

The structural definition of adducts of stoichiometry MX:dppx (1:1) M = Cu^I, Ag^I, X = simple anion, dppx=Ph₂P(CH₂)_xPPh₂, x = 3–6

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Abstract

Single crystal X-ray structural characterizations are recorded for a wide range of adducts of the form MX:dppx (1:1)_(n), M = silver(I) (predominantly), copper(I), X = simple (pseudo-) halide or oxy-anion (the latter spanning, where accessible, perchlorate, nitrate, carboxylate – a range of increasing basicity), dppx=bis(diphenylphosphino)alkane, Ph₂P(CH₂)_xPPh₂, x = 3–6. Adducts are defined of two binuclear forms: (i) [LM(μ-X)₂L], with each ligand chelating a single metal atom, and (ii) [M(μ-X)₂(μ-(P-L-P'))₂M'] where both ligands L and halides bridge the two metal atoms; a few adducts are defined as polymers, the ligands connecting M(μ-X)₂M' kernels, this motif persisting in all forms. Synthetic procedures for all adducts have been reported. All compounds have been characterized both in solution (¹H, ¹³C, ³¹P NMR, ESI MS) and in the solid state (IR).

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1. Introduction

In preceding papers [1–3], in pursuit of our goal of achieving the definition of adducts of simple salts of the univalent group 11 metals copper and silver, MX, with symmetrical simple bis(diphenylphosphino)alkane ligands, Ph₂E(CH₂)_xEPh₂, E = P (predominantly), As, 'dpex', we have described studies of adducts of the form MX:dpex (1:1)_(n) for the simplest ligands 'dppm' and, less extensively, 'dpam' (E = P, As; x = 1). 'dppe' (E = P; x = 2) is also a widely used ligand, but our studies of its complexation of MX has shown it to yield, predominantly, adducts of stoichiometry MX:dppe (2:3) [4], while adducts of the higher homologues, 'dppp', 'dppb',

'dppn', 'dpph', (E = P only, x = 3–6), readily yield once more a wide array of adducts of 1:1 stoichiometry. Again, at this stage of our studies, our results pertain predominantly to M = Ag, E = P systems, augmented by a number of copper(I) counterparts. Again we point out that we have found the latter more difficult of access, and, further, that the acquisition of material of useful form for the X-ray studies is sometimes not compatible with the production of analytically pure bulk samples. We further note the aggregation of this body of work over a considerable period of time, employing in some circumstances 'solvents' (such as pyridine ('py'), 2-methylpyridine ('mpy')) which may seem unusual – in a number of cases, these were initially consequent on attempts to produce mixed nitrogen/phosphine ligand adducts, wherein the nitrogen ligand, unlike its more usual behaviour with unidentate phosphine ligand complexes, did not coordinate, but, nevertheless, provided

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an auspicious solvent vehicle for crystallization, leading to more extended systematic arrays in circumstances where the use of more conventional solvents had failed.

Unlike adducts of dppm and dppe, structurally defined complexes of the form MX:dppx (1:1), $x \geq 3$, are very limited in number for $\text{M} = \text{Cu}, \text{Ag}$, comprising, for simple (pseudo-) halide or oxy-anion X , the arrays $\text{CuClO}_4\text{:dppb}$, dpph (1:1), CuNO_3 , $\text{AgClO}_4\text{:dpph}$ (1:1) [5], $\text{AgNO}_3\text{:dppp}$ [6], dppb [7,8] (1:1), AgCl:dppn (1:1) [9], all dimeric (1:1)₂ forms. We report here a number of adducts of the form MX:L (1:1) for these ligands with $\text{X} =$ (pseudo-) halide SCN , OCN , CN , Cl , Br , I , and the oxyanions ClO_4 , NO_3 , and simple carboxylate, the latter series, where complete, providing a spectrum of basicity for oxygen donors. Their spectroscopic features are also described.

2. Experimental

2.1. Materials and methods

All syntheses and handling were carried out in the air. All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C,H,N) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a VXR-300 Varian spectrometer (300 MHz for ^1H , 75.0 MHz for ^{13}C and 121.4 MHz for ^{31}P). H and C chemical shifts are reported in ppm versus SiMe_4 , P chemical shift in ppm versus H_3PO_4 85%. The electrical conductances of the acetone, dichloromethane, DMSO and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. Positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro Isotopic Abundance Simulator Version 2.1 [10]; peaks containing silver(I) and copper ions are identified as the centers of isotopic clusters.

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

2.2. Syntheses

2.2.1. Syntheses of the silver complexes

The colourless complexes described were obtained by crystallization, by slow evaporation and/or cooling, of

solutions of millimolar stoichiometry of AgX or CuX with dppx in a few ml of the specified solvent, analytically acceptable bulk samples being obtained for the following (33 excepted):

2.2.1.1. Synthesis of AgBr:dppp (1:1)₂ (1). dppp (0.41 g, 1.0 mmol) was added at room temperature to an 1:1 MeCN/1,2-diaminoethane solution (10 ml) of AgBr (0.19 g, 1.0 mmol). After the addition, the solution was stirred for 48 h. A colourless precipitate was obtained which was filtered off and washed with MeCN to give complex **1** as a colourless crystalline solid in 75% yield; m.p. 142–144 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.6 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.40 (m br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.17–7.29 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 19.83s, 29.01s ($\text{CH}_{2\text{dppm}}$), 128.7d, 129.7s, 133.0d, 134.7d (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 2.5 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ 6.9 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 571$ Hz, $^1J(^{31}\text{P},^{109}\text{Ag}) = 655$ Hz), 1.1 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 394$ Hz, $^1J(^{31}\text{P},^{109}\text{Ag}) = 452$ Hz). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1560w, 1478w ($\text{C}\cdots\text{C}$); 508s, 485m, 477m, 455w, 431w, 348w, 322w, 202br, 151w, 129m. ESI MS (+): 933 [100] [$\text{Ag}(\text{dppp})_2$]⁺; 1120 [75] [$\text{Ag}_2\text{Br}(\text{dppp})_2$]⁺; 1720 [3] [$\text{Ag}_3\text{Br}_2(\text{dppp})_3$]⁺. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{AgBrP}_2$: C, 54.03; H, 4.37. Found: C, 54.2; H, 4.55%. A_m (CH_2Cl_2 , 10^{-3} M): $2 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.2. Synthesis of AgI:dppp (1:1)₂ (2). Compound **2** has been obtained using a similar procedure to that reported for compound **1**, a colourless micro-crystalline precipitate of the β -form being obtained in 90% yield (The α -form was obtained from piperidine.) m.p. 156–159 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.7 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.38 (pt, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.16–7.36 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 20.76s, 29.23s ($\text{CH}_{2\text{dppm}}$), 128.6d, 129.4s, 133.3d, 135.4d (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –5.0 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ –4.3 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 372$ Hz, $^1J(^{31}\text{P},^{109}\text{Ag}) = 430$ Hz). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1582w, 1566w, 1480m ($\text{C}\cdots\text{C}$); 552br, 510s, 478s, 456w, 432w, 413w, 388w, 348w, 321w, 228w, 202w, 151w, 106m, 74m. ESI MS (+): 933 [100] [$\text{Ag}(\text{dppp})_2$]⁺; 1167 [80] [$\text{Ag}_2\text{I}(\text{dppp})_2$]⁺; 1814 [5] [$\text{Ag}_3\text{I}_2(\text{dppp})_3$]⁺. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{AgIP}_2$: C, 50.11; H, 4.05. Found: C, 50.34; H, 4.22%. A_m (CH_2Cl_2 , 10^{-3} M): $5 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.3. Syntheses of $\text{AgClO}_4\text{:dppp}$ (1:1)₂ (3). dppp (0.41 g, 1.0 mmol) was added at room temperature to an EtOH solution (20 ml) of AgClO_4 (0.21 g, 1.0 mmol). After the addition, the solution was stirred for 24 h. A colourless precipitate was formed which was filtered off and washed with EtOH to give compound **3** as a colourless micro-crystalline solid in 64% yield. It was recrystallised from MeCN giving the α -form; the

