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Structural characterization of silver(I) complexes of diphenylmethanimine and (diphenylmethyleneamino)diphenylphosphine

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Dedicated in honor of Professor R. Usón

Abstract

The reaction of $NH{=}CPH_2$ with the silver species $[AgX(PPh_3)]$ ($X = ClO_4$, SO_3CF_3) affords the derivatives $[Ag(PPh_3)(NH{=}CPh_2)]X$. Complexes $[Ag(Ph_2PN{=}CPh_2)_2]X$ ($X = Cl$, ClO_4, SO_3CF_3) have been obtained from $Ph_2PN{=}CPh_2$ and the corresponding silver salt AgX. X-ray diffraction studies have been carried out for four of the derivatives.

Keywords: Crystal structures; Silver complexes; Ketimine complexes

1. Introduction

Ketimines are among the most widely used functional groups in organic chemistry, notably in the stereoselective synthesis of organic derivatives, which is nowadays a rapidly growing research area. In spite of their importance in organic chemistry, and although an enormous variety and number of nitrogen-containing ligands have been tested in inorganic or organometallic chemistry, ketimines have seldom been used as substrates or ligands. Regarding the coinage metals, for instance, ketimine copper complexes have been proposed as intermediates in the oxidative coupling of ammonia to produce hydrazine, [1–4] but the intermediates have never been characterized. In a few recent studies benzophenoneimine [5,6] or its derivative (diphenylmethyleneamino)diphenylphosphine [7] have been employed as ligands giving rise to various mononuclear gold(I) and silver species that, in some cases, form supramolecular structures via aurophilic or hydrogen bonding. In case of the only reported silver(I) complex the structure consists of a dimer in which a tetrafluoroborate anion connects two $[Ag(NH{=}CPh_2)_2]^+$ units by hydrogen bonding of the form $N{-}H\cdots F$ [6].

We have reported recently the structural characterization of silver(I) complexes of stoichiometries $[Ag(CF_3SO_3)L]$ ($L = PPh_3$, PPh_2Me, SC_4H_8) and $[AgL_2](CF_3SO_3)$ ($L = PPh_3$, PPh_2Me) in which the solid state structures display a wide variety of nuclearities, silver co-ordination numbers, trifluoromethanesulfonate co-ordination modes and secondary interactions; these depend variously on the nature of the neutral ligand and the donor capabilities of the anion [8]. In the present research we synthesized and structurally characterized silver(I) complexes with the nitrogen-donor ligand $NH{=}CPh_2$ and its phosphine derivative $Ph_2P{-}N{=}CPh_2$ starting from silver(I) salts with the anions chloride, perchlorate or trifluoromethanesulfonate.

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2. Results and discussion

The reaction between $AgClO_4$, AgCl or $AgCF_3SO_3$ and 2 equiv. of $Ph_2PN{=}CPh_2$ at room temperature leads to the complexes $[Ag(Ph_2PN{=}CPh_2)_2]X$ ($X = ClO_4$ **1**, Cl **2**, CF_3SO_3 **3**) in high yields (Scheme 1). The products are yellow crystalline solids stable to air and moisture; their composition has been confirmed by elemental analysis. The IR spectra (nujol mulls) show imino stretching frequencies at $\nu = 1602$ (**1**), 1610 (**2**) and 1619 (**3**) cm^{-1}, and bands due to the anions perchlorate [9] or triflate [10] at 1103 and 622 cm^{-1} or 1287, 1244 and 1146 cm^{-1} for complexes **1** and **3**, respectively. Complex **2** also shows a weak band at 376 cm^{-1} which could be assigned to a stretching ν(Ag–Cl) mode and may indicate tricoordination at the silver center. The structural situation is not clear for the other derivatives **1** and **3** because of the overlapping of the vibrational modes. In the ^1H NMR spectra in HDA or $CDCl_3$ solutions only the phenyl resonances are observed. The conductivity in acetonitrile solutions are: 158 (1), 92 (2) and 140 (3) Ω^{-1} cm^2 mol^{-1}, in accordance with a 1:1 ionic formulation; nevertheless the different values are consistent with a greater dissociation of the perchlorate or triflate anions than the chloride, for which the coordinating capability at silver is stronger.

