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The double-helicate terpyridine silver(I) compound $[Ag_2L_2](SO_3CF_3)_2$ (L = 4'-phenyl-terpyridine) as a building block for di- and mononuclear complexes

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ABSTRACT

The double-helicate dinuclear silver(I) complex $[Ag_2L_2](SO_3CF_3)_2$ (1) was obtained by reaction of AgSO_3CF₃ with 4'-phenyl-terpyridine (L). Each Ag⁺ ion is coordinated by two N-atoms from one of the ligands and by one N-atom of the other ligand, forming an irregular Ag_2N_6 bi-triangle geometry, with a metallic bond between the two silver ions. Complex 1 reacts with potentially bidentate ligands (L¹), such as 9,10-bis(diphenylphosphino)anthracene (PAnP), 4,4'-dipyridyl or bis(diphenyl phosphino)methane (DPPM), to give the corresponding dinuclear complexes with bridging L¹, $[Ag_2L_2(\mu-L^1)](SO_3CF_3)_2$ (L¹ = PAnP **2**, 4,4'-dipyridyl **3** or DPPM **4**), whereas on reaction with PPh₃ forms the mononuclear complex [AgL(PPh₃)](SO_3CF_3) **5**. Reaction of **1** with the potentially tridentate ligand tris(2-diphenylphosphino-ethyl)amine (NP₃) results in complete decomposition of the coordination spheres to form [Ag(NP₃)]-(SO₃CF₃) **6**. Compound **1** shows a strong fluorescence in the solid state with its excitation band at 383.5 nm, the emission band at 535.5 nm and the lifetime of 4.20 ns, but the derived complexes do not show fluorescent properties. The photoluminescence of **1** in various solvents was also studied. The complexes were characterized by ¹H NMR, elemental analysis, IR, MS, UV and single crystal X-ray diffraction.

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1. Introduction

Much current attention has been paid to multi-pyridyl complexes [1–9] due to their properties in photoluminescence and catalysis, and their interest as sensors and in molecular electronics. Ligation of these multi-pyridyl ligands to transition metal ions, especially platinum, forming square coordination geometries, shows a rich range of spectroscopic and photo-luminescent properties, as well as the propensity to exhibit metal-metal interactions. Ag⁺ can also form a diversity of structures including stable planar complexes with tri- [10-13], penta- [14,15] and hexa-[16] dentate multi-pyridyl ligands and in a few cases there is a metal-metal bond between two central ions forming double-helicate complexes [11a]. Although the crystal structures of these types of complexes, namely of helical silver species, and their electrical and catalytic properties were studied, their photo-luminescent properties have only seldom been reported [11b] and their reactivity has still been little explored. Hence, the current work aims to prepare silver complexes with a terpyridine ligand, 4'-phenyl-terpyridine, by testing the $[Ag_2(4'-Ph-terpy)_2]^{2+}$ site as a suitable starting material, and to investigate their photo-luminescent behaviour.

In this paper, we report the preparation and characterization of the dinuclear helicate compound $[Ag_2L_2](SO_3CF_3)_2$ **1** (L = 4'-Ph-terpy). It was obtained by reaction of 4'-phenyl-terpyridine with $AgSO_3CF_3$ in mixed CH_2Cl_2 and CH_3CN solvents and its solid state structure (as shown by single crystal X-ray diffraction) displays two twisted coordination triangles, with each Ag^+ coordinated by three N atoms (two from one of the ligands and the third N from the other one). This configuration makes possible a metal-metal bond between the two central metal ions. Its fluorescent properties were also studied. By reaction with several N- or P-compounds, it undergoes a structural rearrangement with Ag–Ag bond cleavage to afford five new complexes which were isolated and characterized by ¹H NMR, IR and electronic spectroscopies, elemental analysis, MS and single crystal X-ray diffraction.

