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Correlation Between ^{31}P NMR Data and Structural Parameters on $Ag(PPh_3)_3X$ Series. Crystal and Molecular Structure of Tris(triphenylphosphine)silver(I)tetrafluoroborate and Tris(triphenylphosphine)silver(I)iodide

M. CAMALLI and F. CARUSO

Istituto di Strutturistica Chimica 'G. Giacomello' C.N.R. C.P. 10, 00016 Monterotondo Stazione, Rome, Italy

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Abstract

The series $Ag(PPh_3)_3X$, $X = BF_4$, NO_3, Cl and I, has been studied with ^{31}P NMR spectroscopy. The crystal and molecular structures for $X = BF_4$ and I have been determined by X-ray diffraction. There are two independent molecules of the iodo complex in the asymmetric unit. Average values of both Ag–P bond distances and P–Ag–P bond angles correlate with the $^1J(^{107}Ag–^{31}P)$ data. Three phosphorus atoms and one atom of the anion bind to the metal in a distorted tetrahedral arrangement which is modified by the coordination ability of the anion so that the system can be described as going from a tetrahedral to a trigonal geometry at the metal. A measure of the basicity of PPh_3 is given by comparing the coupling constant values in the *p*-tolylphosphine equivalent series of complexes Ag(*p*-tolyl)$_3$X. Selected structural data are: Ag–P bond distances = 2.577(3), 2.506(3) and 2.543(3) Å, Ag–F = 2.82(1) Å for the tetrafluoroborate complex whereas Ag–P bond lengths are 2.607(4), 2.572(4) and 2.585(4) Å in one molecule and 2.582(4), 2.613(3) and 2.616(3) Å in the other one, the Ag–I bond distances are 2.855(1) and 2.864(1) Å respectively. The bond angles around the metal are P–Ag–P = 114.9(1)°, 119.3(1)° and 119.0(1)° for the tetrafluoroborate complex and 113.0(1)°, 113.2(1)° and 113.2(1)° in the first molecule and 113.2(1)°, 114.1(1)° and 110.8(1)° in the second one for the iodo complex respectively. By comparison with Cu analog complexes, our series shows larger average P–M–P bond angles, but unlike those complexes the metal–anion direction does not show threefold symmetry.

Introduction

In recent years a number of reports concerned with ^{31}P NMR characteristics of silver–phosphine complexes have been published [1–6]. Our program approaches the structural information in solution through the study of the coupling constant $^1J(^{107}Ag–^{31}P)$ obtained by ^{31}P NMR. Recently [7–9] we have reported X-ray and ^{31}P NMR studies on several series of metal–phosphine complexes, where metals have at least one isotope with spin 1/2 as: Ag(1a)X, 1a = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene [7], Ag(1b)X, 1b = 2,11-bis(di-t-butylphosphinomethyl)benzo[c]phenanthrene [8] and Hg(1a)X$_2$ [9]. These studies show that changes in the values of *J*(M–P) are associated with the capability of the anion X to coordinate to the metal and correlate with the M–P bond distances and P–M–P bond angles similarly to what was reported earlier for the complexes $Hg(PPh_3)_2X_2$ [10], PPh_3 = triphenylphosphine. As an extension of this type of study we present here an equivalent investigation on the series $Ag(PPh_3)_3X$.

Experimental

Preparation of the Complexes

$Ag(PPh_3)_3BF_4$

$AgBF_4$ (143 mg = 0.73 mmol) was suspended in Cl_2CH_2 under nitrogen and mixed with a solution of PPh_3 (575 mg = 2.19 mmol) in Cl_2CH_2 at room temperature, in darkness. The silver salt dissolved immediately, then petroleum ether was added and the solution filtered. Colourless crystals were obtained after evaporation at room temperature (r.t.) in darkness (yield 73%).

$Ag(PPh_3)_3I$

AgI (109 mg = 0.46 mmol) was suspended in a solution of PPh_3 (365 mg = 1.39 mmol) in Cl_2CH_2 and the resulting suspension stirred at r.t. in darkness. After 3 h the suspension was filtered and the solution left to evaporate. A white powder was obtained (yield 62%).

