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Inorganica Chimica Acta 359 (2006) 2183-2193

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis, spectroscopic and structural characterization of novel adducts of some silver(I) salts with the ambidentate donor PPh₂py

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> Received 11 November 2005; accepted 11 December 2005 Available online 8 February 2006

Abstract

Syntheses, spectroscopic (IR, ¹H and ³¹P NMR) and some 'low' -temperature single-crystal X-ray structural characterizations are reported for a wide variety of adducts of AgX:PPh₂py (:S) (n:m(:x)) (X = Cl, Br, I, NO₂, SCN, ClO₄, BF₄, O₂CCF₃ (tfa), O₂CCH₃ (ac), O₂CC₃F₇ (hefb), S₂CN(C₂H₅)₂ (dtc), 1/2 SO₄²⁻; PPh₂py = L = diphenyl-2-pyridylphosphine) stoichiometry. All compounds are binuclear, a wide range of Ag···Ag distances being found, bridging entities being diverse, either anionic X or the P,N-ambidentate ligand PPh₂py. PPh₂py acts as a terminal P-donor in Agdtc: PPh₂py (1:1)₂ and in [(Ph₂py)₂Ag(µ-Cl)₂Ag(PPh₂py)(NCMe)], but fully utilizes its coordinating capabilities in [(MeCN)Ag(µ-PPh₂py)₃Ag(OH₂)](ClO₄)₂ and [(NO₂)Ag(µ-PPh₂py)₂Ag(O₂N)]. Comparison is made between the latter compound and the analogous species [(NO₂)Ag(µ-PPh₂bim)₂Ag(O₂N)] (PPh₂bim = L' = 1-benzyl-2-imidazolyldiphenylphosphine).

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Keywords: Silver; ³¹P NMR; X-ray crystal structure; Ambidentate PN donor; Phosphine ligands

1. Introduction

The coordination chemistry of tertiary phosphines is a well-established field of research that allows systematic investigation of the possible coordination modes of oxyanions such as NO_3^- , ClO_4^- , and NO_2^- to Ag(I) [1–4] and Cu(I) ions [5]. It is well-known that interesting structural variations within the series $MX/(PR_3)_n$ result from the different coordination modes of the anions. A recent series of papers has augmented and summarized the contemporary status of the structural definition of families of simple complexes of the form $MX:EPh_3$ (1:*n*), M = univalent copper or silver, X = simple halide or pseudohalide (Cl, Br, I, SCN) or oxyanion (ClO_4^- , NO_3^- , or simple car-

boxylate), E = P, As, Sb, n = 1 [6,7], 2 [8], 3 [9], 4 [10]. Similar adducts MX:L (1:*n*) (n = 1-4) for ER₂R' ligands ($R \neq R'$) (*n* predominantly 1) have been only sporadically investigated. The multidentate 2-pyridyl-phosphines of the type PPh_xpy_{3-x} (x = 0, 1, 2) are potentially interesting ligands in this respect. They can act in unidentate terminal [11–13], bridging [14,15], or chelating modes [16,17]. Changes in coordination mode from the solid to solution state have been reported [18].

The ambidentate PPh₂py is a suitable ligand for the formation of multinuclear complexes in which the metal atoms are held in close proximity, thus allowing direct metal-metal interactions as in the dinuclear dicationic 1:1 gold complex containing PPh₂py which is distinguished by a very short Au–Au contact [19]. Mixed-metal complexes (Au–Ag and Au–Cu) have also been prepared [20]. A number of papers [21–24] have described other coinage metal derivatives containing PPh₂py, but to date

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no systematic investigation on the interaction between this P,N-donor and silver salts has been reported. Here, we describe the synthesis and spectroscopic characterization of a number of novel AgX:PPh₂py adducts, supported by four single-crystal X-ray studies to assist in understanding the relationships between molecular packing, coordinating ability of X⁻, donor capacity, and the Tolman cone angle of the ancillary ligand PPh₂py. Comparison is also made with an AgNO₂ derivative of the analogous P.N-donor ligand PPh₂bim (PPh₂bim = 1-benzyl-2-imidazolyldiphenylphosphine) [25-28]. Our results demonstrate that remarkably stable neutral silver complexes showing different silver(I) coordination environments can be easily synthesized, ranging from dinuclear systems containing the P,N-donor coordinated as a terminal ligand through the P center, to dinuclear systems containing the same P,N-donor coordinated in a bridging bidentate fashion.

2. Experimental

All syntheses and handling were carried out in the air. All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C,H,N,S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin–Elmer System 2000 FT-IR instrument. ¹H-, ¹³C- and ³¹P NMR spectra were recorded on a VXR-200 (200 MHz for ¹H, 50 MHz for ¹³C) or on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, and 162.1 MHz for ³¹P). H and C chemical shifts are reported in ppm vs. SiMe₄, P chemical shifts in ppm vs. H₃PO₄ 85%. The electrical conductances of the dichloromethane solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

2.1. Spectroscopic data of the ligands

2.1.1. PPh₂py, L, (diphenyl-2-pyridylphosphine)

¹H NMR (CDCl₃, 200 MHz, 293 K): δ 7.04d, 7.06– 7.15m, 7.32–7.40m, (12H, $H_{py} + H_{Ph}$), 7.56–7.51 (m, 1H, H_{py}), 8.70 (d, 1H, H_{py}). ³¹P NMR (CDCl₃): δ –4.0s. IR (nujol mull, cm⁻¹): 1566w, 1555w, 509s, 502s, 486s, 432m, 418m, 402m, 392m, 280w, 269w, 247w.

2.1.2. PPh_2bim , L', (1-benzyl-2-imidazolyl)diphenylphosphine)

¹H NMR (CDCl₃, 400 MHz, 293 K): δ 5.48 (s, 2H, CH₂), 7.08–7.63 (m, 17H, CH_{arom}). ³¹P NMR (CDCl₃): δ –32.6s. IR (nujol mull, cm⁻¹): 618s, 570w, 552w, 542w, 510s, 505s, 465m, 455m, 420w, 285m.

2.2. Syntheses and spectroscopic data of complexes

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.

