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A Tetrahedral Complex of Gold(I). The Crystal and Molecular Structure of $Au(Ph_2PCH_2CH_2PPh_2)_2Cl\cdot 2H_2O$

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The structure of $Au(Ph_2PCH_2CH_2PPh_2)_2Cl\cdot 2H_2O$ *has been determined by single crystal X-ray methods. The compound crystallizes with four formula units in a cell of dimensions* a = *10.057(1),* b = *21.704(2),* c = *21.724(1)* Å, β = *94.06(3)°*, V = *4730* Å^3, *space group* $P2_1/n$. *The structure has been refined by full-matrix least-squares methods to a final* R *index of 0.038 for the 217 variables and 4263 observed data. The coordination about the Au atom is found to be tetrahedral with Au–P bond lengths varying from 2.384(2) to 2.412(2)* Å.

Introduction

Gold(I), unlike univalent copper and silver, rarely exhibits a coordination number of four and few such complexes have been fully characterised by the X-ray method [1–4]. As part of a survey on gold(I) complexes and their reaction products with various reducing agents, $Au_2(dppe)Cl_2$ (dppe ≡ 1,2-bis(diphenylphosphino)ethane) in a chloroform solution was reacted with Na_2S under nitrogen. On evaporation a mixture of products was obtained and X-ray analysis of a colourless, crystalline material resulted in the structure determination of the title compound.

Experimental

$Au_2(dppe)Cl_2$, prepared by a literature method [5], was dissolved in chloroform and reacted with an excess of Na_2S under nitrogen. Several products resulted on evaporation of the solvent and a crystal of one, $(Au(dppe)_2Cl\cdot 2H_2O)$, was mounted in air on a CAD4 diffractometer. The prismatic crystal chosen, which displayed faces of the forms $\{1\ 0\ \bar{1}\}$, $\{\bar{1}\ 0\ 1\}$, $\{0\ 0\ \bar{1}\}$, $\{0\ 1\ 0\}$, $\{0\ \bar{1}\ 0\}$ had a calculated volume of 0.00358 mm^3 and approximate dimensions of 0.37 × 0.10 × 0.09 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, are a = 10.057(1), b = 21.704(2), c = 21.724(1) Å, β = 94.06(3)°. For a cell volume of 4730 Å^3 and a molecular weight of 1065.31 amu ($C_{52}H_{52}AuClO_2P_4$) the density was calculated to be 1.496 g cm^{-3} for four formula weights in the cell. Systematic absences ($h\ 0\ l$, $h + l = 2n + 1$; and $0\ k\ 0$, $k = 2n + 1$ absent) established the space group as $P2_1/n$. A total of 8761 data was collected with Mo-Kα radiation (μ(Mo-Kα) = 31.9 cm^{-1}) using the $\omega/2\theta$ scan technique (θ_{max} = 25.0°). 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 verticl aperture was 4 mm. A maximum scan time of 99 seconds was set for each reflection where $\theta \leqslant 10°$ but this was increased to 120 secs for all higher angle data. The intensities of three standard reflections were monitored during the data collection but the maximum variation was less than 3%. Absorption corrections were applied [6], minimum and maximum transmission factors being 0.680 and 0.767 respectively.

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares technique [7]. The final refinement cycle converged to values of 0.038 and 0.037 for R and R_w respectively for the 217 variables and 4263 data for which $F^2 > 3\sigma(F^2)$. The function minimised was $\Sigma\omega(|F_o| - |F_c|)^2$ with the weight w being defined as $1.1602/[\sigma^2(F) + 0.000488\ F^2]$. In the refinement the atoms of each phenyl ring were treated as a rigid group (C–C, 1.395; C–H, 1.08 Å) with isotropic thermal parameters; for all other non-hydrogen atoms anisotropic thermal motion was assumed. The hydrogens bound to the tetrahedral carbon atoms were included in the calculations at idealised positions

