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Synthesis, characterization, crystal structure and luminescence properties of phosphinic silver(I) complexes with thiourea derivatives

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Abstract

Reaction of phenylisothiocyanate with different aromatic amines allowed the synthesis of compounds containing the thiourea moiety. By reacting silver bis(triphenylphosphine)nitrate with suitable ligands belonging to this family of sulphurated compounds, three new complexes have been afforded. Ligands and complexes were characterized also by X-ray diffraction. The structures reveal remarkable differences in the silver coordination geometry in function of the nature and size of the ligand. The emission properties of all compounds were characterized at 10 and at 298 K.

Keywords: Thioureic ligands; Silver; Structure elucidation; Luminescence

1. Introduction

The reaction of inorganic silver(I) salts with ternary organophosphorus derivatives leads to the formation of different adducts where the metal–ligand ratio varies from one to four depending on the nature of the ligand, the stoichiometric ratio between the reagents and the experimental conditions [1]. These compounds can be usefully employed as precursors of d^{10} metal complexes with mixed ligands having different stoichiometries and geometries. These complexes often show interesting luminescence properties involving charge transfer excited states, whose nature can be assessed only on the basis of reliable calculations [2]. The coordination chemistry of the d^{10} metal centres varies markedly as a function of the electronic and sterical factors peculiar to the ligands. The structural characterization of these compounds is of extreme importance in order to shed light on the factors that influence the reaction mechanism and to gain control over the synthesis towards the formation of complexes with predictable geometric requirements. Moreover, it constitutes the starting point for reliable quantomechanical calculations on these systems.

We have recently undertaken a work about this subject by reacting $[(PPh_3)_2AgNO_3]$ with thiourea derivatives having different geometrical and electronic peculiarities.

In this paper, we report the synthesis and the characterization of derivatives of $[(PPh_3)_2AgNO_3]$ with ligands obtained by condensation of phenylisothiocyanate with 2-aminopyridine, 2-aminomethylpyridine and 2-aminofluorene, namely 1-phenyl-3-(2-pyridyl)-2-thiourea (Phpytu, **1**), 1-phenyl-3-(2-methylpyridyl)-2-thiourea (Phmepytu, **2**) and 1-phenyl-3-(2-fluorenyl)-2-thiourea (Phflotu, **3**), respectively.

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2. Results and discussion

2.1. General

The vibrational spectra of the synthesized compounds have been recorded and some selected bands are summarized and assigned in the experimental section. Based on the spectral comparison, the shifts of the *v*CS and *v*CN bands are indicative of metal–ligand interactions. In particular, the bands assigned to the C=S stretching in the complexes are shifted to lower energies and are less intense if compared with the corresponding bands of the free ligands. This behaviour shows a coordination mode via sulphur atom for all complexes. For complex **5** also the downward shift observed for the pyridine carbon–nitrogen stretching shows an S, N coordination. On the contrary, the stretching assignments of the covalently linked NO_3 group in complex **4** are not so obvious because signals are overlapped with other stretching modes of thioureic absorptions [3]. For the other complexes the bands centred at about 824 cm^{-1} can be reasonably attributed to the ionic NO_3^- group.

It can be concluded that in general the differences between the molecular structures found for Ag(I) complexes with the three thioureic derivatives are determined by topological and rigidity constraints of the used ligands.

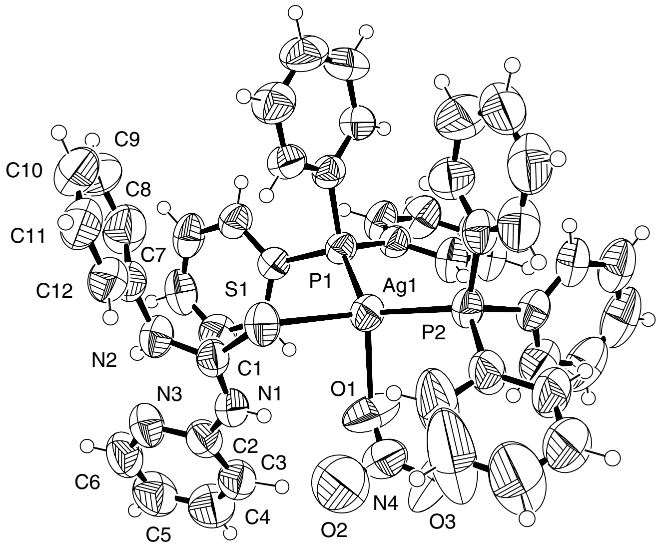

Fig. 1. ORTEP drawing of complex **4** (thermal ellipsoids are drawn at the 50% probability level).

