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Synthesis and structural characterization of adducts of silver(I) carboxylate salts AgX (X = CF_3COO, CH_3COO) with ER_3 (E = P, As; R = Ph, cy, *o*-tolyl) and oligodentate aromatic bases derivative of 2,2′-bipyridyl, L, AgX:PR_3:L (1:1:1)

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

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

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Abstract

Twenty-one adducts of the form AgX:ER_3:L (1:1:1) (X = CF_3COO ('tfa'), CH_3COO ('ac'), E = P, As; R = Ph, cy, *o*-tolyl; L = 2,2′-bipyridyl ('bpy')-based ligand) have been synthesized and characterized by analytical, spectroscopic (IR, far-IR, ^1H, ^{19}F and ^{31}P NMR) and single crystal X-ray diffraction studies. The resulting complexes are predominantly of the form $[(R_3E)AgL]^+X^-$, with a trigonal $EAgN_2$ coordination environment, the planarity of which may be perturbed by the approach of anion or solvent. The carboxylate anions have been found to be uni-, or semi-bidentate, or also completely ionic, as in the complexes $[Ag(PPh_3)(bpy)(H_2O)](tfa)$ and $[Ag(PPh_3)(dpk \cdot H_2O)](tfa)$ ('dpk · H_2O' = bis(2-pyridyl)ketone (hydrated)). The complexes Agac:PPh_3:dpa (1:1:1) and Agac:P(*o*-tol)$_3$:dpa:MeCN (1:1:1:1) are dinuclear, with bridging unidentate acetate and terminal unidentate dpa ('dpa' = bis(2-pyridyl)amine).

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

1. Introduction

Silver carboxylate derivatives have received attention because of a variety of potential applications. Thus, recent papers report on the use of silver trimethylacetate phosphine derivatives as CVD molecular precursors [1–3], alternatives to fluorinated β-diketonate silver complexes [4], because of diminished sensitivity to light and moisture, higher volatility and thermal stability. Other studies of silver fluorinated carboxylate complexes with 4,4′-bipyridine show the formation of supramolecular assemblies of Ag(I) polyhedra containing embedded acetylenediyne [5], while coordination polymers and networks of Ag(I) with binaphthylbis(amidopyridyl) ligands contain trifluoroacetate groups coordinated to silver and involved in hydrogen-bonding with the N–H groups of the donors [6]. In the preceding pair of papers [7,8], we have described a number of quasi-systematic studies of arrays of complexes of silver(I) oxyanion salts, with oxyanions of increasing basicity – perchlorate [7] and nitrate [8] – with mixed group 15 ligand arrays of the form unidentate ER_3 (E = P, As, Sb; R various) and oligodentate nitrogen-donor aromatic ligands L. We now extend the array to encompass the more basic carboxylate anions acetate ('ac') and trifluoroacetate ('tfa') in combination with various ER_3 arrays for E = P, As; R = Ph, cy (=cyclohexyl), *o*-tol (=*o*-tolyl), and ligands L = 2,2′-bipyridyl ('bpy'), 1,10-phenanthroline ('phen'), 2,9-dimethyl,1,10-phenanthroline ('dmp'), 2,2′-biquinolyl

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

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('bq'), bis(2-pyridyl)amine ('dpa'), bis(2-pyridyl)ketone ('dpk') (as its hydrated form 'dpk · H_2O'), the dominant stoichiometry being AgX:ER_3:L (1:1:1); the results are presented hereunder.

2. Experimental

Experimental procedures follow those recorded in an accompanying paper [9]; in a number of cases, following those precedents, crystals were readily obtained from a few mL of MeCN solutions of the reagents on a millimolar scale by slow cooling and/or evaporation in ambience. In a few cases, probably consequent on solubility considerations, methanol proved more congenial.

2.1. Syntheses

2.1.1. Synthesis of Agtfa:PPh_3:bpy (1:1:1) · MeOH (**1** · MeOH)

A solution containing Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol) in 5 mL of methanol was stirred with warming for 1 h and then cooled at room temperature. A colourless crystalline precipitate slowly formed, which was filtered off, washed with methanol (5 mL), dried under reduced pressure and shown to be compound **1** (0.588 g, yield: 92%); m.p. 101–103 °C. *Anal.* Calc. for $C_{30}H_{23}AgF_3N_2O_2P$: C, 56.36; H, 3.63; N, 4.38. Found: C, 56.15; H, 3.76; N, 4.42%. Λ_m (CH_3CN, 10^{-4} M): 115 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 29 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1580m, 1558m ν(C⋯C, C⋯N), 1675vs, 1435s ν(CF_3COO). IR (nujol, cm^{-1}): 523s, 505s, 494s, 445m, 434m, 417m ν(PPh_3), 399w, 262m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 7.40m (15H, $PC_{18}H_{15}$), 7.54m, 7.91dt, 8.20dd, 8.70m (8H, CH_{bpy}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.7s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 13.6dd (^1J(^{31}P–^{109}Ag): 699.4 Hz; ^1J(^{31}P–^{107}Ag): 620.0 Hz).

2.1.2. Synthesis of Agtfa:PPh_3:bpy:H_2O (1:1:1:1) (**2**)

Compound **2** (0.578 g, yield: 88%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol); m.p. >97 °C (dec.). *Anal.* Calc. for $C_{30}H_{25}AgF_3N_2O_3P$: C, 54.81; H, 3.83; N, 4.26. Found: C, 54.85; H, 4.01; N, 4.20%. IR (KBr, cm^{-1}): 3280br ν(H_2O), 1684m δ (H_2O), 1594s, 1580m ν(C⋯C, C⋯N), 1661s, 1465s ν(CF_3COO). IR (nujol, cm^{-1}): 524s, 505s, 493s, 442m, 424m, 414m ν(PPh_3), 394w, 265m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 7.43m (15H, $PC_{18}H_{15}$), 7.56m, 7.987dt, 8.19dd, 8.58m (8H, CH_{bpy}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −75.5s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 14.8dd (^1J(^{31}P–^{109}Ag): 702.1 Hz; ^1J(^{31}P–^{107}Ag): 621.4 Hz).

2.1.3. Synthesis of Agtfa:PPh_3:phen (1:1:1) (**3**)

Compound **3** (0.629 g, yield: 95%) has been prepared following a procedure similar to that reported for **1** by using a methanol solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and phen (0.180 g, 1.0 mmol); m.p. 186–186 °C. *Anal.* Calc. for $C_{32}H_{23}AgF_3N_2O_2P$: C, 57.94; H, 3.49; N, 4.22. Found: C, 57.70; H, 3.62; N, 4.21%. Λ_m (CH_3CN, 10^{-4} M): 109 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 27 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1619m, 1589m, 1569m, 1513s ν(C⋯C, C⋯N), 1687vs, 1435s ν(CF_3COO). IR (nujol, cm^{-1}): 525vs, 504s, 491s, 445m, 431m, 417m ν(PPh_3), 267m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 7.48m (15H, $PC_{18}H_{15}$), 7.75dd, 7.89s, 8.37dd, 9.10dd (8H, CH_{phen}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.7s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 13.5dd (^1J(^{31}P–^{109}Ag): 701.9 Hz; ^1J(^{31}P–^{107}Ag): 620.2 Hz), 10.8d br (^1J(^{31}P–$^{107/109}$Ag): 463.6 Hz). The compound was modelled from the X-ray study as **3**·¾MeOH.

2.1.4. Synthesis of Agac:PPh_3:phen:MeOH (1:1:1:2) · MeOH (**4** · 2MeOH)

Compound **4** (0.545 g, yield: 85%) has been prepared following a procedure similar to that reported for **3** by using a methanol solution of Agac (0.167 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and phen (0.180 g, 1.0 mmol); m.p. 116–118 °C. *Anal.* Calc. for $C_{33}H_{30}AgN_2O_3P$ (monosolvate): C, 61.86; H, 4.72; N, 4.38. Found: C, 61.41; H, 4.48; N, 4.36. Λ_m (CH_3CN, 10^{-4} M): 110 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 30 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3350br ν(CH_3O–H), 1651m δ (CH_3O–H), 1617m, 1507m ν(C⋯C, C⋯N), 1561vs, 1407s ν(CH_3COO). IR (nujol, cm^{-1}): 512s, 502s, 493s, 4437m, 4329m, 420m ν(PPh_3), 281w, 266m, 246m, 228m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.88s (3H, CH_3COO), 2.04s (3H, CH_3OH), 3.48s (1H, CH_3OH), 7.45m (15H, $PC_{18}H_{15}$), 7.67dd, 7.84s, 8.30dd, 9.15dd (8H, CH_{phen}). ^{31}P NMR ($CDCl_3$, 293 K): δ, 12.4br. ^{31}P NMR ($CDCl_3$, 223 K): δ, 12.7br, 8.1d (^1J(^{31}P–$^{109/107}$Ag): 449.8 Hz).

2.1.5. Synthesis of Agtfa:PPh_3:dmp (1:1:1) (**5**)

Compound **5** (0.621 g, yield: 90%) has been prepared following a procedure similar to that reported for **1** by using a methanol/ethanol solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dmp (0.208 g, 1.0 mmol); m.p. 205–207 °C. *Anal.* Calc. for $C_{34}H_{27}AgF_3N_2O_2P$: C, 59.12; H, 3.94; N, 4.06. Found: C, 59.34; H, 4.00; N, 4.12; Λ_m (CH_3CN, 10^{-4} M): 119 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 40 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1619m, 1555m, 1499s ν(C⋯C, C⋯N), 1665vs, 1589s ν(CF_3COO). IR (nujol, cm^{-1}): 520s, 506vs, 490s, 432m br ν(PPh_3), 317w, 272m, 248m ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.85s (6H, CH_{3dmp}), 7.36m, 7.47m (15H, $PC_{18}H_{15}$), 7.62d, 7.83s, 8.29d (6H, CH_{dmp}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.5s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 10.8dd (^1J(^{31}P–^{109}Ag): 516.3 Hz; ^1J(^{31}P–^{107}Ag): 454.0 Hz), 13.1dd (^1J(^{31}P–^{109}Ag): 686.0 Hz; ^1J(^{31}P–^{107}Ag): 599.4 Hz).

2.1.6. Synthesis of Agac:PPh_3:dmp (1:1:1:1) · MeOH (**6** · MeOH)

Compound **6** (0.615 g, yield: 92%) has been prepared following a procedure similar to that reported for **1** by using a

methanol solution of Agac (0.167 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dmp (0.208 g, 1.0 mmol); m.p. 233–235 °C. *Anal.* Calc. for $C_{35}H_{34}AgN_2O_3P$: C, 62.79; H, 5.12; N, 4.18. Found: C, 62.78; H, 4.95; N, 4.40%. Λ_m (CH_3CN, 10^{-4} M): 106 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 41 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3240br ν(CH_3O–H), 1617m, 1586m ν(C⋯C, C⋯N), 1564vs, 1499s ν(CH_3COO). IR (nujol, cm^{-1}): 517vs, 506vs, 495vs, 435m, 422m ν(PPh_3), 549s, 396m, 330w, 310m, 274w, 263w, 251m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.97s (3H, CH_3COO), 2.81s (6H, CH_{3dmp}), 3.33s (3H, CH_3OH), 3.95s (1H, CH_3O*H*), 7.25m, 7.42m (15H, $PC_{18}H_{15}$), 7.51d, 7.72s, 8.217d (6H, CH_{dmp}). ^{31}P NMR ($CDCl_3$, 223 K): δ, 9.5dd (^1J(^{31}P–^{109}Ag): 643.4 Hz; ^1J(^{31}P–^{107}Ag): 559.1 Hz), 9.8dd (^1J(^{31}P–^{109}Ag): 343.0 Hz; ^1J(^{31}P–^{107}Ag): 279.8 Hz).