β -polymorph was obtained from MeCN/pyridine solution; m.p. 273–278 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.8 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.4 (pt, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.2–8.0 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 20.91s, 29.93s ($\text{CH}_{2\text{dppm}}$), 128.23d, 129.75d, 130.67d, 133.23d (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 10.1 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ -5.2 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 223$ Hz); $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 258$ Hz); 1.8 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 417$ Hz), $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 483$ Hz); 11.6 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 362$ Hz), $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 420$ Hz). IR (nujol, cm^{-1}): 3071w, 3045w (CH_{arom}), 1586w, 1485m ($\text{C}=\text{C}$); 1126s, 1105s, 1081s, 1055s, 621s (ClO_4), 552br, 522m, 507m, 481m, 475m, 450m, 437w, 315w, 189w, 82w, 72w. ESI MS (+): 519 [100] $[\text{Ag}_2(\text{dppp})_2]^{++}$; 933 [40] $[\text{Ag}(\text{dppp})_2]^+$; 1139 [20] $[\text{Ag}_2(\text{ClO}_4)(\text{dppp})_2]^+$; 1760 [3] $[\text{Ag}_3(\text{ClO}_4)_2(\text{dppp})_3]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{AgClO}_4\text{P}_2$: C, 52.34; H, 3.94. Found: C, 52.31; H, 4.12%. A_m (CH_2Cl_2 , 10^{-3} M): $18 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.4. Syntheses of $\text{Ag}(\text{ac}): \text{dppp}$ (1:1) $_2 \cdot 2\text{MeCN}$ (4). dppp (0.41 g, 1.0 mmol) was added at room temperature to an MeCN solution (5 ml) of $\text{Ag}(\text{ac})$ (0.166 g, 1.0 mmol). After the addition, the solution was stirred for 48 h and then slowly evaporated until a colourless oil formed which was washed with Et_2O to give compound 4 as a colourless solid in 75% yield. Re-crystallisation from MeCN yielded 4.2 MeCN; m.p. 79 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.8 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.96 (s, 3H, CH_3ac), 2.40 (pt, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.22–7.49 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 22.87s, 24.08, 29.41 (s $\text{CH}_{2\text{dppp}}$ + $\text{CH}_{3\text{ac}}$), 129.02, 129.99, 133.02 (C_{arom}) 177.99 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 1.08 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): 1.7 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 430$ Hz, $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 502$ Hz). IR (nujol, cm^{-1}): 3065w, 3051w (CH_{arom}), 1553s br (CO), 1582sh ($\text{C}=\text{C}$) 515s, 479m, 445w, 317w, 197br, 130w, 116w. ESI MS (+): 933 [100] $[\text{Ag}(\text{dppp})_2]^+$; 1099 [5] $[\text{Ag}_2(\text{ac})(\text{dppp})_2]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{29}\text{AgO}_2\text{P}_2$: C, 60.12; H, 5.05. Found: C, 60.32; H, 5.09%. A_m (CH_2Cl_2 , 10^{-3} M): $23 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.5. Syntheses of $\text{Ag}(\text{tfa}): \text{dppp}$ (1:1) $_2 \cdot \text{H}_2\text{O}$ (5). This compound was obtained in 80% yield by slow evaporation of an EtOH solution of dppp (0.41 g, 1.0 mmol) and $\text{Ag}(\text{tfa})$ (0.22 g, 1.0 mmol), followed by recrystallisation from MeCN; m.p. 126–134 °C dec. ^1H NMR (CD_3OD , 293 K): δ 1.9 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.6 (pq, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.3–7.6 (m, 20H, C_6H_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3OD , 293 K): δ 8.7 br. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.4 (pq, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.3–7.5 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 23.66s, 29.52 (s $\text{CH}_{2\text{dppp}}$), 117.4 (q, CF_3), 129.15, 130.62, 131.97, 133.02 (C_{arom}) 162.0 (q, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 4.6 (m,

$^1J(^{31}\text{P}, \text{Ag}) = 485$ Hz). IR (nujol, cm^{-1}): 3450br (OH) 3052w (CH_{arom}), 1665s, 1622s, 1586s, 1421s, 1435s (CO), 515s, 482m, 461m, 417m, 325m, 275m, 247w, 225w, 200w, 195w, 177w, 151w, 120w, 107w, 98w, 73m. ESI MS (+): 933 [100] $[\text{Ag}(\text{dppp})_2]^+$; 1153 [10] $[\text{Ag}_2(\text{tfa})(\text{dppp})_2]^+$. Anal. Calc. for $\text{C}_{58}\text{H}_{54}\text{Ag}_2\text{F}_6\text{O}_5\text{P}_4$: C, 54.23; H, 4.24. Found: C, 53.98; H, 4.23%. A_m (CH_2Cl_2 , 10^{-3} M): $0.5 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.6. Synthesis of $\text{Ag}(\text{tfs}): \text{dppp}$ (1:1) $_2$ (6). Compound 6 was obtained using a similar procedure to that reported for compound 4 as a colourless solid in 72% yield. It was recrystallised from MeCN; m.p. 257–262 °C dec. ^1H NMR ($\text{DMSO}-d_6$, 293 K): δ 1.6 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.6 (br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.4–7.6 (m, 20H, C_6H_5). ^{13}C NMR ($\text{DMSO}-d_6$, 293 K): δ 23.8, 28.0 (s $\text{CH}_{2\text{dppp}}$), 129.70, 131.44, 132.6, 133.42 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 293 K): δ 3.2 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 467$ Hz, $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 536$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 10.4 (d, $^1J(^{31}\text{P}, \text{Ag}) = 546$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): 10.2 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 508$ Hz, $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 586$ Hz). IR (nujol, cm^{-1}): 3052w (CH_{arom}), 1586w, 1485w ($\text{C}=\text{C}$) 1276s, 1244s, 1224s (SO_3CF_3) 571m, 521s, 516s, 506s, 480s, 449s, 314m, 263w, 210w, 189w, 72w. ESI MS (+): 519 [100] $[\text{Ag}_2(\text{dppp})_2]^{++}$; 933 [45] $[\text{Ag}(\text{dppp})_2]^+$; 1189 [10] $[\text{Ag}_2(\text{tfs})(\text{dppp})_2]^{++}$. Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{AgF}_3\text{O}_3\text{SP}_2$: C, 50.24; H, 3.97; S, 4.79. Found: C, 49.99; H, 4.09; S, 4.56%. A_m (CH_2Cl_2 , 10^{-3} M): $40 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.7. Synthesis of $\text{CuCl}: \text{dppp}$ (1:1) $_2$ (7). dppp (0.41 g, 1 mmol) was added to a CHCl_3 solution/suspension of CuCl (0.10 g, 1.0 mmol). After 10 min a colourless precipitate formed which was filtered off and washed with MeCN to give compound 7 in 68% yield. It was recrystallised from MeCN; m.p. 194–198 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.8 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.4 (br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.0–7.8 (m br, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 19.5br, 20.5br, 28.0br, 28.6br ($\text{CH}_{2\text{dppp}}$), 128.5br, 129.6br, 131.2br, 133.3br (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ -13.9 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): -18.4, -13.5, -13.0, -9.8, -9.4, -8.3, -3.8, -2.7 (s br). IR (nujol, cm^{-1}): 3072w, 3045 (CH_{arom}), 1586w, 1569w ($\text{C}=\text{C}$); 551w, 525w, 511s, 503s, 492s, 479s, 448m, 428m, 416m, 351w, 322w, 310w, 279w, 261w, 225m, 202m, 186m, 165m, 132w, 123w, 110w, 100w, 73m. ESI MS (+): 475 [10] $[\text{Cu}(\text{dppp})_2]^+$; 516 [50] $[\text{Cu}(\text{dppp})(\text{MeCN})]^+$; 887 [100] $[\text{Cu}(\text{dppp})_2]^+$; 987 [10] $[\text{Cu}_2(\text{Cl})(\text{dppp})_2]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{CuClP}_2$: C, 63.41; H, 5.12. Found: C, 63.56; H, 5.23%. A_m (CH_2Cl_2 , 10^{-3} M): $12 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.8. Synthesis of $\text{CuBr}: \text{dppp}$ (1:1) $_2$ (8). Compound 8 was obtained using a similar procedure to that recorded for compound 7 as a colourless microcrystalline solid in