2.2.1. {Bis(diphenyl-2-pyridylphosphine)-

dibromodisilver(*I*))}, [(*L*)₂*Ag*₂*Br*₂)] (*1*) To an MeCN solution containing 0.149 g (0.569 mmol) of PPh₂py, 0.082 g (0.436 mmol) of AgBr was added. The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with MeCN, and identified as compound 1 (77% yield). M.p. 259–261 °C. *Anal.* Calc. for C₁₇H₁₄AgBrNP: C, 45.27; H, 3.13; N, 3.11. Found: C, 45.23; H, 3.10; N, 3.04%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 7.23–7.39 (11H, *H*_{py} + *H*_{Ph}), 7.51–7.64 (m, 1H, *H*_{py}), 7.77 (t, 1H, *H*_{Ph}), 8.65 (d, 1H, *H*_{py}). ³¹P (CDCl₃, 400 MHz, 293 K): 5.7s. ³¹P (CDCl₃, 400 MHz, 293 K): 8.1 (d, ¹*J*(³¹P–Ag): 412 Hz). IR (nujol mull, cm⁻¹): 1563m, 1555m (C --- C and C --- N), 1459w, 1377w, 986m, 768m, 745w, 515w, 504w, 491m, 433s. *A*_m (CH₂Cl₂, conc. = 1.0×10^{-3} M): $2.8 \Omega^{-1}$ cm⁻² mol⁻¹.

2.2.2. {Bis(diphenyl-2-pyridylphosphine)diiododisilver(I)}, $[(L)_2Ag_2I_2](2)$

Compound **2** was prepared by the reaction of 0.149 g (0.569 mmol) of PPh₂py with 0.102 g (0.434 mmol) of AgI. The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with MeCN, and identified as compound **2** (71% yield). M.p. 271–272 °C. *Anal.* Calc. for C₁₇H₁₄AgINP: C, 41.00; H, 2.83; N, 2.81. Found: C, 40.71; H, 2.92; N, 2.71%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 7.18br, 7.25–7.36br (12H, H_{py} + H_{Ph}), 7.50–7.55 (1H, H_{py}), 8.67 (br, 1H, H_{py}). ³¹P (CDCl₃, 400 MHz, 293 K): 0.3s. ³¹P (CDCl₃, 400 Mz) = 0.3s P (CDCl₃, 400 Mz) = 0.3s P (CDCl₃) = 0.3s P (CDCl₃) = 0.3s P (C

2.2.3. Bis {(diphenyl-2-pyridylphosphine)bis(diethyldithiocarbamato)disilver(I)}, $[(L)_2Ag_2(dtc)_2](3)$

Compound 3 was prepared by the reaction of 0.149 g (0.569 mmol) of PPh₂py with 0.111 g (0.437 mmol) of silver diethyltiocarbamate (Agdtc) in acetonitrile (15 ml). The solution was stirred under reflux for 20 h in a roundbottomed flask protected from the light. Upon slow evaporation at room temperature, small crystals formed that were identified as compound 3 (38% yield). M.p. 164-165 °C. Anal. Calc. for C₂₂H₂₄AgN₂P₂: C, 50.87; H, 4.66; N, 5.39; S, 12.35. Found: C, 50.42; H, 4.88; N, 5.33; S, 12.21%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 1.31 (t, 6H, CH_{3dtc}), 3.99 (q, 4H, CH_{2dtc}), 7.23–7.26, 7.33–7.40 (m, 12H, $H_{py} + H_{Ph}$), 7.54–7.64 (1H, H_{py}), 8.73 (d, 1H, H_{py}). ³¹P NMR (CDCl₃, MHz, 294.1 K): 10.5s. ³¹P NMR (CDCl₃, MHz, 218.2 K): 11.7 br. IR (nujol mull, cm⁻¹): 1459w, 1376w, 1261s, 1202m, 1155m, 1086br, 1010, 976br (C=S), (C-N), 721m, 691w, 669s, 618s

(C–S), 562s, 507w, 409s, 277s. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): $1.2 \ \Omega^{-1} \ {\rm cm}^{-2} \ {\rm mol}^{-1}$.

2.2.4. {Bis(diphenyl-2-pyridylphosphine)sulfatodisilver(I)}, $[(L)_2Ag_2(SO_4)]$ (4)

Compound **4** was prepared by the reaction of 0.149 g (0.569 mmol) of PPh₂py with 0.68 g (0.218 mmol) of Ag₂SO₄ in MeCN. The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A gray precipitate formed, which was filtered off, washed with MeCN and identified as compound **4** (33% yield). M.p. 229–230 °C. *Anal.* Calc. for C₃₄H₂₈Ag₂-N₂O₄P₂S: C, 48.71; H, 3.37; N, 3.34; S, 3.82. Found: C, 48.31; H, 3.22; N, 3.45; S, 3.93%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 7.15–7.27 (m, 24H, $H_{py} + H_{Ph}$), 7.43 (m, 2H, H_{py}), 8.93 (d, 2H, H_{py}). ³¹P NMR (CDCl₃, 400 MHz, 293 K): 14.5s. ³¹P NMR (CDCl₃, 400 MHz, 223 K): 15.3 (d, ¹J(³¹P-Ag): 648 Hz). IR (nujol mull, cm⁻¹): 1561m (C C and C N), 1454w, 1373w, 1137s, 1104s, 1074s br, 1026s, 989m, 941m, 739m, 720m, 600w, 591w, 521w, 517w, 502s, 492sh, 445br, 420br, 399br, 280s. A_{m} (CH₂Cl₂, conc. = 1.0×10^{-3} M): $3.4 \Omega^{-1}$ cm⁻² mol⁻¹.

2.2.5. {Bis(diphenyl-2-pyridylphosphine)dinitritodisilver(I)}, [(L)₂Ag₂(NO₂)₂] (5)

Compound 5 was prepared by the reaction of 0.290 g (1.14 mmol) of PPh₂py with 0.100 g (0.65 mmol) of AgNO₂ in methanol (20 mL). The reaction was stirred under reflux for 8 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with diethyl ether and shown to be compound 5 (75% yield). Material for the X-ray work was recrystallized from methanol solution. Mp. 114-115 °C. Anal. Calc. for C₁₇H₁₄AgN₂O₂P: C, 48.95; H, 3.38; N, 6.72. Found: C, 49.01; H, 3.45; N, 6.72%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 7.1 (d, 1H, H_{py} or H_{Ph}), 7.2–7.6 (m, 11H, $H_{py} + H_{Ph}$), 7.7 (m, 1H, H_{py}), 8.90 (d, 1H, H_{py}). ³¹P NMR (CDCl₃, 400 MHz, 223 K): 17.8 (d, ${}^{1}J({}^{31}P-Ag)$: 648 Hz). IR (nujol mull, cm⁻¹): 1683s, 1651s, 1557s, 1455s, 1373s, 1152s 1096s (NO₂) 829s, 772m, 740m, 722s, 691m, 633s, 523m, 503m, 487m, 450s, 432s. Am (CH₂Cl₂, conc. = 1.0×10^{-3} M): $0.5 \Omega^{-1}$ cm⁻² mol⁻¹.

