Copper(I) and Gold(I) Complexes with *cis*-Bis(diphenylphosphino)ethylene. Crystal Structures and ^{31}P Cross-polarization Magic Angle Spinning Nuclear Magnetic Resonance Studies*

Susan J. Berners-Price,[a] Lynda A. Colquhoun,[a] Peter C. Healy,[a] Karl A. Byriel[b] and John V. Hanna[c]
[a] *School of Science, Griffith University, Brisbane, Queensland 4111, Australia*
[b] *Department of Chemistry, University of Queensland, Brisbane 4072, Australia*
[c] *C.S.I.R.O. Division of Coal and Energy Technology, North Ryde, New South Wales 2113, Australia*

The synthesis, structural and solid-state ^{31}P cross-polarization magic angle spinning (CP MAS) NMR characterization of *cis*-bis(diphenylphosphino)ethylene (dppey) and the copper(I) and gold(I) complexes $[M(dppey)_2]PF_6$ has been carried out. The complexes, which have been shown to exhibit cytotoxic and antitumour activity, belong to the relatively rare class of copper(I) and gold(I) complexes with tetrahedral CuP_4 and AuP_4 co-ordination spheres. Crystals of dppey **1** are monoclinic with space group $P2_1/c$ and a = 12.861(8), b = 13.097(2), c = 14.228(8) Å, β = 116.15(3)°; R was 0.047 for 3117 'observed' reflections. The solid-state CP MAS ^{31}P NMR spectrum consists of an AB multiplet with $\delta(P_A)$ −24.2, $\delta(P_B)$ −27.2 and J(P–P) = 126 Hz. Crystals of $[Cu(dppey)_2]PF_6$ **2** are orthorhombic with space group $P2_12_12_1$ and a = 14.479(5), b = 16.703(4), c = 20.891(4) Å; R was 0.046 for 3138 'observed' reflections. The CuP_4 co-ordination sphere is regular within the constraints of chelation with Cu–P in the range 2.276(2)–2.289(2) Å. The copper atom lies on a pseudo two-fold axis of symmetry bisecting the C=C bonds. Charge-transfer interactions between phenyl rings on each ligand contribute to the stabilization of the structure of the cation. The solid-state ^{31}P NMR spectrum consists of four broad bands ($\Delta\nu_{\frac{1}{2}}$ = 300 Hz) centred at δ 8 with J(Cu–P) ≈ 820 Hz. Distortion of the quartet spacings by quadrupolar interaction with the copper nuclei is minimal. Crystals of $[Au(dppey)_2]PF_6$ **3** are isomorphous with **2** with a = 14.644(4), b = 16.703(1), c = 20.699(5) Å; R was 0.025 for 3947 'observed' reflections. The Au–P distances lie in the narrow range 2.377(2)–2.388(2) Å. Solid-state CP MAS ^{31}P NMR of this complex and the analogous nitrate and chloride complexes at magnetic field strengths of 2.11, 7.05 and 9.40 T reveal splitting of the phosphorus signal into a quartet ascribed to Au–P spin–spin coupling effects with J(Au–P) estimated to be 200 Hz. As for the copper complex, distortion of the quartet spacings is minimal and indicative of a small ^{197}Au quadrupolar coupling constant. Solution and solid-state ^{31}P NMR chemical shift parameters are similar, supporting the hypothesis that the tetrahedral bis(chelated) cations are also stable in solution. Spin–spin coupling to the quadrupolar (^{197}Au or $^{63/65}Cu$) nuclei was not resolved in the solution spectra, however, due to rapid quadrupolar relaxation.

The bidentate diphosphine $Ph_2P(CH_2)_2PPh_2$ (dppe) and related phenyl-substituted diphosphines exhibit cytotoxic and antitumour activity in several murine tumour models.[1] Their potency is significantly increased when co-ordinated to gold(I) and compounds of the type [XAu(dppe)AuX] (*e.g.* X = chloride or thioglucose) containing linearly co-ordinated gold(I) are active against a range of tumours *in vivo*.[2,3] Phosphorus-31 NMR studies[4] show that in the presence of thiols and blood plasma these compounds readily undergo ring-closure reactions to form a four-co-ordinate cation $[Au(dppe)_2]^+$. Salts of this cation exhibit a broad spectrum of antitumour activity[5] as do analogous silver(I) and copper(I) diphosphine complexes.[6,7] In general, for complexes of the type $[M\{R_2P(CH_2)_nPR_2\}_2]^+$, where M = Au^I, Ag^I or Cu^I, the highest activity has been observed when R = Ph and n = 2 or 3 and analogous complexes with *cis*-$Ph_2PCH{=}CHPPh_2$ (dppey).[3] By contrast, dppe complexes of platinum(II) and palladium(II) have been found to be less active than the phosphine alone.[2,8]

Since the tetrahedral complexes of the Group 11 metal ions have kinetically labile metal–phosphine bonds it has been proposed that the metal acts as a delivery system for the cytotoxic diphosphines.[3,9] The mechanism of the cytotoxic activity is, however, still unknown, although for $[Au(dppe)_2]Cl$ the major lesion responsible for cytoxicity appears to involve DNA–protein cross-links.[5] Toxic side effects, particularly to heart, liver and lung, have been attributed to disruption of mitochondrial function.[10] The lipophilic tetrahedral cation readily permeates mitochondria and uncouples oxidative phosphorylation by collapsing the inner mitochondrial membrane potential.[11]

Part of the effort to determine the mechanism for cytotoxicity and antitumour activity of this novel class of anticancer agents has been to identify features of the structural and solution properties of this series of bis(chelated) complexes of the Group 11 metal ions that may be important for activity. Extensive solution ^{31}P NMR investigations have been carried out on the complexes in this series.[4,6,7,12–15] The results generally support the existence of stable tetrahedral bis(chelated) cations in solution as found in the solid state from the X-ray crystal structures of $[Cu(dppe)_2]X$ {X = $[Cu(C_6H_2Me_3$-

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

2,4,6)$_2$]$^-$[16] or [CF$_3$CO$_2$]$^-$[17]} and [Au(dppe)$_2$]X (X = [SbF$_6$]$^-$[12] or Cl$^-$[18]). Recently, however, X-ray structures of 2:1 complexes of dmpe [1,2-bis(dimethylphosphino)ethane] with copper(I) reveal the existence of both a bis(chelated) complex[19] and a binuclear complex[20] in which one dmpe molecule is chelated and the other acts as a bridging ligand between the two copper atoms. The ^{63}Cu and ^{31}P NMR data for this system is reported to be consistent with either the mono- or di-meric form in solution. In order to investigate the relationship between the structures of the complexes in the solid state and in solution, we have extended the previous work on the solution NMR properties of the bis(chelated) copper(I) and gold(I) complexes of dppey[7,13] to a solid-state ^{31}P cross-polarization magic angle spinning (CP MAS) NMR spectroscopic analysis and X-ray structural determination of the complexes [Cu(dppey)$_2$]PF$_6$ and [Au(dppey)$_2$]PF$_6$, together with that of the previously unreported structure of dppey. The results are presented here.