75% yield and was recrystallised from MeCN; m.p. 229–232 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.4 (br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.0–7.8 (m br, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 19.5br, 20.5br, 28.0br, 28.6br ($\text{CH}_{2\text{dppp}}$), 128.5br, 129.6br, 131.2br, 133.3br (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –16.0, –10.0 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): –14.2, –11.7, –4.6, –1.4 (s br). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1569w ($\text{C}\cdots\text{C}$); 552br, 503s, 491s, 480m, 448m, 427m, 416m, 279w, 259w, 246w, 2226w, 175w, 152w, 148w, 138w, 100w, 91w, 73w. ESI MS (+): 475 [5] $[\text{Cu}(\text{dppp})]^+$; 516 [60] $[\text{Cu}(\text{dppp})(\text{MeCN})]^+$; 887 [100] $[\text{Cu}(\text{dppp})_2]^+$, 1031 [5] $[\text{Cu}_2(\text{Br})(\text{dppp})_2]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{CuBrP}_2$: C, 58.34; H, 4.71. Found: C, 58.56; H, 4.84%. A_m (CH_2Cl_2 , 10^{-3} M): $5\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.9. Synthesis of $\text{CuI}:\text{dppp}$ (1:1) $_2$ (9). Compound **9** was obtained using a similar procedure to that recorded for compound **7** as a colourless microcrystalline solid in 60% yield and was recrystallised from MeCN; m.p. 234–238 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 2.0 (m br, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.44 (br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.2 (m br, 12H, C_6H_5), 7.5 (m br, 8H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 19.5br, 20.5br, 28.0br, 28.6br ($\text{CH}_{2\text{dppm}}$), 128.5br, 129.6br, 131.2br, 133.3br (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –24.9br, –16.2br, –14.5br, –6.6br, –5.0br. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ –29.4s, –25.7s, –25.0s, –23.3s, –17.3s, –16.3s, –15.5s, –13.8s, –11.3s, –10.8s, –10.5s, –6.3br. IR (nujol, cm^{-1}): 3071w, 3039 (CH_{arom}), 1481sh ($\text{C}\cdots\text{C}$); 504s, 490m, 480m, 446w, 425w, 416w, 348br, 250w, 232w. ESI MS (+): 475 [10] $[\text{Cu}(\text{dppp})]^+$; 516 [70] $[\text{Cu}(\text{dppp})(\text{MeCN})]^+$; 887 [100] $[\text{Cu}(\text{dppp})_2]^+$, 1079 [5] $[\text{Cu}_2\text{I}(\text{dppp})_2]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{26}\text{CuIP}_2$: C, 53.79; H, 4.35. Found: C, 53.45; H, 4.51%. A_m (CH_2Cl_2 , 10^{-3} M): $6\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.10. Synthesis of $\text{AgBr}:\text{dppb}$ (1:1) $_2$ (10). dppb (0.43 g, 1.0 mmol) was added at room temperature to an MeCN solution (15 ml) of AgBr (0.19 g, 1.0 mmol). After the addition, a colorless precipitate formed which was filtered off, washed with MeCN to give compound **10** as a colourless solid in 80% yield. It was recrystallised from MeCN; m.p. 268 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.5 (br, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.4–7.6 (m, 20H, C_6H_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –15.6s br. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ –3.8d (d, $^1J(^{31}\text{P},^{107}\text{Ag}) = 433\ \text{Hz}$). IR (nujol, cm^{-1}): 3059w, 3050w (CH_{arom}), 1584m, 1570w, 1538w ($\text{C}\cdots\text{C}$) 510s, 502s, 487m, 478m, 46w, 447m, 433w, 420w, 405w, 396w, 356w, 3001w, 262w, 202w, 151w, 105m, 99m, 90m, 73m. ESI MS (+): 534 [100] $[\text{Ag}(\text{dppb})]^+$; 1148 [45] $[\text{Ag}_2\text{Br}(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{AgBrP}_2$: C, 54.75; H, 4.59. Found: C, 54.87; H, 4.56%. A_m (CH_2Cl_2 , 10^{-3} M): $1\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.11. Synthesis of $\text{AgI}:\text{dppb}$ (1:1) $_2$ (11). dppb (0.43 g, 1.0 mmol) was added at room temperature to an MeCN solution (20 ml) of AgI (0.23 g, 1.0 mmol). After the addition, the solution was stirred for 2 h. A colourless precipitate was formed which was filtered off and washed with EtOH to give compound **11** as a colourless micro-crystalline solid in 84% yield. It was recrystallised from MeCN; m.p. 280–285 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.53 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.0 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.2–7.3 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 27.82, 28.03 ($\text{CH}_{2\text{dppb}}$), 128.51d, 128.7s, 132.9d, 139.0d (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –5.0 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ –4.5 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 370\ \text{Hz}$, $^1J(^{31}\text{P},^{109}\text{Ag}) = 428\ \text{Hz}$). IR (nujol, cm^{-1}): 3052w (CH_{arom}), 1582w ($\text{C}\cdots\text{C}$); 552br, 508s, 485m, 477m, 461m, 446m, 430w, 419w, 396w, 353w, 300w, 255w, 225w, 151w, 99m, 88m, 74m, 56w. ESI MS (+): 534 [100] $[\text{Ag}(\text{dppb})]^+$; 1195 [45] $[\text{Ag}_2\text{I}(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{AgIP}_2$: C, 50.86; H, 4.27. Found: C, 51.23; H, 4.56%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.12. Synthesis of $\text{AgCN}:\text{dppb}$ (1:1) $_2$ (12). Compound **12** was obtained using a similar procedure to that recorded for compound **11** as a colourless micro-crystalline solid in 90% yield. It was recrystallised from MeCN; m.p. 189–193 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.4 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.2–7.3, 7.5 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 14.35s, 22.92, 29.59, 32.15 ($\text{CH}_{2\text{dppb}}$), 128.84, 129.6, 133.24 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –1.7 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 404\ \text{Hz}$; $^1J(^{31}\text{P},^{109}\text{Ag}) = 440\ \text{Hz}$); –0.7 (d br, $^1J(^{31}\text{P},\text{Ag}) = 370\ \text{Hz}$). IR (nujol, cm^{-1}): 3045m (CH_{arom}), 2155w, 2101w (CN), 1599m, 1531w, 1481w ($\text{C}\cdots\text{C}$); 516s, 477m, 464wbr, 408w br, 306w. ESI MS (+): 960 [15] $[\text{Ag}(\text{dppb})_2]^+$; 1095 [25] $[\text{Ag}_2(\text{CN})(\text{dppb})_2]^+$; 1103 [100] $[\text{Ag}_2\text{Cl}(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{28}\text{AgNP}_2$: C, 62.16; H, 5.04; N, 2.50. Found: C, 61.98; H, 5.36; N, 2.33%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.13. Synthesis of $\text{AgClO}_4:\text{dppb}$ (1:1) $_2$ (13). dppb (0.43 g, 1.0 mmol) was added at room temperature to an MeCN solution (20 ml) of AgClO_4 (0.21 g, 1.0 mmol). After the addition, the solution was stirred for 24 h. The colourless precipitate which was formed was filtered off and washed with EtOH to give compound **13** as a colourless micro-crystalline solid in 84% yield. It was recrystallised from MeCN; m.p. 270–275 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 2.0 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.43 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.2–7.3, 7.5 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 25.7, 27.5 ($\text{CH}_{2\text{dppb}}$), 129.95, 130.17, 133.28 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 2.0 (d br, $^1J(^{31}\text{P},\text{Ag}) = 484\ \text{Hz}$). IR (nujol, cm^{-1}): 3071w, 3050w (CH_{arom}), 1582w, 1485m ($\text{C}\cdots\text{C}$); 1120sh, 1100s,

