79. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions

Part XVI[1])

X-Ray Structural and ^{31}P-NMR Solution Studies of 2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrenesilver(I) Perchlorate

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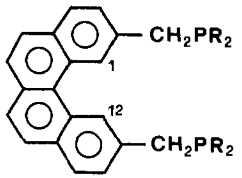
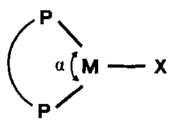
The preparation of complexes {AgX(**1c**)} (X = Cl, Br, I, NO_3, and ClO_4; **1c** = 2,11-bis(diethylphosphinomethyl)benzo[*c*]phenanthrene) is reported. The ^{31}P-NMR spectra of the above complexes were recorded and the $^1J(^{107}Ag, ^{31}P)$ values are compared with the corresponding data for related complexes. The X-ray crystal structure of [Ag(**1c**)](ClO_4) was determined. There are two crystallographically independent molecules in the unit cell each containing two-coordinate silver, the O-atoms of the perchlorate anions being outside bonding range from the central atom. The two molecules, however, show different bonding parameters: Thus for 'molecule 1' P(1)–Ag(1)–P(2) = 167.6(1)°, Ag(1)–P(1) = 2.389(3), and Ag(1)–P(2) = 2.393(3) Å, while for 'molecule 2' P(3)–Ag(2)–P(4) = 164.8(1)°, Ag(2)–P(3) = 2.377(3), and Ag(2)–P(4) = 2.378(3) Å. These differences are probably due to packing forces in the crystal lattice.

Introduction. – The ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1a**) easily forms square-planar complexes of the type [MX_2(**1a**)], where M is a divalent d^8 transition-metal ion, in which the chelating phosphine spans *trans*-positions [2]. This ligand, however, can also chelate to metal centres with other coordination numbers [3] and/or geometries in which the P–M–P bond angles may deviate significantly from 180°, *e.g.*, with Cu(I) and Ag(I) with formation of complexes of the type [MX(**1a**)] (**2**) having a distorted trigonal coordination or with Hg(II) where the complexes [HgX_2(**1a**)] exhibit a



1a R = Ph
b R = *t*-Bu
c R = Et



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pseudo-tetrahedral coordination [4] [5]. Studies of the Ag(I) complexes of the type [MX(**1**)] have been particularly rewarding, as changes in phosphine and anion have induced significant changes in coordination geometry. Extensive structural investigations of those complexes have shown that: *1)* at parity of anionic ligand X the P–Ag–P bond angle, α, is influenced by the nature of the terminal substituents on the P-atom, *e.g.*, α is 151.5° in [Ag(ClO$_4$)(**1a**)] [6] and 161.5° in [Ag(ClO$_4$)(**1b**)] [1]; *2)* at parity of chelating diphosphine changes of anionic ligand X induces significant changes in the P–Ag–P bond angle, α, *e.g.* for complexes [AgX(**1a**)] $\Delta\alpha$(ClO$_4$,Cl) = 11° [6]; *3)* the value of $\Delta\alpha$(ClO$_4$, Cl) changes with the nature of the terminal substituents on ligand **1**, *i.e.*, it is 11°, when R = Ph, **1a**, and *ca.* 20° when R = *t*-Bu [1] [5]. However, an unambiguous interpretation of these changes on the basis of existing data is not possible. Thus, the widening of the P–Ag–P bond angle on replacing the Ph ligand **1a** with that containing *t*-Bu group **1b** could be intuitively attributed to steric effects. However, it cannot, *a priori*, be excluded that these changes are, at least in part, caused by electronic effects, *e.g.*, the differences in donor capacity of the P-atom which, in one case, carries two terminal aryl groups (**1a**) and in the other two alkyl groups (**1b**). An estimate of these differences can be obtained by comparing *Tolman*'s electronic parameter, ν which for PPh$_2$Bz is 2068.4 cm^{-1} and for PBz(t-Bu)$_2$ can be calculated as being *ca.* 2060 cm^{-1} [7].

To gain additional information about the relative contribution of electronic and steric effects on structural parameters in three-coordinate Ag(I) complexes advantage was taken of a recent study describing the preparation of several alkyl-substituted ligands of type **1** [8]. Thus, the complexes [AgX(**1c**)] (**1c** = 2,11-bis(diethylphosphinomethyl)benzo[*c*]phenanthrene; X = Cl, Br, I, NO$_3$, and ClO$_4$) were prepared and the X-ray crystal structure of [Ag(**1c**)](ClO$_4$) was determined.

