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¹D and ²D Nuclear magnetic resonance of new silver(I) complexes with achiral and chiral bases as ligands: Crystal structure of $[Ag\{(S)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)C_6H_5\}(PPh_3)_2](O_3SCF_3)$

Olga Cifuentes^a, Raúl Contreras^{a,*}, Antonio Laguna^{b,*}, Olga Crespo^b

^a Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-6094411, Chile ^b Departamento de Química Inorgánica, Universidad de Zaragoza-CSIC, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Pedro Cerbuna 12, 50009 Zaragoza, Spain

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ABSTRACT

Treatment of equimolar amounts of substituted aniline or amine with substituted benzaldehyde leads to the corresponding achiral or chiral Schiff bases (L). The reaction of the bases with $[Ag(O_3SCF_3)(PPh_3)]$ leads to the preparation of three or four coordinated cationic complexes, $[Ag(k^1-L)(PPh_3)_n]^+$ (n = 1 or 2) which have been characterized by IR, ¹D and ²D NMR spectroscopy. The crystal structure of $[Ag{(S)-(6-CH_3)C_5H_3N-C+H(\alpha-CH_3)C_6H_5}](PPh_3)_2](O_3SCF_3)$ is reported.

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1. Introduction

The chemistry of silver(I) complexes has attracted an increased interest during last years, due to both their structural features and their potential applications. Silver(I) complexes with nitrogen ligands have proved to be valuable candidates in medicine, catalysis or materials science. Polydentate ligands should offer different coordination sites, thus dictating different coordination geometries around the metal centre and the possibility to obtain monomeric or polymeric species [1-27]. The use of Schiff bases as ligands can increase the biological activity of many of their metallic coordination complexes, i.e. as anti-influenza, antibacterial or as antitumoral agents [28-36]. Nevertheless, not many complexes of this type have been described until now with silver(I) [37-46]. Among them, different types of Schiff bases, e.g. containing heteroaromatic benzimidazole and benzithiale rings [40], N,N chelating moieties [41], cryptands [38] or other substituents, have been used as ligands in the silver(I) chemistry.

Herein we describe the synthesis, characterization and reactivity of silver three or four coordinated complexes with the Schiff bases shown in Fig. 1 as ligands.

* Corresponding authors.

E-mail address: alaguna@unizar.es (A. Laguna).

2. Experimental

2.1. General

The starting complex $[Ag(O_3SCF_3)(PPh_3)]$ [47] and the Schiff bases [48–52] were synthesized by similar procedures to those described in literature. FT-IR spectra (KBr pellet) were obtained on a model Vector-22 Bruker spectrophotometer. ¹H, ¹⁹F, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on a Bruker AC-200P and Bruker-400 spectrometers. Chemical shifts are reported in ppm relative to SiMe₄ (¹H, ¹³C) and 85% H₃PO₄ in D₂O (³¹P) (positive shifts downfield) as external standards, respectively. The values of the coupling constants (¹J_{C-H}) of the ligands and complexes synthesized were determined by means of the experiment of HMBC (²D NMR).

2.2. Synthesis of the Schiff bases

The new Schiff bases used in this work (Fig. 1): $O_2NC_6H_4$ -CHN-CH₂C₆H₄(4-CH₃) (**L**₁), (CH₃)₂NC₆H₄-CHN-CH₂C₆H₅ (**L**₂), (CH₃)₂NC₆H₄-CHN-CH₂C₆H₄(4-CH₃) (**L**₃), C₆H₄N-CHN-CH₂C₆H₅ (**L**₄), C₆H₄N-CHN-CH₂C₆H₄(4-Cl) (**L**₅), C₆H₄N-CHN-CH₂C₆H₄(4-CH₃) (**L**₆), (S)-(-)-(6-CH₃)C₅H₃N-CHN-C*H(α -CH₃)C₆H₅ (**L**₇-***C**₅) and (S)-(-)-C₅H₄N-CHN-C*H(α -CH₃)C₆H₅ (**L**₈-***C**₅) were synthesized by similar methods to those described in the bibliography [48– 52], by condensing equimolar amounts of different amines and





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Fig. 1. Schiff bases L₁-L₈.

the respective substituted aldehydes, under continuous stirring. Reaction times and temperature (room or refluxing temperature) conditions are detailed below.

2.2.1. Monodentate achiral Schiff bases (L_1-L_3)

2.2.1.1. $O_2NC_6H_4$ -*CHN*-*CH*₂*C*₆*H*₄(4-*CH*₃) (*L*₁). A solution of 4-methylbenzylamine (1000 mg, 8.3 mmol), 4-nitrobenzaldehyde (1250 mg, 8.3 mmol) and glacial acetic acid (0.2 mL) in 3 mL of dichloromethane was stirred for 3 days at room temperature and protected from light. The solution was evaporated under vacuum and the beige residue washed with cold dichloromethane. Yield, 97%. FT-IR: $v_{(C=N)im} = 1638.2 \text{ cm}^{-1}$. *Anal.* Calc. for $C_{15}H_{14}N_2O_2$ (*M* = 254.29 g/mol): C, 70.85; H, 5.55; N, 11.0. Found: C, 71.2; H, 5.8; N, 11.9%. ¹H NMR (acetone-d₆): δ 8.60 (s, ¹H_d), 8.29 (d, 2H_{b,b}, ³*J* = 8.8 Hz,), 8.05 (d, 2H_{c,c}, ³*J* = 8.8 Hz,), 7.25 (d, 2H_{f,f}, ³*J* = 8.0 Hz,), 7.16 (d, 2H_{g,g}, ³*J* = 8.0 Hz,), 4.82 (s, 2H_e), 2.30 (d, ¹H_h). ¹³C{¹H} NMR (acetone-d₆): δ 149.1 (C₂), 123.7 (C_{3,3}, ¹*J* = 173.5 Hz), 129.0 (C_{4,4'}, ¹*J* = 168.0 Hz), 142.1 (C₅), 159.6 (C₆, ¹*J* = 162.8 Hz), 64.5 (C₇, ¹*J* = 135.4 Hz), 136.4 (C₈), 128.0 (C_{9,9'}, ¹*J* = 156.2 Hz), 128.9 (C_{10,10'}, ¹*J* = 156.2 Hz), 136.3 (C₁₁), 20.3 (C₁₂, ¹*J* = 125.0 Hz).

2.2.1.2. (*CH*₃)₂*NC*₆*H*₄-*CHN*-*CH*₂*C*₆*H*₅ (*L*₂). A solution of benzylamine (500 mg, 4.7 mmol) and 4-(dimethylamine)benzaldehyde (450 g, 3.0 mmol) in 3 mL of ethanol was stirred for 3 days at room temperature and protected from light. Upon cooling a beige solid precipitated, which was filtered, washed with cold ethanol and dried under vacuum. Yield, 41%. *Anal.* Calc. for C₁₆H₁₈N₂ (*M* = 238.33 g/mol): C, 80.63; H, 7.61; N, 11.75. Found: C, 79.64; H, 9.18; N, 11.64%. FT-IR: $v_{(C=N)im} = 1638.6 \text{ cm}^{-1}$. ¹H NMR (acetone-d₆): δ 8.31 (s, ¹H_d), 7.65 (d, 2H_{c,C}, ³*J* = 9.0 Hz), 7.34 (dd, 2H_{f,f}, ³*J* = 7.6 Hz, ⁴*J* = 1.6 Hz), 7.32 (t, 2H_{g,g'}, ³*J* = 7.6 Hz), 7.22 (dt, H_h, ³*J* = 7.6 Hz, ⁴*J* = 1.6 Hz), 6.75 (d, 2H_{b,b'}, ³*J* = 9.0 Hz), 4.71 (s, 2H_e), 3.00 (s, 6H_a). ¹³C{¹H} NMR (acetone-d₆): δ 40.3 (C₁, ¹*J* = 144.1 Hz), 153.3 (C₂), 112.5 (C_{3,3'}, ¹*J* = 155.1 Hz), 130.4 (C_{4,4'}, ¹*J* = 155.1 Hz), 125.8 (C₅), 162.1 (C₆: ¹*J* = not resolved), 65.5 (C₇, ¹*J* = 137.7 Hz), 141.8 (C₈), 128.8 (C_{9.9'}, ¹*J* = 158.8 Hz), 129.1(C_{10.10'}; ¹*J* = 158.8 Hz), 127.4 (C₁₁, ¹*J* = 155.1 Hz).