1035s, 996s, 620s (ClO_4), 518m, 504s, 478m, 452m, 433w, 428w, 359w, 325w, 290w, 261w, 223w, 186w, 151w, 99w, 88w, 81w, 73m. ESI MS (+): 534 [100] $[\text{Ag}(\text{dppb})]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{AgClO}_4\text{P}_2$: C, 53.06; H, 4.45. Found: C, 53.23; H, 4.62%. A_m (CH_2Cl_2 , 10^{-3} M): $40 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.14. Synthesis of $\text{AgNO}_3:\text{dppb}$ (1:1)₂ (14**).** Compound **14** has been prepared as a colourless solid in 76% yield, using a similar procedure to that reported for compound **13**, but with a MeCN:EtOH 1:1 mixture as solvent. It was recrystallised from MeCN; m.p. 272–276 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.81br, 1.95 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.32br, 2.38br (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.2–7.3, 7.5 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 25.5, 28.1 ($\text{CH}_{2\text{dppb}}$), 128.89d, 130.0d, 130.6d, 133.49s (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 0.80 (d br, $^1J(^{31}\text{P},\text{Ag}) = 471$ Hz), 2.96 (dd br, $^1J(^{31}\text{P},\text{Ag}) = 480$ Hz). IR (nujol, cm^{-1}): 3052w (CH_{arom}), 1586w, 1537w ($\text{C}\cdots\text{C}$); 1455s, 1433s, 1393s, 1312s (NO_3); 552w, 512s, 496s, 479s, 451s, 420s, 354w, 332w, 299s, 242w, 204w, 148m, 131m, 120m, 92mbr. ESI MS (+): 534 [100] $[\text{Ag}(\text{dppb})]^+$; 960 [90] $[\text{Ag}(\text{dppb})_2]^+$; 1130 [40] $[\text{Ag}_2(\text{NO}_3)(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{AgNO}_3\text{P}_2$: C, 56.39; H, 4.73; N, 2.35. Found: C, 56.76; H, 4.72; N, 2.41%. A_m (CH_2Cl_2 , 10^{-3} M): $15 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.15. Synthesis of $\text{Ag}(\text{tfa}):\text{dppb}$ (1:1)₂ (15**).** Compound **15** has been prepared in 65% yield as a colourless solid, using a similar procedure to that reported for compound **13**. It was recrystallised from MeCN; m.p. 230–234 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.4 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.2–7.3, 7.5 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 25.4, 27.2 ($\text{CH}_{2\text{dppb}}$), 128.8br, 129.9br, 133.3br (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 0.01 (d br, $^1J(^{31}\text{P},\text{Ag}) = 480$ Hz), 1.94 (dd br, $^1J(^{31}\text{P},\text{Ag}) = 480$ Hz). IR (nujol, cm^{-1}): 3052w (CH_{arom}), 1660sbr, 1460s (CO), 1586w, 1537w ($\text{C}\cdots\text{C}$); 552w, 509s, 485s, 478s, 463m, 447m, 438w, 424w, 399w, 381w, 352w, 295w, 277wm, 260m, 224w br, 175wbr, 151w, 100w, 89w, 77w, 71w. ESI MS (+): 534 [100] $[\text{Ag}(\text{dppb})]^+$; 960 [40] $[\text{Ag}(\text{dppb})_2]^+$; 1104 [95] $[\text{Ag}_2\text{Cl}(\text{dppb})_2]^+$, 1181 [20] $[\text{Ag}_2(\text{tfa})(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{28}\text{AgF}_3\text{O}_2\text{P}_2$: C, 55.66; H, 4.36. Found: C, 55.30; H, 4.18%. A_m (CH_2Cl_2 , 10^{-3} M): $2 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.16. Synthesis of $\text{CuCl}:\text{dppb}$ (1:1)₂·4CHBr₃ (16**).** Compound **16** deposited in 80% yield as a colourless crystalline solid from a CHCl_3 solution containing dppb (0.43 g, 1.0 mmol) and CuCl (0.10 g, 1.0 mmol) over 72. Recrystallisation from CHBr_3 yielded **16**; m.p. 278 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.8 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.6 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.0–7.8 (m br, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K):