2. Results and discussion

The double-helicate silver(1) complex $[Ag_2L_2](SO_3CF_3)_2$ (1, L = 4'-Ph-terpy) was synthesized by treatment of a CH_2Cl_2

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Compounds	1	2	3	4	5	6
Formula	C44H30Ag2-	C ₈₃ H ₅₈ Ag ₂ Cl ₂ -	C ₅₄ H ₃₈ Ag ₂ -	C ₇₅ H ₆₇ Ag ₂ F ₆ -	C40H30AgF3-	C43H42AgF3-
	$F_6N_6O_6S_2$	$F_6N_6O_6P_2S_2$	$F_6N_8O_6S_2$	$N_6O_{7.50}P_2S_2$	N ₃ O ₃ PS	NO ₃ P ₃ S
Formula Weight	1132.60	1762.05	1288.78	1628.15	828.57	910.62
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	Triclinic	Trigonal
Space group	C2/c	ΡĪ	P2(1)/n	P2(1)/c	ΡĪ	P32
a (Å)	19.6347(8)	9.5175(6)	8.5373(3)	13.4086(8)	10.4936(8)	17.740(3)
b (Å)	18.132(1)	15.241(1)	15.8799(7)	24.4640(19)	12.4263(9)	17.740(3)
c (Å)	14.6506(6)	15.884(1)	18.5540(6)	23.5042(12)	15.1431(9)	11.446(2)
α (°)	90	117.807(2)	90	90	104.929(2)	90
β (°)	124.567(1)	90.632(3)	93.398(1)	106.114(2)	92.541(4)	90
γ (°)	90	98.294(4)	90	90	108.099(3)	120
V (Å ³)	4295.0(3)	2008.6(3)	2516.8(2)	7407.1(8)	1796.9(2)	3119.5(9)
Ζ	4	1	2	4	2	3
D_{calc} (Mg m ⁻³)	1.752	1.457	1.701	1.460	1.531	1.454
μ (mm ⁻¹)	1.092	0.716	0.945	0.701	0.723	0.703
Independent reflection,	4930, 4332	8622, 7339	5450, 4498	12711, 9521	8036, 7305	4768, 3800
observed reflection						
Goodness-of-fit (GOF)	1.012	1.052	1.072	1.042	1.057	1.033
$R_1 \left[I > 2\sigma(I) \right]$	0.0347	0.0487	0.0304	0.0792	0.0338	0.0254
wR ₂	0.0995	0.1373	0.0920	0.2452	0.0956	0.0675

Table 1						
Crystal data	for	the	title	com	pound	ls.

solution of L with a CH₃CN solution of AgSO₃CF₃. It was isolated as a colourless crystalline solid which was characterized by ¹H NMR, IR, MS, elemental and X-ray diffraction analyses. Details of the crystal parameters, data collections and refinements are summarized in Table 1.

The obtained compound **1** in solid state is in its stable dinuclear (2Ag:2L) form, which is the only one isolated whether the silver salt solution was added to the 4'-Ph-terpy solution or the reverse. The corresponding mononuclear 1:1 (Ag:L) form of this complex was not obtained under these conditions. Constable et al. reported [11a] the two related silver compounds with multi-pyridyl ligands $[Ag_2(tpy)_2(MeCN)_2][PF_6]_2$ (tpy = 2,2':6',2"-terpyridine) and $[Ag(dptpy)(MeCN)][BF_4]$ (dptpy = 6,6"-diphenyl-2,2':6',2"-terpyridine), while Hou et al. reported [11b] the tetranuclear compound $[Ag_2L_2]_2[PF_6]_4$ (CH₃COCH₃)₂ with the same 4'-phenyl-terpyridine ligand of our study. The molecular structure of [Ag₂(tpy)₂- $(MeCN)_2$ [PF₆]₂ [11a] displays a metal-metal bond between the two metal ions whose coordination geometry is square-planar. In the structure of [Ag₂L₂]₂[PF₆]₄·(CH₃COCH₃)₂ [11b], two doublehelicate dinuclear subunits are linked by a ligand-unsupported Ag–Ag bond and each terpyridyl bridging two Ag(I) atoms acts as a bi- and a monodentate ligand. One Ag(I) atom is four-coordinate and the other is two-coordinate. By comparison of these with our results, we can conclude that the observed differences are not only caused by a variation of the ligands but also by the distinct synthetic processes that were used. Depending on the experimental conditions, terpyridine ligands and counterions, different structures of the terpyridine silver compounds can be obtained [13].

