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Synthesis of [2-{(dimethylamino)methyl}phenyl-C^1N]-(phenyl)gold(III) complexes. Crystal structure of two modifications of chloro[2-{(dimethylamino)methyl}-phenyl-C^1N](phenyl)gold(III)

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Abstract

The reaction (1/1) between $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)Cl}_2]$ and $[\text{HgPh}_2]$ gives $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)(Ph)Cl}]$. From this complex, the neutral $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)(Ph)X}]$ (X = Br, I, CN, MeCO_2) complexes are obtained by reaction with X^- salts. Cationic complexes $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)(Ph)L]ClO}_4$ (L = pyridine, tetrahydrothiophene) are obtained by treatment of $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)(Ph)Cl}]$ with ClO_4^- and the relevant ligand L. The complex $[\overline{\text{Au(2-C}_6\text{H}_4\text{CH}_2\text{N}}\text{Me}_2\text{)(Ph)Cl}]$ crystallizes in two modifications, both with three independent molecules in the asymmetric unit. The Au–N and Au–Cl bonds are long, consistent with the appreciable *trans* influence of the C-donor ligands. The molecules differ somewhat in the orientation of the rings.

Introduction

We have shown that organomercury compounds are convenient reagents for the synthesis of aryl complexes of gold(I) and gold(III) [1], palladium(II) [2], platinum(II) [3], rhodium(III) [4] and tin(IV) [5]. We have recently extended this method to thallium(III) [6].

Mono- or di-aryl complexes are obtained in these transmetallation reactions; the nature of the products depends on the nature of the aryl group to be transferred, on

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the metal and on the reaction conditions. In the case of some aryl groups, such as *ortho*-nitrophenyl, both groups seem to be simultaneously transferred from the corresponding $[HgR_2]$ compound to give d^8 ion complexes (Au^{III} [1c,1d], Pd^{II} [2b], Pt^{II} [3a], or Rh^{III} [4]), whereas with others, such as 2-[(dimethylamino)methyl]phenyl or 2-(phenylazo)phenyl, the two are transferred from the corresponding mercury compound to $[AuCl_4]^-$ in a two-step process [1b,e,f,h]. The latter reaction type [1f] allows the synthesis of mixed [2-{(dimethylamino)methyl}phenyl][2-(phenylazo)-phenyl]gold(III) complexes.

In this paper we show that the organomercury route for the synthesis of mixed diarylgold(III) complexes can also be used to prepare complexes with a non-functionalized aryl group such as phenyl. Arylgold chemistry is mainly dominated by perhalophenyl complexes [7], and the only mixed diaryl derivatives are trans-$[Au(C_6F_5)(2,4,6\text{-}C_6F_3H_2)X_2]^-$ (X = Br, I) [8] and those recently reported by us [1f]. We also report the first crystal structure of a neutral arylgold(III) complex containing two different aryl groups.

Results and discussion

The complex $[\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)Cl_2]$ (obtained [1e] by the reaction of $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) with $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ and Me_4NCl (1/1/1)), reacts with $[HgPh_2]$ (1/1) in chloroform at room temperature to give $[\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)(Ph)Cl]$ (**1**) in high yield (86%). The limited solubility in cold chloroform of the by-product, [Hg(Ph)Cl], allows the isolation of **1** from the reaction solution. The reaction between $[\overline{Au(2\text{-}C_6H_4N=}NC_6H_5)Cl_2]$ [1a,1b] and $[HgPh_2]$ gives metallic gold and [Hg(Ph)Cl].

The reaction of **1** with KX (X = Br, I, CN) (1/1) leads to the corresponding complexes $[\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)(Ph)X]$ (X = Br (**2**), I (**3**), CN (**4**)). When KO_2CMe is used, the acetato complex (X = $MeCO_2$ (**5**)) is obtained, along with **1** after 24 h, but the pure complex can be isolated by use of AgO_2CMe (1/1).

Complex **1** reacts with PPh_3 (1/1) to give $[AuCl(PPh_3)]$. It is likely that the coordination of PPh_3 induces a coupling reaction of both aryl groups, as previously observed [1f,h]. We are now investigating this and other similar reactions in order to determine the nature of the organic products and to see whether other diaryl gold(III) complexes exhibit the same behaviour.

