isostructural, being shifted appreciably in the x and z directions with respect to each other.

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial assistance, and Degussa (Hanau) for a generous gift of gold metal. Calculations were performed with the program system *SHELX*76 (which incorporates atomic scattering factors), locally modified by its author Professor G. M. Sheldrick.

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Redetermination of the Structure of Cyano(triphenylphosphine)gold(I)

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Abstract. $[Au(C_6H_5)_3P(CN)]$, $M_r = 485{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}388\,(2)$, $b = 12{\cdot}420\,(2)$, $c = 13{\cdot}057\,(2)$ Å, $V = 1684{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}91$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 8{\cdot}8$ mm^{-1}, $F(000) = 920$, $T = 293$ K. The structure was refined to $R = 0{\cdot}037$ for 4202 unique observed reflections. The absolute structure was determined with an η refinement. The coordination geometry at gold is linear, with Au—P 2·278 (2), Au—C 2·003 (7) Å, P—Au—C 177·0 (2)°. Considerable distortions of the structure (involving the light atoms) were observed until systematic errors (extinction, absolute structure) were minimized.

Introduction. Many linear gold(I) complexes of general formula Ph_3PAuX crystallize isostructurally in space group $P2_12_12_1$ (Barron, Engelhardt, Healy, Oddy & White, 1987; Jones, 1981, 1983, 1984*a*, 1986; Ahrland, Dreisch, Norén & Oskarsson, 1987, and references therein). Presumably the bulky PPh_3 groups determine the packing. An early structure from this series was that of the cyano derivative Ph_3PAuCN (Bellon, Manassero & Sansoni, 1969). The structure was determined from photographic intensity measurements, which limited its precision; the bond lengths at gold were Au—P 2·27 (1), Au—C 1·85 (4) Å, and the bond angle P—Au—C was 169 (2)°. The Au—C bond thus appeared unusually short, and despite its high e.s.d. is often quoted as an example of a short Au—C bond. We decided to redetermine the structure to obtain a more precise value.

Experimental. The title compound was prepared by the method of Nichols & Charleston (1969) and recrystallized as colourless prisms by diffusion of petroleum ether into a solution in dichloromethane.

A crystal 0·6 × 0·2 × 0·1 mm was mounted in a glass capillary on a Stoe–Siemens four-circle diffractometer. Using monochromated Mo $K\alpha$ radiation, 5950 profile-fitted intensities (Clegg, 1981) were measured ($2\theta_{\max}$ 60°, octants $+h+k+l$ and $-h-k-l$). Merging equivalents gave 4874 reflections (R_{int} 0·016, index ranges after merging and reorienting h −14 to 14, k 0 to 17, l 0 to 18). An absorption correction based on φ scans was applied, with transmission factors 0·73–0·96; to avoid problems with Friedel opposites, only reflections with one zero index were used for this correction. Cell constants were refined from 2θ values of 60 reflections in the range 20–25°.

The coordinates of Bellon *et al.* (1969) were used as a starting model. Refinement proceeded to a final $R = 0{\cdot}037$, $wR = 0{\cdot}036$ [full matrix on F, all non-H atoms anisotropic, H-atoms included using a riding model, 4202 reflections $>4\sigma(F)$]. The absolute structure (Jones, 1984*b*) was determined by an η refinement (Rogers, 1981); η refined to −1·08 (3), whereupon the structure was inverted to give the final model. Six low-angle reflections with $F_o \ll F_c$ were omitted; additionally, an extinction correction of the form $F_{\text{corr}} = F_c(1 + xF^2/\sin 2\theta)^{-0{\cdot}25}$ was applied, where x refined to $8\,(1) \times 10^{-7}$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}*
Au	3446·6 (2)	4272·7 (2)	7597·2 (1)	49 (1)
P	5475 (2)	3740 (1)	7170 (1)	46 (1)
C	1638 (7)	4660 (5)	7981 (5)	59 (2)
N	601 (6)	4804 (6)	8219 (5)	87 (3)
C(11)	6236 (5)	2926 (5)	8141 (4)	48 (2)
C(12)	7577 (6)	2941 (6)	8264 (5)	67 (2)
C(13)	8128 (8)	2234 (8)	8991 (6)	87 (3)
C(14)	7394 (9)	1586 (7)	9570 (6)	79 (3)
C(15)	6068 (9)	1580 (5)	9448 (5)	72 (3)
C(16)	5501 (7)	2256 (5)	8739 (5)	58 (2)
C(21)	6572 (6)	4858 (4)	6973 (4)	49 (2)
C(22)	7242 (6)	5036 (6)	6090 (5)	62 (2)
C(23)	8064 (7)	5917 (6)	6033 (7)	78 (3)
C(24)	8210 (6)	6598 (6)	6835 (7)	73 (3)
C(25)	7534 (6)	6444 (6)	7699 (6)	70 (2)
C(26)	6710 (6)	5590 (5)	7781 (5)	59 (2)
C(31)	5469 (6)	2932 (5)	6011 (4)	47 (2)
C(32)	4749 (8)	3268 (5)	5186 (6)	72 (3)
C(33)	4669 (9)	2643 (7)	4308 (6)	86 (3)
C(34)	5280 (8)	1698 (6)	4256 (6)	77 (3)
C(35)	6015 (8)	1349 (7)	5056 (6)	82 (3)
C(36)	6097 (8)	1964 (6)	5945 (5)	71 (3)