2.1.7. Synthesis of Agtfa:PPh_3:bq (1:1:1) (7)

Compound **7** (0.635 g, yield: 86%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol); m.p. 215–217 °C. *Anal.* Calc. for $C_{38}H_{27}AgF_3N_2O_2P$: C, 61.78; H, 3.69; N, 3.79. Found: C, 61.92; H, 3.80; N, 3.84%. Λ_m (CH_3CN, 10^{-4} M): 108 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 38 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1619m, 1552m, 1502s ν(C⋯C, C⋯N), 1659vs, 1594s ν(CF_3COO). IR (nujol, cm^{-1}): 520vs, 505vs, 493vs, 440m, 427m ν(PPh_3), 394m, 270s. ^{1}H NMR ($CDCl_3$, 293 K): δ, 7.45m (15H, $PC_{18}H_{15}$), 7.60dt, 7.67dt, 7.79dd, 8.28d, 8.38dd, 8.46d (12H, CH_{bq}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.3s. ^{31}P NMR ($CDCl_3$, 293 K): δ, 10.2br, 14.6br. ^{31}P NMR ($CDCl_3$, 223 K): δ, 8.9dd (^1J(^{31}P–^{109}Ag): 423.9 Hz; ^1J(^{31}P–^{107}Ag): 350.8 Hz), 9.7dd (^1J(^{31}P–^{109}Ag): 519.0 Hz; ^1J(^{31}P–^{107}Ag): 449.6 Hz), 12.1dd (^1J(^{31}P–^{109}Ag): 685.8 Hz; ^1J(^{31}P–^{107}Ag): 594.2 Hz).

2.1.8. Synthesis of Agtfa:PPh_3:dpa (1:1:1) (8)

Compound **8** (0.602 g, yield: 92%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 164–166 °C. *Anal.* Calc. for $C_{30}H_{24}AgF_3N_3O_2P$: C, 55.01; H, 3.70; N, 6.42. Found: C, 55.28; H, 3.86; N, 6.65%. Λ_m (CH_3CN, 10^{-4} M): 101 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 3 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3322m, 3204m ν(N–H_{dpa}), 1647s, 1575s, 1547m 1530s ν(C⋯C, C⋯N), 1667vs, 1592s ν(CF_3COO). IR (nujol, cm^{-1}): 521s, 503m, 493s, 434m, 425m, 403m ν(PPh_3), 328m, 267m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 7.45m (15H, $PC_{18}H_{15}$), 6.82dt, 7.63dt, 7.72dd, 8.07dd (8H, CH_{dpa}), 9.95br (1H, NH_{dpa}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −75.1s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 10.6d br (^1J(^{31}P–$^{109/07}$Ag): 474.8 Hz), 17.1dd (^1J(^{31}P–^{109}Ag): 732.5 Hz; ^1J(^{31}P–^{107}Ag): 637.2 Hz).

2.1.9. Synthesis of Agac:PPh_3:dpa (1:1:1)$_{(2)}$ (9)

Compound **9** (0.504 g, yield: 84%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agac (0.167 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 134–136 °C. *Anal.* Calc. for $C_{30}H_{27}AgN_3O_2P$: C, 60.01; H, 4.53; N, 7.00. Found: C, 60.29; H, 4.71; N, 7.18%. Λ_m (CH_3CN, 10^{-4} M): 10 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3244m, 3165m ν(N–H_{dpa}), 1605s, 1594s, 1566m ν(C⋯C, C⋯N), 1548vs, 1439s ν(CH_3COO). IR (nujol, cm^{-1}): 516s, 506vs, 494s, 436m, 424m, 417m, 408m ν(PPh_3), 332w, 317w, 259m, 218m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.14s (3H, CH_3COO), 7.42m (15H, $PC_{18}H_{15}$), 6.81dt, 7.55dt, 7.65dd, 8.18dd (8H, CH_{dpa}), 8.55br (1H, NH_{dpa}). ^{31}P NMR ($CDCl_3$, 223 K): δ, 13.8d br (^1J(^{31}P–$^{109/107}$Ag): 653.1 Hz).

2.1.10. Synthesis of Agtfa:PPh_3:dpk · H_2O (1:1:1) · MeCN (10 · MeCN)

Compound **10** (0.558 g, yield: 85%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and dpk (0.184 g, 1.0 mmol); m.p. 87–89 °C. *Anal.* Calc. for $C_{33}H_{28}AgF_3NO_4P$: C, 56.75; H, 4.04; N, 2.01. Found: C, 56.81; H, 3.95; N, 1.94%. Λ_m (CH_3CN, 10^{-4} M): 125 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 44 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3150br ν(O–H_{dpk}), 1583s, 1572m ν(C⋯C, C⋯N), 1678vs, 1434s ν(CF_3COO). IR (nujol, cm^{-1}): 525vs, 507s, 494s, 441m, 425m, 416m, 406w ν(PPh_3), 386w, 376w, 352w, 278w, 263m, 246w, 227w. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.02s (3H, CH_3CN), 7.47m (15H, $PC_{18}H_{15}$), 7.26dt, 7.78dt, 8.09dd, 8.32dd (8H, CH_{dpk}), 9.90br (2H, O–H_{dpk}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −76.1s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 18.2dd (^1J(^{31}P–^{109}Ag): 747.1 Hz; ^1J(^{31}P–^{107}Ag): 646.9 Hz).

2.1.11. Synthesis of Atfa:Pcy_3:bpy (1:1:1) (11)

Compound **11** (0.571 g, yield: 87%) has been prepared following a procedure similar to that reported for **1** by using an ethanol solution of Agtfa (0.221 g, 1.0 mmol), Pcy_3 (0.280 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol); m.p. 170–172 °C. *Anal.* Calc. for $C_{30}H_{41}AgF_3N_2O_2P$: C, 54.80; H, 6.29; N, 4.26. Found: C, 54.94; H, 6.25; N, 4.47%. Λ_m (CH_3CN, 10^{-4} M): 104 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 14 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1618m, 1590m, 1574w ν(C⋯C, C⋯N), 1680vs, 1461s ν(CF_3COO). IR (nujol, cm^{-1}): 543s, 515s, 472m, 460m, 410s ν(Pcy_3), 389w, 267s. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.28m, 1.88m (33H, $PC_{18}H_{33}$), 7.42dd, 7.93dt, 8.39dd, 8.71dd (8H, CH_{bpy}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.9s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 46.1dd (^1J(^{31}P–^{109}Ag): 719.1 Hz; ^1J(^{31}P–^{107}Ag): 622.4 Hz).

2.1.12. Synthesis of Agtfa:Pcy_3:dmp (1:1:1) (12)

Compound **12** (0.653 g, yield: 92%) has been prepared following a procedure similar to that reported for **1** by using an ethanol solution of Agtfa (0.221 g, 1.0 mmol), Pcy_3 (0.280 g, 1.0 mmol), and dmp (0.208 g, 1.0 mmol);

m.p. 203–205 °C. *Anal.* Calc. for $C_{34}H_{45}AgF_3N_2O_2P$: C, 57.55; H, 6.39; N, 3.95. Found: C, 57.24; H, 6.30; N, 4.04%. Λ_m (CH_3CN, 10^{-4} M): 107 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 18 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1622m, 1591m, 1558m, 1505s ν(C⋯C, C⋯N), 1689vs, 1446s ν(CF_3COO). IR (nujol, cm^{-1}): 547s, 513s, 492m, 439m, 434m ν(Pcy_3), 398m, 384m, 377m, 352w, 314m, 280w, 265s, 248w. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.30m, 1.85m (33H, $PC_{18}H_{33}$), 2.94s (6H, CH_{3dmp}), 7.79d, 7.93dt, 7.94s, 8.43d (6H, CH_{dmp}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.8s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 31.1dd ($^1J(^{31}P–^{109}Ag)$: 517.6 Hz; $^1J(^{31}P–^{107}Ag)$: 447.9 Hz), 31.4dd ($^1J(^{31}P–^{109}Ag)$: 518.7 Hz; $^1J(^{31}P–^{107}Ag)$: 448.0 Hz), 38.2dd ($^1J(^{31}P–^{109}Ag)$: 701.8 Hz; $^1J(^{31}P–^{107}Ag)$: 618.9 Hz).

2.1.13. Synthesis of Agtfa:Pcy_3:bq (1:1:1) (**13**)

Compound **13** (0.712 g, yield: 94%) has been prepared following a procedure similar to that reported for **1** by using an ethanol solution of Agtfa (0.221 g, 1.0 mmol), Pcy_3 (0.280 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol); m.p. 192–194 °C. *Anal.* Calc. for $C_{38}H_{45}AgF_3N_2O_2P$: C, 60.24; H, 5.99; N, 3.70. Found: C, 60.42; H, 5.82; N, 3.87%. Λ_m (CH_3CN, 10^{-4} M): 112 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 26 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1617m, 1589m, 1534m, 1501s ν(C⋯C, C⋯N), 1680s, 1459s ν(CF_3COO). IR (nujol, cm^{-1}): 512s, 483s, 449m, 441m, 420m ν(Pcy_3), 398m, 385w, 352w, 327w, 303w, 279m, 264s, 247s, 231w, 224m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.28m, 1.86m (33H, $PC_{18}H_{33}$), 7.60dt, 7.77dt, 7.90dd, 8.28d, 8.41d, 8.80d (12H, CH_{bq}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.7s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 31.3dd ($^1J(^{31}P–^{109}Ag)$: 701.8 Hz; $^1J(^{31}P–^{107}Ag)$: 618.9 Hz), 38.9dd ($^1J(^{31}P–^{109}Ag)$: 516.4 Hz; $^1J(^{31}P–^{107}Ag)$: 449.2 Hz).

2.1.14. Synthesis of Agtfa:Pcy_3:dpa (1:1:1) (**14**)

Compound **14** (0.618 g, yield: 92%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), Pcy_3 (0.280 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 173–175 °C. *Anal.* Calc. for $C_{30}H_{42}AgF_3N_3O_2P$: C, 53.58; H, 6.29; N, 6.25. Found: C, 53.81; H, 6.34; N, 6.33%. Λ_m (CH_3CN, 10^{-4} M): 101 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3328m, 3204m, 3137m ν(N–H_{dpa}), 1592m, 1578s, 1533m ν(C⋯C, C⋯N), 1684vs, 1474s ν(CF_3COO). IR (nujol, cm^{-1}): 527vs, 515vs, 472m, 462m, 413s ν(Pcy_3), 390w, 326m, 280w, 267m, 247w, 229w. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.27m, 1.86m (33H, $PC_{18}H_{33}$), 6.86dt, 7.63dt, 7.67dd, 8.14dd (8H, CH_{dpa}), 8.55br (1H, NH_{dpa}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −75.2s. ^{31}P NMR ($CDCl_3$, 223 K): δ, 44.2dd ($^1J(^{31}P–^{109}Ag)$: 720.2 Hz; $^1J(^{31}P–^{107}Ag)$: 625.7 Hz).

2.1.15. Synthesis of Agtfa:$Ascy_3$:bpy (1:1:1) (**15**)

Compound **15** (0.547 g, yield: 78%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), $Ascy_3$ (0.324 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol); m.p. 122–124 °C. *Anal.* Calc. for $C_{30}H_{41}AgAsN_2O_2F_3$: C, 51.37; H, 5.89; N, 3.99. Found: C, 51.53; H, 5.82; N, 4.12%. Λ_m (CH_3CN, 10^{-4} M): 124 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 38 Ω^{-1} cm^2 mol^{-1}.

2.1.16. Synthesis of Agtfa:$Ascy_3$:dpa (1:1:1) (**16**)

Compound **16** (0.602 g, yield: 84%) has been prepared following a procedure similar to that reported for **1** by using an ethanol solution of Agtfa (0.221 g, 1.0 mmol), $Ascy_3$ (0.324 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 142–145 °C. *Anal.* Calc. for $C_{30}H_{42}AgAsF_3N_3O_2$: C, 50.29; H, 5.91; N, 5.86. Found: C, 50.23; H, 5.84; N, 5.96%. Λ_m (CH_3CN, 10^{-4} M): 119 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 34 Ω^{-1} cm^2 mol^{-1}.

