289. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. III[1]). Preparation and Solution Studies of Complexes [MX(1)] (M = Cu, Ag and Au; X = Anionic Ligand; 1 = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene)

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(22. IX. 76)

Summary. The preparation of monomeric complexes [MX(**1**)] is reported where M = Cu, Ag, Au; X = I, Cl, NO_3, BF_4 and **1** = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene. The solution structure of the complexes is discussed on the basis of molecular weight, conductivity and NMR. measurements. In acetonitrile and nitromethane, the nitrate and fluoroborate complexes exist as ionic species $[M(\mathbf{1})]^+X^-$ whereas the halo-complexes are present as equilibrium mixtures of 'covalent' and 'ionic' forms. All the complexes are associated in CH_2Cl_2-solutions. The values of $^1J_{^{107}Ag-^{31}P}$ show that this association in $[Ag(NO_3)(\mathbf{1})]$ and $[Ag(BF_4)(\mathbf{1})]$ is best described in terms of ion-pairing while that for species $[AgX(\mathbf{1})]$ (X = Cl, Br and I) is mainly 'covalent' in nature. Evidence is presented for the formation of the complex ion $[Ag(CH_3CN)_n(\mathbf{1})]^+$ in acetonitrile solution.

Introduction. – The chemistry of tertiary phosphine and ditertiaryphosphine complexes of copper(I), silver(I) and gold(I) is characterised by the wide range of stoichiometric and structural types obtained [1–3]. This results from the widespread occurrence of such effects as bridging by anionic ligands and by diphosphines [4–9], the formation of cluster compounds [4] [10] and the formation of a variety of ionic complexes based on the cation $[ML_4]^+$ in which the anion may also contain the coinage metal [4] [5] [11] [12] (L_2 = two monodentate phosphines or a bidentate diphosphine; M = Cu, Ag, Au).

Comparatively few of the complexes with stoichiometry 'MXL_2' (X = anionic ligand) have simple monomeric structures and only in isolated cases [13] has it been firmly established whether these mononuclear species are 2-coordinate ionic species $[ML_2]X$ or 3-coordinate covalent complexes $[MXL_2]$. Particularly with monodentate phosphines, the interpretation of solution data for 'MXL_2' species is difficult since, in addition to equilibria between ionic and covalent forms (eq. (1)), equilibria of the type shown in eq. 2–5 can also occur [12] [14].

$$[MXL_2] \rightleftharpoons [ML_2]^+ + X^- \quad (1)$$

$$[MXL_2] \rightleftharpoons [MXL] + L \quad (2)$$

$$2\,[MXL_2] \rightleftharpoons [MXL_3] + [MXL] \quad (3)$$

$$2\,[MXL_2] \rightleftharpoons [ML_4]^+[MX_2]^- \quad (4)$$

$$2\,[MXL_2] \rightleftharpoons [M_2X_2L_4] \quad (5)$$

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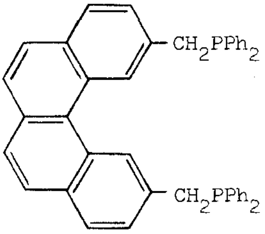
[1]) Part II: See [1].

This has, for example, given rise to considerable disagreement over the structure of bis(triphenylphosphine)gold(I)-halides in solution, these complexes being variously reported as covalent by one group of workers [10a] and as ionic by others [14] [15] whilst a third group [16] has found evidence for the existence of both ionic and covalent forms.

As a result of the irregular occurrence of monomeric 'MXL_2' species and of the difficulty in interpreting solution data for such complexes there exist few systematic studies of the factors affecting the ionic character of the M-X bond in these systems, with the exception of a study by *Muetterties* & *Alegranti* [17]. These workers were able to examine the effects of changing X in a series of complexes $[AgX((p\text{-tol})_3P)_2]$ in methylene chloride solutions at −80°, a temperature at which exchange reactions have essentially ceased. Whilst the use of chelating diphosphines, LL, would also be expected to minimise complications due to phosphine exchange and disproportionation reactions (eq. 2–4), it is rare [2] for such ligands to give monomeric complexes [MX(LL)] due to their pronounced tendency towards the formation of diphosphine-bridged and $[M(LL)_2]^+$ cationic complexes.

In the course of our studies of sterically-constrained ligands, we have prepared a diphosphine ligand, 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**), the properties of which [18] seem well suited for the preferential formation of monomeric 2- and 3-coordinate species of the types **2** and **3** respectively.



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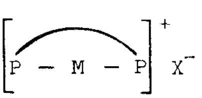

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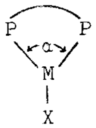

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A linear arrangement of metal and phosphorus atoms, as occuring in **2**, is present in complexes $[MX_2(\mathbf{1})]$ (M = Ni, Pd and Pt; X = halide) [19]. There is also evidence [19] suggesting that the comparatively bulky and rigid backbone of ligand **1** renders it far less prone to form diphosphine bridged oligomers than are analogous diphosphines with more flexible backbones. Finally, examination of molecular models indicate that:

1) it is not possible to chelate two molecules of ligand **1** to one metal atom to form species of the type $[M(\mathbf{1})_2]^+$ and

2) trigonal planar structures with P-M-P bond-angles of not less than 120° should also be possible, although these might require distortions from normal values of bond lengths and angles.

