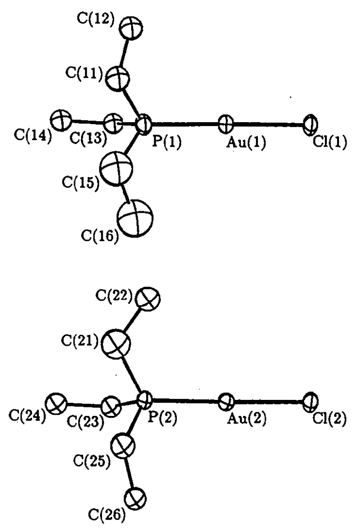


Fig. 1. Molecular structure and numbering scheme for the two molecules in the asymmetric unit of $Et_3PAuCl$ (*ORTEP*II, Johnson, 1971).

eters in Table 2* and the numbering scheme used is shown in Fig. 1, which was drawn with *ORTEP*II (Johnson, 1971) at 15% probability ellipsoids.

**Related literature.** Metal phosphines, in particular gold phosphine complexes, have useful medicinal properties (Berners-Price & Sadler, 1987; Parish & Cottrill, 1987). $Et_3PAuCl$, which is known to interact with DNA (Mirabelli, Sung, Zimmerman, Hill, Mong & Crooke, 1986), has a similar coordination geometry to that reported for the triphenylphosphine analogue $Ph_3PAuCl$ (Baenziger, Bennett & Soboroff, 1976).

G. A. Koutsantonis is thanked for the gift of $Et_3PAuCl$. The Australian Research Grants Scheme is thanked for support.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and all bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51779 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 2,6-Bis(diphenylphosphorylmethyl)pyridine Ethanol Solvate 2·5-Hydrate

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**Abstract.** $C_{31}H_{27}NO_2P_2.C_2H_6O.2\cdot5H_2O$, $M_r = 598\cdot62$, monoclinic, $P2_1/c$, $a = 9\cdot392$ (3), $b = 18\cdot903$ (6), $c = 17\cdot736$ (6) Å, $\beta = 96\cdot81$ (3)°, $V = 3127$ (2) Å$^3$, $Z = 4$, $D_x = 1\cdot272$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot75$ cm$^{-1}$, $F(000) = 1268$, $T = 299$ K, final $R = 0\cdot073$, $wR = 0\cdot077$ for 1569 reflections. The title compound results from the reaction of the corresponding phosphine with $Au_2Cl_6$. The bond lengths are normal.

**Experimental.** The ligand 2,6-bis(diphenylphosphinomethyl)pyridine, PCpyCP, was prepared by a modification of the synthesis reported by Dahlhoff & Nelson

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Table 1. *Atomic coordinates* (× $10^4$) *and equivalent isotropic thermal parameters* (Å$^2$ × $10^3$)

| | *x* | *y* | *z* | *U** |
|---|---|---|---|---|
| N | 7819 (8) | 1190 (5) | 963 (5) | 41 (3) |
| C(1) | 7607 (10) | 1078 (6) | 1697 (6) | 46 (4) |
| C(2) | 7830 (12) | 1632 (7) | 2219 (7) | 59 (5) |
| C(3) | 8224 (12) | 2279 (7) | 1963 (7) | 58 (5) |
| C(4) | 8431 (11) | 2384 (6) | 1211 (8) | 58 (5) |
| C(5) | 8233 (11) | 1829 (7) | 722 (6) | 50 (4) |
| C(1*a*) | 7106 (10) | 368 (6) | 1901 (5) | 47 (4) |
| P(1) | 5224 (3) | 231 (2) | 1587 (2) | 41 (1) |
| C(11) | 4696 (8) | 797 (4) | 2995 (4) | 62 (5) |
| C(12) | 3778 | 1078 | 3480 | 92 (7) |
| C(13) | 2360 | 1235 | 3205 | 93 (7) |
| C(14) | 1860 | 1109 | 2445 | 89 (6) |
| C(15) | 2778 | 828 | 1959 | 71 (5) |
| C(16) | 4196 | 671 | 2234 | 50 (4) |
| C(11′) | 4676 (9) | −984 (5) | 2399 (4) | 71 (6) |
| C(12′) | 4490 | −1713 | 2463 | 79 (6) |
| C(13′) | 4599 | −2151 | 1839 | 77 (6) |
| C(14′) | 4894 | −1860 | 1152 | 67 (5) |
| C(15′) | 5080 | −1131 | 1088 | 48 (4) |
| C(16′) | 4971 | −693 | 1712 | 46 (4) |
| C(5*a*) | 8505 (10) | 1870 (6) | −112 (5) | 47 (4) |
| P(2) | 10323 (3) | 1563 (2) | −208 (2) | 44 (1) |
| C(21) | 11320 (8) | 1840 (4) | −1601 (4) | 59 (5) |
| C(22) | 11408 | 1701 | −2367 | 78 (6) |
| C(23) | 10546 | 1179 | −2742 | 60 (5) |
| C(24) | 9595 | 796 | −2352 | 80 (6) |
| C(25) | 9508 | 935 | −1586 | 68 (5) |
| C(26) | 10370 | 1457 | −1211 | 44 (4) |
| C(21′) | 12918 (10) | 2047 (4) | 439 (5) | 67 (5) |
| C(22′) | 13936 | 2557 | 695 | 87 (6) |
| C(23′) | 13592 | 3274 | 627 | 92 (7) |
| C(24′) | 12230 | 3481 | 303 | 88 (6) |
| C(25′) | 11212 | 2971 | 47 | 65 (5) |
| C(26′) | 11555 | 2255 | 115 | 53 (5) |
| O(1) | 4849 (6) | 465 (4) | 795 (3) | 43 (2) |
| O(2) | 10625 (7) | 894 (4) | 221 (4) | 51 (3) |
| *W*(1) | 7562 (7) | 144 (4) | 5 (4) | 58 (3) |
| *W*(2) | 8895 (50) | 310 (16) | 5713 (11) | 262 (25)† |
| *W*(3) | 6739 (35) | 685 (16) | 5836 (13) | 171 (15)† |
| *W*(4) | 5622 (28) | 131 (17) | 4840 (20) | 206 (19)† |
| C(1′) | 8861 (13) | 459 (7) | 3845 (5) | 69 (5) |
| C(2′) | 8118 (12) | 1134 (7) | 4105 (6) | 64 (5) |
| O′ | 7340 (15) | 1513 (7) | 4493 (8) | 172 (7) |

