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Synthesis, spectroscopy and structural characterization of silver(I) complexes containing unidentate N-donor azole-type ligands

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Abstract

From the interaction between azole-type ligands L and AgX (X = NO_3 or ClO_4) or $[AgX(PPh_3)_n]$ (X = Cl, $n = 3$; X = $MeSO_3$, $n = 2$), new ionic mononuclear $[Ag(L)_2]X$ and $[Ag(PPh_3)_3L][X]$ or neutral mono-($[Ag(PPh_3)_nL(X)]$) or di-nuclear ($[\{Ag(PPh_3)(L)(\mu\text{-}X)\}_2]$) complexes have been obtained which have been characterized through elemental analysis, conductivity measurements, IR, ^1H NMR and, in some cases, also by $^{31}P\{^1H\}$ NMR spectroscopy, and single-crystal X-ray studies. Stoichiometries and molecular structures are dependent on the nature of the azole (steric hindrance and basicity), of the counter ion, and on the number of the P-donor ligands in the starting reactants. Solution data are consistent with partial dissociation of the complexes, occurring through breaking of both Ag–N and Ag–P bonds.

Keywords: Azole; Silver; Phosphine; X-ray

1. Introduction

There has been a growing contemporary interest in the coordination chemistry of silver(I) derivatives containing azole ligands, due to potential applications in photography or silver-plating by electrochemical processes [1–4]. Some of them also display antimicrobial and anticancer activity [5–7], and macrocyclic silver(I) compounds undergo very slow acid-dependent decomplexation and therefore may be useful for ^{111}Ag-based radioimmunotherapy [8,9].

As a continuation of our previous studies on the structural and spectroscopic properties of mixed phosphine/N-donor derivatives of silver(I) [10], we have synthesized some new silver(I) complexes containing azole-type ligands (imH = imidazole, imb = 1-benzylimidazole, imet = 2-ethylimidazole, meim = 1-methylimidazole, imme = 2-methylimidazole, imph = 4-phenylimidazole, bzim = benzoimidazole, pzH = pyrazole, mpz = 3-methylpyrazole, dmpz = 3,5-dimethylpyrazole, and tzH = triazole), characterizing a representative array by X-ray diffraction studies and spectroscopic and analytical measurements.

2. Experimental

2.1. Materials and methods

Solvents were used as supplied or distilled using standard methods. All chemicals were purchased from Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried in vacuum to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points are uncorrected

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and were measured on an SMP3 Stuart Scientific Instrument, and on a capillary apparatus. IR spectra were recorded from 4000 to 200 cm^{-1} using a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H and ^{31}P NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H and 121.4 MHz for ^{31}P) and on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for ^{1}H, 162.1 MHz for ^{31}P). Proton chemical shifts are reported in ppm versus Me_4Si while phosphorus chemical shifts are reported in ppm versus 85% H_3PO_4. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. The electrical conductances (Λ_M, reported as $\Omega^{-1}\,cm^2\,mol^{-1}$) of acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

2.2. Syntheses

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

The precursor $AgCl(PPh_3)_3$ was synthesized by the procedures previously reported [11]. The precursor $Ag(SO_3Me)(PPh_3)_2\cdot H_2O$ was prepared as follows: to an ethanol solution (30 ml) of PPh_3 (0.524 g, 2 mmol), $AgSO_3Me$ (0.203 g, 1 mmol) was added. The clear solution was refluxed for 2 h, then cooled and left overnight to evaporate. Upon addition of diethyl ether (10 ml), a colorless precipitate deposited, which was filtered off, washed with diethyl ether (5 ml) and dried to constant weight. Yield: 75%. *Anal.* Calc. for $C_{37}H_{35}AgO_4P_2S$: C, 59.61; H, 4.73; S, 4.30. Found: C, 59.95; H, 4.94; S, 4.08%. IR (nujol, cm^{-1}): 3340br ν(O–H···O), 1666m δ(O–H···O), 1172s, 1164s $\nu(SO_3Me)$, 516s, 502s, 492s ν(*y*-mode of PPh_3), 446m, 435m ν(*t*-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ, 1.8s br (2H, H_2O), 2.54s (3H, SO_3CH_3), 7.25–7.55m (30H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 10.5s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 9.8 (dd, $^{1}J(^{109}Ag–^{31}P)$: 539 Hz, $^{1}J(^{107}Ag–^{31}P)$: 467 Hz).

2.2.1. Synthesis of $[Ag(imH)_2](NO_3)$ (1)

Derivative **1** has been prepared by a procedure similar to that previously reported [12,13]. It was re-crystallized from hot chloroform. Analytical and spectral data are consistent with those reported in the literature [12,13].

2.2.2. Synthesis of $[Ag(imb)_2](ClO_4)$ (2)

1-Benzylimidazole (imb) (0.312 g, 2 mmol) was added to a solution of $AgClO_4$ (0.207 g, 1 mmol) in ethanol (20 ml). A colorless precipitate immediately formed, which was filtered off, washed with Et_2O (10 ml) and shown to be compound **2** (yield 76%). It was re-crystallized from acetonitrile. Compound **2** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 180 °C dec. Λ_M (acetonitrile, 10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$): 134.8. *Anal.* Calc. for $C_{20}H_{20}AgClN_4O_4$: C, 45.87; H, 3.85; N, 10.70. Found: C, 45.28; H, 3.92; N, 10.43%. IR (nujol, cm^{-1}): 3148w, 3123m $\nu(C_{arom}–H)$, 1519sbr ν(C=C + C=N), 1090vs br, 622s $\nu(ClO_4)$. ^{1}H NMR ($CDCl_3$): δ, 5.16s (3H, $NCH_2C_6H_5$), 6.94s, 7.09s (2H, $H_{4imb} + H_{5imb}$), 7.24t, 7.35t, 7.79d (5H, $NCH_2C_6H_5$), 8.21s (1H, H_{2imb}).