2.2. Crystal structure

The structure of compound **4** consists of neutral complexes represented in Fig. 1. The silver atom presents a distorted tetrahedral geometry involving two triphenylphosphine phosphorus atoms, a sulphur of the ligand

Table 1
Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **4**–**6**

1		**2**		**4**		**5**		**6**	
S1–C1	1.682(2)	S1–C1	1.683(3)	Ag1–S1	2.550(2)	Ag1–S1	2.5992(4)	Ag1–S1	2.529(1)
N1–C1	1.369(3)	N1–C1	1.334(3)	Ag1–P1	2.479(2)	Ag1–P1	2.4685(5)	Ag1–P1	2.478(1)
N1–C2	1.398(3)	N1–C2	1.454(4)	Ag1–P2	2.439(2)	Ag1–P2	2.4867(8)	Ag1–P2	2.483(1)
N2–C1	1.333(3)	N2–C1	1.343(4)	Ag1–O1	2.408(4)	Ag1–N3	2.4755(3)	S1–C1	1.700(3)
N2–C7	1.424(3)	N2–C8	1.426(4)	S1–C1	1.694(4)	S1–C1	1.693(3)	N1–C1	1.352(4)
N3–C2	1.328(3)	N3–C3	1.336(4)	N1–C1	1.350(7)	N1–C1	1.335(2)	N1–C2	1.434(4)
N3–C6	1.346(3)	N3–C7	1.337(6)	N1–C2	1.395(6)	N1–C2	1.455(3)	N2–C1	1.338(4)
C2–C3	1.392(3)	C2–C3	1.503(6)	N2–C1	1.311(5)	N2–C1	1.348(3)		
C3–C4	1.374(3)	C3–C4	1.367(5)	N2–C7	1.414(7)	N2–C8	1.441(2)		
C4–C5	1.371(4)	C4–C5	1.379(6)			N3–C3	1.334(5)	S1–Ag1–P1	114.38(4)
C5–C6	1.366(4)	C5–C6	1.353(5)	S1–Ag1–P1	104.07(5)	C2–C3	1.511(2)	S1–Ag1–P2	114.38(4)
		C6–C7	1.362(6)	S1–Ag1–P2	119.35(5)			P1–Ag1–P2	125.40(4)
C1–N1–C2	130.14(18)			S1–Ag1–O1	98.9(1)	S1–Ag1–P1	111.55(1)	Ag1–S1–C1	107.9(1)
C1–N2–C7	125.96(18)	C1–N1–C2	122.1(3)	P1–Ag1–P2	124.64(5)	S1–Ag1–P2	106.61(1)		
C2–N3–C6	117.5(2)	C1–N2–C8	127.0(3)	P1–Ag1–O1	102.6(1)	S1–Ag1–N3	101.54(8)		
S1–C1–N1	118.79(15)	C3–N3–C7	116.7(3)	P2–Ag1–O1	102.7(1)	P1–Ag1–P2	124.25(1)		
S1–C1–N2	124.42(17)	S1–C1–N1	122.9(2)	Ag1–S1–C1	106.9(2)	P1–Ag1–N3	109.55(7)		
N1–C1–N2	116.78(18)	S1–C1–N2	119.9(2)	Ag1–O1–N4	122.2(4)	P2–Ag1–N3	100.61(8)		
N1–C2–N3	118.7(2)	N1–C1–N2	117.2(3)			Ag1–S1–C1	104.0(1)		
N1–C2–C3	118.61(19)	N1–C2–C3	113.7(3)			Ag1–N3–C3	118.7(3)		
N3–C2–C3	122.7(2)	N3–C3–C2	117.0(3)			Ag1–N3–C7	118.7(3)		
C2–C3–C4	118.1(2)	N3–C3–C4	122.4(3)						
C3–C4–C5	120.0(3)	C2–C3–C4	120.6(3)						
C4–C5–C6	118.1(3)	C3–C4–C5	119.0(4)						
N3–C6–C5	123.6(2)	C4–C5–C6	119.6(4)						
N2–C7–C8	118.91(18)	C5–C6–C7	117.8(4)						
N2–C7–C12	121.23(19)	N3–C7–C6	124.5(4)						
		N2–C8–C9	118.3(3)						
		N2–C8–C13	121.9(3)						

