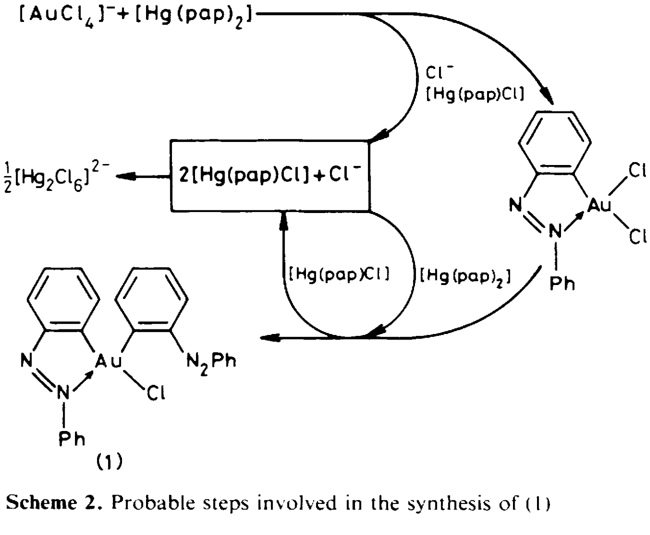
† *Supplementary data available* (No. SUP 23820, 15 pp.): structure factors, anisotropic thermal parameters, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme 1. Syntheses of bis[2-(phenylazo)phenyl]gold(III) complexes: (*i*) $-\frac{1}{2}[NMe_4]_2[Hg_2Cl_6]$; (*ii*) $+AgClO_4$, $-AgCl$; (*iii*) $+QX$, $-QClO_4$ [$Q = PPh_3(CH_2Ph)^+$, (1); Na^+, (3); K^+, (4)—(6)]; (*iv*), $+[NMe_4][AuCl_4]$, $-[NMe_4]ClO_4$; (*v*) $+[Hpy]ClO_4$, $-MeCO_2H$ [for the reaction of complex (6) only]



Scheme 2. Probable steps involved in the synthesis of (1)

also be used to symmetrize [Hg(pap)Cl] (dichloromethane, 2 : 1, 15 h, room temperature, 78% yield).

Scheme 2 summarizes the probable steps involved in the synthesis of (1), based on these experimental results. Complex (1) is formulated as neutral in view of its low conductivity in acetone (see Table 1) and the presence in its i.r. spectrum of a strong band at 305 cm^{-1} assignable to ν(Au−Cl).

Although five-co-ordination is not excluded we believe complex (1) to be a four-co-ordinate square-planar complex with only one 2-(phenylazo)phenyl group, co-ordinated through a nitrogen atom to give a five-membered ring (see Scheme 1). This is based on the following arguments. (*i*) The position of the band assigned to ν(Au−Cl) in (1) and that assigned to ν(Au−Cl) *trans* to the phenyl group in [Au(pap)Cl$_2$],[19a] where a square-planar geometry is expected, are identical. The other band assigned in [Au(pap)Cl$_2$] to ν(Au−Cl) *trans* to the nitrogen atom of the azo-group appears at 370 cm^{-1}. Hence, if complex (1) is square-planar the chloro-ligand must be *trans* to the phenyl group of the 2-(phenylazo)phenyl ligand which is co-ordinated through both C and N giving a structure in which both phenyl groups are *cis*, in accordance with the crystal structure of [Au(pap)$_2$]$^+$ (see later). This argument is supported by the recent report [24] on the crystal structure of [Au{C(Ph)=C(Ph)−C(Ph)=C(Ph)}Cl(phen)] (phen = 1,10-phenanthroline) where a very distorted five-co-ordinate structure is found. One of the N−Au bonds is much longer (0.6 Å) than the N−Au bond that lies in an almost perfect plane together with the chloro-ligand and two carbon atoms of the organic group. This complex shows ν(Au−Cl) at 280 cm^{-1} which is lower than that observed in the related four-co-ordinate complex, [Au{C(Ph)=C(Ph)−C(Ph)=C(Ph)}Cl(py)] (300 cm^{-1}). Therefore, ν(Au−Cl) is very sensitive to a N−Au axial interaction even if it is very weak. (*ii*) Several 2-(phenylazo)phenyl complexes have been formulated where this ligand bonds in a unidentate manner.[1] The crystal structure of *trans*-[Pd(pap)Cl(PEt$_3$)$_2$] [25] shows this type of co-ordination.