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.
† Site-occupancy factor of 0·5.

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

E.s.d.'s of torsion angles are 0·2°.

| | | | |
|---|---|---|---|
| *W*(4)—*W*(4*a*) | 1·446 (61) | O′—C(2′) | 1·281 (19) |
| N—C(1) | 1·357 (14) | N—C(5) | 1·353 (15) |
| C(1)—C(2) | 1·397 (17) | C(1)—C(1*a*) | 1·481 (16) |
| C(2)—C(3) | 1·371 (18) | C(3)—C(4) | 1·385 (18) |
| C(4)—C(5) | 1·361 (17) | C(5)—C(5*a*) | 1·531 (15) |
| C(1*a*)—P(1) | 1·808 (10) | P(1)—C(16) | 1·790 (8) |
| P(1)—C(16′) | 1·780 (9) | P(1)—O(1) | 1·474 (6) |
| C(5*a*)—P(2) | 1·831 (10) | P(2)—C(26) | 1·797 (8) |
| P(2)—C(26′) | 1·794 (9) | P(2)—O(2) | 1·485 (7) |
| C(1′)—C(2′)—O′ | 157·7 (12) | C(1)—N—C(5) | 121·5 (9) |
| N—C(1)—C(2) | 119·4 (10) | N—C(1)—C(1*a*) | 117·6 (9) |
| C(2)—C(1)—C(1*a*) | 123·0 (10) | C(1)—C(2)—C(3) | 118·4 (11) |
| C(2)—C(3)—C(4) | 121·4 (11) | C(3)—C(4)—C(5) | 118·7 (11) |
| N—C(5)—C(4) | 120·6 (11) | N—C(5)—C(5*a*) | 116·0 (10) |
| C(4)—C(5)—C(5*a*) | 123·4 (11) | C(1)—C(1*a*)—P(1) | 112·5 (7) |
| C(1*a*)—P(1)—C(16) | 108·5 (4) | C(1*a*)—P(1)—C(16′) | 104·0 (5) |
| C(16)—P(1)—C(16′) | 106·6 (4) | C(1*a*)—P(1)—O(1) | 111·4 (4) |
| C(16)—P(1)—O(1) | 112·7 (4) | C(16′)—P(1)—O(1) | 113·1 (4) |
| P(1)—C(16)—C(11) | 123·6 (2) | P(1)—C(16)—C(15) | 116·1 (2) |
| P(1)—C(16′)—C(11′) | 122·6 (2) | P(1)—C(16′)—C(15′) | 117·4 (2) |
| C(5)—C(5*a*)—P(2) | 109·7 (6) | C(5*a*)—P(2)—C(26) | 105·1 (4) |
| C(5*a*)—P(2)—C(26′) | 108·2 (5) | C(26)—P(2)—C(26′) | 107·8 (4) |
| C(5*a*)—P(2)—O(2) | 110·2 (5) | C(26)—P(2)—O(2) | 112·8 (4) |
| C(26′)—P(2)—O(2) | 112·3 (4) | P(2)—C(26)—C(21) | 121·8 (2) |
| P(2)—C(26)—C(25) | 118·0 (2) | P(2)—C(26′)—C(21′) | 116·9 (3) |
| P(2)—C(26′)—C(25′) | 123·1 (3) | | |
| N—C(1)—C(1*a*)—P(1) | −75·7 | N—C(5)—C(5*a*)—P(2) | −83·6 |
| C(2)—C(1)—C(1*a*)—P(1) | 102·5 | C(4)—C(5)—C(5*a*)—P(2) | 94·4 |
| C(1)—C(1*a*)—P(1)—C(16) | −78·5 | C(5)—C(5*a*)—P(2)—C(26) | 168·0 |
| C(1)—C(1*a*)—P(1)—C(16′) | 168·2 | C(5)—C(5*a*)—P(2)—C(26′) | −77·0 |
| C(1)—C(1*a*)—P(1)—O(1) | 46·0 | C(5)—C(5*a*)—P(2)—O(2) | 46·2 |
| C(1*a*)—P(1)—C(16)—C(11) | −27·1 | C(5*a*)—P(2)—C(26)—C(21) | 119·4 |
| C(1*a*)—P(1)—C(16)—C(15) | 159·2 | C(5*a*)—P(2)—C(26)—C(25) | −65·8 |