2.2.3. Synthesis of $[AgCl(imH)(PPh_3)_2]$ (3)

Imidazole (imH) (0.136 g, 2 mmol) was added to a suspension of $AgCl(PPh_3)_3$ (0.465 g, 1/2 mmol) in diethyl ether (30 ml). The suspension was allowed to stir at room temperature for 24 h, and the precipitate then filtered off, washed with Et_2O (10 ml) and shown to be compound **3** (yield 85%). It was re-crystallized from $CHCl_3$. Compound **3** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 209–211 °C. Λ_M (acetonitrile, 10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5.4. *Anal.* Calc. for $C_{39}H_{34}AgClN_2P_2$: C, 63.65; H, 4.66; N, 3.81. Found: C, 63.88; H, 4.84; N, 4.01%. IR (nujol, cm^{-1}): 3120br ν(N–H), 3068w $\nu(C_{arom}–H)$, 1521sbr ν(C=C + C=N), 515s, 502s, 493s ν(*y*-mode of PPh_3), 440m, 427m ν(*t*-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ, 6.10br (1H, N–H_{imH}), 7.05s (2H, $H_{4imH} + H_{5imH}$), 7.20–7.50m (30H, CH_{arom}), 7.69s (1H, H_{2imH}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 10.8s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 12.5 (d br, $^{1}J(Ag–^{31}P)$: 721 Hz), 7.4 (d br, $^{1}J(Ag–^{31}P)$: 448 Hz).

2.2.4. Synthesis of $[AgCl(imet)(PPh_3)_2]$ (4)

2-Ethylimidazole (imet) (0.192 g, 2 mmol) was added to a suspension of $AgCl(PPh_3)_3$ (0.465 g, 1/2 mmol) in diethyl ether (30 ml). The suspension was allowed to stir at room temperature for 24 h, and the precipitate then filtered off, washed with Et_2O (10 ml) and shown to be compound **4** (yield 88%) which was re-crystallised from $CHCl_3$. Compound **4** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 181–184 °C. Λ_M (acetonitrile, 10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$): 7.1. *Anal.* Calc. for $C_{41}H_{38}AgClN_2P_2$: C, 64.45; H, 5.01; N, 3.67. Found: C, 64.67; H, 5.13; N, 3.39%. IR (nujol, cm^{-1}): 3123br ν(N–H), 3074w $\nu(C_{arom}–H)$, 1520sbr ν(C=C + C=N), 511s, 500s, 494s ν(*y*-mode of PPh_3), 437m, 426m ν(*t*-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ, 1.26t, 2.75q (5H, $CH_{2imet} + CH_{3imet}$), 5.50br (1H, NH_{imet}), 6.88s (2H, $H_{4imet} + H_{5imet}$), 7.18–7.45m (30H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 6.1s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 7.2 (d br, $^{1}J(Ag–^{31}P)$: 431 Hz), 3.1 (d br, $^{1}J(Ag–^{31}P)$: 310 Hz).

2.2.5. Synthesis of $[AgCl(imme)(PPh_3)_2]$ (5)

Derivative **5** was prepared similarly as that for **4** but using 2-methylimidazole (imme). Compound **5** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. Yield: 74%. M.p. 202–203 °C. Λ_M (acetonitrile, 10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5.4. *Anal.* Calc. for $C_{40}H_{36}AgClN_2P_2$: C, 64.06; H, 4.84; N, 3.74. Found: C, 63.55; H, 4.98; N, 3.65%. IR (nujol, cm^{-1}): 3120br ν(N–H), 3065w $\nu(C_{arom}–H)$, 1583m, 1556m ν(C=C + C=N), 511s, 504s, 494s ν(*y*-mode of PPh_3), 437m, 426m ν(*t*-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ, 2.34s (3H, CH_{3imme}), 3.70br (1H, N–H_{imme}),

6.93s (2H, H_{4imme} and H_{5imme}), 7.25–7.45m (30H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 10.3s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 11.5 (d br, ^{1}J(Ag–^{31}P): 625 Hz), 7.3 (d br, ^{1}J(Ag–^{31}P): 422 Hz).

2.2.6. Synthesis of [Ag(imph)(PPh$_3$)$_3$]Cl (6)

Derivative **6** was prepared similarly as that for **4** but using 4-phenylimidazole (impH). Compound **6** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. Yield: 94%. M.p. 174–176 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 151.6. *Anal.* Calc. for $C_{63}H_{53}AgClN_2P_3$: C, 70.43; H, 4.97; N, 2.61. Found: C, 69.88; H, 5.16; N, 2.90%. IR (nujol, cm^{-1}): 3115m ν(N–H), 3071w ν(C$_{arom}$–H), 1583br ν(C=C + C=N), 513s, 499s, 494s ν(*y*-mode of PPh$_3$), 440m, 417w ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 4.70br (1H, NH_{imph}), 7.15s (2H, $H_{4imH} + H_{5imH}$), 7.20–7.45m, 7.62t, 7.70d (50H, CH_{arom} + CH$_{imH}$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 6.6s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 6.4 (d br, ^{1}J(Ag–^{31}P): 345 Hz).

2.2.7. Synthesis of [AgCl(meim)(PPh$_3$)] (7)

Derivative **7** was prepared by the same procedure as that reported for **4** but using 1-methylimidazole (meim). Compound **7** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. Yield: 63%. M.p. 163–167 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 4.8. *Anal.* Calc. for $C_{22}H_{21}AgClN_2P$: C, 54.18; H, 4.34; N, 5.74. Found: C, 53.98; H, 4.50; N, 5.62%. IR (nujol, cm^{-1}): 3065w ν(C$_{arom}$–H), 1546m, 1526m ν(C=C + C=N), 513s, 499s ν(*y*-mode of PPh$_3$), 431m ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 2.21s (3H, N–CH_{3meim}), 6.89s, 7.03s (2H, $H_{4meim} + H_{5meim}$), 7.25–7.50m (15H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 10.0s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 12.0 (d br, ^{1}J(Ag–^{31}P): 650 Hz), 7.4 (d br, ^{1}J(Ag–^{31}P): 444 Hz).