Complex **1** reacts with $AgClO_4$ in acetone to give AgCl and a solution from which we were not be able to isolate the expected perchlorato complex as a pure compound. However, the residue after evaporation of the acetone is soluble in dichloromethane, and addition of an excess of tetrahydrothiophene (tht) to this solution gives the cationic complex $[\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)(Ph)L]ClO_4$ (L = tht (**6**)). If PPh_3 (1/1) is used a product that analyzes as the corresponding cationic complex (L = PPh_3) can be obtained, but the result is not easily reproducible. If PPh_3 (2/1) is used reduction to $[Au(PPh_3)_2]ClO_4$ occurs. It is likely that the above mentioned coupling reaction take place in both reactions of **1** with PPh_3.

Complex **6**, and the related pyridine complex (L = py (**7**)), can also be obtained from the reaction between **1**, $NaClO_4$ and L (1/1/1). However, the reaction with L = PPh_3 gives the reduction product $[Au(PPh_3)_2]ClO_4$. The use of $NaClO_4$ instead of the silver salt (see above) could have an effect similar to that of an excess of PPh_3, because of a slow replacement of Cl^- by ClO_4^-. The same explanation could apply to the observation that complex **7** reacts with PPh_3 (1/1) to give a mixture of **7** and $[Au(PPh_3)_2]ClO_4$. If a 1/2 molar ratio is used only $[Au(PPh_3)_2]ClO_4$ is obtained.

Complex **7** can also be obtained by the reaction of the acetato-complex **5** with $[pyH]ClO_4$ (1/1). However, the same method, whose usefulness we have previously demonstrated [1h,9], failed when **5** was treated (1/1) with $[LH]ClO_4$ ($L = PPh_3$, 1,10-phenanthroline or PPh_3CHCO_2Et). The reaction when $L = PPh_3$ gives a mixture of **7** and $[Au(PPh_3)_2]ClO_4$, and when L = 1,10-phenanthroline there is decomposition to metallic gold. With the phosphonium salt there is no reaction. Complex **5** does not react with 8-hydroxyquinoline or 2-aminothiophenol.

Complexes **1**–**7** show molar conductivities in accord with their formulations. The corresponding data along with some NMR spectroscopic, analytical and other data are included in the Experimental section.

IR Spectra

The main difference between the IR spectrum of the starting complex $[\overline{Au(2\text{-}C_6H_4CH_2NMe_2})Cl_2]$ (**A**) [1e] and those of complexes **1**–**7** is the presence in these complexes of a new band at 490(m) cm^{-1}. A band at around 510(m, w) cm^{-1} in **1**–**7** could be related to that appearing at 530(w) cm^{-1} in **A**. These two bands could be assigned to ν(Au–C) modes corresponding to the phenyl (490 cm^{-1}) and the $2\text{-}C_6H_4CH_2NMe_2$ (510 cm^{-1}) groups.

The bands at 350(s) and 300(s) cm^{-1} in complex **A** [1e], are replaced in **1** by a weak and a very strong band, respectively. Because the structure of **1** could not be assigned unambiguously from the IR spectrum only, its crystal structure was determined (see below) and this showed it to be the isomer with the chloro ligand *trans* to the phenyl of the chelating ligand. Accordingly, the strong band at 300 cm^{-1} in **1** can be assigned to ν(AuCl).

The solution of the crystal structure of **1** confirms our previous structural and IR spectral assignments [1,9] in which we assumed that the *trans* influence scale (mainly based on platinum complexes) could be used to assign ν(AuCl) modes in gold(III) complexes. We have assigned the bands around 300 and 360 cm^{-1} to ν(AuCl) *trans* to a phenyl group and a nitrogen donor ligand, respectively, in several gold(III) complexes, based on the assumption of a decrease in *trans* influence. This assignment now has a structural basis. In addition, some previous structural assignments are now confirmed. Thus for example, the complex $[\overline{Au(2\text{-}C_6H_4CH_2NMe_2})Cl(PPh_3)]Cl$ was assumed to be the isomer with the chloro ligand *trans* to the phenyl group [1e] on the basis of the presence of a strong band at 310 cm^{-1}, and this is now supported by the IR spectrum and crystal structure of **1**.

