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Synthesis and structural characterization of adducts of silver(I) nitrate with ER_3 (E = P, As, Sb; R = Ph, cy, *o*-tolyl, mes) and oligodentate aromatic bases derivative of 2,2′-bipyridyl, L, $AgNO_3$:ER_3:L (1:1:1)

Corrado Di Nicola [a], Effendy [b,c], Fabio Marchetti [a], Claudio Pettinari [a,*], Brian W. Skelton [b], Allan H. White [b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Via S. Agostino 1, 62032 Camerino MC, Italy*
[b] *Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009, Australia*
[c] *Jurusan Pendidikan Kimia, FMIPA Universitas Negeri Malang, Jalan Surabaya 6, Malang 65145, Indonesia*

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Abstract

Twenty-one adducts of the form $AgNO_3$:ER_3:L (1:1:1) (E = P, As, Sb; R = Ph, cy, *o*-tolyl, mes; L = 2,2′-bipyridyl ('bpy')-based ligand), together with $AgNO_3$:Pcy_3:tpy (2:2:1) and $AgNO_3$:PPh_3:tpy (1:2:1) ('tpy' ≡ (2,2′:6,2″-terpyridine)), have been synthesized and characterized by analytical, spectroscopic (IR, far-IR, ^1H and ^{31}P NMR) and single crystal X-ray diffraction studies. The resulting complexes are predominantly of the form $[(R_3E)AgL]^+NO_3^-$, with trigonal $EAgN_2$ coordination environments, the planarity of which is perturbed by the approach of the nitrate anion. The nitrate ion shows uni- or (semi-)bidentate coordination, excepting the complex $AgNO_3$:P(*o*-tol)$_3$:dpca (1:1:1) (dpca = bis(2-picolyl)amine) where the anion is uncoordinated, the donor dpca being a pincer-tridentate. The complex $AgNO_3$:Pcy_3:tpy (2:2:1), also reported, is dinuclear with a bridging unidentate nitrate and a terpyridine, the latter bridging through its central ring, with the peripheral rings forming chelates to either side, whereas the complex $AgNO_3$:PPh_3:tpy (1:2:1) is ionic with a five-coordinate silver, bonded to tridentate tpy and two phosphines.

Keywords: Silver nitrate; Phosphine; Aromatic N-bases; Single crystal X-ray studies; NMR

1. Introduction

Silver(I) systems containing aromatic nitrogen donor ligands have potential applications in photography or silver plating by electrochemical processes [1–4]. Further, some silver(I) derivatives exhibit antimicrobial and antitumor activity [5–7], and some studies have revealed that macrocyclic silver(I) complexes undergo very slow acid-dependent decomplexation [8,9], a feature useful for ^{111}Ag-based radioimmunotherapy. Recently, silver(I) derivatives with N-donor ligands such as 3,4′-dipyridylamine [10] or tris{2-[2-(1-methyl)imidazolyl]-methyliminoethyl}amine [11] have shown in the solid state a mononuclear and dinuclear nature, respectively, which interconnect via hydrogen-bonding to afford interesting supramolecular structures with new topologies, with potential applications in host–guest chemistry [12–16]. Previous studies have defined arrays for various AgX/unidentate N-base/unidentate P-base combinations [17,18], and, concurrently with the present, we now publish further studies combining bidentate N- and bidentate E-base forms [19,20]. In the preceding paper [21], we extended this work further to encompass the study of the nature of adducts of

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[*] Corresponding author. Tel.: +390737 402234; fax: +39 0737 637345.
E-mail address: claudio.pettinari@unicam.it (C. Pettinari).

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the form AgX:ER$_3$:L (1:1:1), where E could be P (extended here, and in the following paper [22] to also include As, Sb), R = Ph, cy (=cyclohexyl), *o*-tol (=*o*-tolyl), mes (=mesityl), L similarly diverse in electronic and steric characteristics, as an oligo-dentate nitrogen base, here 2,2′-bipyridyl (‘bpy’), 1,10-phenanthroline (‘phen’), 2,9-dimethyl,1,10-phenanthroline (‘dmp’), 2,2′-biquinolyl (‘bq’), bis(2-pyridyl)amine (‘dpa’), bis(2-pyridyl)ketone (‘dpk’), 2,2′:6′,2″-terpyridyl (‘tpy’), and bis(2-picolyl)-amine (‘dpca’). In Ref. [21], we addressed the adducts of silver(I) perchlorate, as the first of a series of studies of arrays of increasing oxyanion basicity. In this paper, we describe an array of complexes obtained for X = NO$_3$, a further array for X = carboxylate being described in the following paper [22].

2. Experimental

Experimental procedures follow those recorded in an accompanying paper [19]; in the majority of cases, crystals suitable for the X-ray work were readily obtained from a few milliliters of MeCN solutions of the reagents on a millimolar scale by slow cooling and/or evaporation in ambience.

2.1. Syntheses

2.1.1. Synthesis of AgNO$_3$:PPh$_3$:bpy (1:1:1) (**1**)

A solution containing AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol) in 5 mL of CH$_3$CN was stirred with warming for 1 h and then cooled at room temperature. A colourless crystalline precipitate was slowly formed, which was filtered off, washed with CH$_3$CN (5 mL), dried under reduced pressure and shown to be compound **1** (0.562 g, yield 95%). M.p. 182–185 °C. *Anal.* Calc. for C$_{28}$H$_{23}$AgN$_3$O$_3$P: C, 57.16; H, 3.94; N, 7.14. Found: C, 57.30; H, 3.90; N, 7.21%. Λ_m (CH$_3$CN, 10^{-4} M): 118 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 37 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1590w, 1573w, 1566w ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1452m, 1313mbr, 834m ν(NO$_3$), 522s, 496vs, 434m, 419m, 409m, 400m ν(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 7.50m (15H, PC$_{18}H_{15}$), 7.56m, 7.96dt, 8.21dd, 8.70dd (8H, CH_{bpy}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 11.6dd (^1J(^{31}P–^{109}Ag): 449.2 Hz; ^1J(^{31}P–^{107}Ag): 389.3 Hz), 18.8dd (^1J(^{31}P–^{109}Ag): 740.6 Hz; ^1J(^{31}P–^{107}Ag): 640.9 Hz).

2.1.2. Synthesis of AgNO$_3$:PPh$_3$:phen (1:1:1) (**2**)

Compound **2** (0.590 g, yield 96%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and phen (0.180 g, 1.0 mmol). M.p. 149–151 °C. *Anal.* Calc. for C$_{30}$H$_{28}$AgN$_3$O$_3$P: C, 58.84; H, 3.97; N, 6.86. Found: C, 58.72; H, 3.91; N, 6.74%. Λ_m (CH$_3$CN, 10^{-4} M): 120 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 35 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1619w, 1587w, 1572w, 1510m ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1454m, 1309m, 846s ν(NO$_3$), 524vs, 504s, 493s, 444m, 435m, 417m ν(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 7.45m, 757m (15H, PC$_{18}H_{15}$), 7.79dd, 7.92s, 8.41dd, 9.05dd (8H, CH_{phen}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 14.0dbr (^1J(^{31}P–$^{109/107}$Ag): 674.6 Hz).

2.1.3. Synthesis of AgNO$_3$:PPh$_3$:dmp (1:1:1) (**3**)

Compound **3** (0.563 g, yield 88%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and dmp (0.208 g, 1.0 mmol). M.p. 250–252 °C. *Anal.* Calc. for C$_{32}$H$_{27}$AgN$_3$O$_3$P: C, 60.01; H, 4.25; N, 6.56. Found: C, 59.74; H, 4.33; N, 6.35%. Λ_m (CH$_3$CN, 10^{-4} M): 123 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 38 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1617w, 1585w, 1576w, 1511m ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1455m, 1311m, 855s ν(NO$_3$), 526vs, 505s, 489s, 444m, 435m, 416m ν(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 2.82s (6H, C$H_{3\text{dmp}}$), 7.42m, 756m (15H, PC$_{18}H_{15}$), 7.63d, 7.81s, 8.28d (6H, CH_{dmp}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 11.4dd (^1J(^{31}P–^{109}Ag): 534.7 Hz; ^1J(^{31}P–^{107}Ag): 463.7 Hz), 13.8dd (^1J(^{31}P–^{109}Ag): 701.9 Hz; ^1J(^{31}P–^{107}Ag): 606.6 Hz). The compound was modelled in the X-ray study as **3**·½ MeOH.

2.1.4. Synthesis of AgNO$_3$:PPh$_3$:bq (1:1:1) (**4**)

Compound **4** (0.578 g, yield 84%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol). M.p. 261–263 °C. *Anal.* Calc. for C$_{36}$H$_{27}$AgN$_3$O$_3$P: C, 62.81; H, 3.95; N, 6.10. Found: C, 62.56; H, 4.11; N, 6.73%. Λ_m (CH$_3$CN, 10^{-4} M): 113 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 35 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1747w, 1738w ν(NO$_3$), 1617m, 1593s, 1571sh, 1554m, 1546m, 1504s ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1436s, 1317s, 828s ν(NO$_3$), 521vs, 507s, 499s, 487s, 480s, 441m, 433m, 424m, 394m ν(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 7.38m, 752m (15H, PC$_{18}H_{15}$), 7.64m, 8.14d, 8.28d, 8.32dd (12H, CH_{bq}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 13.9dd (^1J(^{31}P–^{109}Ag): 695.7 Hz; ^1J(^{31}P–^{107}Ag): 603.0 Hz).

2.1.5. Synthesis of AgNO$_3$:PPh$_3$:dpa (1:1:1) (**5**)

Compound **5** (0.530 g, yield 88%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol). M.p. 230–232 °C. *Anal.* Calc. for C$_{28}$H$_{24}$AgN$_4$O$_3$P: C, 55.74; H, 4.01; N, 9.29. Found: C, 55.38; H, 4.13; N, 8.98%. Λ_m (CH$_3$CN, 10^{-4} M): 98 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 5 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 3300m, 3250m, 3190m ν(N–H$_{\text{dpa}}$), 1742w, 1738w ν(NO$_3$), 1630s, 1575s, 1526m, ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1412s, 1338s, 826m ν(NO$_3$), 520vs, 506s, 493s, 440m, 427m, 407s ν(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 7.47m (15H, PC$_{18}H_{15}$), 6.83m, 7.34m, 7.66dd, 8.03dd (8H, CH_{dpa}), 10.10br (1H, NH_{dpa}).

^{31}P NMR ($CDCl_3$, 223 K): δ, 17.4dd ($^1J(^{31}P–^{109}Ag)$: 744.7 Hz; $^1J(^{31}P–^{107}Ag)$: 645.8 Hz).

*2.1.6. Synthesis of $AgNO_3$:PPh_3:dpk (1:1:1) (**6**)*

Compound **6** (0.573 g, yield 93%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dpk (0.184 g, 1.0 mmol). M.p. 141–143 °C. *Anal.* Calc. for $C_{29}H_{23}AgN_3O_4P$: C, 56.51; H, 3.76; N, 6.82. Found: C, 57.82; H, 3.82; N, 6.64%. Λ_m (CH_3CN, 10^{-4} M): $124\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $56\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 1750w, 1738w ν(NO_3), 1654s, 1611w, 1590m, 1567m ν(C$\cdots$C, C$\cdots$N), 1434s, 1315s, 833s, 821s ν(NO_3), 513s, 504vs, 458w, 4425m, 414m, 403w ν(PPh_3), 386m, 304w, 280w, 262m, 247w, 228w, 221w. ^1H NMR ($CDCl_3$, 293 K): δ, 7.32m (15H, $PC_{18}H_{15}$), 7.59dt, 7.94dt, 8.09dd, 8.86dd (8H, CH_{dpk}). ^{31}P NMR ($CDCl_3$, 223K): δ, 11.4dd ($^1J(^{31}P–^{109}Ag)$: 535.9 Hz; $^1J(^{31}P–^{107}Ag)$: 466.2 Hz), 13.7dd ($^1J(^{31}P–^{109}Ag)$: 749.5 Hz; $^1J(^{31}P–^{107}Ag)$: 649.4 Hz).

*2.1.7. Synthesis of $AgNO_3$:$AsPh_3$:bpy (1:1:1) (**7**)*

Compound **7** (0.575 g, yield 91%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), $AsPh_3$ (0.306 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol). M.p. 174–176 °C. *Anal.* Calc. for $C_{28}H_{23}AgAsN_3O_3$: C, 53.19; H, 3.67; N, 6.65. Found: C, 53.44; H, 3.80; N, 6.47%. Λ_m (CH_3CN, 10^{-4} M): $137\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $23\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 1587m, 1574m, 1523w, ν(C$\cdots$C, C$\cdots$N), 1461s, 1305s, 824m ν(NO_3), 470vs, 408m ν($AsPh_3$), 333m, 321s. ^1H NMR ($CDCl_3$, 293 K): δ, 7.40m (15H, $AsC_{18}H_{15}$), 7.50m, 7.89dd, 8.15dd, 8.71dd (8H, CH_{bpy}).

*2.1.8. Synthesis of $AgNO_3$:$AsPh_3$:dpa (1:1:1) (**8**)*

Compound **8** (0.556 g, yield 86%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), $AsPh_3$ (0.306 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol). M.p. 205–207 °C. *Anal.* Calc. for $C_{28}H_{24}AgAsN_4O_3$: C, 51.96; H, 3.74; N, 8.66. Found: C, 52.12; H, 3.90; N, 8.62%. Λ_m (CH_3CN, 10^{-4} M): $110\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $3\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 3310m, 3240m, 3190m ν(N–H_{dpa}), 1742w, 1738w ν(NO_3), 1626s, 1575s, 1526m, ν(C$\cdots$C, C$\cdots$N), 1412s, 1340s, 825m ν(NO_3), 525m, 478s, 471vs, 458s, 406s ν($AsPh_3$), 339m, 325s, 317s. ^1H NMR ($CDCl_3$, 293 K): δ, 7.43m (15H, $AsC_{18}H_{15}$), 6.83m, 7.32m, 7.62m, 8.10m (8H, CH_{dpa}), 9.50br (1H, NH_{dpa}).

