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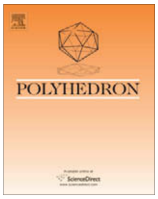

Silver(I) tertiary phosphine complexes: Influence of the anion on the structural and spectroscopic properties

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ABSTRACT

Two-, three- and four-coordinate silver(I) complexes, AgX (X = CN^-, PF_6^-, and SbF_6^-), with triphenyl phosphine, tricyclohexyl phosphine, diphenylcyclohexyl phosphine, and dicyclohexylphenyl phosphine have been synthesised and characterised by single crystal X-ray diffraction, elemental analysis, infrared spectroscopy, and ^{13}C and ^{31}P NMR spectroscopy. From the reaction of a metal salt to phosphine ligand ratio of 1:1 the various compounds crystallize as 1:2, 1:3, and 1:4 compounds $[Ag(PPh_2Cy)_3(CN)]\cdot 5H_2O$ (**1**), $[Ag(PCy_3)_2]\cdot PF_6$ (**2**), $[Ag(PPh_3)_4)]\cdot SbF_6\cdot CHCl_3$ (**3**), $[Ag(PCy_3)_2]\cdot SbF_6$ (**4**), $[Ag(PPh_2Cy)_2(C_3H_6O)]\cdot SbF_6$ (**5**), and $[Ag(PPhCy_2)_2]\cdot SbF_6.CHCl_3$ (**6**) monomers, with a wide variety of geometries around the central silver(I) atom. Compounds **1** and **3** have slightly distorted tetrahedral geometry around the silver(I) atom. The compounds **2**, **4**, and **6** show linear geometry around the metal centre, while compound **5** has a distorted trigonal planar geometry. The elemental analysis and NMR spectroscopic results are consistent with the single crystal structural analyses.

1. Introduction

Silver(I) exhibits a remarkable diversity in its structural chemistry and this is illustrated by the wide variety of structural types that are encountered in complexes of silver(I) salts. In silver(I) mononuclear and multinuclear complexes with neutral phosphine and amine ligands the silver(I) atom exhibits variable coordination numbers [1–5]. Reactions of AgX (X = NO_3^-, ClO_4^-, $C_2H_3O_2^-$, CN^-, SCN^-, PF_6^-, SbF_6^-, Cl^-, Br^-, and I^- etc.,) with monodentate tertiary phosphine and multidentate nitrogen donor bases yielded a diverse array of two-, three- and four-coordinate complexes with structural and spectroscopic properties that are determined by, specific choices of the phosphine and the other ligands, the stoichiometry and to a lesser extent by the choice of the anion [6–10]. Tertiary phosphine complexes of silver(I) of the type $[AgXL_n]$, where L = tertiary phosphine; $n = 1–4$; X = coordinating or non-coordinating anion, were first prepared in 1937 [11]. The general method of preparation involves the reaction of stoichiometric amounts of the phosphine ligand with the appropriate silver(I) salt. The reaction of silver(I) salts with monodentate tertiary phosphines in a 1:2 stoichiometric ratio generally results in the formation of either monomeric $[AgX(PR_3)_2]/[Ag(PR_3)2]\cdot X$ or dimeric complexes $[\{AgX(PR_3)_2\}_2]$, depending on the donor properties of the phosphine ligand, the bulkiness of the ligand, the substituents and the donor properties of the anion [12–27]. These complexes show a diversity of structural types and several reviews on this topic has been published [28–31]. The metal centre in the majority of the neutral $[AgX(PR_3)_2]$ and $[\{AgX(PR_3)_2\}_2]$ complexes are predominantly four-coordinate with the anion acting as either as a bidentate chelating ligand or as a bridging ligand, with two or three coordination found only in circumstances where the anion is a weak donor or the substituents on the phosphine ligand are bulky [16,19–24].

There is great interest to understand about how the molecular properties of the ligands affect the evolving structures of the complexes and their physical, chemical and biological properties [32,33]. Much effort has been devoted to the design and syntheses of pre-organised ligands that are able to control the structure and properties of complexes [34–37]. Silver(I) complexes with various N, S, O, P, and C donor ligands are of growing interest owing to their wide variation in structural format and rich physical, photo-physical, biological and chemical properties [38–43].

In our current investigations into the dependence of the structural and spectroscopic properties of these compounds on the choice of monodentate tertiary phosphine and coordinating and non-coordination anions, we have sought to extend the array of available data for two-, three-, and four-coordinate complexes of silver(I) with triphenyl phosphine, tricyclohexyl phosphine, cyclohexyldiphenyl phosphine, and dicyclohexyl(phenyl) phosphine (Scheme 1).

Spectroscopic data has been obtained from infrared spectroscopy and ^1H, ^{13}C and ^{31}P NMR spectroscopy. Along with X-ray diffraction techniques, there are several potentially useful

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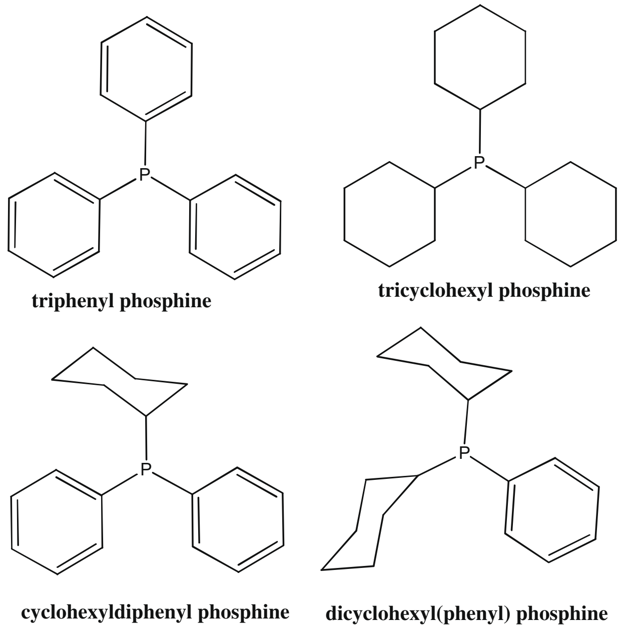

Scheme 1. Chemdraw structures of tertiary phosphine ligands.

spectroscopic techniques for characterising compounds in the solid state and solution. Thus IR, and NMR spectroscopy have proved to be useful techniques for the determination of the structures of silver(I) complexes [44,5,45,46]. Silver(I)-phosphine complexes and their single crystal X-ray structures, IR absorption spectra and NMR spectroscopic properties are discussed here.