Complexes **2** and **3** have almost identical IR spectra to **1**, except for the 300 cm^{-1} band. The other neutral complexes show the expected bands corresponding to the X groups (**4**: 2140(w) cm^{-1}, ν(CN); **5**: 1610 cm^{-1}, $\nu_{asym}(CO_2)$, 1310 cm^{-1}, $\nu_{sym}(CO_2)$). The position of the $\nu(CO_2)$ bands [1f,9a] and their wavenumber difference [10] allow us to assign to the acetato ligand the same position as the chloro ligand in **1**. Both cationic complexes **6**–**7** show bands at 1080 (br, s) and 620 (m, s).

Crystal structure of complex 1

An unusual feature of the crystal structure of **1** is that there are two modifications, both with three independent molecules in the asymmetric unit. (Use of a variety of lattice geometry programs failed to give any hint of higher symmetry). There are thus six molecules of the same compound available for structural comparison. The reliability of these comparisons is reduced somewhat by the imprecisely determined structure of the C-centred modification, and by the fact that one molecule of the primitive modification is disordered, but the following features are noteworthy.

All six molecules show the expected square planar coordination geometry (highest mean deviation 0.057 Å). The aromatic rings adopt slightly different conformations with respect to the ligand plane; the dihedral angles lie in the range 78–107° for the unsubstituted ring, 1–16° for the substituted (see Table 3).

We have studied a series of compounds containing the 2-[(dimethylamino)methyl]phenyl ligand coordinated to Au^{III} [1f,9b,13]. The Au–C bond length is insensitive to the nature of the other ligands, lying in the range 2.014–2.033 Å; in our six molecules, there is one anomalous bond length of 1.947 Å, all others lying in the range 1.970–2.011 Å *. The $Au-NMe_2$ bond length, in contrast, is sensitive to its *trans* ligand. For various ligands with O, N, S, P and C donors *trans* to NMe_2, the $Au-NMe_2$ bond length varied from 2.054–2.166 Å. **1C** and **1P** show an average Au–N bond length of 2.169 Å, consistent with the presence of the C donor ligand. The average Au–Cl bond length is 2.356 Å; Au^{III}–Cl *trans* to P or C ligands are usually ca. 2.35 Å [14], and this may be interpreted as consistent with a large *trans* influence of such ligands.

The C–C–C bond angles at the *ipso* carbons of the unsubstituted phenyl groups are slightly less than the ideal 120° in **1P** (av. 117.4°). This effect is much more marked in C_6F_5 complexes [7b]. The corresponding groups in **1C** were constrained to idealised geometry (see Experimental) because of the poor quality of the data; this would lengthen the apparent Au–C bond lengths systematically.

Experimental

IR and NMR spectra, C, H, N and Au analyses, conductance measurements and melting point determinations were performed as described elsewhere [11]. Reactions were carried out at room temperature with magnetic stirring, without special precautions to exclude light or moisture unless otherwise stated. The starting mercury [12] and gold [1e] complexes were made by published methods. All the complexes are colourless. NMR spectra were measured from $CDCl_3$ solutions. δ in ppm with respect to TMS. Molar conductivities (Λ_M) in $\Omega^{-1}cm^2mol^{-1}$.

[$\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)(Ph)Cl$] (1)

To a suspension of [$\overline{Au(2\text{-}C_6H_4CH_2}NMe_2)Cl_2$] (150 mg, 0.37 mmol) in chloroform (2 cm^3) was added solid [$HgPh_2$] (131 mg, 0.37 mmol). After 1 h the mixture was cooled to ca. 0°C. The white precipitate of [Hg(Ph)Cl] was filtered off and the filtrate concentrated under vacuum to ca. 1 cm^3. Addition of n-hexane (10 cm^3)

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* The anomalous bond length, Au(2)–C(211) in **1C**, can be attributed to a large residual absorption peak near Au(2). If the phenyl ring is refined freely, C(211) is drawn into this peak and an impossible Au–C bond length of 1.6 Å results. Such residual errors may be the cause of some anomalous Au–C bond lengths in the literature.

afforded **1** (86% yield, m.p. 130 °C, dec.). $\Lambda_M = 1$. ^1H NMR: δ, 2.95 (s, 6H); 4.08 (s, 2H); 7–7.5 (m, 9H). Analytical data. Found: C, 39.9; H, 3.7; N, 3.0; Au, 43.9. $C_{15}H_{17}AuClN$ calc.: C, 40.6; H, 3.9; N, 3.2; Au, 44.4%.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(Ph)Br]$ *(2)*