| C(16′)—P(1)—C(16)—C(11) | 84·4 | C(26′)—P(2)—C(26)—C(21) | 4·1 |
| C(16′)—P(1)—C(16)—C(15) | −89·3 | C(26′)—P(1)—C(26)—C(25) | 178·9 |
| O(1)—P(1)—C(16)—C(11) | −150·9 | O(2)—P(2)—C(26)—C(21) | −120·5 |
| O(1)—P(1)—C(16)—C(15) | −35·3 | O(2)—P(2)—C(26)—C(25) | 54·3 |
| C(1*a*)—P(1)—C(16′)—C(11′) | 86·1 | C(5*a*)—P(2)—C(26′)—C(21′) | 149·4 |
| C(1*a*)—P(1)—C(16′)—C(15′) | −93·8 | C(5*a*)—P(2)—C(26′)—C(25′) | −31·3 |
| C(16)—P(1)—C(16′)—C(11′) | −28·4 | C(26)—P(2)—C(26′)—C(21′) | −97·4 |
| C(16)—P(1)—C(16′)—C(15′) | 151·6 | C(26)—P(2)—C(26′)—C(25′) | 81·9 |
| O(1)—P(1)—C(16′)—C(11′) | −152·8 | O(2)—P(2)—C(26′)—C(21′) | 27·5 |
| O(1)—P(1)—C(16′)—C(15′) | 27·2 | O(2)—P(2)—C(26′)—C(25′) | −153·2 |

(1971). The PCpyCP ligand (1·2 mmol) in $C_2H_5OH$ was cooled in ice and $Au_2Cl_6$ (0·30 mmol) in $C_2H_5OH$ was added slowly. After several recrystallizations from $C_2H_5OH$, crystals suitable for an X-ray study were obtained. A colorless crystal, 0·27 × 0·13 × 0·11 mm, was used. The X-ray data were measured using a Nicolet *R*3*m* diffractometer with Mo *Kα* radiation and a graphite monochromator. Cell constants were determined from 25 reflections in the 2*θ* range 6·7–19·4°. One set of data was collected at a 4° min$^{-1}$ scan rate, a second set at a variable scan rate of 2·0–29·3° min$^{-1}$. The 2*θ* range was 2·0–45·0° corresponding to *hkl* values of 0 to 12, 0 to 22 and −21 to 21, respectively. $R_{merge}$ was 0·013 for the 4128 unique reflections; 1578 reflections with $F_o \geq 6\sigma(F_o)$ were used in the analysis. No absorption corrections were applied because of the small value of *μ*. Two standard reflections measured after every 98 reflections dropped by 8% over the time used to measure the two data sets. A decay correction curve was derived from the two standard reflections and applied to the data. A trial structure was obtained by direct methods and refined

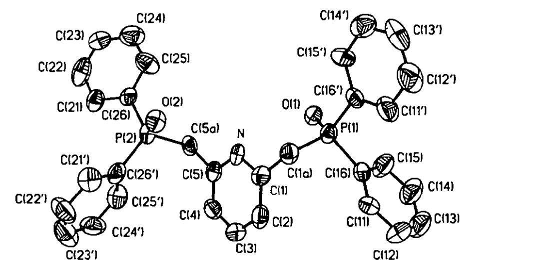


Fig. 1. A view of the 2,6-bis(diphenylphosphorylmethyl)pyridine molecule showing the atomic numbering and 50% thermal ellipsoids. The H atoms are not included for clarity. The four phenyl rings were treated as rigid bodies.

