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P NMR Study on the Ag(triphos)X Series (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, X = anion). Crystal and Molecular Structure of Ag(triphos)I

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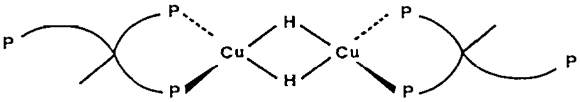
Abstract

The series of complexes Ag(triphos)X, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, X = I, Cl, CH_3COO, NO_3, ClO_4, has been synthesized. P NMR data, in solution, show that anions with lower basicity are associated with higher chemical shifts and higher coupling constants. Only two complexes, X = NO_3 and ClO_4, have available $^1J(^{107}Ag-^{31}P)$, the other complexes are still dynamic at 193 K. The two coupling constants appear higher than expected for complexes of the type 'AgP_3'. The crystalline species Ag(triphos)I is orthorhombic, space group $Pna2_1$, $a = 20.534(6)$, $b = 10.363(3)$, $c = 17.724(4)$ Å, and isomorphous with other tetrahedral complexes of triphos (Ni(triphos)I, Ni(triphos)SO_2). An analysis of complexes of triphos so far reported shows that Ag(triphos)I has the longest (M–P) bond distance and the smallest (P–M–P) bond angle.

Introduction

The triphosphine ligand (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) shows versatile properties in coordination chemistry. Thus, it is able to stabilize coordination number seven as in Mo(triphos)$(CO)_3I_2$ [1]; coordination number six, which is favored for *fac*-octahedral complexes as in Co(triphos)P_3 [2]; coordination number five in two types of geometry: square-pyramidal (Co(triphos)SO_4 [3]) or trigonal-bipyramidal (Ir(triphos)Cl(CO) [4]); coordination number four in tetrahedral (Ni(triphos)I [5]) or square-planar geometry (Ni(triphos)Br_2 [6]). However, the last case is not favored because only two P atoms of the phosphine are coordinated to the metal, with the third one free. Unexpectedly, this binding fashion was also found in a recent tetrahedral copper species, $[Cu(triphos)H]_2$.



This is considered evidence that H atoms can bind to metals stronger than P (phosphine) atoms [7]. The third P atom can also be bound to another metal atom, obtaining in this case polynuclear species like $[Co(triphos)(CO)_2]_2$ [8]. On the other hand we are studying complexes of type ML_nX_m, M = a metal that has at least one isotope of spin = 1/2, L = phosphine, X = anion, from structural and NMR points of view. In our series of complexes, for a given phosphine, the anion X is systematically changed so that its variation in Lewis basicity is related with structural changes of the coordination sphere, as seen by diffraction methods, and changes in the coupling constant NMR, $^1J(M-P)$, obtained by recording ^{31}P NMR spectra in solution. J is composed of three terms: orbital, dipolar and contact. The latter, also known as the Fermi term, is the most important and can be related with structural parameters as indicated by Pople and Santry [9]

$$^1J(M-P) = C(^3\Delta E)^{-1}[S_M(0)]^2[S_P(0)]^2(P'S_MS_P)^2$$

where the term $(P'S_MS_P)^2$ increases directly with the s-character of the acceptor orbital of the metal and the s-character of the donor orbital of the phosphorus atom. Recently we studied the series $Ag(PPh_3)_3X$ [10], Ph = phenyl, where the variation of the P–Ag–P bond angle, strongly linked to the s-characters mentioned above, occurs with two limits: one is the tetrahedral value (109.4°), corresponding to an anion that is strongly bound to the metal, and the other is the trigonal value (120°), which is related to an anion out of the coordination sphere. The associated variations of ^1J(Ag–P) are *c.* 100 Hz. Because the geometrical characteristics of triphos were considered useful in order to extend this structural variation towards angles smaller than 109.4°, the isoelectronic series Ag(triphos)X was synthesized and studied. The related results are reported and discussed in the present work.

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Experimental

Preparation of the Complexes

Silver iodide was obtained from an aqueous solution of $AgNO_3$ by adding KI. The precipitate was later dried. The other salts were purchased from Merck and triphos was purchased from Strem. The general procedure for the preparation of the complexes was by mixing stoichiometric amounts of the phosphine and the corresponding silver salt. A slightly different reaction was used for the chloride complex.