To an acetone (2 cm^3) solution of **1** (75 mg, 0.17 mmol) was added solid KBr (50 mg, 0.43 mmol). After 48 h the suspension was evaporated to dryness, the residue extracted with CH_2Cl_2 (3×6 cm^3), and the extract filtered through anhydrous $MgSO_4$. The solution was concentrated (to ca. 1 cm^3) and n-hexane (10 cm^3) slowly added to afford **2** (88% yield, m.p. 151 °C dec.). $\Lambda_M = 1$. Analytical data. Found: C, 36.5; H, 3.7; N, 2.7; Au, 41.1. $C_{15}H_{17}AuBrN$ calc.: C, 36.9; H, 3.5; N, 2.9; Au, 40.4%.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(Ph)I]$ *(3)*

To an acetone (3 cm^3) solution of **1** (51 mg, 0.12 mmol) was added solid KI (46 mg, 0.28 mmol). After 4.5 h work-up as for **2**, but with 4×5 cm^3 of CH_2Cl_2 used for extraction and final addition of 15 ml of n-hexane gave **3** (87% yield, m.p. 145 °C dec.) $\Lambda_M = 2$. Analytical data. Found: C, 32.8; H, 3.4; N, 2.6; Au, 36.4. $C_{15}H_{17}AuIN$ calc.: C, 33.7; H, 3.2; N, 2.6; Au, 36.8%.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(Ph)CN]$ *(4)*

To an acetone (4 cm^3) solution of **1** (80 mg, 0.18 mmol) was added solid KCN (29 mg, 0.45 mmol). After 24 h work-up as for **3** but with final addition of 10 ml of n-hexane gave **4** (67% yield, m.p. 189 °C dec.) $\Lambda_M = 1$. Analytical data. Found: C, 44.4; H, 4.1; N, 6.9; Au, 45.0. $C_{16}H_{17}AuN_2$ calc.: C, 44.3; H, 4.0; N, 6.5; Au, 45.4%.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(Ph)(OOCCH_3)]$ *(5)*

To an acetone (5 cm^3) solution of **1** (70 mg, 0.16 mmol) was added solid AgO_2CMe (27 mg, 0.16 mmol). After 17.5 h work-up as for **3** but with 3×3 cm^3 of the CH_2Cl_2 for extraction gave **5** (56% yield, m.p. 160 °C dec.) $\Lambda_M = 0$. ^1H NMR: δ, 1.95 (s, 3H); 2.91 (s, 6H); 4.04 (s, 2H); 7–7.5 (m, 9H). Analytical data. Found: C, 42.7; H, 3.9; N, 2.9; Au, 41.2. $C_{17}H_{20}AuNO_2$ calc.: C, 43.6; H, 4.3; N, 3.0; Au, 42.1%.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(Ph)L]ClO_4$ *(L = tht (6), py (7))*

To an acetone (10 cm^3) solution of **1** (52.8 mg, 0.12 mmol) were added neat L (tht or py) (0.1 cm^3) and solid $NaClO_4 \cdot H_2O$ (17 mg, 0.12 mmol). After 21 h, the suspension was concentrated to dryness and the residue extracted with CH_2Cl_2 (3×5 cm^3). The extract was filtered through celite and concentrated (to ca. 1 cm^3). Addition of diethyl ether (15 cm^3) gave **6** (70% yield, m.p. 142 °C dec.) $\Lambda_M = 112$ or **7** (67% yield, m.p. 152 °C dec.) $\Lambda_M = 117$. Analytical data complex **6**. Found: C, 38.0; H, 4.3; N, 2.3; Au, 32.4. $C_{19}H_{25}AuClNO_5$ calc.: C, 38.3; H, 4.2; N, 2.4; Au, 33.0. Analytical data complex **7**. Found: C, 41.4; H, 4.2; N, 5.3; Au, 32.7. $C_{20}H_{27}AuClN_2O_4$ calc.: C, 40.9; H, 3.8; N, 4.8; Au, 33.6%.