$Ag(PPh_3)_3NO_3$

A solution of $AgNO_3$ (86 mg = 0.50 mmol) in CH_3CN was mixed with a suspension of PPh_3 (400 mg = 1.50 mmol) in the same solvent. The phosphine

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TABLE I. Summary of Crystal Data for the Compounds $Ag(PPh_3)_3X$

Compound	$X = BF_4$	$X = I$
Formula	$C_{54}H_{45}AgP_3F_4B$	$C_{54}H_{45}AgIP_3$
Formula weight	981.62	1021.65
a (Å)	19.029(6)	14.097(5)
b (Å)	13.764(4)	14.384(4)
c (Å)	18.018(5)	23.413(7)
α (°)	90	92.61(2)
β (°)	94.26(2)	91.85(2)
γ (°)	90	91.12(2)
V (Å^3)	4706(2)	4739(2)
Z	4	4
Space group	$P2_1/n$	$P\bar{1}$
Crystal dimension (mm)	0.20 × 0.20 × 0.40	0.15 × 0.30 × 0.30
Radiation	Mo Kα graphite monochromated	
μ (cm^{-1})	5.39	5.52
Diffractometer	Nicolet R3	
Scan mode	ω	
Scan range (°)	0.9	
Background counts	1/2 of scan time at ±0.5 from the center of the scan range	
2θ limits (°)	3–56	
Reflections collected no.	12232	31730
No. unique data	3801	7120
Final no. of variables	235	307
Final R, R_w	0.078, 0.078	0.056, 0.056

dissolved immediately. A white powder was obtained after evaporation at r.t. in darkness (yield 66%).

$Ag(PPh_3)_3Cl$

This complex was prepared as described by Cassel [11].

Collection and Reduction of X-ray Intensity Data

Colourless single crystals of $Ag(PPh_3)_3BF_4$ suitable for diffraction analysis were grown from Cl_2CH_2/petroleum ether solutions whereas crystals of $Ag(PPh_3)_3I$ were obtained from Cl_2CH_2/CH_3CN solutions. Monitoring of standard reflections indicated no decay during the data collection. Shape anisotropy correction was applied to the iodo complex [12]. A summary of crystal data along with details of the data collection is given in Table I.

Solution and Refinement of the Structures

The solution of the two structures was carried out using a three-dimensional Patterson function to determine the position of the heavy atoms, *i.e.* I, Ag and P for the iodo complex, and Ag and P for the tetrafluoroborate complex, and Fourier methods to determine the other non-H atoms. Refinement by least-squares procedures was applied subsequently. The structures were solved with Shel-X program [13]. In the final cycles of least-squares each phenyl group was treated as a rigid body restricted to its idealized geometry (6/*mmm* symmetry, d(C–C) = 1.395 Å) with an individual isotropic thermal parameter for each C atom. The fixed contribution of the H atoms was included into the calculations with idealized positions (d(C–H) = 0.96 Å) and isotropical thermal parameter equal to that of the nearest C atom. Weights were of the type $= 1/[\sigma^2(F_o) + b(F_o{}^2)]$ where the constant b was chosen so as to minimize the dispersion of $\langle w(|F_o| - |F_c|)^2\rangle$ over ranges of reflections. The b values were 0.000609 and 0.000359 for the tetrafluoroborate and the iodo complexes respectively. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for Crystallography [14]. See also 'Supplementary Material'.

NMR Spectra

$^{31}P\{^1H\}$ NMR spectra were run at 80.96 MHz on a Bruker WP Spectrometer of the NMR Service of the CNR Research Area of Montelibretti (Rome) using 10 mm sample tubes in Cl_2CH_2/Cl_2CD_2 (3:1). Coupling constants were measured at −90 °C.

Results and Discussion

Description of the Structures

The crystal structures consist of discrete molecular units with no close intermolecular contacts. Selected geometrical parameters are given in Table II where the complex with X = Cl is also reported for comparison [11].