Experimental

Procedures and Materials.—*cis*-Bis(diphenylphosphino)-ethylene **1** (dppey) was obtained from Strem Chemicals. The compound [Cu(MeCN)$_4$]PF$_6$ was synthesized by the reaction of Cu$_2$O and HPF$_6$ in acetonitrile according to published procedures.[21]

Preparation of Compounds.—Complex [Cu(dppey)$_2$]PF$_6$ **2** was prepared following a variant to a procedure previously reported for the synthesis of [Cu(dppey)$_2$]Cl.[7] The compound [Cu(MeCN)$_4$]PF$_6$ (0.31 g, 0.8 mmol) was added to a solution of **1** (0.66 g, 1.65 mmol) in warm acetonitrile (40 cm^3) and the reaction mixture stirred for 1–2 h. The volume of the resultant clear solution was reduced to *ca.* 5 cm^3 by rotary evaporation, filtered and then cooled to 4 °C overnight to give a colourless crystalline precipitate of the complex which was recrystallized from the minimum volume of warm acetonitrile to give crystals suitable for X-ray diffraction (Found: C, 62.2; H, 4.3; P, 15.7. Calc. for $C_{52}H_{44}CuF_6P_5$: C, 62.4; H, 4.4; P, 15.5%).

Complex [Au(dppey)$_2$]PF$_6$ **3** was prepared by a procedure analogous to that reported for the chloride salt [Au(dppey)$_2$]Cl **5**.[13] A solution of Na[AuCl$_4$]·0.5H$_2$O (0.25 g, 0.6 mmol) and NH$_4$PF$_6$ (1.75 g, 10.7 mmol) in water (5 cm^3) was reduced to gold(I) by the addition of a solution of thiodiglycol [2,2′-thiobis(ethanol)] (0.165 g, 1.35 mmol) in acetone (2 cm^3). This gold(I) solution was then added slowly to a warm solution of dppey (0.54 g) in acetone (35 cm^3). The resultant clear yellow solution was rotary evaporated to give a crystalline precipitate of the complex. The crystals were recrystallized from acetonitrile to provide crystals suitable for X-ray diffraction (Found: C, 54.9; H, 3.5; P, 13.6. Calc. for $C_{52}H_{44}AuF_6P_5$: C, 55.1; H, 3.9; P, 13.6%). The analogous nitrate salt [Au(dppey)$_2$]NO$_3$ **4** was prepared following a similar procedure, utilizing NaNO$_3$ as the source of the nitrate anion (Found: C, 59.7; H, 4.0; P, 11.7. Calc. for $C_{52}H_{44}AuNO_3P_4$: C, 59.4; H, 4.2; P, 11.8%). The determination of chlorine in these two salts (**3** 1.1%, **4** 0.7%) was indicative of co-crystallization of a small percentage of the chloride salt in each final product.

Structure Determinations.—Unique data sets were measured at *ca.* 297 K within the specified 2θ maximum limit using an Enraf–Nonius CAD-4 four-circle diffractometer (ω–2θ scan mode, monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å); *N* independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the block matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Residual electron density in the lattice of **2** was modelled as a 50% occupied solvated molecule of acetonitrile constrained at estimated values. The corresponding lattice points in **3** were featureless. Conventional residuals at convergence, R, R' on $|F|$ are quoted; statistical reflection weights derivative of $w = 1/[\sigma^2 F_o + (n_w \times 10^{-4})F_o^2]$ being used. Neutral complex scattering factors were employed;[22] computation used the SHELX computational package.[23]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Crystal data. Ph$_2$PCH=CHPPh$_2$ **1**. $C_{26}H_{22}P_2$, M = 396.4, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 12.861(8), b = 13.097(2), c = 14.228(8) Å, β = 116.15(3)°, U = 2151(1) Å^3, D_c = 1.22 g cm^{-3}, Z = 4, F(000) = 832, μ(Mo-Kα) = 2.1 cm^{-1}. Specimen: 0.10 × 0.10 × 0.60 mm. No absorption correction. $2\theta_{max}$ = 50°, N = 5610, N_o = 3117, n_w = 3.84, R = 0.047 and R' = 0.054.

[Cu(Ph$_2$PCH=CHPPh$_2$)$_2$]PF$_6$ **2**. $C_{52}H_{44}CuF_6P_5$, M = 1001.3, orthorhombic, space group $P2_12_12_1$ (D_4^2, no. 19), a = 14.479(5), b = 16.703(4), c = 20.891(4) Å, U = 5052 Å^3, D_c = 1.32 g cm^{-3}, Z = 4, F(000) = 2056, μ(Mo-Kα) = 6.6 cm^{-1}. Specimen: 0.15 × 0.19 × 0.37 mm. Empirical absorption correction. $2\theta_{max}$ = 50°, N = 4942, N_o = 3138, n_w = 10.6, R = 0.046 and R' = 0.050 (preferred chirality).

[Au(Ph$_2$PCH=CHPPh$_2$)$_2$]PF$_6$ **3**. $C_{52}H_{44}AuF_6P_5$, M = 1134.8, orthorhombic, space group $P2_12_12_1$, a = 14.644(4), b = 16.703(1), c = 20.699(5) Å, U = 5062 Å^3, D_c = 1.49 g cm^{-3}, Z = 4, F(000) = 2256, μ(Mo-Kα) = 32.2 cm^{-1}. Specimen: 0.48 × 0.69 × 0.77 mm. Empirical absorption correction. $2\theta_{max}$ = 50°, N = 4951, N_o = 3947, n_w = 7.17, R = 0.025 and R' = 0.026 (preferred chirality).

NMR Spectroscopy.—Solid-state ^{31}P CP MAS spectra of compounds **1**–**3** were obtained on a Bruker CXP-300 (B = 7.05 T) spectrometer at 121.47 MHz using ^{1}H–^{31}P cross-polarization with radiofrequency fields of 8 and 20 G for ^{1}H and ^{31}P respectively with a Bruker 7 mm double air-bearing system at spinning speeds of 3 kHz. Phosphorus-31 CP MAS spectra of the gold complexes **3**–**5** were also recorded at magnetic fields strengths of 2.11, 7.05 and 9.40 T on Bruker CXP-90, MSL-300 and MSL-400 spectrometers respectively, operating at the ^{31}P frequencies of 36.43, 121.47 and 161.92 MHz. Spectra at 2.11 T were obtained with a 7 mm Doty single air-bearing electromagnet probe spinning at 4 kHz. Those at 7.05 and 9.40 T were obtained with a Bruker 4 mm double air-bearing system at spinning speeds of 12 kHz. All chemical shift data were referenced externally to 85% H$_3$PO$_4$ through solid triphenylphosphine [δ(PPh$_3$) −9.9]. Solution ^{31}P-{^{1}H} NMR spectra in CDCl$_3$ solution were recorded in 10 mm tubes on the Bruker CXP-300; 85% H$_3$PO$_4$ was used as an external reference with δ(PPh$_3$)(CDCl$_3$) −6.0.

