Stable Gold(I) Complexes with Chelate Rings: Solution Studies of Bis(phosphino)ethane Complexes and *X*-Ray Crystal Structure of Bis[1,2-bis(diphenylphosphino)ethane]gold(I) Hexafluoroantimonate–Acetone (1/1) †

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Bis-chelated four-co-ordinate gold(I)–phosphine complexes of 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diethylphosphino)ethane (depe) exhibit exceptionally high thermodynamic and kinetic stability both in the solid state and in solution at ambient temperatures. Their formation in solution has been studied by conductivity and ^{31}P n.m.r. titrations. Complexes of $[Au(depe)_2]^+$ and $[Au(dppe)_2]^+$ have been prepared and characterized. These species exist in solution even at Au : bis(phosphine) ligand ratios of 1 : 0.75. The mixed species $[Au(depe)(dppe)]^+$ exhibited a *trans*-gold ^{31}P–^{31}P n.m.r. coupling of 52 Hz. The title complex was crystallized and shown by *X*-ray crystallography to contain gold(I) with a flattened tetrahedral (closely D_{2d}) co-ordination geometry (P–Au–P, 85—130°) chelated by two dppe ligands with Au–P bond lengths of 2.39—2.42 Å. Crystals are monoclinic, space group $P2_1/n$, with a = 18.685(2), b = 19.414(2), c = 15.096(1) Å, β = 91.69(1)°, and Z = 4; 4 811 reflections refined to R 0.062.

The apparent overwhelming preference of Au^I for linear two-co-ordination has made complexes of higher co-ordination special curiosities. A few three-co-ordinate complexes are known,[1] and, in the last few years, the existence of four-co-ordination has been substantiated [2-5] including two complexes with near tetrahedral symmetry: [6,7] $[Au(PMePh_2)_4]^+$ and $[Au(SbPh_3)_4]^+$. Reports of chelated Au^I complexes have been confined [1,8,9] to bidentate ligands with rigid backbones: $[Au(pdma)_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)] and bis[*cis*-bis(diphenylphosphino)ethylene]gold(I). However, the latter ligand (L) also readily forms the ring-opened complex $[(AuCl)_2L]$,[10] a type of species also formed by bis(diphenylphosphino)methane.[11] Flexible, bidentate bis(phosphino)ethane ligands are usually assumed [12] to preserve linear co-ordination for Au^I *via* formation of annular binuclear complexes. During our ^{31}P n.m.r. studies of solutions containing Au^I and 1,2-bis(diphenylphosphino)ethane (dppe) it became apparent that significant amounts of a possible four co-ordinate complex were present even at ambient temperature and low Au^I : bis(phosphine) ratios (*e.g.*, 1 : 0.75). By *X*-ray crystallography this very stable complex has been shown to contain gold(I) with a flattened tetrahedral co-ordination geometry provided by two chelated bis(phosphine) ligands, the first example of the chelation of gold(I) by a flexible bidentate ligand. Variable-temperature ^{31}P n.m.r. studies of both dppe and 1,2-bis(diethylphosphino)ethane (depe) gold(I) complexes are also reported, and used to confirm the existence of a four-co-ordinate mixed-ligand complex in solution.

Experimental

1,2-Bis(diphenylphosphino)ethane and 1,2-bis(diethylphosphino)ethane were purchased from Strem Chemicals. Sodium chloroaurate was purchased from Johnson Matthey PLC and thiodiglycol [2,2′-thiobis(ethanol)] from Sigma.

Preparations.—$[(AuCl)_2(dppe)]$. $Na[AuCl_4]\cdot 2H_2O$ (0.45 g, 1.1 mmol) was reduced to Au^I by thiodiglycol (0.28 g, 2.2 mmol) in aqueous acetone (2.5 : 1, 7 cm^3). When the solution became colourless, dppe (0.22 g, 0.55 mmol) in acetone (10 cm^3) was added dropwise over 5 min. After stirring for 1 h, the white solid product was filtered off, washed with H_2O (2 × 5 cm^3) and acetone (2 × 5 cm^3). Yield 93%, m.p. 262—267 °C (Found: C, 36.35; H, 2.80; P, 6.75. Calc. for $C_{26}H_{24}Au_2Cl_2P_2$: C, 36.2; H, 2.80; P, 7.20%).

$[(AuCl)_2(depe)]$. $Na[AuCl_4]\cdot 2H_2O$ (1 g, 2.5 mmol) was reduced to Au^I by thiodiglycol (0.61 g, 5 mmol) in aqueous ethanol (3 : 1, 13 cm^3). In an N_2 atmosphere, depe (0.25 g, 1.25 mmol) in EtOH (3 cm^3) was added dropwise giving an immediate white precipitate. After stirring for 2 h, this was filtered off, and recrystallized from $CHCl_3$–EtOH, washed with water and acetone, and dried *in vacuo*. Yield 31%, m.p. 168—169 °C (Found: C, 18.1; H, 3.35; Cl, 10.75; P, 9.70. Calc. for $C_{10}H_{24}Au_2Cl_2P_2$: C, 17.9; H, 3.60; Cl, 10.55; P, 9.25%).