Complex (1) reacts with PPh$_3$ (dichloromethane, 1 : 1, 15 min, room temperature) or [PPh$_3$(CH$_2$Ph)]Cl (dichloromethane, 1 : 1, 3 h, room temperature) to form the gold(I) complexes, [AuCl(PPh$_3$)] (67% yield) or [PPh$_3$(CH$_2$Ph)][AuCl$_2$] (80% yield), respectively. In the reaction of (1) with pyridine (diethyl ether, 1 : 1, 1 h, room temperature) (1) is recovered unchanged although some metallic gold is produced. The complex [Au(pap)$_2$(CN)] (5) reacts similarly with PPh$_3$

Table 1. Physical and analytical data for complexes

Complex	M.p. (°C)	Colour	Λ_M [a]/Ω^{-1} cm^2 mol^{-1}	Analysis [b] (%) C	H	N	Au	Yield (%)
(1) $[Au(pap)_2Cl]$	117 (decomp.)	Orange	11.3	49.30	3.25	9.30	33.70	92
				(48.45)	(3.05)	(9.40)	(33.10)	
(2) $[Au(pap)_2]ClO_4$	223 (decomp.)	Brick red	112.9	43.75	2.75	8.50	30.45	83
				(44.00)	(3.15)	(8.50)	(30.00)	
(3) $[Au(pap)_2Br]$	125 (decomp.)	Brown	1.3	45.30	3.05	8.15	30.35	91
				(45.10)	(2.85)	(8.75)	(30.80)	
(4) $[Au(pap)_2I]$	84 (decomp.)	Brick red	3.8	41.30	2.70	8.30	28.35	67
				(42.00)	(2.65)	(8.15)	(28.70)	
(5) $[Au(pap)_2(CN)]$	143 (decomp.)	Orange	0.6	50.90	3.50	11.80	33.10	75
				(51.20)	(3.10)	(11.95)	(33.65)	
(6) $[Au(pap)_2(O_2CMe)]$	78 (decomp.)	Orange	0.8	50.30	3.25	9.45	31.45	50
				(50.50)	(3.40)	(9.05)	(31.85)	
(7) $[Au(pap)_2][AuCl_4]$	152 (decomp.)	Orange	95.0	32.65	2.15	5.45	43.60	70
				(32.10)	(2.00)	(6.15)	(43.85)	
(8) $[Au(pap)_2(py)]ClO_4$	110	Orange	107.6	46.85	3.05	9.40	26.20	95
				(47.20)	(3.10)	(9.50)	(26.70)	

[a] In acetone (*ca.* 10^{-4} mol dm^{-3}). [b] Calculated values are given in parentheses.

(diethyl ether, 1 : 1, 30 min, room temperature) to give $[Au(CN)(PPh_3)]$ (88% yield). It seems likely that cleavage of the N–Au bond by PPh_3 or Cl^- promotes the splitting of the C–Au bonds due to the very sterically congested situation with two mutually *cis* unidentate 2-(phenylazo)phenyl groups. In fact we have been unable to prepare complexes of the types $[Au(pap)_2XL]$ or $[Au(pap)_2L_2]^+$ (X = anion, L = neutral ligand). Thus, for example, in the reaction of $[Au(pap)_2]ClO_4$ (2) with PPh_3 (acetone, 1 : 2, 10 min, room temperature) the only pure compound obtained was $[Au(PPh_3)_2]ClO_4$. Even when equimolar quantities of PPh_3 or py are used (acetone, 15 min), compounds containing such ligands along with 2-(phenylazo)phenyl and ClO_4^- (by i.r.) are obtained, but we could not obtain analytically pure samples. The probable result of the last reaction, $[Au(pap)_2(py)]ClO_4$ (8), could only be obtained in pure state through a longer process (see Scheme 1).

Complexes $[Au(pap)_2X]$ [X = Br (3), I (4), CN (5), or O_2CMe (6)] lack the band assigned to ν(Au–Cl) in complex (1). The corresponding ν(Au–Br) or ν(Au–I) in (3) or (4) are expected to fall below the range of our spectrophotometer. In complex (5) the ν(CN) band appears as a very weak absorption at 2 159 cm^{-1}. The two bands assignable to ν(C=O) and ν(C–O) in complex (6) appear at 1 620 and 1 295 cm^{-1} in accordance with the unidentate nature of the acetato-ligand.