δ 19.0br, 19.5br, 28.0br, 28.5br ($\text{CH}_{2\text{dppb}}$), 128.5br, 129.1br, 130.9, 131.1, 132.2, 133.3br (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –12.9 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): –12.9. IR (nujol, cm^{-1}): 3072w, 3052w (CH_{arom}), 1585w, 1571w ($\text{C}\cdots\text{C}$); 514s, 482s, 467m, 444m, 432w, 417m, 370w, 345w, 279w, 244w, 185s, 165br, 119m, 100w, 87w, 77w. ESI MS (+): 490 [20] $[\text{Cu}_2(\text{dppb})_2]^{++}$; 531 [30] $[\text{Cu}(\text{dppb})(\text{MeCN})]^+$; 916 [100] $[\text{Cu}(\text{dppb})_2]^+$, 1005 [15] $[\text{Cu}_2\text{Cl}(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{CuClP}_2$: C, 64.00; H, 5.37. Found: C, 64.12; H, 5.43%. A_m (CH_2Cl_2 , 10^{-3} M): $5 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.17. Synthesis of $\text{CuBr}:\text{dppb}$ (1:1)₂·4CHBr₃ (17**).** Compound **17** was obtained as a colourless crystalline solid, using a similar procedure to that reported for compound **16**; m.p. 278 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.9 (m br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 2.7 (br, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.0–7.8 (m br, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 19.0br, 19.5br, 28.0br, 28.5br ($\text{CH}_{2\text{dppb}}$), 128.5br, 129.1br, 130.9, 131.1, 132.2, 133.3br (C_{arom}). IR (nujol, cm^{-1}): 3072w, 3052w (CH_{arom}), 1585w, 1571w ($\text{C}\cdots\text{C}$); 514s, 482s, 462m, 445m, 427w, 417w, 370w, 347w, 279w, 246w, 189br w, 150w, 133m, 122m, 100w, 87w, 77w. ESI MS (+): 490 [20] $[\text{Cu}_2(\text{dppb})_2]^{++}$; 531 [30] $[\text{Cu}(\text{dppb})(\text{MeCN})]^+$; 916 [100] $[\text{Cu}(\text{dppb})_2]^+$, 1005 [15] $[\text{Cu}_2\text{Br}(\text{dppb})_2]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{CuBrP}_2$: C, 59.01; H, 4.95. Found: C, 58.86; H, 4.81%. A_m (CH_2Cl_2 , 10^{-3} M): $5 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.18. Synthesis of $\text{AgCl}:\text{dppn}$ (1:1)_(\infty/\infty)·py·H₂O (18**).** dppn (0.44 g, 0.1 mmol) was added to a pyridine (py) solution of AgCl (0.14 g, 0.1 mmol). Slow evaporation of the solution yielded colourless crystals of compound **18** in 75% yield after 8 days; m.p. 162–165 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.6, 1.8, 2.5 (m br, 10H, (CH_2)₅), 7.2–7.4 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 24.37s, 27.18s, 29.42s ($\text{CH}_{2\text{dppn}}$), 128.71, 129.46, 133.30, 134.36 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ –3.0 (d br, $^1J(^{31}\text{P},\text{Ag}) = 361$ Hz). IR (nujol, cm^{-1}): 3400br (OH), 3045w (CH_{arom}), 1582w, ($\text{C}\cdots\text{C}$); 552w, 514s, 493m, 481br, 450w, 438w, 280w, 180m, 169w, 121w, 100w, 92w, 78w. ESI MS (+): 548 [55] $[\text{Ag}(\text{dppn})]^+$; 1131 [100] $[\text{Ag}_2\text{Cl}(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{34}\text{H}_{37}\text{AgClNOP}_2$: C, 59.97; H, 5.48; N, 2.06. Found: C, 60.12; H, 5.48; N, 1.96%. A_m (CH_2Cl_2 , 10^{-3} M): $2 \Omega^{-1} \text{ mol}^2 \text{ cm}^{-1}$.

2.2.1.19. Synthesis of $\text{AgBr}:\text{dppn}$ (1:1)₂ (19**).** Compound **19** has been prepared in 56% yield, using a similar procedure to that reported for compound **1**, using MeCN as solvent. Crystals for the diffraction study were obtained from 2-methylpyridine solution; m.p. 135–137 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.5, 2.2 (m br, 10H, (CH_2)₅), 7.2–7.4 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 24.4br, 27.3br, 30.3br ($\text{CH}_{2\text{dppn}}$),

128.7, 129.2, 133.0, 136.1 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ -4.7 (d, $^1J(^{31}\text{P},\text{Ag}) = 396$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ -4.2 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 383$ Hz, $^1J(^{31}\text{P},^{109}\text{Ag}) = 442$ Hz). IR (nujol, cm^{-1}): 3071w, 3045w (CH_{arom}), 1586w, ($\text{C}\cdots\text{C}$); 552w, 516s, 510sh, 486m, 477m, 443w, 437w, 422w, 407w, 383w, 352w, 280w, 250w, 203w, 177w, 119, 99w, 89w, 73w. ESI MS (+): 548 [55] $[\text{Ag}(\text{dppn})]^+$; 988 [100] $[\text{Ag}(\text{dppn})_2]^+$; 1176 [80] $[\text{Ag}_2(\text{Br})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{30}\text{AgBrP}_2$: C, 55.44; H, 4.81; N. Found: C, 55.65; H, 4.76%. A_m (CH_2Cl_2 , 10^{-3} M): $4\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.20. Synthesis of AgI:dppn (1:1) $_2$ (20). Compound **20** has been prepared in 62% yield as a colourless solid, using a similar procedure to that reported for compound **1**, but with MeCN as solvent. Crystals for the diffraction study were obtained from pyridine solution; m.p. 233–237 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.6, 1.7, 2.3 (m br, 10H, $(\text{CH}_2)_5$), 7.2–7.4 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 24.20s, 27.14s, 29.72s ($\text{CH}_{2\text{dppn}}$), 128.46, 129.20, 133.39, 134.80 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ -11.67 (d br, $^1J(^{31}\text{P},\text{Ag}) = 366$ Hz). IR (nujol, cm^{-1}): 3074w, 3054w (CH_{arom}), 1583w, ($\text{C}\cdots\text{C}$); 552w, 521m, 504m, 483m, 411brm 279w, 2226w, 151m, 121m, 105m, 99m, 89m, 80m. ESI MS (+): 548 [35] $[\text{Ag}(\text{dppn})]^+$; 988 [100] $[\text{Ag}(\text{dppn})_2]^+$; 1223 [10] $[\text{Ag}_2(\text{I})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{30}\text{AgIP}_2$: C, 51.48; H, 4.48; N. Found: C, 51.39; H, 4.72%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.21. Synthesis of AgNCO:dppn (1:1) $_{2(\infty|\infty)}\cdot\text{py}$ (21). Compound **21** has been obtained as a colourless crystalline solid in 70% yield, using a similar procedure reported to that for compound **18**; m.p. 158 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.5, 1.7, 2.3 (m br, 10H, $(\text{CH}_2)_5$), 7.2–7.4 (m, 22H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{py}$), 7.7 (m, 1H, $\text{C}_6\text{H}_5\text{py}$), 8.6 (m, 2H, $\text{C}_6\text{H}_5\text{py}$). ^{13}C NMR (CDCl_3 , 293 K): δ 24.70s, 27.28s, 29.57s ($\text{CH}_{2\text{dppn}}$), 128.88, 129.81, 132.96, 133.85 (C_{arom}) 123.90, 136.10, 150.06 (C_{py}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 2.18 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ -1.7 (d br, $^1J(^{31}\text{P},\text{Ag}) = 412$ Hz). IR (nujol, cm^{-1}): 3071sh, 3052w (CH_{arom}), 2143s (CNO), 1579w, 1478m ($\text{C}\cdots\text{C}$); 550br, 514s, 491m, 471m, 451w, 432w, 406w, 366w, 283w, 213br, 137m, 119br, 99m, 83w, 76w. ESI MS (+): 548 [100] $[\text{Ag}(\text{dppn})]^+$; 1122 [10] $[\text{Ag}_2(\text{CN})(\text{dppn})_2]^+$; 1131 [40] $[\text{Ag}_2(\text{Cl})(\text{dppn})_2]^+$; 1138 [5] $[\text{Ag}_2(\text{CNO})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{30}\text{AgNOP}_2$: C, 61.03; H, 5.12; N, 2.37. Found: C, 61.39; H, 5.03; N, 2.18%. A_m (CH_2Cl_2 , 10^{-3} M): $1\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.22. Synthesis of AgNCS:dppn (1:1) $_{2(\infty|\infty)}\cdot\text{py}$ (22). Compound **22** has been obtained in 90% yield as a colourless crystalline solid, using a similar procedure