2.2.6. {(Acetonitrile)tris(diphenyl-2-pyridylphosphine)dichlorodisilver(I)}, $[(L)_3Ag_2Cl_2(MeCN)]$ (6)

To an MeCN solution containing 0.149 g (0.569 mmol) of PPh₂py, 0.063 g (0.439 mmol) of AgCl was added. The reaction was stirred under reflux for 20 h in a round-bot-tomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with MeCN, and identified as compound **6** (52% yield). Crystals for the X-ray work were obtained from MeCN solution. M.p. 201–202 °C. *Anal.* Calc. for C₅₃H₄₅Ag₂Cl₂N₄P₃: C, 56.96; H, 4.06; N, 5.01. Found: C, 57.03; H, 4.43; N, 5.21%. ¹H NMR (CDCl₃, 200 MHz, 293 K): δ 2.0 (s, 3H, CH₃CN), 7.23–7.39 (33H, $H_{py} + H_{Ph}$), 7.64–7.51 (3H, H_{py}), 7.77 (t, 3H, H_{Ph}), 8.72 (d, 3H, H_{py}). ³¹P (CDCl₃, 400 MHz,

293 K): 9.28s. ³¹P (CDCl₃, 400 MHz, 223 K): 4.4 (d, ¹*J*(³¹P–Ag): 362 Hz), 8.7 (d, ¹*J*(³¹P–Ag): 426 Hz), 10.4 (d, ¹*J*(³¹P–Ag): 572 Hz). IR (nujol mull, cm⁻¹): 1566m (C---C and C---N), 1459w, 1429m, 1377m, 1094m, 980m, 768m, 739w, 514s, 501w, 394s. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): 0.9 Ω⁻¹ cm⁻² mol⁻¹.

2.2.7. {(Aqua)tris(diphenyl-2-pyridylphosphine)dithiocyanatodisilver(I)} [$(L)_3Ag_2(SCN)_2(H_2O)_2$] (7)

Compound 7 has been prepared by reaction of 0.149 g (0.569 mmol) of PPh₂py with 0.072 g (0.437 mmol) of AgSCN in MeCN (20 mL). The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A colorless precipitate formed, which was filtered off, washed with MeCN and identified as compound 7 (25% yield). M.p. 156-157 °C. Anal. Calc. for C₅₃H₄₆Ag₂₋ N₅O₂P₃S₂: C, 54.98; H, 4.00; N, 6.05; S, 5.54. Found: C, 55.24; H, 4.22; N, 6.31; S, 5.60%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 1.60 (s, 2H, H₂O), 7.24-7.46 (m, 36H, $H_{pv} + H_{Ph}$), 7.55–7.62 (m, 1H, H_{py}), 8.69 (d, 3H, H_{py}). ^{31}P (CDCl₃, 400 MHz, 293 K): 10.1s. ^{31}P (CDCl₃, 400 MHz, 223 K): 5.7 (d, ¹J(³¹P-Ag): 378 Hz), 11.6 (d, ${}^{1}J({}^{31}P-Ag)$: 546 Hz). IR (nujol mull, cm⁻¹): 3300br (OH), 2110m, 2066m (SCN), 1461w, 1380w, 1085s, 1310s, 739m, 518m, 506w, 501m, 458w, 277s. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): 66.6 Ω^{-1} cm⁻² mol⁻¹.

2.2.8. {(Aqua)(acetonitrile)tris(diphenyl-2pyridylphosphine)bis(perchlorato)disilver(I)}, [$(L)_3Ag_2(ClO_4)_2(H_2O)(MeCN)$] (8)

Compound 8 has been obtained by the reaction of 0.150 g (0.57 mmol) of PPh₂py with 0.091 (0.44 mmol) of AgClO₄ in MeCN. The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A colorless precipitate formed, which was filtered off, washed with MeCN, and identified as compound 8 (32% yield). The compound was re-crystallised from MeCN. M.p. 264 °C. Anal. Calc. for C₅₃H₄₇Ag₂Cl₂. N₄O₉P₃: C, 50.38; H, 3.75; N, 4.43. Found: C, 50.45; H, 3.56; N, 4.23%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 1.68 (br, 2H, H₂O), 6.8br, 7.0br, 7.10-7.38m (36H, $H_{\rm pv} + H_{\rm Ph}$), 7.5–7.7 (br, $H_{\rm pv}$), 9.6 (br, 1H, $H_{\rm pv}$). ³¹P NMR (CDCl₃, 200 MHz, 293 K): 11.6 (d, ${}^{1}J({}^{31}P-Ag)$: 453 Hz), 11.5br. ${}^{31}P$ NMR (CDCl₃, 200 MHz, 218.2 K): 10.8 (d, ¹J(³¹P-Ag): 490 Hz), 10.9br. ³¹P NMR (CDCl₃, 400 MHz, 293 K): 11.3 (d, ¹J(³¹P-Ag): 462 Hz), 11.4br. ³¹P NMR (CDCl₃, 400 MHz, 223 K): 10.5 (d, ¹J(³¹P-Ag): 467 Hz), 10.6 (br), 19.6 (d, ¹J(³¹P-Ag): 611 Hz). IR (nujol mull, cm⁻¹): 2921w, 2862w, 1586s (C---C and C---N), 1459w, 1436w, 1377w, 1162s, 1097w, 1058s (ClO₄⁻), 918s, 748m, 638s, 621w (ClO₄⁻), 521w, 506w, 488m, 442s. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): 7.6 Ω^{-1} cm⁻² mol⁻¹.

2.2.9. {Tris(diphenyl-2-pyridylphosphine)-

bis(tetrafluoroborato)disilver(I), $[(L)_3Ag_2(BF_4)_2](9)$

Compound 9 was prepared by the reaction of 0.300 g (1.14 mmol) of PPh₂py with 0.156 g (0.8 mmol) of AgBF₄

in EtOH (15 mL). The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off and identified as compound **9** (43% yield). M.p. 264 °C. *Anal.* Calc. for C₅₁H₄₂Ag₂B₂F₈N₃P₃: C, 51.95; H, 3.59; N, 3.56. Found: C, 52.13; H, 3.48; N, 4.00%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 6.9–7.0, 7.18–7.38 (m, 36H, $H_{py} + H_{Ph}$), 7.56–7.77 (m, 1H, $H_{py}py$), 9.40 (d, 1H, H_{py}). IR (nujol mull, cm⁻¹): 1584s and 1570m (C····O, C····C and C····N), 1455w, 1374w, 1285m, 1090m, 1051m (BF₄⁻), 846m, 771w (BF₄⁻), 745w, 722m, 520w (BF₄⁻), 506w, 487m, 417s, 251s. A_m (CH₂Cl₂, conc. = 1.0×10^{-3} M): 17.2 Ω^{-1} cm⁻² mol⁻¹.