X-Ray structure determination of complex 1

Colourless crystals were obtained by diffusion of n-hexane into a solution of **1** in dichloromethane. They proved to consist of two different crystalline modifications,

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **1P** (Primitive modification)

	x	*y*	*z*	*U*(eq) [a]
Au(1)	7528.2(2)	2116.3(2)	1783.8(2)	45(1)
Cl(1)	6743(2)	1121(2)	821(2)	67(1)
N(1)	8473(5)	1331(4)	2674(5)	58(3)
C(11)	8759(7)	1725(7)	3504(6)	83(5)
C(12)	9218(7)	1224(8)	2461(7)	102(6)
C(13)	8088(8)	548(6)	2749(7)	98(6)
C(111)	6726(4)	2921(5)	1042(4)	37(3)
C(112)	6088(5)	3305(5)	1246(5)	50(3)
C(113)	5579(5)	3907(5)	763(5)	53(4)
C(114)	5697(6)	4160(5)	56(5)	60(4)
C(115)	6309(5)	3793(5)	−160(5)	54(4)
C(116)	6822(5)	3179(5)	318(5)	52(3)
C(121)	8281(5)	2915(5)	2629(5)	47(3)
C(122)	8842(6)	2579(6)	3393(6)	66(4)
C(123)	9477(7)	3053(9)	4023(7)	91(5)
C(124)	9486(7)	3852(9)	3919(7)	89(6)
C(125)	8883(6)	4183(7)	3173(6)	77(5)
C(126)	8269(6)	3712(6)	2538(5)	66(4)
Au(2)	3476.1(2)	2524.5(2)	4407.2(2)	44(1)
Cl(2)	4253(2)	3553(2)	5321(2)	85(1)
N(2)	2495(4)	3289(4)	3493(4)	52(3)
C(21)	2167(7)	2857(6)	2668(5)	69(4)
C(22)	1756(6)	3408(6)	3742(6)	71(4)
C(23)	2836(7)	4062(6)	3374(7)	87(6)
C(211)	4332(4)	1747(5)	5192(5)	43(3)
C(212)	4272(5)	1509(7)	5935(5)	68(4)
C(213)	4852(6)	942(7)	6447(6)	74(4)
C(214)	5486(6)	608(6)	6240(6)	68(4)
C(215)	5569(6)	866(6)	5533(6)	68(4)
C(216)	4999(6)	1417(6)	5010(6)	62(4)
C(221)	2715(5)	1701(5)	3612(5)	45(3)
C(222)	2098(6)	1990(6)	2839(5)	58(4)
C(223)	1456(6)	1496(7)	2256(6)	72(5)
C(224)	1449(7)	720(7)	2418(7)	77(5)
C(225)	2069(6)	410(6)	3151(6)	68(5)
C(226)	2703(5)	900(5)	3748(5)	52(4)
Au(3)	5585.6(2)	2656.3(2)	3225.1(2)	49(1)
Cl(3)	4565(2)	3625(2)	2435(2)	83(1)
N(3)	6459(5)	3458(5)	4175(5)	63(3)
C(31′)	7396(12)	3085(13)	4525(12)	66(5)
C(32′)	6129(13)	3467(14)	4863(13)	77(6)
C(33′)	6553(15)	4257(16)	3865(14)	90(7)
C(31″)	6865(14)	3063(15)	4991(14)	83(6)
C(32″)	7116(13)	3761(14)	3843(13)	80(6)
C(33″)	5977(15)	4183(16)	4381(14)	91(7)
C(311)	4864(5)	1840(5)	2417(5)	51(3)
C(312)	4097(6)	1536(6)	2452(6)	64(4)
C(313)	3613(6)	958(6)	1904(7)	75(5)
C(314)	3866(7)	663(6)	1316(6)	71(4)
C(315)	4611(7)	954(6)	1248(6)	69(5)
C(316)	5110(6)	1541(6)	1799(5)	61(4)
C(321)	6490(5)	1869(5)	3947(5)	50(3)

Table 1 (continued)

	x	y	z	U(eq) [a]
C(322)	7188(9)	2197(8)	4653(8)	117(7)
C(323)	7866(8)	1736(9)	5225(7)	106(6)
C(324)	7878(7)	962(8)	5119(7)	84(6)
C(325)	7185(7)	623(7)	4442(7)	82(5)
C(326)	6517(6)	1072(6)	3867(6)	65(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

one primitive monoclinic (**1P**) and one C-centred monoclinic (**1C**). Both modifications were subjected to an X-ray diffraction study. The structure of one of the crystallographically independent molecules is shown in Fig. 1.

