# Crystal and Molecular Structure of Bis(tricyclohexylphosphine)silver(I)nitrate and Bis(tricyclohexylphosphine)silver(I)perchlorate; Correlation of the Structures with the Silver–Phosphorus Coupling Constants

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## Abstract

Two (1:2) silver monophosphine complexes have been studied by X-ray diffraction methods and in solution by P NMR spectroscopy. Both are monomeric and tricoordinated in the solid state but one of them, the perchlorate compound, is probably associated as a dimer species in solution from the lower $^1J(^{107}Ag-^{31}P)$ value when compared to the nitrate analogue. Previous structural correlations found in other silver–phosphine complexes have been confirmed for these new compounds. Thus, larger P–Ag–P bond angles are associated with shorter Ag–P bond distances, longer Ag–anion bond distances and lower Lewis basicity of the anions. Selected structural data are: P–Ag–P bond angle of 139.04(9)°, Ag–P bond lengths of 2.440(3) and 2.445(3) Å for the nitrate complex and 147.34(3)°, 2.429(1) Å and 2.432(1) Å, for the perchlorate one. $J(^{107}Ag-^{31}P)$ is 457 Hz and 447 Hz, respectively. The complexes are triclinic, $Z = 2$, with the parameters: $a = 9.258(2)$, $b = 9.828(2)$, $c = 23.385(5)$ Å, $\alpha = 94.73(2)°$, $\beta = 96.35(2)°$, $\gamma = 116.42(1)°$ (nitrate) and $a = 9.505(2)$, $b = 9.790(2)$, $c = 23.667(6)$ Å, $\alpha = 99.03(2)$ $\beta = 95.44(2)$ $\gamma = 115.97(1)°$ (perchlorate).

## Introduction

Recently we reported several studies in coordination chemistry in which correlation amongst metal–phosphorus coupling constants and structural aspects were investigated [1–4]. $^1J(M-P)$ were obtained from P NMR spectroscopy in solution, and the structural features pinpointed via X-ray diffraction methods. The relation between $J(M-P)$, where M is a metal with at least one isotope of spin 1/2, and the structure is better shown when a series of complexes is considered. In our case families of compounds of the type $ML_nX_m$, L = phosphine, X = anion, were studied by following the systematic variation in $J$ values and in structure, obtained when the anion X is changed. The Lewis basicity of monoanions follows the order $CN > I > Br \cong SCN > Cl > CH_3COO \cong NO_3 > ClO_4 \cong BF_4 \cong PF_6$ as indicated by increasing $J(Ag-P)$ values in the series $Ag(P(p\text{-}tolyl)_3)_nX$, $n = 1, 2, 3$ [5]. Recently, we have shown that this type of variation can be associated with enlargement of P–M–P bond angles and shortening of M–P bond distances [1–4]. As an extension of this type of study we present a similar investigation on compounds of the type $Ag(PCy)_3)_2X$, $PCy_3$ = tricyclohexylphosphine.

## Experimental

### Preparation of the Complexes

*$Ag(PCy_3)_2NO_3$*

$PCy_3$ (305 mg = 1.08 mmol) was suspended in $CH_3CN$ under nitrogen. $AgNO_3$ (92 mg = 0.54 mmol) was added and the suspension stirred in the dark. After complete dissolution, the filtered solution was left to evaporate at room temperature. A white powder was obtained.

*$Ag(PCy_3)_2ClO_4$*

$PCy_3$ (334 mg = 1.19 mmol) and $AgClO_4 \cdot H_2O$ (125 mg = 0.60 mmol) were treated as for the nitrate complex. The solute dissolved in half an hour and crystals were obtained during evaporation at room temperature in the dark. The perchlorate complex was handled with caution.