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

Table 2. *Bond lengths* (Å) *and angles* (°)

Au—P	2·278 (2)	Au—C	2·003 (7)
P—C(11)	1·804 (6)	P—C(21)	1·814 (6)
P—C(31)	1·816 (6)	C—N	1·136 (10)
C(11)—C(12)	1·402 (9)	C(11)—C(16)	1·374 (8)
C(12)—C(13)	1·413 (11)	C(13)—C(14)	1·342 (12)
C(14)—C(15)	1·387 (13)	C(15)—C(16)	1·381 (10)
C(21)—C(22)	1·365 (9)	C(21)—C(26)	1·400 (8)
C(22)—C(23)	1·390 (10)	C(23)—C(24)	1·355 (12)
C(24)—C(25)	1·342 (11)	C(25)—C(26)	1·368 (9)
C(31)—C(32)	1·376 (9)	C(31)—C(36)	1·370 (9)
C(32)—C(33)	1·387 (11)	C(33)—C(34)	1·336 (12)
C(34)—C(35)	1·365 (11)	C(35)—C(36)	1·392 (11)

P—Au—C	177·0 (2)	Au—P—C(11)	113·3 (2)
Au—P—C(21)	113·2 (2)	C(11)—P—C(21)	104·7 (3)
Au—P—C(31)	111·2 (2)	C(11)—P—C(31)	106·1 (3)
C(21)—P—C(31)	107·9 (3)	Au—C—N	175·0 (6)
P—C(11)—C(12)	120·6 (4)	P—C(11)—C(16)	119·7 (5)
C(12)—C(11)—C(16)	119·6 (6)	C(11)—C(12)—C(13)	118·1 (6)
C(12)—C(13)—C(14)	121·4 (8)	C(13)—C(14)—C(15)	120·2 (7)
C(14)—C(15)—C(16)	119·8 (7)	C(11)—C(16)—C(15)	120·9 (7)
P—C(12)—C(22)	124·3 (5)	P—C(21)—C(26)	117·0 (4)
C(22)—C(21)—C(26)	118·7 (6)	C(21)—C(22)—C(23)	119·0 (7)
C(22)—C(23)—C(24)	121·3 (7)	C(23)—C(24)—C(25)	120·1 (7)
C(24)—C(25)—C(26)	120·3 (7)	C(21)—C(26)—C(25)	120·5 (6)
P—C(31)—C(32)	119·1 (5)	P—C(31)—C(36)	122·4 (5)
C(32)—C(31)—C(36)	118·4 (6)	C(31)—C(32)—C(33)	120·7 (7)
C(32)—C(33)—C(34)	120·3 (7)	C(33)—C(34)—C(35)	120·4 (7)
C(34)—C(35)—C(36)	119·8 (7)	C(31)—C(36)—C(35)	120·3 (7)

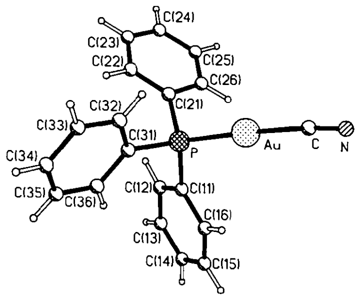

Fig. 1. The molecule of Ph_3PAuCN in the crystal, showing the atom-numbering scheme. Radii are arbitrary.

Further details of refinement: 200 parameters, $S = 1{\cdot}2$, max. $\Delta/\sigma = 0{\cdot}001$, max. $\Delta\rho = 1{\cdot}5$ e $Å^{-3}$ near Au.

Final atomic coordinates are presented in Table 1,* with derived bond lengths and angles in Table 2. A view of the molecule is given in Fig. 1.

Discussion. As would be expected from the use of modern methods, the new structure determination of Ph_3PAuCN is considerably more precise than that of 1969; in particular, the number of reflections used in the refinement is almost five times as large. The coordination geometry at gold is now described by the parameters Au—C 2·002 (7), Au—P 2·278 (2) Å, C—Au—P 177·0 (2)°. The Au—P bond length agrees well with the earlier determination and is typical for an Au—P bond *trans* to a C atom with strong σ donating capacity (see references in the *Introduction*). The bond angle and Au—C bond length are however appreciably different; the deviation from linearity is much less and the Au—C bond length may be regarded as normal [*cf.* 1·97 (2) Å in Et_3PAuCN (Hormann, Shaw, Bennett & Reiff, 1986, and references therein)].