2.2.10. {Diaquatris(diphenyl-2-pyridylphosphine)diacetatodisilver(I)}, [(L)₃Ag₂(O_2 CCH₃)₂(H₂O)₂] (**10**)

Compound **10** was prepared by reaction of 0.149 g (0.569 mmol) of PPh₂py with 0.72 g (0.43 mmol of AgO₂-CCH₃) in ethanol (15 mL). The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. The solution was evaporated and the residue extracted with dichloromethane. The solution was evaporated and an oil formed which was identified as compound **10** (29% yield). *Anal*. Calc. for C₅₅H₅₂Ag₂N₃O₆P₃: C, 56.96; H, 4.52; N, 3.62. Found: C, 56.62; H, 4.65; N, 3.51%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 2.05 (br, 7H, *H*₂O + CH₃), 7.22–7.42 (m, 39H, *H*_{py} + *H*_{Ph}), 7.49–7.56, 7.65 (m, 3H, *H*_{py}), 8.78 (d, 3H, *H*_{py}). ³¹P NMR (CDCl₃, 400 MHz, 223 K): 8.7 (d, ¹*J*(³¹P–Ag): 447 Hz), 8.7 (br). IR (nujol mull, cm⁻¹): 3300br, 1630br, 1461w, 1376m, 1096s, 504s, 153m. $A_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): 17.0 Ω^{-1} cm⁻² mol⁻¹.

2.2.11. {Triaquatris(diphenyl-2pyridylphosphine)bis(trifluoroacetato)-disilver(I)}, $[(L)_3Ag_2(O_2CCF_3)_2(H_2O)_3]$ (11)

Compound 11 has been prepared by reaction of 0.300 g (1.14 mmol) of PPh₂py with 0.097 g (0.43 mmol) of AgO₂- CCF_3 (Agtfa) in methanol (15 mL). The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. The solution was then left for 48 h at -10 °C. A microcrystalline precipitate formed that has been identified as compound 11 (29% yield). Anal. Calc. for C₅₅H₄₈Ag₂F₆O₇P₃N₃: C, 51.38; H, 3.76; N, 3.27. Found: C, 51.19; H, 3.84; N, 3.11%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 2.05 (br, 6H, H₂O), 7.2-7.6 (m, 36H, $H_{py} + H_{Ph}$), 7.7 (m, 3H, H_{py}), 8.8 (d, 3H, H_{py}). ³¹P (CDCl₃, 400 MHz, 293 K): 11.3s. ³¹P (CDCl₃, 400 MHz, 223 K): 8.6 (d, ¹J(³¹P–Ag): 445 Hz), 8.6 (br). IR (nujol mull, cm⁻¹): 3300br (OH) 1675s (CO), 1635br (OH) 1460sh, 1195m, 1169m, 1156m, 1123m, 1097m, 560w, 542m, 515s, 503s, 490s, 399. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): 13.6 Ω^{-1} cm⁻² mol⁻¹.

2.2.12. {Diaquatris(diphenyl-2-pyridylphosphine)-bis(heptafluorobutanoato)-disilver(I)}, $[(L)_3Ag_2(O_2CC_3F_7)_2(H_2O)_2]$ (12)

Compound 12 has been prepared by reaction of 0.300 g(1.14 mmol) of PPh₂py with 0.138 g (0.431 mmol) of AgO₂CC₃F₇ in ethanol (15 mL). The reaction was stirred under reflux for 20 h in a round-bottomed flask protected from the light. The solution was then evaporated and the residue washed with diethyl ether. A microcrystalline precipitate formed that has been identified as compound **12** (55% yield). *Anal.* Calc. for C₅₉H₄₆Ag₂F₁₄N₃O₆P₃: C, 48.28; H, 3.16; N, 2.86. Found: C, 48.42; H, 3.05; N, 2.91%. ¹H NMR (CDCl₃, 200 MHz, 293 K): 2.05 (br, 2H, *H*₂O), 6.8–7.6 (m, 39H, *H*_{py} + *H*_{Ph}), 9.3 (br, 3H, *H*_{py}). ³¹P (CDCl₃, 400 MHz, 293 K): 13.0s. ³¹P (CDCl₃, 400 MHz, 223 K): 17.2 (d, ¹*J*(³¹P–Ag): 652 Hz), 8.0 (d, ¹*J*(³¹P–Ag): 465 Hz), 8.0 (br). IR (nujol mull, cm⁻¹): 3300br, 1679s, 1650s, 1576m, 1564m, 1163s, 1104m, 1070m, 997m, 960m, 919m, 542w, 516m, 503m, 480m, 444br, 399br, 264br. *A*_m (CH₂Cl₂, conc. = 1.0×10^{-3} M): 13.7 Ω⁻¹ cm⁻² mol⁻¹.

2.2.13. {Bis(1-benzyl-2-imidazolyldiphenylphosphine)dinitritodisilver(I)}, $[(L')_2Ag_2(NO_2)_2]$ (13)

To a stirred acetonitrile solution (10 mL) of PPh₂bim (0.40 g, 1.16 mmol), AgNO₂ (0.153 g, 1.0 mmol) at room temperature was added. The solution was then stirred under reflux for 24 h, then left to evaporate until small crystals of the analytical sample were obtained. (40% Yield). *Anal.* Calc. for C₂₂H₁₉AgN₃O₂P: C, 53.25; H, 3.86; N, 8.47. Found: C, 53.11; H, 3.75; N, 8.41%. ¹H NMR (CDCl₃, 400 MHz, 293 K): δ 5.15, (s, 2H, CH₂), 6.62 (s br, 2H, CH_{arom}), 7.0–7.3 (m, 3H, CH_{arom}), 7.3–7.6 (m, 11H, CH_{arom}), 7.73 (s, 1H, CH_{arom}). ³¹P NMR (CDCl₃): δ –6.3 (br). IR (nujol mull, cm⁻¹): 1373s, 1152s, 1096s, (NO₂) 618s, 573w, 550w, 537s, 500s, 470w, 455w, 280m. $A_{\rm m}$ (CH₂Cl₂, conc. = 1.0×10^{-3} M): $1.2 \Omega^{-1}$ cm⁻² mol⁻¹. Recrystallised from MeOH as 13 · 2MeOH.