$[Au_2Cl_2(depe)_2]$. This was prepared from $[(AuCl)_2(depe)]$ by addition of a further mol equiv. of depe in $CHCl_3$, followed by evaporation of the solvent and solidification of the resultant white gum by triturating in ether, m.p. 196—210 °C. The product gave a single {^{1}H}-^{31}P n.m.r. resonance at δ 31.6 p.p.m. ($CDCl_3$) (Found: C, 27.75; H, 5.50; P, 14.2. Calc. for $C_{20}H_{48}Au_2Cl_2P_4$: C, 27.4; H, 5.50; P, 14.1%). A similar sample was kindly provided by Dr. D. T. Hill of Smith, Kline, and French Laboratories (Philadelphia).

$[Au(dppe)_2]SbF_6\cdot Me_2CO$. $[(AuCl)_2(dppe)]$ (0.2 g, 0.23 mmol) was added with stirring to a solution of dppe (0.28 g, 0.7 mmol) in acetone (10 cm^3) giving a clear colourless solution. After 1 h, $Na[SbF_6]$ (0.12 g, 0.46 mmol) in H_2O (3 cm^3) was added dropwise. On standing at room temperature fine white crystals suitable for crystallographic studies were obtained: m.p. 197—202 °C. Crystallization from $CHCl_3$–EtOH proved unsuitable as crystals rapidly lost solvent (Found: C, 51.0; H, 4.4; P, 9.7. Calc. for $C_{55}H_{54}AuF_6OP_4Sb$: C, 51.3; H, 4.25; P, 9.60%). The compound gave a single {^{1}H}-^{31}P n.m.r. ($CDCl_3$) peak at 20.8 p.p.m. The BPh_4^- complex was prepared using a similar procedure.

$[Au(depe)_2]SbF_6$. $[(AuCl)_2(depe)]$ (50 mg, 0.075 mmol) was suspended in $CHCl_3$ (3 cm^3) and depe (50.7 mg, 0.25 mmol) was added giving a clear, colourless solution which was stirred for 30 min. Addition of $Na[SbF_6]$ (39 mg, 0.149 mmol) in acetone (1 cm^3) immediately gave a white precipitate. After

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† *Supplementary data available* (No. SUP 23872, 35 pp.): thermal parameters, structure factors, full bond length and bond angle data .See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Final positional parameters (Au × 10^5, others × 10^4) for the non-hydrogen atoms * with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Au	20 616(2)	20 987(3)	23 216(3)
P(1)	2 173(2)	1 286(2)	3 506(2)
P(2)	1 552(2)	3 229(2)	2 309(2)
P(3)	3 102(2)	2 643(2)	1 714(2)
P(4)	1 499(1)	1 177(2)	1 480(2)
C(11)	1 640(7)	558(7)	3 127(8)
C(111)	3 044(5)	908(6)	3 724(8)
C(112)	3 604(7)	1 063(8)	3 187(9)
C(113)	4 275(7)	738(9)	3 332(11)
C(114)	4 366(7)	266(8)	4 009(10)
C(115)	3 790(8)	105(7)	4 557(9)
C(116)	3 165(7)	416(7)	4 403(8)
C(121)	1 838(7)	1 523(9)	4 578(10)
C(122)	2 256(10)	1 742(11)	5 262(10)
C(123)	1 976(15)	1 989(12)	6 054(12)
C(124)	1 237(14)	2 044(12)	6 113(18)
C(125)	764(12)	1 845(12)	5 390(16)
C(126)	1 085(10)	1 584(11)	4 639(13)
C(21)	2 230(7)	3 776(7)	1 736(9)
C(211)	1 429(8)	3 728(7)	3 303(11)
C(212)	1 205(9)	4 388(8)	3 265(12)
C(213)	1 115(10)	4 773(9)	4 024(13)
C(214)	1 257(9)	4 479(11)	4 839(14)
C(215)	1 491(8)	3 828(10)	4 894(11)
C(216)	1 585(8)	3 435(9)	4 126(10)
C(221)	727(7)	3 339(7)	1 669(9)
C(222)	743(7)	3 247(9)	744(10)
C(223)	112(10)	3 304(9)	246(13)
C(224)	−524(12)	3 411(11)	655(21)
C(225)	−538(10)	3 462(12)	1 546(18)
C(226)	97(8)	3 441(9)	2 060(13)
C(31)	2 708(7)	3 394(8)	1 136(8)
C(311)	3 704(7)	3 043(7)	2 519(9)
C(312)	4 253(9)	3 466(8)	2 242(12)
C(313)	4 734(9)	3 760(11)	2 885(15)
C(314)	4 636(10)	3 633(11)	3 768(15)
C(315)	4 078(10)	3 231(9)	4 040(11)
C(316)	3 626(7)	2 932(8)	3 421(10)
C(321)	3 656(7)	2 219(8)	916(9)
C(322)	3 415(10)	2 090(12)	84(11)
C(323)	3 866(14)	1 709(15)	−483(13)
C(324)	4 496(10)	1 479(14)	−204(15)
C(325)	4 752(10)	1 577(10)	614(15)
C(326)	4 346(8)	1 955(8)	1 225(11)
C(41)	1 775(7)	417(7)	2 137(8)
C(411)	529(7)	1 117(7)	1 466(8)
C(412)	129(8)	1 615(8)	1 825(11)
C(413)	−610(8)	1 551(11)	1 842(14)
C(414)	−938(7)	976(9)	1 447(13)
C(415)	−560(8)	494(10)	1 093(11)
C(416)	195(7)	548(9)	1 050(10)
C(421)	1 719(6)	1 006(7)	335(8)
C(422)	2 102(8)	436(9)	71(9)
C(423)	2 266(8)	362(10)	−841(11)
C(424)	2 054(9)	846(12)	−1 438(10)
C(425)	1 685(10)	1 424(12)	−1 159(10)
C(426)	1 521(9)	1 498(9)	−275(10)
Sb	3 244(1)	8 815(1)	6 960(1)
F(1)	3 978(7)	9 372(8)	6 491(11)
F(2)	3 847(8)	8 030(6)	6 886(11)
F(3)	2 512(7)	8 257(8)	7 431(11)
F(4)	2 642(8)	9 599(6)	7 035(11)
F(5)	3 613(8)	8 990(9)	8 125(5)
F(6)	2 878(8)	8 640(9)	5 796(5)
Solvent molecule			
C(1)	4 091(39)	5 003(24)	8 744(22)
C(2)	4 022(24)	4 531(22)	9 356(34)
O(1)	3 938(25)	4 557(14)	10 154(20)
C(3)	4 068(22)	3 863(26)	9 209(25)

