The Crystal and Molecular Structure of Dichloro-1,2-bis(diphenylphosphino)-ethanedigold(I)

PAUL A. BATES and JOYCE M. WATERS*

Chemistry Department, University of Auckland, Auckland, New Zealand

Received July 2, 1984

Abstract

The structure of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ has been determined by single crystal X-ray methods. The compound crystallizes with four formula units in a cell of dimensions a = 12.815(2), b = 11.160(2), c = 19.054(4) Å, β = 109.33(1)°, V = 2571 Å^3, space group $P2_1/n$. The structure has been refined by full-matrix least-squares methods to a final R index of 0.035 for the 127 variables and 1360 observed data. The coordination about the Au atoms is linear with mean Au–P and Au–Cl bond lengths of 2.239 and 2.315 Å respectively. Pairs of molecules are held together by weak intermolecular Au···Au interactions of 3.189 Å.

Introduction

Currently, multinuclear gold complexes are attracting considerable interest and X-ray techniques have provided a powerful tool for their characterisation [1]. Such complexes are usually stabilized by tertiary, monodentate, phosphine ligands but more recently the structures of several gold clusters containing bidentate phosphines have been reported [2–5] as well as their potential Au(I) precursors [6, 7]. We have just synthesized and elucidated the structure [8] of a high nuclear, Au–S cluster which involves the bidentate, 1,2-bis(diphenylphosphino)ethane—dppe—ligand, and this has prompted the structural characterization of its precursor, $Au_2(dppe)Cl_2$, (**1**).

Experimental

Colourless crystals of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$, prepared by a literature method [9], were obtained by evaporation of a 2:1 dichloromethane:ethanol solution. The diamond-shaped crystal selected for X-ray diffractometry was of approximate dimensions 0.14 × 0.10 × 0.04 mm. On the basis of morphology and photography the crystal was assigned to the monoclinic system. Cell dimensions, determined from a least-squares refinement of the setting angles of 25 reflections, measured on an Enraf-Nonius CAD4 diffractometer, are a = 12.815(2), b = 11.160(2), c = 19.054(4) Å, β = 109.33(1)°. For a cell volume of 2571 Å^3 and a molecular weight of 863.27 amu ($C_{26}H_{24}Au_2Cl_2P_2$) the density was calculated to be 2.230 g cm^{-3} for four formula weights in the cell. Systematic absences ($h\,0\,l$, $h + l$ = 2n + 1; $0\,k\,0$, k = 2n + 1 absent) established the space group as $P2_1/n$. A total of 1618 unique data was collected with Mo-K$_\alpha$ radiation (μ(Mo-K$_\alpha$) = 112.88 cm^{-1}) using the $\omega/2\theta$ scan technique (θ_{max} = 20.0°). A variable ω scan width of $(0.7 + 0.347 \tan\theta)°$ was calculated for each reflection and this was extended by 25% at both ends of the scan for background measurements. A variable horizontal aperture width of $(1.7 + 1.2 \tan\theta)$mm was calculated. The vertical aperture was 4 mm. The scan speed was chosen to return a constant $\sigma(I) = 0.022\ I$ with a maximum scan time of 99 seconds for each reflection with $\theta \leqslant 12°$. The maximum scan time was increased to 120 seconds for all higher angle data. The intensities of three standard reflections were monitored at 2-hourly intervals during the data collection but any variation was less than 2%. Empirical absorption corrections were applied [10], maximum and minimum transmission factors being 0.998 and 0.848 respectively.

The structure was solved by Patterson & Fourier methods and refined by a full-matrix least-squares technique [11]. The final refinement cycle converged to values of 0.035 and 0.036 for R and R_w respectively for the 127 variables and 1360 data for which $F^2 > 3\sigma(F^2)$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $0.9482/[\sigma^2(F) + 0.000952F^2]$. In the refinement the atoms of each phenyl ring were treated as a rigid group (C–C, 1.395 Å; C–H, 1.08 Å) with isotropic thermal parameters; for all other non-hydrogen atoms anisotropic thermal motion was assumed. The hydrogen atom thermal parameters

---

*Author to whom correspondence should be addressed. Present address: Chemistry Department, Massey University, Palmerston North, New Zealand.