There has been also extensive study of the ^{31}P-NMR spectra of phosphine complexes of Ag and Hg as the coupling constants $^1J(^{107,109}\text{Ag},^{31}\text{P})$ and $^1J(^{199}\text{Hg},^{31}\text{P})$ have been related to coordination geometry in solution and to the nature of the metal-donor bond [1] [5] [6] [9]. Therefore, the ^{31}P-NMR spectra of complexes [AgX(**1c**)] were recorded and the $^1J(^{107,109}\text{Ag},^{31}\text{P})$ values are compared to those for related complexes.

Results and Discussion. – The compounds [AgX(**1c**)] (X = Cl, Br, I, NO$_3$, and ClO$_4$) are obtained by mixing the reagents in an appropriate solvent. They are colourless, air-stable but photosensitive crystalline solids.

The X-ray crystal structure of [Ag(**1c**)](ClO$_4$) shows that there are two independent molecules in the unit cell. A selection of bond lengths and angles are listed in *Table 1* and

Table 1. *A Comparison of Structural Parameters of Complexes [Ag(ClO$_4$)(**1**)]*

Ligand	Ag–P (Å)	Ag–O[a]) (Å)	P–Ag–P (°)
1a	2.417(3) 2.401(3)	2.75(1)[a]) 2.81(1)	151.5(1)
1b	2.394(2) 2.393(2)	2.91(1)[a]) 4.51(1)	161.5(1)
1c Molecule 1	2.389(3) 2.393(3)	3.05(1)[a]) 3.16(1)	167.6(1)
Molecule 2	2.377(3) 2.378(4)	3.22(1)[a]) 5.05(1)	164.8(1)

[a]) Shortest Ag–O contact.

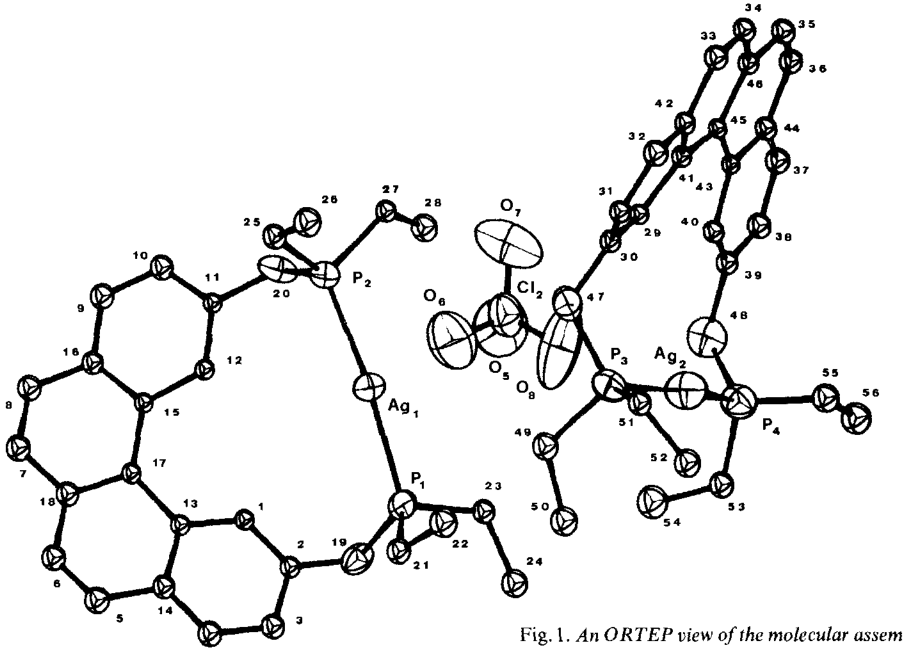

Fig. 1. *An ORTEP view of the molecular assembly in [*(**1c**)*Ag(μ-ClO$_4$)Ag*(**1c**)*]$^+$*