2.2.8. Synthesis of [Ag(bzim)$_3$(PPh$_3$)]Cl (8)

Derivative **8** was prepared similarly as that for **4** but using benzimidazole. Compound **8** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. Yield: 45%. M.p. 179–183 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1}cm^2 mol^{-1}): 148.0. *Anal.* Calc. for $C_{39}H_{33}AgClN_6P$: C, 61.63; H, 4.38; N, 11.06. Found: C, 61.32; H, 4.51; N, 10.68%. IR (nujol, cm^{-1}): 3110m ν(N–H), 3064w ν(C$_{arom}$–H), 1585m ν(C=C + C=N), 519s, 506s, 492s ν(*y*-mode of PPh$_3$), 443m, 424m ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 4.50br (3H, NH_{bzim}), 7.15–7.45m, 7.60m (27H, CH_{arom} + CH_{bzim}), 8.15s (3H, H_{2bzim}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 12.0s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 12.8 (dd, $^{1}J(^{109}Ag–^{31}P)$: 658 Hz, $^{1}J(^{107}Ag–^{31}P)$: 573 Hz), 7.1 (dbr, ^{1}J(Ag–^{31}P): 402 Hz).

2.2.9. Synthesis of [Ag(MeSO$_3$)(pzH)(PPh$_3$)$_2$] (9)

Pyrazole (pzH) (0.068 g, 1 mmol) was added to a suspension of $AgSO_3Me(PPh_3)_3 \cdot H_2O$ (0.746 g, 1 mmol) in diethyl ether (30 ml). The suspension was allowed to stir at room temperature for 24 h, and the precipitate then filtered off, washed with Et_2O (10 ml) and shown to be compound **9** which is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. Yield: 88%. M.p. 168–170 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 18.4. *Anal.* Calc. for $C_{40}H_{37}AgN_2O_3P_2S$: C, 60.39; H, 4.69; N, 3.52; S, 4.03. Found: C, 60.85; H, 4.92; N, 3.59; S, 4.24%. IR (nujol, cm^{-1}): 3180br ν(N–H), 3073w ν(C$_{arom}$–H), 1586m ν(C=C + C=N), 1166s, 1161s, 1154s ν(SO$_3$CH$_3$), 534m, 519s, 508s, 486s ν(*y*-mode of PPh$_3$), 434m, 428m, 417m ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 2.55s (3H, SO$_3$CH_3), 6.29br (1H, H_{4pzH}), 7.25–7.45m (30H, CH_{arom} of PPh$_3$) 7.55br (2H, $H_{3pzH} + H_{5pzH}$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 8.7s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 7.9 (dd, $^{1}J(^{109}Ag–^{31}P)$: 475 Hz, $^{1}J(^{107}Ag–^{31}P)$: 417 Hz).

2.2.10. Synthesis of [Ag(MeSO$_3$)(mpz)(PPh$_3$)$_2$] (10)

Derivative **10** was prepared similarly as that for **9**in 78% yield. It was re-crystallized from $CHCl_3$. Compound **10** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 168–171 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 16.6. *Anal.* Calc. for $C_{41}H_{39}AgN_2O_3P_2S$: C, 60.82; H, 4.86; N, 3.46; S, 3.96. Found: C, 60.32; H, 4.98; N, 3.46; S, 3.89%. IR (nujol, cm^{-1}): 3300br ν(N–H), 3103w, 3078w ν(C$_{arom}$–H), 1582m ν(C=C + C=N), 1166s, 1157s ν(SO$_3$CH$_3$), 528s, 512s, 507s, 492s ν(*y*-mode of PPh$_3$), 441m, 426m ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 2.20s (3H, CH_{3mpz}), 2.54s (3H, SO$_3$CH_3), 6.05br (2H, $H_{4mpz} + H_{5mpz}$), 7.25–7.45m (30H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 8.4s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 13.9 (d br, ^{1}J(Ag–^{31}P): 597 Hz), 7.8 (d br, ^{1}J(Ag–^{31}P): 445 Hz).

2.2.11. Synthesis of [Ag(MeSO$_3$)(dmpz)(PPh$_3$)$_2$] (11)

Derivative **11** was prepared similarly as that for **9** in 73% yield. Compound **9** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 167–170 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 21.0. *Anal.* Calc. for $C_{42}H_{41}AgN_2O_3P_2S$: C, 61.25; H, 5.02; N, 3.40; S, 3.89. Found: C, 60.86; H, 5.15; N, 3.42; S, 4.13%. IR (nujol, cm^{-1}): 3350br ν(N–H), 3106w, 3066w ν(C$_{arom}$–H), 1583m ν(C=C + C=N), 1172s, 1164s ν(SO$_3$CH$_3$), 515sbr, 504s, 493s ν(*y*-mode of PPh$_3$), 439m, 421w ν(*t*-mode of PPh$_3$). ^{1}H NMR ($CDCl_3$): δ, 2.15s (6H, CH_{3dmpz}), 2.54s (3H, SO$_3$CH_3), 5.00br (1H, NH_{dmpz}), 5.82br (1H, H_{4dmpz}), 7.25–7.40m (30H, CH_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ, 7.8s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ, 7.1 (dd, $^{1}J(^{109}Ag–^{31}P)$: 495Hz, $^{1}J(^{107}Ag–^{31}P)$: 432 Hz), 5.6 (d br, ^{1}J(Ag–^{31}P): 235 Hz).

2.2.12. Synthesis of [Ag(MeSO$_3$)(tzH)(PPh$_3$)$_2$] (12)

Derivative **12** was prepared similarly as that for **9** in 64% yield. Compound **12** is soluble in DMSO, acetonitrile, acetone and chlorinated solvent. M.p. 175–177 °C. Λ_M (acetonitrile, 10^{-3} M, Ω^{-1} cm^2 mol^{-1}): 24.3. *Anal.* Calc. for $C_{39}H_{36}AgN_3O_3P_2S$: C, 58.80; H, 4.56; N, 5.27; S, 4.02. Found: C, 58.47; H, 4.71; N, 5.02; S, 4.03%. IR (nujol, cm^{-1}): 3200br ν(N–H), 1575w ν(C=C + C=N), 1170s,

1165s $\nu(SO_3CH_3)$, 536m, 516s, 505s, 492s, 483s ν(*y*-mode of PPh_3), 436m, 424m ν(*t*-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ, 2.58s (3H, SO_3CH_3), 7.25–7.45m (30H, CH_{arom}), 8.04br (1H, $H_{3tzH} + H_{5tzH}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ, 10.0s. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ, 9.8 (d br, $^1J(Ag–^{31}P)$: 463 Hz), 7.9 (d br, $^1J(Ag–^{31}P)$: 317 Hz).