All the complexes show conductivities according to their formulations (see Table 1).

The structure of $[Au(pap)_2][AuCl_4]$ (7) consists of discrete ions linked by van der Waals and ionic forces. The shortest interionic distances are Au(1) · · · Cl(32) 3.454(8), Au(1) · · · Cl(21) 3.589(7), Au(2) · · · C(2) 3.56(1), and Au(3) · · · C(20) 3.75(1) Å, where the shortest distance is 0.2 Å longer than the sum of Au and Cl ionic radii (see Figure 1).

The gold atoms in $[AuCl_4]^-$ are located on inversion centres and display a regular square-planar co-ordination. The average Cl–Au–Cl angles and Au–Cl distances are 90.0(4)° and 2.284(9) Å, the latter being similar to that appearing in the literature.[26]

The gold atom in $[Au(pap)_2]^+$ (see Figure 2 and Table 2) is four-co-ordinated in a distorted square-planar structure surrounded by two *cis* nitrogen atoms and two *cis* carbon atoms [average C–Au–N bond angle 77.4(7)°, N–Au–N 107.1(6)°, and C–Au–C 98.1(9)°].

The mean Au–C bond distance [2.00(2) Å] is the same as that reported for *cis*-$[Au(C_6H_5)Cl_2(SPr^n_2)]$ [27] but smaller than the values found in some pentafluorophenyl complexes: *cis*-$[Au(C_6F_5)_2Cl(PPh_3)]$ (2.18 and 2.19 Å),[28] $[Au(C_6F_5)_3Cl]^-$ (2.028, 2.064, and 2.071 Å); and $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]^+$ (2.071 and 2.094 Å).[29]

The reported Au^{III}–N bond lengths can be classified into: (*i*) Au^{III}–N(*sp*^{3}) bond type present in four fully determined structures corresponding to square-planar complexes [30] and (*ii*) Au^{III}–N(*sp*^{2}) bond type present in several five-co-ordinate complexes containing chelate ligands. In type (*i*) the mean value of Au–N [31] is 2.04 Å (average of nine values) and in type (*ii*) the reported structures can be described as distorted square pyramidal. In [Au(tpp)Cl] (tpp = 5,10,15,20-tetraphenylporphyrinate) the average Au–N bond length [32] is 2.00 Å. For a series of complexes $[AuX_3(L-L)]$ [X = Cl, L–L = 2,2′-biquinolyl; [33] X = Cl or Br, L–L = 2,9-dimethyl-1,10-phenanthroline; [34] X = Cl or Br, L–L = 2-(2′-pyridyl)-quinoline [35]] and [Au{C(Ph)=C(Ph)–C(Ph)=C(Ph)}Cl(phen)] [24] one nitrogen atom lies in a plane along with, respectively, the $AuCl_3$ or the Au{C(Ph)=C(Ph)–(Ph)=C(Ph)}Cl moieties, but the second nitrogen atom cannot adopt the ideal axial position because the ' bite ' of the ligand is too small. For the $[AuCl_3(L-L)]$ complexes the mean value of the longer Au–N bond is 2.58 Å (average of five values) and the shorter is 2.11 Å (average of five values). The latter is somewhat shorter than the corresponding Au–N distance in the tetraphenylbutadienediyl complex [2.184(4) Å] perhaps owing to the greater *trans* influence of the carbon donor ligand with respect to the chloro- or bromo-ligands.

By comparing the Au–N bond length in (7) [2.17(2) Å (av.)] with the value [2.184(4) Å] found in the tetraphenylbutadienediyl complex it may be concluded that this is the normal Au^{III}–N(*sp*^{2}) bond length *trans* to a carbon donor ligand.

The geometrical differences between the two 2-(phenylazo)-phenyl moieties are within three times the standard deviations. The N–N bond distances [1.27(2) Å] are in agreement with other values found in similar complexes of Pt^{II},[36] Rh^{III},[37] and Sn^{IV} [20] (mean value 1.28 Å, average of seven values) but are longer than the average value (1.23 Å) found in azobenzene and its derivatives.[38] The C–N bond distances exterior to the five-membered rings [1.46(3) Å], and the mean values of C–C bond lengths in the four benzene rings [1.40(3) Å] are normal.