We report here the preparation of a series of complexes [MX(**1**)] (M = Cu, Ag, Au; X = I, Cl, NO$_3$, BF$_4$) the solution properties of which are discussed in terms of the nature of the M-X bond.

Results and Discussion. – The complexes [MX(**1**)] were obtained as colourless crystalline solids either by direct reaction of **1** with the corresponding metal salt or by ligand exchange reactions from analogous triphenylphosphine complexes. Their analytical data are given in Table 1. The solid complexes are neither light- nor air-sensitive and are, for the most part, moderately soluble in methylene chloride, acetonitrile and benzonitrile and sparingly soluble in acetone, chlorobenzene and nitromethane, the halide complexes being generally the least soluble species.

Table 1. *Analytical data for the complexes* [MX(**1**)]

Complex		Dec.p. (°C)	Elemental Analysis % Found (% Calculated)					Molecular[a] weight Found (Calculated)
			C	H	P	X	N	
M = Cu, X =	I	>250	64.55 (64.83)	4.22 (4.20)	7.50 (7.60)	15.47 (15.57)		824 (815)
	Cl	>250	72.35 (73.02)	4.73 (4.74)	8.38 (8.50)	5.18 (4.90)		731 (724)
	NO$_3$	>250	70.89 (70.46)	4.63 (4.54)	8.34 (8.26)		1.77 (1.87)	743 (750)
M = Ag, X =	I	>250	62.05 (61.49)	4.09 (3.99)	6.86 (7.21)	14.61 (14.76)		726 (860)
	Cl	slow dec. >170	68.72 (68.81)	4.58 (4.46)	8.12 (8.07)	4.77 (4.62)		745 (768)
	NO$_3$	>250	66.47 (66.51)	4.37 (4.31)	7.78 (7.80)		1.67 (1.76)	[b]
	BF$_4$	slow dec. >230	64.89 (64.50)	4.31 (4.18)	7.18 (7.56)			811 (819)
M = Au, X =	I	>250	55.54 (55.71)	3.77 (3.61)	6.36 (6.53)	13.27 (13.38)		[b]
	Cl	>250	61.76 (61.66)	4.13 (4.00)	7.07 (7.23)	4.36 (4.14)		872 (857)
	NO$_3$	slow dec. >210	59.73 (59.80)	3.96 (3.88)	7.12 (7.01)		1.75 (1.58)	872 (884)

[a] Measured by vapour phase osmometry in methylene chloride solution.
[b] Insufficient solubility precluded measurement.

An X-ray study of complexes [MCl(**1**)] (M = Cu, Ag and Au) [20] shows that, in the solid state, the metal centres are three-coordinate with basic structures of type **3** with α-bond angles 132, 141 and 176° respectively. As pointed out [20], the widening of this bond angle is accompanied by an increase in ionic character of the M-Cl bond.

The solution structures of the complexes were investigated by conductivity and NMR. measurements and the results are discussed below.

Conductivity Studies. – Wherever possible, conductivities were measured both in acetonitrile and in nitromethane solutions and, when the solubility of the complexes and the magnitude of their specific conductances permitted, molar conductance values were obtained at a number of different concentrations in order to test whether the solutions obeyed *Onsager*'s law [21]. These results are presented in Tables 2 and 3 and shown graphically in Fig. 1 and 2.

Table 2. *Conductivity data for complexes* [MX(**1**)], *in acetonitrile solution, at 25°*[a])

[CuI(**1**)]		[Cu(NO$_3$)(**1**)]		[AgCl(**1**)		[Ag(NO$_3$)(**1**)]		[Ag(BF$_4$)(**1**)		[AuCl(**1**)]		[Au(NO$_3$)(**1**)]	
Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$
20.2	0.0502	122.2	0.0501	18.4	0.0318			132.5	0.0630	83.0	0.0309	124.1	0.0508
29.6	0.0328	125.3	0.0448	22.4	0.0246	108.4	0.0490	132.8	0.0549	87.4	0.0253	127.9	0.0454
45.2	0.0207	128.4	0.0401	30.7	0.0174	110.7	0.0438	133.2	0.0446	101.5	0.0179	130.8	0.0406
77.3	0.0104	130.6	0.0335	33.4	0.0127	115.6	0.0392	134.8	0.0388	113.8	0.0126	133.8	0.0320
102.8	0.0073	133.2	0.0281	48.3	0.0090	117.2	0.0328	133.9	0.0315	123.8	0.0089	142.5	0.0248
		135.3	0.0217	71.8	0.0064	119.6	0.0274	135.9	0.0244			146.1	0.0143
		140.1	0.0138			120.7	0.0213	134.2	0.0173				
						119.1	0.0134	134.1	0.0122				
						119.6	0.0095						

[a]) Λ_m-values are given in ohm^{-1}cm^{2}mol^{-1}. The normal range of Λ_m-values for 1:1 electrolytes at 1.0×10^{-3}M solutions ($\sqrt{c}$ = *ca.* 0.031) is 120–160.