### Collection and Reduction of X-ray Data

Colourless single crystals of $Ag(PCy_3)_2NO_3$ were grown from acetone whereas crystals of $Ag(PCy_3)_2ClO_4$ were obtained from $CH_3CN$. Monitoring of standard reflections indicated that no decay occurred during the data collection and a $\phi$-scan of some suitable reflections did not show absorption

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TABLE I. Summary of Crystal Data for the Compounds $Ag(PCy_3)_2X$

| | $X = NO_3$ | $X = ClO_4$ |
|---|---|---|
| Formula | $C_{36}H_{66}NO_3P_2Ag$ | $C_{36}H_{66}O_4PClAg$ |
| Formula weight | 730.75 | 768.19 |
| $a$ (Å) | 9.258(2) | 9.505(2) |
| $b$ (Å) | 9.828(2) | 9.790(2) |
| $c$ (Å) | 23.385(5) | 23.667(6) |
| $\alpha$ (°) | 94.73(2) | 99.03(2) |
| $\beta$ (°) | 96.35(2) | 95.44(2) |
| $\gamma$ (°) | 116.42(1) | 115.97(1) |
| $V$ (Å$^3$) | 1873.0(6) | 1921.9(8) |
| $Z$ | 2 | 2 |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Crystal dimension (mm) | 0.25 X 0.20 X 0.10 | 0.50 X 0.25 X 0.15 |
| Radiation | Mo K$\alpha$ graphite monochromated | |
| $\mu$ (cm$^{-1}$) | 6.48 | 7.01 |
| Diffractometer | Nicolet R3 | |
| Scan mode | $\omega$ | $2\theta-\theta$ |
| Scan range (°) | 0.9 | 1.2 |
| Background counts | 1/4 of scan time at ± 0.5 from the center of scan range | 1/4 of scan time at the end of scan range |
| $2\theta$ limits (°) | 3,54 | 3,56 |
| Reflections collected no. | 5946 | 9854 |
| No. unique data | 3873 | 7494 |
| Final no. variables | 208 | 397 |
| Final $R$, $R_w$ | 0.076, 0.085 | 0.042, 0.065 |

phenomena. Table I summarizes crystal parameters and details of collection data.

### Solution and Refinement of the Structures

The structures were solved using three-dimensional Patterson function to determine the position of the heavy atoms, *i.e.* Ag and P, and Fourier methods to determine the other non-H atoms. Refinement by least-square 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) = 0.96 Å and C–C–H angle = 109.5°). The nitrate compound was solved using SHEL-X program [6] with weights 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 $w\langle|F_o| - |F_c|\rangle$ over ranges of reflections; the $b$ value was 0.002309. The perchlorate complex was solved using CAOS program [7]. Weights were of the type $w = (a + F_o + cF_o^2)$ where $a$ and $c$ are of the order of $2F_o$(min) and $2/F_o$(max) [8]. The calculations were performed on Eclipse MV/8000 II Data General computer. Atomic scattering factors and anomalous dispersion terms were taken from ref. 9.

### NMR Spectra

$^{31}P\{H\}$ 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 mm sample tubes in $Cl_2CH_2/Cl_2CD_2$ (3:1). Coupling constants were measured at room temperature (20 °C).

### Description of the Structures

The crystal structures of the title compounds are built up from well separated discrete molecules with no crystallographically imposed symmetry. There are no intermolecular contacts significantly shorter of van der Waals' radii. Selected geometrical parameters are given in Table II. The two complexes crystallize in the triclinic system, $P\bar{1}$ and $Z = 2$, with similar cell parameters. However they are not isomorphous though the atomic $z$ coordinates show some similarity.

#### $Ag(PCy_3)_2NO_3$

Atomic coordinates are given in Table III. Figure 1 shows a computer generated drawing of the complex. The coordination around the metal is formally tetrahedral with two P atoms of the phosphine and two O atoms of the nitrate anion. If the anion is considered as a ligand the complex can be described as tricoordinated. The tetrahedral arrangement is considerably distorted and the anion is bound asymmetrically (see Table II). This complex can be compared with the compound 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrenesilver(I)nitrate which has the same type of coordination around the metal [2]. Although important rings effects may be present due to the rigidity of the diphosphine, the

