

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

Part XV¹⁾

X-Ray Structural and ³¹P-NMR Solution Studies of Some Three-Coordinate Silver Complexes of 2,11-Bis[di(*tert*-butyl)phosphinomethyl]benzo[*c*]phenanthrene and Related Ligands

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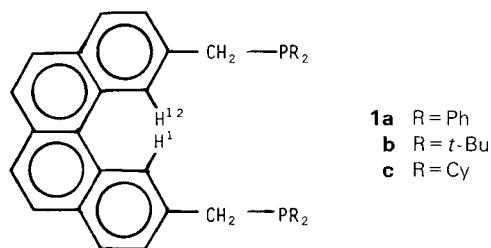
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Summary

A series of three-coordinate bis(dialkylphosphinomethyl)benzo[*c*]phenanthrene Ag(I) complexes, alkyl = *t*-Bu, (**1b**), and cyclohexyl, (**1c**), anion = BF₄, ClO₄, NO₃, Cl, Br, I, have been prepared and their ³¹P-NMR characteristics recorded. The solid state structures of [Ag(**1b**)Br], [Ag(**1b**)Cl] and [Ag(**1b**)ClO₄] have been determined by X-ray diffraction. The Ag atom in these complexes shows distorted trigonal geometry. Selected bond lengths and angles are as follows: Ag-P = 2.463(4) Å and 2.433(5) Å, P-Ag-P = 141.6(2)° in the bromo complex, Ag-P = 2.457(2) Å and 2.427(2) Å, P-Ag-P = 142.6(1)° in the chloro complex, and Ag-P = 2.394(2) and 2.393(2) Å, P-Ag-P = 161.5(1)° in the perchlorato complex.

1. Introduction. – Three-coordinate complexes of Ag(I) with tertiary phosphine ligands normally have trigonal micro-geometry about the metal atom. As the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1a**) has been shown to prefer spanning *trans*-positions in square-planar and octahedral complexes [2], it was expected that its complexes with Ag(I) would exhibit considerable distortion from 120° angles. Indeed, crystallographic studies of the complexes [M(**1a**)Cl] (M = Cu(I), Ag(I) and Au(I)) have shown that although the metal atoms are three-coordinate, the P-M-P angles are 132, 141 and 176°, respectively [3]. ³¹P-NMR studies for the complexes [Ag(**1a**)X], X = BF₄, NO₃, Cl, I, in solution have shown that changes in the values ¹*J*(¹⁰⁷Ag, ³¹P) correlate with the capability of the anion, X, to coordinate to silver [4]. Moreover, for X = ClO₄, NO₃, SnCl₃ (bound *via* Cl), this coupling constant correlates with the bond separations <Ag-P> and the bond angles P-Ag-P [5] in a way similar to

¹⁾ Part XIV: see [1].



that reported earlier for the Hg complexes $[\text{HgX}_2(\text{PR}_3)_2]$ [6]. Unfortunately, the X ligands used are not sufficient to show the full range of possible changes in the structural parameters. Consequently, to extend these correlations and, specifically, to estimate the possible contribution of steric effects to the molecular geometry, we have prepared a series of Ag complexes using the ligands **1b** and **1c**. As their donor atoms should differ both in basicity and steric requirements relative to **1a**, their structural and NMR data were expected to provide additional information about the Ag-P interaction. We report here the solid state structures for $[\text{Ag}(\mathbf{1b})\text{Br}]$, $[\text{Ag}(\mathbf{1b})\text{Cl}]$ and $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$ and solution ^{31}P -NMR measurements for these and related complexes.

2. Results and Discussion. – A. *Solid State Structures.* The crystals of the three Ag(I) complexes are composed of discrete molecular units with no close intermolecular contacts. Interatomic distances and interbond angles are given in *Table 1*.