The solution structure was first studied by means of $^{31}P\{^1H\}$ NMR experiments. In the three complexes the data are indicative of a regioselective coordination of the silver centre to the phosphorus atoms. Thus, the NMR spectra at room temperature show resonances at 46.8(m) and 51.2(m) for **1**, at 44.7(m) and 50.1(m) for **2** and at 42.9(m) and 46.5(m) for **3**, different from that of the free ligand ($\delta = 36.4$ ppm). The fluxionality in these complexes seems to be responsible for the broad resonances observed. In fact, this fluxionality is typical in the co-ordination chemistry of silver and can be attributed to exchange phenomena involving the neutral ligands. These processes can be stopped in some cases at low temperature, showing the coupling constants of a unique kind of magnetically active phosphorus with the ^{107}Ag and ^{109}Ag isotopomers. Thus in the spectra for complexes **1** and **3** in HDA at −50 °C the multiplet signals split into two doublets centered at 42.2 ppm [$J(^{107}Ag–P) = 511.6$; $J(^{109}Ag–P) = 590.5$ Hz] **1** and 43.1 ppm [$J(^{107}Ag–P) = 510.5$; $J(^{109}Ag–P) = 589.1$ Hz] **3**, respectively. These coupling constants are in accordance with an *s* contribution to the hybridization at the silver centres corresponding to a linear geometry, as reported for other phosphine complexes [8,11]. No signal splitting is observed for complex **2**; in the NMR spectrum in $CDCl_3$ at −50 °C, nevertheless, the multiplet separation of about 448 Hz is smaller than for the triflate and perchlorate derivatives and is in accordance with a decrease of the P–Ag–P angle [11]. This result has been confirmed in structural studies (see below).

Complexes **1** and **2** (Figs. 1 and 2, Tables 1 and 2) each consist of a three-coordinate silver centre bonded to the two phosphorus atoms of two different $Ph_2PN{=}CPPh_2$ ligands and to one oxygen atom of a perchlorate group (**1**) or a chlorine ligand (**2**). In compound **2** the silver and chlorine atoms lie on a twofold axis and thus the metal coordination is exactly planar. The silver atom in compound **1** is essentially coplanar with the donor atoms P(1), P(2) and O(1) (mean deviation of four atoms 0.014 Å). The angles around the metal centers are dissimilar. Compound 1 exhibits a P(**1**)–Ag–P(2) angle of 154.22(2)°, are P(1)–Ag–O(1) 109.23(4)°, P(2)–Ag–O(2) 96.46 with (4)°. In compound **2** the P#1–Ag–P angle is 134.62(3)°; P–Ag–Cl 112.690(14)°. This may be attributed to the weaker coordination of the triflate ligand than the chloride, with a concomitant decrease in the perturbation of the otherwise ideally linear geome-

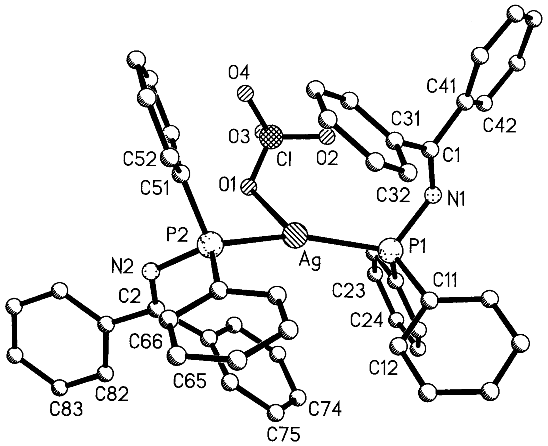
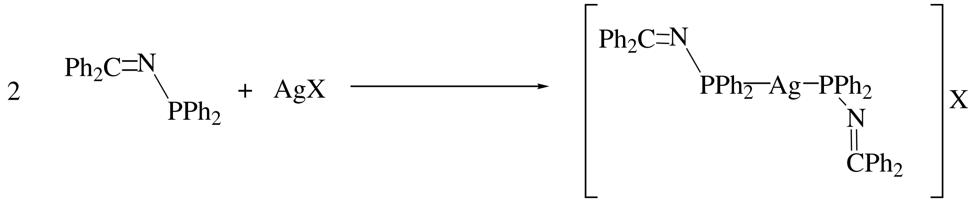


Fig. 1. Molecular structure of compound **1**. Hydrogen atoms are omitted for clarity. Radii are arbitrary.