Results and Discussion

The single-crystal X-ray structure determination of *cis*-Ph$_2$PCH=CHPPh$_2$ **1** shows that the compound crystallizes as discrete molecules in the space group $P2_1/c$. This compound has been previously reported[24] to crystallize in the space group Pn or $P2/n$ with a = 12.732(3), b = 5.627(1), c = 15.796(4) Å, β = 106.59(2)° and U = 1084.6 Å^3. However, structure refinement in this space group did not proceed satisfactorily and no significant geometric results were obtained. A plot of the molecule is presented in Fig. 1, atomic coordinates are given in Table 1, and relevant bond lengths and angles listed in Table 2. Rings 13 and 23 are related by a pseudo mirror plane of symmetry bisecting the C=C bond. Exact mirror symmetry for the molecule overall is negated, however, by significant differences in rotation of the phenyl rings 12 and 22 about P(1)–C(121) and P(2)–C(221) respectively with P(2)–P(1)–C(121)–C(122) 8 and P(1)–P(2)–C(221)–C(222) 39°. The solid-state CP MAS ^{31}P NMR spectrum consists of an AB multiplet [δ(P$_A$) −24.2, δ(P$_B$) −27.2, J(P–P) = 126 Hz], consistent with the structural data where the two ^{31}P nuclei are found to be

Table 1 Non-hydrogen atomic coordinates for *cis*-$Ph_2PCH{=}CHPPh_2$ **1**

	$n = 1$			$n = 2$		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
P(*n*)	0.143 67(6)	0.157 07(5)	0.200 95(5)	0.267 55(6)	0.337 63(5)	0.126 32(5)
C(*n*1)	0.073 3(2)	0.215 3(2)	0.071 3(2)	0.124 0(2)	0.289 2(2)	0.041 8(2)
C(*n*21)	0.016 7(2)	0.106 4(2)	0.212 6(2)	0.271 3(3)	0.456 7(2)	0.060 8(2)
C(*n*22)	−0.048 2(3)	0.174 2(2)	0.238 6(3)	0.378 5(3)	0.495 5(2)	0.076 3(2)
C(*n*23)	−0.144 9(3)	0.142 4(3)	0.251 0(3)	0.387 4(3)	0.591 9(3)	0.038 8(3)
C(*n*24)	−0.175 7(3)	0.041 1(3)	0.238 3(3)	0.289 5(4)	0.649 1(2)	−0.015 3(3)
C(*n*25)	−0.112 1(3)	−0.028 2(3)	0.213 1(3)	0.183 9(4)	0.612 2(3)	−0.031 5(3)
C(*n*26)	−0.015 5(3)	0.003 4(2)	0.201 1(2)	0.174 0(3)	0.515 7(2)	0.005 9(3)
C(*n*31)	0.207 8(2)	0.041 9(2)	0.176 6(2)	0.359 4(2)	0.253 8(2)	0.092 0(2)
C(*n*32)	0.274 6(3)	−0.018 2(2)	0.262 5(2)	0.440 3(3)	0.194 3(2)	0.171 3(2)
C(*n*33)	0.325 4(3)	−0.107 2(2)	0.250 2(3)	0.512 7(3)	0.130 3(3)	0.152 4(4)
C(*n*34)	0.314 0(3)	−0.134 9(2)	0.153 1(3)	0.506 9(3)	0.124 3(3)	0.054 1(4)
C(*n*35)	0.249 5(3)	−0.075 2(3)	0.067 3(3)	0.425 7(4)	0.181 0(3)	−0.027 4(3)
C(*n*36)	0.197 0(3)	0.012 8(2)	0.079 0(2)	0.351 2(3)	0.246 6(2)	−0.008 5(2)

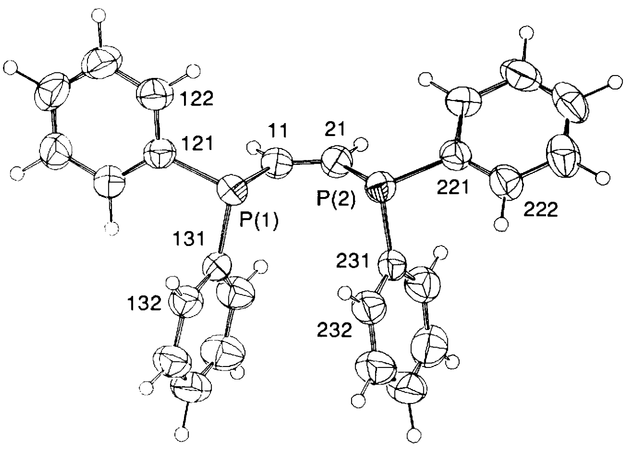

Fig. 1 Molecular structure of *cis*-$Ph_2PCH{=}CHPPh_2$ **1**. Thermal ellipsoids (20%) are shown for non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å

crystallographically inequivalent. This contrasts with dppe which has crystallographically and magnetically equivalent phosphorus nuclei[26] and which exhibits a single resonance line in the solid-state ^{31}P NMR spectrum.[27] An AB multiplet with a coupling constant of 210 Hz has also been previously observed in the CP MAS ^{31}P NMR spectra of the bidentate phosphine $Ph_2PCH_2PPh_2$ (dppm).[27] This coupling constant is larger than observed for **1** and is consistent with the shorter P ··· P ligand bite distance of 2.97 Å in dppm[24] compared to 3.28 Å in **1**. The ^{31}P solution NMR spectrum of **1** in $CHCl_3$ consists of a single resonance at δ −22.7 (lit.,[28] δ −23.1) indicating magnetic equivalence of the phosphorus nuclei under these conditions. The chemical shift is slightly downfield of the centre of the AB multiplet in the solid-state spectrum (−25.7 ppm).

Reaction of *cis*-$Ph_2PCH{=}CHPPh_2$ **1** with $[Cu(MeCN)_4]PF_6$ in stoichiometric amounts in acetonitrile affords air-stable crystals of the bis(chelated) complex, $[Cu(dppey)_2]PF_6$ **2**. The single-crystal X-ray structure determination shows atom connectivity consistent with discrete molecular $[Cu(dppey)_2]^+$ cations and $[PF_6]^-$ anions. A view of the cation is given in Fig. 2 with relevant structural parameters presented in Table 2. Atomic coordinates are listed in Table 3. The CuP_4 co-ordination sphere is a distorted tetrahedron with intraligand P–Cu–P angles of 89.69(7) and 89.90(7)° and the interligand P–Cu–P angles ranging between *ca.* 110 and 130°. The copper atom lies on a pseudo two-fold axis of symmetry bisecting the C=C bonds. Each ligand adopts a sterically 'comfortable' conformational structure with the PPh_2 units rotated about the P(*n*)–C(*n*1) bond and the phenyl ring planes within each ligand mutually orthogonal. Charge-transfer interactions between phenyl rings on each ligand contribute to stabilization of the structure of the cation. This structural arrangement is facilitated by a twisting of the PCH=CHP planes relative to each other with a dihedral angle of 72°. No significant differences are observed between the four Cu–P distances which lie in the range 2.276(2)–2.289(2) Å [mean, 2.285(6) Å]. By comparison, these distances are longer in $[Cu(dppe)_2]X$, where X = $[Cu(C_6H_2Me_3\text{-}2,4,6)_2]^-$ [16] or $[CF_3CO_2]^-$ [17] [2.305(4)−2.365(4) Å; mean, 2.32(2) Å], and shorter in $[Cu(dmpe)_2][Cu\{Co(CO)_4\}_2]$[19] [2.248(3)–2.254(3) Å; mean, 2.253(4) Å] and $[Cu(PMe_3)_4]X$, where X = Cl^-,[29] Br^-,[29] I^- [29] or $[CuMe_2]^-$ [30] [2.253(3)–2.282(4) Å; mean, 2.27(1) Å]. All these distances are, however, considerably shorter than those found in $[Cu(PPh_3)_4]X$, where X = $[PF_6]^-$ [29] or $[ClO_4]^-$ [31] [2.465(2)–2.605(7) Å, mean 2.54(6) Å].[31] The overall symmetry of the complex results in a similar structural environment for each of the four (chiral) phosphorus atoms, in contrast with the phosphorus environments, in **1**. These conformational changes do not, however, affect the C=C and P ··· P distances in **1**–**3** (Table 2).