*2.1.9. Synthesis of $AgNO_3$:$AsPh_3$:bq (1:1:1) (**9**)*

Compound **9** (0.688 g, yield 94%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), $AsPh_3$ (0.306 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol). M.p. >220 °C (dec.). *Anal.* Calc. for $C_{36}H_{27}AgAsN_3O_3$: C, 59.04; H, 3.72; N, 5.74. Found: C, 59.18; H, 3.92; N, 5.73%. Λ_m (CH_3CN, 10^{-4} M): $135\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $23\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 1622m, 1591s, 1524m, 1503s ν(C$\cdots$C, C$\cdots$N), 1434s, 1310s, 828vs ν(NO_3), 502m, 481s, 470vs, 462s, 397m, 377m ν($AsPh_3$), 347s, 322s, 316s. ^1H NMR ($CDCl_3$, 293 K): δ, 7.29m, 7.38m (15H, $AsC_{18}H_{15}$), 7.50dt, 7.60dt, 7.73dd, 8.14d, 8.26d, 8.39d (12H, CH_{bq}). The compound was modelled in the X-ray study as **9**·MeCN.

*2.1.10. Synthesis of $AgNO_3$:$SbPh_3$:dpa (1:1:1) (**10**)*

Compound **10** (0.646 g, yield 95%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), $SbPh_3$ (0.353 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol). M.p. 168–170 °C. *Anal.* Calc. for $C_{28}H_{24}AgN_3O_3Sb$: C, 48.45; H, 3.49; N, 8.07. Found: C, 48.42; H, 3.61; N, 8.16%. Λ_m (CH_3CN, 10^{-4} M): $144\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $3\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 3335m, 3240m, 3180m ν(NH_{dpa}), 1744w, 1736w ν(NO_3), 1627s, 1578s, 1575s, 1527s, ν(C$\cdots$C, C$\cdots$N), 1432s, 1339s, 825m ν(NO_3), 525m, 460s, 453s, 442m, 406m, 345w, 328w ν($SbPh_3$), 283s, 265vs. ^1H NMR ($CDCl_3$, 293 K): δ, 7.46m (15H, $SbC_{18}H_{15}$), 6.74m, 7.35m, 7.55m, 8.11dd (8H, CH_{dpa}), 9.35br (1H, NH_{dpa}).

*2.1.11. Synthesis of $AgNO_3$:$SbPh_3$:bq (1:1:1) (**11**)*

Compound **11** (0.670 g, yield 86%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile/ethanol solution of $AgNO_3$ (0.170 g, 1.0 mmol), $SbPh_3$ (0.353 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol). M.p. 238–240 °C. *Anal.* Calc. for $C_{36}H_{27}AgN_3O_3Sb$: C, 55.49; H, 3.49; N, 5.39. Found: C, 55.72; H, 3.58; N, 5.26%. Λ_m (CH_3CN, 10^{-4} M): $135\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $24\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 1617m, 1594m, 1575w, 1556w, 1546w, 1503s ν(C$\cdots$C, C$\cdots$N), 1432s, 1402m, 1334s, 819s ν(NO_3), 501m, 488m, 482m, 456vs, 426w, 399w, ν($SbPh_3$), 279m, 267s, 224m. ^1H NMR ($CDCl_3$, 293 K): δ, 7.30m, 7.45m (15H, $SbC_{18}H_{15}$), 7.49dt, 7.58dt, 7.63dt, 8.11d, 8.24d, 8.50d (12H, CH_{bq}). The compound was modelled in the X-ray study as **11**·1½EtOH.

*2.1.12. Synthesis of $AgNO_3$:Pcy_3:bpy (1:1:1) (**12**)*

Compound **12** (0.466 g, yield 77%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), Pcy_3 (0.280 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol). M.p. 144–146 °C. *Anal.* Calc. for $C_{28}H_{41}AgN_3O_3P$: C, 55.45; H, 6.93; N, 6.93. Found: C, 55.41; H, 6.88; N, 7.12%. Λ_m (CH_3CN, 10^{-4} M): $134\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_m (CH_2Cl_2, 10^{-4} M): $35\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (nujol, cm^{-1}): 1745w, 1736w ν(NO_3), 1614m, 1594s, 1572m ν(C$\cdots$C, C$\cdots$N), 1454s, 1310vs, 823m ν(NO_3), 515vs, 471m, 460m, 410s, 391m, 383m ν(Pcy_3). ^1H NMR ($CDCl_3$, 293 K): δ, 1.36m, 1.91m (33H, $PC_{18}H_{33}$), 7.57dt, 8.07dt, 8.42dd, 8.66dd (8H, CH_{bpy}). ^{31}P NMR ($CDCl_3$, 223 K): δ, 46.2dd ($^1J(^{31}P–^{109}Ag)$: 723.8 Hz; $^1J(^{31}P–^{107}Ag)$: 627.3 Hz). The compound was modelled in the X-ray study as **12**·3/8MeCN.

2.1.13. Synthesis of *AgNO$_3$:Pcy$_3$:phen (1:1:1)* (***13***)

Compound **13** (0.523 g, yield 83%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of AgNO$_3$ (0.170 g, 1.0 mmol), Pcy$_3$ (0.280 g, 1.0 mmol), and phen (0.180 g, 1.0 mmol). M.p. 237–239 °C. *Anal.* Calc. for C$_{30}$H$_{41}$AgN$_3$O$_3$P: C, 57.15; H, 6.55; N, 6.66. Found: C, 57.41; H, 6.52; N, 6.53%. Λ_m (CH$_3$CN, 10^{-4} M): 111 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 57 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1741w ν(NO$_3$), 1617m, 1590m, 1570m, 1512s, 1500m ν(C$\underline{\cdots}$C, C$\underline{\cdots}$N), 1425s, 1307s, 844vs ν(NO$_3$), 520vs, 471s, 458m, 416m, 392w, 380w ν(Pcy$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ, 1.38m, 1.94m (33H, PC$_{18}H_{33}$), 7.95dd, 8.07s, 8.56dd, 9.04dd (8H, CH_{phen}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 46.3dd ($^1J(^{31}$P–^{109}Ag): 725.1 Hz; $^1J(^{31}$P–^{107}Ag): 627.3 Hz), 33.0dd ($^1J(^{31}$P–^{109}Ag): 529.7 Hz; $^1J(^{31}$P–^{107}Ag): 458.9 Hz).

2.1.14. Synthesis of *AgNO$_3$:Pcy$_3$:bq (1:1:1)* (***14***)

Compound **14** (0.649 g, yield 92%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of AgNO$_3$ (0.170 g, 1.0 mmol), Pcy$_3$ (0.280 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol). M.p. 184–186 °C. *Anal.* Calc. for C$_{36}$H$_{45}$AgN$_3$O$_3$P: C, 61.19; H, 6.42; N, 5.95. Found: C, 61.33; H, 6.48; N, 5.90%. Λ_m (CH$_3$CN, 10^{-4} M): 115 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 52 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1732w, 1718w ν(NO$_3$), 1618m, 1593s, 1555m, 1549m, 1535w, 1504s ν(C$\underline{\cdots}$C, C$\underline{\cdots}$N), 1446s, 1420w, 1309s, 828s ν(NO$_3$), 564w, 547m, 533w, 514m, 501w, 484s, 472w, 443w, 420w, 399m ν(Pcy$_3$), 280m, 224m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 1.24m, 1.83m (33H, PC$_{18}H_{33}$), 7.62dt, 7.74dt, 7.82dt, 8.33d, 8.38d, 8.62d (12H, CH_{bq}). ^{31}P NMR (CDCl$_3$, 223 K): δ, 37.3dd ($^1J(^{31}$P–^{109}Ag): 701.9 Hz; $^1J(^{31}$P–^{107}Ag): 609.2 Hz), 32.9dd ($^1J(^{31}$P–^{109}Ag): 528.6 Hz; $^1J(^{31}$P–^{107}Ag): 457.8 Hz).

2.1.15. Synthesis of *AgNO$_3$:Pcy$_3$:dpa (1:1:1)* (***15***)

Compound **15** (0.540, yield 87%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of AgNO$_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.262 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol). M.p. 190°C (dec.). *Anal.* Calc. for C$_{28}$H$_{42}$AgN$_3$O$_3$P: C, 54.11; H, 6.81; N, 9.01. Found: C, 53.78; H, 6.71; N, 8.83%. Λ_m (CH$_3$CN, 10^{-4} M): 102 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 3 Ω^{-1} cm^2 mol^{-1}.

2.1.16. Synthesis of *AgNO$_3$:Ascy$_3$:bq (1:1:1)* (***16***)

Complex **16** was obtained by crystallization of millimolar stoichiometries of AgNO$_3$ with Ascy$_3$ and bq, from acetonitrile solution by standing and evaporation in ambience. M.p. 187–90 °C. *Anal.* Calc. for C$_{36}$H$_{45}$AgAsN$_3$O$_3$: C, 57.61; H, 6.04; N, 5.60. Found: C, 57.54; H, 6.01; N, 5.52%. Λ_m (CH$_3$CN, 10^{-4} M): 122 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 48 Ω^{-1} cm^2 mol^{-1}.

2.1.17. Synthesis of *AgNO$_3$:P(o-tol)$_3$:bpy (1:1:1)* (***17***)

Compound **17** (0.580 g, yield 92%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of AgNO$_3$ (0.170 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol). M.p. 212–214°C. *Anal.* Calc. for C$_{31}$H$_{29}$AgN$_3$O$_3$P: C, 59.06; H, 4.64; N, 6.67. Found: C, 58.78; H, 4.77; N, 6.83%. Λ_m (CH$_3$CN, 10^{-4} M): 132 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 40 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1747w, 1738w, 1732w ν(NO$_3$), 1633w, 1587m, 1573w, 1564w ν(C$\underline{\cdots}$C, C$\underline{\cdots}$N), 1439m, 1392m, 1302s br, 822s, 802s ν(NO$_3$), 564s, 557sh, 519m, 511m, 468vs, 461vs, 440w, 411m ν(P(*o*-tol)$_3$), 279m, 267m, 227m, 205m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 2.54s (9H, P(C$_6$H$_4$-*ortho*-CH_3)$_3$), 6.91dd, 7.21t, 7.38m (12H, P(C$_6H_4$-*ortho*-CH$_3$)$_3$), 7.45dt, 8.02dt, 8.34d, 8.44dd (8H, CH_{bpy}). ^{31}P NMR (CDCl$_3$, 223 K): δ, −18.4d br ($^1J(^{31}$P–$^{109/107}$Ag): 672.5 Hz). The compound was modelled in the X-ray study as **17**·½MeCN.

2.1.18. Synthesis of *AgNO$_3$:P(o-tol)$_3$:bq (1:1:1)* (***18***)

Compound **18** (0.613 g, yield 84%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of AgNO$_3$ (0.170 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol). M.p. 255–257 °C. *Anal.* Calc. for C$_{39}$H$_{33}$AgN$_3$O$_3$P: C, 64.12 H, 4.55; N, 5.75. Found: C, 64.40; H, 4.71; N, 5.85%. Λ_m (CH$_3$CN, 10^{-4} M): 129 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 41 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1619m, 1594s, 1574m, 1564m, 1554m, 1546m, 1504s ν(C$\underline{\cdots}$C, C$\underline{\cdots}$N), 1455s, 1433m, 1417w, 1338m, 1307s br, 833s, 822m ν(NO$_3$), 564vs, 521m, 514m, 488s, 473vs, 468vs, 461vs, 440m ν(P(*o*-tol)$_3$), 399m, 278m, 272m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 2.39s (9H, P(C$_6$H$_4$-*ortho*-CH_3)$_3$), 7.08m, 7.45m (12H, P(C$_6H_4$-*ortho*-CH$_3$)$_3$), 7.63dt, 7.75dt, 7.92m, 8.53d, 8.71d (12H, CH_{bq}). ^{31}P NMR (CDCl$_3$, 223 K): δ, −8.6 br.

2.1.19. Synthesis of *AgNO$_3$:P(o-tol)$_3$:dpa (1:1:1)* (***19***)

Compound **19** (0.567 g, yield 88%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of AgNO$_3$ (0.170 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol). M.p. 171–173 °C. *Anal.* Calc. for C$_{31}$H$_{30}$AgN$_4$O$_3$P: C, 57.69; H, 4.68; N, 8.68. Found: C, 57.55; H, 4.60; N, 8.34%. Λ_m (CH$_3$CN, 10^{-4} M): 105 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH$_2$Cl$_2$, 10^{-4} M): 4 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1740w, 1733w, 1698w ν(NO$_3$), 1638s, 1588s, 1578s, 1547w, 1531s, 1514w ν(C$\underline{\cdots}$C, C$\underline{\cdots}$N), 1440s, 1413s ν_{as}(NO$_3$), 1290s, 824m, 803s ν_s(NO$_3$), 565s, 558sh, 519s, 469vs, 460vs, 440w, 405m ν(P(*o*-tol)$_3$), 326m, 279m, 226m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 2.43s (9H, P(C$_6$H$_4$-*ortho*-CH_3)$_3$), 6.91dd, 7.21t, 7.40m (12H, P(C$_6H_4$-*ortho*-CH$_3$)$_3$), 6.76m, 7.35m, 7.62dd, 7.80dd (8H, CH_{dpa}), 9.80br (1H, NH_{dpa}). ^{31}P NMR (CDCl$_3$, 223 K): δ, −17.3d ($^1J(^{31}$P–$^{109/107}$Ag): 673.8 Hz). The compound was modelled in the X-ray study as **19**·½EtOH.

2.1.20. Synthesis of $AgNO_3$:P(o-tol)$_3$:dpca:H_2O (1:1:1:1) (**20**)

Compound **20** (0.641 g, yield 93%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol) and dpca (0.199 g, 1.0 mmol). M.p. 195–197 °C. *Anal.* Calc. for $C_{33}H_{34}AgN_4O_4P$: C, 57.49; H, 4.97; N,8.13. Found: C, 57.60; H, 5.06; N, 8.14%. Λ_m (CH_3CN, 10^{-4} M): 139 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 56 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 3360v br ν(N–H$_{dpca}$ + H_2O), 1644m δ(H_2O), 1590s, 1567m ν(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 1441s ν_{as}(NO_3), 1313s br, 828m, 799m ν_s(NO_3), 564s, 557sh, 521s, 504s, 464vs, 440m, 409m, 402m ν(P(*o*-tol)$_3$), 303m, 268vs. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.39s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 4.07s (4H, CH_{2dpac}), 4.80br (2H, H_2O), 7.17t, 7.28m, 7.40dt (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.87t, 7.03dt, 7.64dt, 7.72d (8H, CH_{dpca}), NH_{dpca} not observed. ^{31}P NMR ($CDCl_3$, 223 K): δ, −17.5d br (^1J(^{31}P–$^{109/107}$Ag): 640.8 Hz). The compound was modelled in the X-ray study as **20**·½H_2O.