* For numbering system see Figure 3. Carbons in PCH_2CH_2P bridges are numbered according to the bonded P: *e.g.* C(11) is bonded to P(1) and C(41) to P(4); similarly for the phenyl rings, *e.g.* the two phenyl rings attached to P(1) are C(111)—C(116) and C(121)—C(126).

further concentration by evaporation, this was filtered off, thoroughly washed with H_2O, and recrystallized from aqueous acetone. Yield 60%, m.p. 198—235 °C (Found: C, 28.65; H, 5.70; P, 13.95. Calc. for $C_{20}H_{48}AuF_6P_4Sb$: C, 28.4; H, 5.70; P, 14.65%). The compound gave a single $\{^1H\}$-^{31}P n.m.r. ($CDCl_3$) peak at 15.8 p.p.m.

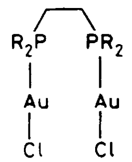
N.M.R. Measurements.—These were made on JEOL FX60 (24.15 MHz) and Bruker HFX90 machines (36.4 MHz, University of London Intercollegiate Research Service) in 10-mm tubes using $CDCl_3$ as solvent at 298 K, unless otherwise stated. The shift reference was H_3PO_4–D_2O (85 : 15 v/v).

Crystallography.—Crystals were not suitable for *X*-ray diffraction unless they were mounted in a glass capillary to avoid loss of the acetone molecule.

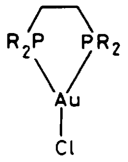
Crystal data. $C_{55}H_{54}AuF_6OP_4Sb$ (acetone solvate), monoclinic, $M = 1\,287.58$, space group $P2_1/n$, $a = 18.685(2)$, $b = 19.414(2)$, $c = 15.096(1)$ Å, $\beta = 91.69(1)°$, $U = 5\,473.8$ Å^3, $F(000) = 2\,416$, $Z = 4$, $D_c = 1.55$ g cm^{-3}. Intensity data [5 843 reflections, 4 811 with $I_o > 2\sigma(I_o)$, $3.5 < \theta < 60°$, measured at 20 °C] were obtained using a CAD-4 diffractometer with Ni filter and Cu-K_α radiation ($\lambda = 1.541\,8$ Å). Empirical absorption corrections were applied ($\mu = 99.7$ cm^{-1}). The Au atom was located in a three-dimensional Patterson map and successive difference syntheses were applied. The F atoms of the SbF_6^- anion were found to be disordered in a manner which could not be readily characterised; a rigid SbF_6^- configuration was therefore imposed for the final cycles of refinement. The final convergence was reached with $R = 0.062$ and $R' = 0.067$. Final positional parameters are listed in Table 1 and bond lengths and angles in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for non-hydrogen atoms with e.s.d.s in parentheses