Table 3. *Conductivity data for Complexes* [MX(**1**)], *in nitromethane solution, at 25°*[a])

[CuI(**1**)]		[CuCl(**1**)]		[AgCl(**1**)]		[Ag(BF$_4$)(**1**)]		[AuI(**1**)]		[AuCl(**1**)]		[Au(NO$_3$)(**1**)]	
Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$	Λ_m	$\sqrt{c}$
4.9	0.0317	7.2	0.0312	10.3	0.0311	80.4	0.0505	30.1	0.0219	52.2	0.0505	78.1	0.0501
						83.1	0.0391			55.3	0.0450	80.0	0.0388
						85.0	0.0303			58.9	0.0391	81.3	0.0301
						87.2	0.0214			63.4	0.0348	83.0	0.0213
						89.9	0.0135			66.5	0.0303	85.7	0.0135
										68.6	0.0270		
										72.1	0.0209		

[a]) Λ_m-values are given in ohm^{-1}cm^{2}mol^{-1}. The normal range of Λ_m-values for 1:1 electrolytes at 1.0×10^{-3}M solutions ($\sqrt{c}$ = *ca.* 0.031) is 75–95.

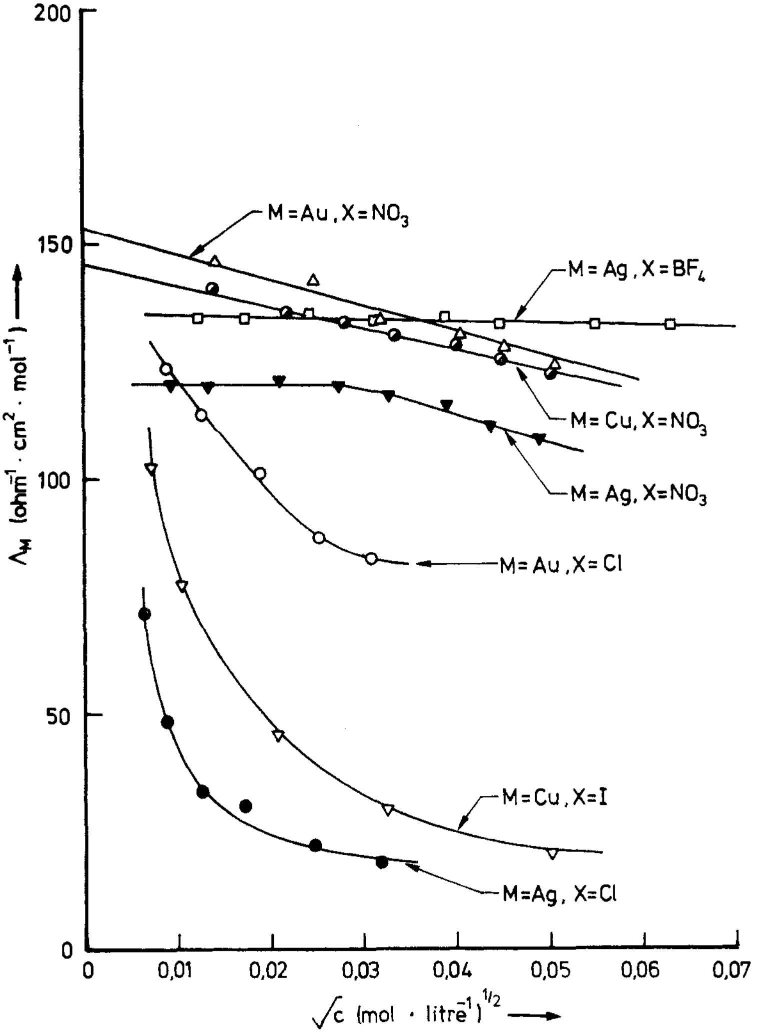

Fig. 1. *Concentration-dependence of the molar conductivity of complexes* [MX(**1**)] *in acetonitrile solution at 25°*. (The normal range of Λ_m-values for 1:1 electrolytes at 1.0×10^{-3} M ($\sqrt{c}$ = *ca.* 0.031) is 120–160 ohm^{-1}cm^{2}mol^{-1} [21])

It is apparent that, for all three metals, the nitrate and fluoroborate complexes behave as 1:1 electrolytes in acetonitrile and nitromethane whereas the halide complexes all show some degree of association, even in these ionising solvents. In acetonitrile solutions, the complexes [$Cu(NO_3)$(**1**)] and [$Au(NO_3)$(**1**)] show linear *Onsager* plots with slopes of the magnitude expected for 1:1 electrolytes whilst complexes [$Ag(NO_3)$(**1**)] and [$Ag(BF_4)$(**1**)] have molar conductances at 1×10^{-3} M which lie within the expected range for 1:1 electrolytes. However, the *Onsager* plot for