to that reported for compound **18**; m.p. 172–175 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.5, 1.6, 2.5 (m br, 10H, $(\text{CH}_2)_5$), 7.2–7.4 (m, 22H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{py}$), 7.78 (m, 1H, $\text{C}_6\text{H}_5\text{py}$), 8.62 (m, 2H, $\text{C}_6\text{H}_5\text{py}$). ^{13}C NMR (CDCl_3 , 293 K): δ 24.49s, 26.91, 29.47 ($\text{CH}_{2\text{dppn}}$), 128.85, 129.82, 133.11, 133.82 (C_{arom}) 124.05, 136.38, 149.86 (C_{py}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ -0.2 (d br, $^1J(^{31}\text{P},\text{Ag}) = 392$ Hz). IR (nujol, cm^{-1}): 3071sh, 3052w (CH_{arom}), 2091 (SCN), 1586w, 1573 ($\text{C}\cdots\text{C}$); 550br, 515s, 475s, 457w, 442m, 418m, 413m, 406m, 385w, 339w, 275w, 233w, 204w, 163w, 115w, 100w, 80w, 75w, 119br, 99m, 83w, 76w. ESI MS (+): 548 [100] $[\text{Ag}(\text{dppn})]^+$; 1131 [45] $[\text{Ag}_2(\text{Cl})(\text{dppn})_2]^+$; 1154 [10] $[\text{Ag}_2(\text{SCN})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{30}\text{AgNOP}_2$: C, 61.03; H, 5.12; N, 2.37. Found: C, 61.39; H, 5.03; N, 2.18%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.23. Synthesis of $\text{Ag}(\text{ac}):dppn$ (1:1) $_{(\infty|\infty)}$ (23). Compound **23** has been prepared as a colourless solid, using a similar procedure to that reported for compound **12**. Crystals for the diffraction study were obtained from 2-methylpyridine solution; m.p. 186–188 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.5, 2.2 (m br, 10H, $(\text{CH}_2)_5$), 1.97 (s, 3H, CH_3ac), 7.2, 7.4 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 24.11s, 25.85, 27.37, 32.0 ($\text{CH}_{2\text{dppn}} + \text{CH}_3\text{ac}$), 129.01, 130.00, 130.3, 133.16 (C_{arom}) 178.12 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 2.5 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 293 K): δ 2.5 (dd, $^1J(^{31}\text{P},^{107}\text{Ag}) = 429$ Hz, $^1J(^{31}\text{P},^{109}\text{Ag}) = 494$ Hz). IR (nujol, cm^{-1}): 3049w (CH_{arom}), 1551s (CO), 1585m ($\text{C}\cdots\text{C}$); 515s, 486m, 464m, 421, 380br, 225w, 204w, 170w, 151w, 119w, 99w, 73w. ESI MS (+): 547 [100] $[\text{Ag}(\text{dppn})]^+$; 1133 [20] $[\text{Ag}_2(\text{Cl})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{31}\text{H}_{33}\text{AgO}_2\text{P}_2$: C, 61.30; H, 5.48. Found: C, 61.12; H, 5.64%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.24. Synthesis of CuBr:dppn (1:1) $_2\cdot 2\text{MeCN}$ (24). Compound **24** has been prepared in 65% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **7**. Recrystallisation from MeCN yielded **24**; m.p. 173–175 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.5, 1.6, 2.4 (br, 10H, $\text{CH}_{2\text{dppn}}$) 7.0–7.4 (m br, 20H, C_6H_5). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1586w, 1569w ($\text{C}\cdots\text{C}$); 514s, 500m, 482s, 449m, 423w, 352w, 325w, 302w, 280m, 247w, 224w, 202wbr, 176w br, 151m, 131w, 121w, 105w, 99w, 78w. ESI MS (+): 504 [55] $[\text{Cu}(\text{dppn})]^+$; 1088 [100] $[\text{Cu}_2(\text{Br})(\text{dppn})_2]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{30}\text{CuBrP}_2$: C, 59.65; H, 5.12. Found: C, 59.23; H, 5.38%. A_m (CH_2Cl_2 , 10^{-3} M): $2\ \Omega^{-1}\ \text{mol}^2\ \text{cm}^{-1}$.

2.2.1.25. Synthesis of CuI:dppn (1:1) $_2$ (25). Compound **25** has been prepared in 83% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **7**. It was recrystallised from MeCN; m.p. 222–224 °C dec. ^1H NMR (CDCl_3 , 293 K): δ 1.4,

1.5, 1.6, 2.5 (br, 10H, CH₂dppn) 7.0–7.3 (m br, 20H, C₆H₅). IR (nujol, cm⁻¹): 3065w, 3045w (CH_{arom}), 1586w, 1569w (C=C); 513s, 482s, 451s, 424w, 417w, 363, 279w, 146w, 222w, 151w, 120w, 100w, 89w, 77w, 57w. ESI MS (+): 504 [100] [Cu(dppn)]⁺; 1135 [60] [Cu₂(I)(dppn)₂]⁺. Anal. Calc. for C₂₉H₃₀CuIP₂: C, 55.21; H, 4.79. Found: C, 55.21; H, 5.00%. A_m (CH₂Cl₂, 10⁻³ M): 3 Ω⁻¹ mol² cm⁻¹.

2.2.1.26. Synthesis of Cu(ac)(Hac):dppn (1:1)_(∞|∞) (26). Compound **26** has been prepared in 60% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **7**. It was recrystallised from MeCN; m.p. 199–203 °C dec. ¹H NMR (CDCl₃, 293 K): δ 1.4, 1.6, 2.2 (br, 16H, CH₂dppn + CH₃ac), 7.0–7.6 (m br, 20H, C₆H₅). ¹³C NMR (CDCl₃, 293 K): δ 15.7 (CH₂dppn), 128.8, 130.0, 133.2 (C_{arom}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 16.0br, -10.1 br. ³¹P{¹H} NMR (CDCl₃, 218 K): δ 16.3br, -11.2s, -10.1s br. IR (nujol, cm⁻¹): 3065w, 3045w (CH_{arom}), 1657s, 1651s, 1644s (CO) 1586w, (C=C); 542m, 514s, 483s, 455s, 413s, 296w, 278w, 256w, 203w, 107s br, 72m, 56m. ESI MS (+): 504 [100] [Cu(dppn)]⁺; 1067 [45] [Cu₂(ac)(dppn)₂]⁺. Anal. Calc. for C₃₃H₃₇CuO₄P₂: C, 63.61; H, 5.98. Found: C, 63.94; H, 5.85%. A_m (CH₂Cl₂, 10⁻³ M): 1 Ω⁻¹ mol² cm⁻¹.