an ORTEP view of the two independent cationic complexes are shown in *Fig. 1*. The bonding parameters of the organic ligand fall in the range previously observed in related complexes [1–6]. An extended list of bond lengths and angles is available as supplementary material. The ClO$_4^-$ anions show high isotropic displacement parameters for the O-atoms and one of them is disordered. This disorder was not analysed in detail, as it was found that the shortest distance between any of the possible positions for the O-atoms and either of the Ag-atoms was *ca.* 5.34 Å. Indeed, this disorder may be associated with the lack of Ag–O interactions. The ClO$_4^-$ anion which is not disordered bridges the two different Ag-atoms, although the interaction with the Ag-atom of *molecule 1* is stronger than that with the Ag-atom of *molecule 2* as shown by the Ag–O contacts which are: Ag(1)–O(5) = 3.05(1); Ag(1)–O(6) = 3.16(1) for the former; Ag(2)–O(7) = 5.05(1) and Ag(2)–O(8) = 3.22(1) Å for the latter. Given these Ag–O distances and those of the related compounds [Ag(**1a**)](ClO$_4$) and [Ag(**1b**)](ClO$_4$) (see *Table 1*), one can assume that there is only a weak electrostatic interaction between anion and cation. However, it is noteworthy that as the ligands are changed from **1a** to **1c** the longer of the Ag–O distances are associated with the wider P–Ag–P angles, although this relationship is not observed, when the two independent molecules of **1c** are compared.

It is also worth pointing out that the ClO$_4^-$ anion can strongly bind to metal centres such as Ni(II), as recently shown by *House et al.* [10], who find that the Ni–O distances in a five-coordinate complex range from 2.199(6) to 2.334(7). Even accounting for the differences in ionic radii between Ni^{2+} and Ag$^+$ (*ca.* 0.4 Å [11]), our Ag–O values can be taken as indicating only weak electrostatic interactions. Thus, in this molecule the Ag$^+$ ions shows the coordination number 2 which is not very common in phosphine complexes of this metal centre [12].

The most striking feature of this structure is the difference in P–Ag–P bond angles between the two molecules (164.8(1)° and 167.6(1)°) (see *Table 1*). There are also differences in Ag–P bond lengths, but these are slight compared with the standard deviations.

To test whether the two molecules differ in any other structural feature a conformational study of the chelate ring in [Ag(**1c**)](ClO$_4$) was carried out, and the parameters obtained were compared with those for other complexes of ligands of type **1**. The chelate ring conformations of complexes of ligands of type **1** fall into two groups: *a)* those in which the P–C* (C* = CH$_2$ group joining the P-atom to benzo[*c*]phenanthrene) are arranged in a parallel fashion relative to the aromatic backbone ('conformation P'), and *b)* those in which these vectors are arranged in anti-parallel fashion ('conformation A').

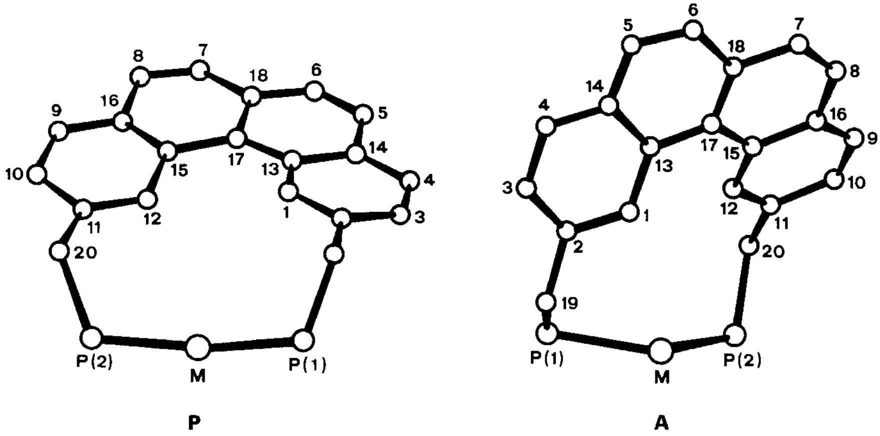

Fig. 2. *Limiting ligand conformations containing the fragment* 'M(1)'. ψ_1 = C(1)–C(2)–C(19)–P(1); ψ_2 = C(2)–C(19)–P(1)–M; ψ_3 = C(12)–C(11)–C(20)–P(2); ψ_4 = C(11)–C(20)–P(2)–M. (Molecule 1: ψ_1 = 84°, ψ_2 = –65°, ψ_3 = –49°, ψ_4 = 75°; molecule 2: ψ_1 = 81°, ψ_2 = –56°, ψ_3 = –59°, ψ_4 = 73°).