0020-1693/85/$3.30

TABLE I.

(a) Positional Parameters ($\times 10^4$) with their estimated standard deviations for the non-hydrogen non-group atoms of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Au(1)	27349(8)	1901(8)	−7029(5)
Au(2)	−5120(7)	13250(8)	10439(5)
Cl(1)	2248(5)	−254(5)	−1957(3)
Cl(2)	−1586(5)	2996(5)	572(3)
P(1)	3346(5)	627(5)	514(3)
P(2)	658(5)	−214(5)	1425(3)
C(1)	2284(16)	829(18)	941(11)
C(2)	1587(16)	−336(19)	910(11)

(b) Anisotropic thermal parameters ($\times 10^3$) with their estimated standard deviations for the non-hydrogen non-group atoms of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au(1)	39.8(6)	47.7(7)	36.9(6)	−1.3(5)	10.2(5)	−1.2(5)
Au(2)	40.9(6)	35.5(6)	35.4(6)	1.4(5)	9.9(4)	−0.1(5)
Cl(1)	48(4)	55(4)	32(3)	−3(3)	9(3)	−8(3)
Cl(2)	70(4)	32(3)	37(3)	21(3)	13(3)	5(3)
P(1)	35(4)	36(4)	34(4)	2(3)	16(3)	−1(3)
P(2)	38(4)	32(3)	27(3)	1(3)	10(3)	−4(3)
C(1)	42(15)	35(14)	28(14)	26(12)	1(11)	4(11)
C(2)	36(14)	42(15)	29(14)	−12(12)	−8(11)	1(11)

[a] The form of the anisotropic thermal parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

in individual phenyl rings were constrained to be equal. Similar constraints were applied to hydrogen atoms attached to each of the bridging carbon atoms. The atomic scattering factors were taken from the tabulations of Cromer and Mann [12]; anomalous dispersion corrections were those of Cromer and Liberman [13]. The numbering system is given in Fig. 1; final parameters for the non-group atoms are given in Table I. Table II presents parameters for the group atoms and Table III* those for all hydrogen atoms. A listing of $10|F_o|$ and $10|F_c|$, in electrons, for the data used in the refinement, is given in Table IV*. Bond distance and angle data are given in Tables V and VI.

Results and Discussion

X-ray analysis shows a digold molecule (Fig. 1) with approximately linear coordination about each gold atom and with values for P–Au–Cl of 173.1(2) and 175.4(2)°. Within experimental error the chemically equivalent bonds about the two halves of the molecule are identical. The mean Au–Cl bond length, 2.315 Å, is equivalent to the sum of the appropriate covalent radii [14, 15] but the mean Au–P bond length, 2.239 Å, shows a significant

TABLE II. Derived Positional ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) with Their Estimated Standard Deviations for the Non-hydrogen Rigid-group Atoms of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
C(111)	4127(11)	2011(11)	715(8)	35(5)
C(112)	5249(11)	2017(11)	1136(8)	44(6)
C(113)	5833(11)	3095(11)	1274(8)	66(8)
C(114)	5297(11)	4166(11)	992(8)	73(8)
C(115)	4175(11)	4159(11)	570(8)	74(8)
C(116)	3591(11)	3081(11)	432(8)	69(8)
C(121)	4235(10)	−507(11)	1076(7)	32(5)
C(122)	4599(11)	−1428(11)	715(7)	44(6)
C(123)	5319(10)	−2298(11)	1130(7)	76(8)
C(124)	5675(10)	−2257(11)	1905(7)	63(7)
C(125)	5311(10)	−1341(11)	2265(7)	58(7)
C(126)	4591(10)	−466(11)	1851(7)	41(6)
C(211)	1563(11)	−62(12)	2371(6)	33(5)
C(212)	2385(11)	−915(12)	2674(6)	61(7)
C(213)	3113(11)	−776(12)	3398(6)	70(8)
C(214)	3021(11)	217(12)	3818(6)	75(8)
C(215)	2200(11)	1070(12)	3515(6)	67(8)
C(216)	1471(11)	931(12)	2791(6)	39(6)
C(221)	25(10)	−1680(10)	1359(7)	28(5)
C(222)	−91(10)	−2455(10)	764(7)	47(6)
C(223)	−668(10)	−3530(10)	714(7)	56(7)
C(224)	−1128(10)	−3829(10)	1260(7)	53(7)
C(225)	−1011(10)	−3054(10)	1855(7)	74(8)
C(226)	−435(10)	−1980(10)	1905(7)	51(6)

---

*Tables III and IV have been deposited with the editor.