2.1.21. Synthesis of $AgNO_3$:PPhmes$_2$:tpy (1:1:1) (**21**)

Compound **21** (0.630 g, yield 84%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of $AgNO_3$ (0.170 g, 1.0 mmol), PPhmes$_2$ (0.346 g, 1.0 mmol), and tpy (0.233 g, 1.0 mmol). M.p. 205–208 °C. *Anal.* Calc. for $C_{39}H_{38}AgN_4O_3P$: C, 62.49; H, 5.11; N, 7.47. Found: C, 62.62; H, 5.10; N, 7.32%. Λ_m (CH_3CN, 10^{-4} M): 116 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 45 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1603s, 1589s, 1578s ν(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 1445s ν_{as}(NO_3), 1328s br, 828m, 800m ν_s(NO_3), 570m, 560vs, 543m, 524m, 512w, 482s, 447vs, 430vs, 410m, 401m ν(PPhmes$_2$), 303m, 268vs. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.90s, 2.26s (18H, P(C_6H_5)(C_6H_2-2,4,6-(CH_3)$_3$)$_2$), 6.76s, 6.77s (4H, P(C_6H_5)($C_6$$H_2$-2,4,6-($CH_3$)$_3$)$_2$), 7.23t, 7.27t, 7.41d (5H, P($C_6$$H_5$)($C_6H_2$-2,4,6-($CH_3$)$_3$)$_2$), 7.45br, 7.91t, 8.08sbr, 8.18t, 8.30dd (11H, CH_{tpy}). ^{31}P NMR ($CDCl_3$, 298 K): δ, −11.2s. ^{31}P NMR ($CDCl_3$, 223 K): δ, −12.1dd (^1J(^{31}P–^{109}Ag): 710.3 Hz; ^1J(^{31}P–^{107}Ag): 615.3 Hz).

2.1.22. Synthesis of $AgNO_3$:Pcy$_3$:tpy (2:2:1) (**22**)

Compound **22** (0.499 g, yield 88%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of $AgNO_3$ (0.170 g, 1.0 mmol), Pcy$_3$ (0.280 g, 1.0 mmol), and tpy (0.233 g, 1.0 mmol). M.p. 174–176 °C. *Anal.* Calc. for $C_{51}H_{77}Ag_2N_5O_6P_2$: C, 54.03; H, 6.84; N, 6.18. Found: C, 53.84; H, 6.75; N, 6.37%. Λ_m (CH_3CN, 10^{-4} M): 250 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 32 Ω^{-1} cm^2 mol^{-1}. IR (nujol, cm^{-1}): 1741w, 1733w ν(NO_3), 1592s, 1573m, 1567m, 1560m ν(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 1438vs, 1406s, 1353vs, 1290vs, 850s, 830m, 818m ν(NO_3), 542w, 515vs, 487m, 471m, 459w, 450w, 416s, 392m, 383m ν(Pcy$_3$), 351w, 288m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.18m, 1.70m (33H, P$C_{18}$$H_{33}$), 7.45dd, 8.00dt, 8.18dt, 8.27dd, 8.70d (11H, CH_{tpy}). ^{31}P NMR ($CDCl_3$, 223 K): δ, 33.1dd (^1J(^{31}P–^{109}Ag): 528.6 Hz; ^1J(^{31}P–^{107}Ag): 457.8 Hz), 42.7dd (^1J(^{31}P–^{109}Ag): 740.9 Hz; ^1J(^{31}P–^{107}Ag): 647.1 Hz).

2.1.23. Synthesis of $AgNO_3$:PPh$_3$:tpy (1:2:1) (**23**)

Compound **23** (0.834 g, yield 90%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of $AgNO_3$ (0.170 g, 1.0 mmol), PPh$_3$ (0.524 g, 2.0 mmol), and tpy (0.233 g, 1.0 mmol). M.p. 180°C (dec.). *Anal.* Calc. for $C_{51}H_{41}AgN_4O_3P_2$: C, 66.03; H, 4.45; N, 6.04. Found: C, 65.78; H, 4.47; N, 5.80%. Λ_m (CH_3CN, 10^{-4} M): 165 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 23 Ω^{-1} cm^2 mol^{-1}.

2.2. Structure determinations

General procedures are described in an accompanying paper [19]; specific details are as follows. For **1**, **2**, *T* was ca. 300 K. CCDC Nos. 605475–605497.

2.2.1. Crystal/refinement data

2.2.1.1. *$AgNO_3$:PPh$_3$:bpy (1:1:1) (**1**).* $C_{28}H_{23}AgN_3O_3P$, $M = 588.4$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 18.267(2)$, $b = 9.689(1)$, $c = 8.139(1)$ Å, $\alpha = 112.496(2)°$, $\beta = 96.410(2)°$, $\gamma = 100.032(2)°$, $V = 1285$ Å^3. D_{calc} ($Z = 2$) = 1.52_0 g cm^{-3}. $\mu_{Mo} = 8.8$ cm^{-1}; specimen: $0.62 \times 0.28 \times 0.12$ mm; 'T'$_{min/max} = 0.85$. $2\theta_{max} = 58°$; $N_t = 14338$; $N = 6259$ ($R_{int} = 0.022$), $N_o = 4401$; $R = 0.031$, $R_w = 0.035$. $(x, y, z, U_{iso})_H$ refined.

2.2.1.2. *$AgNO_3$:PPh$_3$:phen (1:1:1) (**2**).* $C_{30}H_{23}AgN_3O_3P$, $M = 612.4$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 17.192(2)$, $b = 8.913(1)$, $c = 17.994(2)$ Å, $\beta = 105.726(2)°$, $V = 2654$ Å^3. D_{calc} ($Z = 4$) = 1.53_2 g cm^{-3}. $\mu_{Mo} = 8.6$ cm^{-1}; specimen: $0.20 \times 0.15 \times 0.10$ mm; 'T'$_{min/max} = 0.67$. $2\theta_{max} = 58°$; $N_t = 29634$, $N = 6707$ ($R_{int} = 0.028$), $N_o = 3613$; $R = 0.036$, $R_w = 0.037$. $(x, y, z, U_{iso})_H$ refined.

2.2.1.3. *$AgNO_3$:PPh$_3$:dmp (1:1:1) · ½MeOH (**3** · ½MeOH).* $C_{32}H_{27}AgN_3O_3P \cdot ½CH_3OH$, $M = 656.4$. Monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), $a = 48.535(3)$, $b = 8.3275(5)$, $c = 37.678(2)$ Å, $\beta = 129.604(1)°$, $V = 11733$ Å^3. D_{calc} ($Z = 16$) = 1.48_6 g cm^{-3}. $\mu_{Mo} = 7.8$ cm^{-1}; specimen: $0.35 \times 0.27 \times 0.20$ mm; 'T'$_{min/max} = 0.80$. $2\theta_{max} = 58°$; $N_t = 64761$, $N = 14878$ ($R_{int} = 0.025$), $N_o = 9403$; $R = 0.037$, $R_w = 0.042$. $(x, y, z, U_{iso})_H$ refined.

Variata. Solvent difference map residues were modelled as 0.5MeOH.

2.2.1.4. *$AgNO_3$:PPh$_3$:bq (1:1:1) (**4**).* $C_{36}H_{27}AgN_3O_3P$, $M = 688.5$. Triclinic, space group $P\bar{1}$, $a = 16.673(2)$, $b = 10.488(1)$, $c = 10.040(2)$ Å, $\alpha = 63.65(1)°$, $\beta = 86.19(1)°$, $\gamma = 86.843(1)°$, $V = 1569$ Å^3. D_{calc} ($Z = 2$) = 1.45_7 g cm^{-3}. $\mu_{Mo} = 7.3$ cm^{-1}; specimen: $0.08 \times 0.38 \times 0.79$ mm; 'T'$_{min/max} = 0.82$. $2\theta_{max} = 50°$; $N = 5506$, $N_o = 3586$; $R = 0.047$, $R_w = 0.046$.

*2.2.1.5. AgNO$_3$:PPh$_3$:dpa (1:1:1) (**5**).* $C_{28}H_{24}AgN_4O_3P$, $M = 603.4$. Monoclinic, space group $P2_1/n$ (C^5_{2h}, No. 14 (variant)), $a = 17.189(2)$, $b = 9.171(1)$, $c = 18.013(2)$ Å, $\beta = 113.618(2)°$, $V = 2602$ Å^3. D_{calc} ($Z = 4$) $= 1.54_0$ g cm^{-3}. $\mu_{\text{Mo}} = 8.7$ cm^{-1}; specimen: $0.38 \times 0.16 \times 0.11$ mm; 'T'$_{\text{min/max}} = 0.87$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 30216$, $N = 6553$ ($R_{\text{int}} = 0.028$), $N_{\text{o}} = 5685$; $R = 0.023$, $R_w = 0.019$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.6. AgNO$_3$:PPh$_3$:dpk (1:1:1) (**6**).* $C_{29}H_{23}AgN_3O_4P$, $M = 616.4$. Triclinic, space group $P\bar{1}$, $a = 13.283(5)$, $b = 10.902(2)$, $c = 9.542(3)$ Å, $\alpha = 90.14(2)°$, $\beta = 108.07(3)°$, $\gamma = 90.34(2)°$, $V = 1313$ Å^3. D_{calc} ($Z = 2$) $= 1.55_8$ g cm^{-3}. $\mu_{\text{Mo}} = 8.7$ cm^{-1}; specimen: $0.04 \times 0.36 \times 0.52$ mm; 'T'$_{\text{min/max}} = 0.78$. $2\theta_{\text{max}} = 50°$; $N = 4612$, $N_{\text{o}} = 3145$; $R = 0.042$ $R_w = 0.041$.

*2.2.1.7. AgNO$_3$:AsPh$_3$:bpy (1:1:1) (**7**).* $C_{28}H_{23}AgAsN_3O_3$, $M = 632.3$. Triclinic, space group $P\bar{1}$, $a = 18.325(2)$, $b = 9.629(1)$, $c = 8.0710(9)$ Å, $\alpha = 112.056(2)°$, $\beta = 95.443(2)°$, $\gamma = 100.402(2)°$, $V = 1277$ Å^3. D_{calc} ($Z = 2$) $= 1.64_4$ g cm^{-3}. $\mu_{\text{Mo}} = 21$ cm^{-1}; specimen: $0.40 \times 0.20 \times 0.20$ mm; 'T'$_{\text{min/max}} = 0.75$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 14426$, $N = 6093$ ($R_{\text{int}} = 0.018$), $N_{\text{o}} = 5355$; $R = 0.022$, $R_w = 0.030$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.8. AgNO$_3$:AsPh$_3$:dpa (1:1:1) (**8**).* $C_{28}H_{24}AgAsN_4O_3$, $M = 647.3$. Monoclinic, space group $P2_1/n$, $a = 17.313(1)$, $b = 9.2056(1)$, $c = 18.049(2)$ Å, $\beta = 112.842(1)°$, $V = 2651$ Å^3. D_{calc} ($Z = 4$) $= 1.62_2$ g cm^{-3}. $\mu_{\text{Mo}} = 20$ cm^{-1}; specimen: $0.42 \times 0.22 \times 0.12$ mm; 'T'$_{\text{min/max}} = 0.76$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 30469$, $N = 6565$ ($R_{\text{int}} = 0.018$), $N_{\text{o}} = 5961$; $R = 0.018$, $R_w = 0.028$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

Variata. This complex is isomorphous with its E = Sb counterpart, **10** (see below), and was refined in the same cell and coordinate setting.

*2.2.1.9. AgNO$_3$:AsPh$_3$:bq (1:1:1) · MeCN (**9** · MeCN).* $C_{38}H_{30}AgAsN_4O_3$, $M = 773.5$. Monoclinic, space group $P2_1/c$, $a = 8.957(2)$, $b = 17.989(1)$, $c = 20.910(4)$ Å, $\beta = 100.872(3)°$, $V = 3309$ Å^3. D_{calc} ($Z = 4$) $= 1.55_3$ g cm^{-3}. $\mu_{\text{Mo}} = 16.5$ cm^{-1}; specimen: 0.10 mm (cuboid); 'T'$_{\text{min/max}} = 0.85$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 38846$, $N = 8420$ ($R_{\text{int}} = 0.028$), $N_{\text{o}} = 6897$; $R = 0.029$, $R_w = 0.037$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.10. AgNO$_3$:SbPh$_3$:dpa (1:1:1) (**10**).* $C_{28}H_{24}AgN_3O_3Sb$, $M = 694.1$. Monoclinic, space group $P2_1/n$, $a = 17.562(2)$, $b = 9.2343(8)$, $c = 18.079(2)$ Å, $\beta = 111.307(1)°$, $V = 2732$ Å^3. D_{calc} ($Z = 4$) $= 1.68_8$ g cm^{-3}. $\mu_{\text{Mo}} = 17.4$ cm^{-1}; specimen: $0.55 \times 0.24 \times 0.10$ mm; 'T'$_{\text{min/max}} = 0.77$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 31309$, $N = 6846$ ($R_{\text{int}} = 0.026$), $N_{\text{o}} = 6499$; $R = 0.033$, $R_w = 0.038$.

Variata. This complex is isomorphous with its E = As counterpart (see above) and was refined in the same cell and coordinate setting.

*2.2.1.11. AgNO$_3$:SbPh$_3$:bq (1:1:1) · 1½EtOH (**11** · 1½EtOH).* $C_{39}H_{36}AgN_3O_{4.5}Sb$, $M = 848.4$. Triclinic, space group $P\bar{1}$, $a = 9.571(1)$, $b = 11.690(1)$, $c = 16.826(2)$ Å, $\alpha = 70.283(2)°$, $\beta = 82.962(2)°$, $\gamma = 75.957(2)°$, $V = 1717$ Å^3. D_{calc} ($Z = 2$) $= 1.64_0$ g cm^{-3}. $\mu_{\text{Mo}} = 14.0$ cm^{-1}; specimen: $0.25 \times 0.15 \times 0.13$ mm; 'T'$_{\text{min/max}} = 0.83$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 9513$ (hemisphere), $N = 7321$ ($R_{\text{int}} = 0.013$), $N_{\text{o}} = 6331$; $R = 0.024$, $R_w = 0.027$.

Variata. One of the solvent molecules was modelled as disordered about a crystallographic inversion centre.