Table 1. *Selected Interatomic Distances (Å) and Interbond Angles (deg) for $[\text{Ag}(\mathbf{1b})X]$*

	X = Br	X = Cl	X = ClO ₄
Distances			
Ag-P(1)	2.463(4)	2.457(2)	2.394(2)
Ag-P(2)	2.433(5)	2.427(2)	2.393(2)
Ag-Y ^a)	2.681(2)	2.569(2)	2.913(13)
Cl-O(1)			1.422(12)
Cl-O(2)			1.412(9)
Cl-O(3)			1.380(9)
Cl-Y			1.371(12)
Angles			
P(1)-Ag-P(2)	141.6(2)	142.6(1)	161.5(1)
P(1)-Ag-Y	101.4(1)	100.5(1)	90.2(2)
P(2)-Ag-Y	116.8(1)	116.7(1)	107.8(2)
Ag-Y-Cl			146.7(8)
Y-Cl-O(1)			110.0(8)
Y-Cl-O(2)			111.0(6)
Y-Cl-O(3)			112.3(7)
O(1)-Cl-O(2)			106.7(6)
O(1)-Cl-O(3)			105.4(6)
O(2)-Cl-O(3)			111.1(5)

^a) Y is the anion, or atom of the anion, bonded to Ag.

$[Ag(1b)Br] \cdot CH_2Cl_2$. A computer-generated drawing of this molecule is shown in Fig. 1. The coordination about Ag, consisting of one Br and two P atoms, is distorted trigonal. The metal atom is almost coplanar with the three donor atoms and deviates 0.06 Å from their plane. The Ag-Br bond length (2.681(2) Å) is 0.02 Å longer than the sum (2.66 Å) of the tetrahedral covalent bond radius of Ag and the single covalent radius of Br, but is 0.53 Å shorter than the sum of ionic radii (3.21 Å) [7]. Thus the Ag-Br bond can be considered as having prevailingly covalent character. Interestingly, the Ag-Br vector does not bisect the P-Ag-P angle the two Ag-P bonds are significantly different, (2.457(2) and 2.427(2) Å) although both fall in the range (2.38–2.52 Å) normally found for Ag-phosphine complexes [8]. The shorter Ag-P bond is associated with the smaller P-Ag-Br angle (101.4(1)°) and the longer with the larger angle (116.8(1)°).

$[Ag(1b)Cl] \cdot CH_2Cl_2$. This compound is isostructural with the Br complex. Once again the metal shows a distorted trigonal coordination with bonding to one Cl and two P atoms. As before, the metal deviates 0.06 Å from the plane defined by these three atoms. The Ag-Cl bond length (2.569(2) Å) is 0.06 Å longer than the distance given by the sum (2.51 Å) of the tetrahedral covalent radius of Ag and the covalent radius of Cl but considerably shorter than the standard ionic bond length 3.07 Å [7]. The two Ag-P bond lengths fall in the normal range but again are significantly different, 2.457(2) and 2.427(2) Å. The shorter Ag-P bond is associated with the smaller P-Ag-Cl angle (100.5(1)°) and the longer one with the larger angle (116.7(1)°).

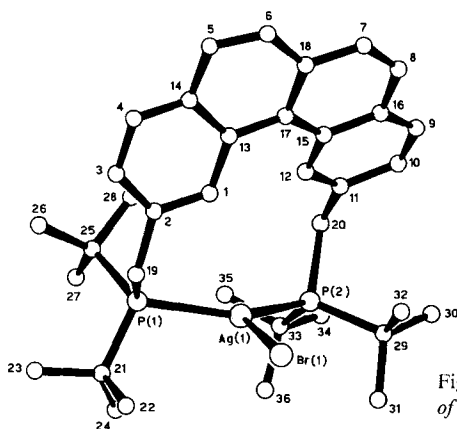


Fig. 1. A computer-generated drawing of the molecule $[Ag(1b)Br]$

$[Ag(1b)ClO_4] \cdot CH_3COCH_3$. A computer-generated drawing of this molecule is shown in Fig. 2. As in the previous complexes the Ag ion adopts a distorted trigonal arrangement of donor atoms these being the two P atoms with one O of the ClO_4^- anion. In this complex the metal deviates 0.07 Å from the plane of coordination. The Ag-O bond at 2.91(1) Å is only 0.11 Å shorter than the calculated ionic (3.02 Å) and 0.63 Å longer than the calculated covalent distance (2.28 Å) [7], suggesting that the Ag-O bond has predominantly ionic character. The ClO_4^- group shows distorted tetrahedral geometry with average Cl-O bond lengths of 1.39(1) Å and O-Cl-O angles ranging from 105.4(6)° to 112.3(7)°. The coordinated O shows a short O-Cl bond length, 1.37(1) Å. In contrast to the other two structures the Ag-P bonds are identical (2.394(2) and 2.393(2) Å) although the O-Ag-P angles are different (107.8(2) and 90.2(2)°).