2.1.17. Synthesis of Agac:$P(o\text{-tol})_3$:bpy (1:1:1) · H_2O (**17** · H_2O)

Compound **17** (0.613 g, yield: 95%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile/water solution of Agac (0.167 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and bpy (0.156 g, 1.0 mmol); m.p. 130–132 °C. *Anal.* Calc. for $C_{33}H_{34}AgN_2O_3P$: C, 61.41; H, 5.31; N, 4.34. Found: C, 61.45; H, 5.23; N, 4.36%. Λ_m (CH_3CN, 10^{-4} M): 6 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 2 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1589s, 1573s ν(C⋯C, C⋯N), 1561vs, 1401s ν(CH_3COO). IR (nujol, cm^{-1}): 564m, 557m, 520m, 463vs, 418w, 403m ν(P(*o*-tol)$_3$), 278m, 268s, 255w, 247w, 227m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.84s (3H, CH_3COO), 2.08s (2H, H_2O), 2.56s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.82dt, 7.40m (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 7.18dt, 7.84dt, 8.38dd, 8.69d (8H, CH_{bpy}). ^{31}P NMR ($CDCl_3$, 223 K): δ, −17.6d br ($^1J(^{31}P–^{109/107}Ag)$: 700.6 Hz).

2.1.18. Synthesis of Agtfa:$P(o\text{-tol})_3$:phen:H_2O (1:1:1) · H_2O (**18** · H_2O)

Compound **18** (0.665 g, yield: 92%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile/water solution of Agtfa (0.221 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and phen (0.180 g, 1.0 mmol); m.p. 127–219 °C. *Anal.* Calc. for $C_{35}H_{31}AgF_3N_2O_3P$: C, 58.11; H, 4.32; N, 3.87. Found: C, 57.92; H, 4.34; N, 3.56%. Λ_m (CH_3CN, 10^{-4} M): 12 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 2 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1617m, 1587m, 1567m, 1508s ν(C⋯C, C⋯N), 1671vs, 1459s ν(CF_3COO). IR (nujol, cm^{-1}): 559m br, 518m, 460s, 414m, 402m ν(P(*o*-tol)$_3$), 278m, 264m, 254s, 247m, 227m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.12s (2H, H_2O), 2.58s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.97t, 7.23t, 7.45m (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 7.86dd, 7.99s, 8.53dd, 8.83dd (8H, CH_{bpy}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −75.3s. ^{31}P NMR ($CDCl_3$, 223 K): δ, −18.0d br ($^1J(^{31}P–^{109/107}Ag)$: 678.7 Hz).

2.1.19. Synthesis of Agtfa:$P(o\text{-tol})_3$:bq (1:1:1) (**19**)

Compound **19** (0.687 g, yield: 88%) has been prepared following a procedure similar to that reported for **1** by

using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and bq (0.256 g, 1.0 mmol); m.p. 221–223 °C. *Anal.* Calc. for $C_{41}H_{33}AgF_3N_2O_2P$: C, 63.01; H, 4.26; N, 3.58. Found: C, 62.92; H, 4.35; N, 3.54%. Λ_m (CH_3CN, 10^{-4} M): 105 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 26 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 1617m, 1591s, 1564m, 1552m, 1502s ν(C⋯C, C⋯N), 1670vs, 1452s ν(CF_3COO). IR (nujol, cm^{-1}): 565m, 550m, 531s, 519m, 509m, 479vs, 465vs, 433w ν(P(*o*-tol)$_3$), 395w, 278m, 268s, 255m, 247m, 225m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.47s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.95dt, 7.20t, 7.42m (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 7.61dt, 7.68dt, 7.91dd, 8.08dd, 8.45d, 8.80dd (12H, CH_{bq}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −74.7s. ^{31}P NMR ($CDCl_3$, 223 K): δ, −8.8br.

2.1.20. Synthesis of Agtfa:P(*o*-tol)$_3$:dpa (1:1:1) (**20**)

Compound **20** (0.585 g, yield: 84%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agtfa (0.221 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 170–171 °C. *Anal.* Calc. for $C_{33}H_{30}AgF_3N_3O_2P$: C, 56.91; H, 4.34; N, 6.03. Found: C, 56.86; H, 4.43; N, 6.28%. Λ_m (CH_3CN, 10^{-4} M): 113 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3333m, 3210m, 3142m ν(N–H$_{dpa}$), 1594s, 1578s, 1551m, 1533s ν(C⋯C, C⋯N), 1678vs, 1474s ν(CF_3COO). IR (nujol, cm^{-1}): 563s, 520s, 509m, 463vs, 443w, 418w, 404m ν(P(*o*-tol)$_3$), 326m, 303w, 278m, 268s, 254m, 247m, 227m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.51s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.84dt, 7.24t, 7.40m (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.75dt, 7.64dt, 7.68dd, 7.93dd (8H, CH_{dpa}), 9.57br (1H, NH_{dpa}). ^{19}F NMR ($CDCl_3$, 223 K): δ, −75.2s. ^{31}P NMR ($CDCl_3$, 223 K): δ, −17.5d (^1J(^{31}P–$^{109/107}$Ag): 687.3 Hz). The compound was modelled from the X-ray study as **20**·½MeCN.

2.1.21. Synthesis of Agac:P(*o*-tol)$_3$:dpa (1:1:1)$_{(2)}$ (**21**)

Compound **21** (0.565 g, yield: 88%) has been prepared following a procedure similar to that reported for **1** by using an acetonitrile solution of Agac (0.167 g, 1.0 mmol), P(*o*-tol)$_3$ (0.304 g, 1.0 mmol), and dpa (0.171 g, 1.0 mmol); m.p. 155–157 °C. *Anal.* Calc. for $C_{33}H_{33}AgN_3O_2P$: C, 61.69; H, 5.18; N, 6.54. Found: C, 61.42; H, 5.30; N, 6.75%. Λ_m (CH_3CN, 10^{-4} M): 7 Ω^{-1} cm^2 mol^{-1}. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): 3249m, 3165m ν(N–H$_{dpa}$), 1605s, 1588s, 1532s ν(C⋯C, C⋯N), 1564vs, 1465s ν(CH_3COO). IR (nujol, cm^{-1}): 562s, 523s, 516m, 460vs, 443m, 413m, 407sh ν(P(*o*-tol)$_3$), 384w, 351w, 332m, 303w, 279m, 269m, 254w, 247m, 224m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 2.09s (3H, CH_3COO), 2.54s (9H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.85dt, 7.16t, 7.42m (12H, P(C_6H_4-*ortho*-CH_3)$_3$), 6.76dt, 7.62m, 8.14dd (8H, CH_{dpa}), 8.35br (1H, NH_{dpa}). ^{31}P NMR ($CDCl_3$, 223 K): δ, 18.1d br (^1J(^{31}P–$^{109/107}$Ag): 667.7 Hz). The compound was modelled from the X-ray study as **21**·2MeCN.

2.2. Structure determinations

General procedures are described in an accompanying paper [9]; specific details are as follows. Data for **2**, **7**, **10** and **15** were measured at ca. 298 K using a single-counter instrument (Gaussian absorption corrections, $2\theta/\theta$ scan mode, $I > 3\sigma(I)$ 'observed'). CCDC Nos. 602570–602590.

2.2.1. Crystal/refinement data

*2.2.1.1. Agtfa:PPh$_3$:bpy (1:1:1) · MeOH (**1**).* $C_{31}H_{27}AgF_3N_2O_3P$, $M = 671.4$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.0126(6)$ Å, $b = 10.5085(7)$ Å, $c = 16.114(1)$ Å, $\alpha = 93.397(1)°$, $\beta = 97.819(1)°$, $\gamma = 92.064(1)°$, $V = 1508$ Å^3. D_{calc} ($Z = 2$) = 1.47$_9$ g cm^{-3}. $\mu_{Mo} = 7.7$ cm^{-1}; specimen: 0.30 × 0.18 × 0.12 mm; '$T_{min/max}$' = 0.81. $2\theta_{max} = 58°$; $N_t = 17478$; $N = 7338$ ($R_{int} = 0.014$), $N_o = 6143$; $R = 0.026$, $R_w = 0.036$.

Variata. The CF_3 group was modelled as rotationally disordered over two sets of sites set at equal occupancy after trial refinement.

*2.2.1.2. Agtfa:PPh$_3$:bpy:H$_2$O (1:1:1:1) (**2**).* $C_{30}H_{25}AgF_3N_3O_3P$, $M = 657.4$. Triclinic, space group $P\bar{1}$, $a = 15.270(2)$ Å, $b = 10.694(1)$ Å, $c = 8.9651(8)$ Å, $\alpha = 93.804(8)°$, $\beta = 92.33(1)°$, $\gamma = 106.58(1)°$, $V = 1397$ Å^3. D_{calc} ($Z = 2$) = 1.56$_2$ g cm^{-3}. $\mu_{Mo} = 8.3$ cm^{-1}; specimen: 0.28 × 0.44 × 0.40 mm; '$T_{min/max}$' = 0.90. $2\theta_{max} = 50°$; $N = 4910$, $N_o = 4153$; $R = 0.028$, $R_w = 0.032$. (x, y, z, U_{iso})$_H$ refined.

*2.2.1.3. Agtfa:PPh$_3$:phen (1:1:1) · ¾ MeOH (**3** · ¾-MeOH).* $C_{32}H_{23}AgF_3N_2O_2P \cdot 0.75CH_4O$, $M = 687.4$. Triclinic, space group $P\bar{1}$, $a = 8.772(3)$ Å, $b = 10.451(4)$ Å, $c = 17.042(6)$ Å, $\alpha = 85.202(6)°$, $\beta = 87.561(6)°$, $\gamma = 84.357(6)°$, $V = 1548$ Å^3. D_{calc} ($Z = 2$) = 1.47$_4$ g cm^{-3}. $\mu_{Mo} = 7.6$ cm^{-1}; specimen: 0.35 × 0.20 × 0.15 mm; '$T_{min/max}$' = 0.66. $2\theta_{max} = 58°$; $N_t = 17551$, $N = 7548$ ($R_{int} = 0.040$), $N_o = 3566$; $R = 0.057$, $R_w = 0.062$.

Variata. The fluorine atoms were modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement; difference map residues were modelled as solvent methanol, site occupancy 0.75.

*2.2.1.4. Agac:PPh$_3$:phen (1:1:1) · 2MeOH (**4** · 2MeOH).* $C_{34}H_{34}AgN_2O_4P$, $M = 673.5$. Triclinic, space group $P\bar{1}$, $a = 8.7309(6)$ Å, $b = 10.6579(7)$ Å, $c = 16.892(1)$ Å, $\alpha = 100.500(2)°$, $\beta = 93.087(2)°$, $\gamma = 93.049(2)°$, $V = 1540$ Å^3. D_{calc} ($Z = 2$) = 1.45$_2$ g cm^{-3}. $\mu_{Mo} = 7.5$ cm^{-1}; specimen: 0.25 × 0.20 × 0.15 mm; '$T_{min/max}$' = 0.81. $2\theta_{max} = 70°$; $N_t = 27823$, $N = 13401$ ($R_{int} = 0.045$), $N_o = 11091$; $R = 0.053$, $R_w = 0.085$.

Variata. The second solvent molecule was modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement, associated hydrogen atoms not located.

