Copper(I), Silver(I) and Gold(I) Complexes with the Hybrid Ligand 1-(Diphenylphosphino)-2-(2-pyridyl)ethane (ppye). Variable-temperature Nuclear Magnetic Resonance Investigations and the Crystal Structure of $[Au(ppye\text{-}P)_2]PF_6$†

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Copper(I), silver(I) and gold(I) complexes with the ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye) of general formula $M(ppye)_2PF_6$ have been prepared and characterized by means of IR and multinuclear (^1H, ^{13}C and ^{31}P) NMR spectroscopy. The copper(I) and silver(I) complexes are bis(chelate) with a tetrahedral geometry around the metal atom. On the contrary, the gold(I) derivative exhibits a digonal structure with monodentate P-bound ppye ligands co-ordinated to the metal centre. The complex $[Au(ppye\text{-}P)_2]PF_6$ has been characterized in the solid state by X-ray diffraction analysis. Crystal data: triclinic, space group $P\bar{1}$, $a = 9.972(1)$, $b = 10.299(2)$, $c = 10.521(2)$ Å, $\alpha = 69.90(2)$, $\beta = 66.03(1)$, $\gamma = 78.51(1)°$, $Z = 1$, $R = 0.039$. The gold atom, which lies on a symmetry centre, is linearly co-ordinated by the P atoms of ppye (P–Au–P, 180°). Variable-temperature NMR studies show that the $[M(ppye\text{-}P,N)_2]^+$ species rearrange in solution by inversion at the tetrahedral metal centre. Furthermore, all three ppye derivatives undergo ligand-exchange processes. The reactions of the cations $[M(ppye\text{-}P,N)_2]^+$ and $[Au(ppye\text{-}P)_2]^+$ with ppye have been investigated.

Metal complexes with unsymmetrical bidentate ligands, especially those containing P and N[1] or O[2] donor atoms, are of increasing interest because of their structural features, reactivity and catalytic applications. In this context, we have been investigating the co-ordination chemistry of the ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye) containing P and N donor atoms (Fig. 1). This ligand exhibits a versatile co-ordinating behaviour, and several transition-metal complexes have been reported in which it acts either as a chelating or as a P-bound monodentate ligand.[3–9] The majority of the studies have been focused on the chemistry of the platinum-group metals, while the co-ordinating ability of ppye toward Group 11 metals has been little investigated. Only copper(I) derivatives of the composition CuX(ppye) (X = Cl and Br) have been briefly mentioned by Uhlig and Maaser.[3] By contrast, complexes of Cu^I, Ag^I and Au^I with the closely related P,N ligand 2-(diphenylphosphino)pyridine are well known.[10–13] We have now studied the co-cordination chemistry of ppye toward univalent coinage metals, and we report here the synthesis and characterization of the bis(chelate) $[M(ppye\text{-}P,N)_2]PF_6$ (M = Cu **1** or Ag **2**) and two-co-ordinate $[Au(ppye\text{-}P)_2]PF_6$ **3** complexes. We decided to investigate the co-ordinating behaviour of ppye toward Cu^I, Ag^I and Au^I also in view of a comparison with the related diphosphine complexes. The chemistry of these species has been a topic of interest in the last years mainly because of their potential biological significance.[14] In particular, cationic derivatives $[M(diphosphine)_2]^+$ have been extensively investigated, and a considerable number of studies have been devoted to their structural characterization in the solid-state by X-ray crystallography[15] and, more recently, by ^{31}P cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance.[15j]

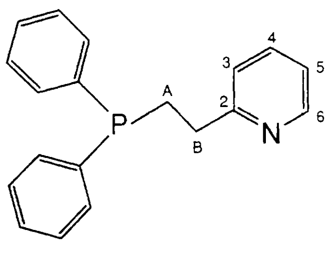

Fig. 1 The ligand ppye with the numbering of the carbon atoms

Complexes **1** and **2** were shown to adopt a tetrahedral geometry both in the solid state and in solution. It should be noted that tetrahedral bis(chelate) complexes with unsymmetric bidentate ligands are enantiomeric with Δ and Λ absolute configurations.[16] By contrast, in agreement with the strong but not exclusive tendency of gold(I) for linear two-co-ordination, in **3** the two ppye ligands act as P-bound monodentate. The structure of **3** in the solid-state has been established by single-crystal X-ray analysis. Moreover, variable-temperature ^1H, ^{13}C and ^{31}P NMR investigations of **1**–**3** show that inversion at the tetrahedral metal centre (**1** and **2**) and ligand-exchange processes take place in solution.

Results and Discussion

Syntheses of the Complexes and Properties.—The ligand ppye forms with each of the three metal ions Cu^I, Ag^I and Au^I air-stable crystalline complexes of the composition $M(ppye)_2PF_6$. Elemental analyses and conductivity data are reported in Table

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Conductivity and elemental analysis data

Complex	Λ_M[a]	Analysis[b] (%)		
		C	H	N
1 $[Cu(ppye\text{-}P,N)_2]PF_6$	89	57.50 (57.70)	4.50 (4.60)	3.55 (3.55)
2 $[Ag(ppye\text{-}P,N)_2]PF_6$	81	54.55 (54.65)	4.20 (4.35)	3.30 (3.35)
3 $[Au(ppye\text{-}P)_2]PF_6$	88	49.00 (49.35)	3.90 (3.90)	3.10 (3.05)
4 $Au(ppye)PF_6$	93	36.10 (36.05)	2.80 (2.85)	2.20 (2.20)

[a] Ω^{-1} cm^2 mol^{-1} for 1 × 10^{-3} mol dm^{-3} nitromethane solutions, at 295 K. [b] Calculated values in parentheses.