2.2.1.3. $(CH_3)_2NC_6H_4$ -CHN- $CH_2C_6H_4(4$ - $CH_3)$ (L_3). A solution of 4-methylbenzylamine (200 mg, 1.65 mmol) and 4-(dimethylamine)benzaldehyde (160 mg, 1.07 mmol) in 3 mL of ethanol was stirred for 3 days at room temperature and protected from light. Upon cooling a beige solid precipitated, which was filtered, washed with cold ethanol and dried under vacuum. Yield, 66%. *Anal.* Calc. for $C_{17}H_{20}N_2.0.75H_2O$ (M = 264.87 g/mol): C, 77.09; H, 8.18; N, 10.58. Found: C, 77.26; H, 9.75; N, 10.24%. FT-IR: $v_{(C=N)im} = 1634.7$ cm⁻¹. ¹H NMR (acetone-d₆): δ 8.29 (s, ¹H_d), 7.64 (d, $2H_{c,c'}$, ³J = 8.8 Hz), 7.22 (d, $2H_{f,f}$, ³J = 8.0 Hz), 7.13 (d, $2H_{g,g'}$, ³J = 8.0 Hz,), 6.75 (d, $2H_{b,b'}$, ³J = 8.8 Hz), 4.67 (s, $2H_e$), 3.00 (s, $6H_a$), 2.30 (s, $3H_h$). ¹³C{¹H} NMR (acetone-d₆): δ 40.3 (C₁, ¹J = 140.3 Hz), 153.3 (C₂), 112.5 (C_{3,3'}, ¹J = 155.8 Hz), 130.3 (C_{4,4'}, ¹J = 155.8 Hz); 125.9 (C₅), 161.8 (C₆, ¹J = not resolved), 65.4 (C₇, ¹J = 131.2 Hz), 138.7 (C₈), 128.7 (C_{9,9'}, ¹J = 124.4 Hz).

2.2.2. Bidentate achiral Schiff bases (L_4-L_6)

2.2.2.1. C_5H_4N -CHN-CH₂ C_6H_5 (L_4). A solution of benzylamine (200 mg, 1.87 mmol) and 2-pyridinecarboxaldehyde (200 mg, 1.87 mmol in 3 mL of water was stirred for 3 days at refluxing temperature and protected from light. During this time it is observed the formation of a yellow oil, which was isolated. Yield, 65%. *Anal.* Calc. for $C_{13}H_{12}N_2.0.5H_2O$ (M = 205.26 g/mol): C, 76.07; H, 6.38; N, 13.65. Found: C, 76.92; H, 8.22; N, 13.50%. FT-IR: $v_{(C=N)im} = 1647.2$, $v_{(C=N)py} = 1586.7$ cm⁻¹. ¹H NMR (acetone-d₆): δ 8.65 (d, H_d, ³J = 4.8 Hz), 8.51 (s, H_e), 8.08 (d, H_a, ³J = 8.0 Hz), 7.83 (t, H_b, ³J = 8.0 Hz), 7.41 (dd, H_{g.g'}, ³J = 6.0 Hz, ⁴J = 1.2 Hz, 2H), 7.39 (t, H_c, ³J = 6.4 Hz), 7.37 (t, H_{h·h'}, ³J = 7.2 Hz, 2H), 7.27 (dt, H_i, ³J = 7.2 Hz, ⁴J = 1.2 Hz), 4.87 (s, H_f, 2H). ¹³C{¹H} NMR (acetone-d₆): δ 121.4 (C_1 , ¹J = 144.1 Hz), 137.3 (C_2 , ¹J = 167.7 Hz), 125.8 (C_3 , ¹J = 167.7 Hz), 150.3 (C_4 , ¹J = 182.2 Hz), 155.8 (C_5), 163.7 (C_6 , ¹J = 165.3 Hz); 65.3 (C_7 , ¹J = 135.6 Hz), 140.4 (C_8), 129.0 ($C_{9.9}$, ¹J = 160.2 Hz), 129.3 ($C_{10.10}$, ¹J = 160.2 Hz), 127.8 (C_{11} , ¹J = 156.5 Hz).

2.2.2.2. C_5H_4N -CHN-CH₂ $C_6H_4(4$ -Cl) (L_5). Following a procedure similar to the reported for L_4 , from a solution of 4-chlorobenzylamine (200 mg, 1.41 mmol) and 2-pyridinecarboxaldehyde (370 mg,

3.45 mmol) a yellow oil was isolated. Yield, 76%. *Anal.* Calc. for $C_{13}H_{11}N_2Cl$ (M = 230.69 g/mol): C, 67.68; H, 4.81; N, 12.14. Found: C, 67.74; H, 6.05; N, 12.25%. FT-IR: $v_{(C=N)im} = 1650.4$, $v_{(C=N)py} = 1586.8$ cm⁻¹; ¹H NMR, (CDCl₃): δ 8.62 (d, H_d, ³*J* = 4.4 Hz, ¹H); 8.47 (s, H_e, ¹H); 8.03 (d; H_a, ³*J* = 8.0 Hz, ¹H); 7.68 (dt, H_b, ³*J* = 7.6 Hz; ⁴*J* = 1.2 Hz, ¹H); 7.27(m, H_{gyg}; H_{h•h'}; H_c, 5H); 4.78 (s, H_f, 2H).¹³C{¹H} NMR (CDCl₃) δ 121.3 (C₁, *J* = 166.7 Hz); 136.5 (C₂; ¹*J* = 163.4 Hz); 124.9 (C₃; ¹*J* = 161.9 Hz); 149.4 (C₄; ¹*J* = 179.0 Hz); 154.4 (C₅); 163.1 (C₆, ¹*J* = 161.9 Hz); 64.0 (C₇, ¹*J* = 144.2 Hz); 132.8 (C₈); 128.6 (C_{9,9}, ¹*J* = 165.9 Hz); 129.4 (C_{10,10}, ¹*J* = 161.0 Hz); 137.4 (C₁₁).

2.2.2.3. C_5H_4N -*CHN*-*CH*₂ $C_6H_4(4$ -*CH*₃) (*L*₆). Following a procedure similar to the reported for **L**₄, from a solution of hot 4-methylben-zylamine (230 mg, 1.9 mmol) and 2-pyridinecarboxaldehyde (230 mg, 2.15 mmol) a yellow oil was isolated. Yield, 74%. *Anal.* Calc. for $C_{14}H_{14}N_2$ ·H₂O (M = 228.29 g/mol): C, 73.66; H, 7.06; N, 12.27. Found: C, 70.76; H, 6.98; N, 11.79%. FT-IR: $v_{(C=N)im} = 1647.5$, $v_{(C=N)py} = 1603.0$ cm⁻¹. ¹H NMR (acetone-d₆): δ 8.65 (d, H_d, ³*J* = 4.8 Hz, ¹H), 8.50 (s, H_e, ¹H), 8.08 (d, H_a, ³*J* = 8.0 Hz, ¹H), 7.79 (dt, H_b, ³*J*_{bc} = 7.8 Hz, ⁴*J* = 1.2 Hz, ¹H), 7.37 (ddd, H_c, ³*J* = 4.8 Hz, ³*J* = 7.6 Hz, ⁴*J* = 1.2 Hz, ¹H), 7.27 (d, H_{g.g'}, ³*J* = 8.0 Hz, 2H), 7.16 (d, H_{h,h'}, ³*J* = 8.0 Hz, 2H), 4.82 (s, H_f, 2H), 2.30 (s, H_i, 3H). ¹³C{¹H} NMR (acetone-d₆): δ 121.4 (C₁, ¹*J* = 167.0 Hz), 136.5 (C₂, ¹*J* = 163.6 Hz), 125.6 (C₃, ¹*J* = 165.4 Hz), 150.2 (C₄, ¹*J* = 180.6 Hz), 155.8 (C₅), 163.4 (C₆, ¹*J* = 162.5 Hz), 65.0 (C₇, ¹*J* = 135.4 Hz), 137.2 (C₈, C₁₁), 128.9 (C_{9.9'}, ¹*J* = 159.7 Hz), 129.9 (C_{10,10'}, ¹*J* = 156.2 Hz), 21.2 (C₁₂, ¹*J* = 124.1 Hz).