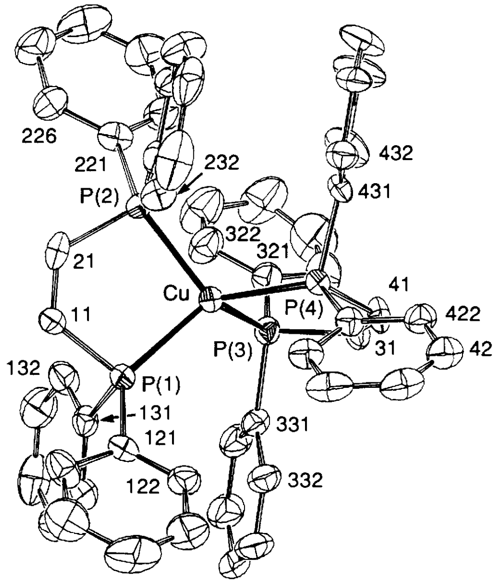

Fig. 2 Molecular structure of $[Cu(dppey)_2]PF_6$ **2** projected normal to the PCH=CHP plane of ligand 1

The solid-state ^{31}P CP MAS NMR spectrum of $[Cu(dppey)_2]PF_6$ **2** is dominated by four relatively broad peaks ($\Delta\nu_{\frac{1}{2}}$ 300 Hz) at δ *ca.* −2.8, 4.2, 11.1 and 17.8 [Fig. 3(*a*)] with a smaller

Table 2 Bond lengths (Å) and angles (°) for the MP_4 unit in *cis*-$Ph_2PCH{=}CHPPh_2$ and the $[M(dppey)_2]^+$ cation for M = Cu, Ag or Au

		M		
	dppey	Cu	Ag[25]	Au
M–P(1)		2.276(2)	2.472(2)	2.378(2)
M–P(2)		2.288(2)	2.476(2)	2.388(2)
M–P(3)		2.289(2)	2.479(2)	2.388(2)
M–P(4)		2.287(2)	2.463(2)	2.377(2)
P(1)–C(11)	1.825(3)	1.799(8)	1.817(7)	1.829(6)
P(1)–C(121)	1.836(3)	1.851(8)	1.813(4)	1.826(7)
P(1)–C(131)	1.824(3)	1.803(7)	1.804(3)	1.813(7)
P(2)–C(21)	1.817(3)	1.809(8)	1.818(6)	1.810(6)
P(2)–C(221)	1.828(3)	1.827(7)	1.807(5)	1.817(7)
P(2)–C(231)	1.830(3)	1.819(8)	1.824(4)	1.823(7)
P(3)–C(31)		1.815(7)	1.825(6)	1.816(6)
P(3)–C(321)		1.805(8)	1.815(3)	1.824(7)
P(3)–C(331)		1.824(7)	1.790(5)	1.808(7)
P(4)–C(41)		1.833(8)	1.805(6)	1.812(6)
P(4)–C(421)		1.809(7)	1.806(4)	1.831(6)
P(4)–C(431)		1.818(7)	1.808(3)	1.814(7)
C(11)–C(21)	1.334(4)	1.337(12)	1.349(9)	1.330(9)
C(31)–C(41)		1.322(11)	1.325(7)	1.342(9)
P(1) ··· P(2)	3.278(3)	3.218(3)	3.311(3)	3.276(3)
P(3) ··· P(4)		3.233(3)	3.304(3)	3.276(3)
M–P(1)–C(11)		103.7(3)	104.0(2)	103.7(2)
M–P(2)–C(21)		103.7(3)	104.4(2)	104.7(2)
M–P(3)–C(31)		103.5(2)	104.2(2)	103.8(2)
M–P(4)–C(41)		102.8(3)	105.2(2)	104.4(2)
P(1)–M–P(2)		89.69(7)	84.1(1)	86.87(5)
P(1)–M–P(3)		110.19(7)	123.8(1)	110.95(5)
P(1)–M–P(4)		131.76(8)	127.8(1)	134.16(6)
P(2)–M–P(3)		130.89(7)	117.8(1)	133.21(5)
P(2)–M–P(4)		109.96(7)	124.2(1)	111.69(5)
P(3)–M–P(4)		89.90(7)	83.9(1)	86.90(5)
P(1)–C(11)–C(21)	121.9(2)	122.2(6)	123.5(5)	123.1(5)
P(2)–C(21)–C(11)	122.7(2)	120.6(6)	122.2(5)	121.6(5)
P(3)–C(31)–C(41)		121.4(6)	123.2(5)	122.4(5)
P(4)–C(41)–C(31)		121.8(6)	122.9(5)	122.0(5)

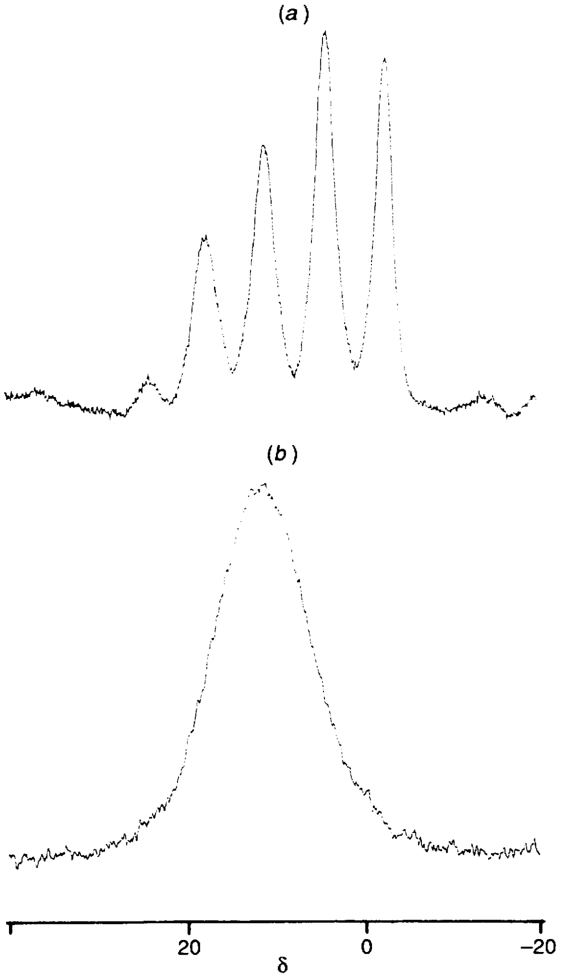

Fig. 3 (*a*) CP MAS solid-state and (*b*) solution ^{31}P NMR spectra of $[Cu(dppey)_2]PF_6$ **2**