The difference between these angles, 17.6° , is similar to that found for $[\text{Ag}(\mathbf{1b})\text{Br}]$, 15.4° , and $[\text{Ag}(\mathbf{1b})\text{Cl}]$, 16.2° .

With the addition of the above data set, we can examine the molecular structure as a function of the substituent on P for the benzo[*c*]phenanthrene derivatives. The Cl and ClO_4 complexes of both $\mathbf{1a}$ and $\mathbf{1b}$ will be considered, since these anions have quite different ligating properties. The most obvious changes (see Table 2) concern the distances $\langle\text{Ag-X}\rangle$, $\langle\text{Ag-P}\rangle$ and the angle P-Ag-P as a function of the substituent. Replacement of the Ph end-groups in $\mathbf{1a}$ by a *t*-Bu substituent in $\mathbf{1b}$ results in an increase of *ca.* 0.05 Å and 0.13 Å in the Ag-Cl and Ag-O lengths, respectively, although the $\langle\text{Ag-P}\rangle$ separations within the two ClO_4 complexes and the two Cl complexes are almost identical.

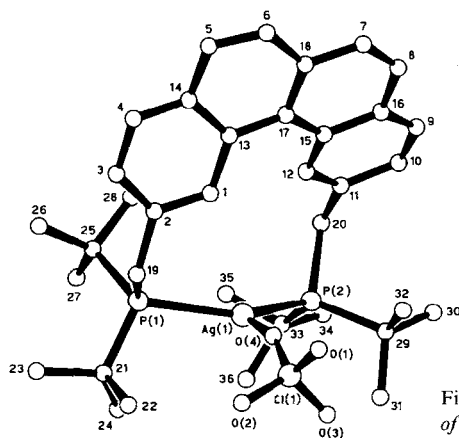


Fig. 2. A computer-generated drawing of the molecule $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$

Table 2. Comparison of Selected Structural Data for the Complexes $[\text{Ag}(\mathbf{1a})\text{X}]$ and $[\text{Ag}(\mathbf{1b})\text{X}]$

Complex	X	$\langle\text{Ag-P}\rangle$ [Å]	$\langle\text{Ag-X}\rangle$ [Å]	$\langle\text{P-Ag-P}\rangle$ [Å]	$^1J(^{107}\text{Ag}, ^{31}\text{P})$ [Hz]
$[\text{Ag}(\mathbf{1a})\text{X}]$	Cl	2.458(3)	2.514(4)	140.7(1)	408
		2.411(3)			
	ClO_4	2.417(3)	2.75(1)	151.5(1)	503
		2.401(3)			
$[\text{Ag}(\mathbf{1b})\text{X}]$	Cl	2.457(2)	2.569(2)	142.6(1)	418
		2.427(2)			
	ClO_4	2.394(2)	2.91(1)	161.5(1)	456
		2.393(2)			

The angle P-Ag-P for $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$ (161.5°) is 10° larger than for $[\text{Ag}(\mathbf{1a})\text{ClO}_4]$ (151.5°), but this difference decreases to *ca.* 2° for the Cl analogs, 142.6° and 140.7° , respectively. For a given ligand, *e.g.*, $\mathbf{1b}$, shorter M-P distances and larger P-Ag-P angles are associated with weaker X donor atoms while the reverse is true for stronger donors. As mentioned earlier, the same trend was found in the $[\text{HgX}_2(\text{PR}_3)_2]$ complexes. Since the structural parameters for these complexes correlate with $^1J(^{199}\text{Hg}, ^{31}\text{P})$ we may expect some correlation of our structural data with the ^{31}P -NMR coupling constant $^1J(^{107}\text{Ag}, ^{31}\text{P})$.