*2.2.1.5. Agtfa:PPh$_3$:dmp (1:1:1) (**5**).* $C_{34}H_{27}AgF_3N_2O_2P$, $M = 691.4$. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 9.5707(9)$ Å, $b = 15.1540(15)$ Å, $c = 21.003(2)$ Å, $V = 3046$ Å^3. D_{calc} ($Z = 4$) = 1.50_7 g cm^{-3}. $\mu_{Mo} = 7.7$ cm^{-1}; specimen: $0.30 \times 0.27 \times 0.20$ mm; '$T_{min/max}$' = 0.76. $2\theta_{max} = 58°$; $N_t = 32\,535$, $N = 4378$ ($R_{int} = 0.025$), $N_o = 3514$; $R = 0.029$, $R_w = 0.035$. $x_{obs} = 0.03(3)$.

*2.2.1.6. Agac:PPh$_3$:dmp (1:1:1) · MeOH (**6** · MeOH).* $C_{35}H_{34}AgN_2O_3P$, $M = 669.5$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14 (variant)), $a = 9.1859(7)$ Å, $b = 21.015(2)$ Å, $c = 16.274(1)$ Å, $\beta = 101.397(2)°$, $V = 3080$ Å^3. D_{calc} ($Z = 4$) = 1.44_4 g cm^{-3}. $\mu_{Mo} = 7.4$ cm^{-1}; specimen: $0.35 \times 0.20 \times 0.13$ mm; '$T_{min/max}$' = 0.88. $2\theta_{max} = 75°$; $N_t = 62\,693$, $N = 16\,144$ ($R_{int} = 0.027$), $N_o = 12\,964$; $R = 0.026$, $R_w = 0.033$. (x, y, z, U_{iso})$_H$ refined (MeOH excepted).

*2.2.1.7. Agtfa:PPh$_3$:bq (1:1:1) (**7**).* $C_{38}H_{27}AgF_3N_2O_2P$, $M = 739.5$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 18.974(2)$ Å, $b = 10.323(1)$ Å, $c = 18.627(3)$ Å, $\beta = 116.30(1)°$, $V = 3271$ Å^3. D_{calc} ($Z = 4$) = 1.50_1 g cm^{-3}. $\mu_{Mo} = 7.2$ cm^{-1}; specimen: $0.33 \times 0.19 \times 0.39$ mm; '$T_{min/max}$' = 0.86. $2\theta_{max} = 50°$; $N = 5751$, $N_o = 3173$; $R = 0.046$, $R_w = 0.044$. (x, y, z, U_{iso})$_H$ refined.

*2.2.1.8. Agtfa:PPh$_3$:dpa (1:1:1) (**8**).* $C_{30}H_{24}AgF_3N_3O_2P$, $M = 654.4$. Monoclinic, space group $P2_1/c$, $a = 9.1934(7)$ Å, $b = 19.691(2)$ Å, $c = 15.514(1)$ Å, $\beta = 101.517(1)°$, $V = 2752$ Å^3. D_{calc} ($Z = 4$) = 1.57_9 g cm^{-3}. $\mu_{Mo} = 8.4$ cm^{-1}; specimen: $0.70 \times 0.50 \times 0.40$ mm; '$T_{min/max}$' = 0.83. $2\theta_{max} = 58°$; $N_t = 31\,144$, $N = 6830$ ($R_{int} = 0.016$), $N_o = 6183$; $R = 0.027$, $R_w = 0.041$. (x, y, z, U_{iso})$_H$ refined.

*2.2.1.9. Agac:PPh$_3$:dpa (1:1:1)$_{(2)}$ (**9**).* $C_{60}H_{54}Ag_2N_6O_4P_2$, $M = 1200.8$. Monoclinic, space group $P2_1/n$, $a = 10.7911(8)$ Å, $b = 8.9787(6)$ Å, $c = 28.135(2)$ Å, $\beta = 96.724(1)°$, $V = 2707$ Å^3. D_{calc} ($Z = 2$ dimers) = 1.47_3 g cm^{-3}. $\mu_{Mo} = 8.4$ cm^{-1}; specimen: $0.28 \times 0.20 \times 0.14$ mm; '$T_{min/max}$' = 0.88. $2\theta_{max} = 58°$; $N_t = 29\,541$, $N = 6861$ ($R_{int} = 0.019$), $N_o = 6377$; $R = 0.029$, $R_w = 0.065$.

*2.2.1.10. Agtfa:PPh$_3$:dpk · H$_2$O (1:1:1) · MeCN (**10** · MeCN).* $C_{31}H_{25}AgF_3N_2O_4P \cdot C_2H_3N$, $M = 726.5$. Triclinic, space group $P\bar{1}$, $a = 13.910(1)$ Å, $b = 12.042(3)$ Å, $c = 10.573(2)$ Å, $\alpha = 105.65(2)°$, $\beta = 90.04(1)°$, $\gamma = 111.04(2)°$, $V = 1582$ Å^3. D_{calc} ($Z = 2$) = 1.52_5 g cm^{-3}. $\mu_{Mo} = 7.5$ cm^{-1}; specimen: $0.82 \times 0.42 \times 0.28$ mm; '$T_{min/max}$' = 0.43. $2\theta_{max} = 50°$; $N = 5618$, $N_o = 4728$; $R = 0.035$, $R_w = 0.041$. (x, y, z, U_{iso})$_H$ refined (MeCN excepted).

*2.2.1.11. Agtfa:Pcy$_3$:bpy (1:1:1) (**11**).* $C_{30}H_{41}AgF_3N_2O_2P$, $M = 657.5$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14 (variant)), $a = 9.438(2)$ Å, $b = 20.984(3)$ Å, $c = 15.586(3)$ Å, $\beta = 90.029(4)°$, $V = 3087$ Å^3. D_{calc} ($Z = 4$) = 1.41_5 g cm^{-3}. $\mu_{Mo} = 7.5$ cm^{-1}; specimen: $0.21 \times 0.04 \times 0.15$ mm; '$T_{min/max}$' = 0.84. $2\theta_{max} = 58°$; $N_t = 34\,390$, $N = 7767$ ($R_{int} = 0.036$), $N_o = 2763$; $R = 0.049$, $R_w = 0.040$.

*2.2.1.12. Agtfa:Pcy$_3$:dmp (1:1:1) (**12**).* $C_{34}H_{45}AgF_3N_2O_2P$, $M = 709.6$. Triclinic, space group $P\bar{1}$, $a = 9.417(1)$ Å, $b = 10.158(1)$ Å, $c = 19.637(2)$ Å, $\alpha = 91.388(2)°$, $\beta = 95.643(2)°$, $\gamma = 116.055(2)°$, $V = 1675$ Å^3. D_{calc} ($Z = 2$) = 1.40_7 gcm^{-3}. $\mu_{Mo} = 7.0$ cm^{-1}; specimen: $0.27 \times 0.17 \times 0.08$ mm; '$T_{min/max}$' = 0.80. $2\theta_{max} = 58°$; $N_t = 19\,468$; $N = 8160$ ($R_{int} = 0.022$), $N_o = 6172$; $R = 0.035$, $R_w = 0.044$.

*2.2.1.13. Agtfa:Pcy$_3$:bq (1:1:1) (**13**).* $C_{38}H_{45}AgF_3N_2O_2P$, $M = 757.6$. Triclinic, space group $P\bar{1}$, $a = 9.829(1)$ Å, $b = 10.670(1)$ Å, $c = 19.047(2)$ Å, $\alpha = 79.496(2)°$, $\beta = 81.478(2)°$, $\gamma = 64.812(2)°$, $V = 1772$ Å^3. D_{calc} ($Z = 2$) = 1.42_0 g cm^{-3}. $\mu_{Mo} = 6.7$ cm^{-1}; specimen: $0.30 \times 0.12 \times 0.03$ mm; '$T_{min/max}$' = 0.79. $2\theta_{max} = 58°$; $N_t = 18\,946$; $N = 8573$ ($R_{int} = 0.025$), $N_o = 4766$; $R = 0.042$, $R_w = 0.038$.

*2.2.1.14. Agtfa:Pcy$_3$:dpa (1:1:1) (**14**).* $C_{30}H_{42}AgF_3N_3O_2P$, $M = 672.5$. Monoclinic, space group $P2_1/n$, $a = 9.4940(1)$ Å, $b = 20.294(1)$ Å, $c = 15.759(2)$ Å, $\beta = 90.932(1)°$, $V = 3036$ Å^3. D_{calc} ($Z = 4$) = 1.47_1 g cm^{-3}. $\mu_{Mo} = 7.7$ cm^{-1}; specimen: $0.65 \times 0.60 \times 0.25$ mm; '$T_{min/max}$' = 0.84. $2\theta_{max} = 58°$; $N_t = 34\,475$; $N = 7581$ ($R_{int} = 0.016$), $N_o = 7125$; $R = 0.043$, $R_w = 0.10$.

Variata. Oxygen and fluorine components of the anion were modelled as disordered over pairs of sites, occupancies refining to 0.86(1) and complement.

*2.2.1.15. Agtfa:Ascy$_3$:bpy (1:1:1) (**15**).* $C_{30}H_{41}AgAsN_2O_2F_3$, $M = 701.5$. Monoclinic, space group $P2_1/n$, $a = 9.473(2)$ Å, $b = 21.178(6)$ Å, $c = 15.718(2)$ Å, $\beta = 90.19(1)°$, $V = 3153$ Å^3. D_{calc} ($Z = 4$) = 1.47_8 g cm^{-3}. $\mu_{Mo} = 17.3$ cm^{-1}; specimen: $0.52 \times 0.36 \times 0.38$ mm; '$T_{min/max}$' = 0.90. $2\theta_{max} = 50°$; $N = 5256$, $N_o = 3664$; $R = 0.036$, $R_w = 0.037$.

*2.2.1.16. Agtfa:Ascy$_3$:dpa (1:1:1) (**16**).* $C_{30}H_{42}AgAsF_3N_3O_2$, $M = 716.5$. Monoclinic, space group $P2_1/n$, $a = 9.506(2)$ Å, $b = 20.519(4)$ Å, $c = 15.833(3)$ Å, $\beta = 90.589(3)°$, $V = 3088$ Å^3. D_{calc} ($Z = 4$) = 1.54_1 g cm^{-3}. $\mu_{Mo} = 17.7$ cm^{-1}; specimen: $0.22 \times 0.15 \times 0.11$ mm; '$T_{min/max}$' = 0.83. $2\theta_{max} = 58°$; $N_t = 35\,878$; $N = 7801$ ($R_{int} = 0.032$), $N_o = 6241$; $R = 0.028$, $R_w = 0.033$. (x, y, z, U_{iso})$_H$ refined.

*2.2.1.17. Agac:P(o-tol)$_3$:bpy (1:1:1) · H$_2$O (**17** · H$_2$O).* $C_{33}H_{34}AgN_2O_3P$, $M = 645.5$. Triclinic, space group $P\bar{1}$, $a = 9.2929(9)$ Å, $b = 10.537(1)$ Å, $c = 15.816(2)$ Å, $\alpha = 87.955(1)°$, $\beta = 88.471(1)°$, $\gamma = 76.600(1)°$, $V = 1505$ Å^3. D_{calc} ($Z = 2$) = 1.42_4 g cm^{-3}. $\mu_{Mo} = 7.6$ cm^{-1}; specimen: $0.38 \times 0.21 \times 0.22$ mm; '$T_{min/max}$' = 0.93. $2\theta_{max} = 58°$;

$N_t =$ 14525; $N = 7220$ ($R_{int} = 0.020$), $N_o = 6276$; $R = 0.030$, $R_w = 0.040$.