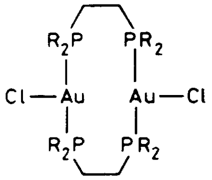
Au–P(1)	2.389(3)	Au–P(2)	2.392(3)
Au–P(3)	2.416(3)	Au–P(4)	2.416(3)
P(1)–C(11)	1.81(1)	P(2)–C(21)	1.88(2)
P(1)–C(111)	1.81(1)	P(2)–C(211)	1.81(2)
P(1)–C(121)	1.81(2)	P(2)–C(221)	1.81(1)
P(3)–C(31)	1.84(1)	P(4)–C(41)	1.84
P(3)–C(311)	1.81(1)	P(4)–C(411)	1.82(1)
P(3)–C(321)	1.81(1)	P(4)–C(421)	1.82(1)
P(1)–Au–P(2)	129.6(1)	P(2)–Au–P(3)	85.4(1)
P(1)–Au–P(3)	121.3(1)	P(2)–Au–P(4)	120.5(1)
P(1)–Au–P(4)	86.1(1)	P(3)–Au–P(4)	117.8(1)
Au–P(1)–C(11)	104.1(4)	Au–P(2)–C(21)	104.3(5)
Au–P(1)–C(111)	117.5(4)	Au–P(2)–C(211)	123.1(5)
Au–P(1)–C(121)	118.4(5)	Au–P(2)–C(221)	116.5(5)
Au–P(3)–C(31)	102.2(4)	Au–P(4)–C(41)	101.5(4)
Au–P(3)–C(311)	115.1(4)	Au–P(4)–C(411)	118.2(4)
An–P(3)–C(321)	122.4(5)	Au–P(4)–C(421)	121.9(4)



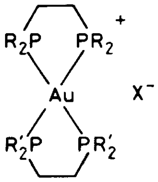
(1a) R = Ph
(1b) R = Et



(2a) R = Ph
(2b) R = Et



(3a) R = Ph
(3b) R = Et



(4a) R = R′ = Ph
(4b) R = R′ = Et
(4c) R = Ph, R′ = Et

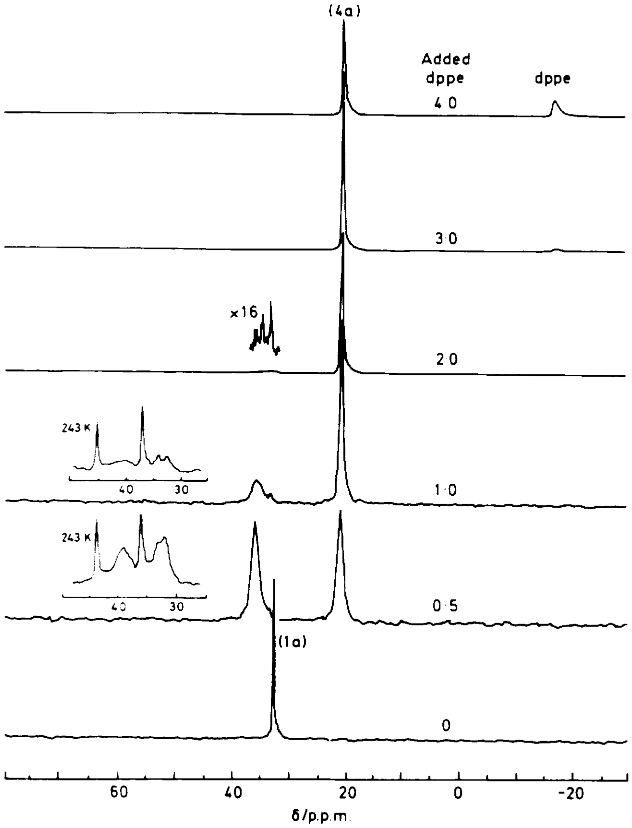


Figure 1. {^{1}H}-^{31}P N.m.r. spectra of [$(AuCl)_2(dppe)$] (1a) (37 mmol dm^{-3} in $CDCl_3$) at 302 K in the presence of 0.5, 1, 2, 3, and 4 mol equiv. of added dppe. The inserts show the region 26—49 p.p.m. at 243 K. Note the appearance of the peak at 20.8 p.p.m. for the chelated complex [$Au(dppe)_2$]$^+$ (4a) even at low dppe : Au ratios. The formation of this species is complete when 3 mol equiv. of dppe have been added to the digold complex (1a), *i.e.* at an Au : dppe ratio of 1 : 2

Conductivity Measurements.—A Griffin conductivity bridge equipped with Pt electrodes was used. Solid dppe was added to a 0.010 mol dm^{-3} solution of [$(AuCl)_2(dppe)$] in $CHCl_3$ (10 cm^3) at 302 K.