In the cation $[Au(pap)_2]^+$ the following sets of planes can be defined, (i): C(1), N(2), Au(1), N(4), C(13); (ii): C(1), C(2), N(1), N(2); (iii): C(13), C(14), N(3), N(4); phenyl rings (iv):

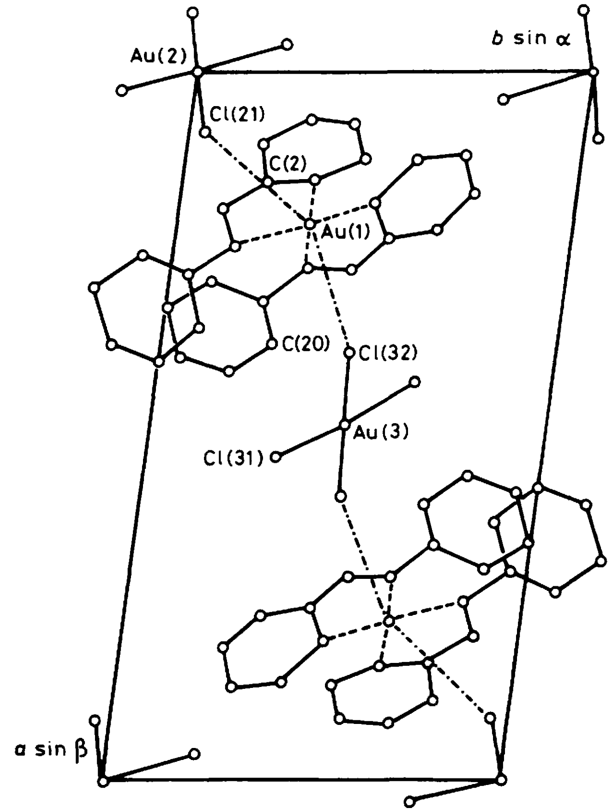


Figure 1. Unit-cell contents of complex (7) projected down *c*, showing interionic interactions and selected atom numbering

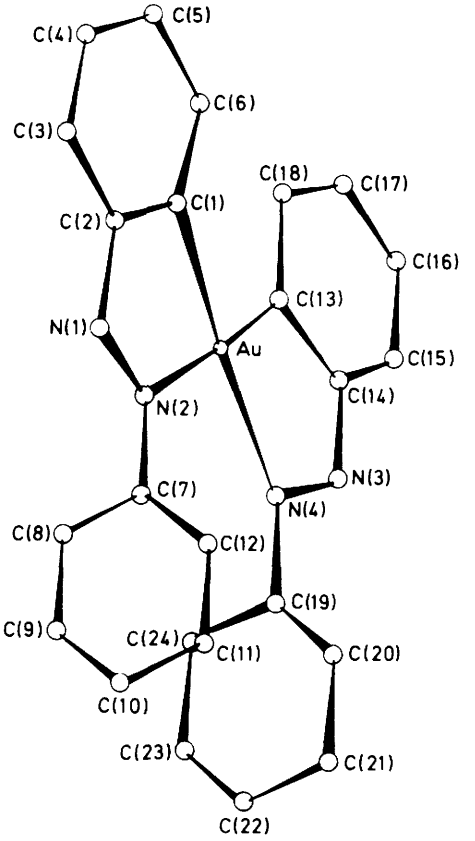


Figure 2. A perspective view of the structure of the cation [Au(pap)$_2$]$^+$ in (7) showing the atom-numbering scheme

C(1)—C(6); (v): C(13)—C(18); (vi): C(7)—C(12); and (vii): C(19)—C(24). The dihedral angles between planes are as follows: (ii)—(i) + 14(1)°, (iii)—(i) − 17(1)°, (iv)—(ii) + 10(1)°, and (v)—(iii) + 10(1)°. Both free phenyl rings (vi) and (vii) are twisted around the corresponding C−N bonds, with torsion angles +45(1)° [N(1)−N(2)−C(7)−(8)] and +46(1)° [N(3)−N(4)−C(19)−C(20)].

Experimental

Infrared spectra were recorded in the range 4 000—250 cm^{-1} on Perkin-Elmer 457 and Nicolet MX-1 spectrophotometers using Nujol mulls between polyethylene sheets and KBr pellets. Conductivities were measured with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine.