downfield peak at δ 24.0. Interpretation of the MAS spectra of spin $I = \frac{1}{2}$ ^{31}P nuclei coupled to the quadrupolar spin $I = \frac{3}{2}$ ^{63}Cu and ^{65}Cu nuclei has been discussed by various authors. Menger and Veeman[32] have reported a calculation of the line positions in terms of the copper nuclear Zeeman interaction, *Z*, the copper nuclear quadrupolar coupling constant, χ, the indirect phosphorus spin–spin coupling constant, *J*, and the ^{31}P–^{63}Cu dipolar coupling constant, *D*. The appearance of the spectrum depends on both the dimensionless parameter *K* which is proportional to the ratio of the copper quadrupolar coupling constant to the copper nuclear Zeeman term (for $I = \frac{3}{2}$, $K = \chi/4Z$), and the ratio *R* of the dipolar to the indirect coupling constant, $R = D/J$. Menger and Veeman have presented an analysis for three cases where the spin $\frac{1}{2}$–spin $\frac{3}{2}$ interaction is purely dipolar, where it is purely scalar and where mixed dipolar–scalar interactions exist (with D/J 0.5). For copper–phosphine complexes, the values of *J* and *D* are found typically to vary from 800 to 2300 Hz and 800 to 1200 Hz, respectively, to yield *R* values in the range 0.5–1.0.[33–36] This approach has been approximated by perturbation theory analysis[37–39] which shows that distortion of the quartets can depend on several other factors, including the anisotropy of the *J* tensor and the angle β between the internuclear Cu–P vector and the electric field gradient tensors through second order Legendre polynomial terms of the type $(3\cos^2\beta - 1)$. It has been proposed, for example, that for complexes such as $[CuX(PPh_3)_3]$, the very small distortions observed in the quartets are not necessarily due to near zero values of χ, but rather β adopting values in the range 103–109° for which the value of $(3\cos^2\beta - 1)$ approaches zero.[37–39] For $[Cu(dppey)_2]PF_6$ **2**, the similar chemical environments of each phosphorus atom suggest minimal chemical shift differences between each phosphorus resonance, resulting in four closely overlapping quartets. The spacings of 830–850 Hz between the four main peaks are similar to those observed in $[Cu(dmpe)_2]_2[BF_4]_2$.[20] The lack of distortion is indicative that the quadrupolar effects outlined above are only small for this complex and suggests a small value for the copper quadrupolar coupling constant. (Here we have assumed that the *z* axis of the electric field gradient tensor is oriented along the bisector of the bidentate ligand and β ≈ 45°.) This result is consistent with the observed relatively high symmetry of the CuP_4 core with the only significant distortions present arising from the chelate effect of the phosphine ligand which diminishes the intraligand P–Cu–P angles to below the tetrahedral angle.

The solution ^{31}P NMR spectrum of **2** in CH_2Cl_2 at 297 K [Fig. 3(*b*)] is very similar to that described previously for the chloride complex[7] and consists of a very broad peak centred at δ 11 ($\Delta\nu_{\frac{1}{2}}$ = 1600 Hz); ^{31}P–$^{63/65}Cu$ couplings were not resolved. On cooling to 223 K the peak shifted to slightly higher frequency (13 ppm) and sharpened considerably ($\Delta\nu_{\frac{1}{2}}$ = 500 Hz). The similarity between the ^{31}P NMR chemical shift in the solid state and solution supports the view that the structure of the bis(bidentate) chelated cation is maintained in solution. The variation in ^{31}P NMR lineshape with decreasing temperature is consistent with the lineshapes calculated by Marker and Gunter[40] for a CuP_4 complex undergoing fast quadrupolar relaxation. Spin–spin couplings of $^{63/65}Cu$–^{31}P are rarely observed in ^{31}P NMR solution spectra of copper(I) phosphine

Table 3 Non-hydrogen atomic coordinates for $[M(dppey)_2]PF_6$ (M = Cu **2** or Au **3**)

