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# Coordination Properties of Silver Diphosphine Complexes. Crystal and Molecular Structures of $Ag_2X_2(m\text{-PP})_2$ (X = I, Cl, $NO_3$; *m*-PP = 1,3-Bis[(diphenylphosphino)methyl]benzene) and $Ag_2X_2(o\text{-PP})_2$ (X = I, Cl; *o*-PP = 1,2-Bis[(diphenylphosphino)methyl]benzene). Synthesis and $^1H$- and $^{31}P$-NMR Spectroscopy of Silver Diphosphine Complexes

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The synthesis and $^1H$- and $^{31}P$-NMR spectra of silver halides and silver nitrate complexes of the ligands 1,3-bis[(diphenylphosphino)methyl]benzene (*m*-PP) and 1,2-bis[(diphenylphosphino)methyl]benzene (*o*-PP) are reported. The crystal and molecular structures of $Ag_2X_2(m\text{-PP})_2$ (X = I, Cl, $NO_3$) and $Ag_2X_2(o\text{-PP})_2$ (X = I, Cl) show that these complexes are binuclear with a rhomboid core consisting of two metals and two anionic ligands. The metal is tetrahedrally surrounded by the two bridging anions and two P atoms. For *m*-PP complexes, each Ag atom is bound to P atoms of different phosphines which also act as bridging ligands. On the other hand, the *o*-PP ligand coordinates in a chelate fashion. This difference in behavior is related to the length of the chain between the phosphine donors, which determines whether chelation can occur in complexes of composition AgX(*o*-PP). The bond angle P−Ag−P, ranging from 110 to 138°, is related to the nucleophilicity of the anions. In the *m*-PP complexes, the shape of the rhomboid core is strongly influenced by the van der Waals interactions of the core atoms. Crystal data are as follows: $Ag_2I_2(m\text{-PP})_2$, monoclinic, $P2_1/c$, $Z = 4$, $a = 12.082(4)$ Å, $b = 22.536(9)$ Å, $c = 22.438(5)$ Å, $\beta = 104.22(2)°$; $Ag_2Cl_2(m\text{-PP})_2$, triclinic, $P\bar{1}$, $Z = 2$, $a = 12.307(3)$ Å, $b = 12.704(3)$ Å, $c = 19.673(5)$ Å, $\alpha = 90.02(2)°$, $\beta = 104.55(2)°$, $\gamma = 96.97(2)°$; $Ag_2(NO_3)_2(m\text{-PP})_2$, triclinic, $P\bar{1}$, $Z = 2$, $a = 12.303(6)$ Å, $b = 12.953(9)$ Å, $c = 19.572(8)$ Å, $\alpha = 88.89(5)°$, $\beta = 74.13(3)°$, $\gamma = 80.95(5)°$; $Ag_2I_2(o\text{-PP})_2$, monoclinic, $P2_1/a$, $Z = 2$, $a = 14.542(2)$ Å, $b = 16.828(3)$ Å, $c = 12.857(2)$ Å, $\beta = 70.71(1)°$; $Ag_2Cl_2(o\text{-PP})_2$, monoclinic, $P2_1/a$, $Z = 2$, $a = 14.046(4)$ Å, $b = 16.882(3)$ Å, $c = 12.845(5)$ Å, $\beta = 68.63(3)°$.

## Introduction

Solution studies of the coordinating properties of the silver ion show that this ion can exhibit coordination numbers ranging from 2 to 4 and that the preference for a given coordination number depends on the nature of the ligand or ligands bound to the metal center.[1]

When phosphine ligands are used, the molecular structures of the complexes are strongly influenced by the combination of two factors, namely, the ligand bulkiness and the coordinating ability of the counterion X. Thus, if the phosphine has bulky substituents and the counterion X has low coordination ability, coordination number 2 is preferred as in $[Ag(P(mesityl)_2)_2]^+X^-$ (X = $ClO_4$, $NO_3$), with the anion being outside the coordination sphere.[2] If the counterion X has higher coordination ability as found with halides, coordination number 2 is still obtained, but compounds[2] are of the type $AgXP(mesityl)_2$.

On the other hand, a smaller phosphine such as L = P(*p*-tolyl)$_3$ forms complexes with coordination number 4, the metal having tetrahedral geometry, as in $[AgL_4]^+X^-$ or $AgL_3X$ as indicated by $^{31}P$-NMR spectroscopy.[3] Both types of compounds have been observed with diffraction methods for the Ag complexes of L = $PPh_3$.[4−7] As for the P−mesityl ligand only anions of weak coordinating ability are outside the coordination sphere.

Furthermore, if the phosphines are small and are not used in excess relative to the metal salt as is the case for the examples above, complexes of the compositions "AgXP" and "$AgXP_2$" are obtained. However, the metal center in these compounds has tetrahedral configuration. Compounds of the former type are tetrameric with each metal surrounded by three halides and one phosphine (each halide bridging three metals) in a cubane-like geometry;[8] compounds of the latter composition are dimeric with each metal surrounded by two halides and two phosphines (the former bridging two metals) as in $Ag_2Cl_2(PPh_3)_4$.[9]

Finally, a phosphine of intermediate bulkiness[10] such as $PCy_3$ forms mononuclear complexes of the type $AgX(PCy_3)_2$ (X = $NO_3$, $ClO_4$), where the anions are weakly bound to the metal.[11]

When bidentate ligands are used, the coordination geometry depends also on the length of the chain between the two donor

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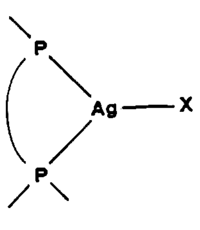
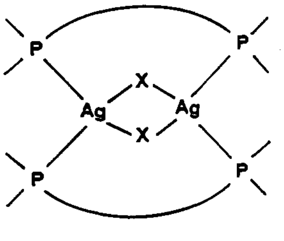
atoms and, with certain ligands, e.g. 2,11-bis[(di-R-phosphino)methyl]benzo[*c*]phenanthrene (R = Ph,[12] *tert*-butyl,[13] ethyl[14]) (R-PP) and 3,3′-oxybis[[(diphenylphosphino)methyl]benzene],[15] three-coordinate species are frequently found (type **A**). They can even assume a T-shaped structure.[14]



A



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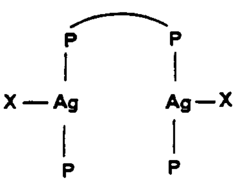

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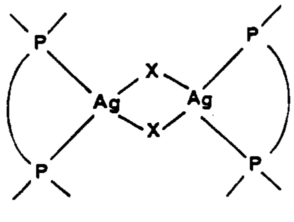

D

However, bidentate ligands such as 1,5-bis(diphenylphosphino)pentane,[16] C-PP, and bis[(diphenylphosphino)ethyl]sulfide,[17] S-PP, give complexes of type **B** while ligands with shorter chains between the donor P atoms[18−20] give complexes of type **C**.

The extent to which the formation of mononuclear species, which are coordinatively unsaturated, can be induced by using suitable ligands has not been actively pursued. We report here the use of the ligands 1,3-bis[(diphenylphosphino)methyl]benzene (*m*-PP) and 1,2-bis[(diphenylphosphino)methyl]benzene (*o*-PP) as they are closely related to the benzo[*c*]phenanthrene ligands (R-PP) used in earlier studies[12−14] and the second ligand places P donor atoms at shorter distances than in the R-PP complexes. We report here the occurrence of yet another type of structure, i.e. **D**, obtained when the ligand *o*-PP is used. Additional interest in these species stems from the fact that recently one silver−diphosphine complex, $Ag(DPPE)_2{}^+NO_3{}^-$ (DPPE = (diphenylphosphino)ethane), has shown antitumor activity.[21] Given that the isoelectronic complex $Au(DPPE)_2{}^+NO_3{}^-$ is also active, the cytotoxicity was ascribed to the diphosphine, which was supposedly released after cleavage of the M−P bond at the target cell.[22] We describe here five Ag−diphosphine molecular structures.

