Structure and Bonding in Gold(I) Compounds. Part 4.† A Phosphorus-31 Nuclear Magnetic Study of the Structure of Some Gold(I) Phosphine Complexes in Solution

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The addition of PEt_3 to dichloromethane solutions of $[Au(PEt_3)_2][PF_6]$ or $[Au(PEt_3)Cl]$ at 175 K leads to the formation in solution of three- and four-co-ordinate gold(I) complexes. These are of the type $[AuL_n]^+$ (n = 3 or 4) and there is no evidence in the case of $[Au(PEt_3)Cl]$ for the presence of the undissociated species $[AuL_nCl]$ ($n > 1$) under these conditions. When $P(OEt)_3$ is added to solutions of the above complexes, mixed species of the type $[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$ (n = 1—3) are formed. If the amount of $P(OEt)_3$ added is such as to give a total ligand : gold ratio of <4 : 1 the two- and three-co-ordinate complexes which are present contain only PEt_3. In no case has free ligand [PEt_3 or $P(OEt)_3$] been observed to be present until the ligand : gold ratio exceeded 4 : 1. At >213 K, ligand exchange is rapid on the n.m.r. time scale in all the systems studied.

GOLD(I) is known to form a large number of complexes with phosphine ligands and the majority of these are two-co-ordinate.[1] Higher co-ordination numbers are sometimes found, however, and examples for which *X*-ray structural data are available include the three-co-ordinate $[Au(PPh_3)_2][B_9SH_{12}]$ [2] and $[(PPh_3)_2AuX]$ (X = Cl [3] or I [4]) and the four-co-ordinate $[Au(PPh_3)_3(SnCl_3)]$.[5] In addition to these examples a number of complexes of the type $[AuL_4]^+$ [L = PPh_3,[6] $P(OMe)_3$,[7] $PPh(OR)_2$,[8] or $PPh_2(OR)$ [8]] have been prepared and these are presumably four-co-ordinate. There is Mössbauer evidence [9] that a number of complexes of the type $[AuL_2X]$ for which *X*-ray data are not available are also three-co-ordinate, although this is not invariably so and $[Au\{P(C_6H_{11})_3\}_2(SCN)]$, for example, is definitely two-co-ordinate.[10]

In solution the situation is much more confused. Schmidbauer and Franks [7] have studied the interaction of $P(OMe)_3$ with $[Au\{P(OMe)_3\}_2]^+$ by i.r. spectroscopy and conclude that only two- and four-co-ordinate species are ever present in solution, and that three-co-ordinate $[Au\{P(OMe)_3\}_3]^+$ must be unstable with respect to disproportionation. On the other hand, Muetterties and Alegranti [11] report that the species $[AuL_2]^+$, $[AuL_3]^+$, and possibly $[AuL_4]^+$ (L = PPh_3) may be identified in solution from ^{31}P n.m.r. and conductivity data. Using the ligand 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane the complexes $[AuL_2(NCMe)]^+$, $[AuL_2]^+$, $[AuL_3]^+$, and $[AuL_4]^+$ have been suggested as being present in acetonitrile solution on the basis of the electronic spectra of such solutions.[12]

In this paper we report the results of our studies using PEt_3 and $P(OEt)_3$ as ligands. Phosphorus-31 n.m.r. studies provide convincing evidence that three- and four-co-ordinate complexes containing PEt_3 are readily formed in dichloromethane solution at the low temperatures (usually below 193 K) which are needed for ligand exchange to become slow on the n.m.r. time scale. The mixed species $[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$ (n = 1—3) have also been identified and this represents the first report of this type of gold(I) complex. By studying the interaction of PEt_3 and $P(OEt)_3$ with $[Au(PEt_3)Cl]$ as well as with $[Au(PEt_3)_2][PF_6]$ we have also been able to investigate whether undissociated species of the type $[AuL_nX]$ ($n > 1$) are present in solution.