	M = Cu			M = Au		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0.183 74(5)	0.506 06(4)	0.360 84(4)	0.187 39(1)	0.508 06(1)	0.360 65(1)
P(1)	0.290 3(1)	0.405 9(1)	0.358 7(1)	0.298 2(1)	0.404 03(8)	0 .358 04(9)
C(11)	0.398 8(5)	0.457 8(5)	0.364 7(4)	0.407 1(4)	0.457 5(4)	0.361 1(4)
C(121)	0.306 9(7)	0.333 2(4)	0.292 8(4)	0.310 8(7)	0.331 5(4)	0.292 7(3)
C(122)	0.231 6(7)	0.310 4(5)	0.259 5(4)	0.237 0(6)	0.311 9(5)	0.256 6(4)
C(123)	0.240 7(9)	0.252 2(6)	0.214 0(5)	0.242 4(8)	0.253 8(6)	0.209 0(5)
C(124)	0.322 6(13)	0.218 9(7)	0.200 3(6)	0.324 9(11)	0.214 7(6)	0.200 2(6)
C(125)	0.402 4(9)	0.245 9(8)	0.234 6(6)	0.399 2(8)	0.235 4(7)	0.234 7(6)
C(126)	0.393 1(7)	0.300 7(6)	0.279 0(4)	0.393 9(6)	0.293 2(6)	0.282 3(4)
C(131)	0.296 3(5)	0.345 1(4)	0.429 9(3)	0.303 2(6)	0.343 8(4)	0.430 8(3)
C(132)	0.307 5(6)	0.382 8(5)	0.489 8(4)	0.313 7(6)	0.382 9(5)	0.489 2(3)
C(133)	0.307 5(8)	0.341 9(7)	0.544 8(4)	0.310 9(7)	0.340 0(6)	0.546 2(4)
C(134)	0.298 5(8)	0.264 9(9)	0.546 2(5)	0.299 9(8)	0.260 0(7)	0.546 7(4)
C(135)	0.285 7(7)	0.220 9(6)	0.489 8(7)	0.286 7(7)	0.220 9(5)	0.489 1(6)
C(136)	0.284 8(6)	0.261 8(5)	0.429 0(4)	0.289 4(5)	0.261 0(4)	0.430 8(4)
P(2)	0.300 3(1)	0.597 9(1)	0.369 7(1)	0.312 4(1)	0.599 45(8)	0.367 63(8)
C(21)	0.403 9(5)	0.537 3(5)	0.370 4(4)	0.413 1(4)	0.536 7(4)	0.366 2(4)
C(221)	0.316 8(7)	0.667 2(4)	0.436 4(3)	0.330 4(6)	0.667 4(4)	0.435 0(3)
C(222)	0.240 1(7)	0.699 1(7)	0.464 7(5)	0.255 7(7)	0.699 5(5)	0.464 0(4)
C(223)	0.247 2(10)	0.755 8(8)	0.513 9(6)	0.265 8(8)	0.757 6(7)	0.512 3(6)
C(224)	0.329 0(13)	0.779 2(7)	0.533 2(5)	0.353 9(10)	0.783 1(7)	0.528 5(5)
C(225)	0.409 3(9)	0.749 5(8)	0.503 2(6)	0.428 7(8)	0.750 1(7)	0.499 9(5)
C(226)	0.403 7(7)	0.690 1(6)	0.456 5(4)	0.418 5(6)	0.693 7(5)	0.452 4(4)
C(231)	0.322 6(6)	0.659 6(5)	0.299 7(4)	0.332 6(5)	0.663 4(4)	0.297 7(3)
C(232)	0.339 4(6)	0.625 0(5)	0.241 8(4)	0.346 9(6)	0.624 9(5)	0.237 7(4)
C(233)	0.351 7(8)	0.672 9(8)	0.187 8(4)	0.355 5(7)	0.673 1(7)	0.183 0(4)
C(234)	0.349 2(8)	0.753 9(8)	0.192 0(5)	0.351 8(7)	0.754 2(8)	0.187 9(5)
C(235)	0.335 1(8)	0.790 7(6)	0.247 4(6)	0.339 5(7)	0.789 3(6)	0.245 0(6)
C(236)	0.318 3(7)	0.746 0(5)	0.301 7(4)	0.328 0(6)	0.744 8(5)	0.299 6(3)
P(3)	0.066 0(1)	0.474 1(1)	0.429 4(1)	0.065 1(1)	0.475 13(9)	0.432 17(7)
C(31)	−0.036 9(5)	0.489 4(5)	0.381 4(3)	−0.036 8(4)	0.495 7(4)	0.385 0(3)
C(321)	0.040 3(5)	0.525 0(4)	0.503 5(4)	0.042 6(5)	0.524 1(4)	0.509 3(3)
C(322)	0.111 7(6)	0.548 9(7)	0.542 8(4)	0.114 8(6)	0.550 5(5)	0.544 9(4)
C(323)	0.094 3(9)	0.585 8(9)	0.599 4(5)	0.101 1(8)	0.581 8(8)	0.606 0(5)
C(324)	0.005 1(10)	0.601 3(8)	0.617 8(6)	0.019 0(10)	0.590 3(9)	0.630 2(5)
C(325)	−0.063 2(9)	0.571 5(9)	0.585 7(7)	−0.057 4(9)	0.564 3(8)	0.596 2(5)
C(326)	−0.047 8(7)	0.537 0(7)	0.526 3(5)	−0.042 7(6)	0.529 3(6)	0.535 4(4)
C(331)	0.052 7(5)	0.368 7(4)	0.450 3(3)	0.051 9(4)	0.369 7(4)	0.449 5(3)
C(332)	0.052 2(6)	0.312 9(5)	0.399 5(4)	0.055 6(6)	0.316 5(4)	0.398 4(3)
C(333)	0.045 3(7)	0.233 0(5)	0.409 3(5)	0.050 2(6)	0.234 6(5)	0.408 9(5)
C(334)	0.040 8(7)	0.205 3(6)	0.470 3(6)	0.040 4(6)	0.205 9(5)	0.469 2(5)
C(335)	0.037 3(7)	0.259 7(7)	0.522 7(5)	0.035 9(7)	0.257 0(5)	0.520 8(4)
C(336)	0.044 7(6)	0.341 7(5)	0.510 7(4)	0.042 4(6)	0.339 6(5)	0.511 6(4)
P(4)	0.078 2(1)	0.548 3(1)	0.286 7(1)	0.073 9(1)	0.553 69(9)	0.287 23(8)
C(41)	−0.032 2(5)	0.519 6(5)	0.323 0(4)	−0.033 3(4)	0.528 0(4)	0.325 7(3)
C(421)	0.065 7(5)	0.517 2(4)	0.204 2(3)	0.057 8(5)	0.521 2(3)	0.203 5(3)
C(422)	−0.016 2(6)	0.532 9(4)	0.170 0(4)	−0.023 8(6)	0.537 5(4)	0.171 3(3)
C(423)	−0.025 7(7)	0.507 0(6)	0.106 7(4)	−0.034 8(6)	0.510 6(5)	0.108 2(4)
C(424)	0.042 6(9)	0.466 8(6)	0.077 3(4)	0.036 2(8)	0.468 8(5)	0.079 1(4)
C(425)	0.124 8(9)	0.448 7(6)	0.109 8(5)	0.114 2(7)	0.454 0(5)	0.109 3(4)
C(426)	0.135 3(6)	0.476 4(5)	0.174 6(4)	0.125 6(5)	0.480 6(4)	0.173 0(3)
C(431)	0.068 9(5)	0.656 7(4)	0.282 7(4)	0.069 8(5)	0.662 0(4)	0.281 6(3)
C(432)	0.041 5(8)	0.697 2(5)	0.337 2(4)	0.041 8(8)	0.705 3(5)	0.335 3(4)
C(433)	0.040 8(10)	0.783 1(6)	0.336 0(7)	0.048 1(10)	0.787 6(5)	0.334 2(5)
C(434)	0.071 1(8)	0.824 6(5)	0.283 0(6)	0.077 6(8)	0.827 1(5)	0.280 2(5)
C(435)	0.100 1(7)	0.783 2(5)	0.231 0(5)	0.104 5(6)	0.786 7(4)	0.228 7(4)
C(436)	0.099 7(6)	0.698 9(4)	0.232 1(4)	0.099 3(5)	0.702 7(4)	0.229 6(3)
P	0.178 8(1)	0.002 7(2)	0.592 6(2)	0.183 8(1)	0.002 3(1)	0.590 6(1)
F(1)	0.253 5(4)	−0.055 9(4)	0.619 1(5)	0.256 4(3)	−0.060 5(4)	0.612 8(4)
F(2)	0.245 5(5)	0.073 7(5)	0.610 7(5)	0.248 4(3)	0.070 4(4)	0.615 6(4)
F(3)	0.126 3(5)	0.004 6(7)	0.657 5(4)	0.133 0(4)	−0.002 6(5)	0.656 6(2)
F(4)	0.104 5(5)	0.059 8(6)	0.567 8(5)	0.111 0(4)	0.063 6(4)	0.567 3(4)
F(5)	0.115 9(4)	−0.072 5(4)	0.577 9(5)	0.121 0(4)	−0.069 2(4)	0.568 6(4)
F(6)	0.233 3(6)	0.004 5(8)	0.530 7(4)	0.234 0(5)	0.006 1(6)	0.525 7(3)
C(S1)	0.409(−)	0.059(−)	0.293(−)*			
C(S2)	0.309(−)	0.064(−)	0.313(−)*			
C(S3)	0.250(−)	0.060(−)	0.320(−)*			

* Population 0.5.