2.3. Structure determinations

For **3** and **4**, unique room-temperature single-counter data sets were measured (T ca. 295 K; $2\theta/\theta$ scan mode, $2\theta_{max} = 50°$), Gaussian absorption corrections being applied; for **1**, **2**, and **10** full spheres of CCD area-detector diffractometer data sets were measured (Bruker AXS instrument, monochromatic Mo Kα radiation ($\lambda = 0.7107_3$ Å), ω-scans; T ca. 300 K for **10**, 153 K for **1** and **2**), yielding $N_{t(otal)}$ reflections, these merging to N unique after 'empirical'/multiscan absorption correction (proprietary software; R_{int} cited), N_o with $F > 4\sigma(F)$ [$I > 3\sigma(I)$] for the single-counter determinations) being considered 'observed' and used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values unless otherwise stated. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$) are cited at convergence. Neutral atom complex scattering factors were employed within various versions of the Xtal program system [14]. Pertinent results are given below and in the tables and figures, the latter showing 20% (room-temperature) or 50% (153 K) probability amplitude displacement envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedure (etc.) are noted as 'variata'.

2.4. Crystal/refinement data

2.4.1. $[Ag(imH)_2](NO_3)$ (**1**) ≡ $C_6H_8AgN_5O_3$, $M = 306.0$

Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 10.929(1)$ Å, $b = 17.535(2)$ Å, $c = 5.0062(5)$ Å, $V = 959.4$ Å^3. D_{calc} ($Z = 4$) $= 2.11_8$ g cm^{-3}. $\mu_{Mo} = 21$ cm^{-1}; specimen: $0.15 \times 0.12 \times 0.08$ mm; 'T'$_{min/max} = 0.77$. $2\theta_{max} = 75°$; $N_t = 19\,101$, $N = 2847$ ($R_{int} = 0.024$), $N_o = 2690$; $R = 0.021$; $R_w = 0.026$ ($n_w = 4$); $x_{abs} = -0.01(3)$. $|\Delta\rho_{max}| = 1.14(6)$ e Å^{-3}. $(x, y, z, U_{iso})_H$ refined. Comment. This compound has been the subject of early room-temperature studies [11,12], the setting of the former being employed (as its inverse).

2.4.2. $[Ag(imb)_2](ClO_4)$ (**2**) ≡ $C_{20}H_{20}AgClN_4O_4$, $M = 523.8$

Monoclinic, space group $C2$ (C_2^3, No. 5), $a = 23.807(3)$ Å, $b = 7.8495(9)$ Å, $c = 5.6352(6)$ Å, $\beta = 98.545(2)°$, $V = 1041$ Å^3. D_{calc} ($Z = 2$) $= 1.67_0$ g cm^{-3}. $\mu_{Mo} = 11.3$ cm^{-1}; specimen: $0.40 \times 0.25 \times 0.04$ mm; 'T'$_{min/max} = 0.70$. $2\theta_{max} = 55°$; $N_t = 4977$, $N = 1210$ ($R_{int} = 0.020$), $N_o = 1210$; $R = 0.017$; $R_w = 0.022$ ($n_w = 9$); $x_{abs} = 0.01(2)$. $|\Delta\rho_{max}| = 0.44(2)$ e Å^{-3}.

Variata. The perchlorate chlorine lies close to a crystallographic *2*-axis (Cl···Cl 0.509(3) Å), about which the anion was modeled as disordered.

2.4.3. $[AgCl(imH)(PPh_3)_2]$ (**3**) ≡ $C_{39}H_{24}AgClN_2P_2$, $M = 736.0$

Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 13.467(2)$ Å, $b = 12.216(2)$ Å, $c = 23.555(2)$ Å, $\beta = 115.99(1)°$, $V = 3483$ Å^3. $D_{calc} = 1.40_3$ g cm^{-3}. $\mu_{Mo} = 7.8$ cm^{-1}; specimen: $0.20 \times 0.21 \times 0.19$ mm; 'T'$_{min,max} = 0.66, 0.83$. $2\theta_{max} = 50°$; $N = 6115$, $N_o = 3852$; $R = 0.037$; $R_w = 0.036$ ($n_w = 9$). $|\Delta\rho_{max}| = 0.41(3)$ e Å^{-3}. $(x, y, z, U_{iso})_H$ refined.

2.4.4. $[AgCl(imet)(PPh_3)_2]$ (**4**) ≡ $C_{41}H_{38}AgClN_2P_2$, $M = 764.1$

Monoclinic, space group $P2_1/c$, $a = 14.220(3)$ Å, $b = 12.285(7)$ Å, $c = 23.875(5)$ Å, $\beta = 118.71(2)°$, $V = 3658$ Å^3. D_{calc} ($Z = 4$) $= 1.38_7$ g cm^{-3}. $\mu_{Mo} = 7.4$ cm^{-1}; specimen: $0.16 \times 0.17 \times 0.29$ mm; 'T'$_{min,max} = 0.79, 0.90$. $2\theta_{max} = 50°$; $N = 5729$, $N_o = 2988$; $R = 0.061$; $R_w = 0.062$ ($n_w = 4$). $|\Delta\rho_{max}| = 1.20(2)$ e Å^{-3}.

Comment. Displacement parameters at the periphery of the pendant substituent ethyl group were elevated, but no disorder was resolvable.