RESULTS AND DISCUSSION

(*i*) $[Au(PEt_3)_2][PF_6]$ *and* PEt_3.—Solutions of $[Au(PEt_3)_2][PF_6]$ in dichloromethane at 175 K gave a single sharp ^{31}P n.m.r. resonance at —43.3 p.p.m.‡ Addition of 0.5 mol equivalent of PEt_3 caused the appearance of a second sharp peak at —38.3 p.p.m. On addition of another 0.5 mol equivalent the first peak disappeared completely while the second peak remained unchanged in its position. More aliquots of PEt_3 resulted in a diminution of intensity of the peak at —38.3 p.p.m. and the growth of a new singlet resonance at 5.7 p.p.m. No further peaks appeared until the phosphine : gold ratio was just greater than 4 : 1. At this point the peak at —38.3 p.p.m. had disappeared and a new sharp peak had appeared at 19.1 p.p.m. which was attributed to the presence of free PEt_3. Addition of more PEt_3 (until the phosphine : gold ratio was 7 : 1) resulted only in an increase in intensity of the peak at 19.1 p.p.m. The peak at 5.7 p.p.m. remained unchanged in position throughout these further additions.

These experiments indicate that the addition of PEt_3 to $[Au(PEt_3)_2]^+$ results in the successive formation of $[Au(PEt_3)_3]^+$ and $[Au(PEt_3)_4]^+$. The fact that none of the three- and four-co-ordinate species is formed until the phosphine : gold ratio is respectively greater than 2 or 3 : 1 suggests that the relative magnitude of the overall stability constants is $\beta_2 > \beta_3 > \beta_4$. On the other hand, the fact that no free ligand is observed until the ratio is greater than 4 : 1 indicates that even β_4 is considerably larger than unity. This suggests that it might not be too difficult to isolate solid complexes containing 3 or 4 mol of PEt_3 per gold(I) atom. These have never been reported, however, and our attempts to crystallise a dichloromethane solution of $[Au(PEt_3)_2][PF_6]$ in the

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† Part 3 is ref. 9.

‡ The resonance due to the $[PF_6]^-$ ion is not referred to in the following discussion. It is a septet which is always clearly distinguishable from other resonances in complexes containing this anion.

presence of a 5 molar excess of PEt_3 gave only the starting material. It can only be assumed that lattice-energy effects favour the two-co-ordinate complex which therefore crystallises preferentially.

On warming the solution containing equimolar quantities of $[Au(PEt_3)_2]^+$ and $[Au(PEt_3)_3]^+$ to >193 K the two peaks at −43.3 and −38.3 p.p.m. broadened and on further warming to >213 K they collapsed to a single resonance. The addition of more PEt_3 at room temperature (r.t.) resulted only in the shift of this resonance towards the position of the free ligand.

(*ii*) $[Au(PEt_3)Cl]$ *and* PEt_3.—In order to obtain an exact phosphine : gold ratio of 2 : 1 a sample of the solid salt $[Au(PEt_3)_2Cl]$ was dissolved in dichloromethane. At 175 K the ^{31}P n.m.r. spectrum of this salt corresponds exactly to that of $[Au(PEt_3)_2][PF_6]$ at the same temperature (Table 1). This suggests very strongly that at 175 K $[Au(PEt_3)_2Cl]$ is essentially completely ionised and that the observed spectrum is due to $[Au(PEt_3)_2]^+$. Conductivity data (Table 3) also indicate that the chloride salt is ionic at 195 K in contrast to silver salts of the type $[AgL_2Cl]$ which have a very low equivalent conductivity under similar conditions.[11]

TABLE 1

Phosphorus-31 parameters for gold(I) phosphine and phosphite complexes

	δ(PEt_3)	δ[$P(OEt)_3$]	^3J(P–P)/ Hz
$[Au(PEt_3)_2][PF_6]$	−43.3		
$[Au(PEt_3)_3][PF_6]$	−38.3		
$[Au(PEt_3)_4][PF_6]$	5.7		
$[Au(PEt_3)\{P(OEt)_3\}_3][PF_6]$	3.4	−125.4	77
$[Au(PEt_3)_2\{P(OEt)_3\}_2][PF_6]$	3.2	−122.9	93
$[Au(PEt_3)_3\{P(OEt)_3\}][PF_6]$	−0.7	−120.0	100
$[Au(PEt_3)Cl]$	−29.0		
$[Au\{P(OEt)_3\}Cl]$		−122.4	
$[Au\{P(OEt)_3\}_4][PF_6]$		−126.0	