It is notable that the apparent Au—C bond length in the title compound was at one stage of the refinement significantly higher, at 2·074 (18) Å; this was before the structure inversion and extinction correction, but the R value was still acceptable (6%). This confirms the principle that light-atom bond lengths in heavy-atom structures are susceptible to systematic errors that may amount to several e.s.d.'s; errors in the model (wrong absolute structure, extinction effects) can cause error ripples near the heavy atom and so influence the light-atom positions near these ripples. A further effect here was on the bond angle C(11)—C(12)—C(13), which was 113° at one stage, but later changed to an acceptable final value of 118°. [Barron *et al.* (1987) also mention difficulties in refining the phenyl rings of Ph_3PAuX complexes.] We have recently drawn attention to even more severe apparent distortions in a gold complex (Vicente, Chicote, Bermúdez, Sanchez-Santano & Jones, 1988).

The C—N bond length is 1·14 (1) Å, but this bond is probably affected by libration (the temperature factors of the N atom are high). A riding-model correction of +0·03 Å was calculated, but the correction itself is subject to the uncertainties inherent in the thermal parameters of light atoms.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51204 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

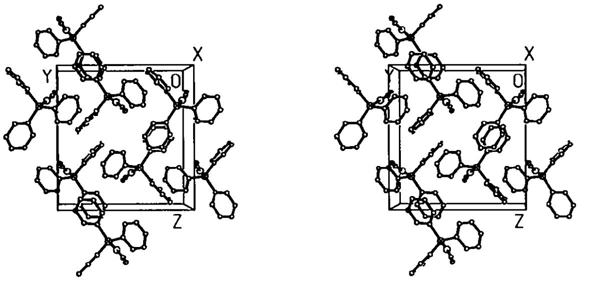

Fig. 2. Stereographic packing diagram of the title compound (H atoms omitted for clarity).

As in other Ph_3PAuX complexes, there are no short Au···Au contacts of the kind often observed for Au^I. The molecular packing is shown in Fig. 2.

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial assistance, and Degussa AG for a gift of gold metal. Calculations were performed with the program system *SHELX*76 (Sheldrick, 1976), locally modified by its author. Professor P. L. Bellon kindly sent us the atom coordinates of his earlier structure determination.

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Structure of Lithium Phthalate Hemitrihydrate

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Abstract. $2(2Li^+.C_8H_4O_4^{2-}.\frac{3}{2}H_2O)$, $M_r=410{\cdot}0$, triclinic, $P\bar{1}$, $a = 7{\cdot}411\ (2)$, $b = 9{\cdot}849\ (2)$, $c = 12{\cdot}511\ (2)$ Å, $\alpha = 93{\cdot}60\ (2)$, $\beta = 91{\cdot}45\ (1)$, $\gamma = 98{\cdot}18\ (3)°$, $V = 901{\cdot}6\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}5103\ (6)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}114$ mm^{-1}, $F(000) = 420$, room temperature, $wR = 0{\cdot}031$ for 1565 reflections $[I > 2{\cdot}5\sigma(I)]$. The structure shows a layer-like sandwich arrangement [parallel to (001)] such that two layers of phthalate ions direct their carboxylic groups towards an inner layer of Li ions. The weak van der Waals forces between these sandwiches cause the observed perfect cleavage along that plane. Of four independent Li ions two have fourfold and two have fivefold coordination.

Introduction. The system Li_2O–phthalic acid–H_2O has gained special interest because of the occurrence of two acid salts containing extremely short hydrogen bonds (Gonschorek & Küppers, 1975; Küppers, Takusagawa & Koetzle, 1985). The existence of the neutral compound with composition $2[Li_2(C_6H_4)(COO)_2].3H_2O$ was reported by Smith, Sturm & Ely (1935) in a study on equilibria in the system mentioned above.

Experimental. Single crystals were grown from an aqueous solution of a stoichiometric mixture of Li_2CO_3 and phthalic acid by slow evaporation of the solvent. The crystals grow as (001) plates which are terminated by small faces of types {100}, {011}, {101}, $\{1\bar{1}0\}$, $\{1\bar{1}1\}$, $\{\bar{1}01\}$ and $\{0\bar{1}1\}$. The crystal used for the present study measured 0·08 × 0·15 × 0·25 mm. Lattice parameters were determined by a least-squares fit to 20 diffractometrically measured Bragg angles in the range $7 < 2\theta < 30°$. 7474 reflections were collected with a Siemens AED2 diffractometer in the θ range 2–30° using θ–2θ scanning technique. 1476 of these were rejected as unobserved. Among the remaining 5998 were 4074 unique (internal R value was 0·013).

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