Table 2 Selected IR and NMR data for complexes **1**–**8**

Complex	IR[a]/cm^{-1}		$^{31}P\text{-}\{^1H\}$[b]		^1H[c]		
	Nujol	CH_2Cl_2	δ	$\nu_{\frac{1}{2}}$/Hz	δ	T/K	Solvent
1	1604	1602	−8.5	265	7.87	363	$CDCl_2CDCl_2$
			−7.8	185	7.88	293	CD_2Cl_2
			−7.4	70	7.80	183	CD_2Cl_2
2	1598	1598	5.4	50	8.05	363	$CDCl_2CDCl_2$
			4.9	540	8.00	293	$(CD_3)_2CO$
			4.3[d]	11	7.94	233	$(CD_3)_2CO$
3	1596, 1585	1592	40.1	9	8.33	363	$CDCl_2CDCl_2$
			39.1	8	8.32	193	CD_2Cl_2
4	1612		30.4	4	8.84	293	$(CD_3)_2CO$
5		1594, 1603	−9.4	320	8.34	293	CD_2Cl_2
			−4.8, −6.9[e]	130, 175	8.35	183	CD_2Cl_2
6		1596	1.3	14	8.34	293	CD_2Cl_2
			2.1[f]	6	8.35	193	CD_2Cl_2
7		1595	−2.9	250	8.42	293	CD_2Cl_2
			−0.1[g]	6	8.43	183	CD_2Cl_2
8		1595	31.2	22	8.39	293	CD_2Cl_2
			36.7	9	8.41	183	CD_2Cl_2

[a] Pyridine-ring stretching absorption. [b] Singlet, unless otherwise stated. [c] The C^6H proton resonance of the pyridine ring (doublet of doublets of doublets). [d] Doublet of doublets, $^1J(^{31}P\text{–}^{107}Ag)$ = 419 Hz. [e] 2:1 intensity ratio, respectively. [f] Doublet of doublets, $^1J(^{31}P\text{–}^{107}Ag)$ = 301 Hz. [g] Doublet of doublets, $^1J(^{31}P\text{–}^{107}Ag)$ = 224 Hz.

1, and relevant IR data have been collected in Table 2. The complex $[Cu(ppye\text{-}P,N)_2]PF_6$ **1** was prepared by the reaction of $[Cu(MeCN)_4]PF_6$[17] with ppye in 1:2 molar ratio in refluxing ethanol. The silver(I) analogue, $[Ag(ppye\text{-}P,N)_2]PF_6$ **2** was synthesized by stirring $AgPF_6$ and ppye in stoichiometric amounts in aqueous acetone at room temperature. The synthesis of $[Au(ppye\text{-}P)_2]PF_6$ **3** was performed in two steps. A product which analyses as $Au(ppye)PF_6$ **4** was obtained by the addition of ppye and NH_4PF_6 to an aqueous acetone solution of $Na[AuCl_4]{\cdot}2H_2O$, which had been reduced to Au^I *in situ* by addition of 2 equivalents of 2,2′-thiodiethanol. Complex **4** was then suspended in acetone and stirred with ppye, in 1:1 molar ratio, until a clear solution formed. Evaporation of the solvent gave analytically pure **3**. Several attempts to prepare **3** in a single step by the reaction of Au^I and ppye in 1:2 molar ratio afforded impure products.

Complexes **1**–**3** behave as 1:1 electrolytes in nitromethane solution (Table 1). The bis(chelate) structure in the solid state of **1** and **2** is supported by their IR spectra in Nujol mull (Table 2), which exhibit the pyridine-ring stretching absorption at 1604 and 1598 cm^{-1}, respectively, as expected for co-ordinated pyridyl groups.[3–9] In CH_2Cl_2 solution both complexes show IR absorptions very close to those exhibited by the Nujol mull samples, thus suggesting that no structural changes occur on going from solid-state to solution. By contrast, the single-crystal X-ray structural analysis (see below) indicates that in **3** both ppye ligands act as P-bound monodentate. It should be noted that the IR spectrum in Nujol mull of **3** shows two signals at 1596 and 1585 cm^{-1}, as usually found when both chelating and P-bound monodentate ppye ligands are co-ordinated to a transition metal.[3–9] On the contrary, the IR spectrum of **3** in CH_2Cl_2 solution exhibits a single absorption at 1592 cm^{-1}, close to the value of free ppye (1589 cm^{-1}). This seems to confirm that the pyridyl groups are unco-ordinated in solution as well as in the solid state. The splitting of the pyridine-ring stretching absorption observed in the spectrum of the Nujol mull sample is probably due to a solid-state effect.

NMR Investigations.—The multinuclear NMR investigations provide further evidence that in **1** and **2** both ppye ligands are chelating in solution. Moreover, the temperature-dependence of the ^1H, ^{13}C and ^{31}P NMR spectra indicates that chemical exchange processes occur in solution for both species.

The $^{13}C\text{-}\{^1H\}$ spectra (phenyl carbon resonances) of **1** in CD_2Cl_2 solution recorded in the temperature range 193–293 K are shown in Fig. 2. At low temperatures two sets of resonances of equal intensity are shown by all the phenyl carbon atoms, thus indicating the presence of two types of phenyl rings, as expected for a tetrahedral bis(chelate) structure (Fig. 3). The differences between the chemical shift values for each pair of magnetically inequivalent nuclei decrease in the order $C_{ipso}(1.62) > C_{para}(0.43) > C_{meta}(0.26) > C_{ortho}(0.14)$, shift differences in ppm are reported in parentheses. With exception of the C_{para} carbons, the resonances of the other phenyl carbons appear as non-binomial triplets as a result of the $^{31}P\text{–}^{13}C\text{–}^{31}P$ spin virtual coupling.[8,9,18] With respect to free ppye, the $^{13}C\text{–}^{31}P$ coupling constants change upon co-ordination to the metal, with a decrease for C_{ortho} and C_{meta} and an increase for C_{ipso} carbons. The $^{13}C\text{–}^{31}P$ coupling constants decrease in the usual order $C_{ipso} > C_{ortho} > C_{meta}$ (Table 3). As the temperature is raised, the resonances broaden and coalesce, so that, at 253 K, an averaged resonance is observed for each type of carbon atoms [Fig. 2(*c*)]. By further raising the temperature, the triplets begin to broaden losing their fine structure. At 363 K ($CDCl_2CDCl_2$ solution), the highest temperature investigated, all the phenyl carbons resonances appear as broad singlets. The