*2.2.1.18. Agtfa:P(o-tol)$_3$:phen (1:1:1) · H$_2$O (**18** · H$_2$O).* $C_{35}H_{31}AgF_3N_2O_3P$, $M = 723.5$. Triclinic, space group $P\bar{1}$, $a = 10.256(2)$ Å, $b = 10.686(2)$ Å, $c = 16.360(3)$ Å, $\alpha = 98.152(3)°$, $\beta = 91.514(3)°$, $\gamma = 114.408(3)°$, $V = 1609$ Å^3. D_{calc} ($Z = 2$) = 1.49$_3$ g cm^{-3}. $\mu_{Mo} = 7.3$ cm^{-1}; specimen: $0.20 \times 0.15 \times 0.10$ mm; '$T_{min/max}$' = 0.66. $2\theta_{max} = 50°$; $N_t = 15895$; $N = 5665$ ($R_{int} = 0.046$), $N_o = 5045$; $R = 0.054$, $R_w = 0.064$.

Variata. The heavy atom components (Ag, P) were modelled as disordered in concert over sets of sites, occupancies refining to 0.946(3) for the major component and 2× (complement/2) for the minor.

*2.2.1.19. Agtfa:P(o-tol)$_3$:bq (1:1:1) (**19**).* $C_{41}H_{33}AgF_3N_2O_2P$, $M = 781.6$. Monoclinic, space group $P2_1/c$, $a = 10.5386(9)$ Å, $b = 10.981(1)$ Å, $c = 30.137(3)$ Å, $\beta = 96.168(2)°$, $V = 3467$ Å^3. D_{calc} ($Z = 4$) = 1.49$_7$ g cm^{-3}. $\mu_{Mo} = 6.8$ cm^{-1}; specimen: $0.18 \times 0.10 \times 0.10$ mm; '$T_{min/max}$' = 83. $2\theta_{max} = 58°$; $N_t = 33511$; $N = 8790$ ($R_{int} = 0.027$), $N_o = 7550$; $R = 0.032$, $R_w = 0.042$.

Variata. Fluorine atoms were modelled over two sets of sites, occupancies set at 0.5 after trial refinement.

*2.2.1.20. Agtfa:P(o-tol)$_3$:dpa (1:1:1) · ½ MeCN (**20** · ½ MeCN).* $C_{34}H_{31.5}AgF_3N_{3.5}O_2P$, $M = 717.0$. Triclinic, space group $P\bar{1}$, $a = 11.519(2)$ Å, $b = 15.814(2)$ Å, $c = 17.459(2)$ Å, $\alpha = 93.595(2)°$, $\beta = 92.993(2)°$, $\gamma = 94.724(2)°$, $V = 3158$ Å^3. D_{calc} ($Z = 4$) = 1.50$_8$ g cm^{-3}. $\mu_{Mo} = 7.4$ cm^{-1}; specimen: $0.40 \times 0.35 \times 0.25$ mm; '$T_{min/max}$' = 0.76. $2\theta_{max} = 58°$; $N_t = 35986$, $N = 15151$ ($R_{int} = 0.023$), $N_o = 12800$; $R = 0.030$, $R_w = 0.042$.

*2.2.1.21. Agac:P(o-tol)$_3$:dpa (1:1:1)$_{(2)}$ · 2MeCN (**21** · 2 MeCN).* $C_{70}H_{72}Ag_2N_8O_4P_2$, $M = 1367.1$. Triclinic, space group $P\bar{1}$, $a = 11.196(1)$ Å, $b = 11.525(1)$ Å, $c = 12.957(1)$ Å, $\alpha = 98.484(2)°$, $\beta = 99.340(1)°$, $\gamma = 100.393(2)°$, $V = 1596$ Å^3. D_{calc} ($Z = 1$ dimer) = 1.42$_3$ g cm^{-3}. $\mu_{Mo} = 7.2$ cm^{-1}; specimen: $0.40 \times 0.25 \times 0.20$ mm; '$T_{min/max}$' = 0.91. $2\theta_{max} = 58°$; $N_t = 15489$, $N = 7696$ ($R_{int} = 0.014$), $N_o = 7052$; $R = 0.025$, $R_w = 0.038$.

3. Results and discussion

3.1. Syntheses

The adducts **1**–**21** (Chart 1) of general formula AgX:ER$_3$:L (1:1:1), have been synthesized by the reaction of one equivalent of *N*,*N*′-bidentate aromatic ligands, L, derivative of 2,2′-bipyridyl, with one equivalent of silver(I) carboxylate and one equivalent of a unidentate ER$_3$ ligand according to

$$AgX + ER_3 + L \xrightarrow{S} AgX : ER_3 : L\ (1:1:1) \quad (1)$$

(X = tfa or ac; E = P or As; R = Ph, cy or *o*-tolyl; L = bpy, phen, dmp, bq, dpa or dpk; S = acetonitrile or ethanol).

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 **2** and **10**. In addition the compounds **1**, **3**–**7**, **11**–**13**, **15** and **17**–**19**, containing weakly coordinated tfa or ac species, undergo complete ionic dissociation, not only in acetonitrile but also in non-ionizing solvents such as dichloromethane, Λ_m in the former solvent being in the range 120–160 and in the latter 40–50 Ω^{-1} cm^2 mol^{-1} [10]. Finally, derivatives **8**, **9**, **14**, **16**, **20** and **21**, containing the dpa ligand, which forms hydrogen-bonding networks in the solid state involving interaction of the N–H components with the carboxylate groups (see crystallographic studies below), are 1:1 electrolytes in acetonitrile but essentially non-electrolytes in dichloromethane [10], presumably in consequence of ion-pair formation.

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-donor and bidentate phosphine or arsine ligands [11]. 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 [12].

In the IR spectra of derivatives **5**–**8**, the difference Δ between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ falls in the range 65–75 cm^{-1}, consistent with the presence of symmetrically bidentate carboxylate groups [13]. Derivatives **2** and **10**, which are ionic in the solid state (see below) show $\Delta\nu(CO_2)$ values of 196 and 243 cm^{-1}, respectively, consistent with the CF_3COO group being involved in some hydrogen-bonding interaction (see below). Derivatives **1**, **3**, **11**–**14**, **18**–**20** show $\Delta\nu(CO_2)$ values in the range 204–252 cm^{-1}, typical of unidentate CF_3COO [13]. Similarly, acetate derivatives **4**, **9**, **17** and **21** present $\Delta\nu(CO_2)$ values between 97 and 160 cm^{-1}, in accordance with unidentate or bridging unidentate CH_3COO [13].

The IR spectra of the dpa-containing derivatives **8**, **9**, **14**, **16**, **20** and **21** exhibit broad bands over 3100 cm^{-1} arising from N–HO(carboxylate) hydrogen-bonding, observed also in their crystal structures. Finally also that of derivative **10**, containing the hydrolyzed dpk · H$_2$O ligand, shows a broad absorption at 3150 cm^{-1}, clearly due to O–H...OC(O)CF$_3$ H-bonding.

In the ^{1}H NMR spectra of derivatives **1**–**21**, all of the signals due to the phosphine and N-donor ligands are found to be detected slightly shifted with respect to those of the free donors, in agreement with the existence of complexes also in solutions in chlorinated solvents.

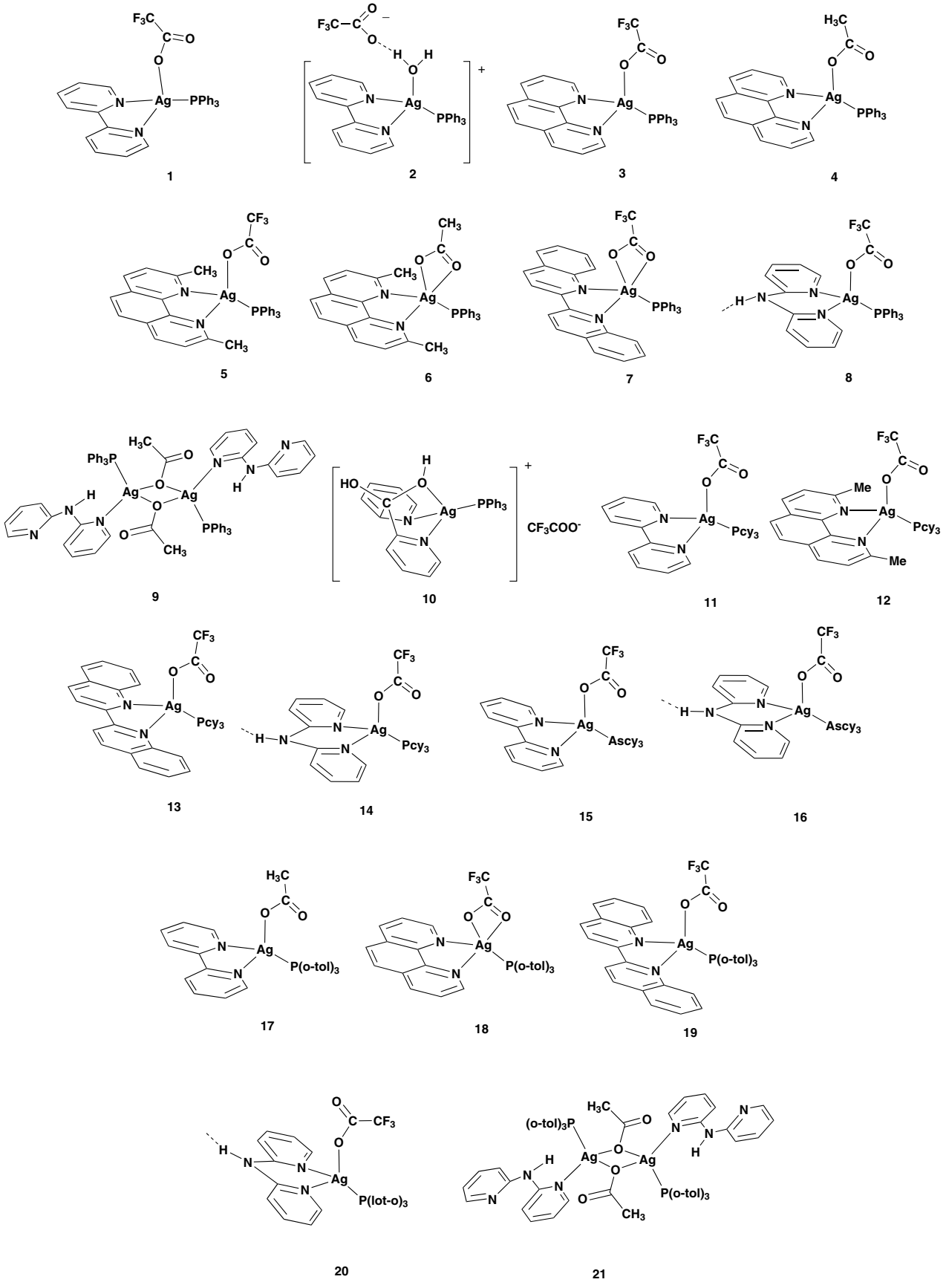

Chart 1.

In the ^{19}F NMR spectra of the tfa-containing derivatives **1**–**3**, **5**, **7**–**8**, **10**–**16** and **18**–**20**, a unique resonance at ca. −75 ppm is always observed, independent of the mode of coordination of the CF_3COO – unidentate, bidentate or ionic – found in the solid state, indicating that the tfa is essentially ionic in nature in chlorinated solvent solution, in accordance also with conductance values (see above).

While at room temperature, the ^{31}P NMR spectra of complexes **1**–**14** and **17**–**21** consist of single broad resonances, presumably due to exchange equilibria which are fast in relation to the NMR time scale, 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 atom, are observed in the accessible temperature range.

We have assigned $AgPN_2$ coordination environments in solution for all derivatives **1**–**14** and **17**–**21** on the basis of their $J_{(Ag–P)}$ (in the range 600–750 Hz) derived from the major ^{31}P resonance. In fact the spin–spin constant (J) between phosphorus and silver depends on the number of coordinated phosphorus atoms in the silver complex, as previously shown by Muetterties and Alegranti [14] and Goel and Pilon [15].