and a nitrate oxygen atom. Selected bond distances and angles are reported in Table 1. The P1–Ag–P2 angle of 124.64(5)° approaches very closely the average value found in similar compounds containing a silver(I) bound to two triphenylphosphines [1a,4–6] but much smaller than the value found in the starting nitrate salt [139.4°] [7]. Consequently, the opposite angle O1–Ag–S1 deviates from the ideal angle for a tetrahedron presenting a value of 98.90(13)°. The Ag–P bond distances agree well with the values found for complexes where the silver atom is tetrahedrally coordinated to two phosphorus atoms [4–7]. The Ag–S bond distance agrees with the mean value found in analogous compounds [8]. The structure of coordinate monodentate ligand **1** can be described as built up from three parts: the phenyl ring, the thiourea fragment and the pyridine ring. The single units are planar and the pyridine ring is almost coplanar with the thiourea fragment [8.2(2)°] thanks to a strong hydrogen bond between the pyridine nitrogen and a protonated thiourea NH group [N2···N3 = 2.675(7) Å]. The phenyl, on the contrary, forms an angle of 71.2(2)° with the thiourea moiety for sterical reasons. The nitrate anion behaves as monodentate and its orientation is affected by a bifurcated hydrogen bond between the thiourea nitrogen N1 and two of the nitrate ion oxygens (O1 and O2) [N1···O1 = 3.068(6) Å, N1–H···O1 = 143(4)° and N1···O2 = 2.955(8) Å, N1–H···O2 = 153(4)°].

In the corresponding free ligand **1** (Fig. 2) the conformation is the same, determined by the strong intramolecular hydrogen bond [N2···N3 = 2.642(3) Å]. Also in this case the single units are planar, the pyridine ring and the thiourea moiety are almost coplanar [5.4(1)°] while the phenyl ring forms an angle of 57.9(1)° with the thiourea moiety. The packing is characterized by dimers formed by N–H···S hydrogen bonds across a centre of symmetry [N1···S1($1-x, -y, -z$) = 3.415(2) Å, N1–H1···S1 = 166.7(1)°] and these dimers are packed by van der Waals interactions.

In complex **5** [Ag(Phmepytu)(PPh$_3$)$_2$]NO$_3$ the organic ligand replaces completely the nitrate anion showing a bidentate N,S behaviour and the methylene spacer allows the formation of a seven-membered chelation ring (Fig. 3). In this fashion the tetrahedral silver coordination geometry becomes more regular and the S–Ag–N3 is 101.54(8)° and the P1–Ag–P2 124.25(1)° (Table 1). The ligand molecule is considerably distorted from planarity and the three components (phenyl ring, thiourea and pyridyl ring) form among them angles of 60.7(2)° and 73.8(1)°, respectively, owing to the insertion of a methylene group that prevents the formation of the intramolecular N2–H2···N3 bond determining the conformation in the free ligand **1** and in its complex **4**. The nitrate ion is bound to the complex through two hydrogen bonds between the two thiourea NH and two oxygens of the inorganic anion [N2···O2 ($2-x, 1-y, 2-z$) = 2.792(6) Å, N2–H···O2 = 147(3)° and N1···O3 ($2-x, 1-y, 2-z$) = 3.029(5) Å, N1–H···O3 = 156(3)°].

The geometry of the free ligand Phmepytu **2** (Fig. 4) differs considerably from that of ligand **1**. The presence of the methylene group between the phenyl ring and the pyridyl thiourea moiety determines a relevant distortion as observed also when the ligand is coordinated *via* N,S in complex **5**. The dihedral angle formed by the phenyl and thiourea planes is 65.3(1)° and that between thiourea and pyridyl ring 83.7(1)°. As in free ligand **1** the packing is characterized by dimers formed by N–H···S hydrogen

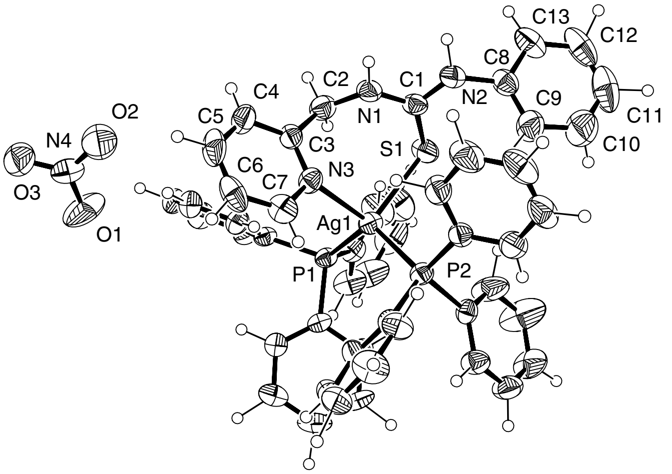

Fig. 3. ORTEP drawing of complex **5** (thermal ellipsoids are drawn at the 50% probability level).

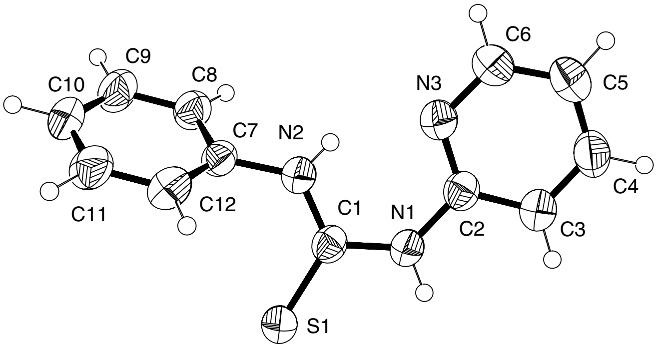

Fig. 2. ORTEP drawing of ligand **1** (thermal ellipsoids are drawn at the 50% probability level).