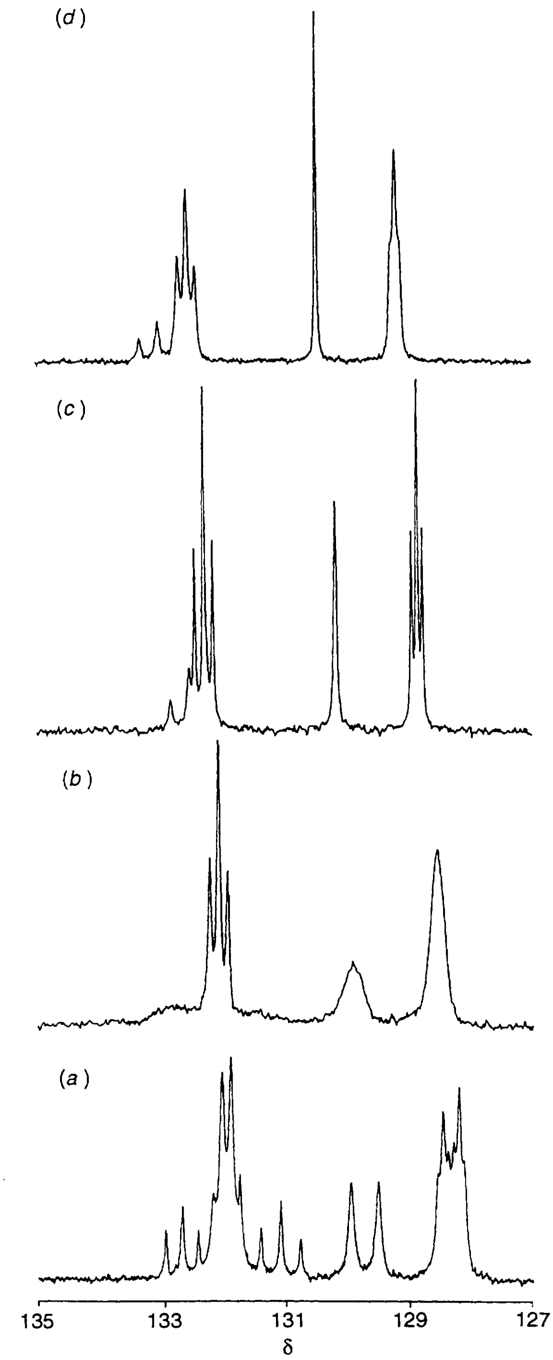


Fig. 2 Variable-temperature $^{13}C-\{^1H\}$ NMR spectra (phenyl carbons) of complex **1** at (*a*) 193, (*b*) 218, (*c*) 253 and (*d*) 293 K

temperature dependence of the ^{13}C NMR spectra of **1**, in the range 253–193 K, can be interpreted in terms of inversion at the tetrahedral Cu^I centre. A similar dynamic NMR behaviour has been found for the complexes $[M(Ph_2PCH_2CH_2PEt_2)_2]^+$ (M = Cu, Ag or Au), and it has been explained in terms of an intramolecular rearrangement involving the rupture of one or more M–P bonds.[19] In the case of **1**, a chelate ring-opening mechanism, with probable cleavage of the Cu–N bonds, appears reasonable in view of the severe steric interactions in the cation, which have been evidenced by the space-filling model. A dissociative intramolecular mechanism was also suggested for complexes of the type $[M(L-L)_2]^+$ (M = Cu, Ag or Au; L–L = diphosphine or diarsine).[20] The NMR pattern above 253 K indicates that a second process occurs at high temperatures. Nevertheless, in absence of the limiting spectrum, the effective nature of this dynamic process cannot be inferred from NMR data.

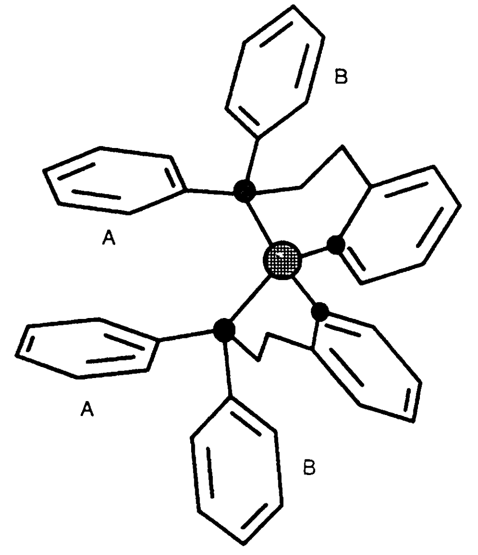


Fig. 3 Representation of one of the enantiomers of the tetrahedral complexes $[M(ppye\text{-}P,N)_2]^+$, showing the two pairs of equivalent phenyl rings (A and B)

Also the ^1H NMR spectra of **1** in CD_2Cl_2 solution display a notable temperature dependence for all resonances of the aliphatic (δ 2.3–3.5) and aromatic (δ 6.8–7.9) region. In particular, in the spectrum recorded at 293 K, the protons of the CH_2CH_2 groups give two broad resonances in 1 : 1 intensity ratio. On cooling the sample to 218 K, the signal at higher field broadens and then splits into two equivalent humps (Fig. 4). The spectrum recorded at 183 K, the lowest available temperature, again shows three broad resonances in a *ca.* 2 : 1 : 1 intensity ratio. In agreement with these results, the space-filling model of **1** shows that the two protons of the PCH_2 fragment are in distinct magnetic environments when the tetrahedral rigid structure is achieved.

Finally, the $^{31}P-\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 solution at 293 K shows a broad singlet at δ −7.8 ($\nu_{\frac{1}{2}}$ = 185 Hz). The $^{31}P-^{63/65}Cu$ couplings are not resolved, as generally found for phosphino derivatives of copper(I) with low symmetry.[21] On cooling the sample, the peak sharpens and at 183 K, the lowest available temperature, $\nu_{\frac{1}{2}}$ is reduced to 70 Hz.

The NMR investigation of **2** was necessarily limited to temperatures higher than 233 K, owing to the insolubility of the complex at lower temperatures in the usual solvents. The $^{31}P-\{^1H\}$ NMR spectra of **2** show a temperature dependence indicative of a ligand-exchange process involving dissociation of the Ag–P bonds. At high temperature (363 K, $CDCl_2CDCl_2$ solution) a broad singlet is observed at δ 5.4 ($\nu_{\frac{1}{2}}$ = 50 Hz). On lowering the temperature, the rate of the exchange process is slowed on the NMR time-scale and at 233 K (CD_2Cl_2 solution) the typical two doublets expected for the spin–spin coupling of magnetically equivalent phosphorus atoms with ^{107}Ag and ^{109}Ag isotopes (in 51.839 and 48.161% natural abundance, respectively[22]) are observed. The ratio of the ^{31}P–Ag coupling constants is 1.152 (close to the ratio of the nuclear magnetic moments of the two metal isotopes). The $^1J(^{31}P-^{107}Ag)$ value of 419 Hz is comparable to those reported for silver(I) derivatives in which two P atoms are co-ordinated to the metal ion.[15c,23] It is noteworthy that for the analogous four-co-ordinate complexes $[Ag(diphosphine)_2]^+$ with the diphosphines $R_2P(CH_2)_nPR_2$ (*n* = 2, R = Et or Ph; *n* = 3, R = Ph) and *cis*-$Ph_2PCH{=}CHPPh_2$, the $^{31}P-^{107/109}Ag$ couplings are observable at room temperature.[24] It seems likely that in **2** the