2.2.3. Bidentate chiral Schiff bases (L₇-*Cs; L₈-*Cs)

2.2.3.1. (S)-(-)-(6-CH₃)C₅H₃N-CHN-C*H(α -CH₃)C₆H₅ (L₇-*C₅). Following a procedure similar to the reported for L₄, from a hot solution of (S)-(-)- α -methylbenzylamine (100 mg, 0.83 mmol) and 6-methylpyridine-2-carboxaldehyde (101 mg, 0.83 mmol) a orange oil was isolated. Yield, 40%. *Anal.* Calc. for C₁₅H₁₆N₂.2.5H₂O (*M* = 269.34 g/mol): C, 66.90; H, 7.86; N, 10.40. Found: C, 67.02; H, 9.17; N, 10.90%. FT-IR: $\nu_{(C=N)im}$ = 1646.6, $\nu_{(C=N)py}$ = 1590.7 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.42 (s, ¹H_e, ¹H), 7.91 (d, H_d, ³J = 7.6 Hz, ¹H), 7.71 (t, H_c, ³J = 8.0 Hz, ¹H), 7.47 (d, H_{h,h'}, ³J = 7.2 Hz, 2H), 7.34 (t, H_{i,i'}, ³J = 7.2 Hz, 2H), 7.26 (d, H_b, ³J = 8.0 Hz, ¹H), 7.24 (t, H_j, ³J = 7.2 Hz, ¹H), 4.66 (q, H_f, ³J = 6.8 Hz, ¹H), 2.52 (s, H_a, 3H), 1.55 (d, H_g, ³J = 6.8 Hz, 3H). ¹³C{¹H} NMR (acetone-d₆): δ 24.4 (C₁, ¹J = 127.5 Hz), 154.4 (C₂), 125.0 (C₃, ¹J = 162.1 Hz), 137.6 (C₄, ¹J = 161.8 Hz), 118.6 (C₅, ¹J = 166.7 Hz), 157.9 (C₆), 161.7 (C₇, ¹J = 160.8 Hz), 70.2 (C₈, ¹J = 137.3 Hz), 146.2 (C₉), 127.5 (C_{10,10}, ¹J = 155.6 Hz), 129.3 (C_{11,11'}, ¹J = 155.6 Hz), 127.7 (C₁₂, ¹J = 155.6 Hz), 25.4 (C₁₃, ¹J = 127.5 Hz).

2.2.3.2. (*S*)-(-)-*C*₅*H*₄*N*-*CHN*-*C***H*(α-*CH*₃)*C*₆*H*₅ (*L*₈-**C*_S). Following a procedure similar to the reported for **L**₄, from a solution of (*S*)-(-)-α-methylbenzylamine (100 mg, 0.83 mmol) and 2-pyridine-carboxaldehyde (95 mg, 0.89 mmol) a orange oil was isolated. Yield, 42%. *Anal.* Calc. for C₁₄H₁₄N₂·2H₂O (*M* = 246.3 g/mol): C, 68.27; H, 5.73; N, 11.37. Found: C, 68.08; H, 6.05; N, 11.38%. FT-IR: $v_{(C=N)im} = 1647.0$, $v_{(C=N)py} = 1586.7 \text{ cm}^{-1}$. ¹H NMR (acetone-d₆): δ 8.64 (d, H_d, ³*J* = 4.8 Hz, 1H), 8.50 (s, H_e, 1H), 8.12 (d, H_a, ³*J* = 8.0 Hz, 1H), 7.82 (dt, H_b, ³*J* = 7.6 Hz, ⁴*J* = 1.2 Hz, 1H), 7.49 (d, H_{h,h'}, ³*J* = 7.6 Hz, 2H), 7.39 (ddd, H_c, ³*J* = 8.0 Hz, ³*J* = 4.8 Hz; 1H), 1.56 (d, Hg, ³*J* = 6.8 Hz, 3H). ¹³C{¹H} NMR (acetone-d₆): δ 121.5 (C₂, ¹*J* = 166.9 Hz), 137.5 (C₃, ¹*J* = 165.0 Hz), 125.7 (C₄, ¹*J* = 164.8 Hz), 150.2 (C₅, ¹*J* = 181.9 Hz), 155.9 (C₆), 161.4 (C₇, ¹*J* = 165.7 Hz), 129.2 (C_{11,11'}, ¹*J* = 155.7 Hz), 127.7 (C₁₂, ¹*J* = 156.0 Hz), 25.4 (C₁₃, ¹*J* = 126.7 Hz).

2.3. Synthesis of the silver(I) complexes

2.3.1. Synthesis of complexes with monodentate achiral Schiff bases

To a saturated solution of the complex $[Ag(O_3SCF_3)(PPh_3)]$ (100 mg, 0.19 mmol) in dichloromethane, a stoichiometric amount of the respective Schiff base (49.2 mg, 0.19 mmol, L_1), (45.0 mg, 0.19 mmol, L_2) or (48.8 mg, 0.19 mmol, L_3) was added in 3 mL of dichloromethane. The mixture was stirred for 45 min at room temperature protected from light. The metallic silver obtained was filtered off through Kieselguhr and the solution was concentrated under reduced pressure to a small volume (2 mL) and the complexes precipitated by addition of diethyl ether.

The white solids of $[Ag(\kappa^{1}-L_{1})(PPh_{3})](O_{3}SCF_{3})$ (1) and $[Ag(\kappa^{1}-L_{n})(PPh_{3})_{2}](O_{3}SCF_{3})$ $[L_{n} = L_{2}$ (2) and L_{3} (3)] were filtered, washed with diethyl ether (3 × 5 mL) and dried under vacuum.

2.3.1.1. $[Ag{\kappa^1-O_2NC_6H_4-CHN-CH_2C_6H_4(4-CH_3)}(PPh_3)](O_3SCF_3)$ (1). Yield, 33%. Thermolabile solid; FT-IR: $v_{(C=N)im} = 1596.7$, $v_{PPh3} = 1094$, 745, 694 and 636, $v_{s(CF3)} = 1274$, $v_{as(CF3)} = 1153$, $v_{s(SO3)} = 1029$ and $\delta_{(CF3)} = 572$ and 514 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.91 (s, H_d, ¹H), 8.11 [AB (H_{A(bb')}, H_{B(c,c')}) system, $v_0 = 3244.65$ Hz. $J_{AB} = 6.0$ Hz, $\Delta v = 12.06$ Hz, 4H], 7.45–7.33 (m, PPh₃, 15H), 7.31 (d, H_{fr}, 2H, ³J_{fg} = 7.9 Hz), 6.99 (d, H_{g.g'}, 2H, ³J_{gf} = 7.9 Hz), 4.86 (s, H_e, 2H), 2.75 (s, H_h, 3H). ³¹P{¹H} NMR (acetone-d₆): δ -79.87 (s).

2.3.1.2. $[Ag\{\kappa^1-(CH_3)_2NC_6H_4-CHN-CH_2C_6H_5\}(PPh_3)_2](O_3SCF_3)$ (2). Yield, 34%. Thermolabile solid. FT-IR: $v_{(C=N)im} = 1604.9$, $v_{PPh3} = 1095$, 745, 695 and 637, $v_{s(CF3)} = 1274$, $v_{s(CF3)} = 1168$, $v_{as(SO3)} = 1031$ and $\delta_{(CF3)} = 60$, 573 and 517 cm⁻¹. ¹H NMR (acetone-d_6): δ 8.77 (s, H_d, 1H), 7.83 (d, H_{c,c'}, $^{3}J_{cb} = 9.0$ Hz, 2H), 7.56 (d, H_{6f}, $^{3}J = 7.6$ Hz, 2H), 7.53 (vt, H_{para}, PPh₃, 6H), 7.40 (vt, H_{meta}, PPh₃, 12H), 7.29 (vt, H_{ortho}, PPh₃, 2H_g, H_h, 15H), 6.50 (d, H_{b,b'}, 2H), 4.84 (s, H_e, 2H), 2.97 (s, H_a, 6H). ¹³C{¹H} NMR (acetone-d_6): δ 40.3 (C₁, ¹J = 138.5 Hz), 153.9 (C₂), 112.7 (C_{3,3'}, ¹J = 164.1 Hz), 129.6 (C_{4,4'}, ¹J = 151.0 Hz), 122.0 (C₅), 166.2 (C₆, ¹J = 161.5 Hz), 66.2 (C₇, ¹J = 134.6 Hz), 140.4 (C₈), 130.7 (C_{9,9'}, ¹J = not resolved), 129.2 (C_{10,10'}, ¹J = 157.6 Hz), 128.6 (C₁₁, ¹J = 151.0 Hz), 130.3 (C_{meta}, ¹J = 168.1 Hz, ³J_{PC} = 19.7 Hz, PPh_3), 132.0 (C_{para}, ¹J = 177.3 Hz, ⁴J_{PC} = not resolved, PPh_3), 134.7 (C_{ortho}, ¹J = 173.3 Hz, ²J_{PC} = 31.7 Hz, PPh_3). ³¹P{¹H} NMR (acetone-d₆): δ -76.9 (s).