*2.2.1.12. AgNO$_3$:Pcy$_3$:bpy (1:1:1) · 3/8MeCN (**12** · 3/8MeCN).* $C_{28}H_{41}AgN_3O_3P \cdot 3/8$MeCN, $M = 621.9$. Triclinic, space group $P\bar{1}$, $a = 19.917(3)$, $b = 15.407(2)$, $c = 10.024(2)$ Å, $\alpha = 82.91(2)°$, $\beta = 78.04(2)°$, $\gamma = 82.45(1)°$, $V = 2968$ Å^3. D_{calc} ($Z = 4$) $= 1.39_2$ g cm^{-3}. $\mu_{\text{Mo}} = 7.7$ cm^{-1}; specimen: $0.30 \times 0.42 \times 0.08$ mm; 'T'$_{\text{min/max}} = 0.85$. $2\theta_{\text{max}} = 55°$; $N = 10406$, $N_{\text{o}} = 5863$; $R = 0.054$, $R_w = 0.054$.

Variata. Difference map residues were modelled (rigid body) as MeCN, site occupancy set at 0.75 after trial refinement.

*2.2.1.13. AgNO$_3$:Pcy$_3$:phen (1:1:1) (**13**).* $C_{30}H_{41}AgN_3O_3P$, $M = 630.5$. Monoclinic, space group $P2_1/c$, $a = 8.7447(4)$, $b = 37.064(2)$, $c = 9.5248(5)$ Å, $\beta = 110.944(1)°$, $V = 2883$ Å^3. D_{calc} ($Z = 4$) $= 1.45_2$ g cm^{-3}. $\mu_{\text{Mo}} = 7.9$ cm^{-1}; specimen: $0.43 \times 0.20 \times 0.05$ mm; 'T'$_{\text{min/max}} = 0.79$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 32904$, $N = 7302$ ($R_{\text{int}} = 0.029$), $N_{\text{o}} = 4587$; $R = 0.040$ $R_w = 0.041$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.14. AgNO$_3$:Pcy$_3$:bq (1:1:1) (**14**).* $C_{36}H_{45}AgN_3O_3P$, $M = 706.6$. Triclinic, space group $P\bar{1}$, $a = 9.5088(9)$, $b = 10.977(1)$, $c = 16.861(2)$ Å, $\alpha = 78.393(1)°$, $\beta = 78.604(1)°$, $\gamma = 80.926(1)°$, $V = 1677$ Å^3. D_{calc} ($Z = 2$) $= 1.39_9$ g cm^{-3}. $\mu_{\text{Mo}} = 6.9$ cm^{-1}; specimen: $0.38 \times 0.28 \times 0.18$ mm; 'T'$_{\text{min/max}} = 0.90$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 18634$; $N = 8155$ ($R_{\text{int}} = 0.012$), $N_{\text{o}} = 7379$; $R = 0.022$, $R_w = 0.031$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.15. AgNO$_3$:Pcy$_3$:dpa (1:1:1) (**15**).* $C_{28}H_{42}AgN_4O_3P_3$, $M = 621.5$. Triclinic, space group $P\bar{1}$, $a = 9.974(2)$, $b = 15.841(3)$, $c = 19.483(4)$ Å, $\alpha = 111.332(2)°$, $\beta = 90.440(2)°$, $\gamma = 91.133(3)°$, $V = 2866$ Å^3. D_{calc} ($Z = 4$) $= 1.44_0$ g cm^{-3}. $\mu_{\text{Mo}} = 8.0$ cm^{-1}; specimen: $0.56 \times 0.32 \times 0.13$ mm; 'T'$_{\text{min/max}} = 0.86$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 32796$; $N = 13828$ ($R_{\text{int}} = 0.016$), $N_{\text{o}} = 12593$; $R = 0.023$, $R_w = 0.035$. $(x, y, z, U_{\text{iso}})_{\text{H}}$ refined.

*2.2.1.16. AgNO$_3$:Ascy$_3$:bq (1:1:1) (**16**).* $C_{36}H_{45}AgAsN_3O_3$, $M = 750.6$. Triclinic, space group $P\bar{1}$, $a = 9.459(1)$, $b = 10.914(1)$, $c = 16.823(2)$ Å, $\alpha = 79.261(2)°$, $\beta = 79.000(2)°$, $\gamma = 81.039(2)°$, $V = 1662$ Å^3. D_{calc} ($Z = 2$) $= 1.50_0$ g cm^{-3}. $\mu_{\text{Mo}} = 16.3$ cm^{-1}; specimen: $0.35 \times 0.15 \times 0.13$ mm; 'T'$_{\text{min/max}} = 0.79$. $2\theta_{\text{max}} = 58°$; $N_{\text{t}} = 19272$;

$N = 8106$ ($R_{int} = 0.021$), $N_o = 7237$; $R = 0.024$, $R_w = 0.033$. $(x, y, z, U_{iso})_H$ refined.

*2.2.1.17. $AgNO_3$:P(o-tol)$_3$:bpy (1:1:1)·½MeCN (**17**·½MeCN).* $C_{32}H_{30.5}AgN_{3.5}O_3P$, $M = 651.0$. Triclinic, space group $P\bar{1}$, $a = 10.013(2)$, $b = 10.384(2)$, $c = 15.545(2)$ Å, $\alpha = 89.801(2)°$, $\beta = 84.765(2)°$, $\gamma = 63.480(2)°$, $V = 1438$ Å^3. D_{calc} ($Z = 2$) $= 1.50_2$ g cm^{-3}. $\mu_{Mo} = 8.0$ cm^{-1}; specimen: $0.20 \times 0.16 \times 0.12$ mm; 'T'$_{min/max} = 0.86$. $2\theta_{max} = 58°$; $N_t = 16888$; $N = 7064$ ($R_{int} = 0.018$), $N_o = 6460$; $R = 0.025$, $R_w = 0.032$. $(x, y, z, U_{iso})_H$ refined (solvent excepted).

Variata. The acetonitrile was modelled as disordered about a centre of symmetry.

*2.2.1.18. $AgNO_3$:P(o-tol)$_3$:bq (1:1:1) (**18**).* $C_{39}H_{33}AgN_3O_3P$, $M = 730.6$. Triclinic, space group $P\bar{1}$, $a = 10.635(1)$, $b = 10.756(2)$, $c = 16.712(3)$ Å, $\alpha = 89.123(2)°$, $\beta = 74.927(2)°$, $\gamma = 62.177(2)°$, $V = 1620$ Å^3. D_{calc} ($Z = 2$) $= 1.49_8$ g cm^{-3}. $\mu_{Mo} = 7.2$ cm^{-1}; specimen: $0.40 \times 0.22 \times 0.13$ mm; 'T'$_{min/max} = 0.89$. $2\theta_{max} = 58°$; $N_t = 18297$; $N = 7862$ ($R_{int} = 0.023$), $N_o = 6635$; $R = 0.030$, $R_w = 0.037$. $(x, y, z, U_{iso})_H$ refined.

*2.2.1.19. $AgNO_3$:P(o-tol)$_3$:dpa (1:1:1)·½EtOH (**19**·½EtOH).* $C_{32}H_{33}AgN_4O_{3.5}P$, $M = 668.5$. Triclinic, space group $P\bar{1}$, $a = 10.116(1)$, $b = 10.470(1)$, $c = 15.687(2)$ Å, $\alpha = 87.157(2)°$, $\beta = 83.252(2)°$, $\gamma = 64.256(2)°$, $V = 1486$ Å^3. D_{calc} ($Z = 2$) $= 1.49_4$ g cm^{-3}. $\mu_{Mo} = 7.7$ cm^{-1}; specimen: $0.10 \times 0.08 \times 0.06$ mm; 'T'$_{min/max} = 0.87.2\theta_{max} = 58°$; $N_t = 14783$; $N = 7280$ ($R_{int} = 0.030$), $N_o = 5649$; $R = 0.036$, $R_w = 0.038$.

Variata. The solvent molecule was modelled as disordered about a centre of symmetry.

*2.2.1.20. $AgNO_3$:P(o-tol)$_3$:dpca (1:1:1)·½H_2O (**20**·½H_2O).* $C_{33}H_{35}AgN_4O_{3.5}P$, $M = 682.5$. Monoclinic, space group $C2/c$, $a = 35.272(6)$, $b = 10.311(2)$, $c = 18.735(3)$ Å, $\beta = 116.493(2)°$, $V = 6098$ Å^3. D_{calc} ($Z = 8$) $= 1.48_7$ g cm^{-3}. $\mu_{Mo} = 7.6$ cm^{-1}; specimen: $0.20 \times 0.13 \times 0.13$ mm; 'T'$_{min/max} = 0.85$. $2\theta_{max} = 56°$; $N_t = 30272$, $N = 7738$ ($R_{int} = 0.030$), $N_o = 6138$; $R = 0.034$, $R_w = 0.041$. $(x, y, z, U_{iso})_H$ refined.

*2.2.1.21. $AgNO_3$:PPhmes$_2$:tpy (1:1:1) (**21**).* $C_{39}H_{38}AgN_4O_3P$, $M = 749.6$. Monoclinic, space group $P2_1/c$, $a = 18.540(2)$, $b = 11.552(1)$, $c = 16.494(2)$ Å, $\beta = 102.425(2)°$, $V = 3450$ Å^3. D_{calc} ($Z = 4$) $= 1.44_3$ g cm^{-3}. $\mu_{Mo} = 6.8$ cm^{-1}; specimen: $0.27 \times 0.23 \times 0.13$ mm; 'T'$_{min/max} = 0.85$. $2\theta_{max} = 75°$; $N_t = 71239$, $N = 18132$ ($R_{int} = 0.049$), $N_o = 10849$; $R = 0.040$, $R_w = 0.040$.

The following pairs of tpy adducts, of less usual stoichiometries, are also recorded:

*2.2.1.22. $AgNO_3$:Pcy$_3$:tpy (2:2:1) (**22**).* $C_{51}H_{77}Ag_2N_5O_6P_2$, $M = 1133.9$. Monoclinic, space group $P2_1/n$, $a = 15.1339(8)$, $b = 9.8940(5)$, $c = 36.136(2)$ Å, $\beta = 102.072(1)°$, $V = 5291$ Å^3. D_{calc} ($Z = 4$) $= 1.42_3$ g cm^{-3}. $\mu_{Mo} = 8.5$ cm^{-1}; specimen: $0.23 \times 0.15 \times 0.05$ mm; 'T'$_{min/max} = 0.78$. $2\theta_{max} = 58°$; $N_t = 56354$, $N = 13355$ ($R_{int} = 0.029$), $N_o = 8134$; $R = 0.033$, $R_w = 0.033$.

Variata. The two nitrate groups were modelled as disordered over pairs of sites, site occupancies refining to 0.875(9) (NO_3(1)) and 0.5 (NO_3(2)) (major components) and complements.

*2.2.1.23. $AgNO_3$:PPh$_3$:tpy (1:2:1) (**23**).* $C_{51}H_{41}AgN_4O_3P_2$, $M = 927.7$. Triclinic, space group $P\bar{1}$, $a = 9.6945(4)$, $b = 14.6436(6)$, $c = 15.0975(6)$ Å, $\alpha = 90.893(1)°$, $\beta = 90.704(1)°$, $\gamma = 99.229(1)°$, $V = 2115$ Å^3. D_{calc} ($Z = 2$) $= 1.45_7$ g cm^{-3}. $\mu_{Mo} = 6.0$ cm^{-1}; specimen: $0.30 \times 0.25 \times 0.20$ mm; 'T'$_{min/max} = 0.91$. $2\theta_{max} = 75°$; $N_t = 43272$, $N = 21695$ ($R_{int} = 0.024$), $N_o = 17950$; $R = 0.031$, $R_w = 0.037$.

Variata. The complex is isomorphous with its perchlorate analogue [23] and was refined in the same cell and coordinate setting.

3. Results and discussion

3.1. Syntheses

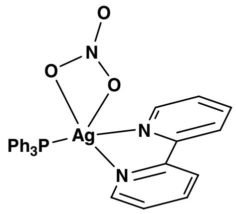
The adducts **1**–**21** (Chart 1), of general formula $AgNO_3:ER_3:L$ (1:1:1), have been synthesized by the reaction of one equivalent of *N*,*N*′-bidentate aromatic ligand, L, derivative of 2,2′-bipyridyl, with one equivalent of silver(I) nitrate and one equivalent of unidentate ER_3, according to the following equation:

$$AgNO_3 + ER_3 + L \xrightarrow{S} AgNO_3 : ER_3 : L \ (1:1:1) \tag{1}$$

(E = P, As or Sb; R = Ph, cy, *o*-tolyl or mes; L = bpy, phen, dmp, bq, dpa, dpk, dpca or tpy; S = acetonitrile or methanol).

Adduct **22** (Chart 1) also has been synthesized by mixing $AgNO_3$, Pcy$_3$ and tpy in 1:1:1 molar ratio, but its formula is $AgNO_3$:Pcy$_3$:tpy (2:2:1). Adduct **23** was obtained similarly, by the use of $AgNO_3$:PPh$_3$:tpy (1:2:1) in that ratio.