Table 3 $^{13}C-\{^1H\}$ NMR data for complexes **1**–**3**[a,b]

	ppye	**1**			**2**			**3**		
T/K	293	363	253	193	363	293	233	363	293	193
C_{ipso}	139.2 (d) [13.7]	133.4 (br)	132.7 (t) [15.1] 132.8 (t) [13.1]	131.2 (t) [16.1]	131.3 (d) [27.9]	131.1 (br)	131.9 (t) [13.1] 132.0 (t) [13.8]	128.5 (d) [51.9]	128.5 (br)	127.1 (t) [28.7]
C_{ortho}	133.1 (d) [18.4]	131.8 (br)	132.4 (t) [7.3] 132.2 (t) [7.5]	132.0 (t) [7.6]	132.3 (d) [15.5]	132.4 (br)	132.7 (t) [8.3]	132.8 (d) [13.1]	133.6 (br)	132.9 (t) [7.0]
C_{meta}	128.8 (d) [10.2]	128.8 (br)	129.0 (t) [4.4] 128.5 (t) [4.2]	128.3 (t) [4.3]	129.1 (d) [9.6]	129.2 (br)	129.1 (t) [4.3]	129.5 (d) [11.1]	130.1 (br)	129.2 (t) [5.5]
C_{para}	128.9	130.0	130.3 130.1	129.6	130.8	130.8	130.8	132.1	132.8	132.0 (br)
C^2	162.2 (d) [13.0]	161.2	161.5	160.8	160.4	160.6	161.1	157.8 (d) [12.2]	158.6 (br)	157.5 (t) [5.0]
C^3	122.9	125.8	126.2	125.8	124.5	124.8	125.1	123.4	123.8	123.2 (br)
C^4	136.5	138.7	139.0	138.5	138.1	138.4	138.7	137.7 (br)	137.5	136.6 (br)
C^5	121.5	122.9	123.3	122.8	122.4	122.6	122.7	122.1	122.5	121.6 (br)
C^6	149.7	150.4 (br)	151.1 (t) [2.7]	150.8 (br)	150.0	150.2	150.7	148.1 (br)	149.4	148.7 (br)
CH_2 (A)	28.2 (d) [12.7]	24.8 (br)	24.6 (t) [9.9]	24.0 (t) [9.3]	25.9 (d) [16.3]	25.8 (br)	25.6 (t) [7.8]	26.5 (d) [31.4]	26.8 (br)	25.4 (br)
CH_2 (B)	34.8 (d) [17.9]	32.1	32.1 (t) [3.6]	31.6 (br)	32.7 (d) [4.8]	32.5 (br)	32.4 (br)	32.3 (br)	32.8	31.2 (br)

[a] The numbering of the carbon atoms is given in Fig. 1. [b] Multiplicity given in parentheses: d = doublet, t = triplet, br = broad singlet; $J(^{13}C-^{31}P)$/Hz in square brackets.

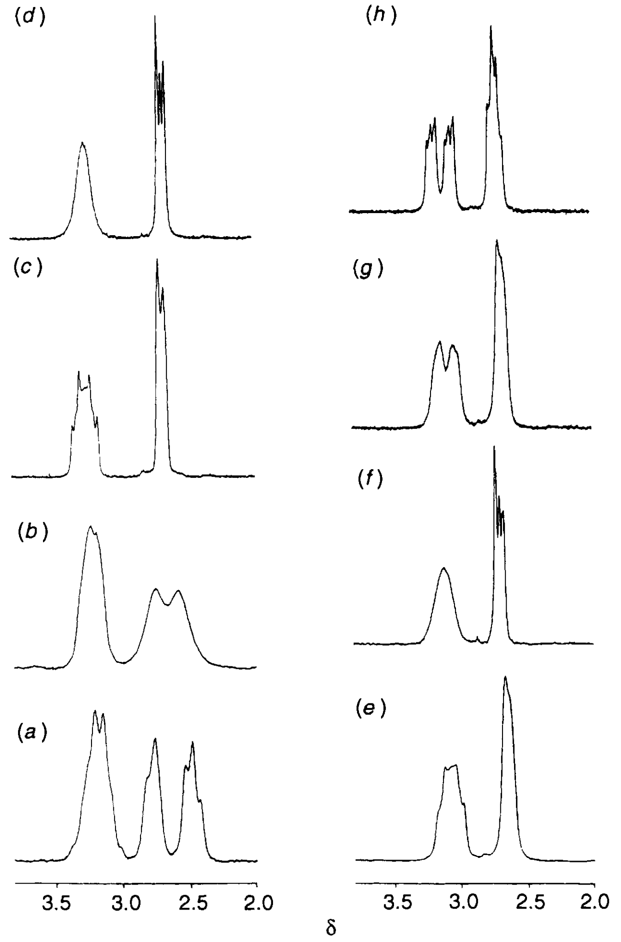


Fig. 4 Variable-temperature ^1H NMR spectra (methylene protons) of complex **1** at (*a*) 193, (*b*) 218, (*c*) 293 and (*d*) 363 K, and complex **2** at (*e*) 233, (*f*) 293, (*g*) 333 and (*h*) 363 K

higher kinetic lability of the ppye ligands requires a lower temperature for the resolution of the coupling constants.