Ag(triphos)I

AgI (73 mg = 0.31 mmol) was added to a hot solution of triphos (194 mg = 0.31 mmol) in CH_3CN, in the dark. After complete dissolution, the filtered solution was left to evaporate at room temperature in the dark. A white powder was obtained.

Ag(triphos)Cl

$(CH_3)_4NCl$ (76 mg = 0.69 mmol) was added to a hot solution of triphos in CH_3CN. Afterwards $AgNO_3$ (177 mg = 0.69 mmol) was added in the dark. When complete dissolution was reached the filtered solution was left to evaporate in the dark. A white powder was obtained.

Ag(triphos)CH_3COO

$AgCH_3COO$ (56 mg = 0.33 mmol) and triphos (210 mg = 0.33 mmol) were reacted as for the iodo complex. A white powder was obtained.

Ag(triphos)NO_3

$AgNO_3$ (47 mg = 0.28 mmol) and triphos (172 mg = 0.28 mmol) were reacted as for the iodo complex. A white powder was obtained.

Ag(triphos)ClO_4

$AgClO_4$ (56 mg = 0.25 mmol) and triphos (156 mg = 0.25 mmol) were reacted as for the iodo complex. A white powder was obtained.

All the complexes were recrystallized from Cl_2CH_2/n-hexane solutions. Only the iodo complex gave crystals suitable for X-ray studies, the other ones gave microcrystalline powders.

Spectroscopic Studies

$^{31}P\{H\}$ NMR spectra were run at 80.96 MHz on a Brucker WP spectrometer of the NMR Service of the CNR Research Area of Montelibretti (Rome) using 10 ml sample tubes in Cl_2CH_2/Cl_2CD_2 (3:1). (See Table 2 for spectroscopic data.) J(Ag–P) was not available for compounds of X = I, Cl and CH_3COO because they are still dynamic at 193 K.

TABLE 1. Summary of crystal data for the compound Ag(triphos)I

Formula	$C_{41}H_{39}AgP_3I$
Formula weight	859.46
a (Å)	20.534(6)
b (Å)	10.363(3)
c (Å)	17.724(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3771.7(17)
Z	4
Space group	$Pna2_1$
Crystal dimension (mm)	0.15 × 0.20 × 0.30
Radiation	Mo Kα
Diffractometer	Nicolet R3
Scan mode	$2\theta-\theta$
Scan range (°)	0.85
Background counts	$\frac{1}{4}$ of scan time at the end of scan range
2θ limits (°)	3–60
No. reflections collected	6327
No. unique data	2148
Final no. variables	414
Final R, R_w	0.056, 0.065

Collection and Reduction of X-ray Data

Monitoring of three standard reflections (−1, 1, 0; 0, 2, −3; 2, 0, 1), taken every 100 reflections, indicated no decay during the data collection and a ψ-scan of some suitable reflections show very low absorption phenomena (*c.* 10–15%) and a sinusoidal form, therefore no correction was applied. Data were corrected by Lorentz and polarization effects. Table 1 summarizes crystal parameters and details of data collection.

Solution and Refinement of the Structure

The structure was solved using the Patterson function to determine the position of the heavy atoms, i.e. I and Ag, and Fourier methods to determine the other non-H atoms with the CAOS program [10]. Refinement by least-square procedures was applied subsequently. The quantity minimized was $\Sigma w(|F_o| - |F_c|)$, with weights of type $w = \sin\theta/\lambda$. All non-H atoms were refined anisotropically. The z coordinate of Ag was fixed after a few cycles of refinement as required by the space group $Pna2_1$. In the final cycles of least-squares the H atoms were included at fixed positions (d(C–H) = 0.96 Å, C–C–H angles = 109.4°) with isotropic displacement parameters of 6.0 Å^2.