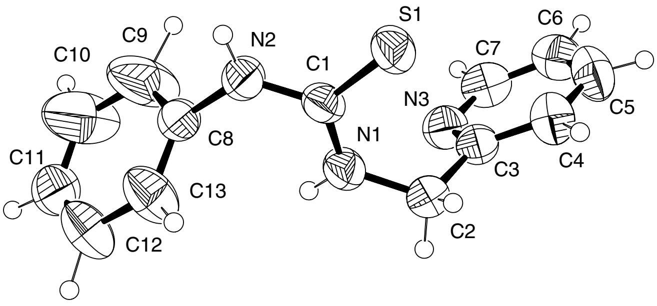

Fig. 4. ORTEP drawing of ligand **2** (thermal ellipsoids are drawn at the 50% probability level).

bonds [N1$\cdots$S1$(1/2 - x, 3/2 - y, -z) = 3.376(3)$ Å, N1–H1$\cdots$S1 168(3)°] and these dimers are packed by van der Waals interactions.

Introducing the bulky and rigid ligand Phflotu **(3)** in the coordination sphere of silver(I) a dramatic change takes place: its coordination geometry becomes planar trigonal with angles of 125.40(4)°, 114.38(4)° and 114.38(4)° for P1–Ag–P2, P1–Ag–S and P2–Ag–S, respectively [9]. The P1–Ag–S and P2–Ag–S angles are identical, but the P_2SAg unit is not perfectly planar (sum of angles at $Ag = 354.16(5)°$) probably because of a π interaction between the Ag atom and the aromatic bond C8–C9 of fluorenyl moiety (the distance Ag–C1M is 3.11(2) Å, where C1M is the mean point of C8–C9 bond). The angle between the Ag–C1M line and the normal to the coordination mean plane is 32.1(2)°. The formula of complex is $[Ag(Phflotu)(PPh_3)_2]NO_3$**(6)** (Fig. 5). The organic ligand, monodentate, shows a remarkable distortion from planarity; in fact the dihedral angles between the thiourea and phenyl ring, phenyl and fluorenyl moiety are 50.5(1)° and 25.0(2)°, respectively. Also in this case the NO_3^- ion is bound through two hydrogen bonds to the two NH of the thiourea fragment [N1$\cdots$O3$(-x, -y, -z) = 2.846(5)$ Å, N1–H$\cdots$O3 156.0(2)° and N2$\cdots$O1$(-x, -y, -z) = 2.782(5)$ Å, N2–H$\cdots$O1 170.3(2)°].

2.3. Emission spectra

A number of Cu(I)- and Au(I)-triphenylphosphine complexes with organic molecules have been extensively investigated in the past for their interesting emission properties [10]. Presently these studies are being extended to the adducts of the Ag(I)-triphenylphosphine. New attractive luminescent compounds have been recently synthesized and their optical spectra have been measured and discussed on the basis of quantum-mechanical calculations [2]. We have measured the 10 (LT) and 298 K (RT) luminescence spectra of the synthesized ligands and complexes in the solid state. At RT the emission intensities are very low and often negligible, so we have concentrated our attention exclusively on the LT spectra. These are shown in Fig. 6. The spectrum of ligand **1** consists of a broadband with maximum at about 460 nm and a complex vibronic structure involving low energy (lattice) phonons. The spectrum of complex **4** is 20 nm shifted towards the lower energies and does not present vibronic structure. It has to be pointed out that the spectrum of pure triphenylphosphine, reported in Ref. [1a], consists of a broadband peaking at 447 nm. The comparison between these spectra indicates that the emission properties cannot be preferentially ascribed to a particular fragment of the complex, but involve the whole molecule. The same holds for ligand **2** and complex **5**, whose spectra are nearly superimposed with maxima at about 480 and 490 nm, respectively, and both present some weak vibrational structure. The spectra of ligand **3** and complex **6** still overlap on to another (maxima at about 500 nm), but in this case they show a vibrational progression involving phonons of the order of $700\ cm^{-1}$, which have correspondence in the IR spectra of both Ag(I)-triphenylphosphine and ligand (δ_{C-HAr}, see Section 4.2.3). From these considerations, it is evident that the definition of the states responsible of the luminescence properties is a difficult task. TD–DFT calculations are in progress in order to obtain information about the compo-