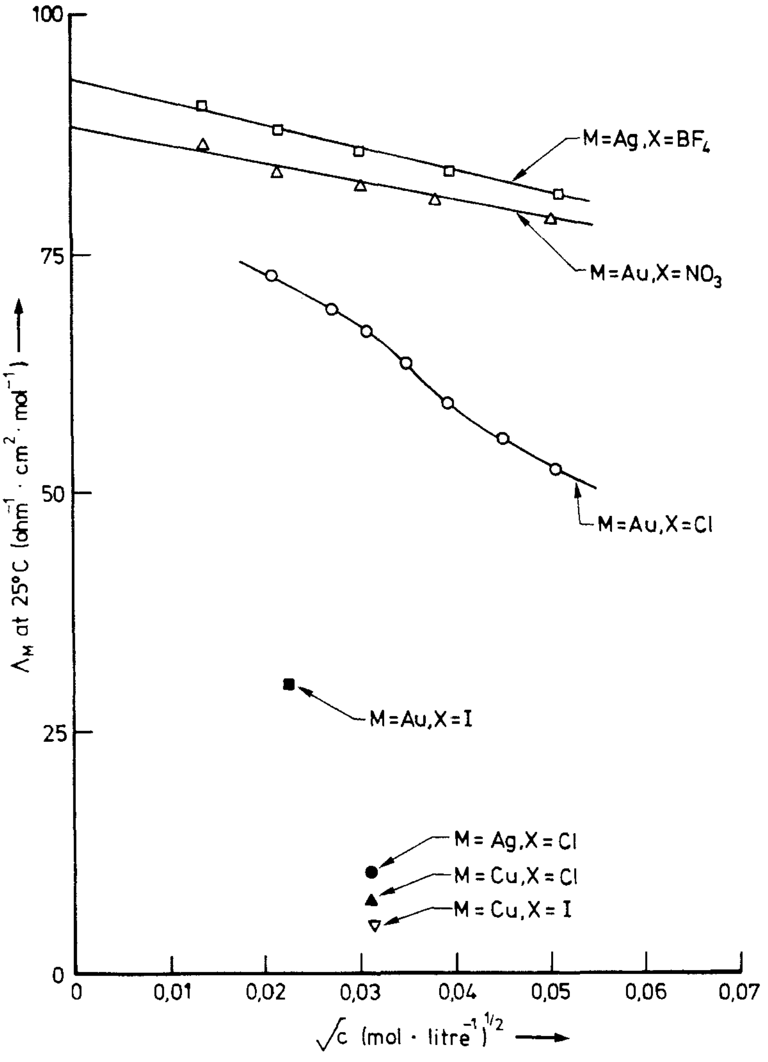

Fig. 2. *Concentration-dependence of the molar conductivity of complexes* [MX(**1**)] *in nitromethane solution at 25°*. (The normal range of Λ_m-values for 1:1 electrolytes at 1.0×10^{-3} M ($\sqrt{c}$ = *ca.* 0.031) is 75–95 ohm^{-1}cm^{2}mol^{-1} [21])

[Ag(BF$_4$)(**1**)] and for [Ag(NO$_3$)(**1**)] at concentrations less than *ca.* 1×10^{-3} M apparently shows a slope close to zero. Based on the observation of a normal slope for the *Onsager* plot of the silver fluoroborate complex in nitromethane solution (Fig. 2) and on the value of its silver-phosphorus coupling constant (see below), it is suggested that the unusual plots obtained for acetonitrile solutions of [Ag(BF$_4$)(**1**)] and [Ag(NO$_3$)(**1**)] are the result of the formation of a complex [Ag(CH$_3$CN)$_n$(**1**)]$^+$ where n is probably 2. The ability of acetonitrile to form complexes with transition metals is well known and there have been previous reports of unusual conductivity behaviour resulting from such complex formation [21]. Presumably, in this case, the formation of an acetonitrile complex of the $[Ag(\mathbf{1})]^+$ ion results in very effective shielding of the charge on the silver atom from electrostatic interaction with the counter ion so that such interactions are very weak even at comparatively high concentrations and are little affected by dilution. It is further evident that the ability of acetonitrile to compete with the anion for the available coordination sites about the silver atom in this way decreases in the order $BF_4 > NO_3 > Cl$.

Given the rare occurrence of complexes containing coordinated fluoroborate [22], the observation that $[Ag(BF_4)(\mathbf{1})]$ is a 1:1 electrolyte is not unexpected. However, the observation that the copper and silver nitrate complexes also apparently exist as ionic species in acetonitrile solution is worthy of comment since the analogous species $[Cu(NO_3)(R_3P)_2]$ (R = phenyl [23], cyclohexyl [24]) have been shown to have covalent, pseudotetrahedral structures in the solid state and it has been suggested [17] that $[Ag(NO_3)((p\text{-tol})_3P)_2]$ exists as a mixture of both ionic and covalent forms in methylene chloride solution. The observation that the nitrato-complexes of ligand **1** are completely dissociated in acetonitrile solutions is likely to be due to the strongly ionising and coordinating nature of this solvent. Unfortunately, due to the instability towards oxidation of $[Cu(NO_3)(\mathbf{1})]$ in nitromethane solution and the insolubility of $[Ag(NO_3)(\mathbf{1})]$ in the same solvent, it was not possible to test whether the observed ionisation of these complexes is a specific effect of the acetonitrile.