TABLE II. Parameters Describing Coordination about Silver in $Ag(PPh_3)_3X$

	X = BF_4	X = Cl	X = I	
Distances (Å)				
Ag–P(1)	2.577(3)	2.552(1)	2.607(4)	2.582(4)
Ag–P(2)	2.506(3)	2.552(1)	2.572(4)	2.613(3)
Ag–P(3)	2.543(3)	2.556(1)	2.585(4)	2.616(3)
Ag–X[a]	2.82(1)	2.556(1)	2.855(1)	2.864(1)
⟨Ag–P⟩	2.54	2.55	2.59	2.60
Ag–(PL)[b]	0.39	0.57	0.68	0.72
Angles (°)				
P(1)–Ag–P(2)	114.9(1)	113.41(4)	113.0(1)	113.2(1)
P(1)–Ag–P(3)	119.3(1)	114.69(5)	113.2(1)	114.1(1)
P(2)–Ag–P(3)	119.0(1)	117.09(4)	113.2(1)	110.8(1)
P(1)–Ag–X	116.9(2)	109.72(5)	106.9(1)	104.9(1)
P(2)–Ag–X	89.8(2)	96.66(5)	105.1(1)	109.0(1)
P(3)–Ag–X	89.5(2)	102.75(5)	103.8(1)	104.1(1)
⟨P–Ag–P⟩	117.7	115.0	113.1	112.7
⟨P–Ag–X⟩	98.7	101.6	107.3	108.6
$^1J(^{107}Ag-^{31}P)$[c]	318	277	262	

[a] A fluorine atom in the BF_4 complex. [b] PL. indicates the plane of the three phosphorus atoms. [c] $^1J(^{107}Ag-^{31}P)$ is 309 Hz for $Ag(PPh_3)_3NO_3$.

TABLE III. Selected Atomic Coordinates of $Ag(PPh_3)BF_4$

Atom	*x/a*	*y/b*	*z/c*
Ag(1)	0.48608(5)	0.31626(7)	0.25697(5)
P(1)	0.53818(16)	0.48365(23)	0.23728(17)
P(2)	0.49818(15)	0.18367(26)	0.15777(17)
P(3)	0.37867(16)	0.30195(23)	0.32874(16)
B(1)	0.6146(10)	0.2193(18)	0.4005(13)
F(1)	0.5722(6)	0.2980(9)	0.3906(7)
F(2)	0.5976(6)	0.1522(14)	0.3608(10)
F(3)	0.6022(12)	0.2012(12)	0.4714(8)
F(4)	0.6798(5)	0.2457(9)	0.4051(8)

TABLE IV. Selected Atomic Coordinates of $Ag(PPh_3)_3I$

Atom	*x/a*	*y/b*	*z/c*
Ag(1)	0.23845(8)	0.25329(7)	0.36972(4)
Ag(2)	0.22661(7)	0.23482(7)	0.86393(4)
I(1)	0.22574(5)	0.18113(7)	0.25403(4)
I(2)	0.21832(8)	0.30604(7)	0.75168(4)
P(1)	0.06692(25)	0.24934(25)	0.40804(14)
P(2)	0.35117(25)	0.14421(24)	0.42172(14)
P(3)	0.30853(26)	0.41948(25)	0.36194(16)
P(4)	0.05491(24)	0.24385(24)	0.89867(14)
P(5)	0.28982(24)	0.06521(23)	0.85744(14)
P(6)	0.34722(25)	0.34655(24)	0.92108(15)

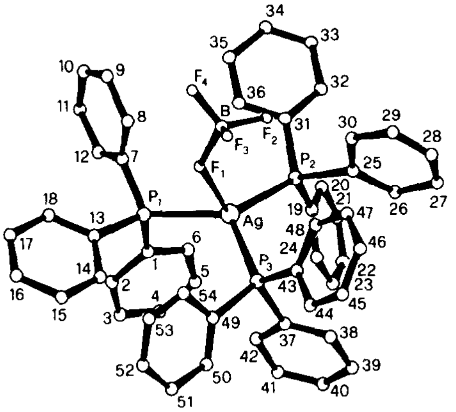

Fig. 1. Perspective view of $Ag(PPh_3)_3BF_4$.