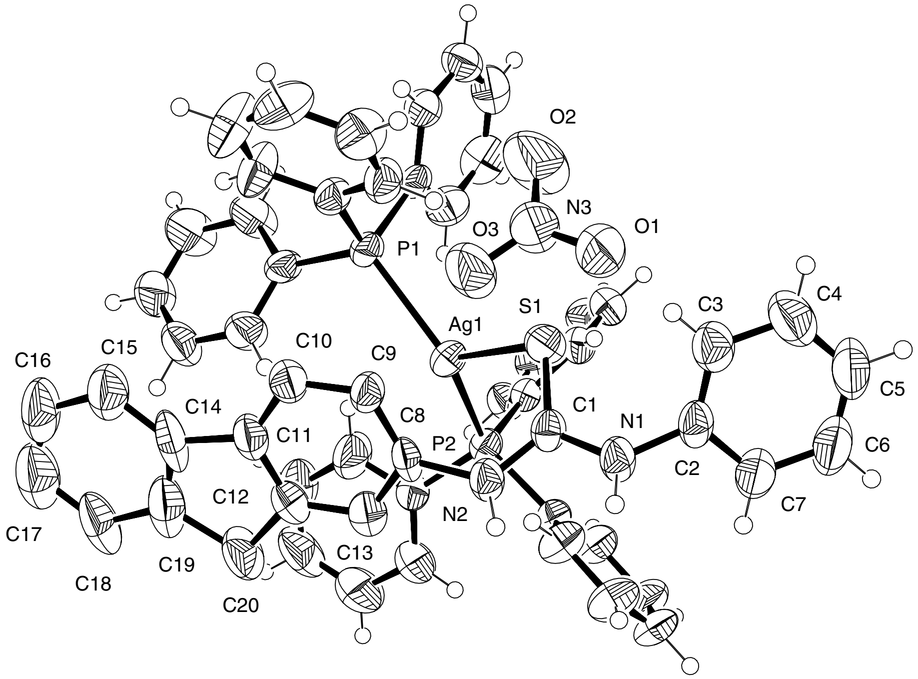

Fig. 5. ORTEP drawing of complex **6** (thermal ellipsoids are drawn at the 50% probability level, the fluorenyl moiety was drawing in its highest s.o.f.).

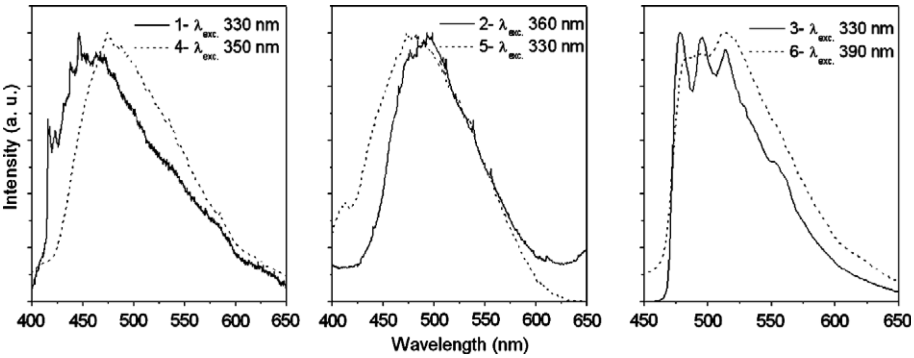

Fig. 6. Emission spectra (10 K) of the synthesized ligands and complexes.

sition of the excited states involved in the optical transitions. On the basis of preliminary results, these can be ascribed to a combination of metal to ligand charge transfer and inter ligand charge transfer processes.

3. Conclusions

In this paper, we report the synthesis of three new thioureic ligands and of their complexes with [$(PPh_3)_2$-$AgNO_3$]. All compounds have been characterized by IR spectroscopy and X-ray diffraction, and their structural and conformational properties have been thoroughly discussed in terms of rigidity and steric hindrance of the ligand units. It is interesting to point out that the coordination geometry around the silver atom varies from tetrahedral in complexes **4** and **5** to trigonal in **6**, owing to the differences in the ligands flexibility and in the intramolecular electronic interactions. Both ligands and complexes are luminescent at low temperature. Their emission spectra evidence a complex structure of the excited states, as confirmed by preliminary TD–DFT calculations.

4. Experimental

4.1. Materials and instruments

All manipulations were performed in air using commercial grade solvents. 2-Aminopyridine (Aldrich, 99%), 2-aminomethylpyridine (Aldrich, 99%), 2-aminofluorene (Aldrich, 99%), phenylisothiocyanate (Aldrich, 99%), triphenylphosphine (Aldrich, 99%), $AgNO_3$ (Carlo Erba) were commercially available and used without further purification.