2.3.1.3. $[Ag{\kappa^{1}-(CH_{3})_{2}NC_{6}H_{4}-CHN-CH_{2}C_{6}H_{4}(4-CH_{3})](PPh_{3})_{2}](O_{3}SCF_{3})$ (**3**). Yield, 38%. Thermolabile solid. FT-IR: $v_{(C=N)im} = 1596.9^{1}$, $v_{PPh3} = 1097$, 747, 694 and 637, $v_{s(CF3)} = 1275$, $v_{as(CF3)} = 1164$, $v_{s(SO3)} = 1030$ and $\delta_{(CF3)} = 573$, 517 and 503 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.68 (s, H_d, 1H), 7.75 (d, H_{c,C'}, ³J_{cb} = 8.9 Hz, 2H), 7.55 (vt, H_{para}, PPh₃, 6H), 7.41 (vt, H_{ortho}, PPh₃, 12H), 7.28 (vt, H_{meta}, PPh₃, 12H), 7.11 (d, H_{f,f}, ³J_{fg} = 8.0 Hz, 2H), 6.94 (d, H_{g,g'}, 2H), 6.53 (d, H_{b,b'}, 2H), 4.74 (s, H_e, 2H), 2.98 (s, H_a, 6H), 2.22 (s, H_h, 3H). ¹³C{¹H}NMR (acetone-d₆): δ 48.2 (C₁, ¹J = 137.3 Hz), 151.9 (C₂), 112.6 (C_{3,3'}, ¹J = 152.9 Hz), 129.3 (C_{4.4'}, ¹J = 164.6 Hz, C_{10,10'}; ¹J = 149.3 Hz), 122.3 (C₅), 164.5 (C₆, ¹J = 160.8 Hz), 65.8 (C₇, ¹J = 131.4 Hz); (C₈, C_{9.9'} and C₁₁ not resolved), 23.0 (C₁₂, ¹J = 127.5 Hz), 130.3 (C_{meta}, ¹J = 160.8 Hz; ³J_{PC} = 19.7 Hz, PPh_3); 132.0 (C_{para}, ¹J = 168.5, ⁴J_{PC} = not resolved, PPh₃), 134.7 (C_{ortho}, ¹J = 164.6 Hz, ²J_{PC} = 31.5 Hz, PPh₃), 130.6 (C_{ipso}, ¹J_{PC} = 61.2 Hz, PPh₃). ³¹P{¹H} NMR (acetone-d₆): δ -76.86 (s).

2.3.2. Synthesis of silver(I) complexes with bidentate achiral Schiff bases

To a saturated solution of the complex $[Ag(O_3SCF_3)(PPh_3)]$ (150 mg; 0.29 mmol) in dichloromethane (20 mL), a stoichiometric amount of the respective Schiff base (37.6 mg, 0.19 mmol, L₄), (44.3 mg, 0.19 mmol, L₅) or (40.3 mg, 0.19 mmol, L₆) was added. The heterogeneous mixture was stirred at room temperature for 1 h protected from light. The metallic silver obtained was filtered off through Kieselguhr and the solutions were concentrated under reduced pressure to a small volume (3 mL) and the complexes precipitated by addition of diethyl ether. The white solids of $[Ag(\kappa^2-L_n)(PPh_3)_2](O_3SCF_3)$ $[L_n = L_4$ (4), L_5 (5) and L_6 (6) and L_7 (7)] were filtered, washed with diethyl ether (3 × 5 mL) and dried under vacuum.

2.3.2.1. $[Ag{\kappa^2-C_5H_4N-CHN-CH_2C_6H_5}(PPh_3)_2](O_3SCF_3)$ (4). Yield, 50%. Anal. Calc. for $C_{50}H_{42}AgF_3N_2O_3P_2S$ (*M* = 977.77 g/mol): C, 61.42; H, 4.33; N, 2.86; S, 3.28. Found: C, 60.96; H, 4.35; N, 3.01; S, 3.12%. FT-IR: $v_{(C=N)py} = 1602.1$, $v_{(C=N)im} = 1589.6$, $v_{PPh3} = 1096$, 782, 745, 694 and 637, $v_{s(CF3)} = 1275$, $v_{as(CF3)} = 1153$, $v_{s(SO3)} = 1031$ and $\delta_{(CF3)} = 572$ and 516 cm⁻¹. ¹H NMR (acetone-d₆): δ 9.07 (s, H_e, 1H), 8.73 (d, H_d, ${}^{3}J$ = 4.8 Hz, 1H), 8.22 (dd, H_a, ${}^{3}J$ = 7.2 Hz, ${}^{4}J$ = 1.6 Hz, 1H), 8.19 (t, H_b, ${}^{3}J$ = 7.2 Hz, 1H), 7.67 (ddd, H_c, ${}^{3}J$ = 7.2 Hz, ${}^{3}J$ = 4.8 Hz, ${}^{4}J$ = 1.6 Hz, 1H), 7.49 (vt, H_{para}, PPh₃, 6H), 7.37–7.28 [m, H_{meta}, H_{ortho} (PPh₃), H_{g,g'}, H_{h,h'}, H_i, 29H], 7.23 (d, H_f, ${}^{4}J_{HP} = 1.2 \text{ Hz}$), 7.21 (d, H_{ff}, ${}^{4}J_{HP} = 2.0 \text{ Hz}$). ${}^{13}C{}^{1}H$ NMR (acetoned₆): δ 123.1 (C₁, ¹*J* = not resolved), 140.2 (C₂, ¹*J* = not resolved), 126.4 (C₃, ${}^{1}J$ = not resolved), 152.2 (C₄, ${}^{1}J$ = not resolved), 157.1 (C_5) , 161.7 $(C_6, {}^1J$ = not resolved) $(C_7, it is probably overlapped with$ the signals of the carbons of the phenyls groups of PPh₃), 142.3 (C_8) , 129.2 $(C_{9,9'}, {}^{1}J = \text{not resolved})$, 130.5 $(C_{10,10'}, {}^{1}J = \text{not resolved})$, (cs), 125.2 (cs), *J* not resolved), 130.2 (C_{meta} , ¹*J* = 163.3 Hz, ³*J*_{PC} = 12.3 Hz, PPh₃), 131.8 (C_{para} , ¹*J* = 159.9 Hz, ⁴*J*_{PC} = not resolved, PPh₃), 134.5 (C_{ortho} , ¹*J* = 56.2 Hz, ²*J*_{PC} = 32.5 Hz, PPh₃), 132.7 (C_{ipso} , ¹*J*_{PC} = 55.4 Hz, PPh₃). ³¹P{¹H} NMR (acetone-d₆, room temperature): δ 10.8 (br). ¹⁹F NMR (acetone-d₆): δ –76.86 (s).