TABLE II. Selected Bond Distances and Angles in Complexes $Ag(PCy_3)_2X$

| | $X = NO_3$ | $X = ClO_4$ |
|---|---|---|
| Distances (Å) | | |
| Ag–P(1) | 2.440(3) | 2.429(1) |
| Ag–P(2) | 2.445(3) | 2.432(1) |
| Ag–O(1) | 2.45(1) | 2.720(7) |
| Ag–O(2) | 2.73(1) | |
| P(1)–C(1) | 1.87(1) | 1.852(4) |
| P(1)–C(7) | 1.85(1) | 1.851(4) |
| P(1)–C(13) | 1.85(1) | 1.861(5) |
| P(2)–C(19) | 1.86(1) | 1.852(4) |
| P(2)–C(25) | 1.85(1) | 1.847(6) |
| P(2)–C(31) | 1.83(1) | 1.867(4) |
| Y–O(1)[a] | 1.16(3) | 1.412(6) |
| Y–O(2) | 1.28(3) | 1.430(8) |
| Y–O(3) | 1.21(2) | 1.420(7) |
| Y–O(4) | | 1.387(7) |
| Angles (°) | | |
| P(1)–Ag–P(2) | 139.04(9) | 147.34(3) |
| P(1)–Ag–O(1) | 110.4(3) | 113.5(2) |
| P(1)–Ag–O(2) | 110.2(3) | |
| P(2)–Ag–O(1) | 109.1(3) | 95.5(2) |
| P(2)–Ag–O(2) | 104.9(3) | |
| O(1)–Ag–O(2) | 45.4(5) | |
| Ag–P(1)–C(1) | 109.0(4) | 112.8(1) |
| Ag–P(1)–C(7) | 113.8(3) | 106.8(1) |
| Ag–P(1)–C(13) | 115.1(5) | 115.5(1) |
| C(1)–P(1)–C(7) | 103.4(5) | 104.5(2) |
| C(1)–P(1)–C(13) | 108.5(6) | 103.9(2) |
| C(7)–P(1)–C(13) | 106.2(7) | 112.9(2) |
| Ag–P(2)–C(19) | 117.3(3) | 118.8(1) |
| Ag–P(2)–C(25) | 111.6(4) | 110.4(1) |
| Ag–P(2)–C(31) | 109.1(4) | 107.6(2) |
| C(19)–P(2)–C(25) | 108.0(5) | 108.0(2) |
| C(19)–P(2)–C(31) | 104.3(6) | 104.9(2) |
| C(25)–P(2)–C(31) | 105.7(5) | 106.4(2) |
| O(1)–Y–O(2) | 111(1) | 101.8(4) |
| O(1)–Y–O(3) | 119(2) | 107.4(5) |
| O(1)–Y–O(4) | | 117.3(5) |
| O(2)–Y–O(3) | 130(2) | 110.5(5) |
| O(2)–Y–O(4) | | 107.7(4) |
| O(3)–Y–O(4) | | 111.6(4) |

[a] Y stands for N in $X = NO_3$ and Cl in $X = ClO_4$.

TABLE III. Atomic Coordinates in $Ag(PCy_3)_2NO_3$[a]