Ag(PPh₃)₃BF₄

Atomic coordinates are given in Table III. Figure 1 shows a view of the complex. The silver atom has a distorted tetrahedral coordination given by three P and one F atoms. The bond angles among these four atoms at the metal are very different to the normal value for tetrahedral geometry. As shown in Table II two P–Ag–P angles are very close to 120° and two P–Ag–F angles very close to 90°. Then the arrangement about the metal could be better described in terms of an almost trigonal coordination in which Ag is bound to the three P atoms and weakly coordinated to the BF_4 group. There is a strong distortion of the plane containing the three P atoms so that the F–Ag direction does not show a threefold symmetry. This complex can be compared with $Cu(PPh_3)_3BF_4$ [15] which has three independent molecules in the asymmetric unit where along each F–Cu direction lies a threefold axis and the P–Cu–P bond angles are 115.9°, 115.2° and 115.8° in each molecule. In our case the average P–Ag–P angle value is 117.7° which displays more trigonal character. The copper complex has the BF_4 anion weakly coordinated [15]. The same consideration about the BF_4 ability to coordinate is deduced from solution studies. In fact the BF_4 and ClO_4 complexes show the highest coupling constant $^1J(^{107}Ag-^{31}P)$ in the trigonal silver phosphine series Ag(1b)X, 1b = 2,11-bis(di-t-butyl)phosphinomethylbenzo[c]phenanthrene, and that indicates the weakest silver–anion bond [8].

Ag(PPh₃)₃I

Selected atomic coordinates are given in Table IV and Fig. 2 shows a view of one molecule of the complex. There are two independent molecules in the asymmetric unit. As with the BF_4 complex, the species has the metal with a distorted tetrahedral arrangement with three P and one I atoms. In this case the Ag–P bond lengths are almost similar in each molecule; the range of variation is 2.57 to

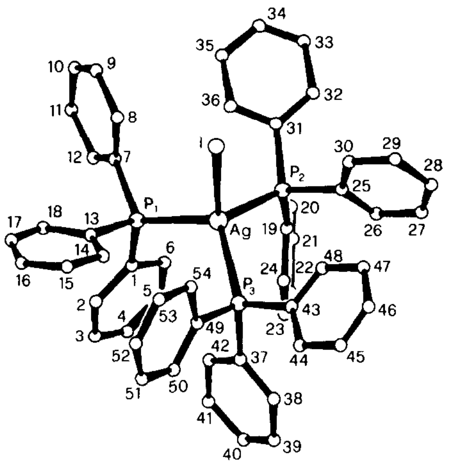

Fig. 2. Perspective view of one molecule of $Ag(PPh_3)_3I$.

2.60 Å for one molecule and 2.58 to 2.61 for the other one against 2.51 to 2.58 for the BF_4 complex. Similarly the variation in the P–Ag–P angles is also smaller, *i.e.* from 113.0° to 113.2° and from 110.8° to 114.1° for the iodo complex against from 114.9° to 119.3° for the other complex. The difference between the two independent molecules is not shown in bond distances; the average Ag–P bond length values are similar, 2.59 and 2.60 Å. Normally these little differences are reflected as large changes in bond angles so that a variation of 0.01 Å is related to 0.4 Å for P–Ag–P and 1.3° for P–Ag–I angles.

Comparison of the Structures and NMR Discussion

We have also included in Table II the structural data for $Ag(PPh_3)_3Cl$ previously described [11]. The related complex $Cu(PPh_3)_3Cl$ [16], which has three independent molecules shows the P–Cu–P angles ranging from 108.4° to 110.5°. These are different from the silver chlorine complex and they have been related to the difference of the tetrahedral covalent radii of the two metals [11]. We have calculated and included in Table II several parameters in order to study trends in the $Ag(PPh_3)_3X$ species as follows:

(a) Average P–Ag–P bond angle. This parameter changes significantly going from BF_4 to the I anion. Its range, 117.7° to 112.7°, can be included in a larger one from 120° to 109.5° that corresponds to a change from a trigonal to a tetrahedral coordination.

