Aurophilic and hydrogen-bonding interactions in [1-(diphenylphosphino)-4-(diphenylphosphinoyl)butane-κP1]iodogold(I) monohydrate

In the title compound, [AuI(C28H28OP2)1]·H2O, the 1-(diphenylphosphino)-4-(diphenylphosphinoyl)butane (dppbO) ligand coordinates through the phosphorus donor to give a linear two-coordinate P–Au–I gold(I) complex. Pairs of [AuI(dppbO)] molecules are linked by symmetric tris-water hydrogen-bond interactions. These dimers associate in zigzag fashion through intermolecular Au···Au interactions between mutually perpendicular P–Au–I groups.

Comment

Mixed bidentate phosphine-phosphine oxide ligands of general formula R2P–Y–P(O)R2, where Y is an organic spacer group, represent an important class of bidentate chelating ligands incorporating both soft (P) and hard (O) donor atoms (Grushin, 2004). Transition metal complexes of these ligands show a variety of structural forms (e.g. Coyle et al., 1998, Saravanabharathi et al., 2002, Faller & Parr, 2000) with evidence for both bidentate and monodentate coordination of the ligand to the metal atom. They have been shown to possess useful catalytic properties (Weber et al., 2000). Recently, we have prepared and structurally characterized the gold(I) complex [(dppmO)AuBr]·CH3CN [dppmO = Ph2P(CH2)P(O)Ph2], by the reaction of dppmO and [Bu4N][AuBr2] in acetonitrile (Williams, Boyd et al., 2003); in this complex, the P–Au–Br and P=O groups are oriented parallel to each other, with an intramolecular Au···O distance of 3.274 (4) Å. We report here the structural characterization of the water solvate of the 1:1 complex of Ph2P(CH2)4P(O)Ph2 with gold(I) iodide, [AuI(dppbO)]·H2O, (I), prepared by the reaction of dppbO and [Bu4N][AuI] in dimethylformamide solution.

The structure of (I) comprises discrete molecules of [AuI(dppbO)] and water (Fig. 1). The hydrocarbon bridge is in
a fully elongated form, with the CH₂ chain adopting an *anti* conformation similar to that recorded for the structures of the ‘parent’ molecules dppbO₂ (Fontes et al., 1991) and [(dppb)(AuI)₂] (Van Calcar et al., 1997). The P–Au–I and the P=O groups are oriented antiparallel to each other, with an Au–P–P=O torsion angle of 170.4 (2)°. The dppbO ligand coordinates to the Au atom through the P atom to yield a linear two-coordinate P–Au–I geometry, with Au–P = 2.264 (2) Å, Au–I = 2.5750 (16) Å and P–Au–I = 172.26 (6)° (Table 1). These parameters are similar to those reported for [(dppb)(AuI)₂] (Van Calcar et al., 1997) and other two-coordinate R₂PAu complexes (Toronto et al., 1996, Bott et al., 2000). The solution ³¹P NMR spectra of the title complex consists of a single broad resonance at 36.1 p.p.m. that is assigned as coincident P(O) and P(AuI) resonances.

The [Au(dppbO)] molecules associate through O–H···O(P) hydrogen bonding and Au···Au aurophilic interactions to give a polymeric chain, as illustrated in Fig. 2. In this structure, pairs of (dppbO)Au molecules are linked by symmetric tris-water hydrogen-bonding bridges, with P=O distances of 2.882 (9) and 2.812 (8) Å (Table 2), to form an R2'(8) ring (Bernstein et al., 1995). While there are many examples of hydrated phosphines with single P=O···OH···H···O=Po water bridges (e.g. Baures & Silverton, 1990; Churchill et al., 1993; Kariuki et al., 1997), to our knowledge, this present hydrogen-bonding motif has not been previously observed in phosphate oxide systems with, in fact, only a few examples recorded where the P=O group acts as a double proton acceptor with water (e.g. Dunbar & Haefner, 1994; Calcagno et al., 2000). The P=O bond length in (I) is 1.501 (6) Å, and appears longer than the distances reported for other tertiary phosphines oxides, for example, dppbO₂ [1.482 (2) Å; Fontes et al., 1991] and [(dppmO)AuBr] – CH₂CN [1.490 (3) Å; Williams, Boyd et al., 2003], or for hydrated oxides, such as Ph₃PO·H₂O [1.487 (2) Å; Baures & Silverton, 1990] and (p-tol)PO·0.5H₂O [1.482 (3) Å; Churchill et al., 1993]. The increase in the P=O bond length is reflected also in the P=O stretching frequency of 1167 cm⁻¹ which is significantly less than the values of 1180–1190 cm⁻¹ typically recorded for arylphosphine oxides (e.g. Williams, Healy et al., 2003; Higgins et al., 1987).