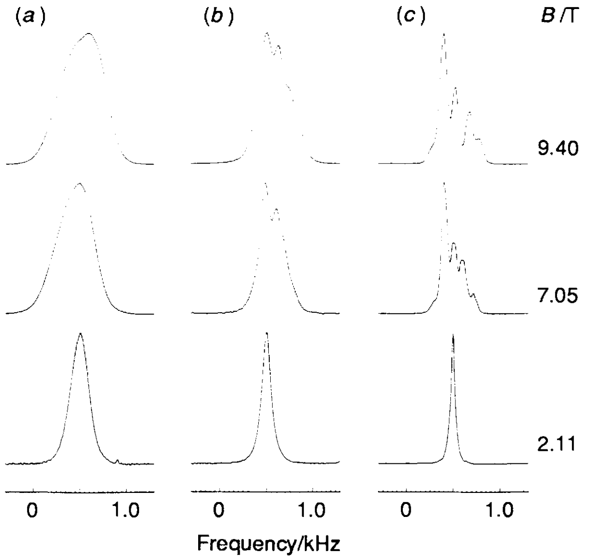

Fig. 4 CP MAS solid-state ^{31}P NMR spectra of $[Au(dppey)_2]X$ [X = (*a*) PF_6^-, (*b*) NO_3^- or (*c*) Cl^-] at magnetic field strengths of 2.11, 7.05 and 9.40 T

complexes and depend on a sufficiently slow rate of quadrupolar relaxation. For example, the ^{31}P NMR spectra of the CuP_4 complexes $[Cu\{P(OMe)_3\}_4]BF_4$[40] and $[Cu(dmpe)_2]_2[BF_4]_2$[20] consist of two overlapping 1:1:1:1 quartets at ambient temperature which broaden as the temperature is decreased. The faster rate of quadrupolar relaxation observed for $[Cu(dppey)_2]PF_6$ **2** compared to $[Cu(dmpe)_2]_2[BF_4]_2$ could be a consequence of either a larger quadrupolar coupling constant, or an increased correlation time for molecular reorientation (τ_q). If the estimation from the ^{31}P CP MAS data of a small value of χ for both complexes is valid, a longer τ_q value may be the major determinant of the faster rate of quadrupolar relaxation. This is not unreasonable in view of the presence of the bulky phenyl substituents in complex **2**.

The single-crystal X-ray structure determination of the gold(I) complex $[Au(dppey)_2]PF_6$ **3** shows it to be isomorphous with **2**. The relevant structural parameters are presented in Table 2. The AuP_4 co-ordination sphere exhibits a similar distortion from tetrahedral symmetry to the copper(I) complex, with intraligand P–Au–P angles of 86.87(5) and 86.90(5)° and interligand angles in the range *ca.* 111–134°. The Au–P distances lie in the narrow range 2.377(2)–2.388(2) Å [mean 2.382(5) Å]. Similar differences in Cu–P and Au–P distances have been observed for other isostructural copper and gold complexes {*e.g.* for $[M(PPh_3)_2]Cl{\cdot}0.5C_6H_6$, Cu–P 2.260(2), 2.272(2) Å, Au–P 2.323(4) and 2.339(4) Å[41]}. Regular four-coordinate AuP_4 geometry for gold(I) complexes is rare having been reported previously only for $[Au(dppe)_2]X$, where X = Cl^- [18] or $[SbF_6]^-$,[12] with Au–P distances in the range 2.384(2)–2.416(3) Å [mean 2.36(9) Å], and for $[Au(PMePh_2)_4]PF_6$[42] where the gold atom is on a four-fold symmetry axis with Au–P 2.449 Å.

The structural chemistry of these copper(I) and gold(I) complexes can be compared with that of the analogous silver(I) complex $[Ag(dppey)_2][SnPh_3(NO_3)_2]$.[25] Here, the Ag–P bond lengths also span a narrow range, 2.463(2)–2.479(2) Å, but are *ca.* 0.20 and 0.10 Å longer than in the copper and gold complexes respectively. Unlike **2** and **3**, the PCH=CHP planes are orthogonal with the silver atom being displaced from each plane by *ca.* 0.4 Å. The conformational structure of the ligands in this complex differ significantly. One ligand adopts essentially the same conformation found for **2** and **3** with a pseudo two-fold axis of symmetry lying in the PCH=CHP plane and perpendicular to C=C. In the second ligand, however, a pseudo two-fold axis is also present, but now perpendicular to PCH=CHP, resulting in a different conformational structure of the ligand and disruption of the interligand charge-transfer interactions between the phenyl rings.

The solution ^{31}P NMR spectrum of the $[Au(dppey)_2]^+$ cation in chloroform consists of a single resonance at δ 23.2, similar to that found for the chloride salt,[13] together with a multiplet for the PF_6^- anion [$\delta(PF_6)$ −143.6, J(P–F) = 714 Hz]. The ^{31}P CP MAS NMR spectrum of $[Au(dppey)_2]PF_6$ **3** at a field strength of 7.05 T consists of a broad, asymmetric peak centred at δ 22. The similarity to the solution ^{31}P NMR chemical shift, again supports the assumption of bis(bidentate) chelation of the cation in both the solid and solution. The observed asymmetry is, however, unusual; typically, solid-state ^{31}P CP MAS spectra of linear gold(I) phosphine complexes consist of a single, symmetrical, relatively broad resonance for each inequivalent phosphorus.[41,43] This is postulated to originate from the very large quadrupolar coupling constants observed for linear complexes {*e.g.* χ for $[AuCl(PPh_3)]$ = 940 MHz[44]} which, even in the solid state, gives rise to efficient quadrupolar relaxation so that the ^{197}Au and ^{31}P spins are effectively decoupled. To investigate further the nature of the asymmetric lineshape, we recorded ^{31}P CP MAS spectra at B = 7.05 T on the analogous nitrate **4** and chloride **5** complexes and, subsequently, spectra on all three complexes at field strengths of 2.11, 7.05 and 9.40 T. These spectra are presented in Fig. 4. At low field (B = 2.11 T), the spectrum of each complex is similar, consisting of a single peak centred at δ 22.2, 22.5 and 22.0 for **3**, **4** and **5** respectively. On increasing B to 9.40 T, the linewidth of **3** increased from 450 to 1100 Hz and the presence of an underlying multiplet structure became apparent as noted above. The spectra of $[Au(dppey)_2]NO_3$ **4** at 7.05 and 9.40 T show partial resolution of this signal into a quartet and in the chloride salt **5** resolution of these lines was such as to enable measurement of line spacings providing values of 200, 200 and 220 Hz at 7.05 T and 250, 300 and 200 Hz at 9.40 T. The profile and line separations of this quartet are best interpreted by assuming a relatively slow rate of quadrupolar relaxation for these complexes so that the signals for each are split into a quartet by indirect spin–spin coupling with the ^{197}Au nucleus. As for the isomorphous copper complex, the symmetrical structure of the cation can be assumed to result in nearly identical chemical shifts for each of the phosphorus atoms, giving rise to unresolved overlap of the quartets from each of the four crystallographically independent phosphorus atoms.

Although accurate measurement of the spin–spin coupling constant $J(^{197}Au–^{31}P)$ is not possible due to the presence of unresolved resonances in the high-field spectra, we estimate the value of J to be of the order of 200 Hz, with the variation observable in the line separations more likely to be attributable to overlap effects rather than the quadrupolar effects discussed above for the copper system. As for the copper system, the lack of distortion of the quartet line spacings suggests that the ^{197}Au quadrupolar coupling constant is small, a situation that is very unusual for gold(I) complexes. Such a prediction is consistent with the high symmetry of the AuP_4 co-ordination sphere, but will require confirmation through direct determination of χ from, for example, the nuclear quadrupole resonance spectrum. The collapse of the spectra to broad single peaks at low field is unexpected. At low fields, χ becomes considerably greater than the magnitude of the Zeeman interaction and in such circumstances, application of the Menger and Veeman analysis[32] (with D = 50 Hz and Z = 1.54 MHz for B = 2.11 T) indicates that the quartet structure is likely to collapse to a triplet or doublet structure, as has been observed for the ^{31}P CP MAS spectra of $[AuCl(PPh_3)]$[45] and (3,4-dimethyl-1-phenylphosphole)gold(I) chloride.[46] At present, we ascribe failure to observe such multiplet structures at low field to residual dipolar broadening effects and overlap of the resonances of the four independent phosphorus atoms in the AuP_4 co-ordination sphere.