B. Ag, P Coupling Constants. Table 3 contains $^1J(^{107}\text{Ag}, ^{31}\text{P})$ coupling-constant data for the new Ag complexes of ligands $\mathbf{1b}$ and $\mathbf{1c}$ and for comparison purposes the data

for the analogs with **1a** are also included. Changing the anion affects $^1J(^{107}\text{Ag}, ^{31}\text{P})$ in the same way for the three phosphines. The halogen donors reduce the $^1J(^{107}\text{Ag}, ^{31}\text{P})$ values relative to the O donors, as previously reported by several groups [4] [9] [10]. These data show that **1b** and **1c** give rise to similar $^1J(^{107}\text{Ag}, ^{31}\text{P})$ values for a given X anion; however, the coupling constants for the **1a** complexes are not readily correlated with those of either **1b** or **1c**. For $[\text{Ag}(\mathbf{1a})\text{Cl}]$, $^1J(^{107}\text{Ag}, ^{31}\text{P})$ (408 Hz) is at the low end of our observed values, below that found for $[\text{Ag}(\mathbf{1b})\text{Cl}]$ (418 Hz); however, the value for $[\text{Ag}(\mathbf{1a})\text{ClO}_4]$ (503 Hz) is much larger than that of $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$ (456 Hz). Comparing the NMR and X-ray data, we note another anomaly. Although there is a 47 Hz difference in $^1J(^{107}\text{Ag}, ^{31}\text{P})$ between $[\text{Ag}(\mathbf{1a})\text{ClO}_4]$ and $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$, the $\langle\text{Ag-P}\rangle$ bond separations vary only slightly (2.409 Å and 2.394 Å, respectively). The Ag-P distances should be significantly different if the difference in $^1J(^{107}\text{Ag}, ^{31}\text{P})$ were mainly a consequence of differing donor capacity of the phosphines. As it is likely that both the steric and electronic effects of **1a** will make a contribution to the NMR parameters, a direct comparison with **1b** and **1c** can be only speculative.

Table 3. NMR Data for the Ag Complexes $[\text{Ag}(\text{ligand})\text{X}]$

Complex	X	$^1J(^{107}\text{Ag}, ^{31}\text{P})$ [Hz]	$\delta(^{31}\text{P})^a)$	$\delta(^1\text{H})^b)$	
				H-C(1), H-C(12)	CH ₂ -Groups
[Ag(1a)X]	I ^{b)}	378	2.6	9.10	3.98
	Br	405	6.4	9.14	3.94
	Cl ^{b)}	408 ^{c)}	7.1 ^{c)}	9.15	3.90
	NO ₃ ^{b)}	461	8.0	9.39	4.10
	ClO ₄	503	11.0	9.29	4.06–4.21
[Ag(1b)X]	I	391	50.0	9.29	3.59
	Br	412	52.0	9.29	3.56
	Cl	418	53.1	8.95	2.87
	NO ₃	444	53.1	9.20	3.42
	ClO ₄	456	58.2	9.06	3.38
	BF ₄	453	59.2	8.94	3.31
[Ag(1c)X]	I	391	20.6	9.05	3.29
	Br	404	23.4	9.10	3.32
	Cl	413	23.4	9.06	3.25
	NO ₃	463	23.9	8.91	3.01
	ClO ₄	469	28.0	9.01	3.21
	BF ₄	469	28.8	9.10	3.28

^{a)} ^{31}P Chemical shifts are in ppm rel. to external H_3PO_4 , CDCl_3 solutions. These data were recorded at 298 K and do not change on lowering the temperature (sharp room-temperature spectra can be obtained only if particular care is taken by the purification of the compounds). ^{b)} See [4]. ^{c)} These values differ slightly from those given in [4].