## Experimental Section

**General Considerations.** All operations were performed under an $O_2$-free Ar or $N_2$ atmosphere. Unless otherwise stated, solvents were dried and deoxygenated prior to use. Elemental analyses were performed by the Microanalytical Laboratory of the Swiss Federal Institute of Technology (ETH). The $^{31}$P-NMR spectra were recorded either at 36.43 MHz on a Bruker HX-90 or at 101.21 MHz on a Bruker WM-250 spectrometer, while for the $^1$H-NMR spectra a Bruker WM-250 spectrometer operating at 250 MHz was used. A positive sign on the chemical shift denotes a resonance to low field of the reference (external $H_3PO_4$ and TMS). Further details have been given elsewhere.[23]

**1,2-Bis[(diphenylphosphino)methyl]benzene, *o*-PP.** This compound was prepared as described elsewhere.[24]

**1,3-Bis[(diphenylphosphino)methyl]benzene, *m*-PP.** $NH_3$ (600 mL) was condensed into a 2-L flask, and Na (12.3 g, 0.534 mol) was added. $PPh_3$ (68.09 g, 0.259 mol) was added to the stirred deep blue solution. $NH_4Cl$ (14.4 g, 0.269 mol) was then slowly added within 1 h to the resulting mixture (red solution with white precipitate). Stirring was continued for an additional 30 min; then 1,3-bis(dichloromethyl)benzene (23.564 g, 0.135 mol) was added within 10 min, and stirring was continued for an additional 2 h. The resulting suspension was treated with 800 mL of moist $Et_2O$. The cooling bath was removed and the ammonia allowed to evaporate over a period of 5 h. The solid residue was filtered off and the filtrate cooled to −22 °C, whereby the product precipitated as colorless crystals. Yield: 47 g. Additional quantities of product could be obtained by evaporating the mother liquor. Total yield: 57 g (85%).

The syntheses of all the silver complexes were carried out under the exclusion of light.

**$Ag_2Cl_2$(*m*-PP)$_2$.** The ligand (1.46 g, 3.08 mmol), dissolved in $CH_2Cl_2$ (200 mL), was treated with $AgCF_3SO_3$ (0.65 g, 2.53 mmol), and the suspension was stirred until a clear solution was obtained (ca. 1 day). Solid NaCl (0.89 g) was then added and the suspension stirred for 1 h. The resulting solid was filtered off over Celite, and the filtrate was covered with a layer of EtOH. On standing, the crystalline product was formed. Yield: 1.18 g (75%). Mp: ca. 245 °C dec. Anal. Calcd: C, 62.21; H, 4.57; Cl, 5.74; P, 10.03. Found: C, 61.74; H, 4.64; Cl, 4.65; P, 9.78.

**$Ag_2Br_2$(*m*-PP)$_2$.** This complex was prepared and purified from $Ag_2(NO_3)_2$(*m*-PP)$_2$ (0.194 g, 0.30 mmol) in $CH_2Cl_2$ (50 mL) and CsBr in acetone (10 mL). Yield: 0.184 g (92%). Mp: ca. 216 °C dec. Anal. Calcd: C, 58.08; H, 4.26; Br, 12.07. Found: C, 57.93; H, 4.15; Br, 11.72.

**$Ag_2I_2$(*m*-PP)$_2$.** This complex was prepared and purified as above from $Ag_2(NO_3)_2$(*m*-PP)$_2$ and CsI. Yield: 91%. Mp: ca. 260 °C dec. Anal. Calcd: C, 54.19; H, 3.98; I, 17.89. Found: C, 53.92; H, 3.84; I, 14.66.

**$Ag_2(NO_3)_2$(*m*-PP)$_2$.** The ligand (0.45 g, 0.95 mmol), dissolved in $CH_2Cl_2$ (100 mL), was treated with $AgNO_3$ (0.17 g, 1 mmol) and the resulting suspension stirred for 1 day. The solution was filtered over Celite, and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from $CH_2Cl_2$/EtOH. Yield: 0.29 g (47%). Mp: ca. 225 °C dec. Anal. Calcd: C, 59.65; H, 4.38; N, 2.17. Found: C, 59.38; H, 4.66; N, 2.08.

The *o*-PP complexes were prepared and purified as given for the *m*-PP analogs.

**$Ag_2Cl_2$(*o*-PP)$_2$.** Yield: 58%. Mp: ca. 255 °C dec. Anal. Calcd: C, 62.21; H, 4.57; Cl, 5.74; P, 10.03. Found: C, 62.09; H, 4.62; Cl, 54.88; P, 9.88.

**$Ag_2Br_2$(*o*-PP)$_2$.** Yield: 86%. Mp: ca. 252 °C. Anal. Calcd: C, 58.03; H, 4.26. Found: C, 58.03; H, 4.34.

**$Ag_2I_2$(*o*-PP)$_2$.** Yield: 88%. Mp: ca. 215 °C dec. Anal. Calcd: C, 54.19; H, 3.98; I, 17.89; P, 8.73. Found: C, 54.12; H, 3.97; I, 17.26; P, 8.14.

**Collection and Reduction of X-ray Data.** Colorless single crystals of the *m*-PP complexes were grown from $CH_2Cl_2/CH_3CN$ (I), $CH_2Cl_2/CH_3COOC_2H_5$ (Cl), and $CH_2Cl_2/(CH_3)_2CO$ ($NO_3$) solutions, whereas

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**Table 1.** Crystallographic Data

| ligand | *m*-PP | *m*-PP | *m*-PP | *o*-PP | *o*-PP |
|---|---|---|---|---|---|
| X | I | Cl | $NO_3$ | Cl | I |
| formula | $C_{64}H_{56}P_4I_2Ag_2$ | $C_{64}H_{56}P_4Cl_2Ag_2$ | $C_{64}H_{56}N_2O_6P_4Ag_2$ | $C_{64}H_{56}P_4Cl_2Ag_2$ | $C_{64}H_{56}P_4I_2Ag_2$ |
| fw | 1418.60 | 1235.38 | 1288.49 | 1235.38 | 1418.60 |
| $a$, Å | 12.082(4) | 12.307(3) | 12.303(6) | 14.046(4) | 14.542(2) |
| $b$, Å | 22.536(9) | 12.704(3) | 12.953(9) | 16.882(3) | 16.828(3) |
| $c$, Å | 22.438(5) | 19.673(5) | 19.572(8) | 12.845(5) | 12.857(2) |
| $\alpha$, deg | 90 | 90.02(2) | 88.89(5) | 90 | 90 |
| $\beta$, deg | 104.22(2) | 104.55(2) | 74.13(3) | 68.63(3) | 70.71(1) |
| $\gamma$, deg | 90 | 96.97(2) | 80.95(5) | 90 | 90 |
| $V$, Å$^3$ | 5922(3) | 2953(1) | 2962(3) | 2836(1) | 2970(1) |
| $Z$ | 4 | 2 | 2 | 4 | 2 |
| space group (No.) | $P2_1/c$ (14) | $P\bar{1}$ (2) | $P\bar{1}$ (2) | $P2_1/a$ (14) | $P2_1/a$ (14) |
| $T$, °C | 25 | 25 | 25 | 25 | 25 |
| $\lambda$, Å | 0.71069 | 0.71069 | 0.71069 | 1.54178 | 0.71069 |
| density,[a] g/cm$^3$ | 1.592 | 1.390 | 1.446 | 1.447 | 1.587 |
| $\mu$, cm$^{-1}$ | 18.470 | 8.834 | 8.073 | 78.813 | 18.417 |
| transm coeff | 1/1 | 1/1 | 1/1 | 0.58/1 | 0.68/1 |
| $R$[b] | 0.064 | 0.078 | 0.062 | 0.035 | 0.038 |
| $R_w$[c] | 0.056 | 0.084 | 0.084 | 0.047 | 0.044 |