Elemental analyses (C, H, N, S) were performed with a Carlo Erba model EA 1108 automatic analyzer. IR spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FT. Mass spectra were run on a Finnigan 1020 spectrometer (CI). Melting points were determined with a Gallenkamp instrument. The emission spectra were measured by means of a modified SPEX Fluorolog system. The samples, in form of pellets, were mounted onto the cold finger of a He closed cycle cryostat (Air Products), and the measurements were carried out at 10 and 298 K.

4.2. Preparation of the ligands

The ligands are obtained in good yields by slowly mixing appropriate amounts of phenylisothiocyanate and amine in absolute ethanol at reflux temperature.

4.2.1. Phpytu (1)

A round-bottom flask was charged with 0.50 g (5.6 mmol) of 2-aminopyridine and 50 mL of absolute ethanol. To this solution phenylisothiocyanate (0.51 mL, 4.3 mmol) was added using a graduated syringe and the resulting mixture was stirred for 2 h under reflux. After cooling colourless needles were separated from the solution. Yield 75%. M.p. 161.5 °C. *Anal.* Calc. for $C_{12}H_{11}N_3S$ (229.29): C, 62.86; H, 4.84; N, 18.32; S, 13.98. Found: C, 62.17; H, 5.01; N, 18.0; S, 14.15%. Selected IR bands: 3218 (ν_{N-H}), 3037 (ν_{C-HAr}), 1590 ($\nu_{C=CAr}$), 1552 (band B thiourea + $\nu_{C=Npy}$), 1427 (band C thiourea), 1268 ($\nu_{C=S}$), 772, 743, 692 (δ_{C-HAr}) cm^{-1}. Mass spectrum *m*/*z*: 229 (M^+).

4.2.2. Phmepytu (2)

To 1.16 mL (9.7 mmol) of phenylisothiocyanate, previously dissolved in 40 mL of absolute ethanol, 1.00 mL (9.7 mmol) of 2-aminomethylpyridine was slowly added. The resultant solution was subsequently stirred for two hours under reflux. After about 1 h a distinct change in colour is observed. At first the solution becomes yellowish and its pH drops, from the original value of 8, to 7 and then the colour turns deep green with a further pH decrease to 6. The solution remains green, also after the separation by filtration of a light yellow crystalline precipitate. Yield 65%. M.p. 114.0 °C. *Anal.* Calc. for $C_{13}H_{13}N_3S$ (243.32): C, 64.17; H, 5.38; N, 17.27; S, 13.18. Found: C, 63.88; H, 5.52; N, 17.22; S, 13.49%. Selected IR bands: 3340 (ν_{N-H}), 3170 (ν_{C-HAr}), 2930 (ν_{C-H}), 1592 ($\nu_{C=CAr}$), 1530 (band B thiourea + $\nu_{C=Npy}$), 1436 (band C thiourea), 1186 ($\nu_{C=S}$), 761, 691 (δ_{C-HAr}) cm^{-1}. Mass spectrum *m*/*z*: 243 (M^+).

4.2.3. Phflotu (3)

To a solution of absolute ethanol containing 0.50 g (2.76 mmol) of 2-aminofluorene was added 0.33 mL (2.76 mmol) of phenylisothiocyanate. After stirring for 1 h under reflux a white microcrystalline solid separates.

Yield 85%. M.p. 223.0°C. *Anal.* Calc. for $C_{20}H_{16}N_2S$ (316.43): C, 75.91; H, 5.10; N, 8.85; S, 10.13. Found: C, 75.83; H, 5.06; N, 8.86; S, 10.20%.

Selected IR bands: 3285 (ν_{N-H}), 3052 (ν_{C-HAr}), 1590 ($\nu_{C=CAr}$), 1538 (band B thiourea + $\nu_{C=Npy}$), 1396 (band C thiourea), 1260 ($\nu_{C=S}$), 824, 767, 756, 734, 699 (δ_{C-HAr}) cm^{-1}. Mass spectrum *m/z*: 316 (M^+).

4.3. Preparation of the complexes

Complexes [Ag(Phpytu)$(PPh_3)_2(NO_3)$] (denoted by **4**), [Ag(Phmepytu)$(PPh_3)_2$]NO_3 (**5**), and [Ag(Phflotu)$(PPh_3)_2$]-NO_3 (**6**), were obtained by mixing in the dark at room temperature the silver salt with equimolar or with a small excess of the corresponding ligand in an acetone/acetonitrile = 1/1 (v/v) mixture. Complexes **5** and **6** were also isolated by mixing equimolar amounts of metal salt and the ligand both dissolved in dichloromethane in the dark at room temperature. The compounds isolated were white or lightly coloured.

