Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Michael L. Williams,[a] Deborah L. Slade,[b] Sue E. Boyd[a] and Peter C. Healy[a]*

[a]Chemical Biology Program, Eskitis Institute, Griffith University, Nathan, Brisbane 4111, Australia, and [b]School of Science, Griffith University, Nathan, Brisbane 4111, Australia

Correspondence e-mail: p.healy@griffith.edu.au

Received 18 November 2004
Accepted 29 November 2004
Online 4 December 2004

In the title compound, $[AuI(C_{28}H_{28}OP_2)]\cdot H_2O$, 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.

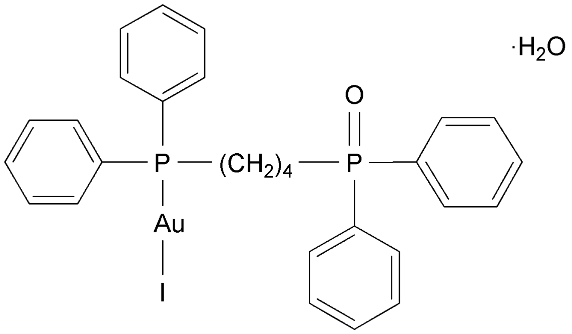
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.012 Å
R factor = 0.033
wR factor = 0.090
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Mixed bidentate phosphine–phosphine oxide ligands of general formula $R_2P—Y—P(O)R_2$, 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 $[(dppmO)AuBr]\cdot CH_3CN$ [dppmO = $Ph_2P(CH_2)P(O)Ph_2$], by the reaction of dppmO and $[Bu_4N][AuBr_2]$ 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 $Ph_2P(CH_2)_4P(O)Ph_2$ with gold(I) iodide, $[AuI(dppbO)]\cdot H_2O$, (I), prepared by the reaction of dppbO and $[Bu_4N][AuI_2]$ in dimethylformamide solution.



(I)

The structure of (I) comprises discrete molecules of [AuI(dppbO)] and water (Fig. 1). The hydrocarbon bridge is in

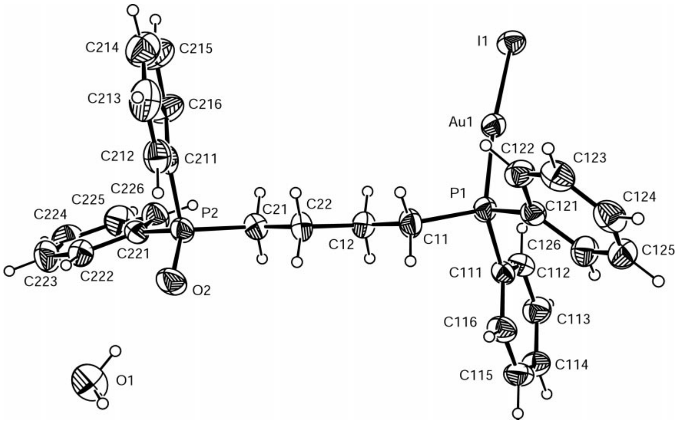


Figure 1
Molecular conformation and numbering scheme for the title compound. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radius.

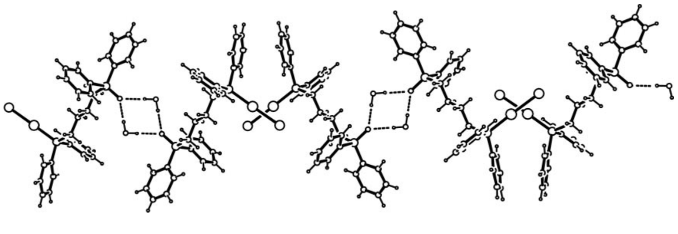


Figure 2
Aurophilic and hydrogen-bonding intermolecular interactions (dashed lines) in (I).