[a] Calculated. [b] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

**Table 2.** $^1$H-NMR Data for Complexes of the Types $Ag_2X_2(m\text{-PP})_2$ and $Ag_2X_2(o\text{-PP})_2$

| ligand | X | $\delta(H_a)$[a] | $\delta(H_b)$[b] | $\delta(H_c)$[c] | $\delta(H_d)$[d] |
|---|---|---|---|---|---|
| *m*-PP | Cl | 3.79 | 8.56 | 6.55 | 6.72 |
| | Br | 3.89 | 9.12 | 6.55 | 6.72 |
| | I | 3.83 | 8.85 | 6.51 | 6.73 |
| | $NO_3$ | 3.72 | 7.96 | 6.34 | 6.62 |
| *o*-PP | Cl | 3.72 | | 6.29 | 6.78 |
| | Br | 3.74 | | 6.32 | 6.81 |
| | I | 3.76 | | 6.33 | 6.81 |

[a] $CH_2$ resonances. Those of the *m*-PP complexes appear as pseudotriplets with $|^2J(P-H) + {}^4J(P-H)| \approx 6$ Hz. [b] Resonances of the aromatic H protons between the two substituents. [c] Resonances of the aromatic H protons in *o*- and *p*-positions to the substituents in *m*-PP and in *o*-positions to the substituents in *o*-PP. [d] Resonances of the aromatic protons in *m*-positions to the substituents in *m*-PP and in *m*- and *p*-positions in *o*-PP.

**Table 3.** $^{31}$P-NMR Data for Complexes of the Types $Ag_2X_2(m\text{-PP})_2$ and $Ag_2X_2(o\text{-PP})_2$[a]

| ligand | X | $\delta$(P) | $^1J(^{107,109}Ag-^{31}P)$, Hz |
|---|---|---|---|
| *m*-PP | Cl | −0.5 | 382, 441 |
| *m*-PP | Br | −2.0 | 377, 434 |
| *m*-PP | I | −9.3 | 337, 388 |
| *m*-PP | $NO_3$ | 5.0 | 457, 525 |
| *o*-PP | Cl | 0.8 | 359, 413 |
| *o*-PP | Br | 0.7 | 353, 404 |
| *o*-PP | I | −4.3 | 328, 378 |

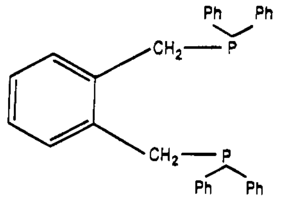
[a] Spectra obtained from $Cl_3CH$ solutions at room temperature.

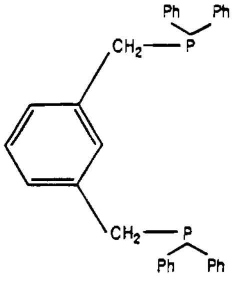
those of the *o*-PP complexes, also colorless, were grown from $CH_2Cl_2/C_2H_5OH$ for both I and Cl complexes. Monitoring of standard reflections, taken every 100 reflections, indicated no decay during data collection, and $\psi$ scans of some suitable reflections showed absorption phenomena only for the *o*-PP complexes (reflections: [1,3,2], [1,6,2], for X = I; [2,3,0], [4,5,0], for X = Cl); for these complexes, the corresponding corrections were applied. Data were also corrected for Lorentz and polarization effects. Table 1 shows crystallographic data.

**Solution and Refinement of the Structures.** The structures were solved using three-dimensional Patterson functions to determine the positions of the heavy atoms of the complexes, e.g. Ag and I for the I complexes and Ag for the others, and Fourier methods to determine the other non-H atoms. Refinement by least-squares procedures was applied subsequently. The quantity minimized was $\Sigma w(|F_o| - |F_c|)$. In the final cycles of least-squares, the H atoms were included at fixed positions ($d$(C−H) = 1.08 Å for $[AgI(m\text{-PP})]_2$ and 0.96 Å for the other complexes, C−C−H angle = 120 or 109.5°). $Ag_2I_2(m\text{-PP})_2$ was solved by using the SHELX program[25] with weights of the type $1/[\sigma(F_o) + b(F_o)^2]$ where the constant $b$ was chosen so as to minimize the dispersion of $\langle w(|F_o| - |F_c|)\rangle$ over ranges of reflections; the $b$ value was 0.00018. In this complex, each aromatic ring, except the *m*-xylene, was treated as a rigid body restricted to its idealized geometry (6/*mmm* symmetry, $d$(C−C) = 1.392 Å, $d$(C−H) = 1.08 Å) with an individual isotropic displacement parameter for each atom. The other complexes were solved with the CAOS program.[26] Weights were of the type $w = 1/(a + F_o + cF_o^2)$ where the constants $a$ and $c$ are of the order of $2F_o(\min)$ and $2/F_o(\max)$.[27] The calculations were performed on an Eclipse MV/8000 II Data General computer. Atomic scattering factors and anomalous dispersion terms were taken from ref 28.

## Results and Discussion

The ligands 1,2-bis[(diphenylphosphino)methyl]benzene, *o*-PP, and 1,3-bis[(diphenylphosphino)methyl]benzene, *m*-PP, react with the silver halides and nitrate, to give complexes of the composition MX(LL). These complexes were characterized by microanalysis, as well as by $^1$H- and $^{31}$P-NMR spectroscopy. The latter data are given in Tables 2 and 3. The $\delta(^{31}P)$ values and the corresponding $^1J(^{107,109}Ag-^{31}P)$ coupling constants fall in the expected range and are similar to those reported for related compounds.[12-14]





Since complexes of the composition given by the chelating ligands 2,11-bis[(di-R-phosphino)methyl]benzo[*c*]phenanthrene, Ph-PP (for R = phenyl), tBu-PP (for R = *tert*-butyl), and Et-PP (for R = ethyl), were mononuclear,[12-14] while those with more flexible systems, e.g. bis[(diphenylphosphino)ethyl] sulfide, S-PP, and 1,5-bis(diphenylphosphine)pentane, C-PP, proved

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to be dimeric complexes,[16,17] the X-ray crystal structures of five of the silver complexes with *o*-PP and *m*-PP were determined and are described below.