All the compounds, air-stable, colourless materials, are insoluble in diethyl ether and alcohols but soluble in chlorinated solvents, acetone, acetonitrile and DMSO. The conductivity measurements are in accordance with the ionic formulation found in the solid state for the derivatives **20**, **22** and **23**. In addition the compounds **1**–**4**, **6**, **7**, **9**, **11**–**17** and **21**, containing the weakly coordinated NO_3, undergo complete ionic dissociation, not only in acetonitrile but also in non-ionizing solvents such as dichloromethane, Λ_m being in the range 120–160 in the former solvent and in the latter 40–50 Ω^{-1} cm^2 mol^{-1} [24]. Moreover, derivatives **5**, **8**, **10**, **15** and **19**, containing the dpa ligand, which forms hydrogen-bonding networks in the solid state involving interaction of its N–H component with the nitrate group (see crystallographic studies below), are 1:1 electrolytes in acetonitrile but non-electrolytes in dichloromethane [24].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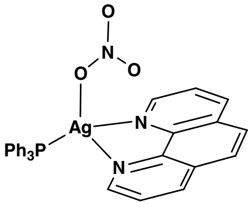
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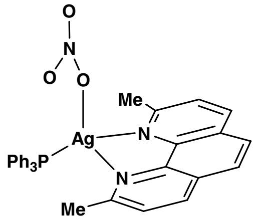
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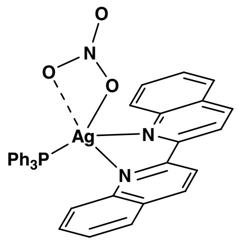
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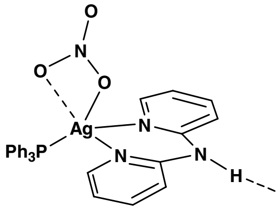
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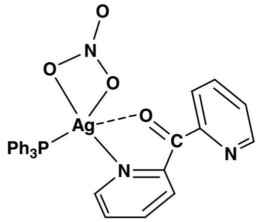
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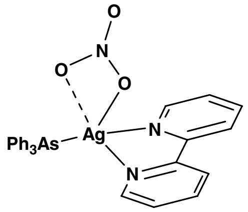
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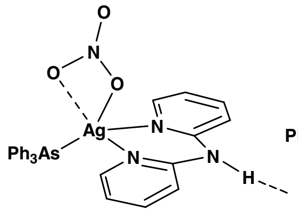
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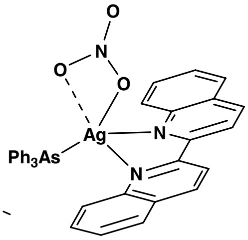
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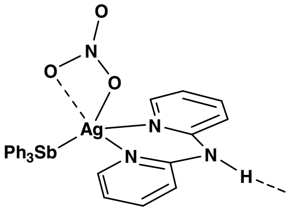
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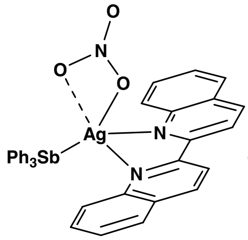
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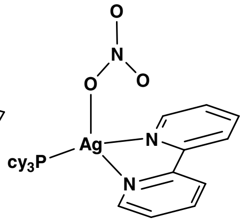
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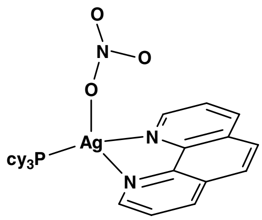
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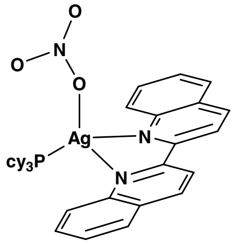
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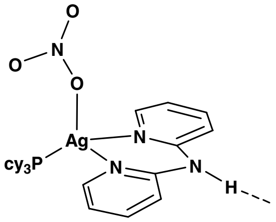
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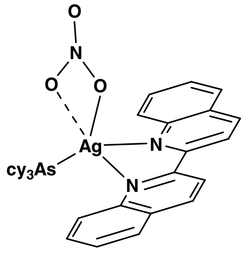
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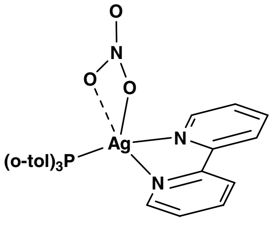
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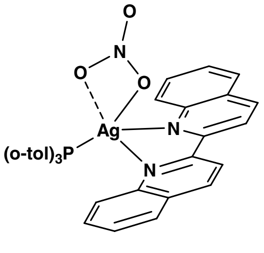
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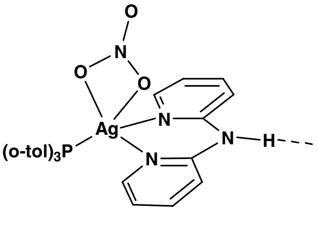
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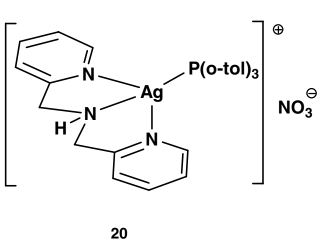
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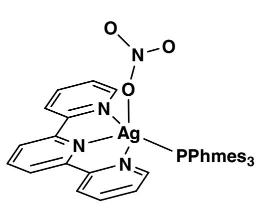
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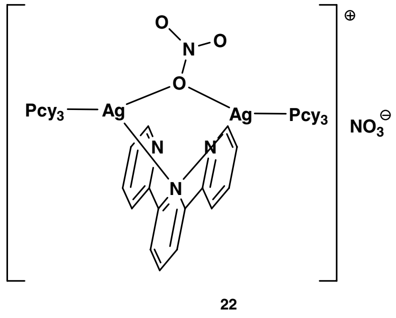
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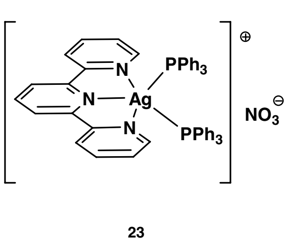
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Chart 1.

3.2. Spectroscopy

The infrared spectra (Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the organic N-donors and bidentate phosphine or arsine ligands [25]. In the far-IR spectra of all phosphino derivatives we assigned, on the basis of previous reports, the broad absorptions near 500 cm^{-1} and those at 480–400 cm^{-1} to Whiffen's y and t vibrations [26].

In the spectra of derivatives **20** and **22**, the ν_2, ν_3 and ν_4 modes of vibration of ionic NO_3^- groups (D_{3h} symmetry) and a unique weak $\nu_1 + \nu_4$ combination band in the overtone region 1700–1800 cm^{-1} have been detected throughout in accordance with their ionic structures [27]. In the spectra of complexes **1**–**12**, **16**–**18** and **21**, the separation between ν_1 and ν_4 is ca. 40 cm^{-1} in accordance with a unidentate nitrato ligand $\nu_1 + \nu_4$ [28]. The weak interactions between the silver(I) cation and the nitrate group in **13**, **14** and **16** are reflected in the small magnitude of the splittings of the asymmetric N–O stretching modes [29]. The presence of several different absorptions due to $\nu(NO_3)$ in the spectrum of derivative **22** is consistent with the presence of both ionic and unidentate NO_3 groups (see below). The IR spectra of the dpa-containing derivatives **5**, **8**, **10** and **19** exhibit broad bands over 3100 cm^{-1} due to $N–H\cdots O–NO_2$ H-bonding, observed also in their crystal structures.

The ^1H NMR spectra of derivatives **1**–**14** and **17**–**22** show the signals due to the phosphine and N-donor ligands, shifted with respect to those found for the free donors, thus indicating the existence of complexes also in chlorinated solvent solution.

At room temperature, the ^{31}P NMR spectra of complexes **1**–**6**, **12**–**14** and **17**–**22** show a unique broad resonance, presumably in consequence of exchange equilibria that are reasonably fast in relation to the NMR time scale. However, the exchange is quenched at low temperature (223 K), and one unresolved doublet or resolved pairs of doublets, arising from coupling between the phosphorus and silver atoms, are observed in the accessible temperature range.

Based on the previous work of Muetterties and Alegranti [30] and Goel and Pilon [31], that showed the spin–spin constant (J) between phosphorus and silver to be dependant on 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, we can assign $AgPN_2$ coordination environments in solution for all derivatives **1**–**6**, **12**–**14** and **17**–**19**, as their $J_{(Ag–P)}$ fall in the range 600–750 Hz. In the low temperature ^{31}P NMR spectra of derivatives **1**, **3**, **6**, **13** and **16**, however, a minor doublet or pair of doublets has been detected, with $J_{(Ag–P)}$ in the range 380–540 Hz, in accordance with the presence in solution of additional AgP_2-containing species, presumably formed from dissociation equilibria such as the following:

$$2[Ag(PR_3)(L)]NO_3 \leftrightarrows [Ag(PR_3)_2(NO_3)] + [Ag(L)_2]NO_3 \quad (2)$$

The low temperature ^{31}P NMR spectrum of derivative **20** shows a broad doublet with a $J_{(Ag–P)}$ value of 640 Hz, in accordance with a AgN_3P coordination environment in solution, as found in the crystal structure (see below). Finally, in the low temperature ^{31}P NMR spectrum of derivative **22** two pairs of doublets have been detected, one at 42.7 ppm ($J_{(Ag–P)}$ of 740.9 and 647.1 Hz) and the other at 33.1 ppm ($J_{(Ag–P)}$ of 528.6 and 457.8 Hz). This behaviour could be explained by the existence in solution of three different Ag-containing species such as those arising from a dissociation equilibrium like the following:

$$2[Ag_2(Pcy_3)_2(L)NO_3]NO_3 \leftrightarrows [Ag(Pcy_3)_2(NO_3)] + [Ag(L)NO_3] \quad (3)$$

where the resonance with higher $J_{(Ag–P)}$ is related to the dinuclear species $[Ag_2(Pcy_3)_2(L)NO_3]NO_3$ containing two AgNOP coordination environments, and that with lower $J_{(Ag–P)}$ is clearly related to the species $[Ag(Pcy_3)_2(NO_3)]$, previously reported and investigated both in the solid state and in solution [32].

3.3. Single crystal X-ray studies

The stoichiometries, connectivities and stereochemistries of complexes **1**–**23**, variously solvated, have also been established by single crystal X-ray diffraction studies. Except for derivative **22**, the complexes are mononuclear, based on a quasi-planar three-coordinate $EAgN_2$ coordination environment in an $[(R_3E)AgL]$ complex, with complementary counterion and, on occasion, accompanying solvent. The usual symmetry of the ER_3 arrays is 3 (or very rarely m) (or less), and that of the ligand is 2 mm (or less), these being normally incompatible, so that it is unsurprising that the asymmetric unit of the structures is never less than one formula unit (thus, devoid of symmetry); in only three cases (**3**, **12**, **15**) does it rise to two. Although the symmetry of the coordination sphere itself can be as high as 2 mm, there is usually a significant asymmetry in the pair of E–Ag–N angles, consequent on the presence of an unsymmetrical disposition of the ER_3 group or other less internal effects. Any potential symmetry of the array may be degraded further by interaction of the (thus far) cationic $[(R_3E)AgL]^+$ species with the counterion or nearby solvent or 'impurity' (H_2O). Solvent or impurity approaches, given the nature of the species employed, should be unidentate; in fact, no close solvent approaches are observed at all, despite the naked aspect of the silver atom within its planar environment, a situation perhaps exploitable in catalysis. Interactions with nitrate anions are widespread and diverse in their nature and strength: all are capable of bidentate approaches, and the species observed may range from O,O'-bidentate to O,O'-semibidentate, one oxygen being more strongly bound than the other, to O-unidentate, to unbound, with a number of interactions lying between the latter pair in strength. In general, the $EAgN_2$ in-plane

Table 1
Silver atom environments, $\mathrm{AgNO_3:ER_3:L(:S)}$ (1:1:1(:1))