a fully elongated form, with the CH_2 chain adopting an *anti* conformation similar to that recorded for the structures of the 'parent' molecules $dppbO_2$ (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 R_3PAuI complexes (Toronto *et al.*, 1996, Bott *et al.*, 2000). The solution ^{31}P 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 [AuI(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)AuI molecules are linked by symmetric tris-water hydrogen-bonding bridges, with O···O distances of 2.882 (9) and 2.812 (8) Å (Table 2), to form an $R_4^2(8)$ ring (Bernstein *et al.*, 1995). While there are a number of examples of hydrated phosphines with single P═O···HOH···O═P 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 phosphine 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, $dppbO_2$ [1.482 (2) Å; Fontes *et al.*, 1991] and $[(dppmO)AuBr]\cdot CH_3CN$ [1.490 (3) Å; Williams, Boyd *et al.*, 2003], or for hydrated oxides, such as $Ph_3PO\cdot H_2O$ [1.487 (2) Å; Baures & Silverton, 1990] and $(p\text{-tol})_3PO\cdot 0.5H_2O$ [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 $\{[AuI(dppbO)]\cdot H_2O\}_2$ dimers associate in zigzag fashion through intermolecular Au···Au aurophilic interactions between mutually perpendicular [AuI(dppbO)] molecules, with a P—Au···Au^i—P^i torsion angle of 108.05 (5)° and a Au···Au^i distance of 3.319 (2) Å [symmetry code: (i) $-x, y, \frac{1}{2}-z$]. Similar Au···Au interactions are observed for $[(dppb)(AuI)_2]$ (Van Calcar *et al.*, 1997) and for $[(Me_2PhP)AuI]$ (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 C12*n* and C12*n*^{i} (*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.* O1···H113^{ii} = 2.65 Å, O1···H114^{ii} = 2.71 Å and O1···H115^{iii} = 2.71 Å; symmetry codes: (ii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$].

Experimental

$[NBu_4][AuI_2]$ (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 $C_{28}H_{30}AuIO_2P_2$: C 42.9, H 3.9%. ν_{max} (KBr, cm^{-1}): 1167 (P═O *str*). δ_H (400 MHz, $CDCl_3$, 298 K, p.p.m.): 7.69–7.55 (8H, *m*, ArH), 7.53–7.36 (12H, *m*, ArH), 2.41 (2H, *m*, CH_2), 2.28 (2H, *m*, CH_2), 1.72 (4H, *m*, 2 × CH_2). δ_P (161.9 MHz, $CDCl_3$, 298 K, p.p.m.): 36.1 p.p.m. (*br s*, 2 × P).

Crystal data

$[AuI(C_{28}H_{28}OP_2)]\cdot H_2O$
M_r = 784.33
Monoclinic, $C2/c$
a = 34.57 (2) Å
b = 14.686 (7) Å
c = 11.740 (4) Å
β = 108.67 (4)°
V = 5647 (5) $Å^3$
Z = 8

D_x = 1.845 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12.6–14.3°
μ = 6.44 mm^{-1}
T = 295 K
Prism, colorless
0.40 × 0.20 × 0.10 mm

Acta Cryst. (2005). E**61**, m30–m32 Michael L. Williams *et al.* • $[AuI(C_{28}H_{28}OP_2)]\cdot H_2O$ **m31**

Data collection

Rigaku AFC-7*R* diffractometer
ω scan
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.170$, $T_{\max} = 0.525$
5863 measured reflections
4984 independent reflections
3672 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
$\theta_{\max} = 25.0^\circ$
$h = -18 \rightarrow 41$
$k = -17 \rightarrow 7$
$l = -13 \rightarrow 13$
3 standard reflections
every 150 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.03$
4984 reflections
308 parameters
H-atom parameters constrained

$w = 1/[\Sigma^2(F_o^2) + (0.0368P)^2 + 13.2508P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.06$ e Å^{-3}
$\Delta\rho_{\min} = -0.86$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00008 (2)

Table 1
Selected geometric parameters (Å, °).

Au1—I1	2.5750 (16)	P2—O2	1.501 (6)
Au1—P1	2.264 (2)	P2—C21	1.795 (8)
P1—C11	1.812 (7)	P2—C211	1.806 (7)
P1—C111	1.808 (6)	P2—C221	1.795 (8)
P1—C121	1.807 (7)		
I1—Au1—P1	172.26 (6)	C211—P2—C221	106.5 (3)
Au1—P1—C11	114.4 (2)	P1—C11—C12	114.7 (5)
Au1—P1—C111	113.7 (2)	P2—C21—C22	112.4 (5)
Au1—P1—C121	113.6 (3)	P1—C111—C116	121.1 (5)
C11—P1—C111	105.8 (3)	P1—C111—C112	119.7 (5)
C11—P1—C121	103.1 (3)	P1—C121—C122	117.6 (5)
C111—P1—C121	105.3 (3)	P1—C121—C126	122.9 (5)
O2—P2—C21	112.7 (3)	P2—C211—C216	122.0 (5)
O2—P2—C211	111.5 (3)	P2—C211—C212	119.6 (6)
O2—P2—C221	112.4 (3)	P2—C221—C222	117.4 (5)
C21—P2—C211	105.8 (3)	P2—C221—C226	123.1 (6)
C21—P2—C221	107.5 (3)		