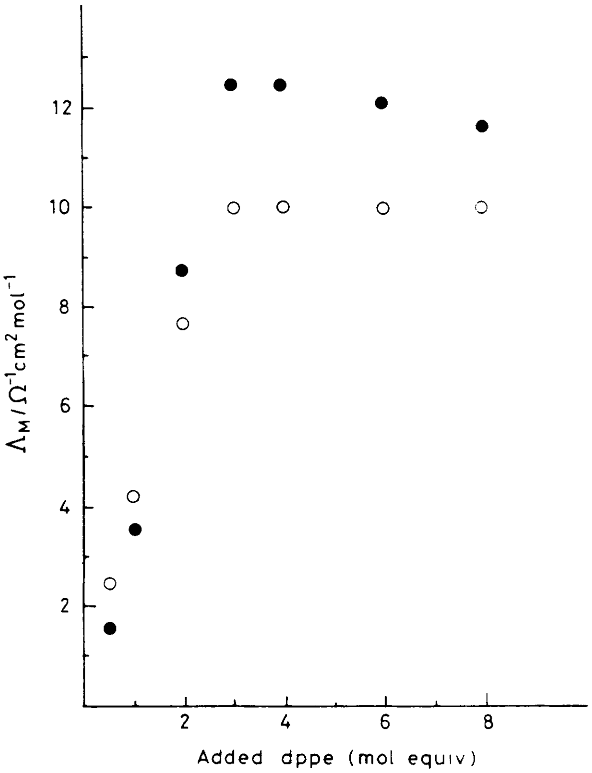


Figure 2. Variation of the molar conductance of 10^{-2} (●) and 10^{-3} (○) mol dm^{-3} solutions of [$(AuCl)_2(dppe)$] (1a) in $CHCl_3$ at 295 K with added dppe. Molar conductances are based on gold concentration, whereas molar equivalents are with respect to the digold complex (1a). The conductance reaches a maximum when 3 mol equiv. of dppe have been added, *i.e.* a Au : dppe ratio of 1 : 2 [A 10^{-3} mol dm^{-3} solution of the isolated complex (4a) (X = Cl^-) in $CHCl_3$ gave a molar conductance of 10.5 Ω^{-1} cm^2 mol^{-1}]

Results and Discussion

The {^{1}H}-^{31}P n.m.r. spectrum of [$(AuCl)_2(dppe)$] in $CDCl_3$ shows a single resonance at 31.5 p.p.m., Figure 1. In this complex, which was reported previously by McAuliffe *et al.*,[13] the bis(phosphine) ligand is assumed to bridge between two Au^{I} ions as in structure (1). The analogous 1,2-bis(diphenylphosphino)ethylene complex has been crystallized.[8] On addition of 0.5 mol equiv. of dppe to the solution of [$(AuCl)_2(dppe)$] (1a) at 302 K, two new broadened ^{31}P n.m.r. peaks appear at 34.6 and 20.8 p.p.m. The broadening appears to be due to chemical exchange since the latter peak is sharp ($\Delta\nu_{\frac{1}{2}}$ = 7 Hz) at 243 K whereas the former splits into four peaks at 41.6, 37.7, 34.9, and 31.8 p.p.m. On further addition of dppe the peak at 20.8 p.p.m. increases in intensity (and sharpens) at the expense of other species so that after addition of 3 mol equiv. (*i.e.* a Au : dppe ratio of 1 : 2) it is the only resonance observed. Subsequently a peak for free dppe appears in the spectrum (Figure 1), slightly broadened by exchange. These data suggested the existence of a new complex ion, [$Au(dppe)_2$]$^+$ (4a). The conductivity of solutions of [$(AuCl)_2(dppe)$] with added dppe reached a maximum at a Au : (total) dppe ratio of 1 : 2 (Figure 2) also suggestive of the formation of a four-co-ordinated gold–phosphine complex.

The complex was isolated and crystallized as an acetone solvate with SbF_6^- as the counter anion (see Experimental section). By *X*-ray crystallography it was shown to contain gold(I) with a flattened (closely D_{2d}) co-ordination geometry