Moreover, variable-temperature ^{13}C NMR studies suggest that **2** undergoes, likewise to the copper(I) analogue **1**, a chemical exchange process involving inversion at the tetrahedral metal centre. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2** recorded at 363 K ($CDCl_2CDCl_2$ solution) the phenyl carbon resonances appear as doublets, with the exception of the C_{para} signal which is a singlet. By lowering the temperature, the doublets broaden and, at 293 K, broad singlets are given by all the phenyl carbon atoms. On cooling the sample to 253 K, the signals due to C_{ipso}, C_{ortho} and C_{meta} carbons resolve into well-shaped triplets due to virtual coupling between two equivalent phosphorus atoms. As the temperature is lowered below 253 K, the triplets begin to broaden and at 233 K, the lowest available temperature, the C_{ipso} carbon resonance splits into two partially overlapped rather broad triplets (Fig. 5). Although the slow-exchange limit spectrum cannot be achieved, the C_{ipso} pattern seems to indicate the incipient 'freezing' of the tetrahedral structure, as found for the copper(I) analogue **1**. Apparently, for the silver(I) derivative the temperature of coalescence is lower, with a higher rate of inversion at the metal centre. It should be noted that for the comparable tetrahedral complexes $[M(Ph_2PCH_2CH_2PEt_2)_2]^+$ (M = Cu, Ag or Au) the rate of inversion increases in the order $Ag^I > Au^I > Cu^I$.[19] Also the ^1H NMR spectra of **2** at different temperatures resemble that of **1** (Fig. 4), but with a lower temperature of coalescence. Probably the dynamic behaviour of **1** and **2** is the same and also the copper(I) complex undergoes at high temperature a ligand-exchange process like the silver(I) analogue.

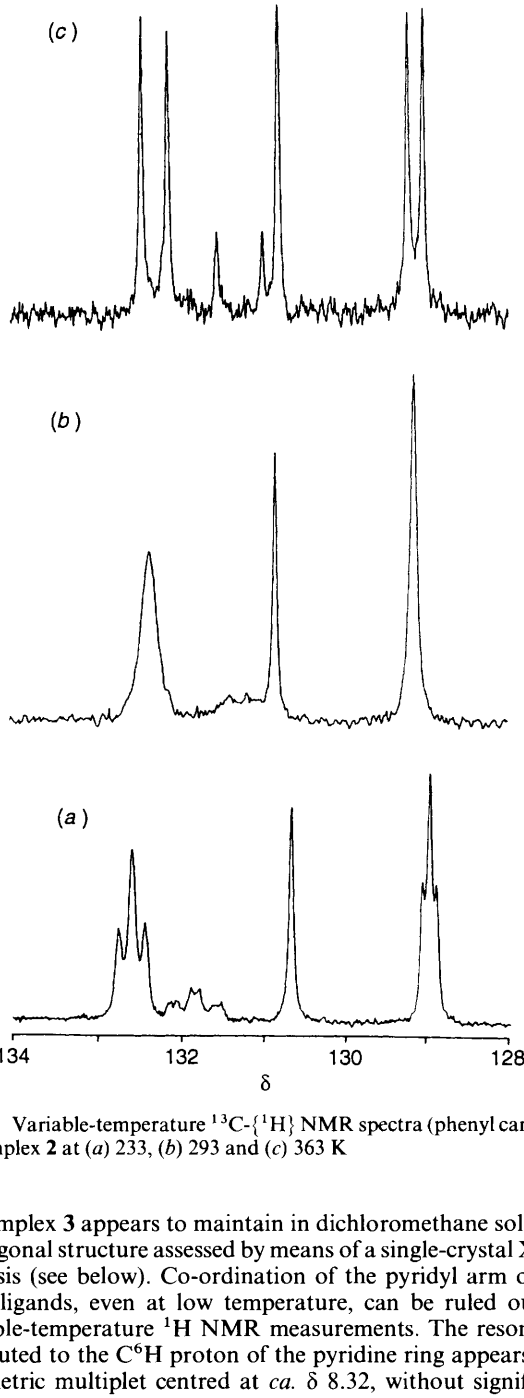


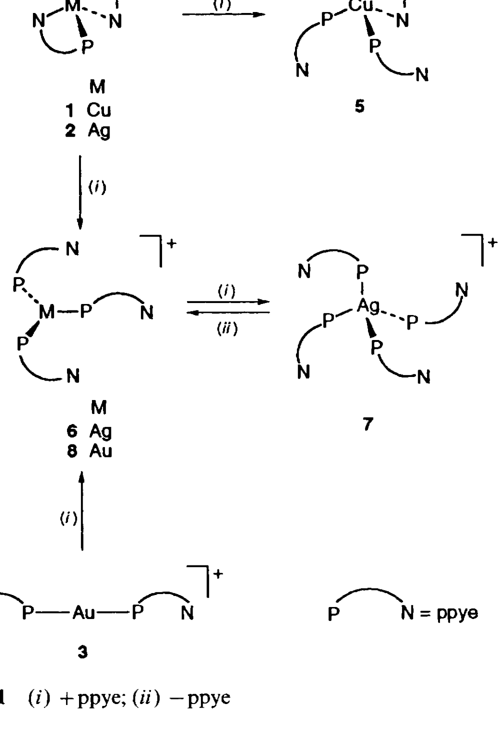
Fig. 5 Variable-temperature $^{13}C\text{-}\{^1H\}$ NMR spectra (phenyl carbons) of complex **2** at (*a*) 233, (*b*) 293 and (*c*) 363 K

Complex **3** appears to maintain in dichloromethane solution the digonal structure assessed by means of a single-crystal X-ray analysis (see below). Co-ordination of the pyridyl arm of the ppye ligands, even at low temperature, can be ruled out by variable-temperature ^1H NMR measurements. The resonance attributed to the C^6H proton of the pyridine ring appears as a symmetric multiplet centred at *ca.* δ 8.32, without significant changes over the temperature range 293–183 K. It should be noted that for the copper(I) and silver(I) complexes $[M(ppye\text{-}P,N)_2]^+$, in which both ppye ligands are chelating, the C^6H protons of the pyridine ring give signals in the range δ 7.80–8.05. On the contrary, the value found for the gold(I) derivative is close to that observed for free ppye (δ 8.51).

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3**, which is not markedly affected by temperature, shows a singlet at δ 39.6 at 293 K. Moreover, the variable-temperature ^{13}C NMR investigation suggests that at high temperature **3** undergoes a ligand exchange process which is fast in the NMR time-scale. Thus, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at 193 K in CD_2Cl_2 solution, the C_{ipso}, C_{ortho} and C_{meta} resonances appear as non-binomial triplets due to $^{31}P\text{–}^{13}C\text{–}^{31}P$ spin virtual coupling. As the temperature is raised, the triplets broaden and, at room-temperature, they appear as broad singlets. At 363 K ($CDCl_2CDCl_2$ solution), they eventually sharpen up into well shaped doublets. Apparently, the ligand-exchange process, owing to the loss of the spin–spin coupling between the phosphorus atoms, implies the cleavage of the Au–P bonds.