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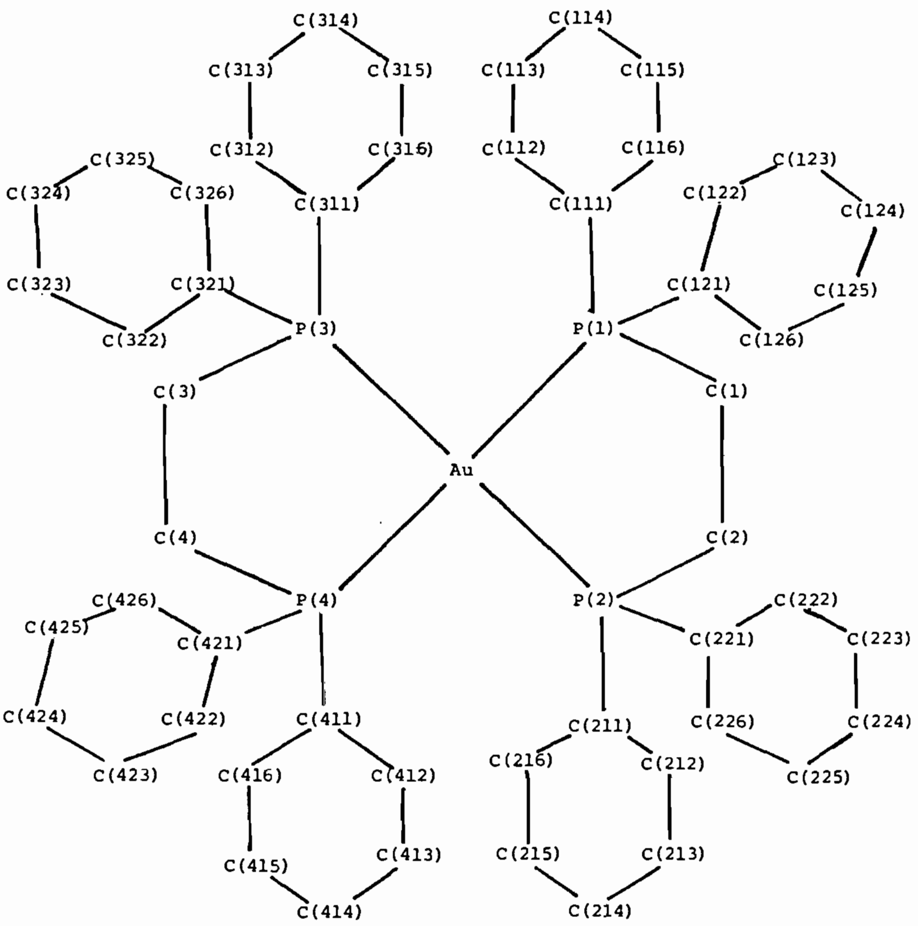

Fig. 1. The numbering system used for the cation of bis[1,2-bis(diphenylphosphino)ethane]gold(I) chloride dihydrate.

TABLE I. Positional and Thermal[a] Parameters with their Estimated Standard Deviations for the Non-group Atoms of Au(dppe)$_2$-Cl·2H$_2$O.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au	0.13959(3)	0.18855(2)	0.23940(2)	269(2)	318(2)	366(2)	19(2)	41(1)	–5(2)
Cl	0.0856(3)	0.1213(2)	0.4968(1)	942(23)	861(23)	712(20)	112(17)	126(17)	84(19)
P(1)	0.3648(2)	0.1848(1)	0.2855(1)	295(11)	425(13)	362(12)	–11(12)	14(10)	–16(13)
P(2)	0.2338(2)	0.2011(1)	0.1425(1)	351(12)	394(15)	341(13)	27(11)	32(10)	–21(10)
P(3)	0.0068(2)	0.1021(1)	0.2667(1)	330(12)	285(13)	391(14)	32(11)	20(11)	–12(10)
P(4)	–0.0162(2)	0.2510(1)	0.2894(1)	320(13)	298(13)	422(14)	10(11)	61(11)	1(10)
O(1)	0.1640(9)	0.2345(4)	0.5844(4)	1193(75)	912(67)	1088(72)	191(57)	408(59)	290(57)
O(2)	0.1548(8)	–0.0155(4)	0.5426(4)	814(59)	1228(74)	787(58)	26(54)	–53(47)	305(54)
C(1)	0.4648(8)	0.1785(5)	0.2182(4)	308(47)	686(73)	380(53)	54(52)	45(39)	–1(48)
C(2)	0.4098(8)	0.2197(4)	0.1653(4)	313(50)	556(63)	506(61)	48(51)	38(45)	–76(45)
C(3)	–0.0754(8)	0.1311(4)	0.3346(4)	329(49)	303(49)	506(60)	0(44)	43(44)	–27(40)
C(4)	–0.1331(8)	0.1958(4)	0.3213(4)	404(48)	351(54)	463(55)	–18(48)	67(40)	62(45)

[a] The Uij values have been multiplied by 10^4.