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

	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O2	0.89	1.99	2.882 (9)	180
O1—H1$B\cdots$O2$^{\text{iv}}$	0.90	1.91	2.812 (8)	179

Symmetry code: (iv) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$.

H atoms were constrained as riding atoms, fixed to their parent C atoms at a C—H distance of 0.95 Å. U_{iso}(H) values were set to $1.2U_{\text{eq}}$ of the parent atom. The water H atoms were not located from Fourier difference maps and were placed at calculated positions along the O1$\cdots$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.

Data collection: *MSC/AFC7 Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC7 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).

The authors thank Griffith University and the Eskitis Institute for Cell and Molecular Therapies for financial support, and Mr Alan White for recording the infrared spectrum of (I).

References

Baures, P. W. & Silverton, J. V. (1990). *Acta Cryst.* C**46**, 715–717.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bott, R. C., Bowmaker, G. A., Buckley, R. W., Healy, P. C. & Senake Perera, M. C. (2000). *Aust. J. Chem.* **53**, 175–181.
Calcagno, P., Kariuki, B. M., Kitchin, S. J., Robinson, J. M. A., Philp, D. & Harris, K. D. M. (2000). *Chem. Eur. J.* **6**, 2338–2349.
Churchill, M. R., See, R. F., Randall, S. L. & Atwood, J. D. (1993). *Acta Cryst.* C**49**, 345–347.
Coyle, R. J., Slovokhotov, Y. L., Antipin, M. Y. & Grushin, V. V. (1998). *Polyhedron*, **17**, 3059–3070.
Dunbar, K. R. & Haefner, S. C. (1994). *Polyhedron*, **13**, 727–736.
Faller, J. W. & Parr, J. (2000). *Organometallics*, **19**, 1829–1832.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fontes, M. R. M., Oliva, G. & Zukerman-Schpector, J. (1991). *Acta Cryst.* C**47**, 2699–2700.
Grushin, V. V. (2004). *Chem. Rev.* **104**, 1629–1662.
Higgins, S. J., Taylor, R. & Shaw, B. L. (1987). *J. Organomet. Chem.* **325**, 285–292.
Kariuki, B. M., Harris, K. D. M., Philp, D & Robinson, J. M. A. (1997). *J. Am. Chem. Soc.* **119**, 12679–12680.
Molecular Structure Corporation (1999). *MSC/AFC7 Diffractometer Control Software for Windows.* Version 1.02. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1997–2001). *TEXSAN for Windows.* Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Saravanabharathi, D., Nethaji, M. & Samuelson, A. G. (2002). *Polyhedron*, **21**, 2793–2800.
Sheldrick, G. M. (1997). *SHELXL97.* University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Toronto, D. V., Weissbart, B., Tinti, D. S. & Balch, A. L. (1996). *Inorg. Chem.* **35**, 2484–2489.
Van Calcar, P. M., Olmstead, M. M. & Balch, A. L. (1997). *Inorg. Chem.* **36**, 5231–5238.
Weber, R., Englert, U., Ganter, B., Keim, W. & Möthrath, M. (2000). *Chem. Commun.* pp. 1419–1420.
Williams, M. L., Boyd, S. E., Dunstan, S. P. C., Slade, D. L. & Healy, P. C. (2003). *Acta Cryst.* E**59**, m768–m770.
Williams, M. L., Healy, P. C., Loh, N. K., Dunstan, S. P. C. & Smith G. (2003). *Acta Cryst.* E**59**, o596–o598.

m32 Michael L. Williams *et al.* • [AuI($C_{28}H_{28}OP_2$)]·H_2O *Acta Cryst.* (2005). E**61**, m30–m32