2.3.2.2. $[Ag{\kappa^2-C_5H_4N-CHN-CH_2C_6H_4(4-Cl)}(PPh_3)_2](O_3SCF_3)(5)$. Yield, 48.4%. Anal. Calc. for C₅₀H₄₁AgClF₃N₂O₃P₂S (M = 1012.21 g/mol): C, 59.33; H, 4.08; N, 2.77; S, 3.17. Found: C, 60.01; H, 4.31; N, 3.76; S, 3.22%. FT-IR: $v_{(C=N)py} = 1642.4$, $v_{(C=N)im} = 1589.2$, $v_{PPh3} = 1095$, 779, 744, 694 and 632, $v_{s(CF3)} = 1265$, $v_{as(CF3)} = 1151$, $v_{s(SO3)} = 1031$ and $\delta_{(CF3)}$ = 572, 516 and 505 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.96 (s, H_e, 1H), 8.42 (d, H_d, ${}^{3}J$ = 4.4 Hz, 1H), 8.12 (t, H_b, ${}^{3}J$ = 7.6 Hz, 1H), 8.07 (dd, H_a , ${}^{3}J = 7.6$ Hz, ${}^{4}J = 0.8$ Hz, 1H), 7.57–7.55 (m, H_c , 1H), 7.52 (vt, H_{para}, PPh₃, 6H), 7.40 (vt, H_{meta}, PPh₃, 12H), 7.19 (m, H_{ortho}, PPh₃, H_{g,g'}, 14H), 7.00 (d, H_{h,h'}, ${}^{3}J = 8.0$ Hz, 2H), 4.83 (s, H_{f,f}, 2H). ¹³C{¹H} NMR (acetone-d₆): δ 126.6 (C₁, ¹J = 167.3 Hz), 139.7 (C₂, ${}^{1}J$ = 161.5 Hz), 128.1 (C₃, ${}^{1}J$ = not resolved), 151.5 (C₄, ${}^{1}J$ = not resolved), (C₅, not resolved), 165.0 (C₆, ${}^{1}J$ = not resolved), 64.5 (C₇; ${}^{1}J$ = 132.2 Hz), 139.6 (C₈), 129.7 (C_{9,9'}, ${}^{1}J$ = not resolved), 131.2 $(C_{10,10'}, {}^{1}J = not resolved), 140.3 (C_{11}), 130.2 (C_{meta}, {}^{1}J = 157.4 \text{ Hz},$ ${}^{3}J_{PC}$ = 19.1 Hz, PPh₃), 131.7 (C_{para}, ${}^{1}J$ = 160.0 Hz, ${}^{4}J_{PC}$ = not resolved, PPh₃), 134.4 (C_{ortho} , ¹*J* = not resolved, ²*J*_{PC} = 32.9 Hz, PPh₃), 133.0 $(C_{ipso}, {}^{1}J_{PC} = 52.8 \text{ Hz}, PPh_{3}). {}^{31}P{}^{1}H} \text{ NMR} (acetone-d_{6}, room temper$ ature): δ 10.8 (br). ¹⁹F NMR (acetone-d₆): δ –76.86 (s).

2.3.2.3. $[Ag{\kappa^2-C_5H_4N-CHN-CH_2C_6H_4(4-CH_3)}](PPh_3)_2](O_3SCF_3)$ (**6**). Yield, 44.2%. Anal. Calc. for $C_{51}H_{44}AgF_3N_2O_3P_2S$ (M = 991.79 g/mol): C, 61.76; H, 4.47; N, 2.82; S, 3.23. Found: C, 61.43; H, 4.60; N, 2.75; S, 2.98%. FT-IR: $v_{(C=N)py} = 1640.8$, $v_{(C=N)im} = 1589.5$, $v_{PPh3} = 1095$, 779, 746, 695 and 637, $v_{s(CF3)} = 1272$, $v_{as(CF3)} = 1149$, $v_{s(SO3)} = 1031$ and $\delta_{(CF3)} = 573$, 516 and 506 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.99 (s, H_e, 1H), 8.34 (d, H_d, ³J = 4.8 Hz, 1H), 8.15 (dt, H_b, ³J = 7.6 Hz, ⁴J = 1.6 Hz, 1H), 8.05 (d, H_a, ³J = 7.6 Hz, 1H), 7.55 (ddd, H_c, ³J = 4.8 Hz, ³J = 7.6 Hz, ⁴J = 1.2 Hz, 1H), 7.51 (vt, H_{para}, PPh₃, 6H), 7.39 (vt, H_{meta}, PPh₃, 12H), 7.18 (vt; H_{ortho}, PPh₃, 12H), 6.97 (d, H_{g.g}, ³J_{gh} = 8.0 Hz, 2H), 6.76 (d, H_{h,h'}, 2H), 4.78 (s, H_{f.f}, 2H), 2.13 (s, H_i, 3H). ¹³C{¹H} NMR (acetone-d₆): δ (C₁, not resolved), 138.5 (C₂, ¹J = not resolved), 128.6 (C₃, ¹J = not resolved), 152.4 (C₄, ¹J = not resolved), (C₅, not resolved), 164.3 (C₆, ¹J = not resolved); 130.4 (C_{10,10}, ¹J = not resolved), 140.4 (C₁₁), 21.3 (C₁₂, ³J = 124.0 Hz), 130.1 (C_{meta}, ¹J = 163.4 Hz, ³*J*_{PC} = 19.3 Hz, PPh₃), 131.7 (C_{para}, ¹*J* = 157.5 Hz, ⁴*J*_{PC} = not resolved, PPh₃), 134.5 (C_{ortho}, ¹*J* = 167.3, ²*J*_{PC} = 32.3 Hz, PPh₃), 132.8 (C_{ipso}, ¹*J*_{PC} = 59.6 Hz, PPh₃). ³¹P{¹H} NMR (acetone-d₆, room temperature): δ 9.2 (br). ¹⁹F NMR (acetone-d₆): δ –76.86 (s).

2.3.3. Synthesis of silver(I) complexes with bidentate chiral Schiff bases

To a saturated solution of the complex $[Ag(O_3SCF_3)(PPh_3)]$ (150 mg, 0.288 mmol) in dichloromethane (20 mL), a stoichiometric amount of the Schiff base L_{n} -*Cs [0.10 mmol, 21.0 mg (n = 7), 59.9 mg (n = 8)] was added. The heterogeneous mixture was stirred at room temperature for 1 h (7) or 15 min (8) and protected from light. The metallic silver obtained was filtered off through Kieselguhr and the solution concentrated under reduced pressure to a small volume (3 mL). Upon addition of diethyl ether (10 mL) a white solid of 7 or 8 was filtered, washed with diethyl ether (3 × 5 mL) and dried under vacuum.

2.3.3.1. [Ag(k²-L₇-*Cs)(PPh₃)₂](O₃SCF₃) (**7**). Yield, 25%. Anal. Calc. for $C_{52}H_{46}AgF_{3}N_{2}O_{3}P_{2}S$ (*M* = 1005.82 g/mol): C, 62.10; H, 4.61; N, 2.79; S, 3.19. Found: C, 61.27; H, 3.92; N, 2.86; S, 4.38%. FT-IR: $v_{(C=N)py} = 1645.9$, $v_{(C=N)im} = 1591.3$, $v_{PPh3} = 1092$, 794, 765, 699 and 638, $v_{s(CF3)} = 1276$, $v_{as(CF3)} = 1155$, $v_{s(SO3)} = 1032$ and $\delta_{(CF3)}$ = 572, 540 and 516 cm⁻¹. ¹H NMR (acetone-d₆): δ 8.81 (d, $^{1}\text{H}_{e}$, $^{4}J_{PH} = 0.8$ Hz, 1H), 7.94 (br, H_d, 1H), 7.61 (t, H_c, $^{3}J = 7.6$ Hz, 1H), 7.57 (d, H_b, ${}^{3}J$ = 7.6 Hz, 1H), 7.52 (vt, H_{para}, PPh₃, 5H), 7.39 (vt, H_{meta}, PPh₃, 10H); 7.33–7.09 (m, PPh₃, H_{h,h'}, H_{i,i'}, H_i, 20H), 4.84 (q, H_f , ${}^{3}J = 6.4$ Hz, 1H), 2.22 (s, H_a , 3H), 1.42 (d, H_g , $^{3}J = 6.4$ Hz, 3H). $^{13}C{^{1}H}$ NMR (acetone-d₆): δ 24.7 (C₁, ^{1}J = not resolved), (C₂, not resolved), 126.8 (C₃; ¹J not resolved), 137.9 (C₄, ${}^{3}J$ = 164.6 Hz), 121.9 (C₅, ${}^{3}J$ = 170.0 Hz), 158.2 (C₆), 162.5 (C₇, ^{1}J = not resolved), (C₈; ^{1}J = not resolved), (C₉, not resolved); 128.6 $(C_{10,10'}, {}^{1}J = 164.6 \text{ Hz}), 127.0 (C_{11,11'}, {}^{1}J = 162.4 \text{ Hz}), 140.4 (C_{12}, {}^{1}J = \text{not} \text{ resolved}), 23.9 (C_{13}, {}^{1}J = \text{not} \text{ resolved}), 129.2 (C_{\text{meta}}, {}^{1}J = \text{not} \text{ resolved})$ ${}^{J}J = 167.8 \text{ Hz}, {}^{3}J_{PC} = 19.0 \text{ Hz}, \text{ PPh}_3$), 130.7 (C_{para}, ${}^{1}J = 157.0 \text{ Hz}, {}^{4}J_{PC} = \text{not resolved}, \text{PPh}_3$), 133.5 (C_{ortho}, ${}^{1}J = 163.5, {}^{2}J_{PC} = 32.1 \text{ Hz}, \text{PPh}_3$), 132.0 (C_{ipso}, ${}^{1}J_{PC} = 50.8 \text{ Hz}, \text{PPh}_3$). ${}^{31}P\{^{1}H\}$ NMR (acetone-d₆, room temperature): δ 5.4 (br). ¹⁹F NMR (acetone-d₆): δ –71.4 (s).