Moreover, in the low temperature ^{31}P NMR spectra of derivatives **3**–**8**, **12** and **13**, one or two minor doublets or pair of doublets have been detected, their $J_{(Ag–P)}$ being in the range 380–540 Hz, in accordance with the presence in solution of additional AgP_2-containing species [14,15], presumably formed from dissociation equilibria such as the following:

$$2[Ag(PR_3)(L)](OOCR) \leftrightarrows [Ag(PR_3)_2(OOCR)] + [Ag(L)_2](OOCR) \quad (R = CF_3 \text{ or } CH_3) \qquad (2)$$

3.3. Single crystal X-ray studies

All adducts **1**–**21** have also been characterized by single crystal X-ray diffraction studies (Fig. 1; Tables 1 and 2). Except in two cases, the complexes are mononuclear, based on a quasi-planar three-coordinate AgN_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), 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 one case, the complex Agtfa:P(*o*-tol)$_3$:dpa (1:1:1), does it rise to two. Although the symmetry of the coordination sphere itself can be as high as m, there is usually a significant asymmetry in the pair of E–Ag–N angles, consequent on the presence of an unsymmetrical disposition relative to 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. By contrast, in the complex where interaction with a water molecule is observed, $[(Ph_3P)Ag(bpy)(OH_2)](tfa)$, **2**, the interaction is close and strong, displacing the potentially ligating tfa anion, which in other situations may be quite strongly bound, an interesting observation in that, given that the crystallizations were effected in ambience, with no special precautions taken to exclude water, its incorporation in the complex is found in only the one case here, and with the carboxylate system, more basic than nitrate or perchlorate where no such interactions are found [7,8]. Interactions with carboxylate anions are widespread and diverse in their nature and strength: all species employed are capable of bidentate approaches and the species observed may range in all cases from *O*,*O*′-bidentate to *O*,*O*′-semibidentate, one oxygen atom being more strongly bound than the other, to *O*-unidentate, to unbound, with a number of interactions between the latter pair in strength. In general, the $EAgN_2$ in-plane 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 Ag–N; for a given anion, the strength of interaction tends to be greater in E = As complexes, cf. counterpart E = P, as expected and in keeping with the diminished base strength of AsR_3, with concomitant change in Ag–N. Although the more basic carboxylate systems interact more strongly generally than the anions of the nitrate and perchlorate counterparts presented in Refs. [7,8], the generally planar, exposed environments of the silver atoms suggest possible application in catalysis for all three types of systems.

The ligands L offer a range of 'bites', those of bpy, phen, dmp, and bq being similar, the latter pair offering different, more hindered profiles, while dpa, with a six- cf. a five-membered chelate ring, has a greater 'bite', also true of dpk – but here with a further O donor (two in the case of the hydrate) introduced between the peripheral pair, the ligand is potentially tridentate, although it could function as a simple chelate or a pair of chelates. Interestingly, in two of the dpa complexes, one with E = P, the other E = As, both with the acetate (rather than the less basic trifluoroacetate) oxyanion, the strength of the anion/base interaction is such as to overcome the chelate effect of the dpa ligand so that it becomes unidentate. In both of these cases, a binuclear species is found, creating, in effect, via the bridging oxygen atoms, an alternative $(\mu\text{-}O)_2$-chelate. 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 dominant determinants of crystal packing in many cases. Core geometries for all of the species are summarized in Tables 1 and 2, with individual

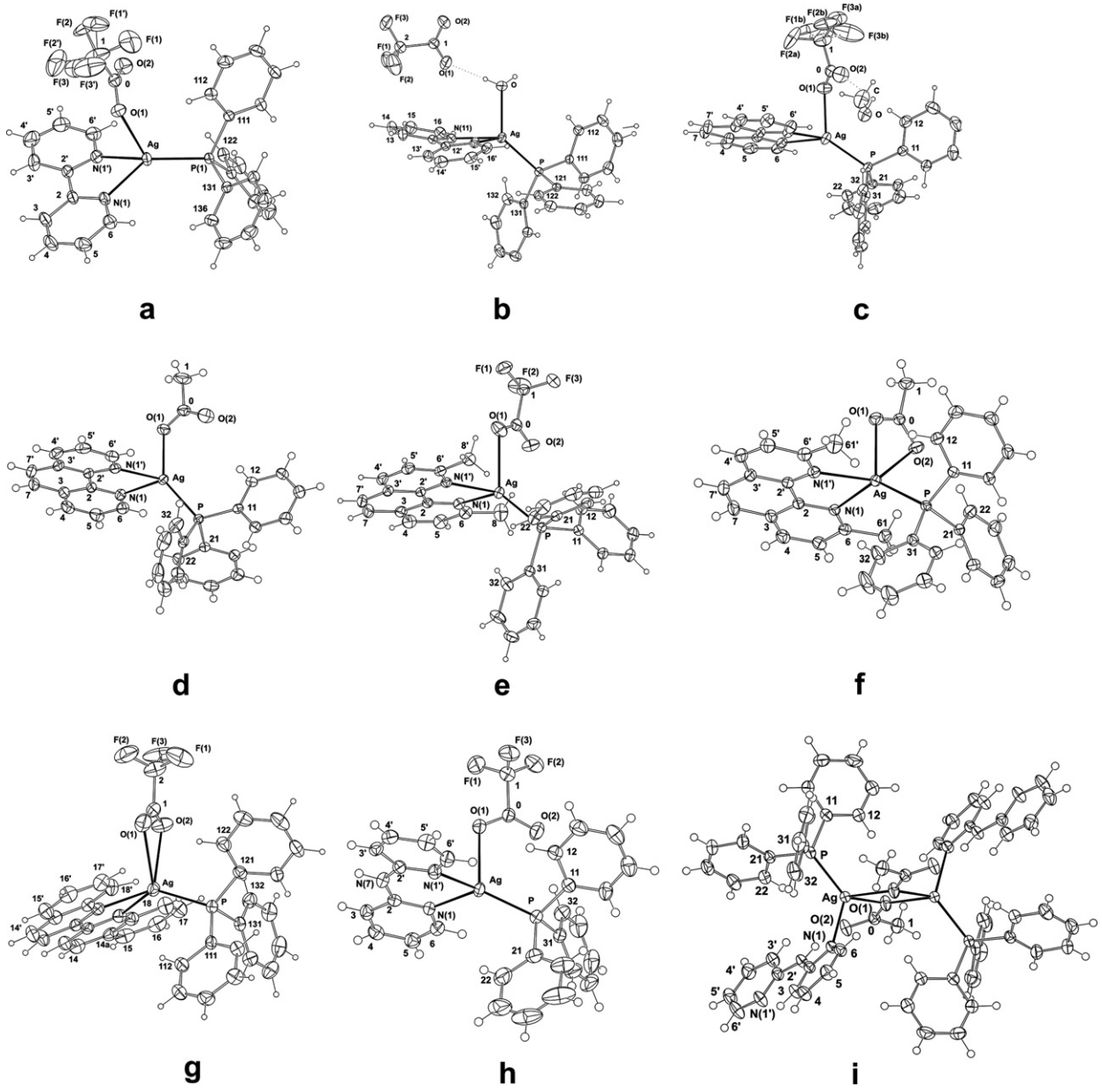

Fig. 1. Projections of the complex aggregates of the following (R_3P)Ag(N,N'-aromatic base)/(ac/tfa) systems: (a) [(Ph_3P)Ag(N,N'-bpy)(O-tfa)] in **1** · MeOH; (b) [(Ph_3P)Ag(N,N'-bpy)(OH_2)]$^+$ in **2**; (c) [(Ph_3P)Ag(N,N'-phen)(O-tfa)] in **3** · ¾MeOH; (d) [(Ph_3P)Ag(N,N'-phen)(O-ac)] in **4** · 2MeOH; (e) [(Ph_3P)Ag(N,N'-dmp)(O-tfa)], **5**; (f) [(Ph_3P)Ag(N,N'-dmp)(O,O'-ac)] in **6** · MeOH; (g) [(Ph_3P)Ag(N,N'-bq)(O,O'-tfa)], **7**; (h) [(Ph_3P)Ag(N,N'-dpa)(O-tfa)], **8**; (i) [{(Ph_3P)Ag(N-dpa)Ag}$_2$(μ-O-ac)$_2$], **9**; (j) [(Ph_3P)Ag{N,N',O-(dpk · H_2O)}](tfa) in **10** · MeCN; (k) [(cy_3P)Ag(N,N'-bpy)(O-tfa)], **11**; (l) [(cy_3P)Ag(N,N'-dmp)(O-tfa)], **12**; (m) [(cy_3P)Ag(N,N'-bq)(O-tfa)], **13**; (n) [(cy_3P)Ag(N,N'-dpa)(O,O'-tfa)], **14**; (o) [(cy_3As)Ag(N,N'-bpy)(O-tfa)], **15**; (p) [(cy_3As)Ag(N,N'-dpa)(O-tfa)], **16**; (q) [{(o-tol)$_3$P}Ag(N,N'-bpy)(O-ac)] in **17** · H_2O; (r) [{(o-tol)$_3$P}Ag(N,N'-phen)(O,O'-tfa)] in **18** · H_2O; (s) [{(o-tol)$_3$P}Ag(N,N'-bq)-(O-tfa)], **19**; (t) [{(o-tol)$_3$P}Ag(N,N'-dpa)(O-tfa)], (mol. 1) in **20** · ½MeCN; (u) [{((o-tol)$_3$P)Ag(N,N'-dpa)}$_2$(μ-O-ac)$_2$] in **21** · 2MeCN.

species depicted in Fig. 1. We comment individually on the various structures as follows:

3.3.1. Agtfa:PPh$_3$:bpy:MeOH (**1** · MeOH)

An imponderable thread throughout the present array is the determinant(s) of mode and strength of interaction of the anion with the 1:1:1 complex substrate, seemingly devoid of systematic behaviour or trend. Here in the present complex, the base tfa affords a unidentate coordination. A salient factor in the present array may be the well-defined methanol solvate molecule, which, with hydrogen atoms smoothly refining, interacts closely with the uncoordinated oxygen of the anion ((MeOH)O,H…O(2) 2.686(3), 1.73(4) Å). The query concerning mode and nature of anion interaction is reinforced in the structure of the adventitious **2**:

3.3.2. Agtfa:PPh$_3$:bpy:H$_2$O (1:1:1:1) (**2**)

This is unequivocally defined as displaying a solvent, rather than an anionic, interaction with the substrate.