Results and Discussion

Table 2 shows P NMR data of the series Ag(triphos)X together with the corresponding values for

TABLE 2. P NMR data in AgLX complexes

X =	L = triphos [a]		L = $(PPh_3)_3$ [a]		L = $(P(p\text{-tolyl})_3)_3$ [b]	
	δ	J(Ag–P)	δ	J(Ag–P)	δ	J(Ag–P)
I	−22.0		−0.89	262	18.8	266
Cl	−15.4		3.15	277	22.7	280
CH_3COO	−13.2					
NO_3	−4.80	489	8.49	309	27.3	312
ClO_4	−4.70	505				

J values in Hertz; chemical shifts in ppm. [a] H_3PO_4 (80%). [b] $P(ethyl)_3$.

TABLE 3. Selected geometrical parameters in Ag(triphos)I

Distances	
Ag–P(1)	2.527(6)
Ag–P(2)	2.555(5)
Ag–P(3)	2.510(5)
Ag–I	2.691(3)
P(1)–C(3)	1.86(2)
P(1)–C(6)	1.84(2)
P(1)–C(12)	1.81(2)
P(2)–C(4)	1.84(2)
P(2)–C(18)	1.82(3)
P(2)–C(24)	1.85(2)
P(3)–C(5)	1.89(2)
P(3)–C(30)	1.85(2)
P(3)–C(36)	1.81(2)
C(1)–C(2)	1.59(3)
C(1)–C(3)	1.61(3)
C(1)–C(4)	1.56(3)
C(1)–C(5)	1.52(3)
Angles	
P(1)–Ag–P(2)	88.9(2)
P(1)–Ag–P(3)	90.3(2)
P(2)–Ag–P(3)	87.8(2)
P(1)–Ag–I	115.5(1)
P(2)–Ag–I	127.5(1)
P(3)–Ag–I	134.0(1)
Ag–P(1)–C(3)	105.6(8)
Ag–P(2)–C(4)	107.1(8)
Ag–P(3)–C(5)	104.9(7)
P(1)–C(3)–C(1)	116(1)
P(2)–C(4)–C(1)	117(1)
P(3)–C(5)–C(1)	116(1)
C(3)–C(1)–C(4)	111(1)
C(3)–C(1)–C(5)	118(1)

the isoelectronic series $Ag(PPh_3)_3X$, Ph = phenyl [10], and $Ag(P(p\text{-tol})_3)_3X$, *p*-tol = *p*-tolyl [12]. The three series of compounds show the same trend on the chemical shifts, i.e. more cationic complexes have higher chemical shifts. This trend is also found in the series Ag(P-P)X, P-P = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene [13], Ag(t-P-P)X, t-P-P = 2,11-bis(di-t-butylphosphinomethyl)benzo[*c*]-phenanthrene [14], $Hg(PPh_3)_2X_2$ [15], and Hg-(P-P)X_2 [16]. Most of the coupling constant values are not available in the triphos series, probably due to dynamic behavior of the species. The two *J*-solved complexes are in agreement with expected values since the perchlorate coupling constant, 505 Hz, is higher than the nitrate one, 489 Hz, as shown in previous studies [10, 12–16]. However, these values are much higher than those of the PPh_3 series. This may be a result from fast exchange of P atoms from complexes with lower coordination number. These complexes may coordinate, in turn, only two of the three arms of the ligand triphos. This supposed exchange would not show the temporarily free P atom in the NMR spectrum if the phenomenon is fast for the NMR time scales. In addition NO_3 and ClO_4 have two oxygen atoms that can simultaneously coordinate on the metal atom completing the tetrahedra that silver normally requires to saturate its electronic capability.

We tried to study also with X-ray methods the structure of the series, unfortunately only one complex gave suitable crystals for this purpose, Ag(triphos)I, and is described below.