Upon reaction of **1** with an aromatic phosphine or 4,4'-dipyridyl, the Ag–Ag bond is broken and the dinuclear 2:2 (Ag⁺:4'-Ph-terpy) structure rearranges to the mononuclear 1:1 form. In fact, as illustrated in Scheme 1, compound **1** reacts with P- or N-species, such as PAnP, 4,4'-dipyridyl, DPPM, PPh₃ or NP₃, yielding products with coordination spheres (AgN₃P or AgN₄) that are different from the initial one (Ag₂N₆). Reactions with potentially bidentate ligands (L¹) give the corresponding dinuclear complexes [Ag₂L₂(μ -L¹)](SO₃CF₃)₂ (L¹ = PAnP **2**, μ , μ '-dipyridyl **3** or DPPM **4**), while the reaction with a monophosphine (L²), such as PPh₃, affords the mononuclear compound [AgL(L²)](SO₃CF₃) **5**. However, upon reaction of **1** with the potentially tridentate ligand NP₃, displacement of the coordinated 4'-Ph-terpy occurs to form the mononuclear NP₃ complex [AgL³](SO₃CF₃) **6**. When a **1**:NP₃ ratio of 3:2 is used (corresponding to 3Ag:1NP₃), only one third of **1** reacts to form

the mononuclear complex **6**, with liberation of the L ligand which was isolated, in accord with the stoichiometry of **6**.

The stability in solution of the bridged compounds depends on the non-terpyridine ligand and in air it tracks the following sequence: 1 > 3 > 4 > 2. Hence, in DMSO solution under air, at room temperature, compound 2 decomposes within one day while the others take several weeks. Additionally, the stability of complexes 5 and 6 are similar to those of 3 and 1, respectively. Moreover, even under inert atmosphere, the formation of silver mirrors on the walls of the containers occurs in several months, for all the compounds.

Compound 1 crystallized in a centrosymmetric space group and both left and right helicates are present in the solid state as shown in Fig. 1a. Each silver ion is coordinated by three pyridyl groups from two ligands and each terpyridyl ligand bridges two Ag(I) atoms acting as a bidentate ligand to one of the metal atoms and in a monodentate mode to the other one. Each silver ion displays one shorter Ag1-N1 bond to one pyridine ring of one ligand (2.273(2)Å) and two longer contacts (Ag1-N2 and Ag1-N3) to two pyridyl rings (2.331(2) and 2.394(2) Å, respectively) of the other ligand, forming an irregular triangle coordination geometry. A disilver head-to-head double-helicate is present with a Ag-Ag distance of 2.9452(4) Å in the dinuclear cation, considerably shorter than the sum of the van der Waals radii (3.40 Å). This distance is even shorter than that reported, 3.170(1) Å, for $[Ag_2(tpy)_2]$ $(MeCN)_2$ [PF₆]₂ [11a], although longer than those (2.8955(6)-2.8441(7) Å range) of $[Ag_2L_2]_2[PF_6]_4 \cdot (CH_3COCH_3)_2$ (L = 4'-phenyl-2,2':6',2"-terpyridine) [11b]. However, while in this case the tetranuclear cations are further aggregated through Ag...Ag intermolecular contacts of 3.215 Å (also shorter than the sum of van der Waals radii, see above), in compound 1 the shortest intermolecular metal contact is 7.638 Å.