(b) Average P–Ag–X bond angle. It ranges from 98.7° to 108.6° and may be included in the range from 90° to 109.5° in agreement with the conclusion at point (a).

(c) Average Ag–P bond distance. This parameter decreases following the same model of coordination change. The variation is less significant.

(d) The distance between the metal and the plane determined by the three phosphorus atoms is also in agreement with the conclusion in (a). It changes significantly from 0.39 to 0.72 Å.

(e) The silver–phosphorus coupling constant is also dependent on the anion. The observed range (from 318 to 262 Hz, including the nitrate value) is in agreement with a progressive decrease of the bond orbital overlapping between Ag and P on the basis of the Fermi contact term [17] that corresponds to a decrease of the Ag–P bond lengths, although other terms could contribute to changing the coupling constant.

Comparing with the $Ag[P(p\text{-tol})_3]_3X$ series [1], *p*-tol = *p*-tolyl group, our complexes show shifts about 3 Hz less for each anion. This feature should be related to the smaller basicity of PPh_3. An extrapolation of our data would indicate a pure trigonal cationic complex without threefold symmetry. In order to confirm this prediction we have also prepared the complex $Ag(PPh_3)_3BPh_4$ where the silver–anion bond is not expected. Unfortunately this compound does not crystallize and the ^{31}P NMR spectra is still dynamic at −90 °C.

Conclusions

From structural studies on the $Ag(PPh_3)_3X$ series, the influence of the anion is confirmed. This is a function of its basicity which induces a large variation in the geometry of the complexes so that the system can be described as going from a tetrahedral to a trigonal configuration at the metal. In addition, ^{31}P NMR solution studies are in agreement with the solid state model. A measure of the basicity of triphenylphosphine related to tri-*p*-tolylphosphine is given by $^1J(Ag–P)$. By comparison with Cu analog complexes our series shows larger average P–M–P bond angles but unlike those complexes the metal–anion direction does not show threefold symmetry.

Supplementary Material

Tables of observed and calculated structure factors, full atomic positions of the two complexes and final thermal parameters are available on request.

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References

1 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, *94*, 6386 (1972).

2 F. J. Hollander, Y. L. Ip and D. Coucouvanis, *Inorg. Chem.*, *15*, 2230 (1976).

3 D. K. Johnson, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta*, *59*, 2691 (1976).

4 R. G. Goel and P. Pilon, *Inorg. Chem.*, *17*, 2876 (1978).

5 P. S. Pregosin and R. W. Kunz, in 'NMR Basic Principles and Progress', Vol. 16, Springer, Berlin, 1979, p. 107.

6 E. C. Alyea, S. A. Diaz and S. Stevens, *Inorg. Chim. Acta*, *44*, L203 (1980).

7 M. Barrow, H. B. Burgi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, *22*, 2356 (1983).

8 M. Camalli, F. Caruso, S. Chaloupka, P. N. Kapoor, P. S. Pergosin and L. M. Venanzi, *Helv. Chim. Acta*, *67*, 1603 (1984).

9 R. W. Kunz, P. S. Pregosin, M. Camalli, F. Caruso and L. Zambonelli, *Helv. Chim. Acta*, *66*, 1661 (1983).

10 H. B. Burgi, R. W. Kunz and P. S. Pregosin, *Inorg. Chem.*, *19*, 3707 (1980).

11 A. Cassel, *Acta Crystallogr., Sect. B*, *37*, 229 (1981).

12 R. Spagna and L. Zambonelli, *J. Chem. Soc. A*, 2544 (1971).

13 G. M. Sheldrick, 'Shel-X 76', a program for crystal structure determination, University of Cambridge, U.K., 1976.

14 'International Tables for X-ray Crystallography', Kynoch Press, Birmingham, U.K., 1974.

15 A. P. Gaughan, Z. Dori and J. Ibers, *Inorg. Chem.*, *13*, 1657 (1974).

16 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. S. Stowens and S. L. Lippard, *Inorg. Chem.*, *15*, 1155 (1976).

17 J. A. Pople and D. P. Santry, *Mol. Phys.*, *8*, 1 (1964).