| | *x* | *y* | *z* |
|---|---|---|---|
| Ag(1) | 0.0682(1) | 0.3493(1) | 0.25344(4) |
| P(1) | 0.1496(3) | 0.2791(3) | 0.3448(1) |
| P(2) | 0.1585(3) | 0.3964(3) | 0.1594(1) |
| N(1) | −0.252(2) | 0.365(2) | 0.2398(6) |
| O(1) | −0.125(1) | 0.452(1) | 0.2657(6) |
| O(2) | −0.264(2) | 0.230(2) | 0.2297(7) |
| O(3) | −0.354(2) | 0.409(3) | 0.2295(8) |
| C(1) | 0.178(1) | 0.104(1) | 0.3286(5) |
| C(2) | 0.018(1) | −0.032(1) | 0.2957(6) |
| C(3) | 0.045(1) | −0.164(1) | 0.2743(6) |
| C(4) | 0.123(1) | −0.213(1) | 0.3245(6) |
| C(5) | 0.275(1) | −0.083(1) | 0.3557(6) |
| C(6) | 0.244(1) | 0.055(1) | 0.3801(6) |
| C(7) | 0.351(1) | 0.4227(9) | 0.3848(5) |
| C(8) | 0.484(1) | 0.441(1) | 0.3479(6) |
| C(9) | 0.655(1) | 0.563(1) | 0.3828(6) |
| C(10) | 0.650(1) | 0.721(1) | 0.3965(6) |
| C(11) | 0.520(1) | 0.698(1) | 0.4330(6) |
| C(12) | 0.351(1) | 0.575(1) | 0.4004(6) |
| C(13) | 0.005(2) | 0.242(2) | 0.3972(7) |
| C(14) | 0.064(1) | 0.242(1) | 0.4620(6) |
| C(15) | −0.064(2) | 0.198(2) | 0.4979(9) |
| C(16) | −0.209(2) | 0.211(2) | 0.4831(9) |
| C(17) | −0.262(2) | 0.209(2) | 0.4192(7) |
| C(18) | −0.128(2) | 0.267(2) | 0.384(1) |
| C(19) | 0.023(1) | 0.4272(9) | 0.1025(5) |
| C(20) | −0.144(1) | 0.282(1) | 0.0872(6) |
| C(21) | −0.255(1) | 0.310(1) | 0.0416(6) |
| C(22) | −0.280(1) | 0.447(1) | 0.0623(6) |
| C(23) | −0.114(1) | 0.594(1) | 0.0792(6) |
| C(24) | −0.003(1) | 0.563(1) | 0.1250(5) |
| C(25) | 0.366(1) | 0.559(1) | 0.1676(5) |
| C(26) | 0.415(1) | 0.632(1) | 0.1135(6) |
| C(27) | 0.594(2) | 0.759(1) | 0.1241(7) |
| C(28) | 0.627(2) | 0.874(1) | 0.1726(7) |
| C(29) | 0.580(2) | 0.812(1) | 0.2268(7) |
| C(30) | 0.396(1) | 0.679(1) | 0.2162(6) |
| C(31) | 0.174(1) | 0.229(1) | 0.1265(6) |
| C(32) | 0.224(1) | 0.228(1) | 0.0655(6) |
| C(33) | 0.230(2) | 0.079(2) | 0.0462(7) |
| C(34) | 0.312(2) | 0.027(2) | 0.0899(8) |
| C(35) | 0.256(1) | 0.024(1) | 0.1450(7) |
| C(36) | 0.261(2) | 0.169(2) | 0.1687(7) |

[a] e.s.d.s given in parentheses.

comparison of the coordination geometries shows the same trend as other silver–phosphine series. In fact, the Ag–P bond distances of 2.424(2) and 2.410(2) Å subtend a bond angle at the metal of 148.6(1)° and in our case the bond distances are 2.440(3) and 2.445(3) Å and subtend an angle of 139.04(9)°. In other words, shorter M–P bond distances are associated with larger P–M–P bond angles, as shown in the $Ag(PPh_3)_3X$ series [4], $PPh_3$ = triphenylphosphine, where the mean value of the P–Ag–P bond angles is correlated with the mean value of the Ag–P bond lengths, or in other series [2, 3]. The Ag–anion bond is given by two Ag–O bond distances, 2.45(1) and 2.73(2) Å in our complex and 2.47(1) and 2.56(1) Å for the diphosphine complex, showing that in the present case the nitrate is more asymmetric. Another complex for comparison is $[Ag(AsPh_3)_3NO_3]_2$ which has three Ag–O contacts at 2.409(6), 2.684(7), and 2.737(6) Å, the last belonging to a second nitrate. The As–Ag–As bond angle is 134.2(1)° *versus* 139.04(9)° for the P–Ag–P value in our complex [10].

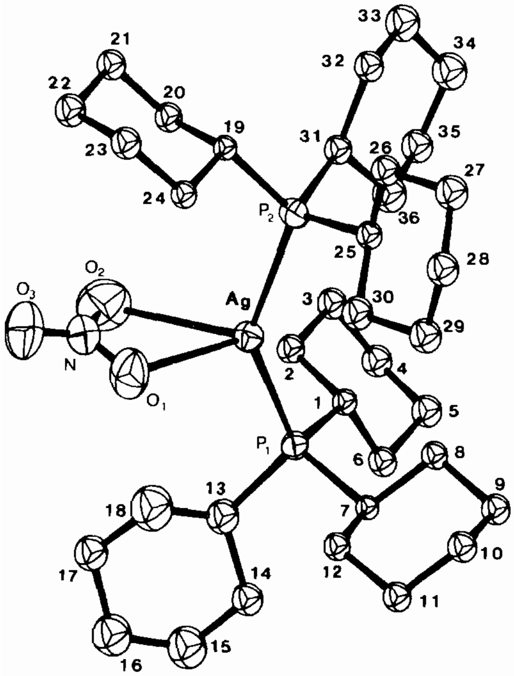

Fig. 1. Perspective view of $Ag(PCy_3)_2NO_3$.