$X = ClO_4$ (**1**), Cl (**2**), CF_3SO_3 (**3**)

Scheme 1.

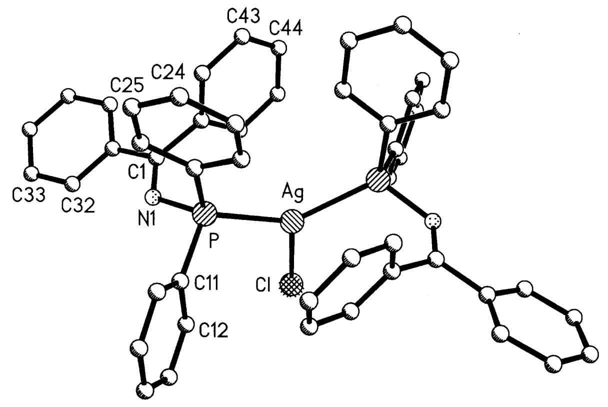


Fig. 2. Molecular structure of compound **2**. Hydrogen atoms are omitted for clarity. Radii are arbitrary.

Table 1
Selected bond lengths (Å) and bond angles (°) for compound **1**

Bond lengths			
Ag–P(1)	2.4020(6)	C(1)–C(31)	1.495(3)
Ag–P(2)	2.4101(6)	C(1)–C(41)	1.496(3)
Ag–O(1)	2.5554(17)	C(2)–N(2)	1.284(3)
P(1)–N(1)	1.7029(18)	C(2)–C(81)	1.482(3)
P(1)–C(11)	1.815(2)	C(2)–C(71)	1.498(3)
P(1)–C(21)	1.823(2)	Cl–O(3)	1.4283(18)
P(2)–N(2)	1.712(2)	Cl–O(2)	1.4377(18)
P(2)–C(61)	1.810(2)	Cl–O(4)	1.4410(17)
P(2)–C(51)	1.818(2)	Cl–O(1)	1.4492(17)
C(1)–N(1)	1.285(3)		
Bond angles			
P(1)–Ag–P(2)	154.22(2)	N(1)–C(1)–C(31)	125.40(19)
P(1)–Ag–O(1)	109.23(4)	N(1)–C(1)–C(41)	117.12(19)
P(2)–Ag–O(1)	96.46(4)	C(31)–C(1)–C(41)	117.44(17)
N(1)–P(1)–C(11)	105.88(10)	N(2)–C(2)–C(81)	118.4(2)
N(1)–P(1)–C(21)	100.42(9)	N(2)–C(2)–C(71)	125.1(2)
C(11)–P(1)–C(21)	103.52(10)	C(81)–C(2)–C(71)	116.50(19)
N(1)–P(1)–Ag	118.83(7)	O(3)–Cl–O(2)	110.66(12)
C(11)–P(1)–Ag	112.93(7)	O(3)–Cl–O(4)	109.63(11)
C(21)–P(1)–Ag	113.48(8)	O(2)–Cl–O(4)	109.46(11)
N(2)–P(2)–C(61)	105.57(10)	O(3)–Cl–O(1)	109.35(11)
N(2)–P(2)–C(51)	99.91(10)	O(2)–Cl–O(1)	109.04(11)
C(61)–P(2)–C(51)	104.24(10)	O(4)–Cl–O(1)	108.67(11)
N(2)–P(2)–Ag	117.68(7)	Cl–O(1)–Ag	116.35(10)
C(61)–P(2)–Ag	114.14(8)	C(1)–N(1)–P(1)	122.64(16)
C(51)–P(2)–Ag	113.55(7)	C(2)–N(2)–P(2)	121.73(17)