The crystal structure of Ag(triphos)I is built up from well separated discrete molecules with no crystallographically imposed symmetry. Selected geometrical parameters of the coordination sphere are given in Table 3, atomic coordinates are given in Table 4, and Fig. 1 shows a view of the molecular structure with Ph and H atoms omitted. The coordination around the metal is tetrahedral with three P atoms of the phosphine and one I atom. This arrangement is considerably distorted since the P angles at the metal site, P–Ag–P, are smaller than the tetrahedral value, 109.4° (see Table 3). These lower angles are counterbalanced by the bond angles P–Ag–I whose values are much larger than 109.4°. One of these angles is very large, P_3–Ag–I = 134.0°. The tetrahedral distortion is due to steric imposition of the ligand triphos whereas it is not clear why P_3–Ag–I is so large. The compound can be compared with the isoelectronic complex $Ag(PPh_3)_3I$ which crystallizes with two independent molecules in the unit cell [10]. Table 5 shows the geometrical parameters of the coordination sphere of the two com-

TABLE 4. Atomic coordinates with e.s.d.s in parentheses

	x	y	z
Ag(1)	0.4296(1)	0.4421(2)	0.3777(0)
I(1)	0.3639(1)	0.5072(2)	0.5034(2)
P(1)	0.4004(3)	0.2257(5)	0.3213(3)
P(2)	0.5498(2)	0.3812(5)	0.3669(3)
P(3)	0.4383(3)	0.5378(5)	0.2480(3)
C(1)	0.507(1)	0.298(2)	0.219(1)
C(2)	0.540(1)	0.229(2)	0.148(1)
C(3)	0.470(1)	0.180(2)	0.261(1)
C(4)	0.566(1)	0.346(2)	0.267(1)
C(5)	0.462(1)	0.398(2)	0.185(1)
C(6)	0.3311(8)	0.215(2)	0.256(1)
C(7)	0.317(1)	0.107(2)	0.213(1)
C(8)	0.265(2)	0.103(3)	0.163(1)
C(9)	0.228(2)	0.212(4)	0.158(2)
C(10)	0.235(1)	0.323(3)	0.203(2)
C(11)	0.2890(9)	0.323(2)	0.250(1)
C(12)	0.3899(9)	0.088(2)	0.383(1)
C(13)	0.358(1)	0.107(3)	0.451(2)
C(14)	0.345(1)	0.009(2)	0.503(2)
C(15)	0.368(1)	−0.112(2)	0.486(1)
C(16)	0.401(1)	−0.134(3)	0.420(2)
C(17)	0.413(1)	−0.033(2)	0.367(2)
C(18)	0.612(1)	0.498(2)	0.394(1)
C(19)	0.673(1)	0.506(2)	0.358(2)
C(20)	0.719(1)	0.591(3)	0.386(2)
C(21)	0.706(2)	0.676(3)	0.442(2)
C(22)	0.645(2)	0.669(3)	0.476(2)
C(23)	0.602(1)	0.578(2)	0.452(1)
C(24)	0.578(1)	0.235(2)	0.417(1)
C(25)	0.539(1)	0.186(2)	0.473(2)
C(26)	0.559(2)	0.081(3)	0.518(2)
C(27)	0.614(3)	0.028(3)	0.505(3)
C(28)	0.656(2)	0.067(4)	0.445(2)
C(29)	0.638(2)	0.179(3)	0.402(2)
C(30)	0.370(1)	0.614(2)	0.197(1)
C(31)	0.362(1)	0.608(3)	0.118(2)
C(32)	0.309(2)	0.672(3)	0.083(2)
C(33)	0.265(2)	0.730(3)	0.126(2)
C(34)	0.270(1)	0.738(2)	0.201(2)
C(35)	0.322(1)	0.677(2)	0.238(2)
C(36)	0.5026(9)	0.654(2)	0.234(1)
C(37)	0.525(1)	0.726(3)	0.296(1)
C(38)	0.569(2)	0.823(3)	0.289(2)
C(39)	0.594(1)	0.858(3)	0.221(3)
C(40)	0.574(2)	0.781(4)	0.157(2)
C(41)	0.531(2)	0.687(4)	0.165(2)

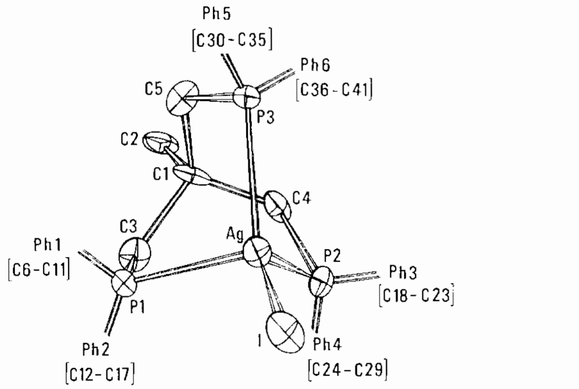

Fig. 1. A view of Ag(triphos)I with H atoms and phenyl groups omitted.