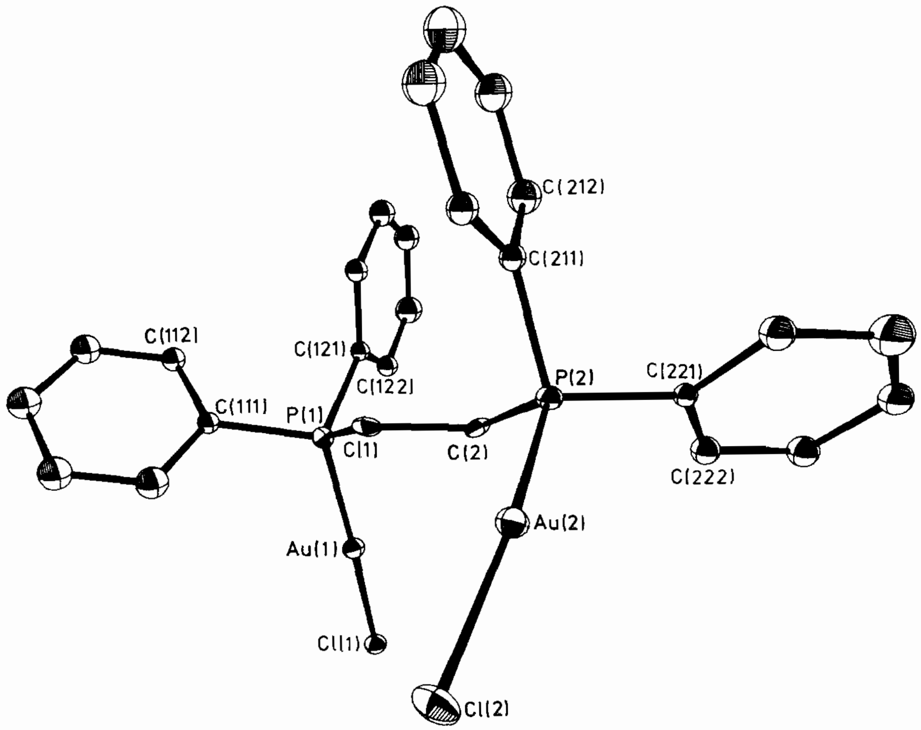

Fig. 1. The complex, $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ showing the numbering system used. Thermal ellipsoids have been drawn at the 15% probability level.