**The Structures of Ag$_2$($\mu$-X)$_2$($\mu$-*m*-PP)$_2$.** The crystal structures of these compounds are built from well-separated discrete molecules with no crystallographically imposed symmetry. Atomic coordinates for X = Cl are given in Table 4 whereas those for X = I and X = NO$_3$ are given as supplementary Tables S1 and S2. Figures 1 and 2 show computer-generated views of the structures of Ag$_2$($\mu$-Cl)$_2$($\mu$-*m*-PP)$_2$ and Ag$_2$($\mu$-O−NO$_2$)$_2$($\mu$-*m*-PP)$_2$, respectively. The corresponding view of Ag$_2$($\mu$-I)$_2$($\mu$-*m*-PP)$_2$ is given as supplementary Figure S1. The complexes contain binuclear units in which the metal is coordinated by two P atoms and two atoms belonging to the anions, i.e. Cl, O, and I, respectively, in a distorted tetrahedral arrangement. The molecule 1,3-bis[(diphenylphosphino)methyl]-benzene, *m*-PP, acts as a bridging ligand with the two P atoms coordinating to different Ag atoms. The metals are also linked by the halide anions (or the O atom in the nitrate complex) so that the core of the complex is a rhomboid with Ag−Ag and X−X (or O−O) diagonals. These four atoms are coplanar (deviations are less than 0.03 Å). Also the four P atoms are approximately coplanar (deviations are within 0.4 Å (I), 0.8 Å (Cl), and 0.9 Å (NO$_3$)). The metals are also contained in this plane, as their deviations are less than 0.1 Å for the three complexes. These two planes are approximately perpendicular, with intersecting angles of 89° (I), 90° (Cl), and 96° (NO$_3$).

Each nitrate is coordinated to both metals through a single O atom. Addison et al. have reviewed the bonding modes of the nitrate ion in complexes.[29] Most bridging nitrate ligands coordinate through two O atoms, each bound to a different metal atom. Only one of the complexes mentioned in this review, i.e. Cu$_2$(NO$_3$)$_2$(pyridine)$_4$, shows the same type of NO$_3$ binding as in our complex.[30] Moreover, the core of this dimeric complex is a rhomboid as in our case. Two isostructural[6,31] complexes with Ag−NO$_3$ cores are Ag$_2$(NO$_3$)$_2$(YPh$_3$)$_4$ (Y = As, P).

In our complexes, the coordination polyhedron around Ag(1) differs slightly from that around Ag(2), as the angles P(1)−Ag(1)−P(3) and P(2)−Ag(2)−P(4) are different (e.g. for X = I these values are 115.5(2) and 117.0(2)° while for X = Cl they are 126.2(2) and 129.5(2)° and for X = NO$_3$ they are 134.2(2) and 138.0(2)°). This is also observed for the X−Ag−X bond angles, which are 111.53(8) and 109.84(8)° (X = I), 93.1(2) and 92.5(2)° (X = Cl), and 69.7(6) and 70.9(6)° (X = NO$_3$). Indeed, the larger the P−Ag−P angle, the smaller the X−Ag−X value. It is not possible to establish whether these angle changes are accompanied by corresponding variation in Ag−P distances, given the magnitudes of the standard deviations.

**Table 4.** Atomic Coordinates for Ag$_2$Cl$_2$(*m*-PP)$_2$ ($U$(eq) = $^1/_3\sum_i\sum_j(a_ia_j)$)

| | $x$ | $y$ | $z$ | $U$(eq), Å$^2$ |
|---|---|---|---|---|
| Ag(1) | −0.1325(1) | −0.1379(2) | −0.2711(1) | 0.063(1) |
| Ag(2) | −0.2921(1) | −0.3355(1) | −0.1784(1) | 0.058(1) |
| Cl(1) | −0.2913(5) | −0.1228(4) | −0.2020(3) | 0.061(2) |
| Cl(2) | −0.1337(5) | −0.3528(5) | −0.2509(3) | 0.071(2) |
| P(1) | 0.0745(4) | −0.1018(4) | −0.2225(3) | 0.049(2) |
| P(2) | −0.2427(4) | −0.3091(4) | −0.0492(3) | 0.040(2) |
| P(3) | −0.2434(5) | −0.0705(5) | −0.3832(3) | 0.063(2) |
| P(4) | −0.4384(5) | −0.4684(5) | −0.2559(3) | 0.057(2) |
| C(1) | 0.101(1) | −0.148(1) | −0.0787(9) | 0.044(4) |
| C(2) | −0.011(2) | −0.173(2) | −0.077(1) | 0.045(4) |
| C(3) | −0.048(1) | −0.155(1) | −0.0171(9) | 0.043(4) |
| C(4) | 0.032(2) | −0.116(2) | 0.044(1) | 0.049(4) |
| C(5) | 0.147(2) | −0.090(2) | 0.042(1) | 0.049(5) |
| C(6) | 0.181(2) | −0.108(2) | −0.020(1) | 0.06(1) |
| C(7) | 0.136(1) | −0.175(2) | −0.145(1) | 0.05(1) |
| C(8) | −0.171(2) | −0.176(2) | −0.016(1) | 0.05(1) |
| C(9) | 0.149(2) | −0.151(2) | −0.286(1) | 0.056(5) |
| C(10) | 0.265(3) | −0.150(2) | −0.267(2) | 0.10(1) |
| C(11) | 0.318(3) | −0.193(3) | −0.318(2) | 0.11(1) |
| C(12) | 0.251(3) | −0.222(3) | −0.381(2) | 0.11(1) |
| C(13) | 0.145(3) | −0.221(3) | −0.400(2) | 0.12(1) |
| C(14) | 0.087(2) | −0.182(2) | −0.350(1) | 0.09(1) |
| C(15) | 0.143(2) | 0.037(2) | −0.202(1) | 0.047(4) |
| C(16) | 0.250(2) | 0.064(2) | −0.162(1) | 0.06(1) |
| C(17) | 0.296(2) | 0.166(2) | −0.156(1) | 0.08(1) |
| C(18) | 0.237(2) | 0.246(2) | −0.188(1) | 0.08(1) |
| C(19) | 0.129(2) | 0.221(2) | −0.224(1) | 0.07(1) |
| C(20) | 0.081(2) | 0.116(2) | −0.231(1) | 0.06(1) |
| C(21) | −0.167(1) | −0.402(1) | 0.0101(9) | 0.037(4) |
| C(22) | −0.177(2) | −0.504(1) | −0.015(1) | 0.047(4) |
| C(23) | −0.117(2) | −0.580(2) | 0.025(1) | 0.06(1) |
| C(24) | −0.046(2) | −0.552(2) | 0.090(1) | 0.054(5) |
| C(25) | −0.038(2) | −0.446(2) | 0.116(1) | 0.06(1) |
| C(26) | −0.098(2) | −0.373(2) | 0.075(1) | 0.053(5) |
| C(27) | −0.374(1) | −0.302(1) | −0.0222(8) | 0.036(4) |
| C(28) | −0.439(2) | −0.228(2) | −0.052(1) | 0.07(1) |
| C(29) | −0.540(2) | −0.216(2) | −0.033(1) | 0.07(1) |
| C(30) | −0.576(2) | −0.281(2) | 0.013(1) | 0.08(1) |
| C(31) | −0.516(2) | −0.360(2) | 0.042(1) | 0.07(1) |
| C(32) | −0.410(2) | −0.371(2) | 0.025(1) | 0.052(5) |
| C(33) | −0.455(2) | −0.196(2) | −0.417(1) | 0.06(1) |
| C(34) | −0.430(2) | −0.277(2) | −0.373(1) | 0.06(1) |
| C(35) | −0.475(2) | −0.383(2) | −0.393(1) | 0.06(1) |
| C(36) | −0.554(2) | −0.400(2) | −0.460(1) | 0.08(1) |
| C(37) | −0.577(2) | −0.315(2) | −0.502(2) | 0.09(1) |
| C(38) | −0.528(2) | −0.215(2) | −0.481(1) | 0.07(1) |
| C(39) | −0.402(2) | −0.087(2) | −0.393(1) | 0.08(1) |
| C(40) | −0.441(2) | −0.479(2) | −0.351(1) | 0.06(1) |
| C(41) | −0.239(2) | −0.119(2) | −0.471(1) | 0.08(1) |
| C(42) | −0.267(2) | −0.056(2) | −0.530(2) | 0.09(1) |
| C(43) | −0.263(3) | −0.105(3) | −0.595(2) | 0.13(1) |
| C(44) | −0.240(3) | −0.205(3) | −0.598(2) | 0.14(1) |
| C(45) | −0.216(3) | −0.265(3) | −0.544(2) | 0.13(1) |
| C(46) | −0.219(3) | −0.215(3) | −0.478(2) | 0.10(1) |
| C(47) | −0.202(2) | 0.075(2) | −0.381(1) | 0.07(1) |
| C(48) | −0.110(2) | 0.114(2) | −0.409(1) | 0.09(1) |
| C(49) | −0.075(3) | 0.225(3) | −0.401(2) | 0.12(1) |
| C(50) | −0.127(3) | 0.290(3) | −0.369(2) | 0.11(1) |
| C(51) | −0.210(3) | 0.253(3) | −0.341(2) | 0.12(1) |
| C(52) | −0.250(3) | 0.144(3) | −0.349(2) | 0.11(1) |
| C(53) | −0.589(2) | −0.466(2) | −0.255(1) | 0.06(1) |
| C(54) | −0.605(2) | −0.433(2) | −0.191(1) | 0.07(1) |
| C(55) | −0.717(2) | −0.429(2) | −0.186(1) | 0.08(1) |
| C(56) | −0.805(2) | −0.458(2) | −0.243(1) | 0.08(1) |
| C(57) | −0.790(3) | −0.489(2) | −0.304(2) | 0.10(1) |
| C(58) | −0.677(2) | −0.498(2) | −0.310(1) | 0.07(1) |
| C(59) | −0.411(2) | −0.602(2) | −0.232(1) | 0.06(1) |
| C(60) | −0.302(2) | −0.618(2) | −0.195(1) | 0.08(1) |
| C(61) | −0.272(2) | −0.719(2) | −0.177(1) | 0.08(1) |
| C(62) | −0.354(2) | −0.804(2) | −0.195(2) | 0.09(1) |
| C(63) | −0.464(3) | −0.793(3) | −0.231(2) | 0.10(1) |
| C(64) | −0.492(2) | −0.691(2) | −0.251(1) | 0.08(1) |