2. Experimental

2.1. Material and physical measurements

All the reactions were carried out in air. All the reactants and solvents were commercial products of Aldrich and ACROS and were used with out further purification. In all cases, the crystalline products were obtained by the slow evaporation method. Microanalyses were carried out by Mr. D. Mooser (Ecole d'ingénieurs de Fribourg, Filière de chimie). The IR spectra were recorded as KBr plates on a Perkin–Elmer Spectrum One FTIR instrument.^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AMX 400 MHz using CD_2Cl_2–d_2 as solvent. The TMS was used as the internal standard.

*2.2. Preparation of $[Ag(PPh_2Cy)_3(CN)]\cdot 5H_2O$ (**1**)*

To the solution of AgCN (0.014 g, 0.1 mmol) in MeOH/distilled water (3:2) (10 mL) was added diphenylcyclohexyl phosphine (0.086 g, 0.3 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for overnight at 50 °C. The colourless solution obtained was filtered to avoid any impurity and cool down to room temperature and evaporated slowly. After 5 days colourless plate like crystals were obtained. A suitable crystal was chosen for X-ray diffraction analysis. The rest of the product was collected by decantation of solvent and yield was found 62%. *Anal.* Calc. for $C_{55}H_{67}AgNO_2P_3$: C, 67.70; H, 6.87; N, 1.43. Found: C, 67.66; H, 6.60; N, 1.76%. IR (υ, cm^{-1}): 3412s, 3070m, 3050m, 2926vs, 2849s, 2344w, 2151w, 2107m, 1638m, 1617s, 1434vs, 1265m, 1183s, 998s, 847m, 743m, 617m, 510m. ^{1}H NMR (CD_2Cl_2–d_2; ppm): 1.5–2.0, 2.5 (m, 11H, cyclohexyl protons), and 7.2–7.8 (m, 10H, phenyl protons). ^{13}C NMR (CD_2Cl_2–d_2; ppm): 24.77–35.58 (cyclohexyl carbons), 118 (CN^- carbon atom) and 128.49–133.69 (phenyl carbons). ^{31}P NMR (CD_2Cl_2–d_2; ppm): 11.93 (s, sharp).

*2.3. Preparation of $[Ag(PCy_3)_2]\cdot PF_6$ (**2**)*

To the solution of $AgPF_6$ (0.025 g, 0.1 mmol) in acetonitrile (5 mL) was added tricyclohexyl phosphine (0.057 g, 0.2 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min at room temperature. The colourless solution obtained was filtered to avoid any impurity and left undisturbed for crystallization. After a couple of days colourless crystals were obtained (Yield 83%) *Anal.* Calc. for $C_{36}H_{66}AgF_6P_3$: C, 53.09; H, 8.11. Found: C, 54.10; H, 8.46%. IR (υ, cm^{-1}): 3549m, 3409m, 2922s, 2825s, 1633m, 1618s, 1451vs, 1293m, 1171s, 1015s, 834vs, 622m, 557s. ^{1}H NMR (CD_2Cl_2–d_2; ppm): 1.6–2.1, 2.4 (m, 33H, cyclohexyl protons). ^{13}C NMR (CD_2Cl_2–d_2; ppm): 25.22–31.96 (cyclohexyl carbons). ^{31}P NMR (CD_2Cl_2–d_2; ppm): 37.71, 40.68 (d, two broad peaks for phosphorous atom of tricyclohexyl phosphine and PF_6^- counter ion).

*2.4. Preparation of $[Ag(PPh_3)_4)].SbF_6\cdot CHCl_3$ (**3**)*

To the solution of $AgSbF_6$ (0.035 g, 0.1 mmol) in acetonitrile (5 mL) was added 2-mercapto thiazoline (0.018 g, 0.2 mmol) in MeOH (5 mL) and triphenyl phosphine (0.027 g, 0.1 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred overnight at 50 °C. The resultant solution was evaporated slowly at room temperature. After three days colourless block crystals of unexpected product was obtained. A suitable crystal was chosen for X-ray diffraction studies. The crystalline product was collected by filtration (Yield 17% with respect to silver salt). *Anal.* Calc. for $C_{73}H_{61}AgCl_3F_6P_4Sb$: C, 57.93; H, 4.03. Found: C, 57.13; H, 4.56%. IR (υ, cm^{-1}): 3551m, 3478s, 3412s, 3075m, 3052m, 1633m, 1615s, 1437vs, 1257m, 1155s, 1013s, 750m, 843m, 646vs, 503m. No NMR measurement was carried out due to the very little amount of the final product.

*2.5. Preparation of $[Ag(PCy_3)_2]\cdot SbF_6$ (**4**)*

To the solution of $AgSbF_6$ (0.035 g, 0.1 mmol) in acetonitrile (5 mL) was added tricyclohexyl phosphine (0.057 g, 0.2 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min at room temperature. Transparent solution obtained was left undisturbed for crystallization at room temperature by slow evaporation. After three days colourless rod like crystals were obtained (Yield 74%). *Anal.* Calc. for $C_{36}H_{66}AgF_6P_2Sb$: C, 47.76; H, 7.29. Found: C, 47.95; H, 7.25%. IR (υ, cm^{-1}): 3553m, 3412m, 2929s, 2823s, 1634m, 1617s, 1447vs, 1291m, 1168s, 1003s, 837vs, 628m, 555s. ^{1}H NMR (CD_2Cl_2–d_2; ppm): 1.5–2.2, 2.5 (m, 33H, cyclohexyl protons). ^{13}C NMR (CD_2Cl_2–d_2; ppm): 25.82–31.77 (cyclohexyl carbons). ^{31}P NMR (CD_2Cl_2–d_2; ppm): 39.38, 42.31(d. two peaks for phosphorous atom of tricyclohexyl phosphine).