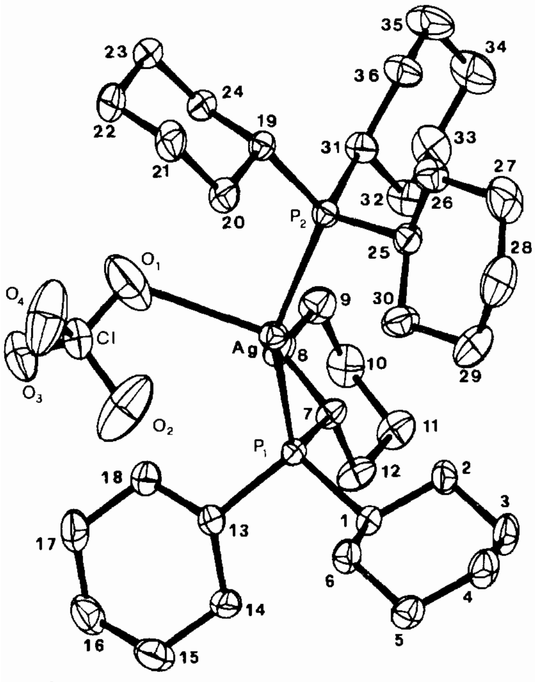

Fig. 2. Perspective view of $Ag(PCy_3)_2ClO_4$.

TABLE IV. Atomic Coordinates in $Ag(PCy_3)_2ClO_4$ [a]

| | *x* | *y* | *z* |
|---|---|---|---|
| Ag(1) | 0.16992(3) | 0.40784(3) | 0.25251(1) |
| P(1) | 0.2063(1) | 0.5717(1) | 0.34660(4) |
| P(2) | −0.0004(1) | 0.2634(1) | 0.15826(4) |
| Cl(1) | 0.5457(1) | 0.4192(2) | 0.2499(1) |
| O(1) | 0.4479(7) | 0.4610(8) | 0.2154(3) |
| O(2) | 0.4626(9) | 0.3817(7) | 0.2970(4) |
| O(3) | 0.6953(4) | 0.5537(5) | 0.2699(2) |
| O(4) | 0.5632(7) | 0.2906(7) | 0.2252(4) |
| C(1) | 0.0534(4) | 0.4738(4) | 0.3896(2) |
| C(2) | −0.1141(4) | 0.4281(5) | 0.3585(2) |
| C(3) | −0.2398(5) | 0.3445(6) | 0.3938(2) |
| C(4) | −0.2302(5) | 0.2008(5) | 0.4066(2) |
| C(5) | −0.0630(5) | 0.2454(5) | 0.4381(2) |
| C(6) | 0.0628(4) | 0.3290(4) | 0.4031(2) |
| C(7) | 0.1722(5) | 0.7363(4) | 0.3322(2) |
| C(8) | 0.2798(5) | 0.8258(5) | 0.2923(2) |
| C(9) | 0.2287(7) | 0.9407(6) | 0.2715(2) |
| C(10) | 0.2214(6) | 1.0497(5) | 0.3219(3) |
| C(11) | 0.1166(7) | 0.9622(5) | 0.3622(2) |
| C(12) | 0.1721(6) | 0.8514(5) | 0.3841(2) |
| C(13) | 0.3982(4) | 0.6361(5) | 0.3964(2) |
| C(14) | 0.4109(5) | 0.7062(6) | 0.4600(2) |
| C(15) | 0.5679(6) | 0.7319(7) | 0.4962(2) |
| C(16) | 0.7107(6) | 0.8290(7) | 0.4729(3) |
| C(17) | 0.6960(5) | 0.7620(7) | 0.4090(3) |
| C(18) | 0.5418(5) | 0.7393(5) | 0.3728(2) |
| C(19) | 0.0768(4) | 0.1731(4) | 0.1028(2) |
| C(20) | 0.1309(5) | 0.0648(5) | 0.1281(2) |
| C(21) | 0.1976(6) | −0.0106(6) | 0.0837(2) |
| C(22) | 0.3346(6) | 0.1108(7) | 0.0639(2) |
| C(23) | 0.2832(5) | 0.2197(6) | 0.0382(2) |
| C(24) | 0.2152(5) | 0.2966(5) | 0.0820(2) |
| C(25) | −0.1926(4) | 0.1106(4) | 0.1676(2) |
| C(26) | −0.2911(5) | −0.0220(5) | 0.1146(2) |
| C(27) | −0.4544(6) | −0.1303(7) | 0.1261(3) |
| C(28) | −0.4403(7) | −0.1942(6) | 0.1786(3) |
| C(29) | −0.3402(7) | −0.0678(7) | 0.2319(3) |
| C(30) | −0.1768(6) | 0.0432(6) | 0.2204(2) |
| C(31) | −0.0466(5) | 0.4017(5) | 0.1239(2) |
| C(32) | −0.0923(7) | 0.4994(6) | 0.1672(2) |
| C(33) | −0.1167(7) | 0.6225(6) | 0.1421(3) |
| C(34) | −0.2339(9) | 0.5540(8) | 0.0857(3) |
| C(35) | −0.1928(9) | 0.4568(8) | 0.0427(3) |
| C(36) | −0.1645(6) | 0.3308(6) | 0.0667(2) |