The rhomboidal arrangement of the Ag$_2$X$_2$ core in the nitrato compound differs from that in the corresponding halo complexes: one of the nitrates is more strongly bound to both silver atoms than the other. Thus, O(1) is 2.47(2) Å from Ag(1) and 2.44(2) Å from Ag(2) while O(4) is 2.69(2) Å from Ag(1) and 2.65(2) Å from Ag(2). The orientations of the nitrates relative to the Ag$_2$O$_2$ core also differ as shown by the angles N(1)−O(1)−Ag(1), 117°, and N(1)−O(1)−Ag(2), 125°, for the more strongly bound nitrate and N(2)−O(4)−Ag(1), 105°, and N(2)−O(4)−Ag(2), 130°, for the other. In addition, interactions between Ag(1) and O(2) (2.99(2) Å) and O(5) (2.94(2) Å) are observed, but no contacts of this type are found with Ag(2) (see Figure 2). Thus, the nitrates seem to be basically monodentate although some additional interaction, albeit weak, appears to be present. In the isostructural complexes mentioned

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(29) Addison, C. C.; Logan, W.; Wallwork, S.; Gardner, S. *Q. Rev. Chem. Soc.* **1971**, *25*, 289.

(30) Cameron, A. F.; Forrest, K. P.; Nutall, R. H.; Taylor, D. W. *J. Chem. Soc., Chem. Commun.* **1970**, 210.

(31) Nardelli, M.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* **1985**, 321.

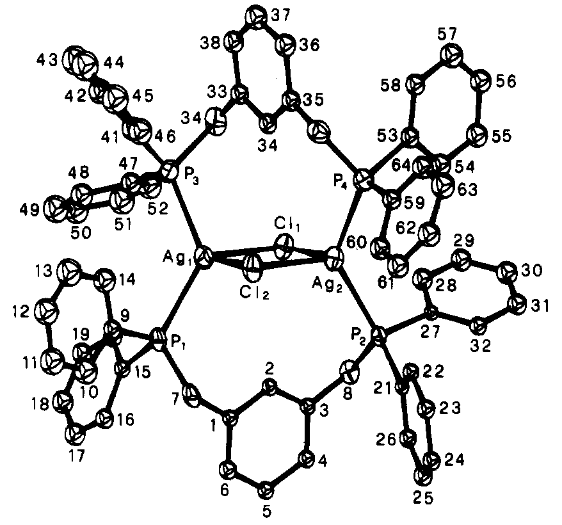


**Figure 1.** View of $Ag_2Cl_2(m\text{-}PP)_2$.

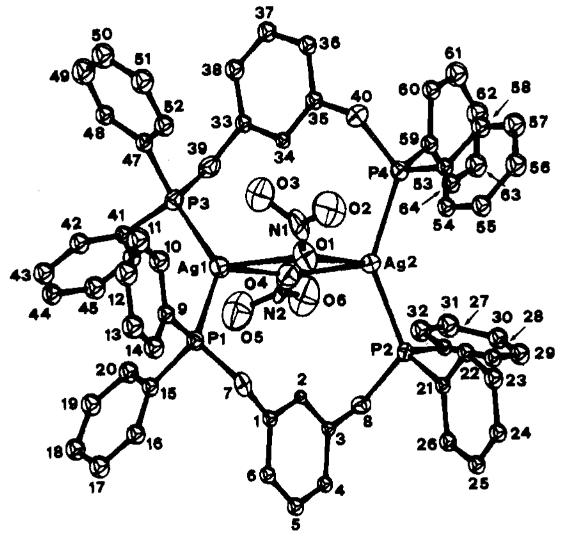


**Figure 2.** View of $Ag_2(NO_3)_2(m\text{-}PP)_2$.

above,[6,31] each silver atom has the same environment because the complexes are centrosymmetric and an additional O atom (nitrate) is bound to silver so that the metal is five-coordinate. In our compound, the O atoms not belonging to the core (O(2), O(3), O(5), O(6)) have displacement parameters higher than those of the other oxygens by approximately a factor of 2.

If the effect of the nucleophilicity of the anions is considered (I > Cl > $NO_3$), the following are observed:

(1) P−Ag−P bond angles are 115.5(2) and 117.0(2)° in the I complex and 138.0(2) and 134.2(2)° in the nitrate complex, while those for the Cl complex have intermediate values, i.e. 129.5(2) and 126.2(2)°. A similar change of P−Ag−P bond angles has been observed in mononuclear complexes.[12,13]

(2) Changes in Ag−P bond lengths are not significant, given the values of the standard deviations, the average values being 2.50(2) and 2.50(2) Å (I), 2.48(2) and 2.49(2) Å (Cl), and 2.45(2) and 2.44(2) Å ($NO_3$). However, similar behavior has been reported for the halide complexes of the ligand $PPh_2(CH_2)_2-S-(CH_2)_2PPh_2$, S-PP.[17]

A comparison of two sets of complexes having the same basic structures shows that interesting differences occur:

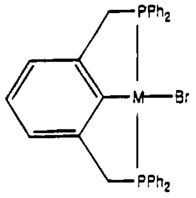
(a) The complexes $Ag_2X_2(S\text{-}PP)_2$ are centrosymmetric.[17]

(b) The P−Ag−P angles in $Ag_2Cl_2(S\text{-}PP)_2$ are smaller (117.7°) than those of the corresponding compound with *m*-PP (127.8(6)° average), while in the corresponding I complexes the opposite is observed: for the S-PP compound this angle is 119.87(7)° while for *m*-PP analog it is an average of 116.2(6)°.