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **2**

Bond lengths			
Ag–P	2.4193(5)	P–C(21)	1.811(2)
Ag–Cl	2.5058(7)	P–C(11)	1.822(2)
P–N(1)	1.7132(18)	N(1)–C(1)	1.285(3)
Bond angles			
P#1–Ag–P	134.62(3)	C(21)–P–Ag	118.89(7)
P–Ag–Cl	112.690(14)	C(11)–P–Ag	110.90(7)
N(1)–P–C(21)	104.65(9)	C(1)–N(1)–P	122.21(15)
N(1)–P–C(11)	100.30(9)	N(1)–C(1)–C(31)	118.01(18)
C(21)–P–C(11)	102.28(9)	N(1)–C(1)–C(41)	125.15(19)
N(1)–P–Ag	117.29(6)		

try. The Ag–P bond distances are similar for both derivatives [2.4020(6), 2.4101(6) Å (1), 2.4193(5) Å (**2**)]. These values are longer than those found in [$Ag_4Cl_4(dppm)_2$] [12] (2.366(**2**) Å for three-coordinated and 2.379(2) Å for four-coordinated silver) or in other '$AgPPh_3$' fragments [13], but they are shorter than in [$Ag(dppf)(PPh_3)$]ClO_4 (dppf = 1,2-bis(diphenylphosphino)ferrocene) [14] (2.4386(3)–2.4870(12) Å) with a trigonal silver centre. The Ag–O distance in **1** (2.5554(17) Å) is similar to the longest found in [$Ag(CF_3SO_3)(PPh_3)$] (two determinations 2.357(2)–2.572(3) Å [8], 2.29(2)–2.546(12) Å [15]). A similar Ag–Cl distance to that found in **2** has been observed in [$AgCl\{P(C_6H_{11})_3\}_2$] (2.489(1) Å) [16]. Possible C–H···O hydrogen bonds in **1**, involving H···O distances of 2.48 and 2.52 Å, are shown in Table 3 and their effect is to link the molecules in chains parallel to the *y* axis.

The reaction of equimolecular quantities of [$AgX(PPh_3)$] (X = ClO_4 **4**, CF_3SO_3 **5**) and benzophenoneimine in dichloromethane at room temperature affords high yields of the corresponding nitrogen–phosphorus-donor ligand complexes [$Ag(PPh_3)(NH{=}CPh_2)$]X as white solids. Reactions with more than 1 equiv. of benzophenoneimine did not lead to an increase of the coordination number and, by spectroscopical methods, the excess ligand was detected unchanged in the reaction mixtures. The composition of the complexes **4** and **5** has been confirmed by elemental analysis. The IR spectra show imino stretching frequencies at 1602 (**4**) and 1609 cm^{-1} (**5**) and the molar conductivities in acetonitrile solutions confirm their ionic nature, with values of 177 (**4**) and 164 Ω^{-1} cm^2 mol^{-1} (**5**) typical of 1:1 electrolytes. Their $^{31}P\{^1H\}$ NMR spectra in acetone solutions show similar features. In both cases at room temperature there are two multiplets at 17.9 and 12.7

Table 3
Hydrogen bonds (Å, °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound 1 [a]				
C(22)–H(22)···O(2)	0.95	2.52	3.420(3)	158.8
C(75)–H(75)···O(4)#1	0.95	2.48	3.425(3)	171.6
Compound 4 [b]				
N–H(01)···O(3)	0.83(2)	2.27(2)	3.051(3)	156(2)
Compound 5 [c]				
N–H(01)···O(1)#1	0.77(3)	2.32(3)	2.933(4)	137(3)
C(23)–H(23)···O(2)#2	0.95	2.37	3.289(5)	162.2
C(16)–H(16)···O(3)#1	0.95	2.56	3.395(5)	146.8

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, y+1, z$.

[b] Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, -y+1/2, z+1/2$. #2 $x, -y+1, z+1/2$.

[c] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1/2$.

ppm (**4**) and 17.6 and 12.1 ppm (**5**), respectively. These split at low temperature into two doublets centred at 14.3 ppm [$J(^{109}\text{Ag–P}) = 743.0$, $J(^{107}\text{Ag–P}) = 643.6$ Hz] **4** and at 14.0 ppm [$J(^{109}\text{Ag–P}) = 744.5$; $J(^{107}\text{Ag–P}) = 644.9$ Hz] **5**, respectively. In the ^{1}H NMR spectra, only a single NH proton is observed for both complexes over the whole temperature range investigated (−50 to + 25 °C). These data seem to indicate that the coordination at silver in both complexes is similar; this situation is different from that mentioned above for the phosphine derivatives **1** and **2**. Attempts to prepare for comparison purposes the corresponding chloride complex by reaction of [$\text{AgCl(PPh}_3)$] and equimolecular amounts of benzophenoneimine left the starting materials unchanged.