$\mathrm{ER_3:L(:S/NO_3)}$	$\mathrm{Ag{-}NO_3(/S)}$ (Å)[a]	Ag–E (Å)	Ag–N,N′ (Å)	$\mathrm{(S/NO_3){-}Ag{-}E}$ (°)	$\mathrm{(S/NO_3){-}Ag{-}N,N'}$ (°)	E–Ag–N,N′ (°)	N–Ag–N′ (°)	∑ (°)
(**1**) $\mathrm{PPh_3}$:bpy:O_2NO	2.603(3), 2.798(3)	2.3528(8)	2.304(2), 2.359(2)	113.02(5) 96.51(7)	85.58(8), 91.34(8) 81.08(9), 131.20(9)	151.86(6), 126.21(6)	71.34(7)	$349._4$
(**2**) $\mathrm{PPh_3}$:phen:O(,ONO)	2.466(3)(,3.320(4))	2.354(1)	2.315(3), 2.334(3)	108.78(8)	100.2(1), 103.5(1)	132.66(9), 131.76(8)	72.6(1)	$337._0$
(**3**) $\mathrm{PPh_3}$:dmp:O(,ONO) (mol. 1)	2.678(3)(,3.008(3))	2.382(1)	2.339(4), 2.352(3)	103.3(1)	103.3(1), 79.8(1)	139.20(6), 143.67(8)	71.7(1)	$354._6$
(**3**) $\mathrm{PPh_3}$:dmp:O(,ONO) (mol. 2)	2.721(5)(,3.012(6))	2.382(1)	2.313(4), 2.355(3)	96.2(1)	112.0(1), 85.3(1)	138.08(6), 143.17(8)	72.2(1)	$353._5$
(**4**) $\mathrm{PPh_3}$:bq:O_2NO	2.512(6), 2.813(6)	2.363(2)	2.326(5), 2.328(5)	112.6(1) 89.9(2)	103.2(2), 86.8(2) 95.4(2), 126.0(2)	133.1(2), 138.0(1)	70.7(2)	$341._8$
(**5**) $\mathrm{PPh_3}$:dpa:O(,ONO)	2.452(2)(,3.020(2))	2.3465(6)	2.280(2), 2.364(2)	119.92(5)	83.61(2), 100.87(6)	135.90(5), 125.24(5)	79.20(8)	$340._3$
(**6**) $\mathrm{PPh_3}$:dpk:O_2NO	2.466(4) 2.790(5)	2.363(2)	2.273(5) 2.700(5)(O)	119.1(1) 104.6(1)	89.4(2), 98.8(2) 90.9(2), 104.6(2)	151.1(1), 110.9(1)	65.4(1)	$327._4$
(**7**) $\mathrm{AsPh_3}$:bpy:O_2NO	2.541(2), 2.789(2)	2.4495(3)	2.306(1), 2.348(1)	110.10(3) 95.93(4)	87.81(6), 94.60(6) 80.63(6), 134.14(6)	151.11(4), 125.41(4)	71.84(5)	$348._4$
(**8**) $\mathrm{AsPh_3}$:dpa:O_2NO	2.458(1), 2.898(2)	2.4427(2)	2.279(6), 2.354(1)	121.02(3) 102.45(3)	85.22(5), 101.88(4) 121.58(4), 80.78(5)	133.79(3), 123.66(4)	79.87(5)	$337._3$
(**9**) $\mathrm{AsPh_3}$:bq:O_2NO	2.514(2), 2.928(2)	2.4482(5)	2.305(2), 2.318(2)	108.09(4) 77.96(4)	90.56(6), 97.45(6) 135.21(6), 99.02(6)	137.72(5), 138.86(5)	71.36(7)	$347._9$
(**10**) $\mathrm{SbPh_3}$:dpa:O_2NO	2.438(2), 2.883(2)	2.5733(3)	2.282(2), 2.336(2)	123.24(5) 98.09(6)	87.23(7), 99.50(8) 127.52(8), 83.94(9)	132.26(5), 122.43(7)	80.50(9)	$335._2$
(**11**) $\mathrm{SbPh_3}$:bq:O_2NO	2.519(2), 2.982(3)	2.6069(3)	2.334(3), 2.339(2)	112.50(5) 87.43(4)	102.00(7), 79.24(7) 98.76(7), 121.06(7)	135.75(4), 140.27(5)	71.32(6)	$347._3$
(**12**) $\mathrm{Pcy_3}$:bpy:O(,ONO) (mol. 1)	2.657(8)(,3.145(7))	2.357(2)	2.328(7), 2.332(6)	106.4(1)	81.7(2), 91.7(2)	147.6(2), 137.8(2)	71.3(2)	$356._7$
(**12**) $\mathrm{Pcy_3}$:bpy:O(,ONO) (mol. 2)	2.561(10)	2.347(2)	2.294(8), 2.319(6)	108.2(3)	84.6(3), 86.2(3)	149.9(2), 134.5(2)	71.8(2)	$356._2$
(**13**) $\mathrm{Pcy_3}$:phen:$O\mathrm{NO_2}$	2.564(2)	2.3557(8)	2.409(3), 2.290(3)	113.52(7)	104.86(9), 85.34(9)	119.62(7), 151.90(7)	71.3(1)	$342._8$
(**14**) $\mathrm{Pcy_3}$:bq:$O\mathrm{NO_2}$	2.508(2)	2.3732(4)	2.343(1), 2.358(1)	114.10(3)	90.02(4), 95.26(4)	137.25(3), 135.93(3)	69.73(4)	$342._9$
(**15**) $\mathrm{Pcy_3}$:dpa:$O\mathrm{NO_2}$ (mol. 1)	2.662(1)	2.3639(5)	2.256(1), 2.376(2)	95.09(3)	91.51(5), 97.94(4)	157.18(4), 119.99(4)	80.47(5)	$357._6$
(**15**) $\mathrm{Pcy_3}$:dpa:$O\mathrm{NO_2}$ (mol. 2)	2.877(1)	2.3617(5)	2.256(1), 2.337(2)	96.94(3)	78.05(4), 99.18(4)	158.37(4), 120.98(4)	80.64(5)	$360._0$
(**16**) $\mathrm{Ascy_3}$:bq:O(,ONO)	2.475(2)(,3.133(2))	2.4535(3)	2.319(2), 2.335(1)	112.28(3)	92.56(5), 97.45(5)	137.73(4), 134.36(4)	70.23(5)	$342._3$
(**17**) P(*o*-tol)$_3$:bpy:O_2NO	2.418(1) 2.850(2)	2.3835(8)	2.333(1), 2.418(4)	134.44(4) 119.95(4)	95.13(5), 89.98(5) 78.88(5), 123.92(5)	127.96(4), 116.03(4)	69.80(6)	$313._8$
(**18**) P(*o*-tol)$_3$:bq:O(,ONO)	2.461(1)(,3.020(2))	2.4199(6)	2.349(2), 2.416(2)	105.38(5)	112.92(6), 86.82(6)	132.92(5), 140.06(5)	69.93(7)	$342._9$
(**19**) P(*o*-tol)$_3$:dpa:O_2NO	2.519(2), 2.839(2)	2.3973(7)	2.318(3), 2.378(3)	136.03(5) 102.27(6)	89.62(8), 84.67(8) 94.48(9), 131.15(8)	128.32(8), 118.63(6)	81.0(1)	$328._0$
(**20**) P(*o*-tol)$_3$:dpca:($\mathrm{NO_3}$)	2.342(2)(N(c))	2.3956(8)	2.417(2), 2.618(2)	166.72(6)	71.33(8), 71.89(7)	119.90(6), 108.03(5)	109.68(8)	$337._6$
(**21**) $\mathrm{PPhmes_2}$:tpy:$\mathrm{ONO_2}$	2.618(2) 2.378(2)(N(c))	2.4348(5)	2.419(2), 2.457(1)	115.53(4) 139.28(4)	77.77(5), 93.81(5) 67.83(5), 67.34(5)	110.61(3), 116.76(4)	130.52(5)	$357._9$
(**22**) $\mathrm{Pcy_3}$:tpy:$\mathrm{ONO_2}$ (Ag(1))	2.696(5)	2.3695(9)	2.563(2), 2.258(3)	106.71(8)	99.7(1), 80.7(1)	139.11(6), 145.2(6)	68.89(8)	$352._2$
(Ag(2))	2.545(2)[b]	2.3850(9)	2.645(2), 2.366(3)	120.3(1)	101.6(1), 108.4(1)	119.70(6), 126.34(6)	66.21(8)	$312._3$

[a] Contacts in parentheses lie between 3 and 3.5 Å.

[b] Ag(2)–O(12) is 2.649(4) Å; O(12)–Ag(2)–P(2),N(1,1′),O(11) are 112.38(8)°, 127.98(9)°, 83.5(1)°, 48.1(1)°; O(11′)–Ag(1,2) are 2.82(2), 2.25(2) Å; O(11′)–Ag(1)–P(1),N(1,1″),O(11) are 95.4(5)°, 92.1(4)°, 105.0(5)°, 30.0(5)°, O(11′)–Ag(2)–P(2),N(1,1′),O(11,12) are 134.7(6)°, 104.6(6)°, 78.6(6)°, 34.1(7)°, 25.1(6)°. Ag(1)···Ag(2) is 3.2765(6) Å.

Table 2
Ligand and anion descriptors, AgX:ER$_3$:L(:S) (1:1:1(:1))

ER$_3$:L(:S/X)	$\theta^{bq/bq}_{py/py}$ (°)	δAg (Å)	$\delta \mathrm{Ag}_{NO_3}$ (Å)	Ag–O(,O′)-Y (°)	Ag–E–C(n1)–C(n2(6)) (°)	E–Ag–O–N (°)	O–N–O (°)
(**1**) PPh$_3$:bpy:O_2NO	12.7(1)	0.361(4), 0.267(5)	0.552(6)	101.7(2), 92.2(2)	42.2(3), 34.8(3), 46.8(2)	−83.5(2) 123.0(2)	118.4(3)
(**2**) PPh$_3$:phen:*O*(,ONO)		0.343(3)	0.352(7)	121.5(2)	−40.8(4), −44.3(3), −53.9(3)	−175.1(2)	119.7(4)
(**3**) PPh$_3$:dmp:*O*(,ONO) (mol. 1)		0.008(3)	1.593(7)	100.5(2)	−34.6(3), −44.4(3), −64.5(4)	−122.8(1)	119.2(3)
(**3**) PPh$_3$:dmp:*O*(,ONO) (mol. 2)		0.039(4)	2.190(7)	107.5(6)	28.6(4), 46.9(3), 74.2(4)	148.7(4)	110.9(6)
(**4**) PPh$_3$:bq:O_2NO	4.6(2)	0.023(9), 0.103(9)	0.52(1)	105.5(5), 92.1(4)	13.1(6), 32.0(6), 71.2(5)	70.2(4) −128.7(5)	116.9(8)
(**5**) PPh$_3$:dpa:*O*(,ONO)	25.04(8)	0.166(4), 1.345(4)	0.100(5)	111.3(2)	12.0(2), 42.1(3), 44.9(2)	−82.5(1)	120.4(2)
(**6**) PPh$_3$:dpk:O_2NO	41.1(3)	0.221(9)	0.14(1)	104.6(4), 89.2(3)	14.7(5), 22.2(4), 28.1(5)	81.4(4) −114.4(4)	118.4(4)
(**7**) AsPh$_3$:bpy:O_2NO	13.06(7)	0.437(3), 0.206(3)	0.035(1)	102.3(1), 90.6(1)	42.0(2), 33.5(2), 47.2(1)	−84.5(1)	118.5(1)
(**8**) AsPh$_3$:dpa:O_2NO	24.42(5)	0.134(2), 1.274(2)	0.142(3)	107.4(1), 86.0(1)	8.4(1), 42.0(2), 43.4(1)	−78.53(9)	120.1(1)
(**9**) AsPh$_3$:bq:O_2NO	5.67(5)	0.356(3), 0.213(3)	0.875(4)	105.0(1), 85.6(1)	7.9(2), 25.7(2), 47.7(2)	−62.6(1)	119.7(2)
(**10**) SbPh$_3$:dpa:O_2NO	23.00(8)	0.125(4), 1.149(4)	0.190(4)	107.1(2), 85.4(2)	2.4(2), 42.3(2), 41.2(2)	−69.7(1)	120.0(2)
(**11**) SbPh$_3$:bq:O_2NO	1.58(5)	0.137(3), 0.130(3)	0.332(5)	108.5(2), 86.0(2)	45.4(2), 51.2(2), 54.3(2)	−64.9(2)	120.0(3)
(**12**) Pcy$_3$:bpy:*O*(,ONO) (mol. 1)	6.4(3)	0.19(1), 0.12(1)	0.36(2)	110.7(6)	−55.4(6), 48.5(7), 20.5(5)	−68.4(5)	119.2(9)
(**12**) Pcy$_3$:bpy:*O*(,ONO) (mol. 2)	11.0(3)	0.06(1), 0.51(1)	0.76(2)	135.1(9)	−57.9(5), 49.1(6), 25.6(5)		
(**13**) Pcy$_3$:phen:*O*NO$_2$		0.018(4)	1.579(7)	115.0(2)	−53.4(5), −30.2(3), 61.2(3)	105.9(2)	120.2(4)
(**14**) Pcy$_3$:bq:*O*NO$_2$	8.11(3)	0.487(2), 0.517(2)	1.419(3)	109.3(1)	64.9(1), −63.0(2), 33.5(1)	−73.4(1)	119.5(2)
(**15**) Pcy$_3$:dpa:*O*(,ONO) (mol. 1)	18.065(5)	0.048(3), 1.008(2)	2.082(3)	124.02(9)	−28.2(1), −43.2(1), 52.4(1)	−49.2(1)	118.4(2)
(**15**) Pcy$_3$:dpa:*O*(,ONO) (mol. 2)	10.73(5)	0.212(2), 0.825(2)	1.833(3)	132.13(8)	59.7(1), −45.2(1), −28.2(1)	−6.3(1)	119.1(1)
(**16**) Ascy$_3$:bq:*O*(,ONO)	7.90(4)	0.405(2), 0.498(2)	1.465(3)	108.3(1)	66.4(1), −62.1(4), 33.2(1)	−73.2(1)	119.8(2)
(**17**) P(*o*-tol)$_3$:bpy:O_2NO	8.11(8)	0.331(4), 0.071(3)	0.510(4)	106.7(1) 86.2(1)	−45.5(1), −44.0(2), −54.7(2)	−98.8(1)	118.7(2)
(**18**) P(*o*-tol)$_3$:bq:*O*(ONO)	23.51(6)	0.152(3), 0.961(3)	0.282(5)	112.0(2)	45.5(2), 46.2(2), 59.0(2)	−117.5(2)	118.7(2)
(**19**) P(*o*-tol)$_3$:dpa:O_2NO	7.3(1)	0.144(6), 0.125(5)	0.343(7)	105.0(2), 89.7(2)	−53.2(2), −40.8(3), −51.8(3)	−57.9(2) 145.9(2)	118.6(2)
(**20**) P(*o*-tol)$_3$:dpca:(NO$_3$)	27.98(9)	0.128(4), 1.535(4)			−55.3(2), −30.5(3), −53.4(2)		
(**21**) PPhmes$_2$:tpy:ONO$_2$	3.45(7), 7.27(7)	0.615(3), 0.285(3)(p,p) 0.483(3)(c)	1.610(4)	127.2(1)	12.7(2), 73.2(1), 30.0(1)	100.3(2)	
(**22**) Pcy$_3$:tpy:ONO$_2$	9.16(7)	[a]	[a]	[a]	42.3(3), −59.7(3), − 70.4(2) 28.7(3), 50.8(3), 56.2(3)	[a]	116.8(4)

[a] Deviations of Ag(1,2) out of the two component planes: −2.288(9), 0.12(1); −1.30(7), 1.74(5) Å; Ag(1,2)–O(11,11′)–N(01) for the two components are 120.9(3)°, 100.4(3)°; 116(1)°, 121(2)°; Ag(2)–O(12)–N(01) 94.6(3)°; P(1,2)–Ag(1,2)–O(11)–N(01) (two components) are 39.4(3)°, −91.6(3)°; −82(2)°, 35(2)°.

angle sum, 360° for a completely planar array, diminishes, as expected, broadly in parallel with the strength of the interaction with the approaching species, asymmetry in the E–Ag–N,N′ angles broadly correlating in the manner expected with the Ag–N distances; for a given anion, the strength of interaction tends to be greater in E = As, Sb complexes, cf. the counterpart E = P arrays, as expected, and in keeping with the diminished base strength of ER_3, with concomitant change in the Ag–N distances.

The ligands L offer a range of 'bites', those of bpy, phen, dmp, and bq being similar, while dpa, with a six- cf. a five-membered chelate ring, has a greater 'bite', also true of dpk, dpca and tpy – but here, with a further O or N donor atom introduced between the peripheral pair of rings, the ligand is potentially tridentate. The ligands generally are extended planar arrays, although in those cases (bpy, bq, and dpa) where there is no central aromatic ring fusing the two donor rings, there may be an appreciable dihedral angle between the latter. The ligand planes, in general, are a dominant determinant of crystal packing. Core and ligand geometries for all of the species are summarized in Tables 1 and 2, with individual species depicted in the figure. We comment individually on the various structures as follows.

3.3.1. *$AgNO_3$:PPh_3:bpy (1:1:1)* (**1**)

The nitrate approach to the silver atom here is that of a somewhat unsymmetrical chelate (Fig. 1(a)), the asymmetry and skewing of the approach perhaps a concomitant of short intra-molecular contacts O(1)···H(32), 2.87(3) and O(2)···H(6) 2.80(3) Å, with angles P–Ag–N,N′(bpy) being very unsymmetrical (151.86(6)°, 121.21(6)°). As in most of the other EPh_3 (and P(*o*-tol)$_3$) arrays presented here, the EPh_3 disposition is quasi-3.

3.3.2. *$AgNO_3$:PPh_3:phen (1:1:1)* (**2**)

This complex in juxtaposition with the above bpy counterpart enhances the dilemma concerning the mode of interaction of the anion, whereas in semi-bidentate mode in the bpy complex, the longer Ag···O interaction is directed nearer the PPh_3 ligand; here we find the nitrate to lie quasi-coplanar with the phosphorus atom with the more weakly interacting oxygen lying over the phen ligand, generally reflecting the rather arbitrary nitrate dispositions throughout the array of complexes. Although the phen is quasi-coplanar with one of the PPh_3 phenyl rings, the P–Ag–N angles are essentially equal.