As shown by the X-ray crystal structural analysis, complex **2** is dinuclear with each silver ion coordinated by three N atoms from 4'-Ph-terpy and one P atom of PAnP, forming an irregular tetrahedral AgN₃P coordination structure as shown in Fig. 1b. The two AgL⁺ groups are bridged by the PAnP ligand, while the two 4'-Phterpy (L) units are parallel to each other, accounting for the symmetry of this complex. The lengths of the Ag1–N1, Ag1–N2 and Ag1–N3 bonds [2.460(3), 2.396(3) and 2.443(3) Å, respectively] are not much different, being slightly shorter than that of Ag1– P1, 2.4799(8) Å, suggesting a stronger coordination of the tripodal 4'-Ph-terpy ligand than that of PAnP. The distances between the



Scheme 1. Reactions of [Ag₂L₂](SO₃CF₃)₂ 1 to form complexes with P- or N-ligands.

two central metal ions and the two P atoms are 10.2874(7) and 6.576(2) Å, respectively, the former being longer than those of Au–Au in complex [{AuX}₂(μ -PAnP)] (X = Cl, Br) [9.154(2), 9.091(4), 7.737(2) and 7.768(1) Å] [17] with a more open coordination sphere. The AgN₃P tetrahedron is distorted with P–Ag–N angles of 103.50(7), 130.88(6) and 112.59(8)°. The SO₃CF₃⁻ ions have weak contacts, 2.734(6) Å, with the central Ag⁺ ions, via an oxygen donor atom. The anthracenyl rings do not curve from central ions in contrast to what was reported [17] for the above Au complexes.

In complex **3** (Fig. 1c), each Ag⁺ ion is coordinated by three N atoms from 4'-Ph-terpy and one N atom from 4,4'-dipyridyl, in a distorted tetrahedral geometry, as for complex **2**. The coordination bond length 2.233(2) Å of 4,4'-dipyridyl, Ag1–N4, is shorter than those of phenyl-terpyridine [i.e. 2.533(2), 2.376(2) and 2.318(2) Å, for Ag1–N1, Ag1–N2 and Ag1–N3, respectively], indicating a slightly stronger coordination of the former chelating ligand. The three N4–Ag1–N angles of 133.58(7), 153.82(7) and 90.88(7)° are also indicative of the distortion of the AgN₄ coordination tetrahedron, as in the structure of **2**.

Complex **4** is also a dinuclear species as shown in Fig. 1d. Two $(AgL)^+$ building blocks are coordinated by the P atoms of the bridging DPPM molecule, in a distorted tetrahedral geometry, as for complex **3**. Unlike the structures of **2** and **3**, the two $(AgL)^+$ structures are in the *cis* conformation and nearly parallel, by the effect of the bridging ligand. There is a Ag–Ag contact of 3.1575(7) Å between the two central metal ions. The distance between the two P atoms is 3.043(2) Å, being longer than that [2.970 or 2.988 Å] of the free ligand [18].

Complex **5** is mononuclear with a distorted square geometry as shown in Fig. 1e, bearing a PPh₃ coordinated to the $(AgL)^+$ centre.

The metal ion is coordinated by three N and one P atoms $(AgN_3P$ coordination form as in complex **2**). The average distance of Ag–N in complex **5** (2.449 Å) is identical to that in complex **4** (2.455 Å), so does the Ag–P bond length [2.3849(5) Å for **5**; 2.399(2) and 2.402(2) Å for **4**]. For **2**, the Ag–P distance (2.4799(8) Å) is longer than that in complexes **4** and **5**, while the average Ag–N bond length (2.433 Å) is shorter than in the latter complexes, what conceivably reflects the high steric hindrance of the anthracenyl group of the PAnP ligand.