In general Ph groups play an ambiguous role where coupling constants are concerned. On one hand, they are electron-withdrawing groups, thus weakening the donor capacity of the phosphine: on the other hand, electron-withdrawing groups on P can enhance the percentage s-character of the P lone pair with a concomitant increase in $^1J(\text{M}, ^{31}\text{P})$ [11] [12]. Note that for the presumed two-coordinate complexes $[\text{Ag}(\text{P}(\text{mesityl})_3)_2]\text{PF}_6$, $^1J(^{107}\text{Ag}, ^{31}\text{P}) = 513$ Hz [13], and $[\text{Ag}(\text{P}(t\text{-Bu})_3)_2]\text{PF}_6$ $^1J(^{107}\text{Ag}, ^{31}\text{P}) = 437$ Hz [9], the mesityl complex shows a much larger one-bond Ag, P coupling constant. This is

presumably arising from the effect of Ph as electron-withdrawing group. In view of these complications a more detailed comparison of **1a** vs. **1b** seems presumptuous.

It is interesting that both $[\text{Ag}(\text{P}(t\text{-Bu})_3)_2\text{NO}_3]$ and $[\text{Ag}(\text{P}(t\text{-Bu})_3)_2\text{ClO}_4]$ show $^1J(^{107}\text{Ag}, ^{31}\text{P})$ values (CH_2Cl_2) of 442 Hz, which differ only slightly from the values for $[\text{Ag}(\text{1b})\text{NO}_3]$ (444 Hz) and $[\text{Ag}(\text{1b})\text{ClO}_4]$ (456 Hz). Since these two $\text{P}(t\text{-Bu})_3$ compounds are 1:1 electrolytes in CH_2Cl_2 [9], either they do not have linear geometry in solution (remember that $[\text{Ag}(\text{1b})\text{ClO}_4]$ shows a P-Ag-P angle of 161.5°) or the correlations of $^1J(^{107}\text{Ag}, ^{31}\text{P})$ with solid state structural parameters does not readily extend to a comparison of different phosphines. It is noteworthy that the cation $[\text{Ag}(\text{P}(\text{NMe}_2)_3)_2]^+$ was recently shown to have a P-Ag-P bond angle of $166.9(1)^\circ$ in the solid state [14].

Summing up, the complexes of both **1a** and **1b** exhibit a range of P-Ag-P angles, which are largely determined by the nature of the anionic ligands. While there is a correlation between the solid state and $^1J(^{107}\text{Ag}, ^{31}\text{P})$ data, this does not extend to a strict comparison of the set of compounds of **1a** with that formed by **1b**. The crystallographic data does not provide compelling evidence to indicate that changes in the geometry about silver are due to a sterically more demanding nature of **1b**.

However, for $[\text{Ag}(\text{1b})\text{ClO}_4]$, the 10° increase in the P-Ag-P bond angle and 0.13 Å increase in Ag-O, relative to the (**1a**) analog could derive from the presence of *t*-Bu groups on P so that this point will require further clarification.

The authors are indebted to the Swiss National Science Foundation for financial support of this work.

Table 4. Summary of Crystal Data and Intensity Measurements, Structure Solution, and Refinement for the Compounds $[\text{Ag}(\text{1b})\text{X}]^{\text{a}}$

Compound	X = Br	X = Cl	X = ClO ₄
Formula	C ₃₇ H ₅₂ AgBrCl ₂ P ₂	C ₃₇ H ₅₂ AgCl ₃ P ₂	C ₃₉ H ₅₆ AgClO ₅ P ₂
F.wt.	732.525	688.069	752.066
Crystal dimension [mm]	0.25×0.25×0.10	0.45×0.40×0.25	0.70×0.40×0.20
<i>a</i> [Å]	11.174(3)	11.163(3)	16.015(4)
<i>b</i> [Å]	24.323(9)	24.382(7)	20.050(4)
<i>c</i> [Å]	14.178(4)	14.094(4)	25.002(5)
β [deg]	102.69(2)	76.88(2)	90.0
<i>V</i> [Å ³]	3759.0(2)	3735.7(18)	8028.3(29)
<i>Z</i>	4	4	8
<i>d</i> _{calc.} [g/cm ³]	1.44	1.37	1.37
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
Diffractometer	Syntex <i>P</i> 2 ₁	Syntex <i>P</i> 2 ₁	Syntex <i>P</i> 2 ₁
Radiation	MoKα graphite monochr.		
μ [m ⁻¹]	18.51	8.83	6.88
Scan mode	ω	ω	ω
Scan range [deg]	0.9	0.9	0.9
Bkd counts	¼ of scan time at ± 0.5° from the center of scan range		
2θ limits [deg]	3–56	3–56	3–56
Reflections collected no	8560	9792	10883
No unique data, <i>F</i> _o ² > 3σ(<i>F</i> _o ²)	2361	4347	3233
Final no. of ref. variables	203	203	243
Final <i>R</i> (<i>R</i> _w)	0.075 (0.073)	0.068 (0.076)	0.063 (0.062)