Crystal data: $C_{15}H_{17}AuClN$, M 443.7. Modification **1P**: space group $P2_1/n$, a 16.472(3), b 17.124(3), c 17.371(3) Å, β 114.76(2)°, V 4449 Å^3, Z 12, D_x 1.99 g cm^{-3}, $F(000)$ 2520, λ(Mo-K_α) 0.71069 Å, μ 10.1 mm^{-1}. Modification **1C**: space group $C2/c$, a 28.36(3), b 18.224(12), c 18.054(10) Å, β 107.46(6)°, V 8902 Å^3, $Z = 24$, D_x 1.99 g cm^{-3}, $F(000)$ 5040, μ(Mo-K_α) 10.1 mm^{-1}.

Data collection and reduction: **1P**: crystal 0.6 × 0.4 × 0.3 mm, colourless prism elongated along $10\bar{1}$. Stoe–Siemens four-circle diffractometer with monochromated Mo-K_α radiation. 10276 profile-fitted intensities [15] measured to $2\theta_{\max}$ 50°, 7908 unique (R_{int} 0.030), 6545 with $F > 4\sigma(F)$ used for all calculations (program system SHELX-76, locally modified by its author Prof. G.M. Sheldrick). Absorption correction based on ψ-scans, with transmission factors 0.51–0.99. Cell constants refined from 2θ values of selected strong reflections in the range 20–24°. **1C**: as for **1P**, but with following differences: crystal 0.45 × 0.45 × 0.4 mm, colourless prism elongated along $\bar{1}02$, 8027 reflections, 7895 unique (R_{int} 0.064), 5303 observed. Transmission factors 0.58–0.96. The reflection shape of **1C** was irregular, and the structure determination is thus less precise than that of **1P**. No better (indeed, no other) crystal of **1C** was discovered.

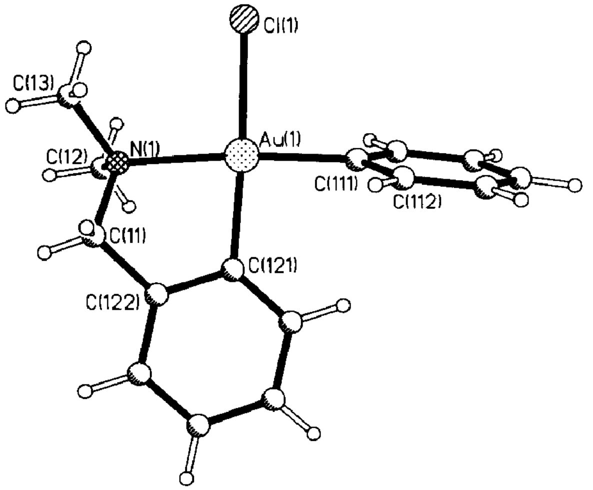

Fig. 1. One of the six crystallographically independent molecules of **1**, showing the atom numbering scheme. Atomic radii are arbitrary. (This is molecule 1 of modification **1P**).

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1C** (C-centred modification)