Complex 6 crystallizes in the trigonal system in the chiral space group P32. The Flack parameter is 0.56(3) here, and 0.44(3) for the inverted structure therefore showing that racemic twinning is present. The compound is mononuclear as shown in Fig 1f, with the silver ion coordinated to the three phosphorus atoms of the NP₃ ligand and presenting an Ag1–O1 (of the SO₃CF₃⁻ counterion) contact distance of 2.756(4) Å, thus completing a distorted tetrahedron around the silver atom. The P-Ag1-P angles (average 114.25°) deviate by a maximum of 9° from the ideal value of 109° as a consequence of the lack of ligand requirements in the fourth coordination position of silver. The Ag-P bond lengths (average 2.4764 Å) are within the overall range of values encountered in the aforementioned Ag complexes. The oxygens and the fluorines in the SO₃CF₃⁻ counter-ion participate in the formation of four long (non-classic) hydrogen bonds (with phenyl-H atoms, D...A bond distances between 3.150 and 3.371 Å), which help to stabilize the structure.

As illustrated in Fig. 2, compound **1** in the solid state shows strong fluorescent properties, with an excitation band at 383.5 nm, an emission band at 535.5 nm and a lifetime of 4.20 ns. The fluorescence may be assigned to $d\sigma^* - p\sigma$ transitions as reported [19,20] for similar discrete d^{10} gold–gold dimers. The



Fig. 1. A view of the complex cations of $[Ag_2L_2](SO_3CF_3)_2$ (1) (a), $[Ag_2L_2(PAPP)](SO_3CF_3)_2$ (2) (b), $[Ag_2L_2(4,4'-dipyridyl)](SO_3CF_3)_2$ (3) (c), $[Ag_2L_2(DPPM)](SO_3CF_3)_2$ (4) (d) and $[AgL(PPh_3)](SO_3CF_3)$ (5) (e), as well as of $[Ag(NP_3)](SO_3CF_3)$ (6) (f), showing the atom labelling schemes. The ellipsoids are drawn at the 50% probability level and the H atoms have been omitted for clarity. Ag-ligand bonds are indicated by solid lines.

fluorescence is quenched upon Ag–Ag bond cleavage, and thus is not observed in any of the derived mononuclear complexes in their solid state or solution in several solvents, such as methanol, acetonitrile or DMF, at ambient or even at low temperature (77 K). In addition, although there is also a Ag–Ag contact in complex **4**, no emission of fluorescence is detected in the conditions mentioned above. This phenomenon may be accounted for by the longer distance between the two central ions in complex **4** (3.1575(7) Å) than in complex **1** (2.9452(4) Å), or may result from the coordination differences in the two complexes (AgN₃ in **1** and AgN₃P in **4**).

The photo-luminescent properties of compound **1** in methanol, acetonitrile (CH₃CN), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and ethanol solutions were also studied and the results are listed in Table 2. It is noteworthy to mention that the Stoke's shifts and the fluorescent intensities increase with the increase of the solvent polarity. The sequence of the Stoke's shifts is as follows: methanol (233 and 295 nm for peak one and two, respectively) \approx CH₃CN (231 and 294 nm for peak one and

two, respectively) > DMF (127 nm) \approx DMSO (125 nm) > ethanol (20 nm). The increase of the polarity of the solvent leads to a red shift of the excitation and emission peaks. There are two peaks of emission in the spectra in methanol and acetonitrile due to the strong polarity of these solvents.

3. Experimental

3.1. Instruments

3.1.1. Physical measurements

Collections of single crystal X-ray data were performed at 293 K on a Rigaku R-AXIS RAPID Weissenberg IP Diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). ¹H NMR spectra were run on a Varian Unity 500 spectrometer. Elemental analyses were determined with an Elementar Vario EL III Elemental Analyser. IR spectra were measured with a Perkin–Elmer Spectrum 2000 or a Magna750 FT-IR spectrophotometer, in KBr



Fig. 2. The fluorescent emission band of compound 1 (excited at 383.5 nm).

 Table 2

 Photo-luminescent data of compound 1 in solutions^a.