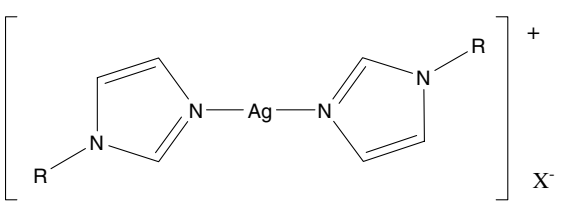
2.4.5. $[Ag(MeSO_2O)(mpz)(PPh_3)_2]$ (**10**) ≡ $C_{41}H_{39}AgNO_3P_2S$, $M = 809.7$

Monoclinic, space group $P2_1/c$, $a = 13.364(1)$ Å, $b = 14.961(1)$ Å, $c = 19.986(2)$ Å, $\beta = 100.218(1)°$, $V = 3933$ Å^3. D_{calc} ($Z = 4$) $= 1.36_7$ g cm^{-3}. $\mu_{Mo} = 6.9$ cm^{-1}; specimen: $0.72 \times 0.35 \times 0.14$ mm; 'T'$_{min/max} = 0.78$. $2\theta_{max} = 58°$; $N_t = 45\,684$, $N = 9926$ ($R_{int} = 0.024$), $N_o = 6422$; $R = 0.036$; $R_w = 0.039$ ($n_w = 4$). $|\Delta\rho_{max}| = 0.80(2)$ e Å^{-3}.

3. Results and discussion

3.1. Syntheses

From the reaction of an equivalent of AgX (X = NO_3 or ClO_4) with two equivalents of imH or imb in ethanol, derivatives **1** and **2** (Fig. 1) have been obtained, respectively. The analytical and spectroscopic data confirm the stoichiometry proposed and conductance measurements



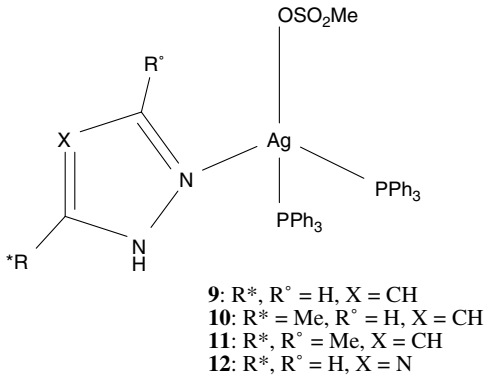
1: X = NO_3, R = H
2: X = ClO_4, R = Bn

Fig. 1. Molecular structures of derivatives **1** and **2**.

carried out in acetonitrile indicate 1:1 ionic compounds [15].

The interaction of $AgCl(PPh_3)_3$ [11] with excesses of several azoles L (L = imH, imet, imme, imph, meim, bzim) with different electronic and steric features, in diethyl ether, has yielded derivatives **3**–**8** (Fig. 2). They show different stoichiometries, ranging from neutral types $[AgCl(L)(PPh_3)_2]$ (compounds **3**–**5**) and $[AgCl(L)(PPh_3)]$ (**7**) to the species $Ag(L)(PPh_3)_3Cl$ (**6**) and $Ag(L)_3(PPh_3)Cl$ (**8**), which probably are ionic both in the solid and in the solution state, the conductance measurements for the latter derivatives clearly indicating the existence in acetonitrile solution of 1:1 electrolytes [15]. The differences in the number of phosphines replaced in the silver environment by azole ligands appear to be mainly consequent on the steric hindrance of the azole substituents.

Finally, the interaction between equivalents of $Ag(SO_3Me)(PPh_3)_2 \cdot H_2O$ and various pyrazoles (pzH, mpz, dmpz) or triazole (tzH) in diethyl ether afforded the compounds **9**–**12**, all characterized with the same stoichiometry $[Ag(L)(PPh_3)_2(MeSO_2O)]$ (Fig. 3).



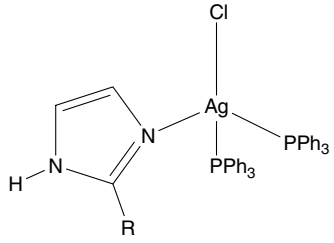
9: R*, R° = H, X = CH
10: R* = Me, R° = H, X = CH
11: R*, R° = Me, X = CH
12: R*, R° = H, X = N

Fig. 3. Molecular structures of derivatives **9**–**12**.

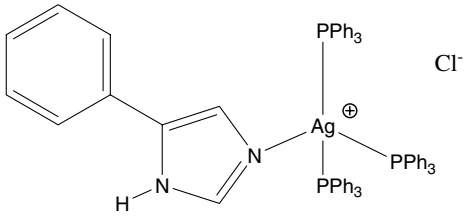
3.2. Spectroscopic characterization

The IR spectra of **1**–**12** show the expected medium to weak absorption bands in the range 1550–1600 cm^{-1} due to the breathing of the azole rings, the bands up to 3100 cm^{-1} for the N–H generally broad, indicative of the presence of extensive H-bonding networks and, for **3**–**12**, also the *y*-mode and *t*-mode of PPh_3 below 600 cm^{-1} [16]. In the IR spectra of derivatives **9**–**12**, containing the SO_3Me group, absorptions in the 1100–1200 cm^{-1} region confirm the presence of co-ordinated methanesulfonate groups [17].

The ^1H spectra of derivatives **1**–**12** have been recorded in deuterochloroform, the resonances and relative integrations further confirming the stoichiometries proposed for **1**–**12**. The signals of the azole donors are displaced to lower fields, an evidence of the existence of complexation in solution, reflecting the changes in the electron density and in π-electron circulation about the heterocyclic ring. In fact, a σ-charge donation from the N-donor ligand to the metal centre removes electron density from the ligand, producing



3: R = H
4: R =Et
5: R = Me



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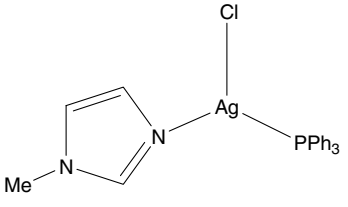

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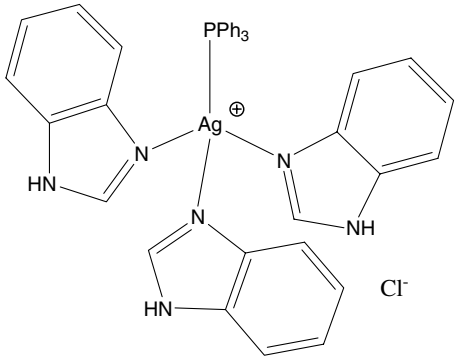

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Fig. 2. Molecular structures of derivatives **3**–**8**.

a deshielding which should attenuate at positions remote from the ligand.