The copper and silver halide complexes gave low, but measureable, molar conductance values and, in acetonitrile solutions, showed *Onsager* plots characteristic of strongly-associated solutes which only approach complete dissociation at very low concentrations (Fig. 1). Since both acetonitrile and nitromethane are solvents of high dielectric constant (36.2 and 35.9 respectively) ion pairing must be considered as unlikely at the concentrations employed in these studies. It is therefore concluded that the associated states of the copper and silver halide complexes involve a high degree of covalency, *i.e.* that these complexes exist as equilibrium mixtures of covalent and ionic forms (analogous to that shown in eq. 1) in which the covalent form predominates at concentrations greater than *ca.* 1×10^{-4}M. Similarly it may be inferred that significant amounts of both ionic and covalent forms exist in acetonitrile and nitromethane solutions of $[AuCl(\mathbf{1})]$ for, whilst molar conductance values for this complex are only slightly lower than those considered normal for 1:1 electrolytes, the non-linearity of its *Onsager* plots in both solvents indicates a significant degree of association. Such a conclusion is in agreement with that reached by *Westland* [16] for the analogous complex $[AuCl(Ph_3P)_2]$. Due to their very low solubilities it was not possible to construct *Onsager* plots for the silver and gold iodide complexes of ligand **1**. However, the single molar conductance measurement obtained for a saturated nitromethane solution of the latter (*ca.* 5×10^{-4}M) suggests that the covalent form is much more dominant for this complex than for $[AuCl(\mathbf{1})]$ at a comparable concentration (Fig. 2). The observation that the gold halide complexes are generally more ionic than their copper and silver analogues is consistent with the well-established observation [1] that gold(I) shows a greater tendency towards 2-coordination than do copper(I) and silver(I).

NMR. Studies. – ^{31}P-NMR. data for the complexes [MX(**1**)] are shown in Table 4. Single line spectra were observed for the copper and gold complexes whilst species [AgX(**1**)] gave the expected four resonances resulting form coupling of ^{31}P to the two spin-active isotopes of silver (^{107}Ag, I = 1/2, natural abundance 51.82%; ^{109}Ag, I = 1/2, natural abundance 48.18%; for convenience only the values of the ^{107}Ag–^{31}P coupling constant are considered in the following discussion, but the same arguments naturally apply to the ^{109}Ag–^{31}P couplings). The copper and silver halide complexes and [Cu(NO_3)(**1**)] showed broad resonances at room temperature, sharper signals being observed at lower temperatures.

Table 4. *^{31}P-NMR. parameters for the complexes* [MX(**1**)]

M	X	Solvent	Temp. (°K)	δ (ppm)	$^1J_{^{107}Ag-^{31}P}$ (Hz)	$^1J_{^{109}Ag-^{31}P}$ (Hz)
Cu	I	CD_2Cl_2	173	− 4.66		
	Cl	CD_2Cl_2	173	− 4.54		
	NO_3	CD_2Cl_2	173	− 4.50		
Ag	I	$CDCl_3$	250	+ 2.57	378	437
	Cl	$CDCl_3$	250	+ 6.25	411	474
		CD_3CN[a]	243	+ 6.82	426	493
	NO_3	$CDCl_3$	293	+ 7.98	461	536
		CD_3CN[b]	293	+ 8.07	460	533
	BF_4	$CDCl_3$	293	+12.06	515	593
		CD_3CN[b]	293	+ 7.99	466	537
		CH_3NO_2	293	+12.01	510	589
Au	I	$CDCl_3$	293	+38.07		
	Cl	$CDCl_3$	293	+40.91		
	NO_3	$CDCl_3$	293	+42.98		

[a] At a concentration of *ca.* 1×10^{-3} M.

[b] The δ- and J-values are unchanged at 250°K.

In contrast to the behaviour of the complexes [MX(**1**)] in acetonitrile and nitromethane solutions, in which all show some degree of dissociation into ionic species, it is apparent from the molecular weight results obtained in methylene chloride (Table 1) that in this solvent (and presumably also in deuteriochloroform) all of the complexes are not dissociated. It has been established [17] that $^1J_{^{107}Ag-^{31}P}$ coupling constants provide a valuable diagnostic tool for the determination of coordination numbers of the silver atom in solution. Thus, [AgCl((*p*-tol)$_3$P)$_2$] shows a J-value of 378 Hz while [Ag((*p*-tol)$_3$P)$_2$][PF_6] shows a J-value of 496 Hz. This decrease in coordination number is also accompanied by a shift to low field of $\delta_{^{31}P}$, *i.e.*, from 21.4 to 33.4 ppm.

The J-values for [AgCl(**1**)] and [Ag(BF_4)(**1**)] are 411 and 515 Hz respectively, indicating that, in CD_2Cl_2-solutions, the former compound is present in the form of a three-coordinate species while the latter compound is to be formulated as containing