[a] e.s.d.s given in parentheses.

### *$Ag(PCy_3)_2ClO_4$*

Atomic coordinates are given in Table IV. Figure 2 shows a view of the structure. In this case the metal atom is tricoordinated with two P phosphine atoms and only one O atom of the perchlorate anion. The metal is 0.25 Å out of the plane determined by the two P atoms and the O atom. The complex can be compared with 2,11-bis(di-t-butylphosphinomethyl)-benzo[*c*]phenanthrenesilver(I)perchlorate which shows a similar coordination sphere [3]. The values in the diphosphine complex, 2.394(2) and 2.393(2) Å for the Ag–P bond distances and 161.5(1)° for the P–Ag–P bond angle, follow the above-mentioned trend when compared with the values of 2.429(1) and 2.432(1) Å and 147.34(3)° respectively. In this case the Ag–O bonds, 2.91(1) and 2.727(7) Å respectively, show that shorter Ag–anion bonds are related to lower P–Ag–P bond angles. Another complex for comparison is 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrenesilver(I)perchlorate [2] where the anion chelates the metal. In this complex, the coordination parameters are: Ag–P bond lengths 2.417(3) and 2.401(3) Å, P–Ag–P bond angle 151.5(1)° and Ag–O bond lengths 2.75(1) and 2.81(1) Å. These parameters also follow the above-mentioned trend. The title compounds have some oxygen atoms with high thermal parameters.