TABLE 5. Selected geometrical parameters[a] for the isoelectronic complexes Ag(triphos)I and $Ag(PPh_3)_3I$ [b]

Parameter	Ag(triphos)I	$Ag(PPh_3)_3I$	$Ag(PPh_3)_3I$
Ag–P(1)	2.527(6)	2.607(4)	2.582(4)
Ag–P(2)	2.555(5)	2.572(4)	2.613(3)
Ag–P(3)	2.510(5)	2.585(4)	2.616(3)
⟨Ag–P⟩	2.531(6)	2.588(4)	2.603(4)
Ag–I	2.691(3)	2.855(1)	2.864(1)
⟨P–Ag–P⟩	88.9(2)	113.1(1)	112.7(1)

[a] Distances in Å, angles in °. [b] Two molecules in the asymmetric unit.

plexes. It is observed that shorter Ag–P bonds are present in the triphos complex. The Ag–P mean value is 2.53 Å versus 2.59 and 2.60 Å respectively. Also the Ag–I bond is shorter, 2.691(3) versus 2.855(1) and 2.864(1) Å, respectively. It is noteworthy that the metal in the chelate complex exhibits strong metal–triphos bonding which might be expected to be counterbalanced by lengthening the Ag–anion bond but is not. Individual comparison among bond angles of the coordination sphere of the two species appears unsuitable because the PPh_3 complex shows angles close to the tetrahedral value while the triphos complex is very much distorted. The two molecules of the PPh_3 complex show mean coordination bond angles (1/6 of the sum of the six bond angles at the metal) slightly wider than the normal tetrahedral value, 109.4°, i.e. 110.2 and 110.6°, while the value for the triphos complex is much lower, 107.3°. In this context the great distortion of P_3–Ag–I (134.0°) in Ag(triphos)I may be seen as a way that the complex seeks to gain more 'tetrahedral' character (namely by increasing the mean tetrahedral value). This possibility can be related to the fact that the silver–anion bond does not exhibit three-fold symmetry in all the complexes of the series $Ag(PPh_3)_3X$ [10] unlike the copper–anion bond in $Cu(PPh_3)_3X$, X = Cl [17] and BF_4 [18]. Perhaps silver is more able to distort the tetrahedral system than copper and this effect is relevant for the bulky ligand triphos. A lack of equivalence in silver bonds is seen also in other examples. Thus, in the series AgLX, L = P-P or t-P-P, if the anion is weakly coordinated ($X = ClO_4$), the two Ag–P bond distances are equivalent, 2.401(3) and 2.417(3) Å (P-P), 2.393(2) and 2.394(2) Å (t-P-P), but if the anion is more basic (Cl), the Ag–P distances become significantly different, 2.458(3) and 2.411(3) Å (P-P), 2.457(2) and

2.427(2) Å (t-P-P) [13, 14]. This significant difference is also present in $Ag(PPh_3)_3I$ and Ag(triphos)I (see Table 5).

The crystal packing of Ag(triphos)I seems to be energetically favored since isomorphous complexes have been reported. Thus, tetrahedral examples are Ni(triphos)SO_2, ($a = 20.451$, $b = 10.246$, $c = 17.349$ Å [19]), Ni(triphos)I ($a = 20.439$, $b = 10.359$, $c = 17.143$ Å [5]); or five-coordinate complexes as Co(triphos)X, X = BH_4 ($a = 20.530$, $b = 10.316$, $c = 17.120$ Å [19]), X = SO_4 ($a = 20.341$, $b = 10.440$, $c = 17.339$ Å [3]), or Ni(triphos)S_2O_4 ($a = 20.472$, $b = 10.475$, $c = 17.759$ Å [3]). It should be noted that this driving force is not enough to guide the Ag(triphos)X complexes (with the exception of X = I) to reach the same intermolecular environment. This may be accounted for if the triphos series follows a different structural trend for the other X anions as indicated by *J*(Ag–P) in solution (X = NO_3 and ClO_4). In any case a closer investigation of the structural properties of the ligand triphos is required.