2.3.3.2. $[Ag(k^2-L_8-*Cs)(PPh_3)](O_3SCF_3)$ (**8**). Yield, 32.3%. Thermolabile solid. FT-IR: $v_{(C=N)py} = 1640.2$, $v_{(C=N)im} = 1591.2$, $v_{PPh3} = 1096$, 747, 695 and 637, $v_{s(CF3)} = 1263$, $v_{as(CF3)} = 1152$, $v_{s(SO3)} = 1030$, and $\delta_{(CF3)} = 572$, 517 and 505 cm⁻¹. ¹H NMR (acetone-d₆): δ 9.45 (s, H_e, 1H), 9.05 (d, H_d, ${}^{3}J = 4.4$ Hz, 1H), 8.60 (dt, H_b, ${}^{3}J = 7.6$ Hz, ⁴J = 1.6 Hz, 1H), 8.46 (d, H_a, ${}^{3}J = 7.6$ Hz, 1H), 8.14 (ddd, H_c, ${}^{3}J = 7.6$ Hz, 1H), 7.95 (vdt, H_{para}, PPh₃, 2H), 7.87 (vdt, H_{para}, H_{meta}, PPh₃, 5H), 7.75 (m, H_{meta}, H_{ortho}, PPh₃, 8H), 7.53 (m, H_{h,h'}, H_{i,i'}, H_j, 5H), 5.49 (q, H_f, ${}^{3}J = 6.4$ Hz, 1H), 2.04 (d, H_g, ${}^{3}J = 6.4$ Hz, 3H). ${}^{31}P$ {¹H} NMR (acetone-d₆, room temperature): δ 14.4 (br). ¹⁹F NMR (acetone-d₆): δ –80.0 (s).

2.4. Crystal structure determination

Suitable crystals for X-ray diffraction of $[Ag(k^2-(S)-(-)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)(C_6H_5)(PPh_3)_2](O_3SCF_3)$ (7) were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The crystal was mounted in inert oil on glass fibers and transferred to the cold gas stream of Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo K_{\alpha} radiation ($\lambda = 0.71073$ Å), scan type ω . Absorption corrections based on multiple scans were applied with the program SADABS [53]. The structure was refined on F^2 using the program SHELXL-97 [54]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details of the data collection and refinement are given in Table 1.

Table 1

Crystallographic data and information about data collection and refinement for 7.

Compound	7
Formula Formula weight T (K) Crystal system Space group	C ₅₂ H ₄₆ Ag F ₃ N ₂ O ₃ P ₂ S 1005.78 100(2) K Monoclinic P2(1)
Unit cell dimensions a (Å) b(Å) c (Å) α (°) β (°) γ (°)	15.158(3) 14.525(3) 22.028(4) 90 104.15(3) 90
V (Å ³) Z Density (calculated, Mg m ⁻³) μ (mm ⁻¹) F(000) Crystal size (mm ³) θ (°) Reflections:collected/independent R_{int}	$\begin{array}{c} 4702.8(16)\\ 4\\ 1.421\\ 0.598\\ 2064\\ 0.13\times0.11\times0.10\\ 4.08-25.00\\ 134246/16391\\ 0.0300\\ \end{array}$
Maximum and minimum transmission Data/restraints/parameters Goodness-of-fit on (GOF) on F^2 Absolute structure parameter wR (F^2 , all reflections) $R(I > 2\sigma(I))$ Maximum χ (e Å ⁻³)	0.9426, 0.9263 16391/4/1159 1.035 0.018(16) 0.0795 0.0338 1.352

3. Results and discussion

3.1. Synthesis and characterization of the Schiff bases

The Schiff bases are synthesized according to a general procedure that consists on the condensation of equimolar amounts of substituted aniline or amine and the respective substituted benzaldehyde, in the presence of magnesium sulfate as a dehydrating agent, in some cases. The synthesized Schiff bases were characterized by FT-IR, and one and two-dimensional NMR spectroscopy.

3.1.1. Monodentate achiral Schiff bases (L_1-L_3)

The monodentate ligands (L_1-L_3) are represented in the Fig. 1. The infrared spectra of the Schiff bases (L_1-L_3) show an intense band in the range of 1634.7–1638.6 cm⁻¹ corresponding to the $v_{(C=N)}$ vibrations [55,56]. The ¹H NMR spectra show two singlet resonances at the ranges 4.82–4.67 and 8.60–8.26 ppm [57–59] attributed to the iminic proton (H_d) and the methylene protons

Table 2 Correlation between hydrogen atoms with different carbon atoms (at two to three bonds). The coupling constants (${}^{1}J_{CH}$) are reported in the Section 2.

Schiff base	Carbon-proton atoms
L ₃	(C_7-H_d) – three bonds
	(C_4-H_d) – three bonds
	(C_5-H_d) – two bonds
	(C_2-H_c) – three bonds
	$(C_6-H_c \text{ and } H_e)$ – three bonds(both)
	(C_3-H_c) – two bonds
	(C_9-H_e) – three bonds
	(C_6-H_e) – three bonds
	(C_2-H_a) – two bonds
	$(C_{10}-H_h)$ – three bonds
	$(C_{11}-H_h)$ – two bonds
	(C_3-H_a) – three bonds

(He), respectively. The ligands L_2 and L_3 also exhibit a singlet at 3.00 ppm, assigned to the dimethylamino group. L_1 and L_3 show a signal at 2.30 ppm, assigned to the protons of the methyl group.

The ¹³C{¹H}, Dept., HSQC and HMBC spectra allow the assignment of most of the carbon atoms of the synthesized ligands. With the help of the HMBC experiment, the correlation between a hydrogen atom with the different carbon atoms (at two to three bonds) and their respective coupling constants may be studied. The HMBC spectrum of the ligand L_3 is shown in Table 2.

3.1.2. Bidentate achiral Schiff bases (L_4-L_6)

The Schiff bases L_4-L_6 (Fig. 1) are obtained as yellow oils from the reaction of 2-pyridinecarboxaldehyde with the respective substituted amines. Infrared spectra show a characteristic intense band in the range 1650.2–1638.1 cm⁻¹, which is attributed to the $v_{(C=N)im}$ vibrations, and a band in the range 1586.7–1603 cm⁻¹, assigned to the $v_{(C=N)py}$ vibrations [60,61]. The ¹H NMR [62–64], ¹³C{¹H}, Dept., HSQC and HMBC spectra allow the assignment of most of the different carbon atoms and their respective coupling constants (Section 2).

3.1.3. Bidentate chiral Schiff bases (L_7 -* C_S and L_8 -* C_S)

The ligands L_7 -* C_S and L_8 -* C_S (Fig. 1) are prepared by reaction between the respective aldehydes and optically pure (S)-(-)- α methylbenzylamine. They are obtained as orange oils. The FT-IR spectra exhibit characteristic intense bands at 1646.6 and 1647.0 cm⁻¹, respectively, due to the $v_{(C=N)}$ vibrations of the iminic (C=N) group. Another band at 1590.7 and 1586.7 cm⁻¹, respectively is assigned to the $v_{(C=N)py}$ vibrations of the pyridinic (C=N) group [79]. The ¹H NMR spectra are reported in the Experimental Section.