Solvent	CH₃OH	CH₃CN	DMF	DMSO	CH ₃ CH ₂ OH
Ex (nm)	415	415	377	380	345
Em (nm)	648, 710	646, 709	504	505	365

^a Ex = excitation band; Em = emission band.

pellets. Electrospray mass spectra (ESI-MS) were recorded on a Finnigan LCQ Mass Spectrometer using dimethylformamide-methanol, methanol, dichloromethane-methanol or acetonitrile-methanol as the mobile phase. Emission and excitation spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928. Emission lifetimes were determined on an Edinburgh Analytical Instruments F900 fluorescence spectrometer using an LED laser at 397 nm excitation, and the resulting emission was detected by a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. The instrument response function at the excitation wavelength was deconvolved from the luminescence decay. UV-Vis absorption spectra in acetonitrile and dichloromethane solutions were measured on a Perkin-Elmer Lambda 25 UV-Vis spectrometer. All reagents used in the experiments were of analytical grade or purified by standard methods. 4,4'-dipyridyl and PPh₃ were purchased from Acros and used as received.

3.2. Synthesis

Ligands: 4'-Ph-terpy [21], 9,10-bis(diphenylphosphino)anthracene (PAnP) [22], bis(diphenylphosphino)methane (DPPM) [23], and tris(2-diphenylphosphinoethyl)amine (NP₃) [23] were prepared by the reported procedures.

3.2.1. [Ag₂L₂](SO₃CF₃)₂ (1)

Dissolution of 4'-Ph-terpy (0.816 g, 2.64 mmol) in CH₂Cl₂ (25 mL) was followed by the slow addition (half an hour) of an CH₃CN solution (25 mL) of AgSO₃CF₃ (0.677 g, 2.64 mmol), under argon. The resulting solution was stirred for 8 h and then refluxed for 5 h. After being concentrated, diethyl ether was added until a large amount of a white solid formed, which was filtered off and washed twice with diethyl ether. This white powder of the product 1 (1.22 g, yield 82%) was recrystallized from acetonitrile by diffusion of diethyl ether to yield colourless crystals, which were suitable for X-ray characterization. All the synthetic processes were

undertaken under argon. *Anal.* Calc. for $[Ag_2C_{42}H_{30}N_6](SO_3CF_3)_2$: C, 46.66; H, 2.67; N, 7.42. Found: C, 46.76; H, 2.27; N, 7.41%. ¹H NMR δ (DMSO- d^6): 7.60 (d, 4H), 7.61 (d, 4H), 7.65 (d, 2H), 8.12 (d, 4H), 8.15 (d, 4H), 8.59 (d, 4H), 8.68 (d, 4H), 8.76 (s, 4H). IR (KBr disk) (cm⁻¹): 3063 (m), 1607 (s), 1595 (s), 1568 (m), 1548 (m), 1477 (s), 1409 (s), 1246 (vs, br), 1163 (s, br), 1028 (s), 1009 (s), 893 (m), 794 (s), 766 (s), 698 (s), 636 (s), 517 (s). UV (CH₃OH): $\lambda_{max} = 279.5$ nm, $\varepsilon_{max} = 5.2 \times 10^4$ L cm⁻¹ mol⁻¹. ESI-MS: $[Ag_2L_2]^{2+}$ (419.1, 96%), $[Ag_2L_2(SO_3CF_3)]^+$ (983.2, 100%).

3.2.2. [Ag₂L₂(PAnP)](SO₃CF₃)₂ (2)