TABLE II. Derived Parameters for the Rigid Group Atoms of $Au(dppe)_2Cl{\cdot}2H_2O$.

Atom	x/*a*	y/*b*	z/*c*	U	Atom	x/*a*	y/*b*	z/*c*	U
C(111)	0.4178(6)	0.1193(2)	0.3334(2)	0.039(2)	C(311)	0.0867(5)	0.0304(2)	0.2920(3)	0.037(2)
C(112)	0.3353(6)	0.1007(2)	0.3790(2)	0.041(2)	C(312)	0.1941(5)	0.0099(2)	0.2601(3)	0.045(2)
C(113)	0.3704(6)	0.0500(2)	0.4161(2)	0.049(3)	C(313)	0.2616(5)	−0.0438(2)	0.2788(3)	0.060(3)
C(114)	0.4879(6)	0.0178(2)	0.4076(2)	0.056(3)	C(314)	0.2219(5)	−0.0770(2)	0.3293(3)	0.052(3)
C(115)	0.5703(6)	0.0365(2)	0.3621(2)	0.059(3)	C(315)	0.1146(5)	−0.0565(2)	0.3611(3)	0.050(3)
C(116)	0.5353(6)	0.0872(2)	0.3250(2)	0.055(3)	C(316)	0.0470(5)	−0.0028(2)	0.3425(3)	0.044(2)
C(121)	0.4335(6)	0.2522(2)	0.3263(3)	0.037(2)	C(321)	−0.1319(5)	0.0797(3)	0.2127(2)	0.038(2)
C(122)	0.3871(6)	0.3105(2)	0.3089(3)	0.050(2)	C(322)	−0.1877(5)	0.0209(3)	0.2137(2)	0.058(3)
C(123)	0.4377(6)	0.3628(2)	0.3398(3)	0.064(3)	C(323)	−0.2960(5)	0.0059(3)	0.1727(2)	0.080(4)
C(124)	0.5346(6)	0.3567(2)	0.3886(3)	0.066(3)	C(324)	−0.3485(5)	0.0498(3)	0.1308(2)	0.069(3)
C(125)	0.5810(6)	0.2983(2)	0.4065(3)	0.067(3)	C(325)	−0.2926(5)	0.1086(3)	0.1298(2)	0.056(3)
C(126)	0.5305(6)	0.2461(2)	0.3756(3)	0.047(2)	C(326)	−0.1843(5)	0.1235(3)	0.1707(2)	0.044(2)
C(211)	0.1841(6)	0.2593(2)	0.0862(3)	0.044(2)	C(411)	−0.1210(5)	0.3041(2)	0.2433(2)	0.036(2)
C(212)	0.0478(6)	0.2670(2)	0.0716(3)	0.055(3)	C(412)	−0.2524(5)	0.3181(2)	0.2549(2)	0.046(2)
C(213)	0.0031(6)	0.3122(2)	0.0294(3)	0.069(3)	C(413)	−0.3244(5)	0.3607(2)	0.2178(2)	0.056(3)
C(214)	0.0947(6)	0.3497(2)	0.0018(3)	0.070(3)	C(414)	−0.2651(5)	0.3893(2)	0.1692(2)	0.057(3)
C(215)	0.2310(6)	0.3419(2)	0.0164(3)	0.079(4)	C(415)	−0.1338(5)	0.3753(2)	0.1577(2)	0.063(3)
C(216)	0.2757(6)	0.2967(2)	0.0586(3)	0.052(3)	C(416)	−0.0617(5)	0.3327(2)	0.1947(2)	0.051(3)
C(221)	0.2409(6)	0.1342(2)	0.0929(3)	0.039(2)	C(421)	0.0489(6)	0.2991(3)	0.3536(3)	0.043(2)
C(222)	0.3278(6)	0.1317(2)	0.0456(3)	0.059(3)	C(422)	0.0512(6)	0.3632(3)	0.3485(3)	0.053(3)
C(223)	0.3234(6)	0.0818(2)	0.0051(3)	0.081(4)	C(423)	0.1131(6)	0.3986(3)	0.3958(3)	0.066(3)
C(224)	0.2322(6)	0.0343(2)	0.0119(3)	0.075(4)	C(424)	0.1728(6)	0.3700(3)	0.4482(3)	0.077(4)
C(225)	0.1454(6)	0.0367(2)	0.0591(3)	0.081(4)	C(425)	0.1706(6)	0.3060(3)	0.4533(3)	0.091(4)
C(226)	0.1497(6)	0.0867(2)	0.0996(3)	0.061(3)	C(426)	0.1087(6)	0.2705(3)	0.4060(3)	0.071(3)