3.3.3. *$AgNO_3$:PPh_3:dmp (1:1:1) · ½MeOH* (**3** · *½MeOH*)

In this array, two independent molecules are found in the asymmetric unit, with one methanol solvent; the latter, not disordered, nevertheless appears not to interact closely with any anion components. In both molecules, the anions are effectively semi-bidentate, but differ somewhat in their orientations vis-a-vis the substrate; displacement parameters on anion 2 are high and may be a foil for unresolved disorder. (The deviation of the silver atom from the nitrate plane (Table 2) is a useful indicator of its inclination to the coordination plane.) The dmp ligand is more highly hindered than its parents phen or bpy, but this appears to have little impact on the overall coordination environment of the metal.

3.3.4. *$AgNO_3$:PPh_3:bq (1:1:1)* (**4**)

Here, despite the electronic similarity between bpy and bq, the nitrate approach is less symmetrical than in the above bpy counterpart.

3.3.5. *$AgNO_3$:PPh_3:dpa (1:1:1)* (**5**)

Here, given some tendency of dpa to bind in unidentate mode in some complexes (e.g. Ref. [22]), it is of interest to observe that, compared to (e.g.) its bq counterpart (above), the geometries in the coordination sphere are similar, the only substantial change concerning the 'bite' of the dpa ligand, which exhibits a substantial dihedral angle between the pair of aromatic ring planes. Interspecies hydrogen-bonding is observed from the (uncoordinated) central N,H of the ligand to the nitrate (O(3)···H,N 2.12(3) (*x*, *y* − 1, *z*), 2.851(3) Å). In this and the other dpa (and dpk) complexes studied, the $EAgN_2$(N,O) angle sums are ⩽340°, perhaps a consequence of the enlarged chelate ring in these complexes; Ag–O(NO_3) are short, ⩽2.5 Å.

3.3.6. *$AgNO_3$:PPh_3:dpk (1:1:1)* (**6**)

Here the possible coordination of the second pyridyl ring is pre-empted by the semi-bidentate chelation of the anion, coupled with coordination by the linker unit to form a five- rather than six-membered chelate. The Ag–O interaction is weak; P–Ag–N,O are concomitantly unsymmetrical, P–Ag–N being larger.

With the weaker donors E = As, Sb displacing P in the EPh_3 component, it might be expected that the remaining ligands might interact more strongly, perhaps with concomitant change in the nature of the complex. Changes in Ag–N,O distances of a qualitative nature are found, as expected, but they are not large, and seem to impact little on the form of the complex in the less extensive arrays studied, the nitrate ions interacting in semi-bidentate mode.

3.3.7. *$AgNO_3$:$AsPh_3$:bpy (1:1:1)* (**7**)

This compound is remarkable for the disparity in the pair of E–Ag–N angles, a feature not observed in the other pair of $AsPh_3$ complexes studied, presumably to be attributed to 'lattice effects' in the absence of any more satisfactory 'intramolecular' hypothesis.

3.3.8. *$AgNO_3$:$AsPh_3$:dpa (1:1:1)* (**8**)

Again, intermolecular dpa-NH···O(NO_3) interactions are found, O(3)···H,N(central) (*x*, *y* − 1, *z*) being 2.00(2), 2.854(2) Å.

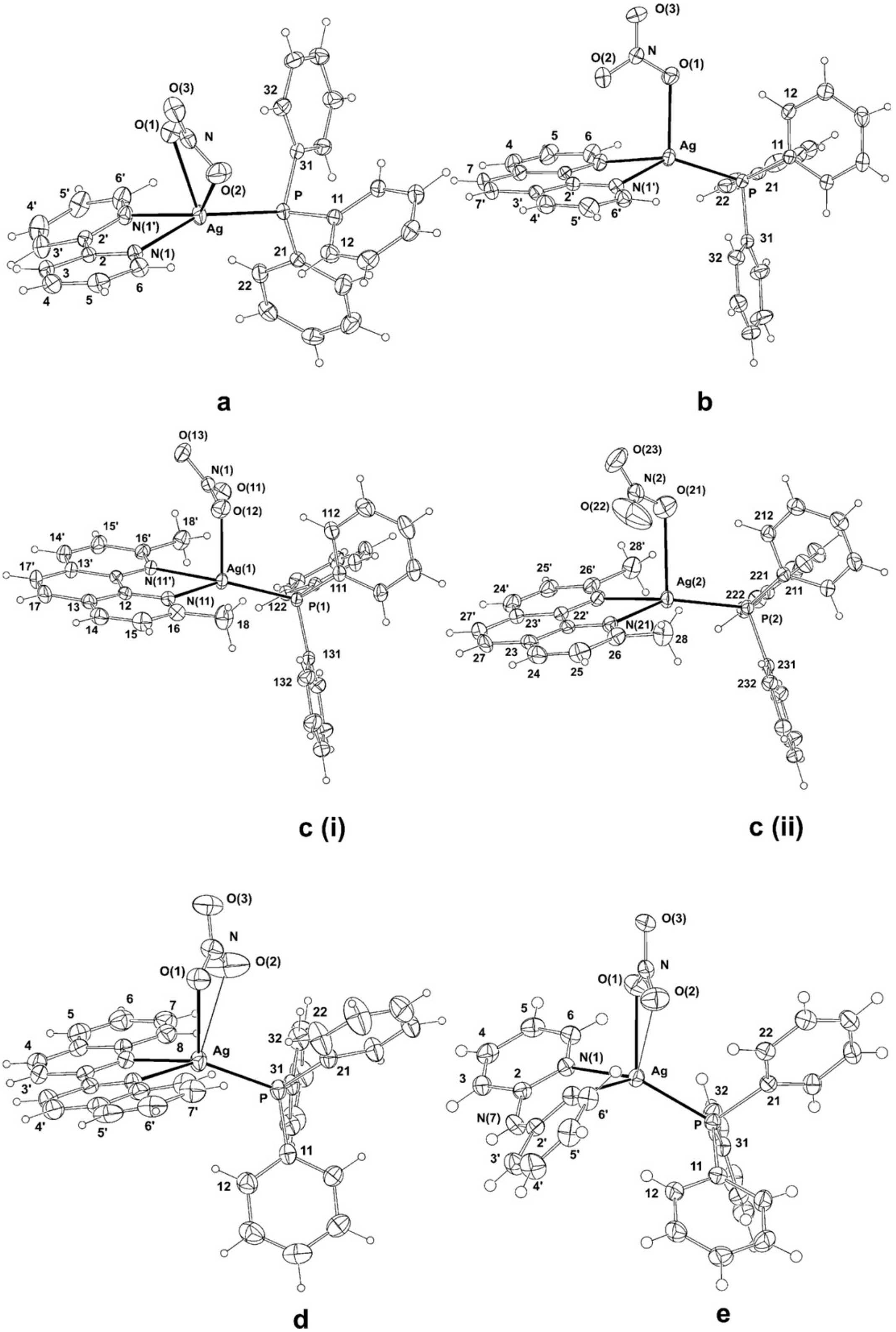

Fig. 1. Projections of the complex aggregates of the following (R$_3$P)Ag(*N*,*N*′-aromatic base)/NO$_3$ systems: (a) [(Ph$_3$P)Ag(*N*,*N*′-bpy)(*O*,*O*′-NO$_3$)] (**1**); (b) [(Ph$_3$P)Ag(*N*,*N*′-phen)(*O*-NO$_3$)] (**2**); (c) [(Ph$_3$P)Ag(*N*,*N*′-dmp)(*O*-NO$_3$)] (two molecules), in **3** · ½MeOH; (d) [(Ph$_3$P)Ag(*N*,*N*′-bq)(*O*,*O*′-NO$_3$)] (**4**); (e) [(Ph$_3$P)Ag(*N*,*N*′-dpa)(*O*-NO$_3$)] (**5**); (f) [(Ph$_3$P)Ag(*N*,*O*′-dpk)(*O*,*O*′-NO$_3$)] (**6**); (g) [(Ph$_3$As)Ag(*N*,*N*′-bpy)(*O*-NO$_3$)] (**7**); (h) [(Ph$_3$As)Ag(*N*,*N*′-dpa)(*O*-NO$_3$)] (**8**) (the E = Sb counterpart, **10**, is isomorphous); (i) [(Ph$_3$As)Ag(*N*,*N*′-bq)(*O*-NO$_3$)], in **9** · MeCN; (j) [(Ph$_3$Sb)Ag(*N*,*N*′-bq)(*O*-NO$_3$)], in **11** · 1½EtOH; (k) [(cy$_3$P)Ag(*N*,*N*′-bpy)(*O*-NO$_3$)] (two molecules), in **12** · 3/8MeCN; (l) [(cy$_3$P)Ag(*N*,*N*′-phen)(*O*-NO$_3$)] (**13**); (m) [(cy$_3$P)Ag(*N*,*N*′-bq)(*O*-NO$_3$)] (**14**); (n) [(cy$_3$P)Ag(*N*,*N*′-dpa)(*O*-NO$_3$)] (two molecules) (**15**); (o) [(cy$_3$As)Ag(*N*,*N*′-bq)(*O*-NO$_3$)] (**16**); (p) [{(*o*-tol)$_3$P}Ag(*N*,*N*′-bpy)(*O*$_2$-NO$_3$)], in **17** · ½MeCN; (q) [{(*o*-tol)$_3$P}Ag(*N*,*N*′-bq)(*O*-NO$_3$)] (**18**); (r) [{(*o*-tol)$_3$P}Ag(*N*,*N*′-dpa)(*O*$_2$-NO$_3$)], in **19** · ½EtOH; (s) [{(*o*-tol)$_3$P}Ag(*N*,*N*,′*N*″-dpca)](NO$_3$), in **20** · ½H$_2$O; (t) [(mes$_2$PhP)Ag(*N*,*N*′,*N*″-tpy)(*O*-NO$_3$)] (**21**); (u) [{(cy$_3$P)Ag}$_2$(*N*,*N*′,μ-*N*′-tpy)(*O*,μ-*O*′-NO$_3$)](NO$_3$) (**22**); (v) [(Ph$_3$P)$_2$Ag(*N*,*N*′,*N*″-tpy)](NO$_3$) (**23**).

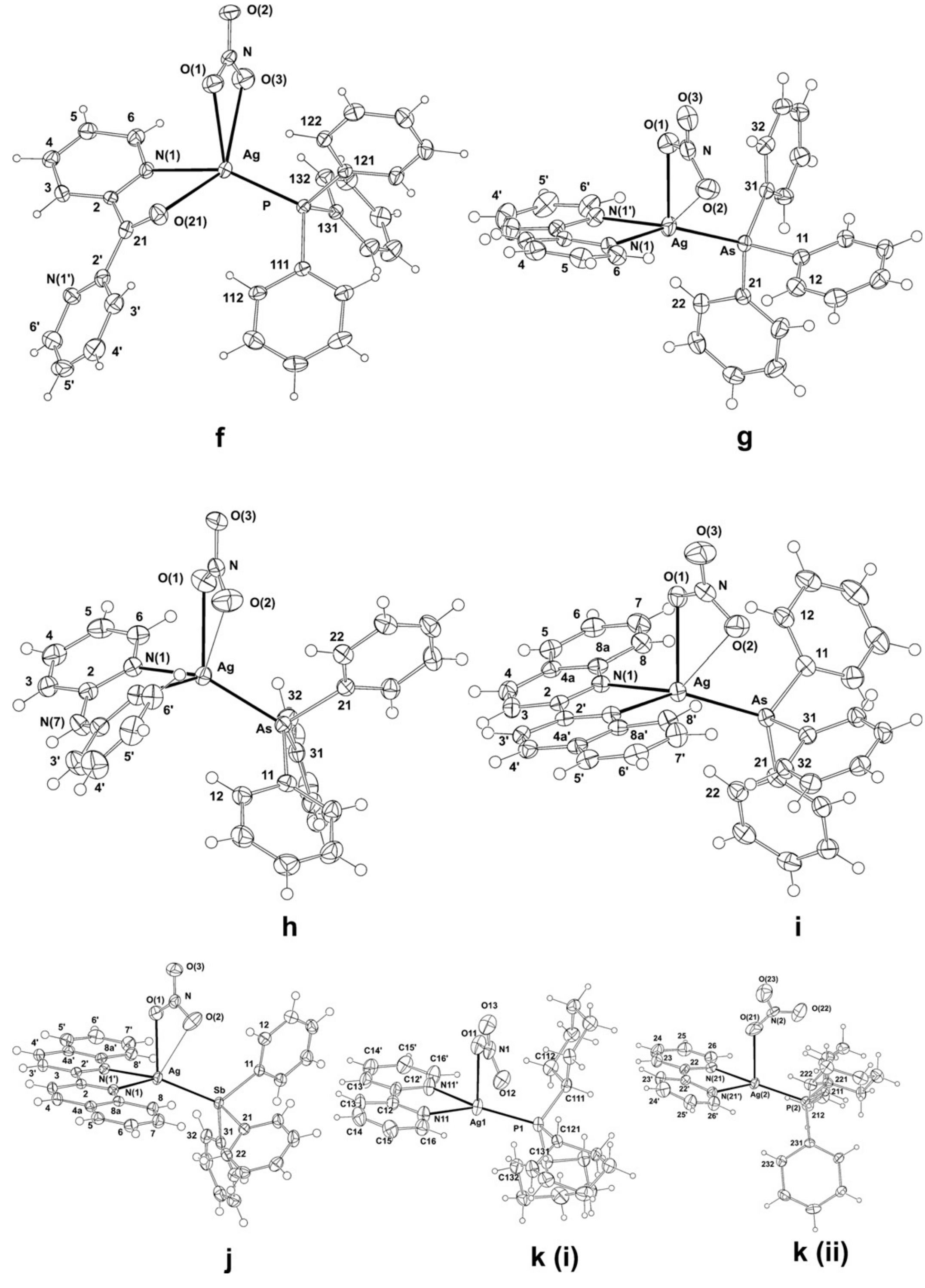

Fig. 1 (*continued*)

3.3.9. $AgNO_3$:$AsPh_3$:bq (1:1:1) · MeCN (**9** · MeCN)

The acetonitrile plays no role in coordination.

3.3.10. $AgNO_3$:$SbPh_3$:dpa (1:1:1) (**10**)

Again, we find intermolecular dpa-NH···O(NO_3) hydrogen-bonding, N,H(central)···O(3) (x, $1+y$, z) being 2.869(3), 1.98(3) Å.