All spectra were measured in $CH_2Cl_2 : CD_2Cl_2$ (1 : 1) at 175 K. Chemical shifts were measured relative to an external PEt_3 reference but are quoted as positive to high field of 85% H_3PO_4 taking PEt_3 as being 19.1 p.p.m. upfield of this primary standard.

At 306 K the ^{31}P chemical shift of $[Au(PEt_3)_2]Cl$ is to low field of the value found at 175 K, whereas that of $[Au(PEt_3)_2][PF_6]$ is to high field of the 175 K value. There are a number of possible explanations of this and it is not possible to choose the correct one on the basis of our data. Anion co-ordination cannot be ruled out, and is responsible for AgL_2X having a lower ^{31}P chemical shift when X = Cl than when X = PF_6.[11] Alternative possibilities which seem more likely for the gold complexes are that equilibria such as (1) and (2) do not lie

$$[Au(PEt_3)_2]Cl \rightleftharpoons [Au(PEt_3)Cl] + PEt_3 \qquad (1)$$

$$2[Au(PEt_3)_2]Cl \rightleftharpoons [Au(PEt_3)_3]Cl + [Au(PEt_3)Cl] \qquad (2)$$

entirely on the side of $[Au(PEt_3)_2]Cl$ at 306 K. At 175 K the ^{31}P n.m.r. spectrum of a 1 : 1 mixture of $[Au(PEt_3)_2]Cl$ and $[Au(PEt_3)Cl]$ shows sharp peaks at −43.3 and −29.0 p.p.m. due to these species. The reactions represented by (1) and (2) therefore take place slowly at 175 K compared to the n.m.r. time scale. It may be concluded that the positions of the equilibria lie well to the left at this temperature, or more than one ^{31}P n.m.r. resonance would have been observed for the solution of $[Au(PEt_3)_2]Cl$ alone. At 306 K the 1 : 1 mixture of $[Au(PEt_3)_2]Cl$ and $[Au(PEt_3)Cl]$ gives rise to a single peak at −33.9 p.p.m. which is significantly different in position from the mean value of the shifts of the individual species at this temperature (Table 2).

TABLE 2

Temperature variation of ^{31}P chemical shifts for some PEt_3 complexes

	δ *			
Complex	306 K	213 K	193 K	175 K
$[Au(PEt_3)Cl]$	−31.09	−29.91	−29.41	−28.97
$[Au(PEt_3)_2Cl]$	−41.51	−43.63	−43.59	−43.31
$[Au(PEt_3)_2][PF_6]$	−46.06	−44.26	−43.78	−43.60

* Apart from temperature, the conditions of measurement are as in Table 1.

This observation may be accounted for in terms of a shift in the position of equilibrium for (1) or (2) to the left on addition of $[Au(PEt_3)Cl]$, and provides some support for the suggestion that (1) or (2) or both do operate. The conductivity data given in Table 3 are certainly compatible with this explanation.

TABLE 3

Equivalent conductivity [a] (S cm^2 equiv.$^{-1}$)

	10^{-2} equiv. l^{-1}		10^{-3} equiv. l^{-1}	
Complex	303 K	195 K	303 K	195 K
$[Au(PEt_3)_2][PF_6]$	32.6	12.2	41.7	17.1
$[Au(PEt_3)_2Cl]$	15.1	10.9	23.7	11.1
$[Ag\{P(C_7H_7)_3\}_2][PF_6]$		10.0 [b]	60.0 [b]	14.0 [b]
$[Ag\{P(C_7H_7)_3\}_2Cl]$	0.2 [b]			

[a] Measured in AnalaR dichloromethane in a cell with platinum electrodes calibrated with 0.01N KCl (aq). [b] Ref. 11.