TABLE III. Calculated Parameters for the Hydrogen Atoms of $Au(dppe)_2{\cdot}Cl{\cdot}2H_2O$.

Atom	x/*a*	y/*b*	z/*c*	Atom	x/*a*	y/*b*	z/*c*
H(11)	0.464	0.131	0.203	H(223)	0.391	0.080	−0.031
H(12)	0.566	0.192	0.232	H(224)	0.229	−0.004	−0.019
H(21)	0.417	0.267	0.180	H(225)	0.075	0.000	0.064
H(22)	0.469	0.213	0.126	H(226)	0.083	0.089	0.136
H(31)	−0.003	0.133	0.374	H(312)	0.225	0.036	0.221
H(32)	−0.155	0.100	0.345	H(313)	0.345	−0.060	0.254
H(41)	−0.218	0.191	0.289	H(314)	0.274	−0.119	0.344
H(42)	−0.165	0.215	0.364	H(315)	0.084	−0.082	0.400
H(112)	0.244	0.126	0.386	H(316)	−0.036	0.013	0.367
H(113)	0.307	0.036	0.451	H(322)	−0.147	−0.013	0.246
H(114)	0.515	−0.021	0.436	H(323)	−0.339	−0.040	0.174
H(115)	0.661	0.012	0.356	H(324)	−0.432	0.038	0.099
H(116)	0.599	0.102	0.290	H(325)	−0.333	0.143	0.097
H(122)	0.312	0.315	0.271	H(326)	−0.141	0.169	0.170
H(123)	0.402	0.408	0.326	H(412)	−0.298	0.296	0.293
H(124)	0.574	0.397	0.413	H(413)	−0.426	0.372	0.227
H(125)	0.656	0.294	0.444	H(414)	−0.321	0.422	0.141
H(126)	0.566	0.201	0.390	H(415)	−0.088	0.398	0.120
H(212)	−0.023	0.238	0.093	H(416)	0.040	0.322	0.186
H(213)	−0.102	0.318	0.018	H(422)	0.005	0.385	0.308
H(214)	0.060	0.385	−0.031	H(423)	0.115	0.448	0.392
H(215)	0.302	0.371	−0.005	H(424)	0.221	0.398	0.485
H(216)	0.381	0.291	0.070	H(425)	0.217	0.284	0.494
H(222)	0.398	0.169	0.040	H(426)	0.107	0.221	0.410

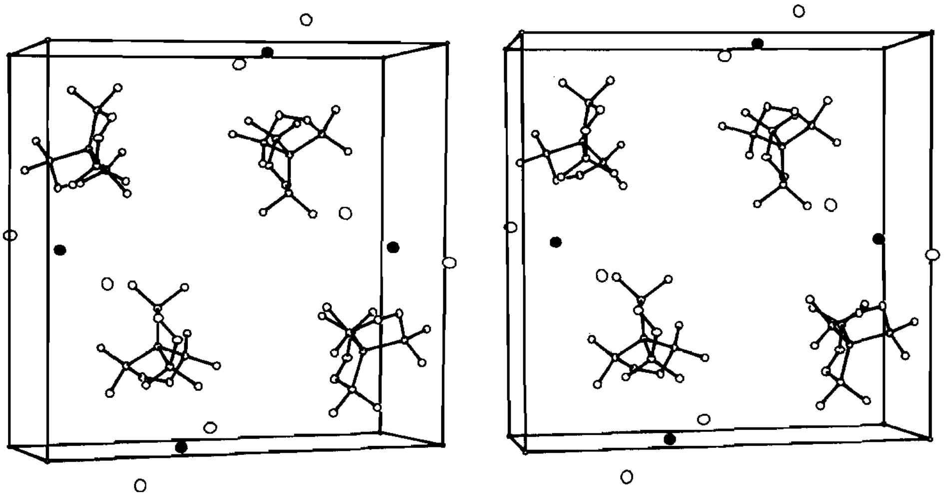

Fig. 2. Stereoview of the unit cell contents of bis[1,2-bis(diphenylphosphino)ethane]gold(I) chloride dihydrate showing the packing of chloride ions and water molecules (chloride ions are filled circles). The phenyl rings of the ligand have been omitted for clarity.