These conformations are schematically shown in *Fig. 2*. While conformation P is typical for square-planar complexes in which the ligand of type **1** spans *trans*-positions [13], conformation A has been observed in complexes such as [Ag(ClO$_4$)(**1a**)] [6] and [Ag(ClO$_4$)(**1b**)] [1]. It should be noted here that while the latter complex shows the chelate-ring conformation A, both forms of [Ag(**1c**)](ClO$_4$) show conformation P. Thus, this is the first Ag complex with a ligand of type **1** to show this conformation which is characteristic of P–M–P bond angles approaching 180° [4].

Conformational changes in complexes containing the fragment 'M(**1**)' are conveniently described by the torsion angles ψ_1, ψ_2, ψ_3, and ψ_4 (see *Fig. 2*). Representative average values for these parameters in complexes with conformation P are: 85, –70, –50, and 70°, respectively [14]. The corresponding data for the two independent molecules of [Ag(**1c**)](ClO$_4$) are listed in *Fig. 2*. As can be seen there, the corresponding ψ values differ for the two molecules, but both sets are not atypical.

Another characteristic feature of complexes of ligands of type **1** is the deviation from planarity of the benzo[*c*]phenanthrene ring caused by overcrowding at C(1) and C(12) [13] [15]. A measure of this distortion is obtained by calculating the tilt angle β between two planes **pl**$_1$ and **pl**$_2$, defined as follows: **pl**$_1$ = best plane intersecting C(9), C(10), C(11), C(12), C(15), and C(16) and **pl**$_2$ = best plane intersecting C(1), C(2), C(3), C(4), C(13), and C(14). Values of β for complexes with conformation P range from 17 to 24° [14]. The β values found in the two molecules of [Ag(**1c**)](ClO$_4$) are 18 and 22°, respectively, *i.e.*, 'normal' values. Thus, also from this point of view, these complexes are unexceptional.

It is then likely that the observed differences in bonding parameters between the two molecules originate from packing forces in the crystal lattice. This hypothesis is plausible as there is extensive structural data showing that potentials for P–Ag–P bond angle deformations are very 'soft' (see below).

The structural differences between the AgClO$_4$ complexes of the three ligands are noteworthy (see *Table 1*). The P–Ag–P bond angle, which is *ca.* 151°, in the complex with the Ph-substituted ligand, **1a**, increases to *ca.* 162°, when the *t*-Bu ligand, **1b**, is present and becomes even larger (*ca.* 165° and *ca.* 168°) in the complex with the Et-substituted ligand, **1c**. Furthermore, *a)* in [Ag(ClO$_4$)(**1a**)], the ClO_4^- anion is still coordinated, albeit weakly, to the Ag^+ ion through *two* O-atoms, *i.e.*, the silver coordination number could be described as being '2 + 2' tending towards a distorted SF$_4$-type coordination; *b)* in [Ag(ClO$_4$)(**1b**)], the ClO_4^- anion is even more weakly coordinated than in the previous complex and, even more significantly, it interacts with the Ag^+ ion only through *one* O-atom, *i.e.*, the silver coordination number could be described as being '2 + 1' tending towards a distorted ClF$_3$-type coordination; *c)* the Ag^+ ion in both independent molecules of [Ag(**1c**)](ClO$_4$) show a distorted digonal coordination, the ClO_4^- anion being outside bonding range. On the basis of these data, it is interesting to speculate as to the possible origin of the differences in terms of steric and electronic effects. These can be discussed on the basis of the following expectations: *1)* the ClO_4^- anion is a weak donor, and the extent of its interaction with the Ag^+ ion, which is expected to be largely ionic in character, will be related to the 'residual positive charge' on silver; *2)* the extent of this residual charge will be related to the donor capacity of the P-atoms which, in turn, will depend on the inductive effect of their terminal substituents; the stronger the donor capacity of the P-atom, the lower the residual charge on silver; *3)* the deviation from linearity of the P–Ag–P unit will increase with increasing Ag–O interactions: *4)* sterically crowded P-donors will prevent the 'optimal' approach of the ClO_4^- anion to silver and cause the formation of a 'more linear' P–Ag–P arrangement relative to the value it would have solely on the basis of electronic effects.

Based on these assumptions, one can deduce that if electronic effects *1* to *3* were dominant, the P–Ag–P bond angle would increase in the order:

1a < **1c** < **1b**.

On the other hand, if steric effects were dominant, the P–Ag–P bond angles would increase in the order:

1c < **1a** < **1b**.