Reactions of Complexes **1**–**3** *with ppye.*—In order to gain more information with respect to the stabilities of the M–P and M–N bonds, we have analysed by means of ^{31}P and ^{1}H NMR spectroscopy the reactions of **1**–**3** with increasing amounts of free ppye in dichloromethane solution. The addition of a slight excess of ppye to a dichloromethane solution of **1** (1.1 : 1 molar ratio) at 293 K results in a broadening of the $^{31}P-\{^{1}H\}$ NMR resonance, which is indicative of a rapid exchange between free and co-ordinated ppye. On cooling the sample to 193 K, the exchange is nearly stopped and the spectrum shows, in addition to the singlet (*ca.* 3% of the total area) due to free ppye (δ −17.8), two still broad signals at δ −4.8 and −6.9 integrating 2 : 1, respectively, which can be reasonably attributed to the complex [Cu(ppye-*P*)$_2$(ppye-*P*,*N*)]PF$_6$ **5** containing one chelating and two P-bound monodentate ligands (Table 2 and Scheme 1). Similar patterns were observed in the spectra of the samples containing increasing amounts of ppye. Apparently, complex **5** seems to be the only copper(I) derivative present in solution even in the presence of a strong excess of ppye. The formation of significant amounts of a species containing four P-bound monodentate ppye ligands is likely to be excluded.

By contrast, **2** reacts with ppye in dichloromethane solution, with stepwise formation of [Ag(ppye-*P*)$_3$]PF$_6$ **6** and [Ag(ppye-*P*)$_4$]PF$_6$ **7**, both containing only P-bound monodentate ligands, as shown by ^{31}P NMR measurements (Table 2 and Scheme 1). Owing to rapid exchange equilibria, the $^{31}P-\{^{1}H\}$ NMR spectra of the samples containing **2** and ppye, in 1 : 1 or 1 : 2 molar ratio, exhibit broad singlets at 293 K. The exchange process is nearly stopped at low temperature, and sharp resonances are observed in the spectra of both samples. At 193 K, the spectrum of the sample containing **2** and ppye in 1 : 1 molar ratio shows a doublet of doublets [δ 2.1, $^{1}J(^{31}P-^{107}Ag)$ = 301 Hz] attributed to complex **6**, which is quantitatively formed. At the same temperature, the spectrum of the sample containing **2** and ppye in 1 : 2 molar ratio shows a doublet of doublets [δ −0.1, $^{1}J(^{31}P-^{107}Ag)$ = 224 Hz] attributed to **7** (*ca.* 90%), together with minor signals due to **6** and free ppye. For the three silver(I) derivatives, the number of ppye molecules co-ordinated to the metal centre is clearly indicated by the magnitudes of the $^{31}P-^{107}Ag$ coupling constants, which decrease in the order **2** (419 Hz) > **6** (301 Hz) > **7** (224 Hz) (Table 2). These values are diagnostic of the co-ordination to the metal-ion of two, three and four P atoms, respectively.[15c,23] In agreement with the presence of P-bound ligands, the IR spectra of solutions of **6** and **7** exhibit the pyridine stretching absorption at *ca.* 1595 cm^{-1}, close to the value of free ppye.



Scheme 1 (*i*) +ppye; (*ii*) −ppye

In order to verify the possible formation of three- and four-co-ordinate complexes of gold(I), the titration of **3** with ppye has been performed and followed by means of ^{31}P NMR spectroscopy. At 293 K, the proton-decoupled spectrum of **3** shows a sharp singlet at δ 39.6. This peak is replaced by a new slightly broad singlet ($\nu_{\frac{1}{2}}$ = 22 Hz) at δ 31.2 when 1 equivalent of ppye is added. On cooling to 183 K, the resonance considerably sharpens and the chemical shift moves to lower field (δ 36.7, $\nu_{\frac{1}{2}}$ = 9 Hz). No signals corresponding to free ppye are present in the NMR spectra in the whole range of temperature investigated. The signal at δ 36.7 can be reasonably attributed to the three-co-ordinated complex [Au(ppye-*P*)$_3$]PF$_6$ **8**. This assumption is supported by the ^{1}H NMR spectra, which exhibit C^{6}H protons resonances at *ca.* δ 8.40, as expected for P-bound monodentate ppye ligands. After further addition of 1 equivalent of ppye to the solution, the $^{31}P-\{^{1}H\}$ spectrum at 293 K shows a broad singlet ($\nu_{\frac{1}{2}}$ = 40 Hz) at δ 23.0. On cooling the sample, the peak considerably broadens and shifts to lower field (δ 30.8, $\nu_{\frac{1}{2}}$ = 1020 Hz, at 193 K). No clear evidence of formation of the four-co-ordinate complex [Au(ppye-*P*)$_4$]PF$_6$ has been obtained. It should be noted that the related ligand PMePh$_2$ forms the stable four-co-ordinate [Au(PMePh$_2$)$_4$]$^+$ derivative.[25]

Description of the Structure of **3**.—Fig. 6 shows an ORTEP[26] view of the [Au(ppye-*P*)$_2$]$^+$ cation and the numbering scheme for the crystallographically independent atoms. For clarity, the PF$_6^-$ anion is not shown. The asymmetric unit contains one half of the cation, with the Au atom on the crystallographic inversion centre at (0, ½, 0). The phosphorus of the PF$_6^-$ anion sits on the symmetry centre at (0, 0, 0), so that only three fluorine atoms are independent. Consequently, only one [Au(ppye)$_2$PF$_6$] formula unit is contained in the centrosymmetric triclinic cell. The digonal co-ordination of the Au atom is regular [P(1)–Au–P(1′), 180°] as imposed by the crystallo-

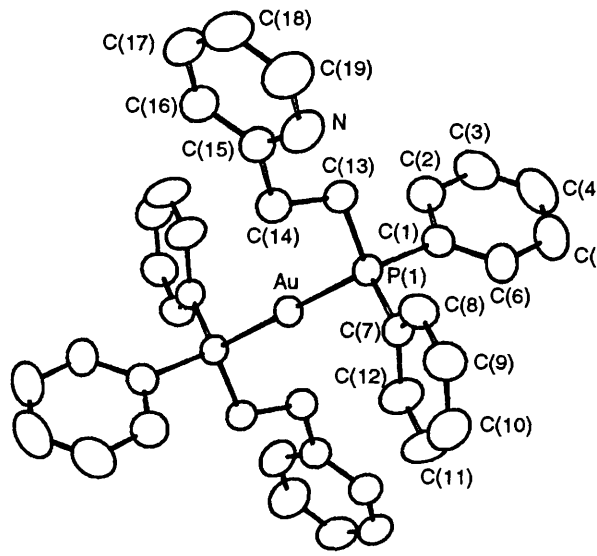


Fig. 6 ORTEP drawing of the [Au(ppye-*P*)$_2$]$^+$ cation. Ellipsoids are drawn at 50% probability

graphic symmetry centre. Both ppye ligands act as P-bound monodentate [the Au$\cdots$N distance is 5.369(6) Å], as previously reported for the square-planar complex *trans*-[IrCl(CO)(ppye-*P*)$_2$].[6] The Au–P(1) distance of 2.3125(9) Å is unexceptional and very close to that found in similar digonal complexes $[Au(PR_3)_2]^+$ [PR$_3$ = PPh$_3$,[27] PBu$^n_3$,[28] PMePh$_2$[29] and P(CH$_2$CH$_2$CN)$_3$[30]].