The [[Au(dppbO)]H₂O]₂ dimers associate in zigzag fashion through intermolecular Au···Au aurophilic interactions between mutually perpendicular [Au(dppbO)] molecules, with a P–Au···Au···P torsion angle of 108.05 (5)° and a Au···Au distance of 3.119 (2) Å [symmetry code: (i) –x, y, 1–z]. Similar Au···Au interactions are observed for [(dppb)(AuI)₂] (Van Calcar et al., 1997) and for [(Me₃Ph-P)AuI] (Toronto et al., 1996), with Au···Au distances of 3.148 (1) and 3.104 (2) Å, respectively. As observed in the structure of [(dppb)(AuI)₂], the aurophilic interactions in (I) are accompanied by face-to-face (π···π) interactions between the phenyl rings C12n and C12n' (n = 1–6), with the three remaining phenyl rings on each molecule engaged in edge-to-face C–H···π interactions. In addition, a number of phenyl H atoms orient towards the water O atom, with H···O contact distances of 2.6–2.7 Å [i.e. C1···H113ii = 2.65 Å, C2···H114ii = 2.71 Å and O1···H115ii = 2.71 Å; symmetry codes: (ii) ½–x, 3–y, 1–z; (iii) ½–x, ½+y, ½–z].

**Experimental**

[NBu₄][AuI₂] (240 mg, 0.35 mmol) and diphenylphosphinobutane monoxide (150 mg, 0.34 mmol) were dissolved in dimethylformamide (5 ml) to give a clear solution. Cooling and slow evaporation of the solvent yielded well-formed colorless crystals of (I). Yield 240 mg, 92%. M.p. 419–424 K. Analysis found: C 42.4, H 3.8%; calculated for C₃₀H₂₈AuIO₂P₂: C 42.9, H 3.9%.

Crystal data

*|AuI(C₂₈H₂₈OP₂)|H₂O*

metal-organic papers
Data collection

Rigaku AFC-7R diffractometer
ω scan
Absorption correction: ψ scan
(North et al., 1968)
T_max = 0.170, T_min = 0.525
5863 measured reflections
4984 independent reflections
3672 reflections with I > 2σ(I)

Refinement

Refinement on F^2:
R(F^2 > 2σ(F^2)) = 0.033
wR(F^2) = 0.090
S = 1.03
4984 reflections
308 parameters
H-atom parameters constrained

w = 1/[σ^2(Fo^2) + (0.0368P)^2 + 13.2508P]

where P = (Fo^2 + 2Fc^2)/3

Δρ_max = 1.06 e Å^−3
Δρ_min = −0.86 e Å^−3

Extinction correction: SHEXL97
Extinction coefficient: 0.00008 (2)

Data collection: MSC/AFCT7 Diffractometer Control Software (Molecular Structure Corporation, 1999); cell refinement: MSC/AFCT7 Diffractometer Control Software; data reduction: TEXSAN for Windows (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: TEXSAN for Windows; program(s) used to refine structure: TEXSAN for Windows and SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 (Farrugia, 1997); software used to prepare material for publication: TEXSAN for Windows and PLATON (Spek, 2003).

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Table 1
Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
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<tbody>
<tr>
<td>Au1—I</td>
<td>2.5750 (16)</td>
</tr>
<tr>
<td>Au1—P1</td>
<td>2.264 (2)</td>
</tr>
<tr>
<td>P1—C11</td>
<td>1.812 (7)</td>
</tr>
<tr>
<td>P1—C111</td>
<td>1.808 (6)</td>
</tr>
<tr>
<td>P1—C121</td>
<td>1.807 (7)</td>
</tr>
<tr>
<td>I1—Au1</td>
<td>172.26 (6)</td>
</tr>
<tr>
<td>Au1—P1—C11</td>
<td>114.4 (2)</td>
</tr>
<tr>
<td>Au1—P1—C111</td>
<td>113.7 (2)</td>
</tr>
<tr>
<td>Au1—P1—C121</td>
<td>113.7 (3)</td>
</tr>
<tr>
<td>Au1—P1—C12</td>
<td>105.3 (3)</td>
</tr>
<tr>
<td>P1—C11—P12</td>
<td>105.3 (3)</td>
</tr>
<tr>
<td>P1—C12—P12</td>
<td>105.3 (3)</td>
</tr>
<tr>
<td>P1—C21—P22</td>
<td>105.3 (3)</td>
</tr>
<tr>
<td>P1—C21—P22</td>
<td>105.3 (3)</td>
</tr>
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</table>

Table 2
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H</th>
<th>H—A</th>
<th>D—A</th>
<th>D—H—A</th>
</tr>
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<tr>
<td>0.89</td>
<td>1.99</td>
<td>2.828 (9)</td>
<td>180</td>
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<tr>
<td>0.90</td>
<td>1.91</td>
<td>2.812 (8)</td>
<td>179</td>
</tr>
</tbody>
</table>

Symmetry code: (w) −x + 1, −y + 1, −z.

H atoms were constrained as riding atoms, fixed to their parent C atoms at a C—H distance of 0.95 Å. Ueq(H) values were set to 1.2Ueq(C) of the parent atom. The water H atoms were not located from Fourier difference maps and were placed at calculated positions along the O1···O2 axis at an O—H distance of 0.90 Å and with an H—O···H angle of 103.4°. The maximum electron-density peak is located 1.01 Å from atom Au1.

References