

William Clegg,^{a*} Andrew J. Scott,^a Christian Wiesauer,^{b,‡} Walter Weissensteiner^b and Todd B. Marder^{c,‡}

^aSchool of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, ^bInstitute of Organic Chemistry, University of Vienna, Waehringerstrasse 38, A-1090 Wien, Austria, and ^cDepartment of Chemistry, University of Durham, Durham DH1 3LE, England

‡ Formerly at Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Correspondence e-mail: w.clegg@ncl.ac.uk

Key indicators

Single-crystal X-ray study
T = 160 K
Mean $\sigma(\text{C}-\text{C}) = 0.018 \text{ \AA}$
Disorder in main residue
R factor = 0.082
wR factor = 0.223
Data-to-parameter ratio = 17.2

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

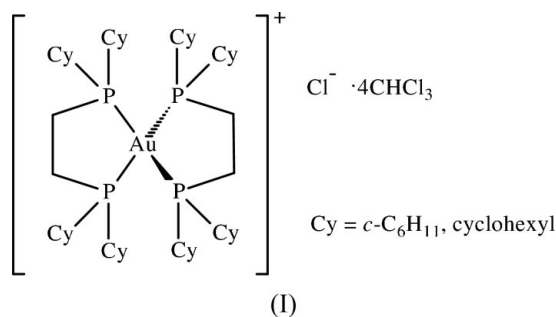
Bis[bis(dicyclohexylphosphino)ethane- κ^2P,P']-gold(I) chloride chloroform tetrasolvate

In the title complex, $[\text{Au}(\text{C}_{26}\text{H}_{48}\text{P}_2)_2]\text{Cl}\cdot 4\text{CHCl}_3$, the cation and anion lie on twofold rotation axes. The Au atom has a distorted tetrahedral coordination geometry, with two chelating diphosphine ligands, and lies far from the anion.

Received 8 June 2004
Accepted 11 June 2004
Online 19 June 2004

Comment

As part of a study of hydroboration catalysis, the title compound, (I), was prepared as a catalyst precursor. Although gold complexes with the ligands DCPE [bis(dicyclohexylphosphino)ethane] and DPPB [bis(diphenylphosphino)butane] are effective alkene diboration catalysts (Baker *et al.*, 1995), we found them to be ineffective for hydroboration of vinylboronate esters.



The crystal structure of the chloroform tetrasolvate has been determined. The complex consists of a bis(diphosphine)gold(I) cation, a chloride anion and four molecules of chloroform. The cation and anion lie on twofold rotation axes in space group $C2/c$ and the asymmetric unit contains two solvent molecules, one of which is disordered.

The Au atom is coordinated by two chelating diphosphine ligands in a distorted tetrahedral geometry (Fig. 1 and Table 1), the main distortion being the small bite angles of the ligands. A similar geometry is found for nine other gold(I) complexes of diphosphinoethane ligands in the Cambridge Structural Database (CSD, Version 5.25 with one update, January 2004; Allen, 2002), and is as expected. The CSD contains 103 structures of complexes of the DCPE ligand (the structure of the uncomplexed ligand has not been reported); almost all of these are with metals of the Fe/Ru/Os, Co/Rh/Ir and (especially) Ni/Pd/Pt transition-metal triads. There are two complexes with Cu, one with Al, and three with Au. In the vast majority of complexes, DCPE coordinates as a chelating ligand, and there are six incidences of DCPE as a bridging ligand, including all of the previously reported gold complexes. In $[(\text{DCPE})_2\text{Au}_2](\text{PF}_6)_2$, two DCPE ligands bridge a pair of Au^{I} atoms with a direct Au—Au bond (Schaefer *et al.*,

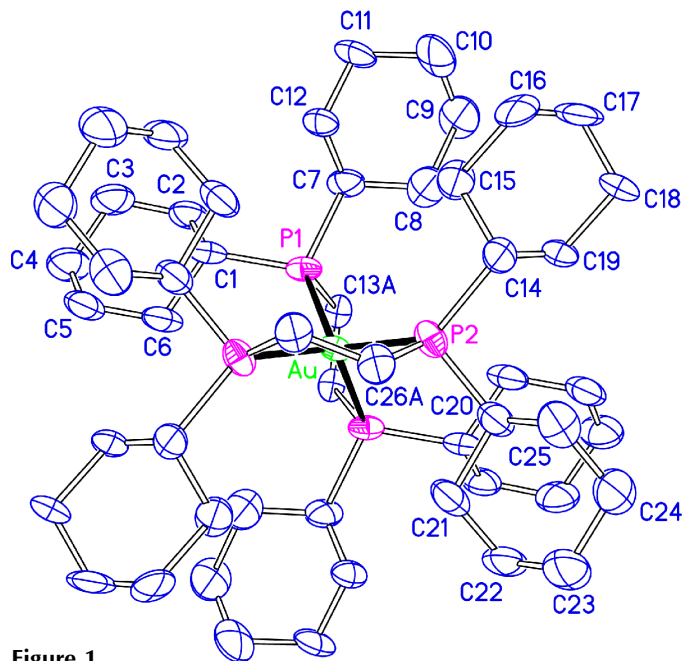


Figure 1
The structure of the cation of (I), shown with atom labels and 40% probability ellipsoids. H atoms and one of the disorder components have been omitted.