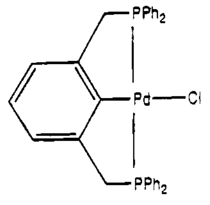
Other related complexes have also been reported, i.e. $Ag_2Cl_2(C\text{-}PP)_2$ (C-PP = $PPh_2(CH_2)_5PPh_2$)[16] and $Ag_2Cl_2(PPh_3)_4$.[9] In these, the P−Ag−P bond angles are 126.5(3) (average) and 122.91(7)°, respectively. There are also changes in X−Ag−X bond angles, the major difference being 110.7(2)° for $Ag_2I_2(m\text{-}PP)_2$ and 96.59(3)° in $Ag_2I_2(S\text{-}PP)_2$. However, all the complexes with bridging bidentate phosphines, as well as that with $PPh_3$, show similar Ag−P bond lengths. Furthermore, Ag−I and Ag−Cl bond lengths are similar for the complexes of the three ligands.

In our complexes, the values of the core diagonals are Ag−Ag = 3.295(2) Å (I), 3.753(3) Å (Cl), 4.175(2) Å ($NO_3$) and X−X = 4.768(2) Å (I), 3.941(8) Å (Cl), 2.95(2) Å ($NO_3$); i.e., the shortest Ag−Ag diagonal in the rhomboid of the I complex increases and becomes similar to the X−X distance in the Cl complex, the rhomboid having become almost a square (the four bond angles within the core fall in the range 88.9(1)−91.1(1)°) while the Ag−Ag distance becomes even longer in the nitrate complex. The H atoms H(1) and H(29), bound to C(2) and C(34), respectively, because of their proximity to the anions, may be important for understanding the structure of the core. Thus, the distances H(1)−I(1) (3.24 Å) and H(29)−I(2) (3.29 Å) are of the order of the sum of the corresponding van der Waals radii (3.35 Å),[32] hence rationalizing the long I−I distance in the core of the I complex. In the Cl complex, the distances H(1)−Cl(1) (3.14 Å), H(1)−Cl(2) (3.10 Å), and H(29)−Cl(1) (2.93 Å) seem to play a similar role (the sum of van der Waals radii is 3.00 Å).[32] By way of contrast, in the nitrate complex only one contact is present, H(1)−O(1) = 2.73 Å (the sum of van der Waals radii is 2.60 Å).[32] This point will be further discussed later together with the structures of *o*-PP complexes.

An interesting question is why *m*-PP does not form a chelate with Ag as other similar diphosphine ligands do.[12−15] In this ligand, the expected P−P distances should range from 4.60 to 4.90 Å as indicated by the X-ray structures of the compounds[33]



(M = Ni, Pd, Pt)



(It should be noted here that these complexes are obtained by reacting the corresponding $MX_2$ salts with *m*-PP by a facile cyclometalation reaction.[34])

As normal Ag−P distances are ca. 2.45 Å, in a mononuclear Ag complex with chelating *m*-PP the central aromatic C−H would strongly interfere with the metal center. It has been proposed that this type of interaction is responsible for the ease of cyclometalation with suitable electrophilic centers such as those mentioned above.[35]

**The Structures of $Ag_2(\mu\text{-}X)_2(o\text{-}PP)_2$.** The crystal structures of these complexes are also built from well-separated discrete molecules. They have crystallographically imposed symmetry, as the molecules themselves are centrosymmetric. The asymmetric unit is half a molecule which relates to the other half through the inversion center at (1/2, 0, 0). Atomic coordinates for X = I are given in Table 5; those for X = Cl are given as

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[32] Pauling L. *The Nature of the Chemical Bond*, 3rd Ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

[33] (a) Rimml, H. Dissertation, ETH Zurich, 1984; No. 7562, p 96−103. (b) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.

[34] Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6.

[35] Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: Weinheim, Germany, 1992; p 440.