As can be seen in *Table 1*, the observed order is:

1a < **1b** < **1c**.

Thus, while electronic effects appear to play a major role in determining bond-angles in these complexes, the reversal in position of those with ligands **1b** and **1c** must be attributed to the superimposition of a steric effect.

The bonding model developed above is fully consistent with the existing structural data on complexes of the type [MX(**1c**)] (M = Cu, Ag, and Au) [1] [4] [6] [9].

In conclusion, the main inference to be drawn from all the data mentioned above shows that P–Ag–P bond angle changes are easily induced. This could also mean that they may be significantly influenced by packing forces in the crystal lattice, as it appears to be the case in [Ag(**1c**)](ClO$_4$). Therefore, further discussion of the more detailed aspects of solid-state coordination geometries in Ag(I) complexes may have to take into account the effects of intermolecular interactions.

Table 2. *Geometrical Data for Compounds of the Type AgXL$_2$*

Complex	P$_1$–Ag–P$_2$	d(Ag–P$_i$)	d(Ag–P$_i$)a)	b)	Ref.
[Ag(NO$_3$)(PCy$_3$)$_2$]	139.0(1)	2.440(3) 2.445(4)	2.44	0.021	[16]
[AgCl(**1a**)]	140.7(1)	2.455(1) 2.412(1)	2.43	0.006	[6]
[AgBr(**1b**)]	141.6(2)	2.463(4) 2.433(5)	2.45	0.027	[1]
[Ag(Cl$_3$Sn)(**1a**)]	142.2(1)	2.451(3) 2.419(3)	2.435	0.018	[6]
[AgCl(**1b**)]	142.6(1)	2.457(2) 2.427(2)	2.44	0.012	[1]
[Ag(NO$_3$)(**1a**)]	148.6(1)	2.424(2) 2.410(2)	2.42	0.012	[6]
[Ag(ClO$_4$)(**1a**)]	151.5(1)	2.417(3) 2.401(3)	2.41	0.018	[6]
[Ag(ClO$_4$)(**1b**)]	161.5(1)	2.394(2) 2.393(2)	2.39	0.012	[1]
[Ag(ClO$_4$)(**1c**)]	164.8(1)	2.378(3) 2.377(4)	2.38	0.021	c)
[Ag{P[N(CH$_3$)$_2$]$_3$}$_2$][BPh$_4$]	166.9(1)	2.395(2) 2.393(2)	2.39	0.012	[17]
[Ag(ClO$_4$)(**1c**)]	167.6(1)	2.393(3) 2.389(3)	2.39	0.018	d)
[Ag{P(mesityl)$_3$}$_2$][PF$_6$]	179.4(5)	2.461(6)			[18]

a) d(Ag–P$_i$) = average between the Ag–P$_1$ and Ag–P$_2$ distances.
b) $\Delta = 3[\sigma(\text{Ag–P}_1) + \sigma(\text{Ag–P}_2)]$.
c) This publication (molecule 2).
d) This publication (molecule 1).

Another interesting structural feature of complexes of the type [AgX(**1**)] is the relationship between P–Ag–P bond angles and Ag–P bond lengths. While P–Ag–P bond angles in mononuclear silver bis-phosphine complexes range from 139 to 179°, the associated Ag–P bond distances vary between 2.46 and 2.38 Å. It should also be noted that in the complexes with the smaller P–Ag–P bond angles, there are significant differences in Ag–P distances within the same molecule (see *Table 2*). However, a rough comparison of such distances and their relationships to bond angles can be made by averaging the Ag–P distances for each compound and plotting the resulting values against the corresponding bond angles. While it is evident that changes in average Ag–P bond distances fall well within 'experimental error', the data, taken over the whole set of compounds, indicate a general trend: larger P–Ag–P angles correspond to shorter average Ag–P distances. The only data that fall outside this trend are those relating to $[Ag\{P(mesityl)_3\}_2]^+$ [18], where the largest P–Ag–P angle is associated with the longest Ag–P distance. Here, however, given the large 'cone-angle' [7] ($\theta = 212°$) of the ligand one might expect 'longer-than-normal' metal–donor distances due to steric repulsions between the organic substituents on the phosphines.