Despite the similarity of the chemical formula of complexes **4** and **5**, the environment at silver is very different. In both complexes the phosphorus atom of a triphenylphosphine ligand and the nitrogen of the HNCPh_2 group are bonded to the metal atom. Nevertheless, compound **5** (Fig. 3) resembles complexes **1** and **2** in the distorted trigonal planar geometry at the silver centre (Ag, P, N and O(3) coplanar to within 0.026 Å, P–Ag–N 155.96(8)°). The Ag–P bond distance (2.3482(10) Å) is shorter than those found in **1** and **2**; that corresponding to the Ag–O bond is 2.616(2) Å. The Ag–N distance in **5** (2.149(3) Å) lies in the range found in [$\text{Ag(NH=CPh}_2)_2$]BF_4 (2.2223(2) Å) [6] and is close to the shortest values found in [$\text{Ag\{P(C}_6\text{H}_4\text{Me–4)}_3\}\{\text{BPh}_2\text{(pz)}_2\}$] (pz = Pyrazolyl) (2.194(4), 2.411(4) Å) [13c]; longer Ag–N bond distances have been found in [Ag(dppf)(phen)]ClO_4 (2.343(3), 2.361(3) Å [14]. A selection of bond lengths and angles is shown in Table 4.

In compound **4** (Fig. 4) the environment of silver is almost linear, with an N–Ag–P angle of 170.34(5)°. This is essentially linear geometry, marginally distorted by the weak coordination to two oxygen atoms of a perchlorate ligand (Ag–O distances (2.9153(17), 3.0166(19) Å). This geometry has been observed in silver–triflurosulphonate derivatives such as [$\text{Ag(CF}_3\text{SO}_3)(\text{PPh}_2\text{Me})_2$] [8]. Despite the different geometry both the Ag–P and Ag–N distances are close to those found in **5**. A selection of bond lengths and angles is given in Table 5. Possible N–H···O hydrogen bonds have been observed in both complexes, involving H···O distances 2.27(2) (**4**), 2.32(3) Å (**5**) (see Table 3). Compound **5** also shows C–H···O hydrogen bonds involving H···O distances of 2.37, 2.56 Å. In this complex the effect of the two shortest hydrogen bonds is to connect the molecules to layers parallel to the *yz* plane (two layers per cell) (see Fig. 5).

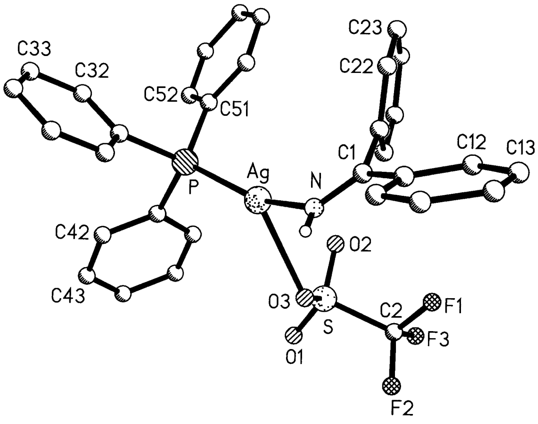


Fig. 3. Structure of compound **5**. Hydrogen atoms except NH are omitted for clarity. Radii are arbitrary.