^a) During the crystallographic analysis a molecule of solvent was found in each complex, i.e. CH_2Cl_2 for X = Br and Cl and acetone for X = ClO₄.

3. Experimental. – *Collection and Reduction of X-Ray Intensity Data.* Colourless single crystals of $[\text{Ag}(\mathbf{1b})\text{Br}] \cdot \text{CH}_2\text{Cl}_2$ suitable for diffraction analysis were grown from CH_2Cl_2 solution, whereas crystals of $[\text{Ag}(\mathbf{1b})\text{Cl}]$ and $[\text{Ag}(\mathbf{1b})\text{ClO}_4]$ were obtained from CH_2Cl_2 /acetone solutions. The crystals of $[\text{Ag}(\mathbf{1b})\text{Br}] \cdot \text{CH}_2\text{Cl}_2$ change with time, probably due to loss of the solvent of crystallization. Therefore a crystal was sealed in a thin-walled capillary before the X-ray analysis.

A *Syntex P2₁* automatic diffractometer was used for the cell constants measurement and the data collection. A summary of the crystal parameters along with details of the data collection is given in *Table 4*.

Monitoring of standard reflections indicated no decay during the data collection and the collected intensities were processed to give structure factor amplitudes with standard deviations.

Solutions and Refinement of the Structures. The solution of the three structures was carried out using a three-dimensional *Patterson* function to determine the position of Ag and P atoms, and *Fourier* methods to determine the other atoms. Refinement by least-squares procedures was applied subsequently.

$[\text{Ag}(\mathbf{1b})\text{Br}] \cdot \text{CH}_2\text{Cl}_2$. After the isotropic refinement converged at $R = 0.090$, the refinement was continued allowing the non-C-, non-H-atoms, except for C(19) and C(20), to vibrate anisotropically. Each Ph ring was treated as a rigid body restricted to its idealized geometry (6/*mmm*-symmetry, $d(\text{C}-\text{C}) = 1.395 \text{ \AA}$, $d(\text{C}-\text{H}) = 0.96 \text{ \AA}$) with individual isotropic thermal parameters per C atom. The fixed contribution of the H atoms was included in the calculations with idealized positions and isotropic thermal parameters of the nearest C atom. Convergence was reached at $R = 0.075$ ($R_w = 0.073$).

Refinement was by full-matrix and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights of the type $w = 1/[\sigma^2(F_o) + bF_o^2]$ with b chosen so as to minimize the dispersion of the mean value of the minimized function over ranges of reflections ($b = 0.000582$).

During the analysis the presence of a molecule of CH_2Cl_2 per molecule of complex became evident. When included in the refinement this solvent shows high thermal parameters (see *Table 2*).

$[\text{Ag}(\mathbf{1b})\text{Cl}] \cdot \text{CH}_2\text{Cl}_2$. The isotropic refinement converged at $R = 0.086$, after which the refinement was continued, applying the same conditions as for the Br complex (see above): convergence was reached at $R = 0.068$ ($R_w = 0.076$). The Cl and Br compounds are isomorphous.