Table 3. *^{31}P-NMR Chemical Shifts* [ppm] *and* ^{1}J(^{107}Ag, ^{31}P) *Values* [Hz] *for Complexes [AgX*(**1**)*]*

X	**1c**	**1a**	**1b**	X	**1c**	**1a**	**1b**
Cl	$\delta = 6.7$	2.6	50.0	NO_3	$\delta = 7.2$	8.0	53.1
	$J = 447$	378	391		$J = 475$	461	444
Br	$\delta = 5.5$	6.4	52.0	ClO_4	$\delta = 9.7$	11.0	58.2
	$J = 435$	405	412		$J = 493$	503	456
I	$\delta = 5.2$	7.1	53.1	BF_4	$\delta = 10.2$	12.3	59.2
	$J = 416$	408	418		$J = 494$	511	453

The ^{31}P-NMR spectra of the complexes [AgX(**1c**)] were recorded and the ^1J(Ag,P) values are listed in *Table 3*. As can be seen there, the J values follow the same trend observed for the complexes with ligands **1a** and **1b** [1]. It is, however, clear that there is no unambiguous correlation between J values and P–Ag–P bond angles in the solid state (*cf. Tables 2* and *3*). While this discrepancy could be explained by assuming that these bond angles are different when the complexes are in solution, given the rough and qualitative nature of the realtionship between ^1J(Ag,P) and P–Ag–P bond angles, the interpretation of the NMR data must be considered as open.

Experimental. – Ligand **1c** was prepared as described in [8]. Physical measurements were carried out as described in [19]. The complexes of ligand **1c** were prepared as described below.

[AgCl(**1c**)*]*. AgCl (300 mg, 2.1 mmol) was added to a soln. of **1c** (865 mg, 2 mmol) in 25 ml of CH_2Cl_2, and the mixture was stirred at r.t. overnight. The suspension was filtered over a short *Celite* column and the soln. evaporated to a small volume *i.v.* Colourless crystals of the product were obtained by floating a layer of Et_2O over the concentrated CH_2Cl_2 soln. and storing the mixture at –2°. The crystals were filtered off and dried at r.t. under high vacuum. Yield 65%. Dec. 132°. Anal. calc. for $C_{28}H_{34}AgClP_2$: C 58.40, H 5.95, Cl 6.16; found: C 58.68, H 5.71, Cl 6.01.

[AgBr(**1c**)*]*. It was prepared and recrystallised analogously to the chloro complex. Yield 70%. Dec. 150°. Anal. calc. for $C_{28}H_{34}AgBrP_2$: C 54.22, H 5.52, Br 10.88; found: C 54.01, H 5.38, Br 13.12.

[AgI(**1c**)*]*. It was prepared as described for the corresponding chloro complex. For the crystallisation, MeOH was used instead of Et_2O. Yield 65%. Dec. 132°. Anal. calc. for $C_{28}H_{34}AgIP_2$: C 50.40, H 5.13, I 19.02; found: C 50.12, H 4.86, I 18.70.

[Ag(NO$_3$)(**1c**)*]*. It was prepared and crystallised as described for the corresponding chloro complex. Yield 63%. Dec. 120°. Anal. calc. for $C_{28}H_{34}AgNO_3P_2$: C 55.83, H 5.69; found: C 56.25, H 5.79.

[Ag(**1c**)*(ClO$_4$)*. It was prepared and purified as described for the corresponding chloro complex. Yield 59%. Dec. 110°. Anal. calc. for $C_{28}H_{34}AgClO_4P_2$: 52.56, H 5.36; found: C 52.73, H 5.51.

[Ag(**1c**)*]/BF$_4$]*. It was prepared and purified as the complex above. Yield 63%. Dec. 109°. Anal. calc. for $C_{28}H_{34}AgBF_4P_2$: C 53.62, H 5.46; found: C 53.83, H 5.61.

Collection and Reduction of X-Ray Intensity Data. These were carried out on colourless crystals of [Ag(**1c**)](ClO_4) grown from CH_2Cl_2/MeOH solns. A summary of crystal data, together with details concerning the measurements are given in *Table 4*.