### *Comparison of the Structures and NMR Discussion*

To our knowledge these two structures are the first reported examples of mononuclear (1:2) silver–monophosphine complexes with the anion coordinated to the metal. The external electronic characteristics of silver(I) are 5s° 5p° orbitals that can accept one to four lone pairs. A number of compounds $Ag(PR_3)_nX$, $n = 1$–4, R = *p*-tolyl, have been studied by P NMR in solution [5]. It seems that, for $n = 2$, Ag(I) prefers to saturate the electronic capacity giving tetrahedral complexes, at least in the solid state, when phosphines are used. For instance, dimer compounds can be obtained for X = halogen, R = Ph, in the solid state and the metal atoms are bridged by the halogens giving tetrahedral species [11]. Another means of obtaining (1:2) silver–monophosphine complexes is to use sterically hindered ligands such as $P(t\text{-butyl})_3$ and weak anions ($NO_3$, $ClO_4$) so that the anion is out of the coordination sphere [12]. Diphosphine ligands can give mononuclear complexes as in the benzo[*c*]phenanthrene phosphines [2–3] or binuclear ones when alkyl chains join the P atoms as in bis(diphenylphosphino)methanesilver(I)nitrate [13]. In this case the P atoms bind different metal atoms and each nitrate chelates the metal in a formally tetrahedral coordination. If instead of the nitrate, a non-chelating anion such as Cl is used, two halogens join the two metals but the same tetrahedral configuration is obtained [13]. Recently using $BPh_4$ anion, the structure of a (1:2) silveraminophosphine cationic complex was obtained [14]. Curiously, the P–Ag–P bond angle is rather far from 180°: the value is 166.9(1)°. In our case we have chosen a phosphine with intermediate steric hindrance, *i.e.* $PCy_3$. A measure of this property is the cone angle parameter [15] whose value, 170°, is between 145° ($PPh_3$) and 182° ($P(t\text{-butyl})_3$). Recent structural studies on $Ag(AsPh_3)_nNO_3$ complexes have confirmed that lower cone angle parameter ligands stabilize $Ag(ligand)_2X$ in the dimeric form [10]. In order to study the general behavior of silver(I) in the coordinatively unsaturated (1:2) mononuclear species we have plotted P–Ag–P bond angles against Ag–P bond distances in Fig. 3 for all the compounds obtained after an investigation on Cambridge Crystallographic Data Base [16] and included the data of the title compounds. We have also included the values of the complex 2,11-bis(diethylphosphinomethyl)benzo[*c*]phenanthrenesilver(I)perchlorate [17] which has two independent molecules in the asymmetric unit. Our data fall well within the trend and perhaps it is possible to detect a straight line when all the data are considered. The last three points [14, 17] on the right of the plot are cationic complexes. We have not included in the plot the cationic complex $Ag[P(mesityl)_3]_2^+$ whose values, Ag–P bond dis-

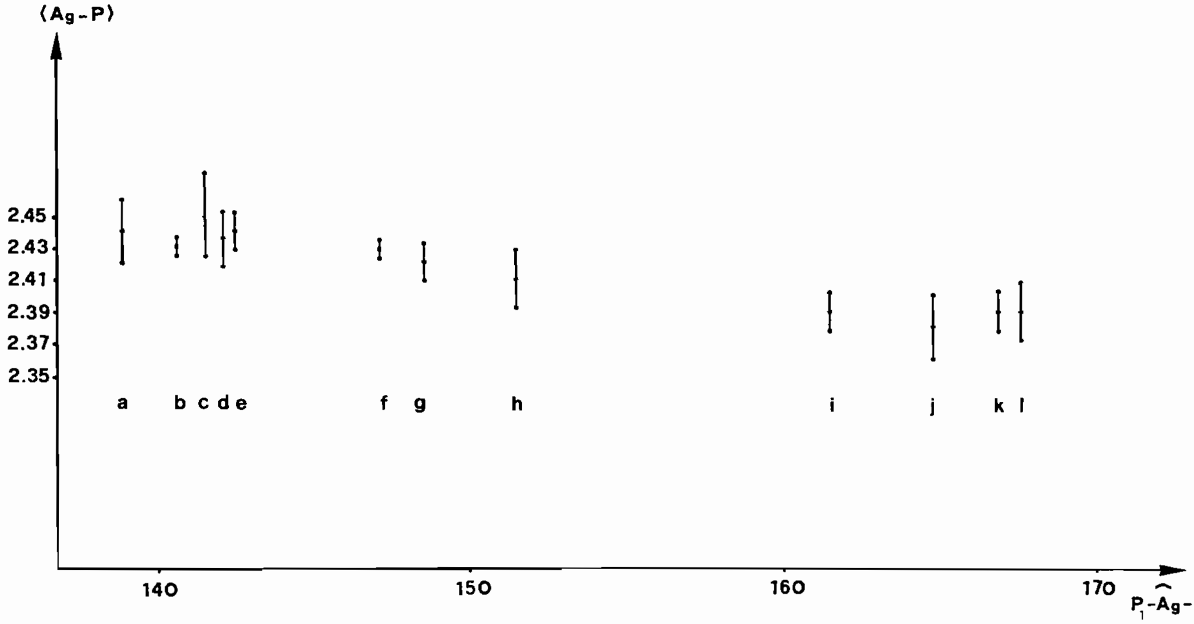

Fig. 3. Mean Ag–P bond distances against P–Ag–P bond angles in mononuclear (1:2) silver–phosphine complexes (see Table V).