3.2. Synthesis and characterization of the silver(I) complexes (1–8) with achiral and chiral Schiff bases

Reaction of $[Ag(O_3SCF_3)(PPh_3)]$ with the corresponding Schiff base leads to the synthesis of complexes of stoichiometry $[Ag(\kappa^1-L)(PPh_3)_n](O_3SCF_3)$ (n = 1 or 2) (**1–8**), which were isolated as solids. Complexes **1–8** were characterized by FT-IR and one- (¹H, ¹³C{¹H}, ³¹P{¹H} or ¹⁹F) and two-dimensional NMR spectroscopy (¹H–¹H COSY, HSQC, HMBC or NOESY).[65–67]

The FT-IR spectra of complexes **1–8** include the characteristic bands of the triphenylphosphine (1092–1091, 745–744, 695–670, 571–540 and 501 cm⁻¹) and the triflate anion ($v_{sym(CF3)}$ = 1276–1267, $v_{asym(CF3)}$ = 1155–1143, $v_{sym(SO3)}$ = 1032–1031, $\delta_{(CF3)}$ = 638–637, 573–572 and 516–511 cm⁻¹) [68]. Also, the corresponding stretching vibrations $v_{(C=N)}$ of the iminic and/or pyridinic groups (**4–8**) of the Schiff free bases (**L**₁–**L**₈), modify their values due to the coordination to the metallic center. They appear in the range 1589–1605 or 1602–1646 cm⁻¹ (**4–8**), respectively.

3.2.1. Silver(I) complexes with monodentate achiral Schiff bases (1-3)

The reaction of $[Ag(O_3SCF_3)(PPh_3)]$ with the monodentate Schiff bases L_1-L_3 in molar ratio 1:1 leads to the cationic complexes $[Ag(\kappa^1-L)(PPh_3)_n](O_3SCF_3)$, where n = 1, $L = L_1$ (1); n = 2, $L = L_2$ (2) or L_3 (3), with one or two PPh₃ groups, in agreement with the ¹H NMR spectra.

The FT-IR spectra of the complexes (1-3) show the characteristic strong absorption of $v_{(C=N)im}$ at 1596.7, 1604.9 and 1596.9 cm⁻¹, respectively. These bands appear at lower energy than those for the corresponding free ligand (1638.3 (**L**₁), 1633.4 (**L**₂) and 1623.1 (**L**₃) cm⁻¹) [69,70]. This suggests that the iminic nitrogen (Schiff base) is coordinated to the silver(I). The ¹H NMR spectrum of complex **1** shows a singlet at







Fig. 3. The HMBC experiment of complex 3.

4.86 ppm attributed to the methylene protons (H_e). At low field it shows a singlet at 8.91 ppm, assigned to the iminic proton (H_d). The resonances of the protons H_d, H_{c,c}, and H_{f,f} and, H_{b,b'} and H_{g,g'}

present displacement to low field and strong displacement to high field, respectively, which indicates the coordination of the iminic nitrogen to the metallic center. Fig. 2 illustrates the ¹H NMR spectrum of complex **3**. It clearly shows the assignment of the different signals.

The singlet at 8.68 ppm in Fig. 2 is assigned to the iminic proton which is shifted to low field in comparison of the free ligand (8.29 ppm). The doublet attributed to $H_{c,c'}$ shifts slightly to low field, due to the coordination of the iminic nitrogen to silver.

The skeleton of the complexes can be drawn with the help of the HMBC experiment. The assignment of the majority of the carbon atoms and their respective coupling constants $({}^{1}J_{C}-_{H})$, are calculated. Due to the great number of phenyl carbon atoms of the triphenylphophines, a decrease of the sensitivity of some carbon atoms of the Schiff base should occur.

The HMBC spectrum of complex **3** (Fig. 3) shows a signal at higher field, at 23.0 ppm (${}^{1}J$ = 127.5 Hz), attributed to the C₁₂ carbon of the methyl group. It also shows a strong interaction between C_{10,10} and C₁₁ with the methyl proton (H_h), at three and two bonds, respectively. The spectrum shows the coupling of C₁ carbon (48.2 ppm) with the methyl protons of the dimethylamino group (H_a) (${}^{1}J$ = 137.3 Hz). The complete assignment of the carbon atoms and their respective coupling constants are shown in the Experimental Section.

3.2.2. Synthesis of the silver(1) complexes with bidentate achiral Schiff bases

The synthesis of the cationic complexes $[Ag(\kappa^2-L_n)(PPh_3)_2](O_3SCF_3)$ [$L_n = L_4$ (**4**), L_5 (**5**) or L_6 (**6**)] is carried out by reacting the precursor complex $[Ag(O_3SCF_3)(PPh_3)]$ with the respective Schiff base in 1:1 molar ratio (Eq. (1)).

$$X = H^{i}(\mathbf{4}); Cl(\mathbf{5}); {}^{12}CH^{i}_{3}(\mathbf{6})$$
(1)

The ¹H NMR spectra of complexes **4–6** show a singlet in the range 9.07–8.96 ppm, which is shifted to low field (average $\Delta \delta = 0.51$) with respect to the signals of the free ligands. It is also observed a doublet of doublets for complexes **4** and **5** that appear at 8.22 (${}^{3}J_{\text{HaHb}} = 7.2$, ${}^{4}J_{\text{HaHc}} = 1.6 \text{ Hz}$) and 8.07 ppm (${}^{3}J_{\text{HaHb}} = 7.6$, ${}^{4}J_{\text{HaHc}} = 0.8 \text{ Hz}$), respectively, assigned to the proton H_a of the pyridinic group. For complex **6** a doublet at 8.05 ppm (${}^{3}J = 7.6 \text{ Hz}$) is observed [71] (see Section 2).

As it was indicated previously, the low sensitivity shown by the carbon atoms of the Schiff bases in the complexes (¹³C{¹H} and 2D-HMBC NMR) is related to the presence of PPh₃ (ligand:triphenylphosphine = 1:2). Table 3 shows some of the coupling constants values (${}^{1}J_{CH}$ and ${}^{n}J_{PC}$, n = 1, 2, 3 or 4) for complexes **4–6**. The ${}^{13}C$ ¹H} NMR spectra of complexes **4–6** show the most characteristic signals. The spectra show two not resolved signals assigned to the carbons C_6 and C_1 , which appear in the range 161.7–165.0 and at 123.1-126.6 ppm, respectively. Moreover, the spectra show two doublets corresponding to the carbon atoms C_{meta} and C_{ortho} of the phenyl groups bonded to the phosphorus atom of the phosphine ligands, due to carbon-phosphorus coupling. The signals appear in the ranges 130.1–130.2 (${}^{3}J_{PC}$ = 12.3–19.3 Hz) and 134.4– 134.5 ppm (${}^{2}J_{PC}$ = 32.3–39.9 Hz), respectively. They also show a singlet in the range 131.7-131.8 ppm, assigned to the C_{para} carbon atoms of the triphenylphosphine.



Table 3

Coupling constants ${}^{1}J_{CH}$ and ${}^{n}J_{PC}$ in Hz (n = 1, 2, 3 or 4) from ${}^{13}C{}^{1}H$ and 2D NMR (HMBC) spectra for complexes **4–6**.

Compound	Assignment	¹ Jс н	ⁿ J _{P-C}
4	C _{meta}	163.3	$^{3}J = 12.3$
	C _{para}	159.9	⁴ J = Not resolved
	Cipso	-	$^{1}J = 55.4$
	Cortho	163.3	$^{2}J = 32.5$
5	C ₁₋ H _e	167.3	-
	C ₂₋ H _d	161.5	-
	C ₇₋ H _{f,f}	132.2	-
	C _{meta}	157.4	$^{3}J = 19.1$
	C _{para}	160.0	⁴ J = not resolved
	Cipso	-	$^{1}J = 52.8$
	C _{ortho}	Not resolved	$^{2}J = 39.9$
6	$C_{7}H_{f,f}$	137.8	_
	C ₁₂ -H _i	124.0	-
	C _{meta}	163.4	$^{3}J = 19.3$
	C _{para}	157.5	⁴ J = Not resolved
	Cipso	-	$^{1}J = 59.6$
	C _{ortho}	167.3	$^{2}J = 32.3$

3.2.3. Synthesis of the silver(I) complexes with bidentate chiral Schiff bases

The complex $[Ag(O_3SCF_3)(PPh_3)]$ reacts with $[(S)-(-)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)(C_6H_5)]$ (L_7-*C_S) or $S)-(-)-C_5H_4N-CHN-C*H(\alpha-CH_3)C_6H_5$ (L_8-*C_S), in a 1:1 M ratio, to give $[Ag(k^2-(S)-(-)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)(C_6H_5))(PPh_3)_2](O_3SCF_3)$ (7) or $[Ag\{k^2-(S)-(-)-C_5H_4N-CHN-C*H(\alpha-CH_3)C_6H_5\}(PPh_3)](O_3SCF_3)$ (8) (Scheme 1).