Table 6 includes representative structural parameters for 16 complexes of triphos that have been studied by diffraction methods. In the Table the complexes are ordered as mean values of metal–phosphorus bonds increase. It should be noted that our complex is not included in the so far known range of ⟨M–P⟩ bonds (2.19–2.38 Å) and that the value is much longer e.g. 2.53 Å. In addition, P–Ag–P shows the minimum ⟨P–M–P⟩ value, 88.9°, of the range of variation (88.9–94.9°) in Table 6 (other complexes of triphos are reported in ref. 27, all of them follow these trends). It is observed that, although with exceptions like $Fe_2H_3(triphos)_2$, Co(triphos)(S_2CO) or $Pd_2P_3(triphos)_2$, longer M–P bond distances can be associated with smaller P–M–P bond angles. Recently, complexes of the type 'AgP_2' were reported as having similar patterns for Ag–P bond distances and P–Ag–P bond angles [20]. The variation of the distances (mean values) between P and the γ-C atoms of the ligand (C(3), C(4) and C(5)) is small (3.09–3.28 Å), and only in three examples is it longer than 3.20 Å. The value in our complex, 3.27 Å, is close to the longest one. Also our complex shows limiting values of the C(*i*)–C(1)–C(*j*) angles ($i = 3$–5, $j = 3$–5, $i \neq j$) e.g. 114.3°, the range being 110.3–114.3°. The related individual maximum values have the range 110.9–118.9° and our complex has the C(4)–C(1)–C(5) angle of 118.1°, that is close to the maximum of the range. The minimum distance among P atoms ranges from 3.09 to 3.51 Å; also our complex has the limiting value (3.51 Å). Another comparison can be made with complexes that only have tetrahedral hybridization, Ni(triphos)I [5] and Ni(triphos)SO_2 [19]. The P–M–X angles are 116.2, 125.0, 125.3° (Ni(triphos)I); 117.5, 121.2, 126.3° (Ni(triphos)SO_2) and 115.5, 127.5, 134.0° (Ag(triphos)I), showing our complex to be more dis-

TABLE 6. Selected geometrical parameters in complexes of the ligand triphos (Tr)