4.3.1. [Ag(Phpytu)$(PPh_3)_2NO_3$](**4**)

A solution obtained by dissolving 0.100 g (0.14 mmol) of $Ag(PPh_3)_2NO_3$ in 20 mL of a mixture 1:1 (v:v) of acetone–acetonitrile was poured in 20 mL of the same solvent mixture containing 0.035 g (0.15 mmol) of Phpytu. The final volume is stirred for 2 h in the dark. After a few days this solution yielded white microcrystals. Recrystallization afforded white crystals suitable for single-crystal X-ray diffraction experiments. Yield 90%. M.p. >300.0 °C. *Anal.* Calc. for $C_{48}H_{41}AgN_4O_3P_2S$ (923.75): C, 62.41; H, 4.47; N, 6.06; S, 3.47. Found: C, 62.07; H, 4.46; N, 6.12; S, 3.14%. Selected IR bands: 3050 (ν_{C-HAr}), 1600 ($\nu_{C=CAr}$), 1540 (band B thiourea + $\nu_{C=Npy}$), 1434, 998 (ν_{P-CAr}), 1385 ($\nu_{N-O\ asym.}$ + band C thiourea), 1299 ($\nu_{N-O\ sym.}$), 1193 ($\nu_{C=S}$), 783, 743, 694 (δ_{C-HAr}) cm^{-1}.

4.3.2. [Ag(Phmepytu)$(PPh_3)_2$]NO_3 (**5**)

In two aliquotes of 20 mL of a mixture acetone–acetonitrile 1:1 (v/v) are dissolved separately 0.09 g (0.097 mmol) of the triphenylphosphinesilver precursor and 0.03 g (0.12 mmol) of the ligand Phmepytu. The two solutions were poured into a round-bottom flask and stirring continued for 2 h protected from light. A white powder precipitated and was then recrystallized in the dark from the same solvent and after a few days the solution gave pale green prismatic crystals. The same product was also obtained by reacting the two reagents in equimolar ratio in 20 mL of dichloromethane. From this reaction crystals form directly from the reaction solution. Yield 92%. M.p. 216.5 °C. *Anal.* Calc. for $C_{49}H_{43}AgN_4O_3P_2S$ (937.78): C, 62.76; H, 4.62; N, 5.97; S, 3.41. Found: C, 62.57; H, 4.69; N, 5.83; S, 3.14%. Selected IR bands: 3052 (ν_{C-HAr}), 1590($\nu_{C=CAr}$), 1555 ($\nu_{C=CAr}$), 1477 (band B thiourea + $\nu_{C=Npy}$), 1434 (ν_{P-CAr}), 1400 (νNO_3^- + band C thiourea), 1140 ($\nu_{C=S}$), 820 (νNO_3^-), 745, 695 (δ_{C-HAr}) cm^{-1}.

4.3.3. [Ag(Phflotu)$(PPh_3)_2$]NO_3 (**6**)

At ambient temperature two solutions are prepared, one made up from 0.09 g (0.28 mmol) of the ligand in 30 mL of solvent (acetone:acetonitrile 1:1 v/v) and the other from 0.19 g (0.26 mmol) of triphenylphosphinesilver precursor dissolved in a solvent mixture having the same composition as the previous one. The two solutions were then mixed together in a round bottom flask and stirred in the dark for 2 h. After three days the solution afforded white crystals suitable for a structure determination by single-crystal X-ray diffraction. Yield 96%. T dec. 168 °C. *Anal.* Calc. for $C_{56}H_{46}AgN_3O_3P_2S$ (1009.87): C, 66.60; H, 4.49; N, 4.16; S, 3.18. Found: C, 66.97; H, 4.26; N, 4.20; S, 3.06%. Selected IR bands: 3052 (ν_{C-HAr}), 1591($\nu_{C=CAr}$), 1556 (band B thiourea), 1434, 998 (ν_{P-CAr}), 1385 (νNO_3^-+ band C thiourea), 1130 ($\nu_{C=S}$), 828 (νNO_3^-), 744, 693 (δ_{C-HAr}) cm^{-1}.

4.4. X-ray crystallography

Relevant data concerning data collection and details of structure refinement are summarized in Tables 2a and 2b. The intensity data for the ligands were collected with Cu Kα radiation for **1** on an ENRAF-NONIUS CAD4 and for **2** on a Siemens diffractometers single-crystal computer controlled by the θ–2θ technique. All intensity data for

Table 2a
Crystal data and structure refinements parameters for ligands **1** and **2**