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **4**

Bond lengths			
Ag–N	2.1402(16)	Ag–P	2.3565(5)
Ag–O(2)	2.9153(17)	Ag–O(4)	3.0166(19)
N–C(1)	1.282(2)	C(1)–C(11)	1.485(3)
C(1)–C(21)	1.490(3)	P–C(31)	1.8158(18)
P–C(41)	1.8185(19)	P–C(51)	1.820(2)
Cl–O(1)	1.4271(16)	Cl–O(4)	1.4300(18)
Cl–O(3)	1.4356(18)	Cl–O(2)	1.4386(17)
Bond angles			
N–Ag–P	170.34(5)	N–Ag–O(2)	87.73(6)
P–Ag–O(2)	101.91(4)	N–Ag–O(4)	73.96(6)
P–Ag–O(4)	113.08(4)	O(2)–Ag–O(4)	46.15(5)
C(1)–N–Ag	134.64(14)	N–C(1)–C(11)	119.30(17)
N–C(1)–C(21)	121.21(17)	C(11)–C(1)–C(21)	119.39(16)
C(31)–P–C(41)	105.92(8)	C(31)–P–C(51)	106.53(9)
C(41)–P–C(51)	103.17(8)	C(31)–P–Ag	110.00(6)
C(41)–P–Ag	119.55(6)	C(51)–P–Ag	110.76(6)
O(1)–Cl–O(4)	110.09(11)	O(1)–Cl–O(3)	110.59(11)
O(4)–Cl–O(3)	108.44(13)	O(1)–Cl–O(2)	110.72(11)
O(4)–Cl–O(2)	108.42(12)	O(3)–Cl–O(2)	108.51(11)

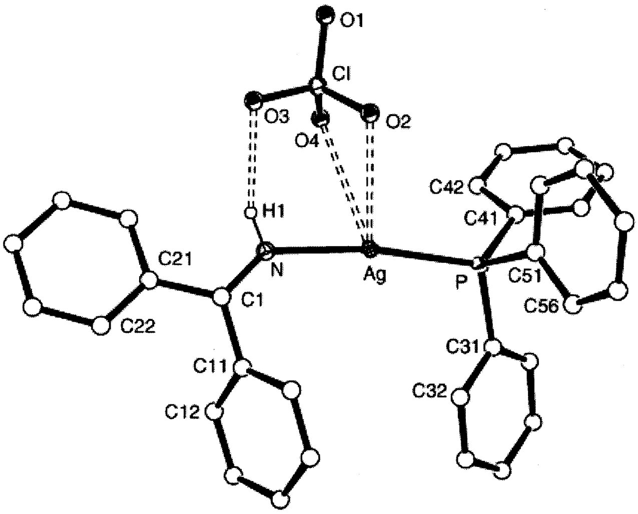


Fig. 4. Molecular structure of compound **4**. Hydrogen atoms except NH are omitted for clarity. Radii are arbitrary.

Table 5
Selected bond lengths (Å) and bond angles (°) for compound **5**

Bond lengths			
Ag–N	2.149(3)	P–C(31)	1.822(3)
Ag–P	2.3482(10)	P–C(51)	1.828(3)
Ag–O(3)	2.616(2)	N–C(1)	1.273(4)
P–C(41)	1.818(3)		
Bond angles			
N–Ag–P	155.96(8)	C(41)–P–Ag	114.50(11)
N–Ag–O(3)	90.07(10)	C(31)–P–Ag	112.06(12)
P–Ag–O(3)	113.56(6)	C(51)–P–Ag	114.22(13)
C(41)–P–C(31)	104.80(16)	C(1)–N–Ag	124.8(2)
C(41)–P–C(51)	106.29(16)	S–O(3)–Ag	121.74(14)
C(31)–P–C(51)	103.98(16)		

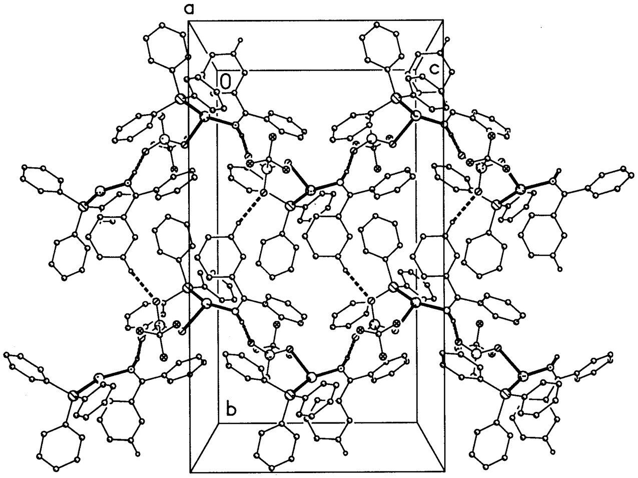


Fig. 5. Arrangement of the molecules in the unit cell (**5**).