Addition of 1 and 2 mol of PEt_3 to the solution of $[Au(PEt_3)_2]Cl$ at 175 K gave respectively $[Au(PEt_3)_3]^+$ and $[Au(PEt_3)_4]^+$ as in the case of the $[PF_6]^-$salt. The addition of more PEt_3 then led to the appearance of a singlet peak at 19.1 p.p.m. due to the free ligand.

(*iii*) $[Au(PEt_3)_2][PF_6]$ *and* $P(OEt)_3$.—The use of two different phosphorus ligands means that coupling-constant as well as chemical-shift data can be used to provide evidence about the co-ordination number of gold(I) complexes in solution. The approach is similar to that used previously by Tolman to investigate related nickel(0) systems.[13] At 175 K the addition of 1 mol of $P(OEt)_3$ to a dichloromethane solution of $[Au(PEt_3)_2]^+$ gives rise to a ^{31}P n.m.r. spectrum showing singlet peaks at −43.3 and −38.3 p.p.m., which may be respectively assigned to $[Au(PEt_3)_2]^+$ and $[Au(PEt_3)_3]^+$. Resonances at 3.4 [q, ^3J(P–P) 77] and −125.4 p.p.m. [d, ^3J(P–P) 77 Hz] must be due respectively to the PEt_3 and $P(OEt)_3$ ligands in the complex $[Au(PEt_3)\{P(OEt)_3\}_3]^+$. A further weaker resonance at 3.2 p.p.m. [t, ^3J(P–P) 93 Hz] is clearly due to co-ordinated PEt_3 in a complex of the type $[Au(PEt_3)_n\{P(OEt)_3\}_2]^+$ ($n = 1$ or 2), but the corresponding $P(OEt)_3$ resonance was too weak to observe using a 1 : 1 ratio of $[Au(PEt_3)_2][PF_6]$ to $P(OEt)_3$. On addition of another mol of phosphite, however, this resonance [−122.9 p.p.m., t, ^3J(P–P) 93 Hz] becomes clearly visible establishing that the complex is $[Au(PEt_3)_2\{P(OEt)_3\}_2]^+$. Although the use of Fourier-transform spectroscopy does not allow exact integration to be carried out, it is obvious from the spectra that at this higher concentration of $P(OEt)_3$ the amount of $[Au(PEt_3)_2\{P(OEt)_3\}_2]^+$ present in solution is much greater than that of $[Au(PEt_3)\{P(OEt)_3\}_3]^+$. Increasing the phosphite : gold ratio beyond 2 : 1 (up to 5 : 1) has little effect on the spectrum already described except for the appearance of a new peak at −137.6 p.p.m. This has an almost identical chemical shift to that recorded for a CD_2Cl_2 solution of $P(OEt)_3$ at 175 K (−138.0 p.p.m.) and is assigned to the presence of the free phosphite. It should be emphasized that the low-temperature limiting spectrum for solutions containing mixed phosphine(phosphite) gold complexes is only just reached at 175 K. Even on warming to 183 K a significant broadening of the peak due to free $P(OEt)_3$ is observed.

The complex $[Au(PEt_3)_3\{P(OEt)_3\}]^+$ was not detected by ^{31}P n.m.r. spectroscopy in any of the experiments involving the addition of $P(OEt)_3$ to $[Au(PEt_3)_2][PF_6]$. On adding 2 mol of PEt_3 to a dichloromethane solution containing $[Au(PEt_3)_2][PF_6]$ and an excess of $P(OEt)_3$ (3 mol) at 175 K, however, this complex was readily identified as being present by the observation of a doublet [−0.7 p.p.m., ^3J(P–P) 100 Hz] in the phosphine region and a quartet [−120.0 p.p.m., ^3J(P–P) 100 Hz] in the phosphite region.