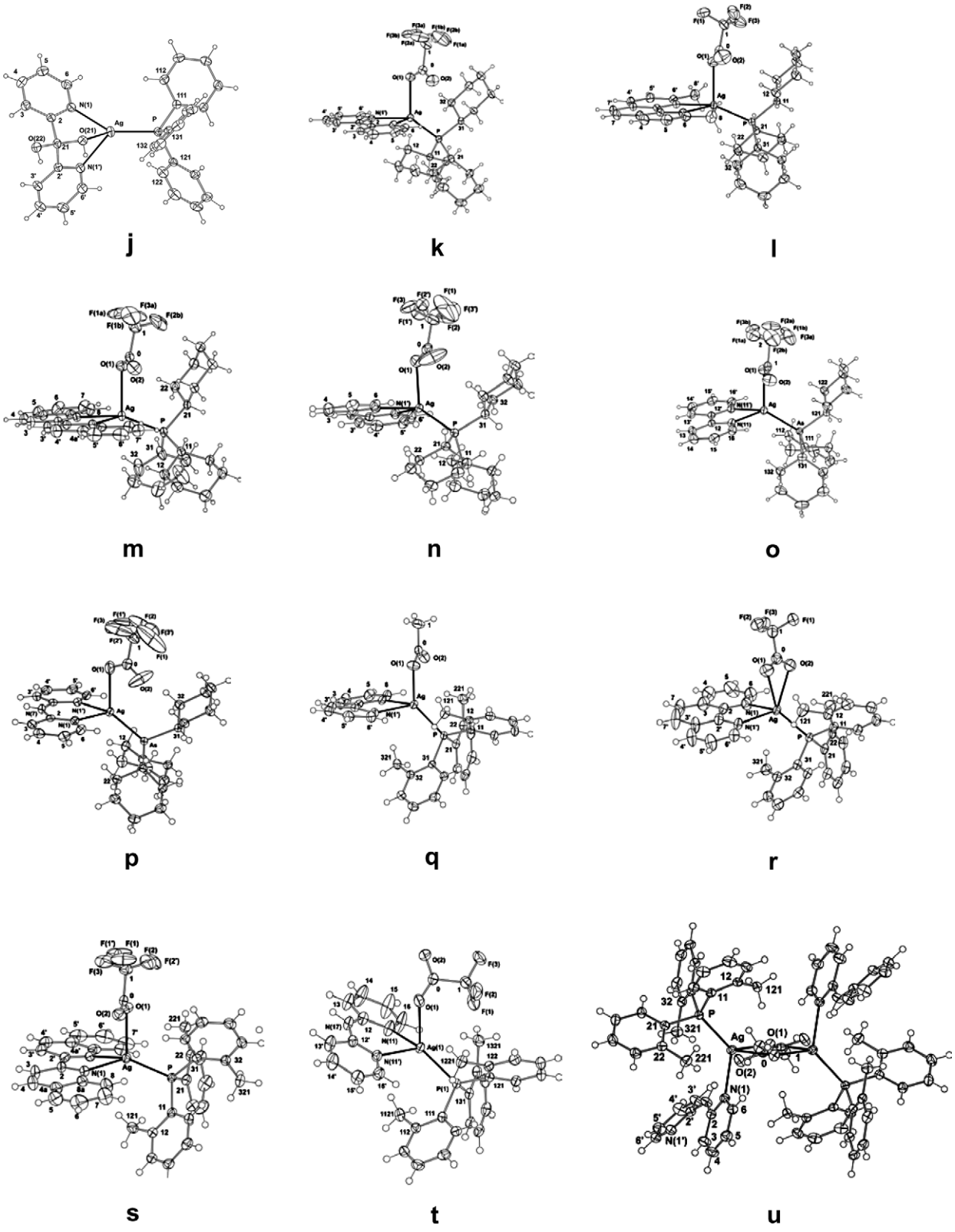

Fig. 1 (*continued*)

Ag–O(H_2), 2.340(3) Å, is one of the shortest/strongest approaches of any oxo-moiety to the substrate in the present array, reflected in the considerable 'distortions' in the silver environment. The compound is thus ionic, $[(Ph_3P)Ag(N,N'\text{-bpy})(OH_2)]^+$('tfa')$^-$, the water molecule bridging a pair of symmetry related anions in the lattice (O,H(2)···O(1), 2.741(4), 1.93(6); O,H(1)···O(2) $(2-x, 1-y, \bar{z})$ 2.751(5), 2.03(5) Å).

Table 1
Silver atom environments, AgX:ER_3:L(:S) (1:1:1(:1))

ER_3:L(:S/X)	Ag–X(/S) (Å)[a]	Ag–E (Å)	Ag–*N*,*N*′ (Å)	(S/X)–Ag–E (°)	(S/X)–Ag–*N*,*N*′ (°)	E–Ag–*N*,*N*′ (°)	N–Ag–N′ (°)	Σ (°)
(**1**) PPh_3:bpy:*O*,(O-tfa)	2.503(2)	2.3547(5)	2.355(2), 2.315(2)	114.11(4)	89.13(6), 86.02(6)	132.50(4), 145.92(5)	71.36(6)	$349._8$
(**2**) PPh_3:bpy:*O*H_2(tfa)	2.340(3)	2.3535(7)	2.330(2), 2.377(3)	130.7(1)	90.6(1), 95.5(1)	129.50(6), 121.60(6)	70.99(8)	$322._1$
(**3**) PPh_3:phen:*O*,(O-tfa)	2.370(6)(,3.416(7))	2.351(2)	2.375(5), 2.319(5)	125.4(1)	88.6(2), 88.2(2)	129.4(1), 135.7(1)	71.7(2)	$336._8$
(**4**) PPh_3:phen:*O*,(O-ac)	2.292(2)(,3.316(3))	2.3541(7)	2.426(3), 2.364(3)	139.55(7)	93.13(7), 88.22(9)	116.52(6), 126.12(7)	70.5(1)	$313._1$
(**5**) PPh_3:dmp:O_2-tfa	2.583(3), 2.824(4)	2.383(1)	2.363(3), 2.372(3)	126.37(7) 105.6(1)	100.97(9), 80.1(1) 92.4(1), 121.0(1)	128.84(8), 129.32(7)	71.2(1)	$329._4$
(**6**) PPh_3:dmp:O_2-ac	2.3993(9), 2.875(1)	2.3792(3)	2.3620(9), 2.4104(9)	122.30(2) 97.52(2)	101.95(3), 89.94(3) 93.11(3), 132.31(3)	128.96(2), 128.11(3)	70.23(3)	$327._3$
(**7**) PPh_3:bq:O_2-tfa	2.671(6), 2.673(6)	2.391(2)	2.354(5), 2.370(7)	106.8(2) 104.9(2)	124.0(2), 92.1(2) 98.1(2), 122.6(2)	126.6(2), 127.8(1)	69.8(2)	$324._2$
(**8**) PPh_3:dpa:*O*,(Otfa)	2.461(1)(,3.403(1))	2.3589(5)	2.293(1), 2.335(1)	116.70(3)	96.07(5), 87.66(4)	132.08(4), 130.51(3)	81.43(5)	$344._0$
(**9**) PPh_3:dpa:μ-O-ac	2.278(1), 2.546(1)	2.3609(5)	2.341(1) (unident.)	129.28(4) 108.06(3)	108.97(5) 92.77(5)	120.04(4)		
(**10**) PPh_3:dpk,OH_2(tfa)	2.596(3)(O(dpk))	2.326(1)	2.276(3), 2.337(3)	121.80(6)	67.3(1), 67.44(9)	148.04(6), 129.41(8)	82.5(1)	$360._0$
(**11**) Pcy_3:bpy:*O*,(O-tfa)	2.439(5)(,3.101(2))	2.368(2)	2.354(5), 2.383(5)	122.5(1)	99.8(2), 91.2(2)	127.1(1), 131.9(1)	69.5(2)	$328._5$
(**12**) Pcy_3:dmp:*O*,(O-tfa)	2.424(3)(,3.469(5))	2.3710(7)	2.352(3), 2.366(2)	113.38(8)	100.7(1), 88.7(1)	133.52(7), 136.55(6)	71.5(1)	$341._6$
(**13**) Pcy_3:bq:*O*,(O-tfa)	2.472(4)(,3.240(4))	2.384(1)	2.378(3), 2.353(3)	109.96(8)	91.6(1), 100.5(1)	136.21(7), 137.1(1)	69.7(1)	$343._0$
(**14**) Pcy_3:dpa:*O*,(O-tfa) (disordered cpt.)	2.508(4)(,3.153(7)) 2.64(1)(,2.97(1))	2.3758(5)	2.357(1), 2.352(2)	131.4(1)/ 102.9(2)	92.4(1), 81.4(1) 90.2(2), 121.7(2)	125.85(4), 129.83(4)	78.79(5)	$334._5$
(**15**) $Ascy_3$:bpy:*O*,(O-tfa)	2.413(4)(,3.054(5))	2.4587(9)	2.351(4), 2.373(4)	121.1(1)	103.2(1), 94.0(1)	125.2(1), 131.0(1)	69.2(1)	$325._4$
(**16**) $Ascy_3$:dpa:*O*,(O-tfa)	2.488(2)(,3.074(3))	2.4680(5)	2.357(2), 2.352(2)	131.80(5)	94.02(7), 85.35(7)	123.38(5), 127.07(5)	79.41(7)	$329._9$
(**17**) P(*o*-tol)$_3$:bpy:O_2-ac	2.322(2), 2.930(2)	2.3828(6)	2.355(2), 2.450(2)	131.68(5) 121.10(4)	99.01(7), 90.12(7) 77.30(6), 119.84(6)	126.40(6), 119.02(5)	68.58(6)	$314._0$
(**18**) P(*o*-tol)$_3$:phen:O_2-tfa (major component)	2.464(4), 2.754(4)	2.374(1)	2.344(4), 2.431(5)	134.2(1) 115.0(1)	87.6(2), 87.3(2) 80.4(1), 129.6(2)	136.7(1), 114.4(1)	70.6(2)	$321._7$
(**19**) P(*o*-tol)$_3$:bq:*O*,(O-tfa)	2.418(2)(,3.048(2))	2.3937(5)	2.349(2), 2.387(2)	113.10(4)	105.36(6), 88.00(6)	133.98(5), 133.83(4)	69.64(6)	$337._5$
(**20**) P(*o*-tol)$_3$:dpa:*O*-tfa (mol. 1)	2.457(2)	2.3855(6)	2.299(2), 2.353(2)	130.22(4)	87.52(7), 84.49(6)	134.30(5), 121.82(5)	80.55(6)	$336._7$
O_2-tfa (mol. 2)	2.493(2), 2.808(2)	2.3952(6)	2.319(2), 2.374(2)	135.53(4) 99.12(5)	89.08(7), 85.03(6) 95.77(7), 134.08(6)	129.34(6), 118.66(6)	80.66(7) 80.66(7)	$328._6$ $328._6$
(**21**) P(*o*-tol)$_3$:dpa:μ-*O*-ac	2.366(1), 2.539(1)	2.4304(4)	2.384(1) (unident.)	126.92(3) 117.55(3)	105.07(4) 88.93(4)	125.82(3)		

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

Table 2
Silver atom environments, $AgX:ER_3:L(:S)$ (1:1:1(:1))