2.3. Structure determinations

Full spheres of low-temperature CCD area-detector diffractometer data were measured (T ca. 153 K; Bruker AXS instrument, w-scans; monochromatic Mo Ka radiation, $\lambda = 0.7107_3$ Å), yielding $N_{t(otal)}$ reflections, these merging to N unique (Rint cited) after 'empirical'/multiscan absorption correction (proprietary software), N_0 with $F > 4\sigma(F)$ being considered 'observed' and used in the full-matrix least-squares refinements, refining anisotropic displacement parameters for the non-hydrogen atoms, $(x, y, z, U_{iso})_{H}$ being included and constrained at estimates. Conventional residuals R, $R_{\rm w}$ (reflection weights: $(\sigma^2(F) + 0.000n_{\rm w}F^2)^{-1})$) are cited at convergence; neutral atom complex scattering factors were employed within the Xtal 3.7 program system [29]. Pertinent results are presented below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 A; individual diversions in procedure are noted under 'variata'. The assignment of the pyridyl nitrogen in all cases was clearcut, on the basis of refinement behaviour and bonding considerations, and the location of other pyridylic hydrogen

atoms. Full.cif depositions have been lodged with the Cambridge Crystallographic Data Centre, CCDC 284591-284595.

2.3.1. Crystallrefinement data

2.3.1.1. Agdtc: $L(1:1)_2$, $\mathbf{3} = C_{44}H_{48}Ag_2N_4P_2S_4$, M = 1038.8. Triclinic, space group $P\bar{1}$ (C_i^1 , No. 2), a = 8.596(2), b = 11.121(3), c = 12.236(3) Å, $\alpha = 80.314(4)$, $\beta = 84.401(4)$, $\gamma = 69.351(4)^\circ$, V = 1078 Å³. D_{calc} (Z = 1) = 1.600 g cm⁻³. $\mu_{Mo} = 1.21$ mm⁻¹; specimen: $0.28 \times 0.26 \times 0.18$ mm; ' $T_{min/max} = 0.83$. $2\theta_{max} = 55^\circ$; $N_t = 8783$, N = 4756 ($R_{int} = 0.024$), $N_0 = 3602$; R = 0.044, $R_w = 0.055$ ($n_w = 0.4$).

Variata. One of the ethyl groups of the dithiocarbamate was disordered with the terminal methyl group disposed to either side of the anion plane, site occupancies set at 0.5 after trial refinement.

2.3.1.2. $AgNO_2$: L $(1:1)_2$, $5 \equiv C_{34}H_{28}Ag_2N_4O_4P_2$, M = 834.3. Triclinic, space group $P\overline{1}$, a = 9.0060(5), b = 9.7977(6), c = 10.2235(6) Å, $\alpha = 68.182(1)$, $\beta = 87.019(1)$, $\gamma = 83.003(1)^\circ$, V = 831.2 Å³. D_{calc} (Z = 1) = 1.666 g cm⁻³. $\mu_{Mo} = 1.32$ mm⁻¹; specimen: $0.28 \times 0.24 \times 0.18$ mm; ' $T_{min/max} = 0.78$. $2\theta_{max} = 75^\circ$; $N_t = 16966$, N = 8516 ($R_{int} = 0.022$), $N_0 = 7654$; R = 0.030, $R_w = 0.036$ ($n_w = 4$).

Variata. $(x, y, z, U_{iso})_{H}$ were refined throughout.

2.3.1.3. AgCl:L:MeCN (2:3:1), $\mathbf{6} \equiv C_{53}H_{45}Ag_2Cl_2N_4P_3$, M = 1117.5. Triclinic, space group $P\bar{1}$, a = 12.360(1), b = 14.420(1), c = 15.846(2) Å, $\alpha = 99.938(2)$, $\beta = 104.846(2)$, $\gamma = 111.594(2)^{\circ}$, V = 2405 Å³. D_{calc} (Z = 2) = 1.545 g cm⁻³. $\mu_{Mo} = 1.07$ mm⁻¹; specimen: $0.15 \times 0.12 \times 0.10$ mm; ' $T_{min/max}^{\circ} = 0.88$. $2\theta_{max} = 70^{\circ}$; $N_t = 49724$, N = 20454 ($R_{int} = 0.035$), $N_0 = 14706$; R = 0.044, $R_w = 0.051$ ($n_w = 7$).

2.3.1.4. $AgClO_4:L:H_2O:MeCN\ (2:3:1:1),\ \mathbf{8} \equiv C_{53}H_{47}Ag_2-Cl_2N_4O_9P_3,\ M = 1263.5.$ Monoclinic, space group $P2_1/n\ (C_{2h}^5,\ \text{No}.\ 14\ (\text{variant})),\ a = 13.058(1),\ b = 18.099(2),\ c = 22.561(2)\ \text{\AA},\ \beta = 98.209(3)^\circ,\ V = 5277\ \text{\AA}^3.\ D_{\text{calc}}\ (Z = 4) = 1.59\ \text{g cm}^{-3}.\ \mu_{\text{Mo}} = 0.99\ \text{mm}^{-1};\ \text{specimen:}\ 0.19 \times 0.16 \times 0.03\ \text{mm;}\ `T_{\text{min/max}} = 0.79.\ 2\theta_{\text{max}} = 65^\circ;\ N_t = 109\,843,\ N = 18\,664\ (R_{\text{int}} = 0.11),\ N_0 = 10\,551;\ R = 0.040,\ R_{\text{w}} = 0.034\ (n_{\text{w}} = 5).$

Variata. $(x, y, z, U_{iso})_{H}$ were refined throughout. Both perchlorates were modelled with disordered oxygen atoms, all of perchlorate 1 over two sets of sites and O(22–24) of perchlorate 2, occupancies refining to 0.761(7) and complement, in each case, presumably concerted.

2.3.1.5. $AgNO_2:L':MeOH$ $(1:1:1)_2$, $13 \equiv C_{46}H_{46}Ag_2$ - $N_6O_6P_2$, M = 1056.6. Triclinic, space group $P\bar{1}$, a =8.7780(9), b = 11.369(1), c = 12.292(1) Å, $\alpha = 73.941(2)$, $\beta = 74.066(2)$, $\gamma = 88.544(2)^\circ$, $V = 1131._8$ Å³. D_{calc} (Z = 1)= 1.551 g cm⁻³. $\mu_{Mo} = 0.99$ mm⁻¹; specimen: 0.40×0.28 $\times 0.26$ mm; ' $T'_{min/max} = 0.84$. $2\theta_{max} = 75^\circ$; $N_t = 23.332$, N = 11.558 ($R_{int} = 0.030$), $N_0 = 9687$; R = 0.042, $R_w =$ 0.060 ($n_w = 8$).