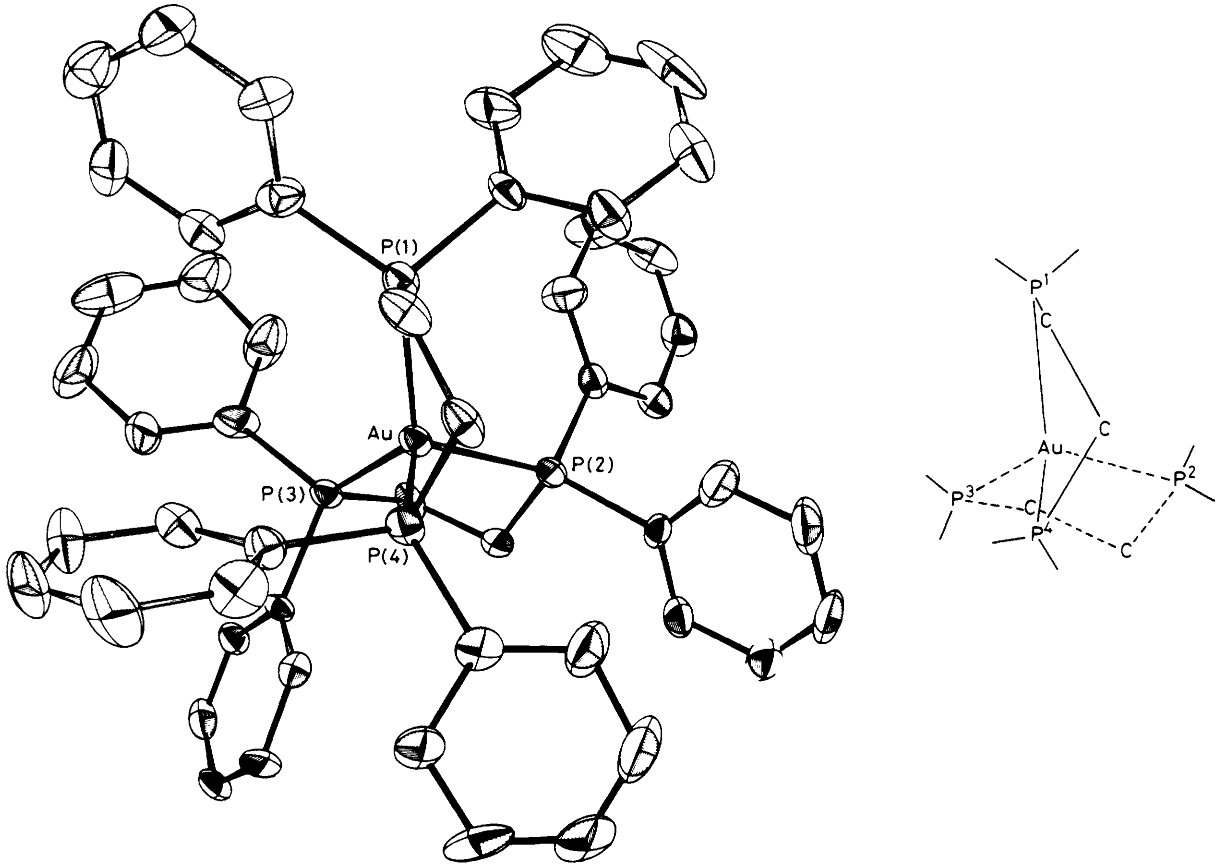


Figure 3. The molecular structure of the $[Au(dppe)_2]^+$ cation determined by *X*-ray crystallography; P(1) and P(4) belong to one dppe ligand and P(2) and P(3) to the second. A line diagram is shown to aid tracing of the chelate rings

(P–Au–P, 85—130°) chelated by two bis(phosphine) ligands [structure (4), R = Ph] with Au–P bond lengths of 2.39—2.42 Å, Figure 3. Tetrahedral co-ordination is prevented by the small bite of the dppe ligand, as in $[Au(pdma)_2]^+$.[9] The Au–P distances (2.389, 2.392, 2.416, and 2.416 Å) are approximately equal and similar to those observed for the three short Au–P bonds of modification (I) of $[Au(PPh_3)_4]BPh_4$ (average 2.402 Å),[3] but shorter than those of the more nearly tetrahedral $[Au(PMePh_2)_4]PF_6$ (2.449 Å).[6] The acetone molecule occupies an open region in the crystal and the geometries of the bis(phosphine) ligands are normal.

When dissolved in $CDCl_3$ these crystals gave the expected single sharp $\{^1H\}$-^{31}P n.m.r. resonance at 20.8 p.p.m. Therefore either the chelated four-co-ordinate $[Au(dppe)_2]^+$ species exists in solution or a very rapid ring opening and closure occurs.

To investigate this further we studied the ^{31}P n.m.r. spectra of $[(AuCl)_2(depe)]$ (1b) with added depe and dppe, the latter with the aim of detecting mixed-ligand species $[Au(dppe)(depe)]^+$ (4c). The titration of $[(AuCl)_2(depe)]$ with depe is shown in Figure 4. In an analogous manner to dppe it is notable that the only resonance present in the $\{^1H\}$-^{31}P spectrum at a Au : depe ratio of 1 : 2 [*i.e.*, a (1b) : depe molar ratio of 1 : 3] is that at 15.8 p.p.m. This was thought to correspond to $[Au(depe)_2]^+$ (4b) and indeed salts containing this can be isolated (see Experimental section). The $\{^1H\}$-^{31}P n.m.r. spectra of titrations of $[(AuCl)_2(dppe)]$ with depe and $[(AuCl)_2(depe)]$ with dppe are shown in Figure 5(*a*) and (*b*). In the presence of a total of 2 mol equiv. of bis(phosphine) a multiplet pattern corresponding to the expected A_2B_2 spin system of $[Au(dppe)(depe)]^+$ (4c) is seen at δ 18.7 p.p.m. and $^2J(P-P)$ = 52 Hz, corresponding to coupling of the phosphorus atoms of dppe with those of depe across gold [simulation shown in Figure 5(*c*)]. We can conclude therefore that any ring opening and closure in these chelated bis(phosphine) complexes occurs at a rate of $\ll 52\ s^{-1}$.

The chelated four-co-ordinate phosphine species described here therefore appear to have a much enhanced kinetic and thermodynamic stability compared to monodentate $[Au(PR_3)_4]^+$ phosphine complexes described previously. It can be seen from Figure 1 that a significant amount of $[Au(dppe)_2]^+$ is present even in solutions containing a Au : dppe ratio of 1 : 0.75, although in intermediate exchange on the n.m.r. time-scale ($<300\ s^{-1}$) with other species at *ca.* 34.6 p.p.m. Curiously there is no $[Au(depe)_2]^+$ (4b) present in solutions of $[(AuCl)_2(depe)]$ (1b) with 0.5 mol equiv. of added depe, Figure 4. We attribute this to the higher stability of the digold open-ring complex (3b) which can be isolated (see Experimental section) from solutions with a Au : depe ratio of 1 : 1 where it is the only species present, as shown by ^{31}P n.m.r. (Figure 4). Further titration of (3b) with depe leads to the same products as with (1). From a consideration of molecular models it appeared that steric interactions in (3a) would destabilize the complex perhaps with respect to the three-co-ordinate chelated complex (2a).