The starting complexes [NMe$_4$][AuCl$_4$][39] and [Hg(pap)$_2$][8] were prepared by literature methods. Solvents were distilled before use. Unless otherwise stated the reactions were carried out at room temperature with magnetic stirring and without special precautions against daylight or moisture.

Preparations.—[Au(pap)$_2$Cl] (1). To a suspension of [NMe$_4$][AuCl$_4$] (100 mg, 0.24 mmol) in dichloromethane (10 cm^3), solid [Hg(pap)$_2$] (136 mg, 0.24 mmol) was added. After 24 h the suspension was filtered off, the resulting solution concentrated (1 cm^3), and n-hexane (10 cm^3) added to precipitate complex (1), which was recrystallized from dichloromethane–n-hexane (1 : 5).

Table 2. Selected bond lengths (Å) and angles (°) for [Au(pap)$_2$]-[AuCl$_4$] (7)

Au(1)−C(1)	1.99(2)	N(3)−N(4)	1.27(2)
Au(1)−N(2)	2.17(1)	Au(2)−Cl(21)	2.289(6)
Au(1)−C(13)	2.00(2)	Au(2)−Cl(22)	2.281(6)
Au(1)−N(4)	2.17(2)	Au(3)−Cl(31)	2.271(7)
N(1)−N(2)	1.27(2)	Au(3)−Cl(32)	2.295(6)
C(1)−Au(1)−N(2)	78.1(7)	N(1)−N(2)−Au(1)	116(1)
C(1)−Au(1)−C(13)	98.1(9)	N(3)−N(4)−Au(1)	118(1)
N(2)−Au(1)−N(4)	107.1(6)	C(14)−N(3)−N(4)	111(2)
N(4)−Au(1)−C(13)	76.8(8)	C(13)−C(14)−N(3)	121(2)
Au(1)−C(1)−C(2)	110(1)	C(14)−C(13)−Au(1)	111(1)
C(1)−C(2)−N(1)	121(2)	Cl(21)−Au(2)−Cl(22)	90.0(3)
C(2)−N(1)−N(2)	112(2)	Cl(31)−Au(3)−Cl(32)	90.6(3)

[Au(pap)$_2$]ClO$_4$ (2). To a suspension of (1) (67.4 mg, 0.11 mmol) in benzene (5 cm^3), solid AgClO$_4$ (22.8 mg, 0.11 mmol) was added. After 15 h the solvent was evaporated and the residue extracted with dichloromethane (3 × 6 cm^3). The resulting solution was concentrated (1 cm^3) and diethyl ether (10 cm^3) slowly added to precipitate complex (2) which was recrystallized from dichloromethane–diethyl ether (1 : 5).

[Au(pap)$_2$X] [X = Br (3), I (4), CN (5), *or* O$_2$CMe (6)]. To a suspension of (2) (~0.1 mmol) in acetone (~10 cm^3) an equimolar amount of solid NaBr [for (3)] or KX [for (4)—(6)] was added. Some time later [1 h for (3) and (4), 14 h for (5), or 30 min for (6)] the solvent was evaporated and the residue extracted with a solvent [dichloromethane (3 × 5 cm^3) for (3) and (5), diethyl ether (3 × 5 cm^3) for (4), and acetone

Table 3. Final fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[Au(pap)_2][AuCl_4]$ (7)

Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	2 187(1)	3 382(1)	−524(1)
C(1)	1 620(12)	3 481(23)	1 458(31)
C(2)	1 533(12)	2 151(22)	2 516(29)
C(3)	1 112(14)	1 897(26)	3 931(33)
C(4)	758(12)	2 977(26)	4 354(33)
C(5)	858(15)	4 252(27)	3 346(35)
C(6)	1 305(15)	4 568(26)	1 875(37)
N(1)	1 968(10)	1 092(19)	2 362(24)
N(2)	2 403(8)	1 488(16)	1 215(24)
C(7)	2 901(13)	467(20)	1 138(29)
C(8)	2 618(14)	−884(23)	1 084(34)
C(9)	3 119(16)	−1 814(32)	995(39)
C(10)	3 935(14)	−1 295(26)	1 076(35)
C(11)	4 170(15)	74(25)	1 159(34)
C(12)	3 677(12)	1 044(24)	1 131(32)
C(13)	1 880(12)	5 083(23)	−2 115(34)
C(14)	2 367(14)	5 509(22)	−3 454(28)
C(15)	2 302(13)	6 694(25)	−4 675(30)
C(16)	1 751(17)	7 535(30)	−4 616(44)
C(17)	1 266(17)	7 113(28)	−3 298(37)
C(18)	1 342(14)	5 912(23)	−2 115(30)
N(3)	2 832(12)	4 596(21)	−3 813(26)
N(4)	2 775(9)	3 460(21)	−2 778(24)
C(19)	3 235(13)	2 464(22)	−3 146(27)
C(20)	3 906(15)	2 915(27)	−3 801(35)
C(21)	4 323(15)	1 912(31)	−4 227(36)
C(22)	4 043(17)	545(37)	−4 035(35)
C(23)	3 330(16)	65(28)	−3 413(34)
C(24)	2 916(15)	1 056(25)	−2 947(32)
Au(2)	0(0)	0(0)	0(0)
Cl(21)	874(4)	362(7)	−1 879(9)
Cl(22)	−367(4)	2 128(7)	−1 074(11)
Au(3)	5 000(0)	5 000(0)	0(0)
Cl(31)	5 517(4)	3 380(7)	2 130(11)
Cl(32)	3 986(4)	4 859(7)	1 441(11)

(3 × 5 cm^3) for (6)]. The suspension was filtered off and the resulting solution concentrated (1 cm^3) and n-hexane (10 cm^3) added to precipitate the corresponding complex which was recrystallized from diethyl ether–n-hexane (1 : 5) [for (4)—(6)] or acetone–n-hexane (1 : 5) [for (3)].

$[Au(pap)_2][AuCl_4]$ (7). To a suspension of (2) (52.7 mg, 0.08 mmol) in dichloromethane (5 cm^3) solid $[NMe_4][AuCl_4]$ (33 mg, 0.08 mmol) was added. After 30 min the suspension was filtered off, the solution concentrated (1 cm^3), and diethyl ether added (10 cm^3) to precipitate (7). Single crystals of complex were obtained in a test tube by slow diffusion of n-hexane (5 cm^3) into a saturated solution of (7) in dichloromethane (2 cm^3).

$[Au(pap)_2(py)]ClO_4$ (8). To a solution of (6) (40 mg, 0.06 mmol) in acetone (5 cm^3) solid $[Hpy]ClO_4$ (11.6 mg, 0.06 mmol) was added. After 4 h the solvent was evaporated to dryness and the residue extracted with dichloromethane (3 × 3 cm^3). The solution was concentrated (1 cm^3) and diethyl ether slowly added (10 cm^3) to precipitate (8), which was recrystallized from dichloromethane–diethyl ether (1 : 5).

Crystal Data for Complex (7).—$C_{24}H_{18}AuN_4\cdot AuCl_4$, $M = 898.18$, triclinic, $a = 18.113(3)$, $b = 9.752(2)$, $c = 7.515(2)$ Å, $\alpha = 82.84(2)$, $\beta = 101.90(2)$, $\gamma = 99.17(1)^\circ$, $U = 1\ 276.5(8)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 2.34$ g cm^{-3}, $F(000) = 832$, Mo-K_α radiation, λ(Mo-K_α) = 0.710 69 Å, and $\mu = 122.86$ cm^{-1}.

A crystal of dimensions 0.08 × 0.08 × 0.12 mm was selected for crystal measurement on a Philips PW-1100 four-circle diffractometer. The unit cell was measured by centring 25 independent reflections and refining the orientation matrix by the least-squares method. 2 753 Independent reflections were measured in the range $2 \leqslant \theta \leqslant 25^\circ$, 2 702 of which were considered observed by applying the condition $I > 2.05\sigma(I)$.

The structure was solved by direct methods, using the MULTAN system of computer programs.[40] An *E* map with the phases from the set with the highest combined figure of merit revealed peaks for Au and Cl atoms; a subsequent Fourier synthesis revealed peaks for the remaining non-hydrogen atoms. Isotropic and anisotropic refinements by full-matrix least-squares methods were carried out using the SHELX 76 computer program.[41] The function minimized was $w[|F_0| - |F_0|]^2$, where $w = [\sigma^2(F_0) + 0.0084|F_0|^2]^{-1}$. The final *R* factor was 0.063 ($R' = 0.067$) for all observed reflections. Selected bond distances and angles are listed in Table 2 and final co-ordinates are in Table 3.

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