Table 4. *Summary of Crystal and Intensity Measurements, Structure Solution, and Refinement*

Compound	[Ag(**1c**)]ClO_4	γ [°]	90
Formula	$C_{28}H_{34}AgClO_4P_2$	V [Å^3]	5613(3)
E wt	639.85	Z	4
Space group	$P2_1/a$	Scan mode	ω
Crystal dimension [mm^3]	0.35 × 0.30 × 0.20	Scan range [°]	0.9
Radiation	Mo*Kα*	Bkgd counts	½ of scan time at ±0.5° from the center of scan range
Diffractometer	*Nicolet P3*		
a [Å]	23.567(9)	2θ limits [°]	3.56
b [Å]	15.720(3)	Observation, total No.	15044
c [Å]	15.245(4)	No. unique data $F_o^2 > 3\sigma(F_o^2)$	4796
α [°]	90	Final No. of variables	397
β [°]	96.35(2)	Final R, R_w	0.061, 0.082

A *Nicolet-P3* automatic diffractometer was used for measurements of the cell constants; angles of 15 reflections were refined by a least-square procedure. Periodic measurements of 3 standard reflections, at an interval of 100 reflections, indicated no decay during the data collection. Intensities were corrected for *Lorentz*, polarization, and shape-anisotropy [20] effects. Atomic scattering factors and anomalous dispersion terms were taken from [21].

The structure was solved by the combination of *Patterson* and *Fourier* methods with CAOS program [22]. Refinement by least-square procedures was applied subsequently. There are two independent molecules of the complex in the asymmetric unit. When all the non-H-atoms were positioned a R factor of 0.178 was obtained, isotropic refinement gave a R value of 0.099. At this point, the fixed contribution of the H-atoms was included in the calculations with idealized position (C–H distance = 1 Å) and isotropic displacement parameter values of 5.0 Å^2. Refinement with anisotropic displacement parameters for Ag, P, C(19), C(20), C(47), and C(48) was carried out. The positions of the H-atoms were updated after refinement. Convergence was reached at $R = 0.061$ ($R_w = 0.082$).

Refinement was by full matrix, and the function minimized was $\Sigma(|F_o| - |F_c|)^2$ with weights of the type $w = (a + bF_o + cF_o^2)$ where a and b are of the order of $2F_o$ (min) and $2/F_o$ (max) [23], resp.

The final positional and displacement parameters are given in *Table 5*. Tables of displacement parameters, calculated H-atom positions and of observed and calculated structure factors are available from *F.C.* upon request.

Table 5. *Positional Parameters and Isotropic Displacement Parameters for [Ag(**1c**)ClO$_4$]*

	x	y	z	U_{eq}		x	y	z	U_{eq}
AG(1)	0.45327(4)	0.3116(1)	0.2896(1)	0.0425(3)	C(21)	0.5205(6)	0.1103(9)	0.266(1)	0.061(4)
AG(2)	0.2558(1)	–0.0017(1)	1.0038(1)	0.0625(4)	C(22)	0.4832(7)	0.086(1)	0.183(1)	0.081(5)
P(1)	0.4831(1)	0.1736(2)	0.3419(2)	0.038(1)	C(23)	0.4224(6)	0.1105(9)	0.3673(9)	0.052(3)
P(2)	0.4304(1)	0.4591(2)	0.2690(2)	0.037(1)	C(24)	0.4345(7)	0.017(1)	0.393(1)	0.070(4)
P(3)	0.3237(1)	0.0391(2)	0.9075(2)	0.047(1)	C(25)	0.4597(6)	0.5179(9)	0.1816(9)	0.057(3)
P(4)	0.2055(2)	–0.0250(2)	1.1285(2)	0.053(1)	C(26)	0.4398(7)	0.486(1)	0.089(1)	0.079(5)
Cl(1)	0.4040(2)	0.1178(2)	0.6367(3)	0.059(1)	C(27)	0.3530(5)	0.4750(8)	0.2499(8)	0.044(3)
Cl(2)	0.3353(2)	0.2442(3)	0.1242(3)	0.065(1)	C(28)	0.3235(7)	0.445(1)	0.325(1)	0.070(4)
O(1)	0.4512(5)	0.1453(8)	0.5949(7)	0.090(5)	C(29)	0.2154(5)	0.1913(8)	0.8790(7)	0.039(3)
O(2)	0.4228(7)	0.104(1)	0.727(1)	0.15(1)	C(30)	0.2586(5)	0.1727(8)	0.8272(8)	0.046(3)
O(3)	0.3801(9)	0.042(1)	0.606(1)	0.17(1)	C(31)	0.2480(5)	0.1747(8)	0.7337(8)	0.045(3)
O(41)	0.377(2)	0.187(2)	0.668(3)	0.15(2)	C(32)	0.1957(6)	0.201(1)	0.696(1)	0.062(4)
O(42)	0.3572(9)	0.168(2)	0.601(2)	0.10(1)	C(33)	0.0990(6)	0.2575(9)	0.7052(9)	0.057(3)
O(5)	0.3334(7)	0.257(1)	0.2151(8)	0.12(1)	C(34)	0.0565(6)	0.2764(8)	0.7533(9)	0.049(3)
O(6)	0.3915(6)	0.254(1)	0.105(1)	0.15(1)	C(35)	0.0101(6)	0.2769(9)	0.8884(9)	0.055(3)
O(7)	0.3025(7)	0.306(1)	0.075(1)	0.15(1)	C(36)	0.0089(6)	0.2594(9)	0.9737(9)	0.055(3)
O(8)	0.3149(9)	0.164(1)	0.099(1)	0.16(1)	C(37)	0.0524(6)	0.197(1)	1.112(1)	0.061(4)
C(1)	0.5966(5)	0.3014(8)	0.4372(7)	0.039(3)	C(38)	0.0936(6)	0.1530(9)	1.1613(9)	0.059(4)