Complex	⟨M–P⟩	⟨P–M–P⟩	⟨P–C3,4,5⟩	P–C1	P1–P2, P1–P3, P2–P3	*Ci*–C1–*Cj* [a]	⟨*Ci*–C1–*Cj*⟩	*CN* [b]	Geometry [c]	Reference
$CoTrP_3$	2.186(1)	93.55(4)	3.127(5)	2.866(5)	3.186(2), 3.186(2), 3.186(2)	111.8(3), 111.8(3), 111.8(3)	111.8(3)	6	OC	2
$NiTrSO_2$	2.205(3)	94.9(1)	3.17(1)	2.89(1)	3.194(6), 3.275(6), 3.278(6)	109.9(8), 111.4(8), 114.2(8)	111.8(8)	4	TE	19
$CoTrP_3Cr(CO)_{10}$	2.204(4)	92.6(2)	3.09(4)	2.84(4)	3.136(6), 3.163(6), 3.263(6)	111(1), 112(1), 114(1)	112(1)	6	OC	2
$TrFeH_3FeTr$	2.21	89	atomic positions not published					6	OC	21
NiTrI	2.222(4)	94.3(1)	3.17(2)	2.87(2)	3.193(8), 3.250(8), 3.324(8)	110(1), 113(1), 115(1)	113(1)	4	TE	5
$CoTrSO_4$	2.238(6)	90.6(2)	3.12(4)	2.87(4)	3.09(1), 3.20(1), 3.25(1)	111(1), 111(1), 112(1)	111(1)	5	SQ-PY	22
$NiTrP_3$	2.243(2)	93.7(1)	3.148(8)	2.892(4)	3.200(3), 3.311(3), 3.331(3)	110.2(5), 111.8(5), 113.2(5)	111.7(5)	6	OC	23
$CoTrBH_4$	2.250(6)	91.4(2)	3.12(2)	2.87(2)	3.09(7), 3.20(7), 3.25(7)	109(1), 111(1), 111(1)	110(1)	5	SQ-PY	19
$CoTr(S_2CO)$	2.258(8)	90.7(3)	3.17(2)	2.86(2)	3.16(1), 3.24(1), 3.25(1)	111(1), 112(1), 115(1)	113(1)	5	SQ-PY	24
$IrTrP_3$	2.277(2)	91.22(7)	3.181(8)	2.865(8)	3.254(4), 3.254(4), 3.254(4)	113.9(5), 113.9(5), 113.9(5)	113.9(5)	6	OC	25
$RhTrP_3$	2.294(1)	91.25(4)	3.162(5)	2.890(5)	3.279(2), 3.279(2), 3.279(2)	111.8(4), 111.8(4), 111.8(4)	111.8(4)	6	OC	25
$NiTr(SeO_4)$	2.332(6)	90.4(2)	3.18(4)	2.90(4)	3.28(1), 3.32(1), 3.34(1)	109(1), 111(1), 112(1)	111(1)	5	SQ-PY	22
$PtTrP_3$	2.339(8)	90.9(1)	atomic positions not published					6	OC	23
$PdTrP_3$	2.368(7)	90.9(2)	3.19(2)	2.89(2)	3.28(1), 3.41(1), 3.43(1)	112(1), 112(1), 118(1)	113(1)	6	OC	26
$TrPdP_3PdTr$	2.378(7)	92.0(2)	3.29(2)	2.89(2)	3.25(1), 3.27(1), 3.30(1)	107(1), 111(1), 118(1)	112(1)	6	OC	26
IrTrClCO	2.380(4)	90.3(1)	3.23(2)	2.86(2)	3.15(1), 3.29(1), 3.38(1)	111(1), 112(1), 119(1)	114(1)	5	TR-BI	4
AgTrI	2.531(6)	88.9(2)	3.27(2)	2.92(2)	3.511(8), 3.559(8), 3.572(8)	111(1), 114(1), 118(1)	114(1)	4	TE	

[a] $i, j = 3$–5, $i \neq j$.

[b] *CN* = Coordination number.

[c] OC = octahedral, TE = tetrahedral, SQ-PY = square-pyramidal, TR-BI = trigonal-bipyramidal.

torted. All these data show that our compound occupies a particular position in the family of triphos complexes. Is this due to the fact that no other tetrahedral complexes belonging to the second transition series have been studied? This is difficult to address because, except for the I derivative, no other silver complexes are crystalline and other metals do not seem suitable for this study. It is observed that there are no complexes of triphos with mean M–P bonds longer than 2.38 Å, (except for Ag(triphos)I).

Conclusions

The series of complexes Ag(triphos)X shows similar P NMR trends (chemical shifts, δ, and coupling constants, $^1J(^{107}\text{Ag}-^{31}\text{P})$) as the isoelectronic series $\text{Ag(PPh}_3)_3\text{X}$, although the values of the available coupling constants in solution ($\text{X} = \text{NO}_3$, ClO_4) are higher. These values suggest that one P atom of the ligand, in turn, is not coordinated to the metal. Dynamic behavior in solution does not allow definitive structure assignment for all of the series and the only suitable complex for solid state study (X = I) has a different structure than that seen for the complexes with $\text{X} = \text{NO}_3$, ClO_4 in solution, namely with three P atoms coordinated. The structure of Ag(triphos)I and a comparison with structural analyses of complexes of triphos so far reported, shows that the I complex has the longest ⟨M–P⟩ bond distance and the smallest ⟨P–M–P⟩ bond angle.

Supplementary Material

Tables of observed and calculated structure factors and anisotropic displacement parameters are available from the authors.

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