(on *F*) by blocked-cascade least-squares methods. A difference Fourier synthesis revealed a poorly defined ethanol molecule, together with several other large peaks. The isolated large peaks were assigned to one ordered and three disordered water molecules with occupancy factors of 0·5. These were included in the subsequent least-squares cycles. The weighting scheme was $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, where $g = 3\cdot37 \times 10^{-3}$. The final values of $R$ and $wR$ were 0·073 and 0·077, respectively. The largest shift/e.s.d. in the last cycle was 0·235. A final difference Fourier synthesis had a maximum peak of 0·54 and a minimum of −0·50 e Å$^{-3}$ and was featureless. All calculations were carried out using the *SHELXTL* program (Sheldrick, 1986) on a Data General Eclipse Model 30 computer. The scattering factors used in the *SHELXTL* program are the analytical form given in *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.* Selected bond lengths, bond angles and torsion angles are given in Table 2. The molecule with the atomic numbering scheme is shown in Fig. 1. The poorly defined solvent molecules are probably related to the decrease in the standard reflections during data collection. The result is a somewhat higher $R$ value.

* 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 51791 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** The P—O distances of 1·474 (6) and 1·485 (7) Å are similar to the P—O distances in triphenylphosphine oxide (Brock, Schweizer & Dunitz, 1985) and related species (Bye, Schweizer & Dunitz, 1982). The various P—C, C—C and C—N distances are similar to those reported in other phosphinomethylpyridines by McNair & Pignolet (1986).

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# Tetraphenylphosphonium Chloride Monohydrate, Tetraphenylphosphonium Bromide and Tetraphenylphosphonium Iodide

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**Abstract.** $[C_{24}H_{20}P]Cl.H_2O$, (1), $M_r = 392\cdot84$, triclinic, $P\bar{1}$, $a = 10\cdot837$ (3), $b = 10\cdot996$ (3), $c = 18\cdot399$ (5) Å, $\alpha = 77\cdot28$ (2), $\beta = 76\cdot45$ (2), $\gamma = 85\cdot69$ (2)°, $V = 2078\cdot5$ (8) Å$^3$, $Z = 4$, 2·0 molecules/asymmetric unit, $D_x = 1\cdot26$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 2\cdot7$ cm$^{-1}$, $F(000) = 824$, $T = 296$ K, $R_F = 5\cdot79\%$ for 3663 reflections and 391 parameters. The two independent cations are chemically indistinguishable, but produce two clearly resolved signals by $^{31}$P solid-state NMR spectroscopy owing to small differences in the cation–anion interactions. Although all were prepared and recrystallized identically, only (1), the chloride, acquired adventitious water. Weak hydrogen bonding links the $Cl^-$ ions and the water molecules. $[C_{24}H_{20}P]Br$, (2), $M_r = 419\cdot27$, triclinic, $P\bar{1}$, $a = 10\cdot031$ (3), $b = 10\cdot688$ (3), $c = 10\cdot678$ (3) Å, $\alpha = 77\cdot45$ (2), $\beta = 83\cdot27$ (2), $\gamma = 71\cdot87$ (2)°, $V = 1060\cdot5$ (5) Å$^3$, $Z = 2$, $D_x = 1\cdot31$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 20\cdot0$ cm$^{-1}$, $F(000) = 428$, $T = 296$ K, $R_F = 5\cdot75\%$ for 2659 reflections and 198 parameters. $[C_{24}H_{20}P]I$, (3), $M_r = 466\cdot28$, tetragonal, $I\bar{4}$, $a = 11\cdot9785$ (14), $c = 6\cdot9809$ (9) Å, $V = 1001\cdot7$ (2) Å$^3$, $Z = 2$, $D_x = 1\cdot55$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 16\cdot63$ cm$^{-1}$, $F(000) = 464$, $T = 296$ K, $R_F = 3\cdot68\%$ for 624 reflections and 81 parameters. A curious feature of these three tetrahedral tetraphosphonium halides is that no two are isomorphous.

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**Experimental.** For (1), colorless crystals from methylene chloride/hexane (0·36 × 0·26 × 0·30 mm); Nicolet $R3m$ diffractometer with graphite monochromator; $\omega$ scans; lattice parameters from least-squares fit of 25 reflections ($20 < 2\theta < 25°$); an absorption correction

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