ER_3:L(:S/X)	$\theta_{py/py}^{bq/bq}$ (°)	δAg (Å)	δAg_x (Å)	Ag–X(,X′)–Y (°)	Ag–E–C(n1)–C(n2(6)) (°)	E–Ag–O–X (°)	O–X–O (°)
(**1**) PPh_3:bpy:*O*(,O-tfa)	13.5(1)	0.010(4), 0.674(4)	0.006(8)	124.1(1)	34.2(2), 57.6(2), 43.2(2)	81.2(2)	131.9(2)
(**2**) PPh_3:bpy:*O*H_2(tfa)	18.5(1)	0.436(5), 0.532(5)			31.2(2), 42.8(2), 56.9(3)		131.2(4)
(**3**) PPh_3:phen:*O*(,O-tfa)		0.151(6)	0.39(2)	120.5(5)	−25.7(6), −42.2(6), −58.7(5)	−82.1(6)	132.0(9)
(**4**) PPh_3:phen:*O*(,O-ac)		0.176(3)	0.091(8)	122.5(2)	−30.0(3), −47.4(3), −57.8(3)	−35.2(3)	125.0(3)
(**5**) PPh_3:dmp:O_2-tfa		0.331(3)	0.118(8)	98.1(3), 86.3(4)	9.6(3), 63.5(3), 32.6(3)	79.3(3)	128.5(4)
(**6**) PPh_3:dmp:O_2-ac		0.343(1)	0.047(3)	104.68(2), 82.16(7)	20.0(1), 45.7(1), 16.9(1)	68.58(8), −125.71(6)	124.2(1)
(**7**) PPh_3:bq:O_2-tfa	2.4(2)	0.05(1), 0.01(1)	0.14(2)	91.9(6), 92.1(5)	24.5(7), 25.3(6), 65.4(7)	93.2(6), −97.3(6)	128.2(9)
(**8**) PPh_3:dpa:*O*(,Otfa)	8.06(6)	0.142(3), 0.423(3)	0.238(3)	116.8(1)	14.8(2), 33.4(2), 49.0(2)	16.5(1)	130.3(2)
(**9**) PPh_3:dpa:μ-O-ac	9.42(5)	0.685(3)	0.027(3), 0.927(4)	108.6(1), 144.2(1)	−12.2(2), −26.7(2), −46.5(2)	−96.8(1)	124.0(2)
(**10**) PPh_3:dpk,OH_2(tfa)	68.4(1)	0.131(6), 0.212(6)		97.1(2)	22.5(3), 44.9(4), 43.8(3)	−168.6(6)	129.6(4)
(**11**) Pcy_3:bpy:*O*(,O-tfa)	2.8(3)	0.10(1), 0.01(1)	0.22(2)	109.7(5)	19.5(5), 51.6(4), −52.0(4)	−78.7(6)	124.7(10)
(**12**) Pcy_3:dmp:O_2(O-tfa)		0.033(2)	0.485(8)	120.9(4)	58.1(2), −58.9(2), 47.7(3)	−81.7(3)	132.5(5)
(**13**) Pcy_3:bq:O_2(O-tfa)	2.9(1)	0.035(6), 0.118(6)	0.42(1)	112.1(4)	55.9(3), −58.3(3), −28.5(7)	−89.3(3)	130.6(6)
(**14**) Pcy_3:dpa:*O*(,O-tfa)	4.80(5)	0.088(3), 0.213(3)	0.376(1)	109.1(3)	20.4(1), 51.5(1), −49.9(1)	−43.5(4)	130.1(4)
(disordered cpt.)			0.350(1)	102.3(7)		126.1(5)	124.4(8)
(**15**) $Ascy_3$:bpy:*O*(,O′ − tfa)	3.2(2)	0.058(9), 0.061(9)	0.18(1)	108.5(4)	18.7(5), −49.5(4), 49.5(4)	−78.5(4)	129.6(8)
(**16**) $Ascy_3$:dpa:*O*(,O-tfa)	5.40(6)	0.005(4), 0.069(4)	0.245(6)	107.6(2)	18.6(2), 50.7(2), −48.8(2)	−36.6(2)	127.9(3)
(**17**) P(*o*-tol)$_3$:bpy:O_2-ac	14.70(9)	0.243(4), 0.538(4)	0.116(6)	107.9(2), 79.2(1)	43.4(2), 46.6(2), 51.5(2)	98.7(2)	124.9(3)
(**18**) P(*o*-tol)$_3$:phen:O_2-tfa	5.4(2)	0.17(1), 0.04(1)	0.37(1)	95.4(4), 82.8(3)	41.9(8), 49.8(4), 51.6(5)	92.3(4), −132.4(3)	130.5(5)
(**19**) P(*o*-tol)$_3$:bq:*O*(,O-tfa)	11.09(6)	0.100(3), 0.522(3)	0.228(4)	106.7(1)	48.6(2), 61.5(2), 16.4(2)	−96.7(1)	129.7(2)
(**20**) P(*o*-tol)$_3$:dpa:*O*-tfa (mol. 1)	9.69(7)	0.406(4), 0.474(3)	0.491(4)	143.4(2)	50.3(2), 44.3(2), 49.7(2)	44.5(3)	129.0(2)
O_2-tfa (mol. 2)	4.8(1)	0.040(5), 0.262(4)	0.242(4)	98.2(1), 83.8(1)	−46.2(2), −43.2(2), −56.1(2)	−52.7(2), 143.3(1)	129.0(2)
(**21**) P(*o*-tol)$_3$:dpa:μ-*O*-*ac*	30.60(6)	0.398(3), 1.420(3)	0.172(3)	108.10(8), 134.24(9)	44.7(2), 47.2(2), 54.8(1)	−98.8(1)	124.2(2)

3.3.3. *Agtfa:PPh$_3$:phen (1:1:1) · ¾MeOH (**3** · ¾MeOH)*

Here the anion plane (C_2O_2) lies effectively normal to the plane containing PAgO and the phen bisector. However, again, despite refinement to a less-than-total occupancy, we find solvent interaction to be significant, the methanol molecule hydrogen-bonding to the uncoordinated anion oxygen ((MeOH)O,H…O(2) 2.74(1), 2.2 (est.) Å) and resulting in an anion orientation similar to that in the bpy counterpart.

3.3.4. *Agac:PPh$_3$:phen (1:1:1) · 2MeOH (**4** · 2MeOH)*

In this species, containing the more basic anion, the coordination mode is similar to the previous. Here there are two solvent molecules of crystallization, one disordered, the second firmly anchored by hydrogen-bonding to the uncoordinated oxygen of the anion, (MeOH)O, H…O(2) being 2.754(5), 1.7_5 Å.

3.3.5. *Agtfa:PPh$_3$:dmp (1:1:1) (**5**)*

The geometry of this molecule is not unusual in the light of the above. 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, in this or its other complexes in the present array.

3.3.6. *Agac:PPh$_3$:dmp (1:1:1) · MeOH (**6** · MeOH)*

In both **5** and **6,** the anions are effectively semi-bidentate, but differ somewhat in their orientations vis-a-vis the substrate; displacement parameters on anion 2 in this case are high and may be a foil for unresolved disorder. The carboxylate anions being prone to semi-bidentate coordination, the less strongly interacting oxygen atom here is hydrogen-bonded by the hydroxylic solvent. (MeOH)O,H…O(2) are 2.724(2), 1.99(3) Å.

3.3.7. *Agtfa:PPh$_3$:bq (1:1:1) (**7**)*

In this (unsolvated) carboxylate complex we find, for the first time, a truly bidentate anion, its plane lying across the molecule. Angles P–Ag–O are less than N–Ag–O as might be expected. The O–C–O angle of the anion is considerably reduced relative to the values observed with uni-/semi-bidentate tfa, but still lies above the values found for the various acetate species. Although like dmp, the bq ligand may be considered to exhibit a 'bulky' profile, this does not appear to impact on the overall geometries of arrays containing it to any noticeable extent.

3.3.8. *Agtfa:PPh$_3$:dpa (1:1:1) (**8**)*

Here O(1) (N.B. coordinated)…H,N $(2 - x, 1 - y, \bar{z})$ are 2.08(2), 2.867(2) Å. This complex is not unusual, albeit the semi-bidentate anion is unaccompanied by any interacting

solvent. Given the behaviour of the ligand in the systems of **9** and **21**, it is of interest to note that the Ag–*N*,*N*′ distances vary quite widely throughout the array of complexes studied, and that the values observed for dpa here and elsewhere, functioning as a bidentate ligand, are not unusually long.

3.3.9. Agac:PPh_3:dpa (1:1:1)$_{(2)}$ (**9**)

With this complex, by contrast, a new form is found. Here the dpa ligand has become unidentate, while the acetate has become *O*-bridging, so that the array is now an (unsolvated) neutral centrosymmetric dimer. The Ag–O–Ag angle is 99.59(5)°. An important factor, perhaps, in determining the stability of this form (and, perhaps, also relevant in other similar situations involving unidentate dpa) is an intra-species hydrogen-bond between the central NH hydrogen and the uncoordinated carboxylate oxygen (N,H...O(2) 2.841(2), 2.04(2) Å). Relaxation of the chelate constraint permits the uncoordinated pyridine ring of the dpa to adopt the *trans*-disposition vis-à-vis the coordinated ring; it is of interest to note here that the N(1′)...H(3) distance is 2.26(2) Å, the angle at the central nitrogen atom being 130.2(2)°. The dihedral angle between the Ag_2O_2 and acetate planes is 22.07(6)°.

3.3.10. Agtfa:PPh_3:dpk · H_2O (1:1:1:1) · MeCN (**10** · MeCN)

Here the pair of pyridine rings can and do function as a chelate ligand; one of the *gem*-OH groups can function in approaching 'solvent' mode, and does so, forming a tridentate and displacing the anion which, unsurprisingly, lies close by, hydrogen-bonded to the ligand, the two hydrogen atoms to the same anion (O,H(21)...O(1a) 2.721(4), 1.93(3); O,H(22)...O(2a) 2.697(4), 1.89(4) Å). The two O...O distances are similar, as are the two carboxylate C–O distances (1.232(6), 1.215(7) Å), suggesting the two hydroxyl groups to be of similar acidity. The carboxylate group being uncoordinated, the complex may be considered ionic in the solid state, albeit presenting as an ion-pair.

Ligands of the form Ecy_3 (E = P or As) normally exhibit a more bulky steric profile than PPh_3 counterparts, as measured by their 'cone angles' [16]; their conformations in projections down the M–P coordinate bond may vary, in a manner discussed elsewhere [17], and here they are parameterized 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 variations therein have little impact on the latter, except to note that the anion approaches in the relatively limited range of compounds studied are as unidentate or weak semi-bidentate ligands. In a number of complexes, the E–Ag–*N*,*N*′ angle pairs are quite disparate, but in others they are essentially equal.

3.3.11. Atfa:Pcy_3:bpy (1:1:1) (**11**)

Here the impact of the anion approach is much more marked, the $PAgN_2$ angle sum falling to 328.$_5$°.

3.3.12. Agtfa:Pcy_3:dmp (1:1:1) (**12**)

Here the combination of hindered dmp with hindered Pcy_3 appears to have little impact on the coordination environment.

3.3.13. Agtfa:Pcy_3:bq (1:1:1) (**13**)

By contrast, in similar circumstances, the trifluoroacetate here is semi-bidentate.

3.3.14. Agtfa:Pcy_3:dpa (1:1:1) (**14**)

In this complex, the semi-bidentate anion is disordered over a pair of sites, the disorder seemingly not echoed in the remainder of the coordination sphere, suggesting the bulk of the anion to encounter little hindrance as a determinant of its orientation or coordination capability, the mode of coordination being unaffected by orientation.

3.3.15. Agtfa:$Ascy_3$:bpy (1:1:1) (**15**)

In the two complexes of $Ascy_3$ defined, the feebler coordination of $Ascy_3$, cf. Pcy_3, is primarily compensated by a closer approach of the anion, but without substantial change in coordination mode, rather than in the Ag–N(L) distances.

3.3.16. Agtfa:$Ascy_3$:dpa (1:1:1) (**16**)

Here the anions are semi-bidentate, as in the preceding array.

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

3.3.17. Agac:P(*o*-tol)$_3$:bpy (1:1:1)·H_2O (**17**)·H_2O

Here the $EAgN_2$ array is well removed from planarity.

3.3.18. Agtfa:P(*o*-tol)$_3$:phen (1:1:1)·H_2O (**18**)·H_2O

Here also the anion is unsymmetrically bidentate and the $EAgN_2$ array well removed from planarity. A curious feature of the structure, not uncommon in other complexes, is the apparent disorder of both silver and phosphorus atoms (minor light atom ligand components not resolved), being displaced to either side of a central Ag–P vector by ca. 1 Å each way (Fig. 1(r)). In the displaced components, Ag–P is shorter (2.33(4), 2.36(4) Å), with Ag moving closer to one of the ligand nitrogen atoms and further from the other, suggesting the possibility of some admixture in the crystal of other coordination isomers, or less likely, minor impurity. Displacement parameters on the residue modelled as water are high, and they do not interact closely with other species in the lattice.

*3.3.19. Agtfa:P(o-tol)$_3$:bq (1:1:1) (**19**)*

Here semi-bidentate anion interaction is found.

*3.3.20. Agtfa:P(o-tol)$_3$:dpa (1:1:1) · ½ MeCN (**20** · ½ MeCN)*

Here two independent molecules comprise the asymmetric unit; in one the anion is unidentate, in the other it is unsymmetrically bidentate, with different dispositions, neither seemingly in the proximity of the (ordered) solvent molecule.

*3.3.21. Agac:P(o-tol)$_3$:dpa (1:1:1)$_{(2)}$ · 2MeCN (**21** · 2MeCN)*

Interestingly, here, we again find a binuclear form, *O*-ac bridged, with unidentate dpa, as in the PPh_3 counterpart, above. The solvent is well removed from any of the substrate components.

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