TABLE V. Bond Distances (in Å) for Au(dppe)$_2$Cl·2H$_2$O. Standard deviations are in parentheses.

Au–P(1)	2.412(2)	Au–P(3)	2.402(2)
Au–P(2)	2.384(2)	Au–P(4)	2.391(2)
P(1)–C(1)	1.837(8)	P(3)–C(3)	1.852(9)
P(1)–C(111)	1.819(5)	P(3)–C(311)	1.818(5)
P(1)–C(121)	1.827(5)	P(3)–C(321)	1.824(5)
P(2)–C(2)	1.849(8)	P(4)–C(4)	1.847(9)
P(2)–C(211)	1.803(5)	P(4)–C(411)	1.814(5)
P(2)–C(221)	1.814(5)	P(4)–C(421)	1.826(5)

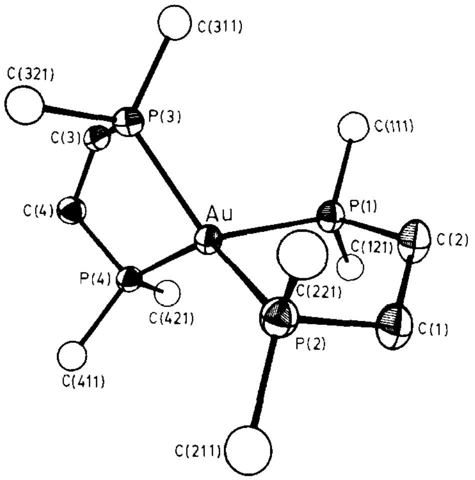

Fig. 3. The complex cation of bis[1,2-bis(diphenylphosphino)ethane]gold(I) chloride dihydrate showing the tetrahedral coordination geometry. The first carbon atom only of each phenyl ring is shown. Thermal ellipsoids have been drawn at the 40% probability level.

(C–H, 1.08 Å). The atomic scattering factors were taken from the tabulations of Cromer and Mann [8], anomalous dispersion corrections were by Cromer and Liberman [9]. The numbering system is given in Fig. 1, final atomic coordinates and thermal parameters in Table I. Table II presents positional and thermal parameters for the group atoms, Table III the calculated positions of all hydrogen atoms. A listing of the values of 10|F$_o$| *vs.* 10|F$_c$| in electrons for the reflections used in the refinement is given in Table IV, deposited with the editor.

Results and Discussion

The crystal structure consists of the packing of monomeric units of the Au(I) complex cation, chloride anions and water molecules. A stereoview of the crystal packing is given in Fig. 2. The shortest, non-hydrogen contact distances are 3.17 and 3.19 Å between Cl···O(1) and Cl···O(2) respectively suggesting the presence of weak, hydrogen bonding interactions between chloride ions and water molecules.

Listings of bond distances and bond angles are given in Tables V and VI respectively. The coordination of each gold atom approximates to ideal tetrahedral geometry (see Fig. 3), the dihedral angles between the 2 planes defined by Au, P(1), P(2) and Au, P(3), P(4) being 89.7°. However, some distor-

TABLE VI. Bond Angles (in °) for $Au(dppe)_2Cl{\cdot}2H_2O$. Standard Deviations are in Parentheses.