	x	y	z	U(eq) [a]
Au(1)	826.8(3)	8022.5(5)	2395.2(5)	48(1)
Cl(1)	866(3)	8887(4)	1447(4)	80(3)
N(1)	765(7)	7095(10)	1614(10)	57(8)
C(11)	573(10)	6489(15)	1972(14)	75(7)
C(12)	1273(11)	6912(16)	1594(18)	96(9)
C(13)	449(12)	7208(18)	831(18)	103(10)
C(112)	1332(5)	9159(9)	3511(9)	66(7)
C(113)	1390	9668	4109	65(6)
C(114)	992	9837	4382	62(6)
C(115)	536	9497	4057	68(7)
C(116)	478	8988	3459	60(6)
C(111)	876	8819	3186	65(7)
C(122)	747(6)	6535(8)	2832(6)	61(6)
C(123)	778	5908	3287	77(8)
C(124)	907	5969	4093	85(8)
C(125)	1006	6657	4444	76(8)
C(126)	975	7284	3989	55(6)
C(121)	846	7223	3182	52(5)
Au(2)	929.7(3)	3021.3(5)	2841.8(5)	51(1)
Cl(2)	1104(3)	3927(4)	3824(3)	73(3)
N(2)	1103(8)	2117(11)	3661(11)	67(9)
C(21)	1309(16)	1569(23)	3338(22)	143(15)
C(22)	649(13)	1949(19)	3833(21)	122(12)
C(23)	1475(16)	2277(23)	4399(23)	151(16)
C(212)	1162(4)	4088(8)	1764(8)	58(6)
C(213)	1032	4612	1175	62(6)
C(214)	540	4826	866	62(6)
C(215)	177	4516	1146	68(7)
C(216)	307	3991	1735	78(7)
C(211)	799	3777	2044	43(5)
C(222)	889(7)	1529(10)	2423(7)	83(8)
C(223)	796	884	1986	121(12)
C(224)	595	919	1181	94(9)
C(225)	487	1598	812	82(8)
C(226)	579	2242	1249	55(6)
C(221)	780	2208	2055	61(6)
Au(3)	2493.6(3)	8621.3(5)	2532.1(5)	42(1)
Cl(3)	2446(3)	7809(4)	1496(4)	87(3)
N(3)	2363(6)	9605(9)	1803(9)	49(7)
C(31)	2149(10)	10139(14)	2228(14)	72(7)
C(32)	2870(9)	9856(13)	1739(13)	65(6)
C(33)	2033(12)	9518(16)	1014(16)	94(10)
C(312)	3056(5)	7465(8)	3528(8)	65(6)
C(313)	3145	6898	4071	73(7)
C(314)	2768	6654	4359	59(6)
C(315)	2301	6978	4103	61(6)
C(316)	2212	7545	3560	45(5)
C(311)	2590	7789	3272	45(5)
C(322)	2457(5)	10089(8)	3088(6)	54(6)
C(323)	2551	10688	3592	68(7)
C(324)	2776	10581	4385	73(7)
C(325)	2907	9876	4673	60(6)
C(326)	2813	9277	4169	51(5)
C(321)	2588	9383	3376	40(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected molecular dimensions for **1** (bond lengths in Å, angles in degrees)

	1P, molecules 1,2,3			**1C**, molecules 1,2,3		
Au–Cl	2.358(2)	2.357(2)	2.351(3)	2.352(7)	2.363(6)	2.357(7)
Au–N	2.146(7)	2.168(6)	2.166(7)	2.175(18)	2.171(20)	2.188(16)
Au–phenyl-C (C(111)) [a]	1.970(7)	2.003(7)	1.985(8)	2.011(24)	1.947(14) [b]	1.986(15)
Au–damp-C (C(121))	2.010(7)	2.005(7)	2.012(8)	2.025(22)	2.009(22)	2.019(19)
C(112)–C(111)–C(116)	117.2(7)	117.6(7)	117.3(8)	[c]		
chelate N–Au–C	82.0(3)	82.0(3)	82.4(3)	82.9(6)	83.0(7)	81.4(5)
dihedral angles:						
phenyl/ligand plane	106	93	78	104	101	101
damp/ligand plane	12	6	16	13	14	1

[a] For numbering scheme, see Fig. 1. [b] Distortion arising from systematic errors, see text. [c] Refined as idealised rigid groups.

Structure solution and refinement: heavy-atom method, followed by full-matrix least-squares refinement on F. For **1P**, all non-H atoms were refined anisotropically. For **1C**, only Au, Cl and N were refined anisotropically, and aromatic rings were constrained to an idealised geometry with C–C 1.395, C–H 0.96 Å, all angles 120°. All other H atoms were included using a riding model. Final details: **1P**, R 0.042, R_w 0.039; weighting scheme $w^{-1} = \sigma^2(F) + 0.0003F^2$; 484 parameters; max. Δ/σ 0.001; max. $\Delta\rho$ 1.1 e Å^{-3}; S 1.6. The chelate ring of the third molecule of **1P** is disordered, and corresponding half-occupied sites were refined for C(31)–C(33). **1C**, R 0.081, R_w 0.079; $w^{-1} = \sigma^2(F) + 0.001 F^2$; 190 parameters; max. Δ/σ 0.002; max. $\Delta\rho$ 5.5 e Å^{-3} (near Au(2); probably attributable to residual absorption errors); S 1.9.

Final atomic coordinates are presented in Tables 1 and 2, with selected molecular dimensions in Table 3. Further details of crystal structure determination (bond lengths and angles, H atom coordinates, temperature factors, structure factors) have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, W. Germany. Any request for this material should quote the reference number CSD 53121 and the full literature citation.

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