3. Results and discussion

The reaction of AgX (X = Br, I, dtc, $1/2SO_4$ and NO₂) with an equimolar quantity of 2-pyridylphosphine (PPh₂py) at room temperature gave rise to the compounds AgX:PPh₂py (1:1)₂ **1–5** (Chart 1). Under the same conditions the reactions between PPh₂py and AgX (X = Cl, SCN, ClO₄, BF₄, ac, tfa, hefb) yield the 3:2 adducts **6–12** (Charts 2 and 3). Finally, the donor PPh₂bim reacts with AgNO₂ yielding the dinuclear species AgNO₂:PPh₂bim (1:1)₂ **13** (Chart 4).

These compounds are generally air-stable, colorless materials, soluble in polar solvents such as acetonitrile, dimethylformamide and dimethylsulfoxide. They are, however, insoluble in water, ether and tetrahydrofuran, but exhibit good solubility in the chlorinated hydrocarbons CH_2Cl_2 and $CHCl_3$. Solid samples of these compounds show generally no sensitivity to light. However, they are unstable in solution, their chlorinated solvent solutions often darkening after 24 h.

Conductivity measurements indicated that only the thiocyanate complex 7 behaves as a 1:2 electrolyte in dichloromethane solution, whereas the values found for all the other species suggest strong silver(I)-X interactions. If this behaviour is postulated for derivatives 1-6 and 13, taking into account the X-ray single crystal studies (see below), then, for the case of derivative 8, structurally characterised, partial dissociation of a P,N-donor ligand and consequent anion reassociation according to Eq. (1) must be hypothesised.





Chart 2.

$$[(H_2O)Ag(\mu-PPh_2py)_3Ag(CH_3CN)]^{++}2[ClO_4^{-}]$$

$$\rightarrow [(O_3ClO)Ag(\mu-PPh_2py)_2Ag(OClO_3)] + PPh_2py$$

$$+ MeCN + H_2O$$
(1)

This hypothesis is supported by the presence in the ${}^{31}P$ NMR spectrum (CDCl₃ solution) of a signal (at ca. 23 ppm) ascribable to O=PPh₂py and by previous reports in the literature on analogous complexes containing the bidentate ligand dppm [30].

In the case of derivatives 7 and 9–12, conductivity measurements support the hypothesized structures in Charts 2 and 3, consistent with the ³¹P NMR spectra (see below). Partial dissociation of 11 in solution with the formation of a dinuclear species [(tfa)Ag(μ -PPh₂py)₂Ag(tfa)] similar to that reported for an analogous dppm derivative [30] is also likely, as further indicated by the ³¹P NMR spectrum.

3.1. Spectroscopy

The infrared spectra of 1–13 (see Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the counterions and of the phosphorus or arsenic donors [31]. The bands due to the phosphine ligands are only slightly shifted with respect to those of the free donors. In the far-IR spectra of all derivatives we have assigned, on the basis of previous reports on phosphino silver(I) derivatives [31–33], the broad absorptions near 500 cm⁻¹ and those at 450–

 400 cm^{-1} to Whiffen's y and t vibrations, respectively. No discernible bands have been detected at low frequencies in the spectra of 1, 2 and 6 that can be assigned to any M-halide stretching vibrations, as is consistent with strongly bonded, bridging halide groups.

In the spectra of **5** and **10–12** there are some bands in the region $300-200 \text{ cm}^{-1}$, similar to those described in the literature for other silver(I)-oxyanion derivatives [34] which can be tentatively assigned to v(Ag-O).

The spectroscopic behaviour of the counter-ion in compound **8** is typical of an ionic outer-sphere group: for an ionic ClO_4^- (T_d geometry), only two vibrations (v_3 and v_4) are expected to be IR active [35], as are in fact found at ca. 1090 and 620 cm⁻¹, consistent with the results found in the single crystal studies. On the other hand, different absorptions have been found in the spectrum of the derivative **9**, a number of broad bands between 1100 and 900 cm⁻¹ and two weak bands at 745 and 722 cm⁻¹, consistent with a coordinated unidentate BF₄⁻ group [36].

In the case of carboxylate derivatives it is generally accepted [37] that it is possible to distinguish between ionic, unidentate, chelating bidentate or bridging bidentate groups on the basis of Δ values (where $\Delta = v_a(\text{COO}) - v_s$ -(COO)), the trend generally being accepted:

 $\Delta_{\text{unidentate}} > \Delta_{\text{ionic}} > \Delta_{\text{bridging bidentate}}$

 $> \Delta$ chelating bidentate



In compounds 10 and 11 the \triangle is ca. 215 cm⁻¹, consistent with unidentate coordination of the carboxylate groups.

³¹P chemical shifts (CDCl₃ solution) and ³¹P-Ag coupling-constants for derivatives 1-13, are reported in Section 2. They have been found to be slightly dependent on the dilution of the solutions, and strongly dependent on the temperature. Our experiments have been carried out at a concentration of 0.005 mol/L. The room temperature ³¹P NMR spectra of complexes 1–7 consist of broad singlets, presumably in consequence of exchange equilibria that are reasonably fast in relation to the NMR time scale. Exchange is quenched at low temperature (223 K), and one and/or two unresolved doublets arising from coupling between the phosphorus and silver atom are observed in the accessible temperature range. The observed ${}^{1}J({}^{107}\text{Ag})/{}^{1}J({}^{109}\text{Ag})$ ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei $\gamma(^{107}\text{Ag})/\gamma(^{109}\text{Ag})$ [38]. For derivatives 8–12, which in the



solid state have been found to contain three bridging ambidentate phosphine ligands, a broad signal or a broad multiplet was observed at room temperature. At 223 K the spectra exhibit broad triplets that at 193 K split into two broad doublets at 193 K. This pattern can be explained assuming that at 223 K, the dynamical processes that average the two environments have rates that afford 107/109Ag107/109Ag/31P 31 P $'_{2}$ spin systems [39]. At low temperature the two 31 P environments are distinguishable. The values of the silver–phosphorus coupling constants for the Ag₂L₃ systems are, as expected [40], much less than those found for the Ag₂L₂ complexes.

In some cases a signal at ca. 23 ppm is present due to the oxidised form of the free ligand, suggesting dissociation of the 3:2 adduct to form a dinuclear 1:1 species and fast oxidation of the free ligand.