$[\text{Ag}(\mathbf{1b})\text{ClO}_4] \cdot \text{CH}_3\text{COCH}_3$. In this case isotropic refinement converged at $R = 0.150$. At this point a cycle of refinement with anisotropic Ag, P, C(19) and C(20) atoms yielded an R -value of 0.121. A subsequent difference *Fourier* map showed a molecule of acetone per molecule of complex and upon the inclusion of these atoms in the least-square refinement the R -value decreased to 0.075. The calculation was continued by including the H atoms at calculated positions and final convergence was reached at $R = 0.063$ ($R_w = 0.062$). As before, each Ph ring was treated as a rigid body and same type of weight was used ($b = 0.00067$).

Table 5. *Analytical Results for Complexes [Ag (L)X]*

Complex	X	% C	% H	% Y
		Found (Calc.)	Found (Calc.)	Found (Calc.)
[Ag(1a)X]	Br	65.39 (65.05)	4.43 (4.22)	9.59 (9.84) ^{a)}
	ClO ₄	63.62 (63.51)	3.95 (4.12)	4.66 (4.26) ^{b)}
[Ag(1b)X]	I	55.06 (55.47)	6.14 (6.47)	8.10 (7.95) ^{c)}
	Br	58.71 (59.03)	6.43 (6.88)	8.30 (8.46) ^{c)}
	Cl	62.93 (62.85)	7.22 (7.33)	5.05 (5.15) ^{b)}
	NO ₃	60.37 (60.50)	7.08 (7.05)	1.96 (1.96) ^{d)}
	BF ₄	61.79 (61.70)	6.99 (6.91)	7.46 (7.58) ^{c)}
	ClO ₄	57.42 (57.49)	6.76 (6.70)	4.50 (4.71) ^{b)}
[Ag(1c)X]	I	59.70 (59.80)	6.40 (6.61)	6.10 (7.01) ^{c)}
	Br	63.01 (63.17)	7.30 (6.99)	9.20 (9.55) ^{a)}
	Cl	66.40 (66.71)	7.31 (7.38)	4.20 (4.47) ^{b)}
	NO ₃	64.45 (64.55)	7.01 (7.14)	7.29 (7.56) ^{c)}
	BF ₄	62.27 (62.65)	6.58 (6.92)	6.95 (7.35) ^{c)}
	ClO ₄	61.43 (61.72)	6.84 (6.83)	7.11 (8.23) ^{c)}

^{a)} Y = Br. ^{b)} Y = Cl. ^{c)} Y = P. ^{d)} X = N. ^{e)} Cl: 4.17 (4.14)

Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-Ray Crystallography* [15]. The calculations were performed on the *IBM 370* computer of the *CNUCE* (Pisa Italy), with the *Shell X 76* system of programs [16], and on the *HP 21 Mx* minicomputer of the CNR Research Area of Rome, with local programs [17].

Tables of observed and calculated structure factors are available from the authors upon request.

Preparation of the Complexes. Analytical data for the new complexes are shown in *Table 5*.

[Ag(1b)BF₄]. AgBF₄ (150 mg, 0.77 mmol) was dissolved in 10 ml acetone and then treated with an acetone solution of **1b** (429.0 mg, 0.78 mmol). The clear solution which resulted was stirred at r.t. overnight under N₂. Filtration through a short silica gel column was followed by concentration. Colourless crystals were obtained from a mixture of acetone and benzene. Yield: 86.7%. Decomp. > 270°.

[Ag(1c)BF₄] was prepared as described for *[Ag(1b)BF₄]*. Yield: 73%.

[Ag(1a)ClO₄]. AgClO₄ · H₂O (1.5 g, 6.6 mmol) was suspended in a solution of **1a** (2.25 g, 3.6 mmol) in 70 ml CH₂Cl₂ and the resulting suspension stirred at r.t. overnight. The excess AgClO₄ was removed *via* filtration through a short silica gel column and the filtrate concentrated. Colourless crystals of the product were obtained from a mixture of CH₂Cl₂ and acetone. Yield: 73.4%. Decomp. > 260°.

[Ag(1b)ClO₄]. AgClO₄ · H₂O (720 mg, 3.2 mmol) was suspended in a solution of **1b** (1.10 g, 2.02 mmol) in 50 ml CH₂Cl₂ and the suspension was stirred overnight. The excess AgClO₄ was removed by filtration over *Celite*, and the filtrate concentrated under N₂. Colourless crystals were obtained from a mixture of CH₂Cl₂ and acetone. Yield: 57%. Decomp. > 260°.