It is interesting that the product distribution of the mixed phosphine(phosphite) gold complexes is not dissimilar to that observed by Tolman for the related nickel(0) complexes.[13] Thus $NiL_2L'_2$ was found to be the most favoured product (L = phosphine, L′ = phosphite) for a number of different L and L′ ligands with $NiLL'_3$ the next most favoured. This was ascribed as being principally due to electronic factors and the same is probably true of the gold system, since $P(OEt)_3$ has a smaller cone angle than PEt_3,[14] and there therefore seem to be no steric reasons which would account for the observed product distribution. It should be noted that, in contrast to the gold(I) system, the equilibria between the various mixed nickel complexes and the free ligands are in general established slowly on the n.m.r. time scale even at r.t. This presumably reflects the slower rate of dissociation of the four-co-ordinate nickel complexes than their gold counterparts.

(*iv*) $[Au(PEt_3)Cl]$ *and* $P(OEt)_3$.—Addition of $P(OEt)_3$ in 0.5 : 1 mol ratio to a solution of $[Au(PEt_3)Cl]$ at 175 K gives rise to a new singlet resonance at −43.3 p.p.m. which may be assigned to $[Au(PEt_3)_2]^+$. The only other PEt_3-containing species present is unchanged $[Au(PEt_3)Cl]$. A singlet peak in the phosphite region at −122.4 p.p.m. is most probably due to $[Au\{P(OEt)_3\}Cl]$ although we were not able to synthesise this complex for comparative purposes. Addition of another 0.5 mol of $P(OEt)_3$ gives a new peak in the phosphite region at −126.0 p.p.m. which we assign to a species of the type $[Au\{P(OEt)_3\}_n]^+$ where n is most probably 4, since this ' pure ' phosphite complex is the only one observed even when much higher phosphite : complex ratios are used. At a 1 : 1 mol ratio of $P(OEt)_3$ to $[Au(PEt_3)Cl]$ a peak due to unchanged $[Au(PEt_3)Cl]$ is still present in the spectrum. On increasing the ratio to 2 : 1, however, the $[Au(PEt_3)Cl]$ peak vanishes from the spectrum; $[Au(PEt_3)_2]^+$ is still present as a major species and resonances due to $[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$ ($n = 1$ or 2) now also become apparent. There are no peaks due to free ligand and these do not appear until the $P(OEt)_3$: $[Au(PEt_3)Cl]$ ratio is increased beyond 3 : 1. A peak due to free $P(OEt)_3$ then appears. The principal metal-containing species present in solution at these higher phosphite concentrations is $[Au(PEt_3)\{P(OEt)_3\}_3]^+$.

In none of the spectra described in this section or in (*iii*) were resonances observed which could have been assigned to the presence of species of the type $[Au(PEt_3)_x\{P(OEt)_3\}_y]^+$ where $x + y < 4$. Indeed the only phosphite-containing complex with a co-ordination number lower than four which we identified in the series of experiments was $[Au\{P(OEt)_3\}Cl]$. The marked preference of $P(OEt)_3$ to be present in four-co-ordinate gold(I) complexes in solution as compared to PEt_3 could be attributed to its lower steric requirements or to electronic factors. It seems likely that both are important.

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded in the pulse mode on a Varian XL-100 instrument at 40.5 MHz using CD_2Cl_2 as a deuterium lock with proton decoupling. The complexes $[Au(PEt_3)_2][PF_6]$ [9] and $[Au(PEt_3)Cl]$ [15] were prepared by literature methods; PEt_3 and $P(OEt)_3$ were used as purchased.

Bis(triethylphosphine)gold(I) *Chloride*.—The complex $[Au(PEt_3)Cl]$ (1.059 g, 3 mmol) was dissolved in dichloromethane (5 cm^3) and a solution of PEt_3 (0.354 g, 3 mmol) was added. The mixture was shaken vigorously for 0.5 h and the solvent was removed *in vacuo*. The white product was recrystallised from ethanol to give white crystals (Found: C, 31.05; H, 6.35. $C_{12}H_{30}AuClP_2$ requires C, 30.75; H, 6.40%).

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