Except for derivatives **2** and **7**, containing 1-substituted imidazoles, and derivative **12** containing triazole, all others exhibit only one broad resonance instead of the two expected for the protons in the 4 and 5 positions of the imidazole ligands and in the 3 and 5 positions of the pyrazoles, in consequence of the fluxional behavior of these compounds in solution, requiring a concomitant prototropy and metallotropy of the ligand [18–20].

The solution ^{31}P NMR spectra of derivatives **3**–**12** at room temperature consist of a broad or narrow singlet, presumably because of the presence of rapid exchange equilibria. On cooling the samples at −55 °C, the single resonances split into one or two double doublets, from which it is possible to determine the $^{1}J(^{109}Ag–^{31}P)$ and $^{1}J(^{107}Ag–^{31}P)$ coupling constants. They are mainly determined by the broad orbital overlap between Ag and P on the basis of the Fermi contact term [21] and can be related to the number of coordinated phosphines and covalent versus ionic character of Ag–P bonds [22]. Derivatives $[AgCl(imH)(PPh_3)_2]$ (**3**) and $[AgCl(imme)(PPh_3)_2]$ (**5**) undergo partial phosphine dissociation in solution, since two resonances have been detected at low temperature, one at lower fields having ^{1}J(Ag–P) values higher than 600 Hz (typical of compounds containing only one phosphine bonded to silver), whereas the second one at higher fields with ^{1}J(Ag–P) values in the range 300–500 Hz indicates the presence of two phosphines bonded to silver. Also, in the ^{31}P NMR spectra of derivatives $[AgCl(meim)(PPh_3)]$ (**7**) and $[Ag(bzim)_3(PPh_3)]Cl$ (**8**), two different resonances have been detected, explicable in terms of partial dissociation of the azole donor(s) and formation of an sp-hybridized ClAgP species. Finally, derivatives **9**–**12**, containing coordinated SO_3CH_3 groups show one or two resonances with ^{1}J(Ag–P) values in the range 300–500 Hz, in accordance with two PPh_3 ligands bonded to silver, except for the derivative $[Ag(MeSO_3)(dmpz)(PPh_3)_2]$ (**11**) which shows a resonance with a ^{1}J(Ag–P) value of 235 Hz, typical of species containing three or four PPh_3 bonded to silver, as a consequence of phosphine redistribution between a pair of metal centres in solution.

3.3. X-ray structural investigation

The results of the single-crystal X-ray studies of complexes **1**–**4** and **10** are consistent in terms of stoichiometry and connectivity with the expected formulations. In all except **2**, one formula unit, devoid of solvent, comprises the asymmetric unit of the structures; in **2**, both complex cation and anion lie on, or close to, crystallographic 2-axes, one-half of each comprising the asymmetric unit of the structure. Compounds **3** and **4** are neutral molecules; in **1**, **2**, and **10**, the associations of the anions with the metal are more tenuous, and the nature of the compounds more 'ionic'.

The structure of $AgNO_3$:imH (1:2) has been the subject of earlier room-temperature studies [12,13], the essential features of which are confirmed in the present more precise low-temperature study. Ag–N are 2.115(2), 2.120(2) Å,

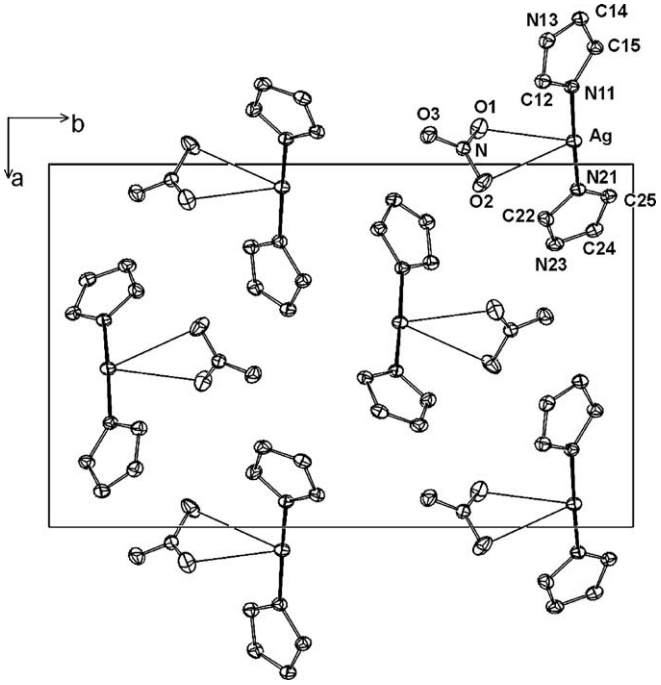

Fig. 4. Unit cell contents of **1**, projected down *c*.