[Ag(1c)ClO₄] was prepared as described for *[Ag(1b)ClO₄]*. Yield: 71%.

[Ag(1b)NO₃]. AgNO₃ (100 mg, 0.59 mmol) was suspended in a solution of **1b** (300 mg, 0.55 mmol) in 50 ml CH₂Cl₂ and the suspension stirred at r.t. overnight. Filtration through a short *Celite* column was followed by concentration. Colourless crystals were obtained from a mixture of CH₂Cl₂ and acetone. Yield: 78%. Decomp. > 280°.

[Ag(1c)NO₃] was prepared as described for *[Ag(1b)NO₃]*. Yield: 68%.

[Ag(1b)Cl]. *[Ag(1b)ClO₄]* (300 mg, 0.40 mmol) was dissolved in 20 ml of CH₂Cl₂ and then treated with 106 mg (0.54 mmol) (Bu)₄NCl. Stirring at r.t. for 2 h was followed by slow removal of solvent under N₂. The colourless crystals obtained were washed three times with 5 ml of CH₂Cl₂/EtOH 1:2 and dried. Yield: 85%. Decomp. > 280°.

[Ag(1c)Cl]. AgCl (100 mg, 0.69 mmol) was suspended in a solution of **1c** (300 mg, 0.46 mmol) in 50 ml CH₂Cl₂ and the suspension stirred at r.t. overnight. Filtration over a short silica gel column was followed by concentration to a small volume. Colourless crystals were obtained from a mixture of CH₂Cl₂ and acetone. Yield: 62.2%. Decomp. > 280°.

[Ag(1a)Br]. AgBr (150 mg, 0.85 mmol) was suspended in a solution of **1a** (500 mg, 0.8 mmol) in 50 ml CH₂Cl₂ and the suspension stirred at r.t. overnight. Filtration over a short *Celite* column was followed by concentration. Colourless crystals were obtained from a mixture of CH₂Cl₂ and acetone. Decomp. > 280°.

[Ag(1b)Br]. *[Ag(1b)ClO₄]* (200 mg, 0.27 mmol) was dissolved in 20 ml of CH₂Cl₂ and then treated with Bu₄NBr (100 mg, 0.31 mmol). Stirring at r.t. for 2 h was followed by slow removal of the solvent under N₂. The colourless crystals obtained were washed with 3 × 5 ml CH₂Cl₂/EtOH 1:3 and dried. r.t./5 · 10⁻³ Torr. Yield: 82%. Decomp. > 280°.

[Ag(1c)Br] was prepared as described for *[Ag(1b)Br]*. Yield: 84.7%. Decomp. > 260°.

[Ag(1b)I]. *[Ag(1b)ClO₄]* (200 mg, 0.27 mmol) was dissolved in 20 ml of CH₂Cl₂ and then treated with Bu₄NI (100 mg, 0.27 mmol). Stirring at r.t. for 2 h was followed by slow removal of the solvent under N₂. The colourless crystals obtained were washed with 3 × 5 ml of CH₂Cl₂/EtOH 1:2 and dried. r.t./5 · 10⁻³ Torr. Yield 81.5%. Decomp. > 270°.

[Ag(1c)I]. AgI (500 mg, 2.13 mmol) was suspended in a solution of **1c** (700 mg, 1.08 mmol) in 80 ml CH₂Cl₂ and the suspension stirred at r.t. overnight. The excess AgI was filtered off through a short *Celite* column and the filtrate concentrated. Colourless crystals of the complex were obtained from a mixture of CH₂Cl₂ and acetone and dried at r.t./5 · 10⁻³ Torr. Yield: 71%. Decomp. > 260°.

NMR Spectra. The ¹H- and ³¹P-NMR spectra were measured at 90 and 36.43 MHz, respectively, on a *Bruker-HX-90* spectrometer. A positive value of the chemical shift denotes a resonance to low field of the reference.

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