Gold(I) Complexes with Amino-acid Derivatives: The Crystal Structure of Triphenylphosphine(hippurato)gold(I)

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The reaction between Ph_3PAuCl and silver salts of *N*-substituted glycines leads to complexes Ph_3PAuX, where X is the substituted glycinate; the *X*-ray structure determination of the hippurato-complex confirms the presence of an Au–O bond.

Gold complexes are used in the treatment of rheumatoid arthritis[1] and also exhibit some anti-tumour activity.[2] However, the mechanisms of action of gold drugs are not well understood. There is evidence that gold species bind to sulphur and, to a lesser extent, nitrogen donor functions of biological molecules such as sulphur-containing proteins;[3] it would therefore be expected that simple amino-acid complexes of gold could act as models for such systems. To the best of our knowledge, no such complex has been subjected to *X*-ray structure analysis and few have been reported.[4] This may be attributed to several factors: (i), gold(III) species are redox active towards some amino-acids;[5] (ii), it is difficult to find suitable solvent systems for amino-acids and gold-containing starting materials (the commonly used $SOCl_2$ reacts with many amino-acids[5]); (iii), even when reactions take place, *e.g.* between (OC)AuCl and lysine, the products are generally insoluble in all common solvents, difficult to obtain pure, and subject to decomposition within a few hours.[6]

We have shown that complexes $Ph_3PAu(O_2CR)$ (R = Me, Ph) are stable crystalline solids.[7,8] We therefore decided to

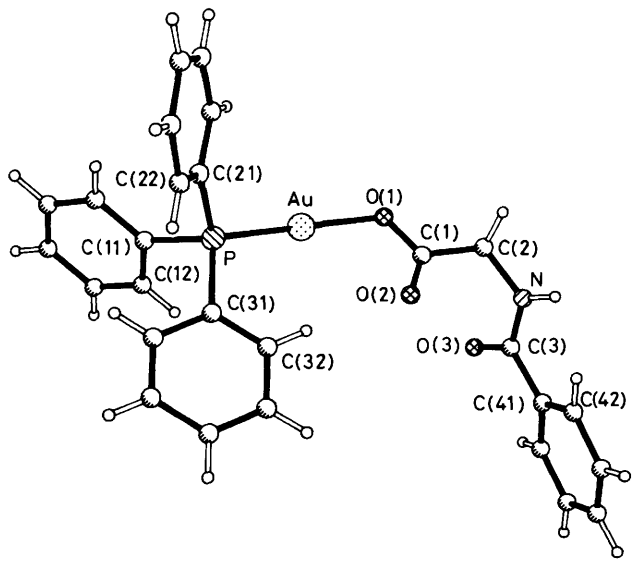

Figure 1. The molecule of the title compound in the crystal (radii arbitrary; one H atom on C(2) is eclipsed).

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depart from the received wisdom that amino-acid complexes of gold(I) must involve S or N donors, and to attempt the preparation of O-bonded complexes. We chose *N*-substituted glycines in order to increase the solubility in organic solvents and to reduce the donor properties and redox activity of the NH_2 group.

The reaction between silver salts $Ag(O_2CCH_2NHC(O)R)$ (R = Me, Ph) and Ph_3PAuCl led to the required products $Ph_3PAu(O_2CCH_2NHC(O)R)$. The silver salts were obtained from the sodium salts and $AgNO_3$ and then stirred with Ph_3PAuCl in benzene for 15 h. AgCl was filtered off and the solution evaporated to dryness under reduced pressure. The resulting gum was recrystallized from CH_2Cl_2/petrol (R = Me) or CH_2Cl_2 alone (R = Ph). Satisfactory ^1H and ^{13}C n.m.r. spectra and elemental analyses were obtained.

An *X*-ray structure determination of the benzoylglycinato ('hippurato') derivative confirmed the expected nature of the product (Figure 1).‡ The co-ordination at gold is linear, with Au–P 2.212(2), Au–O 2.077(5) Å, P–Au–O 174.6(1)°. The molecules are linked by H bonding between N and the benzoyl O (N···O 3.00 Å).

Our results indicate that the possibility of gold–carboxylate interactions in biological systems should not be ignored, at least as a minor effect. We are currently attempting to extend our studies to derivatives of other amino-acids and simple peptides.

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‡ *Crystal structure determination: Crystal data*: $C_{27}H_{23}AuNO_3P$, M_r = 637.4, orthorhombic, *Pbca*, a = 8.990(1), b = 27.050(3), c = 19.307(2) Å, U = 4695 Å^3 (by refinement of 2θ values of 50 reflections in the range 20—23°), Z = 8, D_c = 1.80 Mg m^{-3}, $F(000)$ = 2480, crystal size 0.35 × 0.15 × 0.1 mm (colourless prism), μ(Mo-K_α) = 6.4 mm^{-1}. *Data collection and processing*: Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation, 7650 profile-fitted intensities ($2\theta_{max}$ 50°), 4112 unique (R_{int} 0.023), 3032 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; transmissions 0.63—0.80. *Structure analysis and refinement*: heavy-atom method, full-matrix anisotropic refinement on *F*, H atoms included using riding model. R 0.041, R_w 0.033, 298 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\,F^2$, S 1.3, max. Δ/σ 0.001, max. $\Delta\rho$ 0.8 e Å^{-3}. *Deposition*: Full details of the structure determination (atomic co-ordinates, temperature factors, structure factors, complete bond lengths and angles) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, FRG; any request for this material should quote a full literature citation and the deposition number CSD 53232. Atomic co-ordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

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