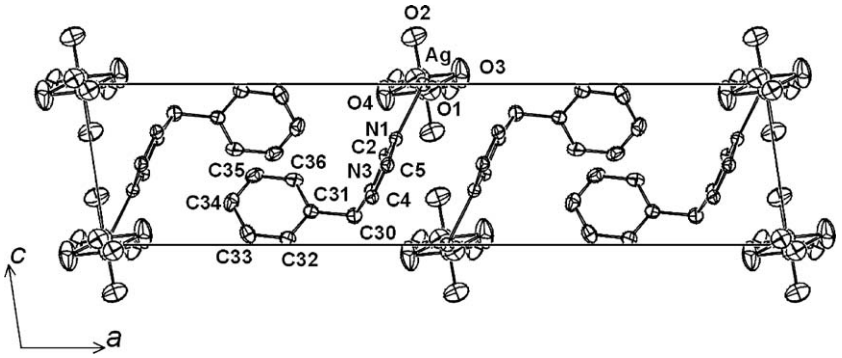

Fig. 5. Unit cell contents of **2**, projected down *b*.

with N–Ag–N 172.78(8)° reflecting the rather distant nitrate approach as a chelate Ag–O 2.945(2), 3.129(2) Å (Fig. 4), the latter impacting somewhat on the associated N–O distances 1.256(3), 1.257(3) Å which are slightly longer than the other non-interacting O–N 1.241(3) Å; the angle opposite the latter is 118.6(2)° with the other pair 120.7(2)°, 120.6(2)°. The imidazole hydrogen has no close contacts. Ag lies 1.745(3) Å out of the NO_3 plane and 0.130(4) Å from the C_3N_2 plane. In **2**, the imidazole hydrogen is replaced by a benzyl group, the cation lying with the silver disposed on a crystallographic 2-axis, with Ag–N 2.131(2) Å and N–Ag–N 170.7(1)°, perchlorate (disordered) oxygens O(1,3) approaching from either side (see Fig. 5) at distances 2.946(5), 2.873(8) Å. Ag lies 0.101(6) Å out of the C_3N_2 plane. Comparative geometries are listed for the parent imH, imH bonded to Ag and, as well, substituted at the 3-position by CH_2Ph in Table 1. Ag–N distances in both are generally comparable with those obtained in a broad array of NAgN pyridine (='py') aromatic heterocycle base donor complexes [23]; also of interest is the comparison with the geometry of $[(Ph_3P)_2Ag(2\text{-meim})_2]^+$ (in the nitrate) [10g], where, in a four-coordinate environment, Ag–N are 2.348(2) (x2); Ag–P 2.4704(6) (x2) Å.

Table 1
Comparative imidazole geometries

System	imH[a]	(Ag) imH (**1**; imH 1, 2)	(Ag)(imb) (**2**)[b]
Distances (Å)			
N(1)–C(2)	1.358(1)	1.326(3), 1.328(3)	1.330(5)
C(2)–N(3)	1.333(1)	1.344(3), 1.344(4)	1.345(4)
N(3)–C(4)	1.389(1)	1.372(3), 1.364(4)	1.381(5)
C(4)–C(5)	1.378(1)	1.366(4), 1.367(4)	1.363(4)
N(1)–C(5)	1.381(1)	1.383(5), 1.379(3)	1.377(4)
Angles (°)			
Ag–N(1)–C(2)		126.7(2), 121.9(2)	124.6(2)
Ag–N(1)–C(5)		126.8(2), 131.8(2)	128.4(2)
C(2)–N(1)–C(5)	107.2(1)	106.0(2), 106.1(5)	106.9(2)
N(1)–C(2)–N(3)	111.8(1)	110.9(2), 110.5(2)	110.3(3)
C(2)–N(3)–C(4)	105.3(1)	107.9(2), 108.3(2)	107.5(3)
N(3)–C(4)–C(5)	109.8(1)	106.1(2), 106.1(2)	106.5(3)
C(4)–C(5)–N(1)	106.0(1)	109.1(2), 109.1(2)	108.7(3)

[a] Derivative of neutron data (103 K), values corrected for libration [26].
[b] N(3)–C(30) is 1.470(4) Å; C(30)–N(3)–C2,5) are 125.5(3)° and 126.7(2)°.

The $AgClNP_2$ environment has previously been described via X-ray studies for the py/PPh_3 system in $[AgCl(py)(PPh_3)_2]$ [24,25]; the geometry for that is compared for those in **3** and **4** (Fig. 6) in Table 2. The values within all three systems are quite similar insofar as distances, and Cl–Ag–N and P–Ag–P angles are concerned, N–Ag–P angles being more diverse, variable and widely ranged; the Ag–P and P–Ag–P descriptors are similar to those found in many other $[(Ph_3P)_2Ag(N\text{-unidentate})_2]$ systems. The present systems are of interest in defining the first such arrays for imidazole bases, **10** likewise for a pyrazole base (Fig. 7). The latter is particularly of interest in defining a $[(Ph_3P)_2$(unidentate N-donor)Ag] array in association with an oxyanion, the interaction of the latter here being invasive, as tested by the $NAgP_2$ angle sum which is diminished well below 360° (being 352.$_8$°) (Table 2); the impact on the S–O (bonded) distance, however, appears negligible