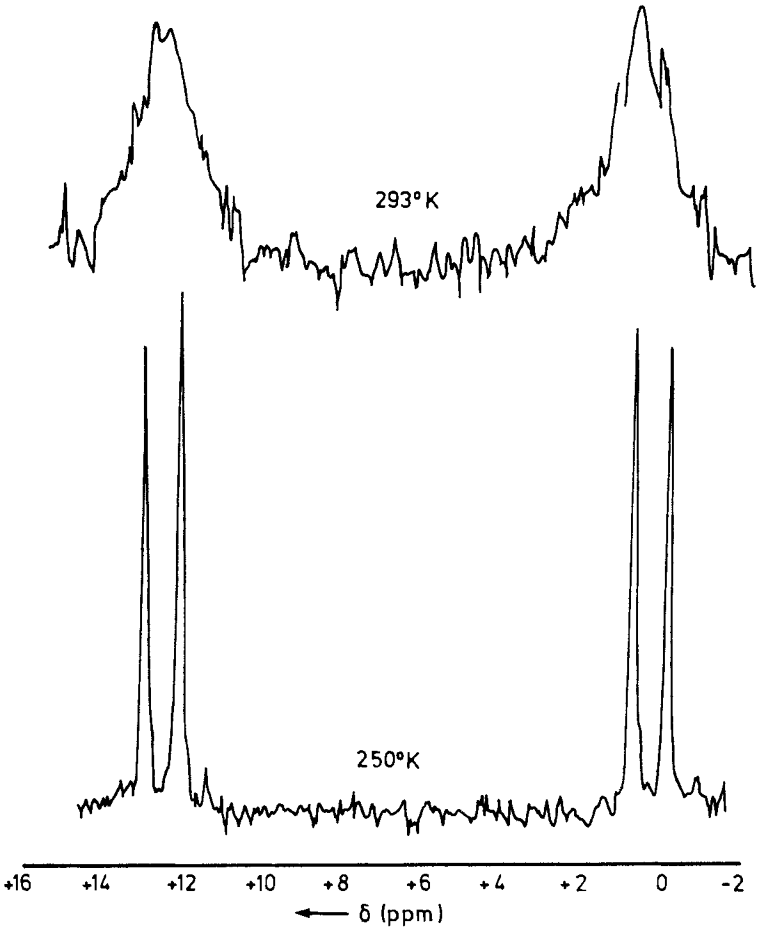

Fig. 3. *Temperature-dependence of the* ^{31}*P-NMR. spectrum of* [AgCl(**1**)]

two-coordinate silver ion-paired to the $[BF_4]^-$-anion. Their $\delta_{^{31}P}$-values, 6.25 and 12.06 ppm respectively, reflect the same trend. The similarity between the two systems extends also to the nitrato-complexes as $[Ag(NO_3)((p\text{-tol})_3P)_2]$ shows a *J*-value of 470 Hz and a δ-value of 9.4 ppm while $[Ag(NO_3)$(**1**)] shows *J*- and δ-values of 461 Hz and 8.0 ppm respectively. *Muetterties & Alegranti* [17] have suggested that the nitrate may be acting as a bidentate ligand and that this complex might be pseudo-tetrahedral in solution. In this context it is worth noting that CD_3CN-solutions of $[Ag(NO_3)$(**1**)] and $[Ag(BF_4)$(**1**)], which are likely to contain the pseudo-tetrahedral $[Ag(CD_3CN)_2$(**1**)$]^+$ cation, give δ- and *J*-parameters which are practically identical with those of $[Ag(NO_3)$(**1**)] in $CDCl_3$ (see Table 4).

Since only single resonances are observed in ^{31}P-NMR. spectra of the copper and gold complexes, it is not possible to obtain similar information as to the associated states of these species. However, we note that the order of chemical shifts observed for the silver complexes [AgX(**1**)] and $[AgX((p\text{-tol})_3P)_2]$ (*i.e.* chemical shifts move to higher fields with increasing covalency in the M-X bonds) is also observed for the gold series (see Table 4). The copper complexes, however, showed only very small coordination chemical shifts (*ca.* 5 ppm) and no conclusions can be drawn from them.

The temperature-dependence of the ^{31}P-NMR. spectra of complexes [MX(**1**)] (M = Cu and Ag; X = halide) (see Table 4 and Fig. 3) is likely to be due to the occurrence of one or more exchange processes of the types shown in eq. 1 to 5. Molecular weight determinations in CH_2Cl_2 show that, within experimental error, all the complexes are present as mononuclear species. Furthermore, a molecular weight determination on [Ag(BF_4)(**1**)] (see Table 1) gives a value corresponding to that of the undissociated species. Thus molecular weight determinations in CH_2Cl_2 are unlikely to show the occurrence of equilibria of the type shown in eq. 1. They do, however, exclude the presence of significant amounts of the species appearing on the right hand side of eq. 3, 4 and 5 (the 'product' of equilibrium 3 for complexes of ligand **1** would be a binuclear complex).

Present studies do not exclude the possibility that the equilibria occurring in solution might be due to processes shown in eq. 3 to 5 if the associated species are present only in small amounts. Steric considerations, however, indicate that exchange is more likely to occur by the reactions shown in eq. 1 and 2, the latter corresponding to the transient formation, at room temperature, of species of the type: P⁀P-M-X. The observation that [AuCl(**1**)] gives sharp spectra, which are temperature-independent, taken in conjunction with the known preference of gold(I) to give linear species of the type R_3P-Au-X and with the result of the crystal structure determination which shows a T-shaped coordination polyhedron [20], lead us to the conclusion that the line-broadening process is most likely to be associated with the structural change (**2**) $\rightleftharpoons$ (**3**).