Table 5 (cont.)

	x	y	z	U_{eq}		x	y	z	U_{eq}
C(2)	0.5881(5)	0.2159(8)	0.4328(8)	0.043(3)	C(39)	0.1428(6)	0.1294(9)	1.1218(9)	0.050(3)
C(3)	0.6346(6)	0.1619(9)	0.4150(9)	0.057(4)	C(40)	0.1478(5)	0.1527(8)	1.0375(8)	0.045(3)
C(4)	0.6872(6)	0.200(1)	0.4049(9)	0.060(4)	C(41)	0.1584(5)	0.2120(8)	0.8419(8)	0.043(3)
C(5)	0.7525(7)	0.324(1)	0.412(1)	0.064(4)	C(42)	0.1506(5)	0.2224(8)	0.7489(8)	0.045(3)
C(6)	0.7603(6)	0.405(1)	0.4269(9)	0.060(4)	C(43)	0.1065(5)	0.1988(7)	0.9844(7)	0.035(2)
C(7)	0.7269(6)	0.553(1)	0.448(1)	0.062(4)	C(44)	0.0559(6)	0.2187(8)	1.0238(8)	0.048(3)
C(8)	0.6858(6)	0.6088(9)	0.4521(9)	0.059(4)	C(45)	0.1102(5)	0.2250(7)	0.8919(7)	0.035(2)
C(9)	0.5854(6)	0.646(1)	0.4362(9)	0.059(4)	C(46)	0.0589(5)	0.2597(8)	0.8455(8)	0.045(3)
C(10)	0.5284(6)	0.6260(9)	0.4154(9)	0.057(4)	C(47)	0.3172(5)	0.1501(9)	0.8712(9)	0.049(4)
C(11)	0.5125(5)	0.5438(7)	0.3909(7)	0.037(3)	C(48)	0.1897(6)	0.0789(9)	1.1772(8)	0.055(5)
C(12)	0.5533(5)	0.4806(7)	0.3940(7)	0.040(3)	C(49)	0.3973(7)	0.038(1)	0.962(1)	0.069(4)
C(13)	0.6487(5)	0.3426(7)	0.4246(8)	0.039(3)	C(50)	0.4159(7)	-0.045(1)	1.007(1)	0.078(5)
C(14)	0.6959(6)	0.2867(9)	0.4121(9)	0.052(3)	C(51)	0.3238(6)	-0.0248(9)	0.8095(9)	0.056(4)
C(15)	0.6124(5)	0.4979(7)	0.4195(7)	0.036(2)	C(52)	0.3178(7)	-0.120(1)	0.826(1)	0.073(4)
C(16)	0.6273(5)	0.5839(8)	0.4379(8)	0.048(3)	C(53)	0.2515(6)	-0.079(1)	1.214(1)	0.062(4)
C(17)	0.6580(5)	0.4345(8)	0.4274(8)	0.040(3)	C(54)	0.3101(9)	-0.040(1)	1.230(1)	0.10(1)
C(18)	0.7153(6)	0.4637(9)	0.4355(9)	0.054(3)	C(55)	0.1403(7)	-0.090(1)	1.118(1)	0.073(4)
C(19)	0.5319(6)	0.1752(7)	0.4444(7)	0.044(4)	C(56)	0.1174(8)	-0.116(1)	1.199(1)	0.09(1)
C(20)	0.4492(5)	0.5247(8)	0.3678(8)	0.050(4)					

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