There are clearly a number of intermediates around 33—37 p.p.m. in the titrations of both $[(AuCl)_2(dppe)]$ and $[(AuCl)_2(depe)]$ with 0.5—2 mol equiv. of added depe or dppe. These may be complexes of the type (2) or phosphine-bridged oligomers similar to those reported for dppe complexes of Cu^I.[14] The complex $[Cu_2Cl_2(dppe)_3]\cdot 2Me_2CO$ has two tetrahedrally co-ordinated Cu^I ions, bridged by one dppe ligand

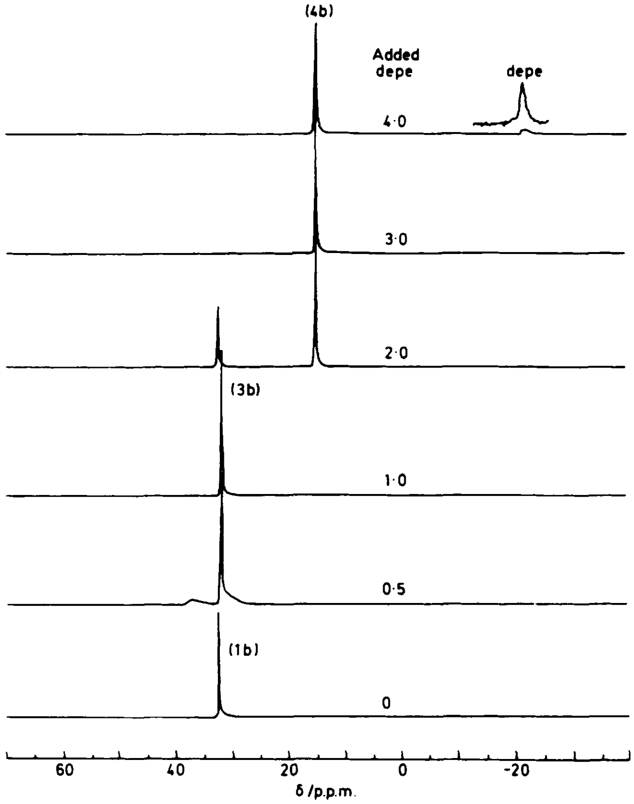
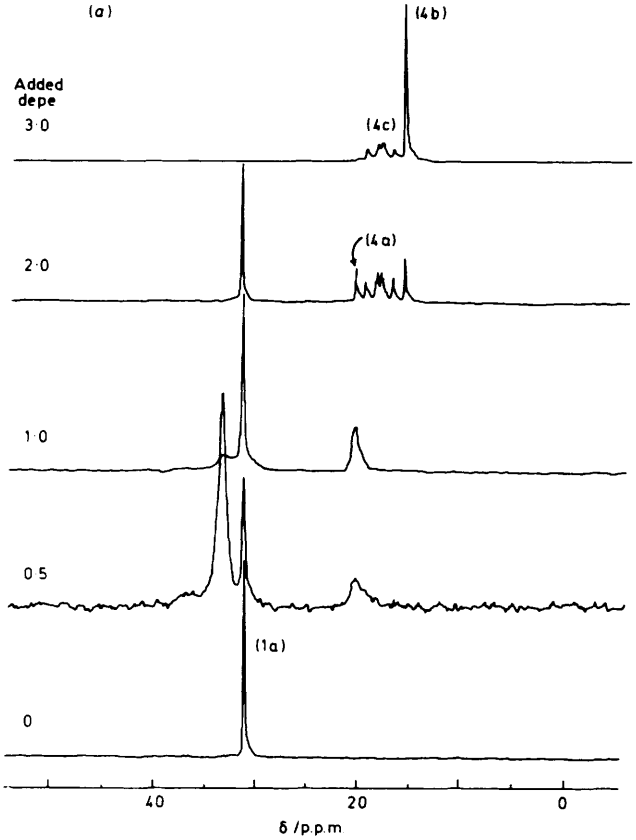
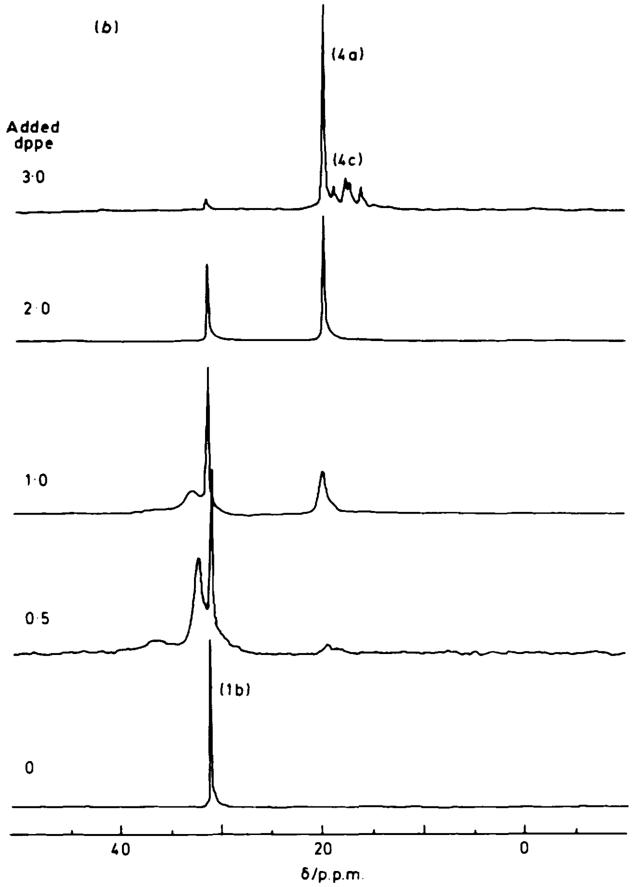