3.3.11. $AgNO_3$:$SbPh_3$:bq (1:1:1) · ½EtOH (**11** · 1½EtOH)

One of the solvent components is disordered (about an inversion centre), albeit it lies in the proximity of the nitrate (O(3)···H,O 1.7 (est.), 2.871(5) Å); the other solvent molecule, more well-defined, also is hydrogen-bonded to the nitrate (O(3)···H,O 2.29(3), 2.95(2) Å).

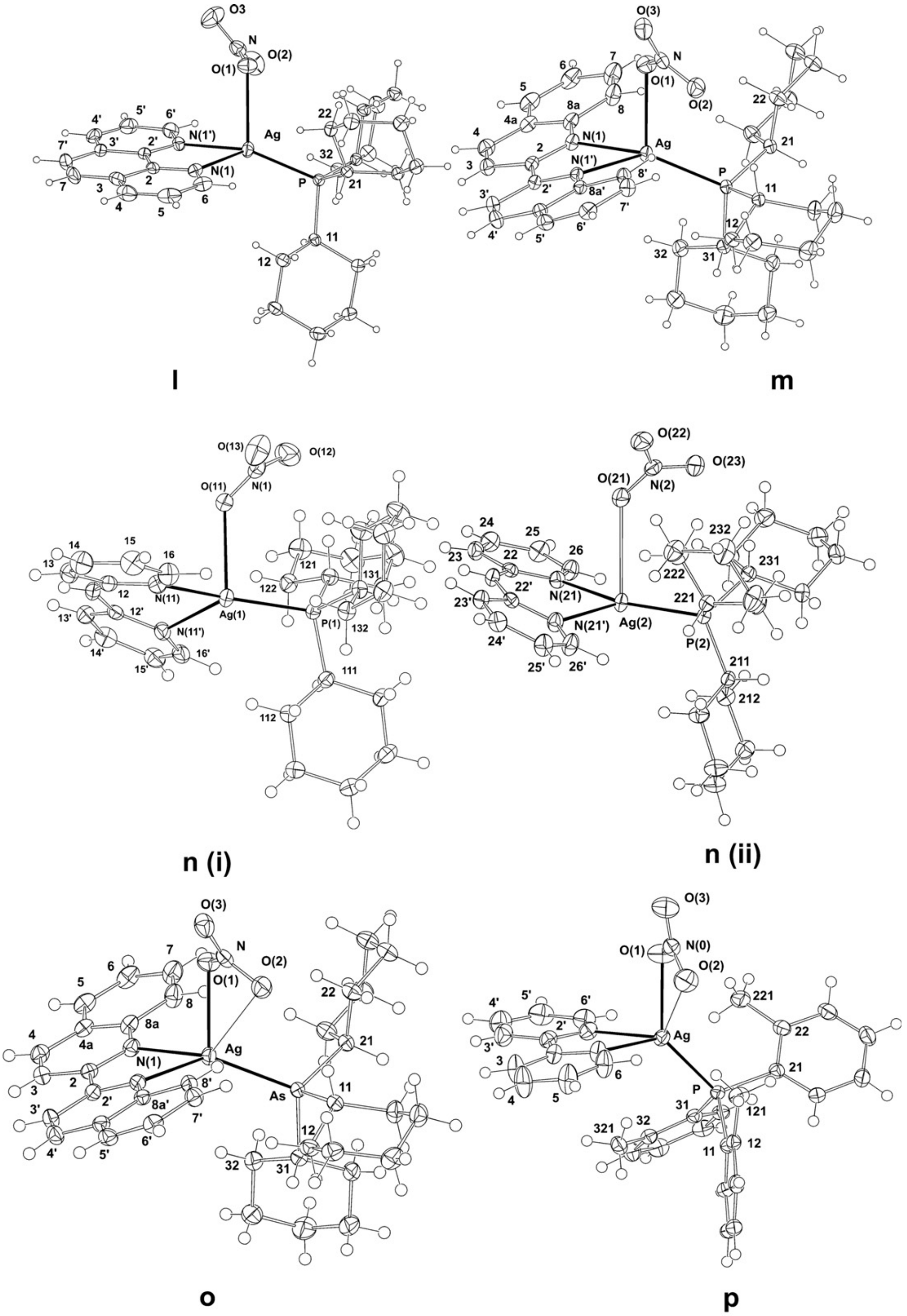

Fig. 1 (*continued*)

Ligands of the form Ecy_3 normally exhibit a more bulky steric profile than their EPh_3 counterparts, as measured by the 'cone angle' [33]; their conformations in projections down the M-P coordinate bond may vary in a manner discussed elsewhere [34], here parametrized by the Ag–E-C–C torsion angle set (Table 1). In general, given the essentially three-coordinate nature of the metal coordination environments, the change has little impact thereon, except to note that the anion approaches in the relatively limited range of compounds studied are

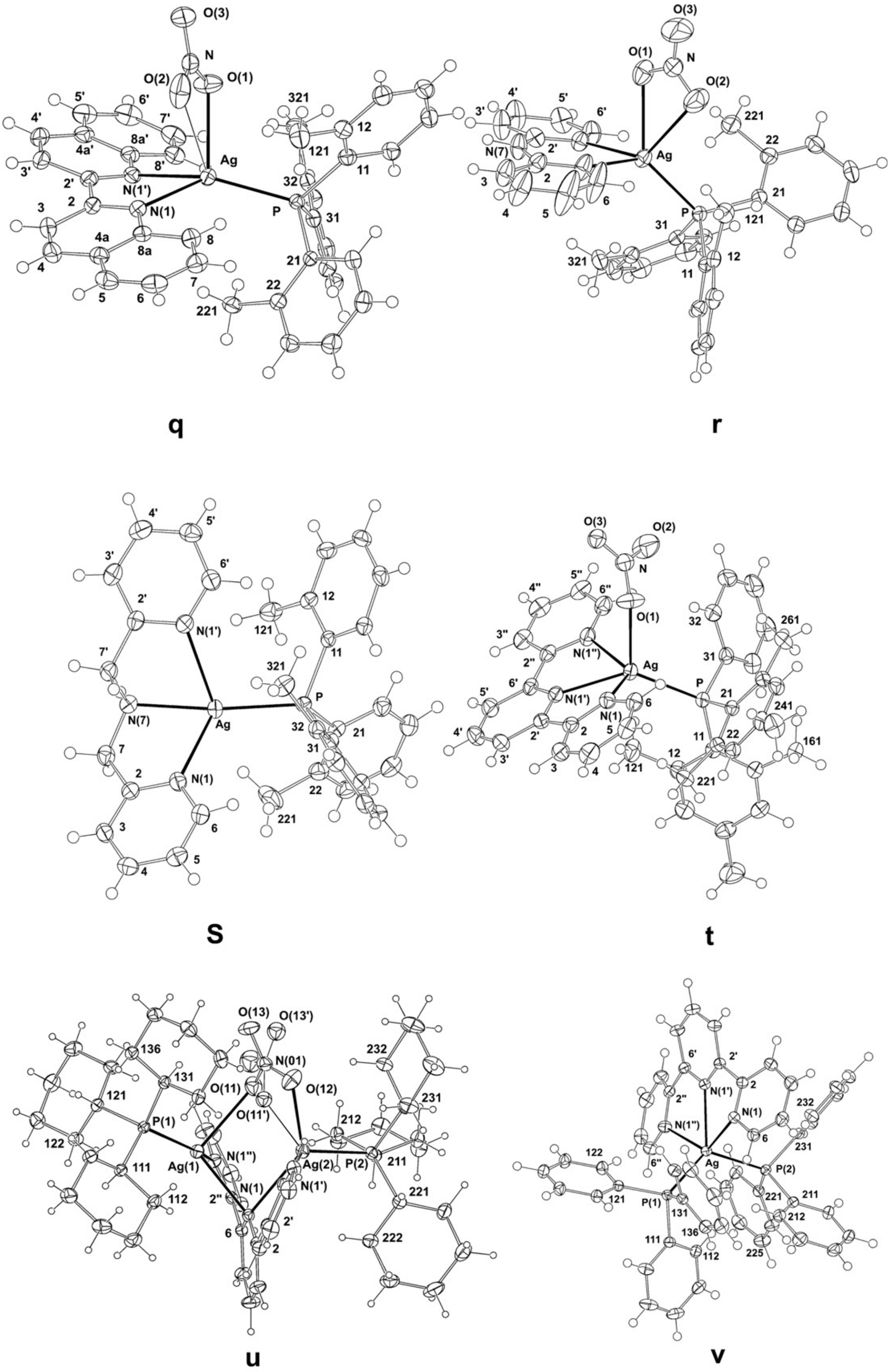

Fig. 1 (*continued*)

as unidentates or weak semi-bidentate ligands. In a number, the E–Ag–N,N′ angle pairs are again quite disparate, but in others essentially equal.

*3.3.12. $AgNO_3$:Pcy_3:bpy (1:1:1) · 3/8MeCN (**12** · 3/8MeCN)*

The solvent seemingly does not interact closely with either of the pair of independent substrate molecules which are found in the asymmetric unit. The two molecules differ somewhat in the orientation of their nitrate planes, although both are similarly semi-bidentate, weakly so, with the $EAgN_2$ angle sums close to 360°.

3.3.13. *$AgNO_3$:Pcy_3:phen (1:1:1) (**13**)*

Here we find for the first time a genuinely unidentate nitrate approach, Ag· · ·O(2) being 3.385(4) Å.

3.3.14. *$AgNO_3$:Pcy_3:bq (1:1:1) (**14**)*

This complex, like the phen counterpart, **13**, above, exhibits a less emphatically unidentate nitrate, Ag· · ·O(2) being 3.158(2) Å.

3.3.15. *$AgNO_3$:Pcy_3:dpa (1:1:1) (**15**)*

Here, in contrast to the other dpa complexes, the $PAgN_2$ angle sums in both of the two independent molecules are close to 360°, the nitrate approaches differing markedly in their dispositions.

3.3.16. *$AgNO_3$:$Ascy_3$:bq (1:1:1) (**16**)*

In this complex the nitrate is semi-bidentate.

Throughout all adducts of $P(o\text{-tol})_3$, the ligand conformation has close to *3*-symmetry about the Ag–P bond, the 2-methyl substituents directed toward the metal rather than within the ligand core. Ag–P are generally slightly longer than in the PPh_3/Pcy_3 counterparts, anion coordination modes being similar.

3.3.17. *$AgNO_3$:$P(o\text{-tol})_3$:bpy (1:1:1) · ½MeCN (**17** · ½MeCN)*

Here the anion is unsymmetrically bidentate. In this complex the $EAgN_2$ array is well-removed from planarity, with Ag–O being correspondingly short.

3.3.18. *$AgNO_3$:$P(o\text{-tol})_3$:bq (1:1:1) (**18**)*

In this complex semi-bidentate anion interaction is found, Ag–P being unusually long.

3.3.19. *$AgNO_3$:$P(o\text{-tol})_3$:dpa (1:1:1) · ½EtOH (**19** · ½EtOH)*

The anion is semi-bidentate; the solvent again is disordered about a crystallographic inversion centre, but with the hydroxylic hydrogen in proximity to the anion, although seemingly without strong hydrogen-bonding interaction. Interestingly, the oxygen atom associated with the shorter Ag–O bond is hydrogen-bonded to the dpa NH group (O(1)..H,N(7) ($1 - x$, $1 - y$, z) 2.24(3), 3.034(6) Å).

3.3.20. *$AgNO_3$:$P(o\text{-tol})_3$:dpca (1:1:1) · ½H_2O (**20** · ½H_2O)*

This complex is ionic, neither anion nor solvent moieties interacting with the metal, and the N_3Ag set of chelate rings unsymmetrical relative to each other, perhaps because of their dispositions relative to the phosphine ligand substituent.

3.3.21. *$AgNO_3$:$PPhmes_2$:tpy (1:1:1) (**21**)*

Here the anion approach is genuinely unidentate, perhaps a consequence of the increased coordination number, coupled with the increased substituent bulk of the phosphine ligand; the phenyl substituent lies nearest to the anion, so that the mes_2 array occupies the void 'behind' the tpy, opposed to the nitrate, one of the associated Ag· · ·H being 2.78(3) Å.

3.3.22. *$AgNO_3$:Pcy_3:tpy (2:2:1) (**22**)*

It is of interest to note that the preceding complexes are all mononuclear as is the following **23** in which coordination of a pair of PPh_3 ligands is no impediment to coordination of a tridentate tpy in that cation, obtained with both perchlorate and nitrate counterions. Nevertheless, in the present array, it may be that the bulk of the Pcy_3 hinders the coordination of a tridentate tpy coplanar with it (even though the bulky $PPhmes_2$ ligand in the previous compound **21** appears to offer no such obstacle). Whatever the cause, the formation of a binuclear complex, in which the tpy ligand rather than being tridentate, behaves as an obliquely coordinated bidentate ligand, to each of a pair of silver atoms, with the central nitrogen atom shared between both (as described elsewhere [35]) is found, the silver atoms also being bridged by one of the nitrate groups, the other being freely ionic. The role of the nitrate group is interesting; it has its oxygen atoms disordered over two sets of sites of unequal occupancy. In the major, unprimed O(11,12) chelate Ag(2) is reasonably symmetrical, with Ag(2) being only 0.12(1) Å out of the plane. Ag(1) lies well out of the plane (2.288(9) Å) and is contacted only by O(11) at a distance of 2.696(5) Å. The $PAgN_2$ angle sum about Ag(1) is $353._2$°, in keeping with the nitrate approach constituting a minor perturbation on what is a possibly awkward planar environment; the $PAgN_2$ counterpart environment is well removed from planarity in keeping with the strong and symmetrical nitrate chelate approach. In the alternative, minor component, disposition, O(11′) is the only oxygen component to contact either silver atom, and is well-removed from Ag(1) (2.82(2) Å), but strongly bound to Ag(2) (2.25(2) Å), maintaining the role of a strong, but now unidentate, donor to the latter, and a negligible one to Ag(1). In this role, the Ag(1,2) out-of-plane deviations are −1.30(7), 1.74(5) Å.

3.3.23. *$AgNO_3$:PPh_3:tpy (2:1:1) (**23**)*

The complex is mononuclear [(tpy-*N*,*N*′,*N*″)$Ag(PPh_3)_2$]-(NO_3), unsolvated, and isomorphous with its perchlorate analogue, which is discussed at length in Ref. [23]. Ag–P are 2.4918(3), 2.5085(3) and Ag–N_c 2.467(1) and Ag–$N_{p,p'}$ are 2.5602(9), 2.6377(10) Å. P–Ag–P′ is 121.79(1)°.

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