^{1}H-NMR. data for the complexes [MX(**1**)] are shown in Table 5. These spectra were similar in general appearance to those previously reported for the complexes

Table 5. *^{1}H-NMR. parameters*[a] *for the complexes* [MX(**1**)]

Complex		1,12 ring protons δ (ppm)	Methylene protons		Temp. (°K)
			δ (ppm)	$\lvert {}^2J_{P-H}+{}^4J_{P-H}\rvert$ (Hz)	
M = Cu, X =	I	9.30	3.98	6.4	328
	Cl	9.35	3.89	6.7	328
	NO_3	9.26	3.73	6.1	298
M = Ag, X =	I	9.10	3.93	6.7	298
	Cl	9.18	3.93	5.9	328
	NO_3	9.39	4.10	[b]	328
	BF_4	9.27	4.15	[b]	328
M = Au, X =	I	9.52	4.63	7.9	298
	Cl	9.93	4.70	9.1	298
	NO_3	9.77	4.49	8.5	298

[a] In $CDCl_3$. [b] Not resolved.

trans-[MX_2(**1**)] (M = Ni, Pd, Pt; X = halide) [19], showing a complex multiplet of aromatic resonances between *ca.* 7 and 8 ppm, a separate resonance to low field of the main aromatic multiplet arising from the protons in the 1 and 12 positions of the benzo[*c*]phenanthrene ring and a resonance in the region 3.5–5.0 ppm due to the methylenic protons. The methylenic proton resonances of the copper and silver complexes, at room temperature, frequently gave unresolved broad absorptions which usually sharpened at 55° to 1:2:1 triplets. Whilst the observation of such 'virtually-coupled' triplets has often been used to infer an approximately linear P-M-P arrangement [19], we are hesitant to draw any structural conclusions from the ^{1}H-NMR. spectra of these complexes, partly in view of their temperature-dependence, which may be a result of equilibria involving different conformations of the ligand skeleton. We have found that the ^{1}H-NMR. spectra of many complexes of ligand **1** are more complicated [25] than those observed for the nickel, palladium and platinum halide complexes [19] and a separate discussion of such spectra will appear elsewhere [26].

Experimental Part. – For generalities see also [18]. Melting points were determined using a Büchi melting point apparatus and are uncorrected. ^{1}H- and ^{31}P-NMR. spectra were recorded on a *Bruker* HX 90 FT spectrometer at frequencies of 90.00 and 36.43 MHz respectively, the deuterium resonance of the deuterated solvent being used as an internal lock. ^{1}H chemical shifts are in ppm with respect to an internal TMS standard whilst the ^{31}P chemical shifts are in ppm relative to an external H_3PO_4 standard. Shifts to higher fields are denoted as negative and those to lower fields as positive. ^{31}P-NMR. spectra were obtained under conditions of broad-band ^{1}H-noise decoupling.

Conductivity measurements were made using a *Philips* model PR 9501 a.c. conductivity meter in conjunction with a *Philips* model PW 9512/01 conductivity cell of measured cell constant 0.745 cm^2. Nitromethane was dried over anhydrous calcium sulfate to give pure solvent of specific conductance 2.02×10^{-6} ohm^{-1}cm^2. Acetonitrile was distilled under nitrogen from calcium hydride and had specific conductance 5.9×10^{-7} ohm^{-1}cm^2.

Elemental analyses and molecular weight determinations were performed by the Microanalytical Laboratory of ETH Zürich.

Preparations of the complexes were carried out under a nitrogen atmosphere in dried and deoxygenated solvents, subsequent work-up and purification of the complexes being carried out in the air unless otherwise specified. Benzene, methylene chloride and acetonitrile were dried over calcium hydride and acetone was dried over anhydrous calcium sulfate. These solvents were freshly distilled under nitrogen before use. Exposure of the silver and gold complexes to direct light during synthesis, purification and storage was avoided wherever possible.

The substrates [$AuX(Ph_3P)$] (X = I, Cl, NO_3) were prepared as previously described [14] [27]. [$Cu(NO_3)(Ph_3P)_2$] was prepared by the method of *Cotton & Goodgame* [28].

[*CuI*(**1**)]. 1.9 g (10 mmol) anhydrous CuI was added to a solution of 0.62 g (1.0 mmol) **1** in 60 ml CH_2Cl_2 and the resulting mixture was stirred overnight. The excess of CuI was filtered off and the filtrate evaporated to dryness *i.V.* to give the crude product. Recrystallization from CH_2Cl_2/Me_2CO 3:2 gave colourless crystals of the pure complex, which were filtered off and dried *i.V.* Yield: 0.69 g (85%).

[*CuCl*(**1**)]. A solution of 0.34 g (2.0 mmol) $CuCl_2 \cdot 6H_2O$ in 60 ml Me_2CO was added drop-wise to a stirred solution of 1.25 g (2.0 mmol) **1** in 120 ml Me_2CO. Initially, the reaction mixture became intense green in colour (presumably due to the formation of an unstable Cu(II) complex), this colour fading towards the end of the addition and giving a dense white precipitate. When precipitation was complete, the crude product was filtered off, washed with 2 × 5 ml Me_2CO and dried i.V. Recrystallization of the crude product from CH_2Cl_2/Me_2CO 2:1 gave colourless crystals of the pure complex, which were filtered off and dried *i.V.* Yield: 0.50 g (69%, based on the assumption that 1.0 mol of **1** was oxidized to a monoxide in the reduction of Cu(II) to Cu(I)).