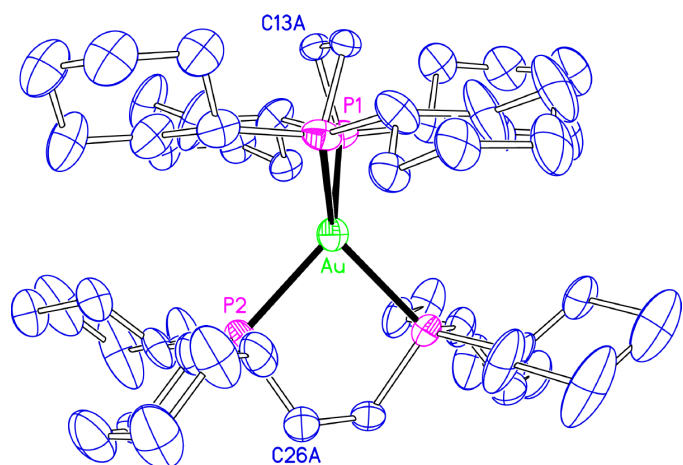


Figure 2
An alternative view of the cation, showing the conformation of the chelate rings.

1991). [BrAu(DCPE)AuCN] has a bridge between two well separated Au atoms (Schaefer *et al.*, 1992). [(DCPE)₃Au₂]-[Au(CN)₂]₂ contains one bridging and two chelating ligands (McCleskey *et al.*, 1993). Thus, there is considerably more variety in the coordination of DCPE to gold(I) than to other metals.

The ethylene linkages in the two DCPE ligands are disordered over two positions each, with staggered conformations, as indicated by P—C—C—P torsion angles of -50 (2), 47 (2), 52 (2) and -52 (2) $^\circ$ (two disorder components of two ligands). There is probably unresolved disorder also in the cyclohexyl groups.

The chloride anion has no significant non-Coulombic interactions and is >6.9 Å from the closest Au atoms. One of the two independent chloroform solvent molecules is disor-

dered over two orientations by rotation about its C—H bond, while no disorder was resolved for the other solvent molecule.

Experimental

The title compound was prepared by the reaction of Au(PEt₃)Cl with two equivalents of DCPE in THF solution. The reaction mixture was stirred for 5 h, then the solvent was removed *in vacuo*, leaving a fine white powder. This was recrystallized from chloroform. ¹HNMR (200 MHz): δ 1.28 (*s, br*, 22H), 1.85 (*s, br*, 22H). ³¹P{¹H} NMR (81 MHz, CD₂Cl₂): δ 29.7.

Crystal data

[Au(C₂₆H₄₈P₂)₂]Cl·4CHCl₃
 $M_r = 1555.06$
 Monoclinic, $C2/c$
 $a = 25.939$ (4) Å
 $b = 13.938$ (3) Å
 $c = 22.685$ (4) Å
 $\beta = 114.050$ (4) $^\circ$
 $V = 7489$ (2) Å³
 $Z = 4$

$D_x = 1.379$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 13280 reflections
 $\theta = 1.7$ – 27.8 $^\circ$
 $\mu = 2.55$ mm⁻¹
 $T = 160$ (2) K
 Plate, colourless
 $0.30 \times 0.24 \times 0.05$ mm

Data collection

Bruker SMART 1K CCD diffractometer
 Thin-slice ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.294$, $T_{\max} = 0.881$
 19047 measured reflections

6599 independent reflections
 4771 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\max} = 25.0$ $^\circ$
 $h = -30 \rightarrow 26$
 $k = -16 \rightarrow 16$
 $l = -26 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.223$
 $S = 1.01$
 6599 reflections
 384 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1563P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 3.63$ e Å⁻³
 $\Delta\rho_{\min} = -3.76$ e Å⁻³
 Extinction correction: SHELXTL
 Extinction coefficient: 0.00045 (13)

Table 1

Selected geometric parameters (Å, $^\circ$).

Au—P1	2.434 (2)	Au—P2	2.470 (2)
P1—Au—P1 ⁱ	85.97 (11)	P1—Au—P2 ⁱ	113.49 (9)
P1—Au—P2	131.15 (9)	P2—Au—P2 ⁱ	87.53 (12)

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

H atoms were positioned geometrically and refined with a riding model, with C—H = 0.99–1.00 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Initial refinement produced highly anisotropic displacement parameters for the C atoms of the two ethylene linkages, which had apparently eclipsed arrangements. Each of these C atoms was successfully refined as two disorder components, the twofold rotation symmetry being retained for each component. Refined occupancy factors for the two linkages were 0.47:0.53 (2) and 0.52:0.48 (3). Twofold disorder was also resolved and refined for one of the chloroform molecules, with occupancies of 0.489:0.511 (9). Restraints were applied to geometry and displacement parameters in the disordered groups. The largest positive and negative features of the final difference map lie close to Au and to the disordered solvent molecule.

Data collection: SMART (Bruker, 2001); cell refinement: local programs; data reduction: SAINT (Bruker, 2001); program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; soft-

ware used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC (UK) and NSERC (Canada) for financial support. CW thanks the Austrian Ministry of Education, Science and Culture for supporting his stay at the University of Waterloo, Canada.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.

Baker, R. T., Nguyen, P., Marder, T. B. & Westcott, S. A. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1336–1338.

Bruker (2001). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.

McCleskey, T. M., Henling, L. M., Flanagan, K. A. & Gray, H. B. (1993). *Acta Cryst.* **C49**, 1467–1469.

Schaefer, W. P., McCleskey, T. M. & Gray, H. B. (1992). *Acta Cryst.* **C48**, 1397–1399.

Schaefer, W. P., Marsh, R. E., McCleskey, T. M. & Gray, H. B. (1991). *Acta Cryst.* **C47**, 2553–2556.

Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL*. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.