*2.6. Preparation of $[Ag(PPh_2Cy)_2(C_3H_6O)]\cdot SbF_6$ (**5**)*

The synthesis was followed by same procedure as described for compound **4**. Here diphenylcyclohexyl phosphine (0.057 g, 0.2 mmol) in CH_2Cl_2 was used instead of tricyclohexyl phosphine. The clear solution obtained was left undisturbed for crystallization. After the evaporation of solvent a transparent solid product was obtained on the walls of evaporation dish. The resultant product was re-dissolved in CH_2Cl_2/acetone (1:2) (15 mL) and kept for slow evaporation; after 3 days colourless block crystals were obtained. The crystalline product was carefully collected and weighed (Yield 56%). *Anal.* Calc. for $C_{39}H_{48}AgF_6OP_2Sb$: C, 49.87; H, 5.11. Found: C, 50.29; H, 5.24%. IR (υ, cm^{-1}): 3550m, 3413s, 3007m, 3069m, 2931s, 2889m, 2859m, 2837m, 1695s,1637m, 1617s, 1436vs, 1229m, 1176m, 1097s, 885m, 749s, 668m, 505s. ^{1}H NMR (CD_2Cl_2–d_2; ppm): 1.3–2.0, 2.6 (m, 11H, cyclohexyl protons), and 7.3–7.7 (m, 10H, phenyl protons). ^{13}C NMR (CD_2Cl_2–d_2; ppm):

25.82–35.10 (cyclohexyl carbons), and 127.64–133.75 (phenyl carbons). ^{31}P NMR (CD_2Cl_2–d_2; ppm): 37.66(d. broad peak for phosphorous atom of tertiary phosphine).

2.7. Preparation of $[Ag(PPhCy_2)_2]\cdot SbF_6\cdot CHCl_3$ (**6**)

The synthesis of compound **6** was done by following the same procedure as described for compound **4** and **5**. To the solution of $AgSbF_6$ (0.035 g, 0.1 mmol) in acetonitrile (5 mL) was added to a solution of dicyclohexylphenyl phosphine (0.055 g, 0.2 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min and colourless solution obtained was filtered to avoid any impurity and left undisturbed for crystallization. After 5 days colourless crystals were obtained. A suitable crystal was chosen for single crystal X-ray diffraction studies. The crystalline product was collected carefully and weighed (Yield 83%). *Anal.* Calc. for $C_{37}H_{55}AgCl_3F_6P_2Sb$: C, 43.88; H, 5.43. Found: C, 43.95; H, 5.21%. IR (υ, cm^{-1}): 3550m, 3478s, 3412s, 3071w, 3051w, 2930vs, 2851s, 1637m, 1617s, 1449vs, 1270m, 1179s, 1001s, 847m, 747m, 659vs, 531m. ^{1}H NMR (CD_2Cl_2–d_2; ppm): 1.4–2.0, 2.5 (m, 22H, cyclohexyl protons), and 7.3–7.8 (m, 5H, phenyl protons). ^{13}C NMR (CD_2Cl_2–d_2; ppm): 25.79–32.47 (cyclohexyl carbons), and 124.75–134.83 (phenyl carbons). ^{31}P NMR (CD_2Cl_2–d_2; ppm): 34.40, 37.48 (d. two peaks for phosphorous atom of tertiary phosphine).

2.8. X-ray Crystallography

The intensity data were collected at 173 K on either, a one circle (ϕ scans) [47], or a two circle (ω and ϕ scans) [48] Stoe Image Plate Diffraction System, using Mo Kα graphite monochromated radiation. The structures were solved by direct methods using the program SHELXS-97 [49]. The refinement and all further calculations were carried out using SHELXL-97 [49]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. In most cases multi-scan absorption corrections were applied using the MULscanABS routine in PLATON [50]. For compound **1** a region of diffuse electron density was treated with the SQUEEZE routine in PLATON [50]: 201 electrons for a volume of 756.5 Å^3, which was estimated to be equivalent to 20 water molecules of crystallization per unit cell, or 5 water molecules per molecule of complex (space group $Pna2_1$, $Z = 4$). All the phenyl rings were made into regular hexagons. Two phenyl rings (C1–C6 and C25–C30) showed positional disorder. They were split and the occupancies were initially refined. The final values were close enough to 0.5/0.5 to be fixed as such in the final cycles of refinement. Atoms in rings C1A–C6A and C1B–C6B were refined anisotropically, however those for rings C25A–C30A and C25B–C30B were only refined isotropically as the anisotropic thermal parameters indicated important thermal disorder. For compound **2** the PF_6 anion was disordered. The F-atoms were split (A and B parts) and the occupancies refined to 0.80(5)/0.20(5). The P–F distances were also refined with distances restraints. Crystals of compound **5** crystallized with a disordered molecule of acetone (occupancies 0.7/0.3). They were also twins and this was corrected for using the TWINrotMAT routine available in PLATON [50]; the final refined BASF factor was 0.15. Figs. 1–6 were drawn using the programs PLATON and Mercury [51]. A summary of crystal data and refinement details for compounds **1**–**6** are given in Table 1, and selected bond lengths and angles are listed in Table 2.

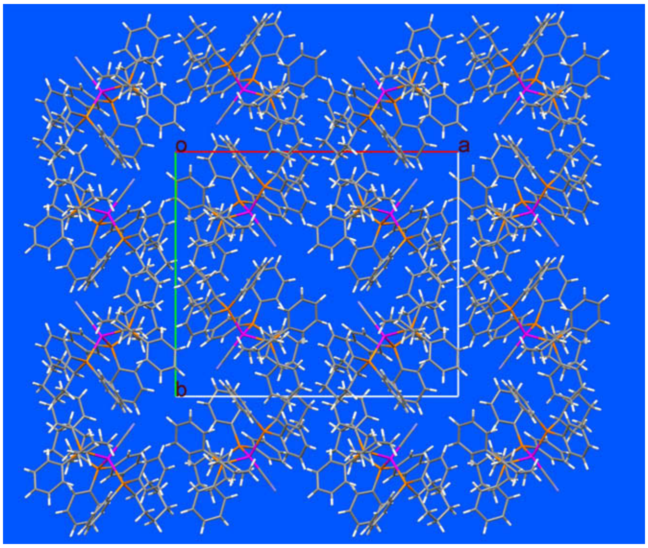

Fig. 1b. View along the *c*-axis of the crystal packing of complex **1**.