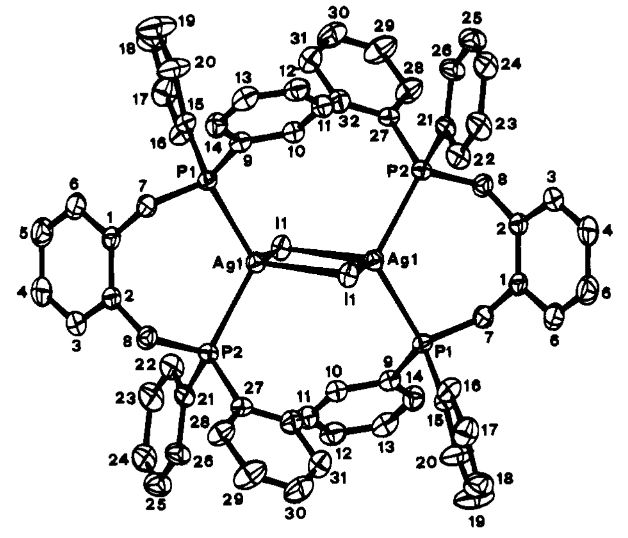

**Figure 3.** View of $Ag_2I_2(o\text{-}PP)_2$.

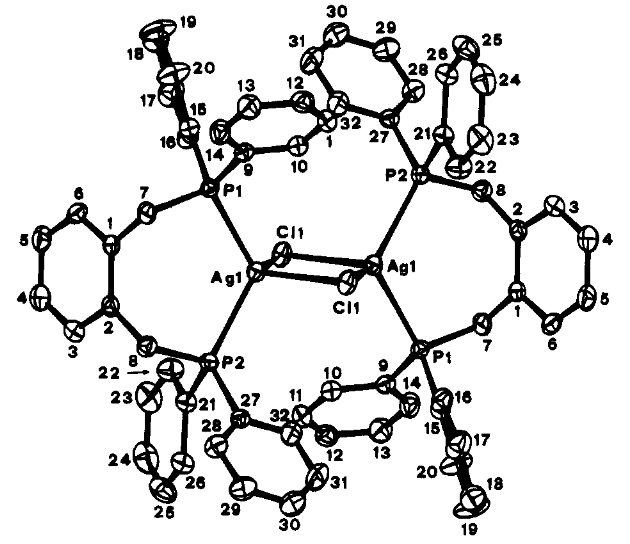

**Figure 4.** View of $Ag_2Cl_2(o\text{-}PP)_2$.

**Table 5.** Atomic Coordinates for $Ag_2I_2(o\text{-}PP)_2$ ($B(\mathrm{eq}) = {}^4/_3\sum_{ij}(a_ia_jb_{ij})$)

| | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|
| Ag(1) | 0.38942(3) | 0.01558(3) | 0.07750(4) | 3.41(1) |
| I(1) | 0.52564(3) | 0.13716(2) | −0.03765(3) | 3.77(1) |
| P(1) | 0.3346(1) | 0.0539(1) | 0.2759(1) | 3.15(4) |
| P(2) | 0.2536(1) | 0.0335(1) | 0.0023(1) | 3.11(4) |
| C(1) | 0.1379(4) | 0.0203(4) | 0.3023(5) | 3.7(2) |
| C(2) | 0.1092(4) | 0.0153(4) | 0.2086(5) | 3.7(2) |
| C(3) | 0.0448(5) | −0.0450(5) | 0.2033(6) | 4.8(2) |
| C(4) | 0.0092(6) | −0.1002(5) | 0.2871(7) | 5.9(3) |
| C(5) | 0.0389(6) | −0.0955(5) | 0.3789(7) | 5.7(2) |
| C(6) | 0.1013(5) | −0.0367(5) | 0.3876(6) | 4.8(2) |
| C(7) | 0.2050(4) | 0.0847(4) | 0.3197(5) | 3.9(2) |
| C(8) | 0.1422(5) | 0.0727(4) | 0.1128(5) | 4.0(2) |
| C(9) | 0.3956(5) | 0.1405(4) | 0.3085(5) | 3.6(2) |
| C(10) | 0.4961(5) | 0.1462(4) | 0.2567(5) | 4.1(2) |
| C(11) | 0.5485(5) | 0.2108(5) | 0.2762(6) | 4.8(2) |
| C(12) | 0.4976(6) | 0.2735(5) | 0.3432(6) | 5.1(2) |
| C(13) | 0.3998(6) | 0.2682(4) | 0.3955(6) | 5.0(2) |
| C(14) | 0.3480(5) | 0.2022(4) | 0.3784(6) | 4.3(2) |
| C(15) | 0.3388(4) | −0.0189(4) | 0.3795(5) | 3.8(2) |
| C(16) | 0.3415(6) | −0.0984(4) | 0.3532(6) | 4.6(2) |
| C(17) | 0.3451(7) | −0.1563(5) | 0.4284(7) | 6.0(3) |
| C(18) | 0.3437(8) | −0.1352(6) | 0.5314(8) | 7.0(3) |
| C(19) | 0.342(1) | −0.0577(7) | 0.5596(8) | 9.0(5) |
| C(20) | 0.3394(9) | 0.0033(6) | 0.4837(7) | 7.0(3) |
| C(21) | 0.2068(4) | −0.0528(3) | −0.0498(5) | 3.5(2) |
| C(22) | 0.2135(5) | −0.1279(4) | −0.0033(6) | 4.7(2) |
| C(23) | 0.1747(6) | −0.1940(4) | −0.0362(8) | 5.5(2) |
| C(24) | 0.1299(6) | −0.1861(5) | −0.1206(7) | 5.3(2) |
| C(25) | 0.1264(7) | −0.1147(5) | −0.1647(7) | 5.5(3) |
| C(26) | 0.1641(5) | −0.0477(4) | −0.1307(6) | 4.6(2) |
| C(27) | 0.2727(4) | 0.1040(3) | −0.1102(5) | 3.4(2) |
| C(28) | 0.2098(6) | 0.1649(4) | −0.1128(6) | 5.1(2) |
| C(29) | 0.2307(8) | 0.2152(5) | 0.2047(7) | 6.8(3) |
| C(30) | 0.3136(8) | 0.2032(5) | −0.2924(7) | 6.4(3) |
| C(31) | 0.3773(6) | 0.1424(6) | −0.2925(7) | 5.9(3) |
| C(32) | 0.3573(5) | 0.0939(5) | −0.2002(6) | 4.7(2) |

supplementary Table S3. Figures 3 and 4 show views of the structures for X = I and Cl, respectively.

As found for the halide complexes with *m*-PP, each Ag atom is distorted tetrahedral and is surrounded by two P atoms and two halogens. The core of the complex, composed of two Ag atoms and two X atoms, is symmetrically coplanar. The four P atoms are also coplanar for symmetry reasons, and the plane they define intersects the core plane at 88.3° (I) and 87.3° (Cl). The major structural difference between the complexes of *o*-PP and those of the other flexible bidentate ligands is the formation of a PAgP chelate ring. This is likely to be due to the size and conformation of this ring, coupled with the bond lengths and angles of the bridging atoms. A recent structural study[24] of this ligand showed that "natural" PMP angles are ca. 105° with the consequence that the longest P−P distance would be too short for the group to act as a bridging ligand in binuclear silver complexes; however, it can still form chelate complexes with P−Ag−P angles close to 109°, as found.

Also in the *o*-PP complexes the P−Ag−P angles are related to the anion nucleophilicity in the expected way;[12,13] i.e., increasing angles are associated with the weaker donor anions. This effect is likely to be caused by a competition for the s character of the Ag atom between the Ag−P and Ag−X bonds. In these two complexes, the stronger Ag−X bonds for the I complex cause a lengthening of Ag−P bonds, 2.493(2) and 2.487(1) Å, relative to those in the Cl complex with values of 2.450(2) and 2.446(2) Å.

The rhomboid core shows shorter Ag−Ag distances than in *m*-PP complexes, and these are similar for both complexes, 3.218(1) Å (I) and 3.238(1) Å (Cl). In this case, no intramolecular contacts between the core and the ligand are apparent.

The folding of the *o*-PP backbone in these complexes can be compared with that in $Pt^0(C_2H_4)(o\text{-}PP)$.[24] In the latter compound, the dihedral angle between the plane Pt−P(1)−P(2)−C(7)−C(8) and that defined by the xylyl moiety is 110° while the corresponding values for the complexes described here are a little smaller, e.g. 107.1° (I) and 108.0° (Cl).

Selected structural parameters of the five structures of this study are compared with those of related compounds of composition "$AgXP_2$" in Table 6. It is observed that the Cl−Cl distance in the $PPh_3$ complex, 3.71(2) Å, is of the order of the the sum of the van der Waals radii (3.60 Å);[32] for C-PP ligand this value is 3.769(4) Å while for the S-PP ligand it is 3.786(8) Å. If the I complexes are considered, the same limiting situation is apparent for the S-PP complex; namely, I−I = 4.323(1) Å (the sum of the van der Waals radii is 4.30 Å).[32] The $NO_3$ complex of the ligand *m*-PP also shows a similar situation because the O−O distance is 2.95(2) Å and the sum of O van der Waals radii is 2.80 Å.[32]

As mentioned above, in silver halide complexes of *m*-PP, intramolecular interactions between halogens and H atoms of the link chain may account for the observation that these halogens are further away than the sum of the corresponding van der Waals radii. Therefore, in Table 6 the only cases with unexplained long anion−anion distances are for complexes of *o*-PP. If we consider the Ag−Ag distances in Table 6, we see this parameter ranging from 3.218(1) to 4.175(2) Å. The shortest values are given for *o*-PP complexes, namely, 3.218(1)