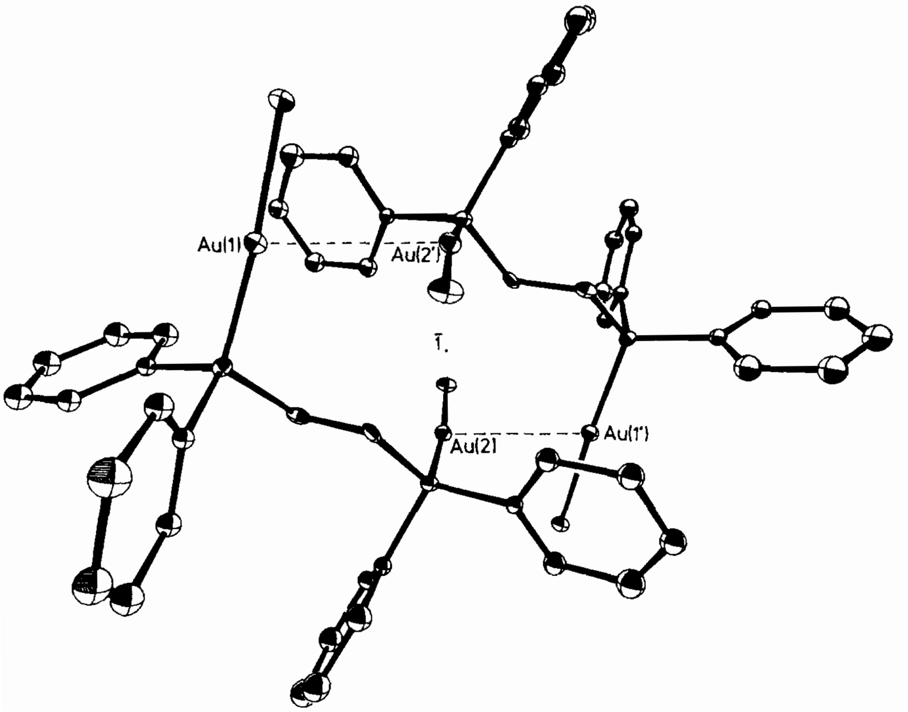

Fig. 2. The two dinuclear molecules of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ related by the centre of symmetry and showing the intermolecular Au••• Au contacts. Thermal ellipsoids have been drawn at the 15% probability level.

contraction [15]. This shortening of the Au–P bonds has been observed in a number of other linear, P–Au–Cl gold(1) complexes [6, 7, 16–18] and has been attributed to d_π–d_π back bonding. The P(1)–C(1)–C(2)–P(2) dihedral angle of 173° allows a large intramolecular Au(1) to Au(2) separation of 6.26 Å, in contrast with the structure [6] of the related 1,2-bis(diphenylphosphino)methane (dppm) ligand complex, $Au_2(dppm)Cl_2$ (2), where the very much shorter intramolecular Au···Au contact distance of 3.351(2) Å is observed. Other short intramolecular Au···Au contacts have been noted in similar complexes which involve bi- or tri-dentate bridging phosphine ligands and which form linear P–Au–Cl moieties [16–18]. For the crystal structure of $Au_2(dppe)Cl_2$ short Au···Au contacts do occur but these are intermolecular contacts and are found between molecules related by a crystallographic centre of symmetry (see Fig. 2). (The Au(1)···Au(2′) and Au(2)···Au(1′) separations are 3.189 Å). No other short intra- or intermolecular approaches are made. In the related complex $Au_2(dppp)Cl_2$ (3), (where dppp ≡ 1,2-bis(diphenylphosphino)propane) intermolecular Au···Au contacts of 3.316 Å [7] are also observed but in this molecule they give rise to a polymeric chain structure throughout the crystal. The shorter, dppe, ligand precludes this same intermolecular pattern for $Au_2(dppe)Cl_2$. In the title complex the P(1)–Au(1)···Au(2′)–P(2′) dihedral angle is 96°. Such a large angle may be necessary to protect the Au···Au contacts from steric pressures. Indeed a relationship between steric factors and Au···Au contacts must exist for gold(1) complexes; the latter are only possible if the former permit. The structure of Ph_3PAuCl [19], with its bulky phosphine ligand, shows no short Au···Au contacts, steric hindrance by the ligands in (1), (2) and (3) allow just one such contact per gold atom whereas complexes with less sterically inhibiting ligands such as $Au(Pte)Cl_2$ [20], (pte ≡ 1,2-bis(phenylthio)ethane) are allowed two giving rise to continuous ···Au···Au···chains throughout the whole crystal lattice. However, as to why such short Au···Au contacts occur at all remains the subject of considerable discussion [1, 21].

TABLE V. Bond Lengths (in Å) for $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$.

Au(1)–Cl(1)	2.314(5)	Au(2)–Cl(2)	2.315(5)
Au(1)–P(1)	2.242(6)	Au(2)–P(2)	2.237(6)
P(1)–C(1)	1.82(2)	P(2)–C(2)	1.78(2)
P(1)–C(111)	1.81(1)	P(2)–C(211)	1.80(1)
P(1)–C(121)	1.80(1)	P(2)–C(221)	1.81(1)
C(1)–C(2)	1.57(3)	Au(1)···Au(2′)	3.189(1)

Acknowledgement

The authors are grateful to the University Grants Committee for funding towards the purchase of equipment.