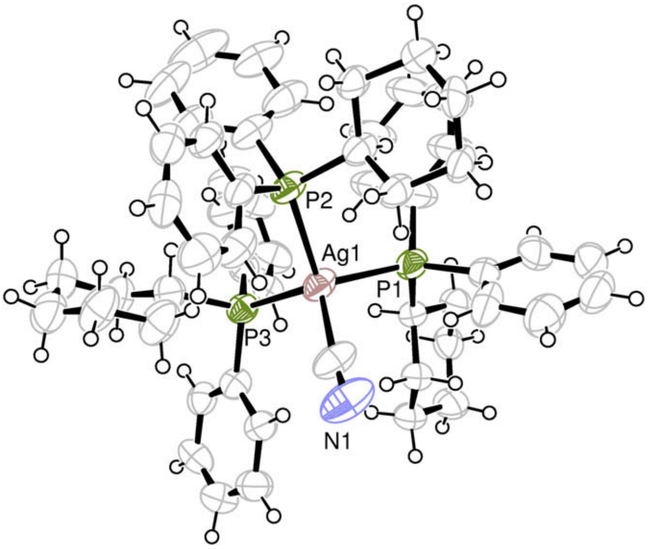

Fig. 1a. View of the molecular structure of complex **1**, with atom labelling scheme and displacement ellipsoids drawn at the 50% probability level.

3. Results and discussions

3.1. Structural descriptions

3.1.1. Crystal structure of $[Ag(PPh_2Cy)_3(CN)]\cdot 5H_2O$ (**1**)

The crystal structure of compound **1** is depicted in Fig. 1a. The complex is isostructural with a considerable family of $[Ag(PR_3)_3(X)]$ arrays [5,40]; the anion being modelled as C-bonded in this complex. The geometry around the silver(I) atom is tetrahedral. Silver(I) atom being coordinated with three phosphorous atoms of monodentate tertiary phosphine ligand molecules and one carbon atom of the cyanide counter ion. Compound **1** crystallizes with five lattice water molecules. The Ag–C bond distance is 2.187(7) Å which is longer than that found in similar silver(I) cyanide phosphine complexes [5,40]. The Ag–P bond distances are 2.5176(15), 2.5240(14), and 2.5226(12) Å. The P–Ag–P bond angles range from 107.02(4)° to 107.74(5)° and P–Ag–C bond angles vary from 109.54(18)° to 113.06(14)°. These bond angles values around the central metal atom are close to the ideal tetrahedral angle 109.5°. The X-ray structure shows that cyclohexyl rings of the tertiary phosphine ligand are present in the chair conformation.

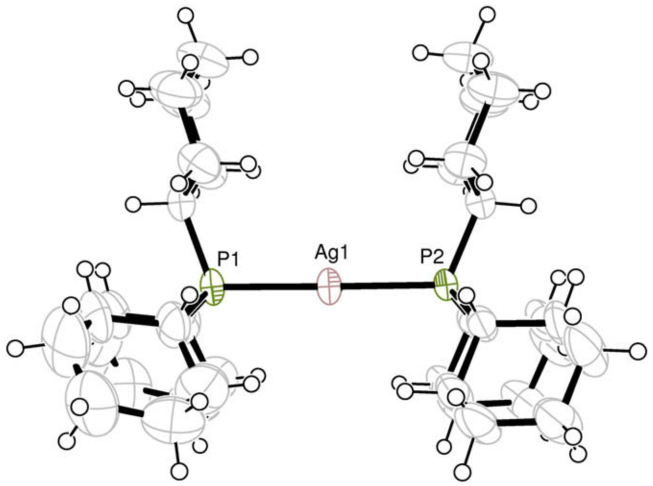

Fig. 2a. A view of the molecular structure of complex **2**, with selected atom labelling scheme and displacement ellipsoids drawn at the 50% probability level (the anion has been omitted for clarity).

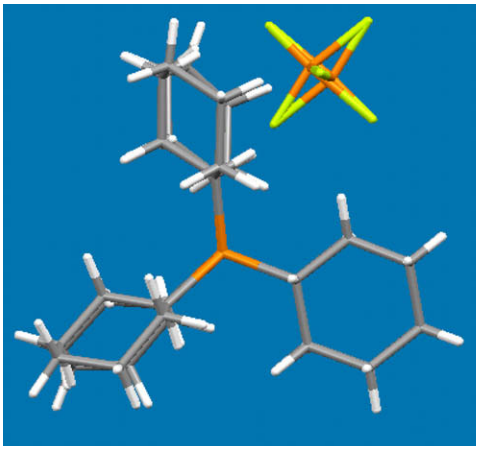

Fig. 2b. Panel showing the almost totally eclipsed arrangement of the two dicyclohexylphenyl phosphine molecules coordinated with silver(I) centre in complex **2**.

3.1.2. Crystal structure of $[Ag(PCy_3)_2]\cdot PF_6$ (2)

The molecular structure of compound **2** is illustrated in Fig. 2a. Here the geometry around the central silver(I) atom is linear. Atom Ag1 is coordinated with two phosphorous atoms of monodentate tertiary phosphine ligand molecules. The PF_6^- anion is well separated from the metal centre and does not show any coordination. The phosphorous atom of the counter ion is hexa-coordinated and an ideal octahedron is observed around phosphorous atom. The P–Ag–P unit is planar [179.42(6)°], and the two phosphine ligand molecules are eclipsed; the cyclohexyl rings are again present in chair conformations.

The molecular structure of compound **2** is highly symmetric and C_2 symmetry is observed here. The phosphorous atom of the counter ion is found to be disordered about the C_2 axis. The Ag–P bond distances are 2.3802(16) and 2.3779(16) Å, considerably shorter than in compound **1**. The Ag–P bond length differences found in complexes **1** and **2**, and other the silver(I) complexes reported here, are attributed to the different crystallographic environments around the central atom, the chemical composition of the tertiary phosphine ligands and to some extent the nature of the counter ions as well.