 $[Ag_2L_2](SO_3CF_3)_2$ (0.150 g, 0.132 mmol) and PAnP (0.072 g, 0.132 mmol) were dissolved in 20 mL of CH₂Cl₂ and the solution was stirred for 48 h under argon. After concentration and separation by column chromatography (silica gel; CH₂Cl₂:MeOH 10:1), a vellow powder of **2** was obtained (0.168 g, vield 66%) upon concentration of the elute. It was recrystallized from acetonitrile by diffusion of diethyl ether, leading to yellow crystals, which were suitable for X-ray characterization. Elemental Anal. Calc. for [Ag₂C₈₀H₅₈N₆P₂](SO₃CF₃)₂: C, 58.65; H, 3.48; N, 5.00. Found: C, 58.49; H, 3.17; N, 4.50%. ¹H NMR δ (DMSO- d^6): 6.86 (s, 4H), 7.42 (t, 20H), 7.54 (s, 2H), 7.62 (d, 8H), 7.97 (s, 4H), 8.01 (d, 4H), 8.10 (d, 4H), 8.33 (s, 4H), 8.66 (d, 4H), 8.74 (s, 4H). IR (KBr disk) (cm⁻¹): 3059 (m), 1605 (s), 1571 (m), 1548 (m), 1548 (m), 1473 (m), 1437 (m), 1406(m), 1276 (vs,br), 1262 (vs,br), 1224(m), 1157(s), 1098 (m), 1031 (s), 794 (m), 764 (s), 753 (s), 696 (s), 638 (s), 554(m), 517 (s). UV (CH₂Cl₂): $\lambda_{max} = 267.3 \text{ nm}$, $\varepsilon_{\rm max} = 1.0 \times 10^5 \, {\rm L} \, {\rm cm}^{-1} \, {\rm mol}^{-1}$. $[Ag_2L_2(PAnP)]^{2+}$ ESI-MS: (688.0, 28%).

3.2.3. $[Ag_2L_2(4,4'-dipyridyl)](SO_3CF_3)_2$ (3)

[Ag₂L₂](SO₃CF₃)₂ (0.183 g, 0.162 mmol) and 4,4'-dipyridyl (0.025 g, 0.162 mmol) were dissolved in 20 mL of CH₂Cl₂ and 20 mL of CH₃CN and the solution was stirred for 48 h under argon. Upon column chromatography separation (silica gel; first CH₂Cl₂, then CH₂Cl₂:MeOH 5:1), the obtained solution was diffused with diethyl ether and the obtained colourless crystals (0.113 g. 54% vield) were suitable for X-ray characterization. Anal. Calc. [Ag₂C₅₂H₃₈N₈](SO₃CF₃)₂: C, 50.33; H, 2.97; N, 8.69. Found: C. 50.68; H, 3.22; N, 8.87%. ¹H NMR δ (DMSO- d^6): 7.59 (m, 4H), 7.62 (s, 2H), 7.65 (d, 4H), 7.86 (m, 4H), 8.12 (t, 4H), 8.16 (d, 4H), 8.57 (d, 4H), 8.68 (d, 4H), 8.74 (m, 4H), 8.75 (s, 4H). IR (KBr disk) (cm⁻¹): 3073 (m), 1597 (s), 1585 (m), 1575(m), 1547 (m), 1475 (s), 1410 (m), 1393 (m), 1264 (vs, br), 1221 (m), 1154 (s, br), 1027 (s), 1003 (m), 812 (m), 771 (s), 728 (m), 699 (m), 636 (s), 517 (m). UV (CH₂Cl₂): λ_{max} = 287.5 nm, ε = 6.9 × 10⁴ L cm⁻¹ mol⁻¹. ESI-MS: [Ag₂L₂(4,4'-dipyridyl)]²⁺ (495.8, 32%).

3.2.4. [Ag₂L₂(DPPM)](SO₃CF₃)₂ (4)

[Ag₂L₂](SO₃CF₃)₂ (0.182 g, 0.161 mmol) and DPPM (0.062 g, 0.16 mmol) were dissolved in CH₂Cl₂ (40 mL) and the solution stirred for 48 h under argon. It was filtered and purified by column chromatography (silica gel; CHCl₃:MeOH 20:1) and a white powder of **4** was obtained (0.140 g, 57% yield) upon concentration. The solid was recrystallized from acetonitrile by diffusion of diethyl ether, yielding colourless crystals which were suitable for X-ray characterization. *Anal.* Calc. for [Ag₂C₆₇H₅₂N₆P₂]-(SO₃CF₃)₂ · 0.5CHCl₃: C, 52.94; H, 3.36; N, 5.33. Found: C, 52.92; H, 3.56; N, 4.81%. ¹H NMR δ (DMSO-d⁶): 3.89 (s, 2H), 7.27 (s, 10H), 7.37 (s, 4H), 7.45 (s, 4H), 7.60 (s, 14H), 8.01 (s, 8H), 8.45 (t, 4H), 8.61 (t, 8H). ESI-MS: [Ag₂L₂(DPPM)](SO₃CF₃)⁺ (1367.3, 100%), [Ag₂L₂(DPPM)]²⁺ (611.5, 2%).