*[Cu(NO)₃(**1**)].* 0.194 g $[Cu(NO_3)(Ph_3P)_2]$ (0.3 mmol) were added to a stirred solution of 0.312 g (0.5 mmol) **1** in 40 ml Me_2CO. The triphenylphosphine complex rapidly dissolved. After stirring overnight, the colourless solution was evaporated to dryness *i. V.* to give a white solid. Free triphenylphosphine was removed from this crude product by washing with 40 ml Me_2CO and the resulting pure complex was dried under high vacuum. Yield: 0.20 g (87%).

*[AgI(**1**)].* 0.16 g (0.68 mmol) AgI were added to a solution of 0.43 g (0.68 mmol) **1** in 50 ml CH_3CN and the resulting suspension was stirred for 7 days at RT. The crude product was filtered off and recrystallized from hot benzonitrile to give colourless crystals of the pure complex which were dried *i. V.* Yield: 0.45 g (77%).

*[AgCl(**1**)].* 1.43 g (10 mmol) AgCl were suspended in a solution of 0.62 g (1.0 mmol) **1** in 60 ml CH_2Cl_2 and the resulting mixture was stirred overnight. Filtration of the excess of AgCl and gradual concentration of the filtrate in a stream of nitrogen gave colourless crystals of the pure complex. The crystalline complex was washed with 2 ml CH_2Cl_2 and dried at 110° *i. V.* Yield: 0.52 g (68%).

*[Ag(NO₃)(**1**)].* A solution of 0.17 g (1.0 mmol) $AgNO_3$ in 10 ml CH_3CN was added drop-wise to a stirred suspension of 0.62 g (1.0 mmol) **1** in 80 ml CH_3CN. The diphosphine rapidly dissolved leaving only traces of an undissolved white solid, which was removed by filtration. Evaporation of the filtrate to dryness *i. V.* gave the crude product as a white solid contaminated with traces of a yellow material.

The crude product was redissolved in 80 ml hot CH_3CN and the resulting yellow solution was stirred with activated charcoal and filtered through alumina. The alumina was washed with 2 × 15 ml CH_3CN and the colourless filtrate and washings were slowly concentrated in a stream of nitrogen to give colourless crystals of the pure complex. The crystalline complex was washed with 2 × 1 ml CH_3CN and dried at 70° *i. V.* Yield: 0.16 g (20%).

*[Ag(BF₄)(**1**)].* A solution of 0.265 g (1.36 mmol) $AgBF_4$ in 20 ml Me_2CO was added to a stirred solution of 0.88 g (1.40 mmol) **1** in 90 ml Me_2CO. The resulting colourless solution was concentrated *i. V.* to *ca.* 30 ml, filtered and diluted with 30 ml benzene. Slow concentration of this solution in a stream of nitrogen precipitated the crude product as a white microcrystalline solid. A second crystallization of this crude product from Me_2CO/benzene 1:1 gave colourless crystals of the pure complex which were washed with 2 × 4 ml benzene and dried *i. V.* Yield: 0.39 g (35%).

*[AuI(**1**)].* 0.100 g (0.17 mmol) $[AuI(Ph_3P)]$ was added to a stirred solution of 0.107 g (0.17 mmol) **1** in 25 ml Me_2CO. The reaction mixture was stirred overnight under nitrogen and the crude product was filtered off and washed with 2 × 5 ml Et_2O to give the pure complex as a white solid. Yield: 0.14 g (86%).

*[AuCl(**1**)].* A solution of 0.62 g (1.0 mmol) **1** in 30 ml CH_2Cl_2 was added drop-wise to a stirred solution of 0.46 g (1.0 mmol) $[AuCl(Ph_3P)]$ in 30 ml CH_2Cl_2 and the resulting colourless solution was evaporated to dryness *i. V.* to give a white glassy solid. This solid residue was extracted with 2 × 20 ml Et_2O and recrystallized from CH_2Cl_2/Me_2CO 3:4 to give the pure complex as a colourless crystalline solid. The latter was washed with 2 × 2 ml CH_2Cl_2/Me_2CO 1:1 and dried *i. V.* Yield: 0.43 g (50%).

*[Au(NO₃)(**1**)].* A solution of 0.62 g (1.0 mmol) **1** in 20 ml CH_2Cl_2 was added drop-wise to a stirred solution of 0.52 g (1.0 mmol) $[Au(NO_3)(Ph_3P)]$ in 25 ml CH_2Cl_2. The resulting solution was evaporated to dryness *i. V.* and the solid residue extracted with 2 × 20 ml Et_2O. Recrystallization from CH_2Cl_2/Me_2CO 1:1 of the white amorphous solid thus obtained gave colourless crystals of the pure complex which were washed with 2 × 2 ml CH_2Cl_2/Me_2O 1:1 and dried *i. V.* Yield: 0.38 g (43%).

The authors are indebted to the Zentenarfonds der ETH for financial support of *D.K.J.* and to Mr *H. Egli* for experimental assistance.

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