2.2.1.27. Synthesis of AgBr:dpph (1:1)₂ (27). Compound **27** has been prepared in 78% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **1**, but with MeCN as solvent. Crystals for the diffraction study were obtained from 2-methylpyridine solution; m.p. 220–228 °C dec. ¹H NMR (CDCl₃, 295 K): δ 1.4, 1.7, 2.1 (m br, 12H, (CH₂)₆), 7.2–7.4 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 293 K): δ 24.0br, 28.5br, 30.4br (CH₂dppn), 128.9, 129.8, 132.9, 134.7 (C_{arom}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -2.7 (d, ¹J(³¹P,Ag) = 371 Hz). ³¹P{¹H} NMR (CDCl₃, 218 K): -1.7 (dd, ¹J(³¹P,¹⁰⁷Ag) = 372 Hz, ¹J(³¹P,¹⁰⁹Ag) = 420 Hz). IR (nujol, cm⁻¹): 3071w (CH_{arom}), 1586w, 1569 w (C=C); 515s, 495m, 480s, 450m, 438w, 410w, 300br, 151m, 132w, 121w, 105w, 90m, 74m, 63m. ESI MS (+): 561 [100] [Ag(dpph)]⁺; 1204 [65] [Ag₂Br(dpph)₂]⁺. Anal. Calc. for C₃₀H₃₂AgBrP₂: C, 56.10; H, 5.02; N. Found: C, 56.34; H, 5.22%. A_m (CH₂Cl₂, 10⁻³ M): 2 Ω⁻¹ mol² cm⁻¹.

2.2.1.28. Synthesis of AgI:dpph (1:1)₂ (28). Compound **28** has been prepared in 65% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **1**, but using MeCN as solvent. Crystals for the diffraction study were obtained from pyridine solution; m.p. 240–260 °C dec. ¹H NMR (CDCl₃, 295 K): δ 1.5, 1.7, 2.2, 2.3 (m br, 12H, (CH₂)₆), 7.2–7.4 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 293 K): δ 22.0br, 23.0br, 24.0br, 27.6br, 28.0br, 30.0br (CH₂dppn), 127.8,

128.8, 129.0, 129.1, 130.0, 130.9, 131.0, 131.2, 132.3, 133.6, 133.8 (C_{arom}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -10.3 (d br, ¹J(³¹P,Ag) = 500 Hz); -8.8 (d br, ¹J(³¹P,Ag) = 340 Hz). ³¹P{¹H} NMR (CDCl₃, 218 K): δ -10.78 (dd, ¹J(³¹P,¹⁰⁷Ag) = 486 Hz; ³¹P,¹⁰⁹Ag = 561 Hz); -8.44 (dd, ¹J(³¹P,¹⁰⁷Ag) = 344 Hz; ³¹P,¹⁰⁹Ag = 397 Hz). IR (nujol, cm⁻¹): 3069m, 3051m (CH_{arom}), 1586m, 1573w (C=C); 517s, 507s, 498s, 474s, 449s, 419m, 391w, 363w, 339w. ESI MS (+): 561 [100] [Ag(dpph)]⁺; 1252 [85] [Ag₂I(dpph)₂]⁺. Anal. Calc. for C₃₀H₃₂AgIP₂: C, 52.27; H, 4.68; N. Found: C, 51.99; H, 4.74%. A_m (CH₂Cl₂, 10⁻³ M): 1 Ω⁻¹ mol² cm⁻¹.

2.2.1.29. Synthesis of Ag(NCO):dpph (1:1)₂ (29). Compound **29** has been prepared in 85% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **1**, but with MeCN as solvent; crystals for the diffraction study were obtained from 2-methylpyridine solution; m.p. 190–193 °C dec. ¹H NMR (CDCl₃, 295 K): δ 1.4, 1.7, 2.2 (m br, 12H, (CH₂)₆), 7.2–7.4 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 293 K): δ 22.0br, 23.2br, 24.0br, 27.6br, 28.0br, 29.6br (CH₂dppn), 128.8, 129.9, 130.9, 133.2 (C_{arom}). ³¹P{¹H} NMR (CDCl₃, 218 K): δ -4.5 (d br, ¹J(³¹P,Ag) = 345 Hz), 1.5 (d br, ¹J(³¹P,Ag) = 429 Hz). IR (nujol, cm⁻¹): 3065w, 3045w (CH_{arom}), 2167m, 2139m (CN) 1585w, 1569w, 1480m (C=C); 509br, 490m, 475br, 453m, 443w, 393w, 354br. ESI MS (+): 561 [100] [Ag(dpph)]⁺; 1150 [50] [Ag₂(CN)(dpph)₂]⁺; 1166 [10] [Ag₂(CNO)(dpph)₂]⁺. Anal. Calc. for C₃₁H₃₂AgNOP₂: C, 61.60; H, 5.34; N, 2.32. Found: C, 61.43; H, 5.54; N, 1.99%. A_m (CH₂Cl₂, 10⁻³ M): 2 Ω⁻¹ mol² cm⁻¹.

2.2.1.30. Synthesis of Ag(NCS):dpph (1:1)₂ (30). Compound **30** has been prepared in 84% yield as a colourless crystalline solid, using a similar procedure to that reported for compound **1**, but with MeCN as solvent. Crystals for the diffraction study were obtained from pyridine solution, the two polymorphs being obtained as a mixture; m.p. 230–235 °C dec. ¹H NMR (CDCl₃, 295 K): δ 1.6, 1.7, 2.4 (m br, 12H, (CH₂)₆), 7.2–7.4 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃, 293 K): δ 22.90s, 23.22s, 27.35s, 28.34, 29.57s, 32.13s (CH₂dppn), 128.8s br, 129.1s br, 130.9d, 133.2s br (C_{arom}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 1.9 (d br, ¹J(³¹P,Ag) = 396 Hz). IR (nujol, cm⁻¹): 3065w, 3045w (CH_{arom}), 2076 (CN) 1583w, 1568w, 1480m (C=C); 523m, 513m, 490m, 479m, 470m, 456m, 416w, 388w. ESI MS (+): 562 [100] [Ag(dpph)]⁺; 1182 [20] [Ag₂(NCS)(dpph)₂]⁺. Anal. Calc. for C₃₁H₃₂AgNSP₂: C, 60.01; H, 5.20; N, 2.26; S, 5.17. Found: C, 60.23; H, 5.34; N, 2.11; S, 5.33%. A_m (CH₂Cl₂, 10⁻³ M): 2 Ω⁻¹ mol² cm⁻¹.