P(1)–Au–P(2)	87.1(1)	P(3)–Au–P(4)	86.4(1)
P(1)–Au–P(3)	113.1(1)	P(2)–Au–P(3)	124.8(1)
P(1)–Au–P(4)	117.2(1)	P(2)–Au–P(4)	130.6(1)
Au–P(1)–C(1)	102.9(3)	Au–P(3)–C(3)	102.6(3)
Au–P(1)–C(111)	119.5(2)	Au–P(3)–C(311)	120.1(2)
Au–P(1)–C(121)	119.2(2)	Au–P(3)–C(321)	117.5(2)
C(1)–P(1)–C(111)	104.1(4)	C(3)–P(3)–C(311)	105.3(3)
C(1)–P(1)–C(121)	104.0(4)	C(3)–P(3)–C(321)	103.9(3)
C(111)–P(1)–C(121)	105.0(3)	C(311)–P(3)–C(321)	105.5(3)
Au–P(2)–C(2)	102.8(3)	Au–P(4)–C(4)	104.9(3)
Au–P(2)–C(211)	124.8(2)	Au–P(4)–C(411)	118.9(2)
Au–P(2)–C(221)	117.9(2)	Au–P(4)–C(421)	117.4(2)
C(2)–P(2)–C(211)	104.1(4)	C(4)–P(4)–C(411)	105.0(3)
C(2)–P(2)–C(221)	117.9(2)	C(4)–P(4)–C(421)	106.8(4)
C(211)–P(2)–C(221)	100.2(3)	C(411)–P(4)–C(421)	102.8(3)
P(1)–C(1)–C(2)	111.4(6)	P(3)–C(3)–C(4)	110.1(6)
P(2)–C(2)–C(1)	111.2(6)	P(4)–C(4)–C(3)	114.9(6)
P(1)–C(111)–C(112)	117.9(2)	P(3)–C(311)–C(312)	117.7(2)
P(1)–C(111)–C(116)	122.1(2)	P(3)–C(311)–C(316)	122.3(2)
P(1)–C(121)–C(122)	118.9(2)	P(3)–C(321)–C(322)	121.6(2)
P(1)–C(121)–C(126)	121.1(2)	P(3)–C(321)–C(326)	118.4(2)
P(2)–C(211)–C(212)	117.4(2)	P(4)–C(411)–C(412)	124.0(2)
P(2)–C(211)–C(216)	122.6(3)	P(4)–C(411)–C(416)	115.9(2)
P(2)–C(221)–C(222)	121.4(2)	P(4)–C(421)–C(422)	121.1(2)
P(2)–C(221)–C(226)	118.4(2)	P(4)–C(421)–C(426)	118.6(2)

tion from the ideal is observed since the 'bite' angles within each chelate ring are of necessity reduced to angles of 87.1(1) and 86.4(1)° for P(1)–Au–P(2) and P(3)–Au–P(4) respectively. These are compensated for by the exterior angles which range from 113.1(1) to 130.6(1)°.

The four Au–P distances are not all identical but can be grouped together in pairs with one longer (Au–P(1) 2.412(2); Au–P(3) 2.402(2) Å) and one shorter set (Au–P(2) 2.384(2); Au–P(4) 2.391(2) Å) within each chelate ring. These values are all shorter than the Au–P distances determined in the tetrahedral complexes $[Au(PPh_2Me)_4][PF_6]$ (2.449(1) Å) [2] and modification II of $[Au(PPh_3)_4]{\cdot}BPh_4$ (av. 2.606 Å) [1]. Non-equivalent M–P bonds have been observed in the structure of $Cu(dppe)_2^+$ [10] but here the pattern of one longer and one shorter bond within the same chelate ring is not repeated. However, the Au–P distances are in line with the pattern noted by Randaccio and his co-workers for the M–P distance in complexes Mp_nX_m [11, 12] where an increase in bond length is observed as the number of P donors increases. A variation in Cu–P bond length as a function of P–Cu–P bond angle has also been noted [11] in Cu(I) complexes and this trend is repeated in the $Au(dppe)_2^+$ cation. Excluding the P–Au–P angle within each chelate ring the longer the 2 Au–P bonds the smaller the angle these two phosphorus atoms subtend at gold. Some distortions from the ideal *gauche* geometry can be seen in the chelate ring. Deviations from the plane, Au, P(1), P(2), of +0.33 and –0.43 Å are observed for atoms C(1) and C(2) respectively. However, atoms C(3) and C(4) deviate from the plane Au, P(3), P(4) by –0.75 and –0.10 Å respectively. This second ring is clearly considerably distorted from its ideal geometry. Further minor variations accompany this distortion as seen in the angles Au–P(4)–C(4) and P(4)–C(4)–C(3) which show small variations from other comparable angles within the molecule. However, inspection of intermolecular contact distance suggests that overall packing forces are likely to be responsible for these effects since there appears to be no one region where steric pressures predominate.

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