References

1 P. G. Jones, *Gold Bulletin, 14,* 102 (1982).

2 J. W. A. van der Velden, J. J. Bour, F. A. Vollenbrock, P. T. Beurskens and J. M. M. Smits, *J. Chem. Soc., Chem. Commun.,* 1162 (1979).

3 J. W. A. van der Velden, F. A. Vollenbrock, J. J. Bour, P. T. Beurskens, J. M. M. Smits and W. P. Bosman, *Rec. Trav. Chim. Pays-Bas, 100a,* 148 (1981).

4 J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, P. T. Beurskens, M. Roseboom and J. H. Noordik, *Inorg. Chem., 21,* 4321 (1982).

5 J. M. M. Smits, J. J. Bour, F. A. Vollenbrock and P. T. Beurskens, *J. Crystallogr. Spectrosc. Res., 13,* 355 (1983).

6 H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama and G. Huttner, *Chem. Ber., 110,* 1748 (1977).

TABLE VI. Bond Angles (in Degrees) for $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$.

Cl(1)–Au(1)–P(1)	175.4(2)	Cl(2)–Au(2)–P(2)	173.1(2)
Au(1)–P(1)–C(1)	115.7(7)	Au(2)–P(2)–C(2)	112.2(7)
Au(1)–P(1)–C(111)	112.5(5)	Au(2)–P(2)–C(211)	113.2(5)
Au(1)–P(1)–C(121)	113.5(5)	Au(2)–P(2)–C(221)	115.8(5)
C(1)–P(1)–C(111)	104.1(8)	C(2)–P(2)–C(211)	103.4(8)
C(1)–P(1)–C(121)	104.0(8)	C(2)–P(2)–C(221)	105.0(8)
C(111)–P(1)–C(121)	106.1(7)	C(211)–P(2)–C(221)	106.3(7)
P(1)–C(1)–C(2)	112.5(1.3)	P(2)–C(2)–C(1)	113.2(1.4)
P(1)–C(111)–C(112)	121.2(5)	P(2)–C(211)–C(212)	119.9(5)
P(1)–C(111)–C(116)	118.8(5)	P(2)–C(211)–C(216)	120.1(5)
P(1)–C(121)–C(122)	118.1(5)	P(2)–C(221)–C(222)	122.7(5)
P(1)–C(121)–C(126)	121.8(5)	P(2)–C(221)–C(226)	117.0(5)
Cl(1)–Au(1)···Au(2′)	76.0(2)	Cl(2)–Au(2)···Au(1′)	88.4(2)
P(1)–Au(1)···Au(2′)	108.0(2)	P(2)–Au(2)···Au(1′)	96.7(2)

7 M. K. Cooper, L. E. Mitchell, K. Henrick, M. McPartlin and A. Scott, *Inorg. Chim. Acta, 84*, L9 (1984).

8 P. A. Bates and J. M. Waters, results to be published.

9 F. Cariati, L. Naldini, G. Simonetta and L. Malatesta, *Inorg. Chim. Acta, 1*, 315 (1967).

10 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A:, 24*, 351 (1968).

11 Using SHELX: G. Sheldrick, 'SHELX-76, Program for Crystal Structure Determination', University of Cambridge, Cambridge, 1976.

12 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A:, 24*, 321 (1968).

13 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53*, 1891 (1970).

14 T. L. Blundell and H. M. Powell, *J. Chem. Soc. A:*, 1685 (1971).

15 L. Pauling, 'The Nature of the Chemical Bond, 3rd edn.', Cornell University Press, Ithaca, New York, 1960.

16 P. G. Jones, *Acta Crystallogr., Sect. B:, 36*, 2775 (1980).

17 M. K. Cooper, K. Henrick, M. McPartlin and J. F. Latten. *Inorg. Chim. Acta, 65*, L185 (1982).

18 R. Uson, A. Laguna, M. Laguna, E. Fernandez, M. D. Villacampa, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1679 (1983).

19 N. C. Baenziger, W. E. Bennett and D. M. Soboroff, *Acta Crystallogr., Sect. B:, 22*, 962 (1976).

20 M. G. B. Drew and M. J. Riedl, *J. Chem. Soc., Dalton Trans.*, 52 (1973).

21 J. J. Guy, P. G. Jones, M. T. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 8 (1977).