3. Experimental

3.1. Materials

All the experiments were carried out under dry purified nitrogen. Glassware was dried and filled with nitrogen, solvents were distilled and kept under nitrogen. NMR: Bruker ARX 300. IR: Perkin–Elmer FT-IR Spectrum 1000. Microanalyses: Perkin–Elmer 240B. Starting materials were prepared according to literature procedures: $Ph_2PN{=}CPh_2$ [17]. $[Ag(CF_3SO_3)(PPh_3)]$ was prepared in a similar way to $[Ag(ClO_4)(PPh_3)]$ [18]. $AgClO_4$ and $AgCF_3SO_3$ were purchased from Aldrich.

3.2. Synthesis

3.2.1. $[Ag(Ph_2PN{=}CPh_2)_2]X$ (X = ClO_4 (**1**), CF_3SO_3 (**3**))

$Ph_2PN{=}CPh_2$ (0.547 mmol, 200 mg) was added to a Et_2O solution (15 ml) of AgX (0.27 mmol, X = ClO_4, 56 mg, CF_3SO_3, 69 mg). After stirring for 45 min the suspension was filtered and the yellow solid obtained washed with OEt_2; yield 210 mg (82%) **1**, 208 mg (77%) **3**. *Anal.* Found (**1**): C, 63.25; H, 4.18; N, 2.65. Calc. for $C_{50}H_{40}N_2O_4AgClP_2$: C, 64.0; H, 4.3; N, 3.0%. *Anal.* Found (**3**): C, 59.39; H, 3.96; N, 2.46. Calc. for $C_{51}H_{40}P_2AgO_3SF_3$: C, 62.01: H, 4.08; N, 2.83%. ^{1}H NMR (**1**) (298 K) 7.94–7.19 (m, Ph–H), (**3**) 7.95–7.11 (m, Ph–H). $^{31}P\{^1H\}$ NMR (**1**) (298 K) 46.8 (m, PPh_2), 51.2 (m, PPh_2), (223 K) $\delta = 42.2$ dd ($J(^{107}Ag–P) = 511.5$; $J(^{109}Ag–P) = 590.5$ Hz), **3** (298 K) 42.9 (m, PPh_2), 46.5 (m, PPh_2), (223 K) $\delta = 43.1$ dd ($J(^{107}Ag–P) = 510.5$; $J(^{109}Ag–P) = 589.1$ Hz).

3.2.2. $[Ag(Ph_2PN{=}CPh_2)_2]Cl$ (**2**)

AgCl (0.139 mmol, 20 mg) was added to an aqueous saturated solution of KCl (20 ml) in order to get a better solubility of AgCl. A solution of $Ph_2PN{=}CPh_2$ (0.279 mmol, 102 mg) in OEt_2 (20 ml) was then added. After stirring for 15 min a yellow solid is filtered off, washed with a saturated solution of KCl in water, ethanol and Et_2O sucessively and recrystallized from a mixture of $CHCl_3$ and Et_2O. Yield 105 mg (86%). *Anal.* Found: C, 68.35; H, 4.3; N, 2.95. Calc. for $C_{50}H_{32}AgClP_2N_2$ C, 68.7; H, 4.6; N, 3.2%. ^{1}H NMR (298 K) 7.68–7.25 (m, Ph–H). $^{31}P\{^1H\}$ NMR (298 K) 44.7 (m, PPh_2), 50.1 (m, PPh_2), (223 K) 44.7 (m, PPh_2), 50.1 (m, PPh_2).

3.2.3. $[Ag(PPh_3)(NH{=}CPh_2)]X$ (X = ClO_4 (**4**), CF_3SO_3 (**5**))