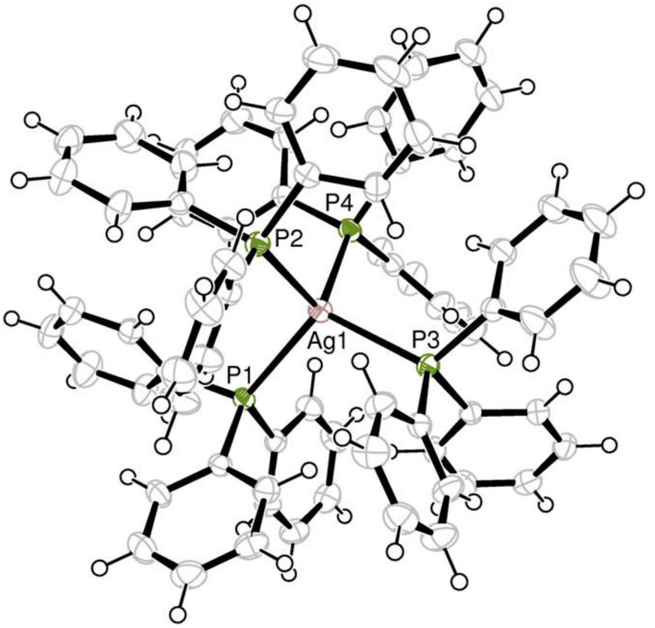

Fig. 3. A view of the molecular structure of compound **3**, with selected atom labelling scheme and displacement ellipsoids drawn at the 50% probability level (the anion and solvated molecule have been omitted for clarity).

3.1.3. Crystal structure of $[Ag(PPh_3)_4)]\cdot SbF_6\cdot CHCl_3$ (3)

The representative view of the crystal structure of complex **3** is shown in Fig. 3. The compound **3** is a solvo polymorph of the complex $[Ag(PPh_3)_4)]\cdot SbF_6$ [52]. In compound **3** the geometrical environment around Ag(I) atom is again close to ideal tetrahedral.

The silver(I) atom is coordinated with four phosphorous atoms of monodentate tertiary phosphine ligand molecules. The compound **3** is solvated by one chloroform molecule as well. In the hexafluoro antimonate counter ion, the Sb(V) atom is hexa-coordinated with an octahedral geometrical environment.

The Ag–P bond distances vary from 2.6197(6) to 2.6282(7) Å. These Ag–P bond distances are longer than that found in compounds **1** and **2** and are shorter than those found in its polymorphic form $[Ag(PPh_3)_4)].SbF_6$ [52]. The P–Ag–P bond angles range from 108.01(2)° to 110.62(2)°; close to ideal tetrahedral angle

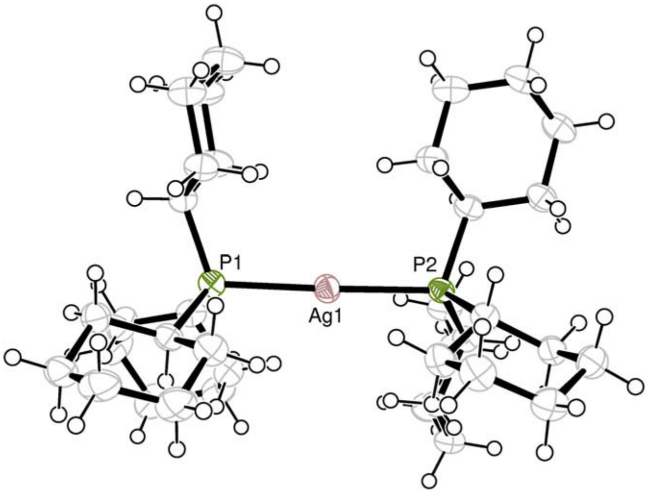

Fig. 4a. Ortep view of the molecular structure of **4**, with selected atom labelling scheme and displacement ellipsoids drawn at the 50% probability level (the anion has been omitted for clarity).

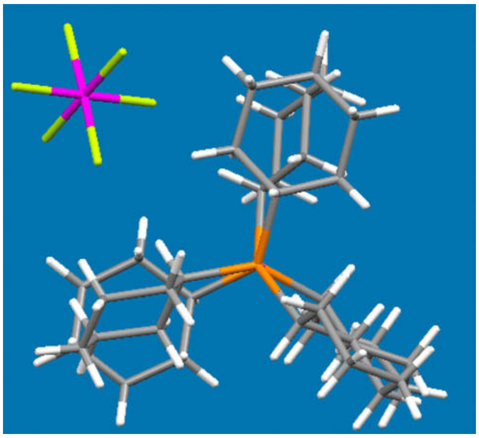

Fig. 4b. View showing the two tertiary phosphine ligand molecules present in a partially eclipsed form in compound **4**.

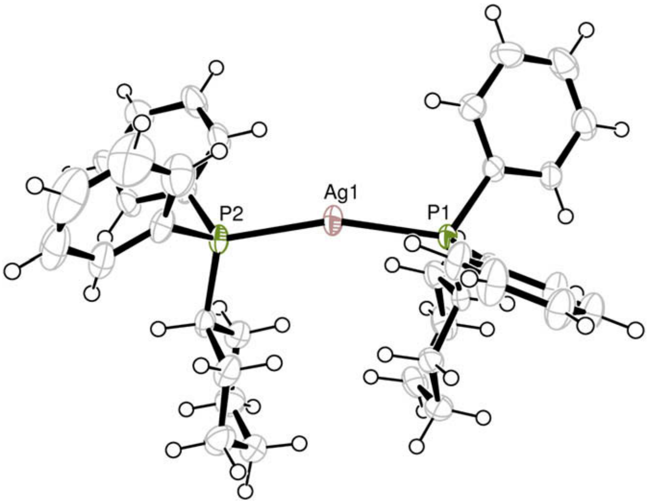

Fig. 5a. A view of the silver(I)phosphine moiety in compound **5**, with partial numbering scheme and displacement ellipsoids drawn at the 50% probability level (the anion and the disordered solvated acetone molecule have been omitted for clarity).