Conclusion

In the copper(I) and silver(I) complexes **1** and **2** the ppye ligands are chelating, while both ligands are P-bound monodentate in the gold(I) derivative **3**. The different co-ordinating behaviour of ppye toward gold(I) agrees with the observation that linear two-co-ordinate cationic gold(I) complexes such as $[Au(PPh_3)_2]^+$ dissolve in pyridine without solvent molecules participating in the inner co-ordination sphere of the metal ion.[31]

It should be noted that the related ligand 2-(diphenylphosphino)pyridine (dppy) reacts with copper(I) and gold(I) salts containing low co-ordinating anions to give binuclear complexes with bridging dppy molecules,[11,13] the tetrahedral geometry being probably disfavoured by its small bite.

On the other hand, the diphosphine Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp), which like ppye can form a six-membered chelate ring, gives four-co-ordinate derivatives of the type $[M(dppp)_2]^+$ with all the metals of Group 11.[14g,24,32] Among the complexes $[Au\{Ph_2P(CH_2)_nPPh_2\}_2]^+$ (n = 1–4), only those containing five- or six-membered chelate rings exist as stable species in solution.[32] Apparently, in the case of the bidentate ligands four-co-ordination for gold(I) is easily achieved with the P$_4$ donor set but not with a P$_2$N$_2$ donor set.

The tetrahedral complexes **1** and **2** rearrange in solution by inversion at the metal centre, with a rate which is higher for the silver(I) derivative. The mechanism implies the cleavage of at least one M–N bond. Furthermore, at high temperature all the complexes undergo a ligand-exchange process which is fast in the NMR time-scale.

With regard to the reactions of **1** and **2** with free ppye, it has been found that the pyridyl arm of the ligand is more easily displaced from the silver ion. The cleavage of only one Cu–N bond is observed in **1**, with formation of a new Cu–P bond, even in the presence of an excess of ppye. On the contrary, the addition of a ppye molecule to **2** is accompanied by the dissociation of both pyridyl arms with formation of the three-co-ordinate **6**, which can then give the four-co-ordinate **7** by addition of a fourth ppye ligand.

Experimental

Materials.—Solvents were dried and distilled according to standard methods, and stored under argon atmosphere on molecular sieves. All chemicals were reagent grade and were used as received. 2,2′-Thiodiethanol, silver hexafluorophosphate and sodium tetrachloroaurate(III) were purchased from Aldrich. The complex [Cu(MeCN)$_4$]PF$_6$ was prepared by a literature procedure.[17] The ligand ppye was synthesized according to the method of Uhlig and Maaser.[3]

Measurements.—Infrared spectra were recorded on a Nicolet FT 550 spectrophotometer; ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded on a Bruker AC 200 F QNP spectrometer equipped with a VT 1000 variable-temperature probe (^{1}H at 200.13, ^{13}C at 50.32 and ^{31}P at 81.02 MHz). Temperatures were calibrated with either methanol or ethylene glycol. Positive ^{31}P chemical shifts are downfield from 85% H$_3$PO$_4$ external standard; ^{1}H and ^{13}C chemical shifts are referenced to SiMe$_4$. Conductance data, for 1×10^{-3} mol dm^{-3} nitromethane solutions of the complexes at 295 K, were measured with a Metrohm E 518 conductivity bridge. Microanalyses were performed by the Microanalytical Laboratory of our Department.

Syntheses.—All manipulations were performed under argon with use of standard Schlenk-line techniques. For the preparation of the silver derivative flasks were protected from light with aluminium foil.

[Cu(ppye-*P*,*N*)$_2$]PF$_6$ **1**. The complex [Cu(MeCN)$_4$]PF$_6$ (0.558 g, 1.50 mmol) and ppye (0.903 g, 3.10 mmol) were suspended in ethanol (25 cm^3) and the slurry was refluxed for 1 h. The white product obtained on cooling was collected by filtration, washed with ethanol and diethyl ether and dried *in vacuo*. Yield: 0.962 g (81%).

[Ag(ppye-*P*,*N*)$_2$]PF$_6$ **2**. (*a*) The ligand ppye (0.583 g, 2.00 mmol) was dissolved in acetone (20 cm^3) and a solution of AgPF$_6$ (0.253 g, 1.00 mmol) in H$_2$O (5 cm^3) was added dropwise. The volume of the solution was reduced to *ca.* 5 cm^3 affording a white-grey gum, which was triturated in propan-2-ol in an ice-bath. The white solid formed was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Recrystallization from dichloromethane–propan-2-ol. Yield: 0.654 g (78%).

(*b*) The salt AgNO$_3$ (0.170 g, 1.00 mmol) and ppye (0.583 g, 2.00 mmol) were stirred in propan-2-ol–dichloromethane (15 cm^3, 2:1) until a clear solution formed. Then NH$_4$PF$_6$ (0.489 g, 3.00 mmol) in propan-2-ol (20 cm^3) was added and the solution concentrated *in vacuo*. The white product formed was filtered, washed with diethyl ether, and dried *in vacuo*. Recrystallization from dichloromethane–propan-2-ol. Yield: 0.608 g (73%).

Au(ppye)PF$_6$ **4**. The complex Na[AuCl$_4$]·2H$_2$O (0.398 g, 1.00 mmol) was reduced to Au^I by 2,2′-thiodiethanol (0.245 g, 2.00 mmol) in water–acetone (5 cm^3, 2.5:1). The ligand ppye (0.291 g, 1.00 mmol) in acetone (10 cm^3) and NH$_4$PF$_6$ (0.326 g, 2.00 mmol) in water (10 cm^3) were added and the mixture stirred for 30 min. The white-grey gum obtained after removing the acetone was triturated in water affording a white solid. This was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Recrystallization from acetone–water. Yield: 0.428 g (68%).