The compound $[AgX(PPh_3)]$ (0.29 mmol, X = ClO_4, 140 mg, CF_3SO_3, 150 mg) was dissolved in 15 ml of CH_2Cl_2 and diphenylmethanimine (0.29 mmol, 51.5 µl) was added. The reagents were allowed to react for 15 min. Then most of the solvent was removed, and 20 ml of hexane was then added to produce a white solid. The solid was filtered and washed with hexane; yield 148 mg, (75%) **4** 166 mg, (81%) **5**. *Anal.* Found (**4**): C, 56.85; H, 4.75; N, 2.55. Calc. for $C_{31}H_{26}NAgClO_4P$: C, 57.29; H, 3.87; N, 2.15%. *Anal.* Found (**5**): C, 54.0; H, 3.5; N, 2.4. Calc. for $C_{32}H_{26}NAgF_3O_3PS$: C, 54.85; H, 3.75; N, 2.0%. ^{1}H NMR (**4**) (298 K) 9.21 (s, 1 H, H–N), 7.76–7.39 (m, 25H, Ph–H); (223 K): 8.97 (s, 1 H, H–N), 7.90–7.32 (m, 25H, Ph–H); **5** (298 K) 9.15 (s, 1 H, H–N), 7.87–7.45 (m, 25H, Ph–H); (223K): 8.96 (s, 1 H, H–N), 7.95–7.33 (m, 25H, Ph–H). $^{31}P\{^1H\}$ NMR (**4**) (298 K) 17.9 (m, PPh_2), 12.7 (m, PPh_2); (223K) $\delta = 14.0$ dd ($J(^{109}Ag–P) = 743.0$, $J(^{107}Ag–P) = 643.6$ Hz, PPh_2); **5** (298 K) 17.6 (m, PPh_2), 12.1 (m, PPh_2); (223 K) $\delta = 14.0$ dd ($J(^{109}Ag–P) = 744.5$, $J(^{107}Ag–P) = 644.9$ Hz, PPh_2).

3.3. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens Smart, Nonius κCCD (**4**) or Siemens P4 (**5**) diffractometers. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were based on psi-scans (**5**), multiple scans (program

Table 6
Details of data collection and structure refinement for complexes **1**, **2**, **4** and **5**

Compound	**1**	**2**	**4**	**5**
Chemical formula	$C_{50}H_{40}AgClN_2O_4P_2$	$C_{50}H_{40}AgClN_2P_2$	$C_{31}H_{26}AgClNO_4P$	$C_{33.5}H_{29}AgF_3NO_{3.5}PS$
Crystal habit	pale yellow plate	yellow prism	colourless prism	colourless irreg. column
Crystal size (mm^3)	0.40 × 0.21 × 0.11	0.34 × 0.13 × 0.13	050 × 0.25 × 0.20	0.80 × 0.30 × 0.20
Crystal system	triclinic	monoclinic	monoclinic	orthorombic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$Pbcn$
a (Å)	10.6466(10)	12.3456(10)	17.4567(3)	22.211(3)
b (Å)	10.7562(11)	16.3453(12)	9.7127(2)	22.642(4)
c (Å)	21.419(2)	20.9283(16)	18.2313(3)	12.7962(16)
α (°)	95.168(3)	90	90	90
β (°)	101.082(3)	100.710(3)	116.4619(6)	90
γ (°)	112.175(3)	90	90	90
U (Å^3)	2193.1(4)	4149.6(6)	2767.29(9)	6435.2(15)
Z	2	4	4	8
D_{calc} (g cm^{-3})	1.421	1.399	1.562	1.506
M	938.10	874.10	650.82	729.48
$F(000)$	960	1792	1320	2960
T (°C)	−130	−130	−100	−100
$2\theta_{max}$ (°)	56	56	56	50
μ(Mo Kα) (mm^{-1})	0.641	0.665	0.921	0.795
Transmission	0.764–0.980	0.781–0.928	0.656–0.837	0.758–0.847
No. of reflections measured	19880	22214	25518	7102
No. of unique reflections	10663	5278	6535	5664
R_{int}	0.0461	0.0528	0.0202	0.0235
R [a] ($F > 4\sigma(F)$)	0.0360	0.0328	0.0271	0.0342
wR [b] (F^2, all reflections)	0.0739	0.0882	0.0616	0.0676
No. of reflections used	10663	5278	6535	5664
No. of parameters	541	254	456	419
No. of restraints	180	0	0	33
S [c]	0.932	1.044	1.044	0.864
Max. $\Delta\rho$ (e Å^{-3})	0.451	1.331	0.370	0.338

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

[c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

SADABS (**1**,**2**) or SORTAV (**4**)). The structures were refined on F^2 using the program SHELXL-97 [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **4** and all NH were refined freely, other rigid methyl groups or using a riding model. Special features of refinement: The acetone solvent molecule of **5** is disordered over a twofold axis. Its H atoms were not located. Further crystallographic details are given in Table 6.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 170808–170811 for complexes **1**, **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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