The different effect of the three anions on the resolution of the ^{31}P resonance is also a notable feature of these CP MAS spectra. The lack of resolution in the high-field spectra of the NO_3^- and particularly the PF_6^- salt may be a consequence of several factors, the most prosaic of these being the presence of the chloride salt, as determined from chemical analysis, in the crystals of each of these complexes, despite several recrystallizations, giving rise to overlapping signals from the two salts. We also note, however, that the broadening increases with size of anion which through differential interaction with the cation may influence the magnitude of the quadrupolar coupling constant and hence quadrupolar relaxation rates in these salts.

Acknowledgements

We thank the Australian Research Council and the National Health and Medical Research Council for support and the award of a R. Douglas Wright Award (to S. J. B. P.). We thank Dr. Rodney Sue for assistance in the collection of the NMR data and Dr. Colin Kennard for assistance with the crystallography and access to the facilities of his laboratory during a period of study leave (by P. C. H.).

References

1 R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe, B. M. Sutton, D. L. Bryan, G. R. Girard and D. T. Hill, *Proc. Am. Assoc. Cancer Res.*, 1985, **26**, 254.
2 C. K. Mirabelli, D. T. Hill, L. F. Faucette, F. L. McCabe, G. R. Girard, D. L. Bryan, B. M. Sutton, J. O'L Bartus, S. T. Crooke and R. K. Johnson, *J. Med. Chem.*, 1987, **30**, 2181.
3 S. J. Berners-Price and P. J. Sadler, *Struct. Bonding (Berlin)*, 1988, **70**, 27.
4 S. J. Berners-Price, P. S. Jarrett and P. J. Sadler, *Inorg. Chem.*, 1987, **26**, 3074.
5 S. J. Berners-Price, C. K. Mirabelli, R. K. Johnson, M. R. Mattern, F. L. McCabe, L. F. Faucette, C.-M. Sung, S.-M. Mong, P. J. Sadler and S. T. Crooke, *Cancer Res.*, 1986, **46**, 5486.
6 S. J. Berners-Price, R. K. Johnson, A. J. Giovenella, L. F. Faucette, C. K. Mirabelli and P. J. Sadler, *J. Inorg. Biochem.*, 1988, **33**, 285.
7 S. J. Berners-Price, R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe and P. J. Sadler, *Inorg. Chem.*, 1987, **26**, 3383.
8 A. R. Khohkar, Q. Xu and Z. H. Siddik, *J. Inorg. Biochem.*, 1990, **39**, 117.
9 S. J. Berners-Price and P. J. Sadler, *Chem. Br.*, 1987, **23**, 541.
10 G. F. Rush, D. W. Alberts, P. Meunier, K. Leffler and P. F. Smith, *Toxicologist*, 1987, **7**, 59; G. D. Hoke, R. A. Macia, P. C. Meunier, P. J. Bugelski, C. K. Mirabelli, G. F. Rush and W. D. Matthews, *Toxicol. Appl. Pharmacol.*, 1989, **100**, 293.
11 G. D. Hoke, G. F. Rush, G. E. Bossard, J. V. McArdle, B. D. Jensen and C. K. Mirabelli, *J. Biol. Chem.*, 1988, **262**, 11203.
12 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1984, 969.
13 S. J. Berners-Price and P. J. Sadler, *Inorg. Chem.*, 1986, **25**, 3822.
14 S. J. Berners-Price, C. Brevard, A. Pagelot and P. J. Sadler, *Inorg. Chem.*, 1985, **24**, 4278.
15 S. J. Berners-Price, C. Brevard, A. Pagelot and P. J. Sadler, *Inorg. Chem.*, 1986, **25**, 596.
16 P. Leoni, M. Pasquali and C. A. Ghilardi, *J. Chem. Soc., Chem. Commun.*, 1983, 240.
17 A. Camus, N. Marisch, G. Nardin and L. Randaccio, *Transition Met. Chem.*, 1976, **1**, 205.
18 P. A. Bates and J. M. Waters, *Inorg. Chim. Acta*, 1984, **81**, 151.
19 D. J. Darensbourg, C.-S. Chao, J. H. Reibenspies and C. J. Bischoff, *Inorg. Chem.*, 1990, **29**, 2153.
20 B. Mohr, E. E. Brooks, N. Rath and E. Deutsch, *Inorg. Chem.*, 1991, **30**, 4541.
21 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90.
22 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.
23 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.
24 H. Schmidbaur, G. Reber, A. Schier, F. E. Wagner and G. Muller, *Inorg. Chim. Acta*, 1988, **147**, 143.
25 C. Franzoni, G. Pelizzi, G. Predieri, P. Tarasconi and C. Pelizzi, *Inorg. Chim. Acta*, 1988, **150**, 279.
26 C. Pelizzi and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1979, **35**, 1785.
27 J. A. Davies, S. Dutremez and A. A. Pinkerton, *Inorg. Chem.*, 1991, **30**, 2380.
28 S. Hietkamp and O. Stelzer, *Inorg. Chem.*, 1984, **23**, 258.
29 G. A. Bowmaker, P. C. Healy, L. M. Engelhardt, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 1697.
30 D. F. Dempsey and G. S. Girolami, *Organometallics*, 1988, **7**, 1208.
31 L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
32 E. M. Menger and W. S. Veeman, *J. Magn. Reson.*, 1982, **46**, 257.
33 G. A. Bowmaker, J. D. Cotton, P. C. Healy, J. D. Kildea, S. B. Silong, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 1462.
34 S. Attar, G. A. Bowmaker, N. W. Alcock, J. S. Frye, W. H. Bearden and J. H. Nelson, *Inorg. Chem.*, 1991, **30**, 4743.
35 G. A. Bowmaker, W. Jirong, R. D. Hart, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1992, 787.
36 P. F. Barron, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Packawatchai, V. A. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1099.
37 A. C. Olivieri, *J. Magn. Reson.*, 1989, **81**, 201.
38 A. C. Olivieri, *J. Am. Chem. Soc.*, 1992, **114**, 5788.
39 J. V. Hanna, M. E. Smith, S. N. Stuart and P. C. Healy, *J. Phys. Chem.*, 1992, **96**, 7560.
40 A. Marker and M. J. Gunter, *J. Magn. Reson.*, 1982, **47**, 118.
41 G. A. Bowmaker, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1089.
42 R. C. Elder, E. H. Kelle Zeiher, M. Onady and R. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1981, 900.
43 J. W. Diesveld, E. M. Menger, H. T. Edzes and W. S. Veeman, *J. Am. Chem. Soc.*, 1980, **102**, 7936.
44 P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1434.
45 L.-J. Baker, G. A. Bowmaker, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1992, 989.
46 S. Attar, W. H. Beardman, N. W. Alcock, E. C. Alyea and J. H. Nelson, *Inorg. Chem.*, 1990, **29**, 425.

Received 6th *July* 1992; *Paper* 2/03557J