[Au(ppye-*P*)$_2$]PF$_6$ **3**. The complex Au(ppye)PF$_6$ **4** (0.633 g, 1.00 mmol) and ppye (0.291 g, 1.00 mmol) were stirred in acetone (10 cm^3) until a clear solution was obtained. Propan-2-ol (10 cm^3) was added and the solution concentrated under vacuum affording a white product, which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.814 g (88%).

X-Ray Crystal Structure Determination.—Colourless single crystals of **3** suitable for X-ray analysis were grown by slow diffusion of propan-2-ol into a dichloromethane solution of the complex under an argon atmosphere.

Crystal data. C$_{38}$H$_{36}$AuF$_6$N$_2$P$_3$, M = 924.6, triclinic, space group $P\bar{1}$, a = 9.972(1), b = 10.299(2), c = 10.521(2) Å, α = 69.90(2), β = 66.03(1), γ = 78.51(1)°, U = 924.0(3) Å^3 (by least-squares refinement of a setting angles of 25 reflections in the range $14 \leqslant \theta \leqslant 18°$, λ = 0.710 73 Å), Z = 1, F(000) = 456, D_c = 1.66 g cm^{-3}, μ(Mo-Kα) = 43.07 cm^{-1}. Colourless plate, 0.3 × 0.2 × 0.1 mm.

Data collection and processing. The ω–2θ technique was used to collect 5640 (5369 unique) reflections in the range $4 \leqslant 2\theta \leqslant 60°$ on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation. Three standards monitored every 300 reflections showed no appreciable change in intensity throughout the data collection. Scans were made in the bisecting position with a maximum time of 60 s for reflections in the final scan. Data were corrected for Lorentz and polarization effects and for absorption based on additional azimuthal scan data. After averaging, 4678 independent reflections with $I > 3\sigma(I)$ were used in the subsequent calculations.

Structure analysis and refinement. The structure was solved

Table 4 Fractional atomic coordinates for complex **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Au	0.000	0.500	0.000
P(1)	0.2169(1)	0.4756(1)	−0.1898(1)
P(2)	0.000	0.000	0.000
F(1)	0.0493(5)	−0.1607(3)	0.0437(4)
F(2)	0.0476(5)	0.0229(5)	0.1153(4)
F(3)	0.1604(5)	0.0296(4)	−0.1179(5)
N	0.2067(5)	0.3535(5)	−0.5681(5)
C(1)	0.3656(5)	0.3876(5)	−0.1261(4)
C(2)	0.3431(6)	0.2543(6)	−0.0291(5)
C(3)	0.4551(7)	0.1802(7)	0.0173(6)
C(4)	0.5851(6)	0.2375(8)	−0.0287(6)
C(5)	0.6074(6)	0.3695(8)	−0.1231(7)
C(6)	0.4975(5)	0.4449(6)	−0.1730(6)
C(7)	0.2810(5)	0.6395(5)	−0.3240(5)
C(8)	0.3532(6)	0.6505(5)	−0.4701(5)
C(9)	0.4025(6)	0.7775(6)	−0.5695(6)
C(10)	0.3787(7)	0.8915(6)	−0.5224(6)
C(11)	0.3055(7)	0.8814(6)	−0.3777(6)
C(12)	0.2554(6)	0.7558(5)	−0.2777(5)
C(13)	0.2067(5)	0.3659(5)	−0.2884(4)
C(14)	0.0801(5)	0.4101(5)	−0.3423(5)
C(15)	0.0902(5)	0.3323(5)	−0.4438(5)
C(16)	−0.0161(5)	0.2457(5)	−0.4110(5)
C(17)	−0.0024(6)	0.1812(5)	−0.5120(6)
C(18)	0.1142(7)	0.2034(6)	−0.6389(6)
C(19)	0.2163(8)	0.2892(7)	−0.6620(6)

Table 5 Bond lengths (Å) and angles (°) for complex **3** with e.s.d.s in parentheses

Au–P(1)	2.3125(9)	C(13)–C(14)	1.517(7)
P(1)–C(1)	1.823(5)	C(14)–C(15)	1.503(8)
P(1)–C(7)	1.820(4)	C(15)–C(16)	1.381(8)
P(1)–C(13)	1.816(6)	C(16)–C(17)	1.39(1)
N–C(15)	1.333(5)	C(17)–C(18)	1.350(7)
N–C(19)	1.33(1)	C(18)–C(19)	1.37(1)
P(1)–Au–P(1′)	180.(0)	P(1)–C(13)–C(14)	113.3(3)
C(1)–P(1)–C(7)	107.4(2)	C(13)–C(14)–C(15)	111.6(4)
C(1)–P(1)–C(13)	102.7(2)	N–C(15)–C(14)	116.1(5)
C(7)–P(1)–C(13)	106.7(2)	N–C(15)–C(16)	122.1(5)
C(15)–N–C(19)	117.4(6)	C(14)–C(15)–C(16)	121.9(4)
P(1)–C(1)–C(2)	116.9(4)	C(15)–C(16)–C(17)	118.8(4)
P(1)–C(1)–C(6)	123.1(3)	C(16)–C(17)–C(18)	119.6(6)
P(1)–C(7)–C(8)	121.7(4)	C(17)–C(18)–C(19)	118.0(7)
P(1)–C(7)–C(12)	118.8(3)	N–C(19)–C(18)	124.2(5)

by conventional Patterson and Fourier synthesis. In the final least-squares cycles, all atoms of the $[Au(ppye\text{-}P)_2]^+$ cation were refined anisotropically, while those of the PF_6^- ion isotropically. The hydrogen atoms were placed in idealized positions (C–H distance set at 0.95 Å) and included in the structure-factor calculations but were not refined. The final cycle of least-squares refinement included 229 parameters $\{$weighting scheme $w = 1/[\sigma(F) + (0.03F)^2 + 1]\}$ and did not shift any parameter by more than 0.05 times its standard deviation. Scattering factors were those of Cromer.[33] The final R and R' values were 0.039 and 0.043, respectively. The difference Fourier map did not reveal chemically significant residual electron density. All calculations were carried out using the MOLEN program package[34] on a VAX 2000 computer and the structure was generated using the ORTEP program.[26]

Atomic coordinates are listed in Table 4, intramolecular bond distances and angles are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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