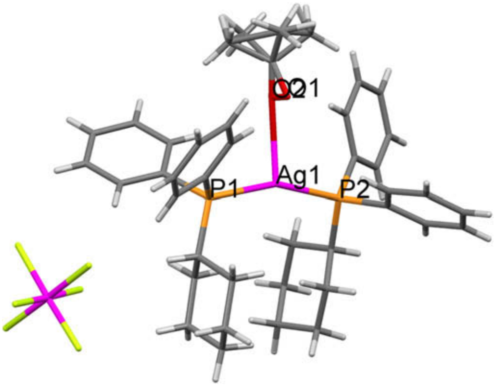

Fig. 5b. A view showing the molecular structure of compound **5** with the disordered solvated acetone molecule, and the SbF_6 anion.

109.5°. The P–Ag–P bond angle values different slightly to those found in complex $[Ag(PPh_3)_4)]\cdot SbF_6$, which has the same geometrical environment around the silver(I) atom and possesses crystallographic C_3 symmetry [52].

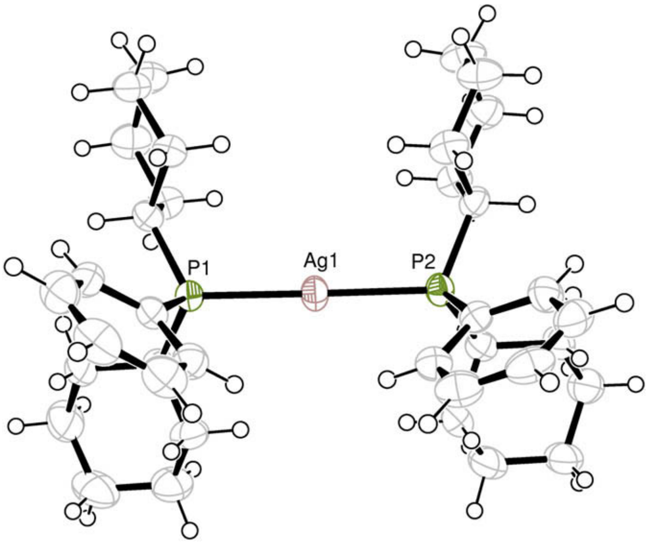

Fig. 6a. Representative view of molecular structure of compound **6** with selected atom labelling scheme and displacement ellipsoids drawn at the 50% probability level (the anion and solvated molecule have been omitted for clarity).

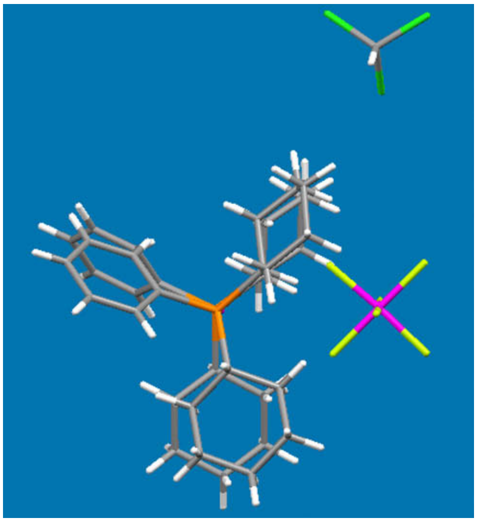

Fig. 6b. A view showing the partially eclipsed tertiary phosphine molecules coordinated to the silver(I) atom in compound **6**.

*3.1.4. Crystal structure of $[Ag(PCy_3)_2]\cdot SbF_6$ (**4**)*

The single crystal structure of the monomer complex **4** is illustrated in Fig. 4a. The geometrical environment around silver(I) atom is linear and the central metal atom is coordinated with two phosphorous atoms of monodentate tertiary phosphine ligand. The molecular structure of compound **4** does not has C_2-symmetry unlike compound **2**. However, the Sb(V) atom has octahedral geometry as found in compound **3**, and is coordinated with six fluorine atoms. The P–Ag–P unit is linear, within experimental error, but slightly less linear found than that found in complex **2**, [175.37(3)° compared to 179.43(6)° for **2**]. The tertiary phosphine ligand molecules are eclipsed and the cyclohexyl rings are present in chair conformations, as in complexes **1** and **2**. The Ag–P1 and Ag–P2 bond distances are 2.3767(10) and 2.3750(10) Å, respectively. These Ag–P distances are shorter than those found in complexes **1** and **3** but comparable with those in **2**.

Table 1
Summery of crystal data and structure refinement details for compounds **1**–**6**.