**Table 6.** Selected Structural Parameters for Dimeric Ag Complexes[a]

| | $Ag_2X_2(m\text{-}PP)_2$ | | | $Ag_2X_2(o\text{-}PP)_2$ | | $Ag_2X_2(S\text{-}PP)_2$ | | $Ag_2X_2(C\text{-}PP)_2$ | $Ag_2X_2(PPh_3)$ |
|---|---|---|---|---|---|---|---|---|---|
| X | I | Cl | $NO_3$ | I | Cl | I | Cl | Cl | Cl |
| P−Ag(1)−P | 115.5(2) | 126.2(2) | 134.2(2) | 109.84(6) | 111.83(6) | 119.87(7) | 117.7(1) | 124.4(1) | 122.91(7) |
| P−Ag(2)−P | 117.0(2) | 129.5(2) | 138.0(2) | 109.84(6) | 111.83(6) | 119.87(7) | 117.7(1) | 128.6(1) | 122.91(7) |
| <P−Ag−P> | 116.2(6) | 127.8(6) | 136.1(6) | 109.84(6) | 111.83(6) | 119.87(7) | 117.7(1) | 126.5(3) | 122.91(7) |
| X−Ag(1)−X | 111.53(8) | 93.1(2) | 69.7(6) | 111.49(2) | 103.04(6) | 96.59(3) | 91.2(1) | 88.9(1) | 88.03(6) |
| X−Ag(2)−X | 109.84(8) | 92.5(2) | 70.9(6) | 111.49(2) | 103.04(6) | 96.59(3) | 91.2(1) | 89.7(1) | 88.03(6) |
| ⟨X−Ag−X⟩ | 110.7(2) | 92.8(6) | 70.3(18) | 111.49(2) | 103.04(6) | 96.59(3) | 91.2(1) | 89.3(3) | 88.03(6) |
| Ag(1)−P(1) | 2.497(6) | 2.470(6) | 2.439(6) | 2.493(2) | 2.450(2) | 2.461(2) | 2.461(4) | 2.472(3) | 2.467(2) |
| Ag(1)−P(2) | 2.496(6) | 2.496(7) | 2.454(6) | 2.487(1) | 2.446(1) | 2.461(2) | 2.481(4) | 2.492(3) | 2.472(2) |
| ⟨Ag(1)−P⟩ | 2.50(2) | 2.48(2) | 2.45(2) | 2.490(6) | 2.448(6) | 2.461(6) | 2.47(1) | 2.482(9) | 2.469(6) |
| Ag(2)−P(3) | 2.497(6) | 2.474(5) | 2.447(5) | 2.493(2) | 2.450(2) | 2.461(2) | 2.461(4) | 2.493(4) | 2.467(2) |
| Ag(2)−P(4) | 2.511(6) | 2.510(7) | 2.439(6) | 2.487(1) | 2.446(1) | 2.461(2) | 2.481(4) | 2.499(4) | 2.472(2) |
| ⟨Ag(2)−P⟩ | 2.50(2) | 2.49(2) | 2.44(2) | 2.490(6) | 2.448(6) | 2.461(6) | 2.47(1) | 2.50(1) | 2.469(6) |
| Ag(1)−X(1) | 2.879(2) | 2.671(5) | 2.47(2) | 2.892(1) | 2.627(2) | 2.879(1) | 2.686(4) | 2.664(4) | 2.596(2) |
| Ag(1)−X(2) | 2.889(2) | 2.758(7) | 2.69(2) | 2.824(1) | 2.576(2) | 2.911(1) | 2.643(4) | 2.718(3) | 2.741(2) |
| ⟨Ag(1)−X⟩ | 2.884(6) | 2.71(2) | 2.58(6) | 2.858(3) | 2.601(6) | 2.895(3) | 2.66(1) | 2.69(1) | 2.668(6) |
| Ag(2)−X(1) | 2.910(2) | 2.715(6) | 2.44(2) | 2.892(1) | 2.627(2) | 2.879(1) | 2.686(4) | 2.663(3) | 2.596(2) |
| Ag(2)−X(2) | 2.916(2) | 2.741(6) | 2.65(2) | 2.824(1) | 2.576(2) | 2.911(1) | 2.643(4) | 2.678(3) | 2.741(2) |
| ⟨Ag(2)−X⟩ | 2.913(6) | 2.73(2) | 2.54(6) | 2.858(3) | 2.601(6) | 2.895(3) | 2.66(1) | 2.670(9) | 2.668(6) |
| Ag−Ag | 3.295(2) | 3.753(3) | 4.175(2) | 3.218(1) | 3.238(1) | 3.852(2) | 3.708(3) | 3.812(1) | 3.840(2) |
| X−X | 4.768(2) | 3.941(8) | 2.95(2) | 4.725(1) | 4.073(2) | 4.323(1) | 3.786(8) | 3.769(4) | 3.710(2) |
| 2vdW(X) | 4.30 | 3.60 | 2.80 | 4.30 | 3.60 | 4.30 | 3.60 | 3.60 | 3.60 |

[a] S-PP = $PPh_2(CH_2)_2{-}S{-}(CH_2)_2PPh_2$; C-PP = $PPh_2(CH_2)_5PPh_2$; vdW(X) = van der Waals radius of anion X.

Å (X = I) and 3.238(1) Å (X = Cl). They are of the order of those found in silver complexes of the ligand dpm = $Ph_2PCH_2PPh_2$, namely, $Ag_2(NO_3)_2(dpm)_4{\cdot}2CHCl_3$ (3.109(1) Å),[18] $Ag_2(NO_3)_2(dpm)_4$ (3.085(1) Å),[19] and $[Ag_4(NO_3)_2(dpm)_4][PF_6]_2$ (3.099(1) Å),[19] which are of type **C** complexes (shown above).

As shown by the five X-ray structures reported here and by literature data, complexes of the composition "$AgXP_2$" show a marked preference for tetrahedral coordination at the silver atom. This is achieved by using the anion as a bridging ligand. When the two P donors form part of a bidentate ligand, one observes that the latter can act either as a chelating or as a bridging ligand, depending on the nature of the chain between the two donors, chelation being preferred when the appropriate ring size can be achieved.

Silver complexes with bidentate phosphine ligands containing $C_1$ to $C_5$ chains between the donors have been prepared, and dimeric complexes of those for $Ph_2PCH_2PPh_2$, dpm ($C_1$), $Ph_2P(CH_2)_3PPh_2$, dpp ($C_3$), and C-PP ($C_5$) have been structurally characterized. The dpm ligand forms two silver nitrate complexes differing in nuclearity: in the dimeric species, the organic ligand bridges the two metal atoms but the characteristic $Ag_2X_2$ four-membered ring is not present. This type of structure (type **C**) is also present in the complex with dpp.[20] Presumably the absence of the $Ag_2X_2$ core is due to the short span of the bidentate ligand. A silver chelate complex with the dpm ligand (type **D**) would imply a six-membered ring with a P−Ag−P bond angle maximum of 95°, which is too far removed from the optimal values mentioned above (around 109°), and the alternative arrangement (type **C**) is preferred. C-PP and S-PP have a five-atom chain which leaves more room for the core that is, therefore, formed. When such a chain is used, the ligands probably could arrange to form a suitable P−Ag−P bond angle approaching the tetrahedral value (in an eight-atom ring) with formation of a chelate ring. However, the observed structures show that these ligands still prefer a bridging arrangement.[16,17] Instead, the ligand *o*-PP, which has a chain of four C atoms, is able to give chelate species.

Our conclusion that the formation of chelate rings in Ag−diphosphine complexes of the type $AgXP_2$ can occur only under very limited conditions, $C_4$ chain length, is in contrast with the complexes $Ag(DPPE)_2{}^+NO_3{}^-$ and $[Ag_2(DMPE)_2]^{2+}(BPh_4{}^-)_2$, which are of the type $AgP_4$. In the former,[21b] both ligands, DPPE, 1,2-bis(diphenylphosphino)ethane, chelate the metal, which has coordination number 4; in the latter,[36] each silver atom is also four-coordinate with one chelating diphosphine DMPE, 1,2-bis(dimethylphosphino)ethane, and two phosphorus atoms from two bridging DMPE ligands. The behavior can be explained in terms of the relative bond strengths Ag−halide > Ag−phosphine > Ag−weak anion. Phosphorus can displace a weak anion from the metal under certain conditions, e.g. in the presence of an excess of phosphine ligand, and the metal can be stabilized notwithstanding a strong deformation of the tetrahedral configuration. In fact, the P−Ag−P bond angle (chelate) is ca. 84° for both of the above complexes and the larger P−Ag−P bond angle is 129° in the former complex[21b] and 144° in the latter.[36]

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**Supplementary Material Available:** Listings of atomic coordinates and isotropic displacement parameters of non-H atoms for $Ag_2X_2(m\text{-}PP)_2$ (X = I, $NO_3$) and $Ag_2Cl_2(o\text{-}PP)_2$ (Tables S1−S3), H coordinates (Table S4), anisotropic displacement parameters (Tables S5−S9), and full crystallographic data (Table S10) and a computer-generated drawing of $Ag_2I_2(m\text{-}PP)_2$ (Figure S1) (17 pages). Ordering information is given on any current masthead page.

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