Compound	**1**	**2**
Formula	$C_{12}H_{11}N_3S$	$C_{13}H_{13}N_3S$
Molecular weight	229.29	243.32
Space group	$P2_1/n$	$C2/c$
a (Å)	5.872(1)	17.488(5)
b (Å)	22.511(6)	8.751(2)
c (Å)	8.750(2)	16.970(5)
α (°)	90.0	90.0
β (°)	98.77(1)	108.78(1)
γ (°)	90.0	90.0
V (Å^3)	1143.1(4)	2459(1)
Z	4	8
$F(000)$	480	512
D_{calc} (Mg/m^3)	1.33	1.31
μ (cm^{-1})	23.0	2.44
λ (Å)	1.54178	0.71069
Radiation	Cu Kα	Mo Kα
θ Range (°)	3–69	3–30
Index ranges	$-7 < h < 7$, $0 < k < 27$, $0 < l < 10$	$-22 < h < 23$, $0 < k < 11$, $0 < l < 22$
Crystal size (mm)	0.7 × 0.6 × 0.4	0.4 × 0.4 × 0.3
Measured reflection	2356	6509
Observed reflection	2034	1302
Refined parameters	145	207
Maximum and minimum ΔF (e Å^{-3})	0.33 and −0.36	0.59 and −0.32
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0495	0.0640
Rw_2	0.1462	0.2140
Weighing scheme	$1/[\sigma^2(F_o^2) + (0.0777 \times P)^2 + 0.41 \times P]$	$1/[\sigma^2(F_o^2) + (0.1464 \times P)^2]$

Table 2b
Crystal data and structure refinements parameters for complexes **4**–**6**

Complex	**4**	**5**	**6**
Formula	$C_{48}H_{41}AgN_4O_3P_2S$	$C_{49}H_{43}AgN_4O_3P_2S$	$C_{56}H_{46}AgN_3O_3P_2S$
Molecular weight	923.75	937.78	1010.87
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.136(8)	13.441(3)	15.296(6)
b (Å)	18.398(7)	16.969(2)	14.473(5)
c (Å)	10.292(6)	11.017(4)	11.993(1)
α (°)	102.74(4)	99.45(1)	113.40(2)
β (°)	112.11(5)	96.26(1)	98.29(2)
γ (°)	91.69(4)	109.85(1)	90.56(4)
V (Å^3)	2230(2)	2294(1)	2405(2)
Z	2	2	2
$F(000)$	948	964	1040
D_{calc} (Mg/m^3)	1.38	1.36	1.40
μ (cm^{-1})	6.15	5.99	5.77
λ (Å)	0.71069	0.71069	0.71069
Radiation	Mo Kα	Mo Kα	Mo Kα
θ Range (°)	3–28	3–30	3–30
Index ranges	$-17 < h < 15$, $-24 < k < 20$, $0 < l < 13$	$-18 < h < 18$, $-23 < k < 23$, $0 < l < 15$	$-21 < h < 21$, $-20 < k < 20$, $0 < l < 16$
Crystal size (mm)	0.7 × 0.7 × 0.5	0.7 × 0.6 × 0.5	0.7 × 0.6 × 0.5
Measured reflection	10352	13360	14014
Observed reflection	4528	4465	6920
Refined parameters	557	714	665
Maximum and minimum ΔF (e Å^{-3})	0.72 and −0.79	0.35 and −0.27	1.24 and −1.05
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0524	0.0358	0.0486
Rw_2	0.1554	0.0836	0.1342
Weighing scheme	$1/[\sigma^2(F_o^2) + (0.106 \times P)^2]$	$1/[\sigma^2(F_o^2) + (0.019 \times P)^2]$	$1/[\sigma^2(F_o^2) + (0.064 \times P)^2]$

complexes were collected with Mo Kα radiation on different single-crystal computer controlled by the θ–2θ technique diffractometers: a Siemens AED for complex **4**, on an ENRAF-NONIUS CAD4 for **5** and on a Philips for **6**. The structures were solved using direct methods (SIR-92 [11] for ligands **1**, **2** and SIR-97 [12] for complexes **4**–**6**). Refinements were carried out by full-matrix least-squares cycles SHELXL97 [13] for all compounds. Anisotropic thermal motion was assumed for all non-hydrogen atoms. In complex **6** the fluorenyl moiety adopted two orientations which were related by a rotation of 180° about the external C8–N2 bond. The refined values of occupation factors were 0.7 and 0.3 for the two orientations, respectively. During the refinement both the phenyl rings was treated as rigid body having D_{6h} symmetry. For ligand **1** the hydrogen atoms were included in the ideal positions and not refined, for **2** the hydrogen atoms were located on a difference map and refined in the last cycle. In complex **4** the hydrogen atoms were partly located on a difference map but not refined and partly were included in the ideal positions and allowed to ride on their respective parent carbon atoms. In complex **5** the hydrogen atoms were located on a difference map and refined, while in complex **6** all hydrogen atoms (except those of the fluorenyl moiety) were included in the ideal positions and allowed to ride on their respective parent carbon. Atomic scattering factors were taken from Ref. [14]. Molecular geometry calculations were performed using the PARST [15] computer program and the structure drawings obtained with the ORTEPIII [16] and PLATON [17] programs.

5. Supplementary material

CCDC 615626, 615627, 615628, 615629 and 615630 contain the supplementary crystallographic data for **1** **2**, **4**, **5** and **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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