	1	**2**
Formula	$C_{55}H_{63}AgNP_3{\cdot}5(H_2O)$	$C_{36}H_{66}AgF_6P_3$
M	1028.92	813.67
Wavelength (Å)	0.71073	0.71073
Temperature (K)	173	173
Crystal symmetry	orthorhombic	triclinic
Space group	$Pna\ 2_1$	$C\ 2/m$
a (Å)	21.5982(15)	24.145(2)
b (Å)	18.7015(13)	17.8524(10)
c (Å)	13.2231(8)	9.7455(8)
α (°)	90	90
β (°)	90	105.671(9)
γ (°)	90	90
V (Å^3)	5341.1(6)	4044.6(5)
Z	4	4
D_{calc} (Mg m^{-3})	1.280	1.336
μ (Mo Kα) (mm^{-1})	0.51	0.67
F(0 0 0)	2168	1712
Crystal size (mm)	0.38 × 0.35 × 0.20	0.30 × 0.27 × 0.11
θ Limits (°)	1.44–25.48	2.10–25.85
Measured reflections	27065	16060
Unique reflections (R_{int})	9418 (0.068)	4065 (0.0614)
Observed reflections	6473	2533
Goodness-of-fit (GOF) on F^2	0.88	0.94
R_1 (F), [a][$I > 2\sigma$ (I)]	0.0427	0.0521
wR_2 (F^2), [b][$I > 2\sigma(I)$]	0.873	0.1335
	3	**4**
Formula	$C_{72}H_{60}AgF_6P_4Sb{\cdot}CHCl_3$	$C_{36}H_{66}AgP_2{\cdot}F_6Sb$
M	1512.07	904.45
Wavelength (Å)	0.71073	0.71073
Temperature (K)	173	173
Crystal symmetry	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	12.0120(5)	14.3626(5)
b (Å)	23.0780(6)	19.1856(10)
c (Å)	23.4887(10)	15.9332(6)
α (°)	90	90
β (°)	90.499(3)	114.936(3)
γ (°)	90	90
V (Å^3)	6511.1(4)	3981.2(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.542	1.509
μ (Mo Kα) (mm^{-1})	1.00	1.30
F(0 0 0)	3048	1856
Crystal size (mm)	0.46 × 0.32 × 0.21	0.50 × 0.27 × 0.23
θ Limits (°)	1.70–29.28	1.61–29.63
Measured reflections	88111	54225
Unique reflections (R_{int})	17605 (0.056)	10766 (0.070)
Observed reflections	12913	8572
Goodness of fit (GOF) on F^2	0.99	1.05
R_1 (F), [a] [$I > 2\sigma(I)$]	0.0371	0.0521
wR_2 (F^2), [b][$I > 2\sigma(I)$]	0.0798	0.1326
	5	**6**
Formula	$C_{36}H_{42}AgF_6P_2Sb{\cdot}C_3H_6O{\cdot}F_6Sb$	$C_{36}H_{54}AgCl_3P_2{\cdot}CHCl_3{\cdot}F_6Sb$
M	938.33	1011.72
Wavelength (Å)	0.71073	0.71073
Temperature (K)	173	173
Crystal symmetry	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pbca$
a (Å)	12.9403(15)	16.3557(14)
b (Å)	13.6997(17)	29.989(3)
c (Å)	14.0354(17)	17.548(2)
α (°)	114.286(13)	90
β (°)	96.745(14)	90
γ (°)	111.183(13)	90
V (Å^3)	2008.4(4)	8607.1(15)
Z	2	8
D_{calc} (Mg m^{-3})	1.552	1.561
μ (Mo Kα) (mm^{-1})	1.30	1.39
F(0 0 0)	944	4080
Crystal size (mm)	0.38 × 0.34 × 0.23	0.35 × 0.15 × 0.08
θ Limits (°)	1.95–26.40	2.10–26.00
Measured reflections	15848	39451
Unique reflections (R_{int})	7346 (0.0)	8329 (0.069)
Observed reflections	5004	4648
Goodness of fit (GOF) on F^2	0.90	0.87
R_1 (F), [a][$I > 2\sigma(I)$]	0.0413	0.0590
wR_2 (F^2), [b][$I > 2\sigma(I)$]	0.1006	0.1501

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

3.1.5. Crystal structure of $[Ag(PPh_2Cy)_2(C_3H_6O)]{\cdot}SbF_6$ (5)

The molecular structure of compound **5** is illustrated in Fig. 5a. A highly disordered acetone molecule of crystallization coordinates to the silver(I) atom, as shown in Fig. 5b. On the basis of this evidence, we suggest a distorted trigonal planar geometry around the silver(I) atom in complex **5**. The central silver(I) atom is further coordinated with two phosphorous atoms of monodentate tertiary phosphine ligand molecules. In the non-coordinating SbF_6^- counter ion, the Sb(V) atom has an octahedral geometry as in compounds **3** and **4**, and is coordinated with six fluorine atoms. The Ag–P1 and Ag–P2 distances are 2.4166(18) and 2.4127(19) Å, respectively. These bond distance values are longer than those in compounds **2** and **4**, and shorter than those found in compounds **1** and **3**. The Ag–O bond distance is 2.664(16) Å, showing weak coordination of the disordered oxygen atom of the solvated acetone molecule. The P–Ag–P bond angle is 158.91(6)° and O–Ag–P1 and O–Ag–P2 bond angles are 95.2(4) and 105.6(4)°, respectively.

The P–Ag–P bond angle 158.91(6)° shows a very large deviation from an ideal linear angle of 180° or an ideal trigonal planar angle of 120°. These bond angles values provide additional evidence of the weak coordination of the acetone molecule to the silver(I) metal centre in **5**. The cyclohexyl rings of the tertiary phosphine molecules are again present in chair conformations.

3.1.6. Crystal structure of $[Ag(PPhCy_2)_2]{\cdot}SbF_6{\cdot}CHCl_3$ (6)

A perspective view of the molecular structure of compound **6** is shown in Fig. 6a. The compound crystallizes in the orthorhombic space group Pbca. The geometrical environment around the silver(I) atom is linear within experimental error. Silver(I) atom is coordinated with two phosphorous atoms of monodentate tertiary phosphine ligand molecules. The complex is solvated with one chloroform molecule, as in compound **3**. The Ag–P1 and Ag–P2 bond distances are 2.3892(17) and 2.3859(17) Å, respectively. These bond distances are more or less comparable with those in compounds **2** and **4** but shorter than those in compounds **1**, **3** and **5**. The P–Ag–P bond angle is 173.33(6)°, smaller than that found in compounds **2** and **4**. The bond angles found around the silver(I) atom indicate quite large deviations from the ideal linear angle of 180°. The differences in bond length and bond angle values found in compounds **2**, **4** and **6** are attributed to different chemical composition of the ligands and to some extent to the counter ions as well.

3.2. ^1H, ^{13}C and ^{31}P NMR spectroscopic studies

In the ^1H NMR spectra of compounds **1, 2** and **4**–**6**, the signals due to the phenyl and cyclohexyl groups of the teriary phosphines

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **1**–**6**.