The signals due to the free phosphine L and L' ligands are always up-field with respect to those of their corresponding silver(I) complexes. It is worthy of note that the presence of two or more different doublets having also very different ³¹P-Ag coupling constants in the case of compounds 3. 6 and 12 suggests the existence of different species in solution. Muetterties and Alegranti [41] and Goel and Pilon [42] indicated that the spin-spin constant (J)between phosphorus and silver changes according to the number of coordinated phosphorus atoms in the silver complex, and that it is possible to determine the number of the latter from measurement of the J values in the ${}^{31}P$ NMR spectra. On the basis of the detected values, an AgPN coordination environment is likely in solution for compounds 4 and 5, partially consistent with the structure found for 5 in the solid state; an AgPX₂ coordination environment is likely for derivatives 1 and 2, whereas the three different signals found at low temperature in the spectrum of 6 are consistent with the three different phosphorus coordination environments found in the solid state. ³¹P NMR low-temperature spectra of derivatives 10-12 are very similar to the spectrum of 8, all showing two different doublets between 7 and 9 ppm, characterized by small silver-phosphorus coupling constants. In the spectrum of 10 there is also a low intensity doublet, for which the

(b)

chemical shift and the coupling constant values suggest a dinuclear structure as found in the solid state for compounds 4 and 5. On the basis of the similarity found

between the spectra of 6 and 7, a dinuclear structure with two silver centers bridged by two SCN moieties has been hypothesised for the former compounds.





(c)







Fig. 1. Projections of the dimeric species (a) AgNO₂:L (2:2), **5**; (b) AgNO₂:L' (2:2), **13**; (c) Agdtc:L (2:2), **3**; (d) $[L_2Ag(\mu-Cl)_2AgL(NCMe)]$, **6**; (e) the $[(MeCN)Ag(\mu-L)_3Ag(OH_2)]^{2+}$ cation of the perchlorate **8**.

3.2. X-ray diffraction studies

A number of the above complexes have been subjected to single-crystal X-ray characterizations, the results comprising the definition of a number of stoichiometric and stereochemical forms, of greater diversity and novelty than anticipated. All are binuclear, a wide range of $Ag \cdots Ag$ distances being found, but the bridging entities are diverse, being either anion or ligand; the heterocycle component of the ligand is not always involved in coordination, in some cases being supplanted by solvent donors, usually regarded as being of lesser donor capacity, despite the ostensible lack of strain inherent in the heterocycle bridging capability. A contemporaneous relevant review is noted [43].

The ligand is found in purely terminal P-donor mode in two of the complexes. In Agdtc: PPh₂py (1:1)₂, **3**, (Fig. 1 and Table 1), centrosymmetric, one Agdtc: PPh₂py unit, devoid of crystallographic symmetry comprises the asymmetric unit of the structure. The independent silver atom is chelated by the *S*,*S'*-dithiocarbamate anion. Ag–S(1) is shorter than Ag–S(2), by virtue of the latter bridging to the inversion related counterpart. The silver atom lies well out of the S₂CNC₂ ligand plane, the latter forming a dihedral angle of 78.26(8)° to the Ag(μ -S(2))₂Ag core plane, Ag(μ -dtc)₂Ag forms of this type being previously established [44]. The coordination sphere is completed by the terminal/unidentate PPh₂py ligand, the pyridine nitrogen directed away from the metal but without any significantly close interdimer contact.

With triphenylphosphine as ligand, binuclear forms are found with the copper(I) halides of stoichiometry CuX (X = Cl, Br, I):PPh₃ (2:3), it being surmised that 2:4 stoichiometry is not achieved because of steric difficulties imposed about the molecular core by ligand crowding; by contrast, binuclear $[(Ph_3P)_2Ag(\mu-X)_2Ag(Ph_3P)_2]$ has been recorded with the larger metal/silver atom [45]. Here, it is of interest to find that with the relatively small halide, 2:4 stoichiometry is not achieved, but, rather, an acetonitrile coordinates instead of one of the putative ligands yielding $[(Ph_2pyP)_2Ag(\mu-Cl)_2Ag(PPh_2py)(NCMe)]$, (Fig. 1 and Table 2), despite its limited donor capacity vis-a-vis excess phosphine or intra- or inter-dimer bridging pyridyl

Table 1				
The silver	environment:	Agdtc:L	$(1:1)_{2}$	3

Atom	r	S(1)	S(2)	S(2'1)
Р	2.381(1)	121.31(4)	111.46(4)	123.13(4)
S(1)	2.563(1)		65.99(5)	106.58(4)
S(2)	2.797(1)			115.05(4)
S(2')	2.531(1)	Ag…Ag′ 2.8696(8) Å		

r Å is the silver-ligand atom distance; other entries in the matrix are the angles subtended by the relevant atoms at the head of the row and column. Ag–S(1)–C(1) is 89.5(2); Ag,Ag'–S(2)–C(1) are 81.2(2), 102.5(2) with Ag–S(2)–Ag' 64.95(3); S(1)–C(1)–S(2) is 120.1(3)°. Ag,Ag' lie -0.933(5), 1.627(4) Å out of the S₂CNC₂ 'plane' (χ^2 722); Ag lies 0.10(1) Å out of the py (C₅N) plane. τ (Ag–P–C(n1)–N,C(n2)) are -177.3(4), -33.2(5), 0.6(4)°.

Table 2	
Silver environment: [$(Ph_2pyP)_2Ag(\mu-Cl)_2Ag(NCMe)(PPh_2py)],$

Atom	r	Cl(2)	P(1,3)	P/N
Cl(1)	2.7102(7) 2.4994(8)	87.73(2) 94.40(2)	104.67(2) 142.32(3)	109.88(2) 82.98(7)
Cl(2)	2.6523(7) 2.5654(8)		116.63(2) 121.98(3)	104.04(4) 122.00(8)
P(1,3)	2.4459(6)	Ag(1)···Ag(3.6416(3) Å	(2)	126.85(2)
	2.3765(8)	$Cl(1) \cdot \cdot \cdot Cl(2) 3.716(1) \text{ Å}$		85.19(7)
P(2) N(01)	2.4558(8) 3.209(3)			

Presentation as for Table 1; values for Ag(2) lie below those for Ag(1). τ (Ag–P(n)–C(n1)–N,C(n2) for the three ligands (n = 1;2;3) are: -58.8(3), -18.8(2), -35.9(3); 178.2(2), 33.9(2), 27.6(2); -43.1(3), -46.2(2), -35.9(3)°.

groups; the full formula unit comprises the asymmetric unit of the structure. Ag-NCMe is long (3.209(3) Å, cf. values ca. 2.25 Å recorded for $[Ag(NCMe)_4](ClO_4)$ [46], with MeCN inclined towards parallelism with the nearby associated Ag–Cl core linkage; the angle sum within the PAg(μ -Cl)₂ complement in the rest of the Ag(2) coordination sphere is 358.7°, suggesting a description as quasi-[(Ph₂pyP)₂Ag(μ -Cl)₂Ag(PPh₂py)] (solvated) not to be inappropriate.