Figure 4. $\{^1H\}$-^{31}P N.m.r. spectra of $[(AuCl)_2(depe)]$ (1b) (40 mmol dm^{-3} in $CDCl_3$) at 302 K in the presence of 0.5, 1, 2, 3, and 4 mol equiv. of added depe. In contrast to Figure 1, note the absence of $[Au(depe)_2]^+$ (4b) (15.8 p.p.m.) after the addition of 0.5 mol equiv. of depe, and with 1 mol equiv. of added depe (*i.e.* a Au : depe ratio of 1 : 1) the complete conversion to the digold open-ring complex (3b)





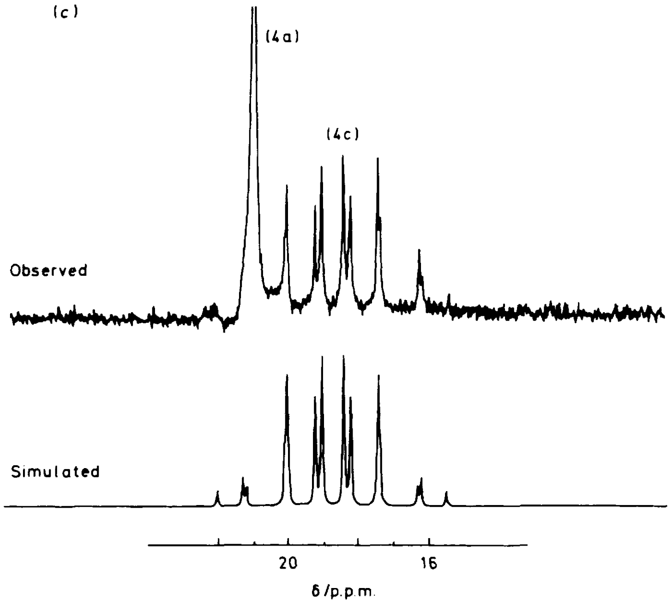


Figure 5. 24-MHz $\{^1H\}$-^{31}P N.m.r. spectra of solutions (35 mmol dm^{-3} in $CDCl_3$, at 302 K) of (*a*) $[(AuCl)_2(dppe)]$ (1a) with 0.5, 1, 2, and 3 mol equiv. of added depe and (*b*) $[(AuCl)_2(depe)]$ (1b) with 0.5 1, 2, and 3 mol equiv. of added dppe. The spectra in (*a*) and (*b*) with Au : dppe : depe ratios of 2 : 1 : 1 are identical showing that equilibrium has been attained. The ratios of $[Au(dppe)_2]^+$ (4a) : $[Au(dppe)(depe)]^+$ (4c) : $[Au(depe)_2]^+$ (4b) with 3 mol equiv. of added bis(phosphine) ligand are similar to those expected statistically. (*c*) The region 16—21 p.p.m. of (*b*) at 36 MHz showing the A_2B_2 pattern for (4c) together with the simulated spectrum

and each bound to a further chelated dppe and a chloride.[14] It is interesting to note that this complex was prepared by reaction of CuCl with excess dppe, conditions which for Au^I would give the bis-chelated complex. The tendency towards ring closure may therefore be even stronger for Au^I than for Cu^I, although $[Cu(dppe)_2]^+$ has been crystallized as the trifluoroacetate salt.[15] The distortions from tetrahedral geometry observed for the latter complex (P–Cu–P, 89—122°) are similar to those reported here for the Au^I complex.

Finally it is noteworthy that the exchange of bound bis(phosphine) ligands in the four-co-ordinate chelate complexes $[Au(depe)_2]^+$ and $[Au(dppe)_2]^+$ with free, excess depe and dppe is comparatively slow on the n.m.r. time-scale ($\ll 800$ s^{-1}) even at room temperature (see Figures 1 and 4, with 4 mol equiv. of added phosphine). This situation contrasts with that for monophosphines.[2,4] The bis(phosphine) ligands used here are not constrained to favour ring closure; indeed the most populated rotamers of free dppe or depe would be expected to be those with the *trans*-P configuration about the C–C bond. It is possible, in general, that chelation in Au^I chemistry is more favourable than has hitherto been assumed.*

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* Since completion of this manuscript we have noted that references to possible $[Au(dppe)_2]Cl$ and $[Au(dppe)_2]BPh_4$ complexes were made in a paper by Cariati *et al.*[16] on gold cluster compounds. These authors commented that they had 'no direct evidence that dppe is chelated.' The work described here clearly confirms that it is.

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