Bond lengths (Å)		Bond angles (°)	
1			
Ag1–P1	2.5176(15)	P1–Ag1–P2	107.63(5)
Ag1–P2	2.5240(14)	P1–Ag1–P3	107.02(4)
Ag1–P3	2.5226(12)	P2–Ag1–P3	107.74(5)
Ag1–C55	2.202(5)	P1–Ag1–C55	109.54(18)
		P2–Ag1–C55	113.06(14)
		P3–Ag1–C55	111.60(4)
2			
Ag1–P1	2.3802(16)	P1–Ag1–P2	179.42(6)
Ag1–P2	2.3779(16)		
3			
Ag1–P1	2.6236(6)	P1–Ag1–P2	109.16(2)
Ag1–P2	2.6261(7)	P1–Ag1–P3	109.39(2)
Ag1–P3	2.6197(6)	P1–Ag1–P4	110.26(2)
Ag1–P4	2.6282(7)	P2–Ag1–P3	110.62(2)
		P2–Ag1–P4	108.01(2)
		P3–Ag1–P4	109.40(2)
4			
Ag1–P1	2.3767(10)	P1–Ag1–P2	175.37(3)
Ag1–P2	2.3750(10)		
5			
Ag1–P1	2.4166(18)	P1–Ag1–P2	158.91(6)
Ag1–P2	2.4127(19)	P1–Ag1–O2^{i}	95.2(4)
Ag1–O2^{i}	2.664(16)	P2–Ag1–O2^{i}	105.6(4)
Symmetry codes:			
(i) $-x+1, -y+1, -z$.			
6			
Ag1–P1	2.3892(17)	P1–Ag1–P2	173.33(6)
Ag1–P2	2.3859(17)		

are observed by their chemical shifts in the regions 7–8 and 1–2.6 ppm, in CD_2Cl_2–d_2 solution. No chemical shifts were observed for the protons of the solvate molecules in the spectra of compounds **1**, **3**, **5** and **6**.

In the ^{13}C NMR spectra of complex **1**, the chemical shifts for the phenyl and cyclohexyl carbons are observed in the range of 128.49–133.69 and 24.77–35.58 ppm, respectively, and a small peak is observed at 118 ppm for the CN^- group (carbon atom). The ^{13}C NMR spectra of complexes **2** and **4** are almost similar and a set of peaks are observed in the range of 25.22–31.96 and 25.82–31.77 ppm (cyclohexyl carbons). The pattern of cyclohexyl resonances is similar to those reported for a gold(I) complex [53]. In ^{13}C NMR spectrum of complex **5**, the chemical shifts for the phenyl and cyclohexyl carbons are observed in the range of 127.64–133.75 and 25.82–35.10 ppm, respectively. No extra signals were observed for the solvate acetone molecule, present in the solid state structure. The ^{13}C NMR spectrum of complex **6** shows two sets of peaks in the range of 25.79–32.47 and 124.75–134.83 ppm for cyclohexyl and phenyl carbons, respectively. Again no peak for the chloroform carbon atom was observed which, is similar to the situation for complex **5**. These complexes appear to lose the solvated molecule of low boiling point solvents at ambient conditions. These results are according to expectations and indicate that the difference between the solution and solid state structures.

^{31}P NMR spectra of silver(I) complexes **1**–**2** and **4–6** were recorded at room temperature. Naturally occurring isotopes of silver (^{107}Ag, 51.82% natural abundance; ^{109}Ag, 48.18%) and their magnetogyric ratios are similar in magnitude [$\gamma(^{109}\text{Ag})/\gamma(^{107}\text{Ag}) = 1.15$]. The ^{31}P NMR spectra of complexes of silver(I) with phosphorous-donor ligands may show splitting due to ^{1}J(P–Ag) coupling. In the ^{31}P NMR spectra of complex **1** a well defined singlet peak was observed at 11.93 ppm, about 17 ppm downfield compared to free diphenycyclohexyl phosphine (~ -6 ppm). The presence of a singlet peak may be due to rapid intermolecular exchange of phosphine between different silver(I) atoms and free phosphine ligand in solution [54]. In the ^{31}P NMR of compounds **2** and **4**, the resonances for the coordinated tricyclohexyl phosphine appear as two sets of intense doublet peaks at 37.71, 40.68 and 39.38, 42.31 ppm, respectively, about 30, 32 and 31, 34 ppm, respectively, downfield compared to the uncomplexed tricyclohexyl phosphine ($\sim$8 ppm). The presence of two sets of doublet peaks may be due to the presence of different types of silver(I) complexes of tricyclohexyl phosphine in the solution. In the ^{31}P NMR of compound **5** the resonance for the coordinated diphenylcyclohexyl phosphine appears as an intense doublet peak at 37.66 ppm, about 31 ppm downfield compared to the uncomplexed dipenylcyclohexyl phosphine. In the ^{31}P NMR of compound **6** the resonances for the coordinated dicyclhexylphenyl phosphine appear as intense doublet peaks at 34.40 and 37.48 ppm, about 31, and 33, 36 ppm, respectively, downfield compared to the uncomplexed dicyclhexylphenyl phosphine ($\sim$1 ppm). Silver(I) complexes with (1:2 stoichiometric ratio) show well resolved pairs of doublets, the resolution of signals for 1:2 species is due to ^{1}J(P–Ag) coupling. The ^{31}P NMR spectral results are in agreement with the previously reported silver(I) phosphine complexes [22–42,44,5]. The differences observed in the ^{31}P NMR spectra of the silver(I) complexes are attributed to the presence of different geometries around the silver(I) atom in the solution form of these complexes.

4. Conclusions

The synthesis of silver(I) tertiary phosphine compounds reveals that the geometry around the silver(I) atom is highly dependent on the type of tertiary phosphine and to some extent on the molar ratio of the reactants used. The tertiary phosphines having bulky groups, like cyclohexyl, impose a linear geometry around the central metal atom with silver(I) salts containing non-coordinating counter ions (SbF_6^- and PF_6^-), and trigonal planar to tetrahedral geometry in the case of silver(I) salts with coordinating anions. Whereas triphenylphosphine, with less bulky groups, imposes tetrahedral geometry around the central metal atom, with silver(I) salts containing coordinating or non-coordinating anions. These silver(I) phosphine precursors have been used successfully for the preparation of mixed ligand coordination polymers with versatile architectures [43].

Supplementary data

CCDC 741314, 741315, 741316, 741317, 741318 and 741319 contain the supplementary crystallographic data for compounds **1**–**6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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