Such an array is an extension of the extant series of AgCl:PPh₂py adducts – the 1:1 adduct takes the form of the usual 'cubane' tetramer [Ag₄Cl₄L₄], L bound only through the phosphorus [47], while an adduct of 2:3 stoichiometry (unsolvated) takes the form [LAg(μ -Cl)₂(μ -N,(L),P)AgL], wherein Ag···Ag' is 3.074 Å, cf. the present 3.6416(3) Å, the pyridyl donor bridging to occupy the site presently occupied by the acetonitrile [48].

The two adducts of silver nitrite with L and L' ligands, 5, 13, both take the same form, being centrosymmetric dimers of $(1:1)_2$ stoichiometry (Fig. 1 and Table 3), the two silvers being bridged by the P and N functionalities of a pair of ligands, the anion, of small bite, chelating the metal atoms in both cases, with the AgO₂N 'plane' quasinormal to the resulting metallacycle 'plane'. Despite the formal similarity of the two dimers, and the centrosymmetric nature of the metallacycles, the latter differ between the two complexes, in respect of their conformations, very considerably - ring torsions in the Ag-N-C-P-Ag strings are 70.9(1), 1.6(1), 73.2(1), -113.06(6) (the PPh₂py complex), $-84.9(2), -16.6(1), -10.3(2), 79.7(2)^{\circ}$ (the L = PPh₂bim complex) so that the resulting $Ag \cdots Ag$ distances are very different. Residues modelled plausibly as lattice methanol (no OH hydrogen located) may be hydrogen-bonded to the nitrite $(O(01) \cdots O(2) (1-x, 1-y, 1-z) 2.874(5) \text{ Å})$ and each other (O(01)···O(02) $(x, y, z; 2 - x, \overline{z}, 1 - z)$ 2.99(1) Å (x2)) (see Table 4).

In the final compound, of $AgX:L(1:1.5)_2$ stoichiometry, 8, the anion, being perchlorate, is uncoordinated, and, the coordinating capabilities of the PPh₂py ligands being fully utilized, a solvated cation is formed, the array being

Table 3 The silver environments: AgNO₂:X (2:2) (X = L_1 L'). 5. 13

		0 2 () (, ,, -, -	
Atom	r	N(12′)	O(1)	O(2)
Р	2.3907(4) 2.3817(5)	117.20(3) 156.94(6)	119.63(6) 111.25(6)	128.48(5) 99.12(5)
N(12')	2.350(2) 2.223(2)		121.24(7) 91.21(8)	85.43(6) 91.58(7)
O(1)	2.341(2) 2.481(4)	Ag···Ag′ 4.0 3.1	0650(2) Å .052(3)	50.55(6) 49.17(9)
O(2)	2.542(2) 2.557(3)			

Presentation as for Table 1. Values for the $L' = PPh_2im$ complex lie below those for the $L = PPh_2py$ complex. Primed atoms are centrosymmetrically related.

In the L;L' complexes, N–O(1,2), Ag–O(1,2)-N, O(1)–N–O(2) are: 1.258(3), 1.235(2) Å, 102.3(1), 93.0(1), 114.2(2)°; 1.254(2), 1.237(5) Å, 99.7(2), 96.4(2), 114.7(3)°, Ag lying 0.048(9); 0.16(1) Å out of the NO₂ planes; Ag–P–C(n1)–N,C(n2) are: 73.2(1), 34.5(1), 45.6(1); -10.3(2), -54.9(2), -54.8(2)°. The bound Ag lie 0.060(3); 0.386(5) Å out of the associated heterocycle planes.

[(MeCN)Ag(μ -L)₃Ag(OH₂)](ClO₄)₂. The ligand being unsymmetrical and with an odd number of ligands, the coordination environments of the two silver atoms are different, one being (S)AgNP₂ and the other (S')AgN₂P. Despite this difference, and the concomitantly different forms of solvation, both silver environments are quasi-trigonal – planar, the AgNP₂ angle sum about Ag(1) being 353.5 and the AgN₂P sum about Ag(2) 357.9°; in the latter there is a more dominant/linear array in P(2)–Ag(2)– N(312), being 149.13(6)° (with concomitantly shorter Ag– N,P distances). The water molecule hydrogens contact diverse perchlorate oxygen components. Here, again, the present structure is an interesting extension of an unsol-

Table 4

Silver environments in [(MeCN)Ag(µ-L)₃Ag(OH₂)](ClO₄)₂, 8

Atom	r	P(3)	N(212)	N(11)
(a) Ag(1)				
P(1)	2.4528(8)	114.68(3)	139.24(7)	96.84(7)
P(3)	2.5260(9)		99.53(6)	110.17(8)
N(212)	2.360(3)			91.1(1)
N(11)	2.452(3)			

Ag(1)–P(1,3)–C(1,311) are 123.2(1), 110.7(1); Ag(1)–N(212)–C(211) is 122.0(2)°. τ (Ag(1)–P(n)–C(n11)–N,C(n12)) are 29.8(3), 50.7(3), 59.7(3); 50.5(2), 19.0(3), 60.0(3)° (*n* = 1,3). Ag(1) lies 0.758(5) Å out of the bound pyridyl C₅N plane. Ag(1)···Ag(2) is 3.0149(4) Å. Ag(1)–N(11)–C(11) is 170.2(3)°.

Atom	r	N(112)	N(312)	O(2)
(b) Ag(2)				
P(2)	2.3805(9)	110.62(7)	149.13(6)	104.88(7)
N(112)	2.393(2)		98.16(9)	85.75(9)
N(312)	2.267(3)			87.68(10)
O(2)	2.559(3)			. ,

Ag(2)–P(2)–C(211) is 120.4(1); Ag(2)–N(112,312)–C(11,311) are 123.8(2), 122.3(2)°. τ (Ag(2)–P(2)–C(211)–N,C(212)) are -42.9(3), -70.5(3), -25.8(3)°. Ag(2) lies 0.333(5), 0.321(5) Å out of (C₅N) pyridyl planes 1,3.

vated precursor, namely AgClO₄:L (2:3) which in the solid state takes the form $[LAg(\mu-N(L)P)_2](ClO_4)_2$, wherein two of the ligands are bridging and one *P*-terminal, with Ag···Ag' 3.072 Å [49].

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