TABLE V. Geometrical Data Related to Fig. 3

| Complex[a] | $d$(Ag–Pi) | ⟨$d$(Ag–Pi)⟩[b] | Δ[c] | $P_1$–Ag–$P_2$ | Figure 3 | Reference |
|---|---|---|---|---|---|---|
| $Ag(PCy_3)_2NO_3$ | 2.440(3)<br>2.445(4) | 2.44 | 0.021 | 139.0(1) | a | this work |
| Ag(**1a**)Cl | 2.455(1)<br>2.412(1) | 2.43 | 0.006 | 140.7(1) | b | 2 |
| Ag(**1b**)Br | 2.463(4)<br>2.433(5) | 2.45 | 0.027 | 141.6(2) | c | 3 |
| Ag(**1a**)$Cl_3Sn$ | 2.451(3)<br>2.419(3) | 2.435 | 0.018 | 142.2(1) | d | 2 |
| Ag(**1b**)Cl | 2.457(2)<br>2.427(2) | 2.44 | 0.012 | 142.6(1) | e | 3 |
| $Ag(PCy_3)_2ClO_4$ | 2.429(1)<br>2.432(1) | 2.43 | 0.006 | 147.34(3) | f | this work |
| Ag(**1a**)$NO_3$ | 2.424(2)<br>2.410(2) | 2.42 | 0.012 | 148.6(1) | g | 2 |
| Ag(**1a**)$ClO_4$ | 2.417(3)<br>2.401(3) | 2.41 | 0.018 | 151.5(1) | h | 2 |
| Ag(**1b**)$ClO_4$ | 2.394(2)<br>2.393(2) | 2.39 | 0.012 | 161.5(1) | i | 3 |
| Ag(**1c**)$^+$ | 2.378(3)<br>2.377(4) | 2.38 | 0.021 | 164.8(1) | j | 17 |
| $Ag\{P[N(CH_3)_2]_3\}_2^+$ | 2.395(2)<br>2.393(2) | 2.39 | 0.012 | 166.9(1) | k | 14 |
| Ag(**1c**)$^+$ | 2.393(3)<br>2.389(3) | 2.39 | 0.018 | 167.6(1) | l | 17 |

[a](1R) = 2,11-bis(di-R-phosphinomethyl)benzo[*c*]phenanthrene; (**1a**) denotes R = phenyl; (**1b**) denotes R = t-butyl; (1c) denotes R = ethyl. [b]⟨$d$(Ag–Pi)⟩ means the average between Ag–$P_1$ and Ag–$P_2$ distances. [c]Δ is $3[\sigma(Ag–P_1) + \sigma(Ag–P_2)]$.

tances of 2.461(6) Å and P–Ag–P bond angle of 179.4(5)°, are probably a result of steric hindrance amongst the mesityl groups of the different phosphine ligands [18]. The coupling constant values are 457 Hz for the nitrate complex and 447 Hz for the perchlorate one. As previously described in silver–phosphine complexes, due to the lower basicity of the perchlorate anion, it is expected that its complex would have a higher $J$ value than the nitrate one [2, 3, 5]. Instead, the value of $J$(Ag–P) is smaller. Our NMR data were measured in solution, so that the anomaly may be due to an association to dimer species for the perchlorate complex in solution, *i.e.* a smaller P–Ag–P angle may be observed in solution from a putative tetrahedral complex.

## Conclusions

The first examples of mononuclear (1:2) silver–monophosphine complexes with the anion coordinated to the metal have been determined in the solid state by diffraction methods. Silver–phosphorus coupling constants indicate that a structural modification exists in solution for the perchlorate complex. Some structural correlations previously described for series of silver–phosphine complexes have been confirmed, *i.e.* larger P–Ag–P bond angles are associated with shorter Ag–P bond distances, longer Ag–anion bond lengths and lower basicity of the anions. The correlation between P–Ag–P bond angles and Ag–P bond distances may be extended to all mononuclear (1:2) silver–phosphine complexes reported to date.

## Supplementary Material

Listings of structure factors, thermal parameters, H positions, and bond lengths and angles (74 pages) are available upon request.

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