3.2.5. [AgL(PPh₃)](SO₃CF₃) (5)

 $[Ag_2L_2](SO_3CF_3)_2$ (0.140 g, 0.124 mmol) and PPh₃ (0.065 g, 0.248 mmol) were dissolved in CH₂Cl₂ (30 mL) and the solution

stirred for 48 h under argon. It was then diffused with diethyl ether and colourless crystals were obtained (0.098 g). Evaporating the left-over solution gave more product (0.077 g) (85% total yield). The solid was recrystallized from acetonitrile by diffusion of diethyl ether, forming colourless crystals which were suitable for X-ray characterization. *Anal.* Calc. for [AgC₃₉H₃₀N₃P](SO₃CF₃): C, 57.98; H, 3.65; N, 5.07. Found: C, 57.86; H, 3.22; N, 5.07%. ¹H NMR δ (DMSO- d^6): 7.31 (t, 6H), 7.46 (d, 6H), 7.52 (s, 3H), 7.53 (s, 2H), 7.60–7.65 (m, 3H), 8.08 (t, 2H), 8.15 (d, 2H), 8.47 (d, 2H), 8.73 (d, 2H), 8.80 (s, 2H). ESI-MS: [AgL(PPh₃)]⁺ (679.8, 94%).

3.2.6. [Ag(NP₃)](SO₃CF₃) (6)

[Ag₂L₂](SO₃CF₃)₂ (0.280 g, 0.25 mmol) and NP₃ (0.052 g, 0.080 mmol) were dissolved in CH₂Cl₂ (20 mL) and CH₃CN (20 mL) and the solution stirred for 48 h under argon. It was filtered and purified by column chromatography (silica gel; CH₂Cl₂:MeOH 10:1) and a white powder of **6** was obtained upon concentration. The solid was recrystallized from acetonitrile by diffusion of diethyl ether, yielding colourless crystals which were suitable for X-ray characterization (0.059 g, 80% yield, calculated relatively to NP₃). *Anal.* Calc. for [AgC₄₂H₄₂NP₃](SO₃CF₃): C, 56.71; H, 4.65; N, 1.54. Found: C, 57.12; H, 4.31; N, 1.17%. ¹H NMR δ (DMSO-d⁶): 2.25 (s, 6H), 2.53 (s, 6H), 7.27 (s, 12H, phenyl), 7.45 (s, 6H, phenyl), 7.63 (s, 12H, phenyl). ESI-MS: [Ag(NP₃)]⁺ (760.7, 100%).

3.3. Crystal structures determination

The crystals were mounted on glass fibers. The data sets were collected on a Rigaku R-AXIS RAPID Weissenberg IP diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å), the scan mode being ω . Data reductions were done [24]. The intensity data of the six title compounds were corrected by *Lp* factors and ψ empirical absorption corrections were done for five complexes [25]. The structures were solved by direct methods (SHELXS-97) [26] and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [26]. All hydrogen atoms of complexes **1–6** were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave R₁ [$I > 2\sigma(I)$] = 0.0347 (0.0995) (**1**); 0.0487 (0.1373) (**2**); 0.0304 (0.0920) (**3**); 0.0792 (0.2452) (**4**); 0.0338 (0.0956) (**5**); 0.0254 (0.0675) (**6**).

4. Supplementary material

CCDC 705121, 705122, 705123, 705124, 705125 and 705126 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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