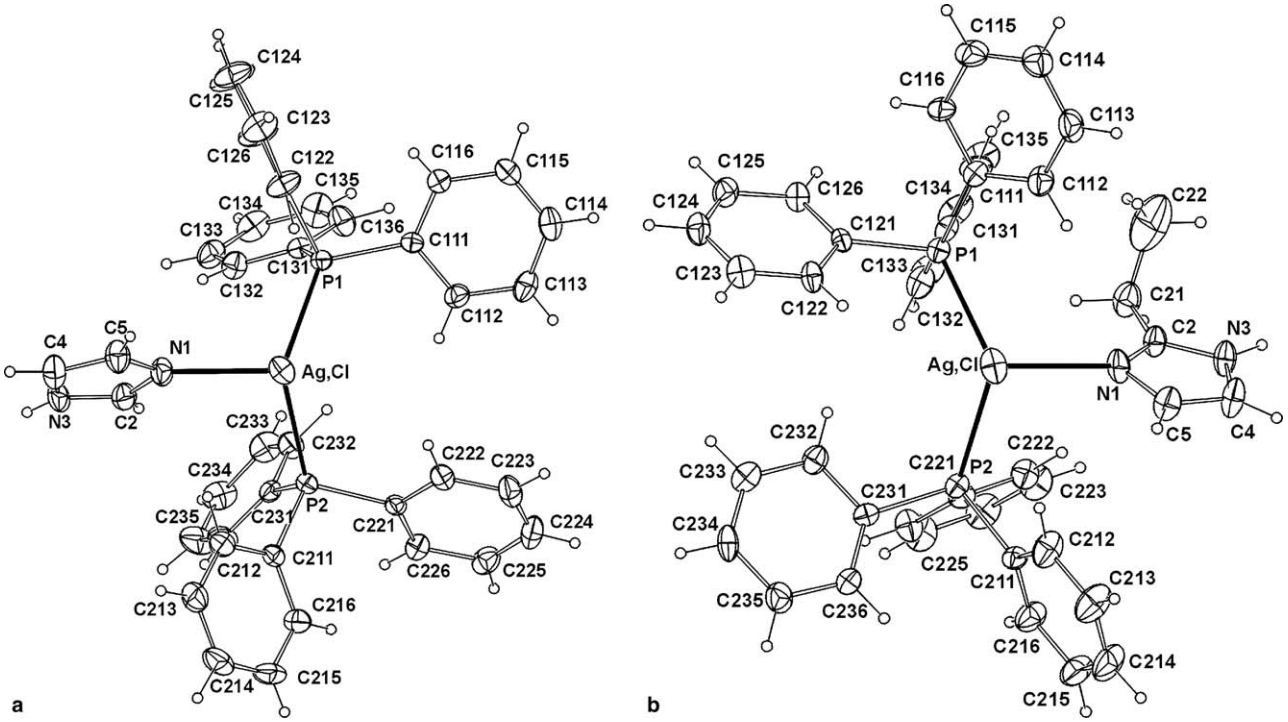

Fig. 6. Molecular projections of: (a) $[AgCl(imH)(PPh_3)_2]$ (**3**) and (b) $[AgCl(imet)(PPh_3)_2]$ (**4**), down the Cl–Ag bonds.

Table 2
Comparative $XAgNP_2$ environments, **3**, **4** and **10** ($[(PPh_3)_2Ag(N\text{-base})X]$ systems)

System	$[ClAg(py)(PPh_3)_2]$[a]	**3** (X = Cl)	**4** (X = Cl)	**10** (X = O, SO_2, Me)[b]
Distances (Å)				
X–Ag	2.517(2)	2.586(1)	2.609(3)	2.505(3)
Ag–N	2.503(4)	2.381(4)	2.359(8)	2.312(2)
Ag–P	2.477(2)	2.454(1)	2.454(4)	2.4393(7)
	2.474(2)	2.466(2)	2.464(4)	2.4663(7)
Angles (°)				
X–Ag–N	94.6(1)	96.1(1)	99.2(2)	95.17(9)
X–Ag–P	115.49(2)	110.60(5)	103.3(1)	90.06(6)
	113.22(7)	112.69(5)	108.7(1)	112.44(7)
N–Ag–P	105.4(1)	106.8(1)	112.2(3)	122.49(7)
	97.1(1)	98.4(1)	102.7(3)	103.91(7)
P–Ag–P	123.60(7)	126.46(5)	127.3(1)	126.40(2)
Ag–P(C(nm1)–C(ortho) torsion angles (°) (acute)				
nm = 11	−56.5(5)	36.0(5)	17(1)	−12.7(2)
12	−39.7(6)	49.1(4)	33(1)	−22.8(2)
13	−32.5(5)	44.5(6)	54(1)	−62.5(2)
21	−45.2(5)	18.1(5)	31(1)	−11.8(2)
22	−50.0(5)	31.2(5)	49(1)	−41.0(2)
23	−29.3(5)	59.2(5)	35(1)	−58.8(2)

[a] Refs. [24,25].
[b] In the anion (ordered), S–O (coordinated; uncoordinated (×2) x are 1.410(3); 1.434(3), 1.399(4) Å.

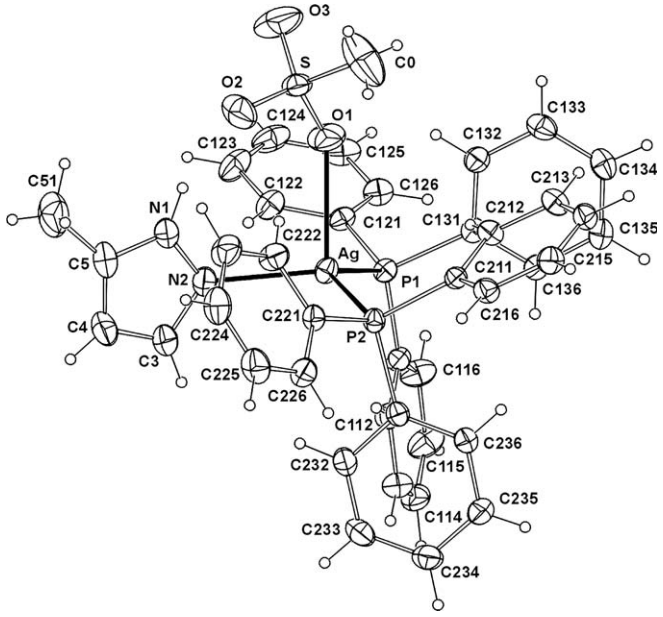

Fig. 7. Molecular projection of $[Ag(MeSO_2O)(mpz)(PPh_3)_2]$ (**10**).

and Ag–N, P are shorter than in the other complexes. A related species of interest is $[(Ph_3P)_2Ag(2\text{-meim})(O_2NO)]$ [10g]; Ag–N is 2.311(7) Å and Ag–P 2.447(3), 2.461(3) Å, with P–Ag–P 129.48(9)° and N–Ag–P 113.6(2)° and 105.6(3)°, suggesting the interaction with the bidentate O_2NO approach (Ag···O 2.75(1), 2.86(1) Å) to be no more effective that the present, PPh_3 ligand conformation throughout the present array are all of (distorted) threefold symmetry, the pair in any given complex being of the same chirality.

4. Supplementary material

X-ray crystallographic files, in *.cif* format, for the structure determinations of derivatives **1**, **2**, **3**, **4**, and **9** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 283883–283887. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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