The ¹H NMR spectra show the iminic protons at 8.81 (d, ${}^{4}J_{HP} = 0.8 \text{ Hz})[67]$ and 9.45 (s) ppm, respectively for complexes **7** or **8**. They also show two doublets at 1.42 (**7**, ${}^{3}J_{HgHf} = 6.4 \text{ Hz}$) and 2.04 ppm (**8**, ${}^{3}J_{HgHf} = 6.4 \text{ Hz}$) for the methyl protons (H_g) and a quartet for the H_f protons at 4.84 (**7**, ${}^{3}J_{HfHg} = 6.4 \text{ Hz}$) and 5.49 ppm (**8**, ${}^{3}J_{HfHg} = 6.4 \text{ Hz}$) [65]. The ${}^{13}\text{C}{}^{1}\text{H}$ and HMBC NMR[72] show the resonances of C₄, C₅, C_{10,10'} and C_{11,11'} of the Schiff base at 137.9 (${}^{1}J = 164.6 \text{ Hz}$), 121.9 (${}^{1}J = 170.0 \text{ Hz}$), 128.6 (${}^{1}J = 164.6 \text{ Hz}$) and 127.0 (${}^{1}J = 162.4 \text{ Hz}$), respectively. Other resonances are reported in the Section 2.

The structure of complex **7** has been resolved by X-ray diffraction studies. Single crystals have been obtained by diffusion of



Scheme 1. Synthesis of complexes 7 and 8.



Fig. 4. The two independent cations of $[Ag((S)-(-)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)(C_6H_5))(PPh_3)_2](O_3SCF_3)$ (7) in the crystal showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

Table 4

Selected bond lengths (Å) and angles (°) for $[Ag(\kappa^2-(S)-(o-CH_3)C_5H_3N-CHN-C*H(CH_3)C_6H_5)(PPh_3)_2](O_3SCF_3)$ (7)[#].

Molecule A		Molecule B	
Bond lengths			
Ag(1)-N(1)	2.334(3)	Ag(2)-N(3)	2.435(4)
Ag(1)-P(1)	2.391(3)	Ag(2)-P(3)	2.5073(12)
Ag(1)-N(2)	2.4333(11)	Ag(2)-N(4)	2.378(4)
Ag(2)-P(2)	2.4730(11)	Ag(2)-P(4)	2.4805(11)
N(1)-C(1)	1.332(5)	N(3)-C(86)	1.323(6)
N(1)-C(6)	1.363(6)	N(3)-C(81)	1.352(5)
N(2)-C(7)	1.254(6)	N(4)-C(87)	1.275(6)
N(2)-C(8)	1.484(5)	N(4)-C(88)	1.487(5)
Bond angles			
P(1)-Ag(1)-P(2)	127.15(4)	P(3)-Ag(2)-P(4)	123.66(4)
N(1)-Ag(1)-N(2)	71.56(12)	N(4)-Ag(2)-N(3)	70.63(12)
P(2)-Ag(1)-N(2)	106.93(9)	P(3)-Ag(2)-N(3)	106.80(9)
P(1)-Ag(1)-N(1)	120.54(8)	P(4)-Ag(2)-N(4)	114.44(9)
P(1)-Ag(1)-N(2)	112.38(9)	P(3)-Ag(2)-N(4)	114.37(9)
P(2)-Ag(1)-N(1)	104.33(9)	P(4)-Ag(2)-N(3)	114.50(8)
Ag(1)-N(1)-C(6)	113.7(3)	Ag(2)-N(3)-C(86)	113.3(3)
Ag(1)-N(2)-C(7)	116.2(3)	Ag(2)-N(4)-C(87)	114.8(3)
Ag(1)-N(2)-C(8)	122.6(3)	Ag(2)-N(4)-C(88)	127.2(3)
N(1)-C(6)-C(7)	116.1(4)	N(3)-C(86)-C(87)	118.3(4)
N(2)-C(7)-C(6)	122.2(4)	N(4)-C(87)-C(86)	122.5(4)
N(2)-C(8)-C(9)	113.3(4)	N(3)-C(81)-C(83)	119.4(5)
C(7)-N(2)-C(8)	120.6(4)	C(87)-N(4)-C(88)	117.6(4)

[#] Two crystallographic independent molecules were observed in the asymmetric unit of **3**.

Table 5

Possible hydrogen bonds for complex 7 [Å and $^\circ\mbox{]}.$

D-H···A	d(D-H)	d(HA)	d(DA)	∠(DHA)
C(85)-H(85)O(1)	0.93	2.54	3.425(7)	158.7
$C(5)-H(5)\cdots O(5)$	0.93	2.51	3.339(8)	149.0
C(7)-H(7)···O(5)	0.93	2.43	3.274(6)	150.7
C(44)-H(44)···O(2)#1	0.93	2.52	3.426(6)	165.7
C(153)-H(153)····F(1)#2	0.93	2.51	3.184(5)	129.7
C(25)-H(25)···O(3)#3	0.93	2.55	3.293(8)	137.3
C(53)-H(53)···F(5)#4	0.93	2.47	3.182(6)	133.3

Symmetry transformations used to generate equivalent atoms:

#1 - x + 1, y - 1/2, -z + 1; #2x, y - 1, z #3 - x + 1, y + 1/2, -z + 1 #4 x, y + 1, z.

diethyl ether into a concentrated dichloromethane solution of the microcrystalline materials to give colorless crystals. A perspective view of the structure of the cation of complex **7** is shown in Fig. 4. In Table 4 there is a selection of bond lengths and angles.

Complex **7** crystallizes in the space group P2(1). The silver atom is coordinated to two phosphorous atoms of two triphenylphosphine ligands and two nitrogen atoms of the Schiff base, displaying a distorted tetrahedral geometry. The major distortion is due to the restricted bite angle of the dinitrogen ligand, which leads to N–Ag– N angles of 70.63(12) and 71.56(12)° (two molecules). Ag–P and Ag–N distances lie in the same range and compare well with those found in similar tetracoordinated silver complexes $[AgL(PPh_3)_2]^+$ with the bidentate ligands (L) (2-(4-dimethylaminophenyl)imidaza(4,5-f)(1,10)phenanthroline) [73] [Ag–N 2.414(3), 2.347(3); Ag– P 2.4608(12), 2.4488(12) Å] or 1,10-Phenanthroline-*N*,*N*' [Ag–N 2.357(1), 2.394(2); Ag–P 2.4694(6), 2.4028(5) Å] [74].

As expected, the configuration of the quiral carbon (S) of the Schiff-base (the same for the two molecules found in the unit cell) does not change upon coordination from that in the free ligand.

Possible C—H···O hydrogen bonds involving H—O distances from 2.55 to 2.43 Å and C—H···F hydrogen bonds involving H–F distances from 2.51 to 2.47 Å (**7**) (Table 5) lead to three dimensional arrays.

3.3. Conclusions

This work presents the synthesis of different silver complexes of the general formula $[Ag(k^1-L)(PPh_3)_n](O_3SCF_3)$ (n = 1 or 2) by reaction of $[Ag(O_3SCF_3)(PPh_3)]$ with mono and bidentate Schiff-bases (L). An exhaustive study with ${}^{13}C{}^{1}H$, ${}^{31}P{}^{1}H$ or ${}^{19}F$ NMR and two-dimensional experiments (${}^{1}H{}^{-1}H$ COSY, HSQC, HMBC or NOESY) has lead to the assignation of the signals to the corresponding carbon or hydrogen atoms in the complexes and ligands. The crystal structure of $[Ag{(S)-(6-CH_3)C_5H_3N-CHN-C*H(\alpha-CH_3)C_6H_5}(PPh_3)_2](O_3SCF_3)$ confirms the tetracoordination of the silver center.

Supplementary material

CCDC 809215 (7) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via "http://www.ccdc. cam.ac.uk/data_request/cif".

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