2.2.1.31. Synthesis of AgNO₃:dpph (1:1)₂ (31). This compound has been prepared as a colourless crystalline solid, using a similar procedure to that for compound

11; m.p. 270–275 °C dec. ^1H NMR (CDCl_3 , 295 K): δ 1.4–1.6, 2.2 (m br, 12H, $(\text{CH}_2)_5$), 7.2–7.6 (m, 20H, C_6H_5). ^{13}C NMR (CDCl_3 , 293 K): δ 14.33, 21.3d, 21.45d, 22.89s, 25.23d, 25.68d, 25.77s, 27.29t, 28.43s, 28.87s, 29.43s, 29.56s, 29.90s, 30.34d, 30.66s, 32.13s (CH_2dpph), 128.8d, 128.9d, 129.45t, 130.87s, 131.5s, 131.3s br, 131.85d, 133.15d, 133.20d, 133.96s (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 218 K): δ 5.5 (dd, $^1J(^{31}\text{P}, ^{107}\text{Ag}) = 469$ Hz; $^1J(^{31}\text{P}, ^{109}\text{Ag}) = 541$ Hz). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1957w, 1898w, 1814w, 1731w, 1456s, 1312s (NO_3), 1584m, 1480m ($\text{C}\cdots\text{C}$); 514s, 505s, 493m, 486m, 474m, 452m, 4123w, 398w, 374w, 339w. ESI MS (+): 561 [100] $[\text{Ag}(\text{dpph})]^+$; 1160 [15] $[\text{Ag}_2(\text{Cl})(\text{dpph})_2]^+$; 1186 [35] $[\text{Ag}_2(\text{NO}_3)(\text{dpph})_2]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{32}\text{AgNO}_3\text{P}_2$: C, 57.71; H, 5.17; N, 2.24. Found: C, 57.65; H, 5.03; N, 2.43%. A_m (CH_2Cl_2 , 10^{-3} M): $19 \Omega^{-1} \text{mol}^2 \text{cm}^{-1}$.

2.2.1.32. CuCN:CuSCN:dppn (2:1:4)·MeCN (32). A few small colourless crystals of **32** were obtained in small quantity by slow recrystallisation of a mixture containing CuSCN (0.12 g, 0.1 mmol) and dppn (0.44 g, 0.1 mmol) from MeCN.

2.3. Structure determinations

A number of determinations were executed using unique room-temperature (ca. 295 K) ‘four-circle’/single-counter/sequential diffractometer data sets ($2\theta/\theta$ scan mode), N_o data with $I > 3\sigma(I)$ being considered ‘observed’ and used in the full matrix/large block least squares refinement after Gaussian (or analytical) absorption correction. Others were executed using full spheres of CCD area-detector diffractometer data (Bruker AXS instrument, ω -scans; monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; T ca. 153 K (unless otherwise specified (as ca. 300 K))), N_{total} reflections merging to N unique (R_{int} quoted) after ‘empirical’/multiscan absorption correction (proprietary software), the ‘observed’ criterion being $F > 4\sigma(F)$. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{\text{iso}})_\text{H}$ being included constrained at estimates. Conventional residuals on $|F|$, R , R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within various versions of the *Xtal* program system [11]. Pertinent results are given below and in the Tables and Figures (the latter showing 20% (room-temperature) or 50% (low temperature) probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å); full cif. depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, # 244562–244601. Individual variations in procedure (difficulties, anomalies, etc.) are cited as ‘variata’.

2.3.1. Crystallrefinement data

2.3.1.1. AgBr:dppp (1:1)₂ (1). $\text{C}_{54}\text{H}_{52}\text{Ag}_2\text{Br}_2\text{P}_4$, $M = 1200.5$. Triclinic, space group $P\bar{1}$ (C_i^1 , No. 2) $a = 12.696(4)$, $b = 10.724(3)$, $c = 10.626(6)$ Å, $\alpha = 70.66(3)$, $\beta = 75.43(3)$, $\gamma = 65.48(2)^\circ$, $V = 1231$ Å³. D_c ($Z = 1$ dimer) = 1.61_9 g cm^{-3} . $\mu_{\text{Mo}} = 25.8 \text{ cm}^{-1}$; specimen: $0.30 \times 0.30 \times 0.03$ mm; $T_{\text{min/max}} = 0.54$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4301$, $N_o = 2632$; $R = 0.043$, $R_w = 0.043$. $|\Delta\rho_{\text{max}}| = 0.84(4) \text{ e Å}^{-3}$. Single-counter instrument, T ca. 295 K.

Variata. The compound is isomorphous with the α -form of the iodide, (2).

2.3.1.2. AgI:dppp (1:1)₂ (2). $\text{C}_{54}\text{H}_{52}\text{Ag}_2\text{I}_2\text{P}_4$, $M = 1294.5$.

α -Form. $a = 12.930(4)$, $b = 10.621(3)$, $c = 10.986(6)$ Å, $\alpha = 69.36(3)$, $\beta = 72.91(4)$, $\gamma = 66.04(2)^\circ$, $V = 1270$ Å³. D_c ($Z = 1$ dimer) = 1.69_2 g cm^{-3} . $\mu_{\text{Mo}} = 21.5 \text{ cm}^{-1}$; specimen: $0.04 \times 0.32 \times 0.20$ mm; $T_{\text{min/max}} = 0.73$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 3746$, $N_o = 2077$; $R = 0.069$, $R_w = 0.074$. $|\Delta\rho_{\text{max}}| = 1.59(4) \text{ e Å}^{-3}$. Single-counter instrument, T ca. 295 K.

β -Form. Triclinic, space group $P\bar{1}$, $a = 10.634(2)$, $b = 14.200(2)$, $c = 16.859(2)$ Å, $\alpha = 97.350(2)$, $\beta = 94.760(2)$, $\gamma = 95.824(2)^\circ$, $V = 2500$ Å³. D_c ($Z = 2$ dimers) = 1.71_9 g cm^{-3} . $\mu_{\text{Mo}} = 21.8 \text{ cm}^{-1}$; specimen: $0.15 \times 0.10 \times 0.08$ mm; $T_{\text{min/max}} = 0.80$. $2\theta_{\text{max}} = 58^\circ$; $N_t = 24425$, $N = 12086$ ($R_{\text{int}} = 0.018$), $N_o = 10222$; $R = 0.029$, $R_w = 0.036$. $|\Delta\rho_{\text{max}}| = 2.50(6) \text{ e Å}^{-3}$. ($x, y, z, U_{\text{iso}})_\text{H}$ refined CCD instrument, T ca. 153 K. ($x, y, z, U_{\text{iso}})_\text{H}$ refined.

2.3.1.3. AgClO₄:dppp (1:1)₂ (3). $\text{C}_{54}\text{H}_{52}\text{Ag}_2\text{Cl}_2\text{O}_8\text{P}_4$, $M = 1239.5$.

α -Form. Triclinic, space group $P\bar{1}$, $a = 11.606(5)$, $b = 13.030(6)$, $c = 10.679(5)$ Å, $\alpha = 113.57(4)$, $\beta = 113.40(3)$, $\gamma = 91.48(3)^\circ$, $V = 1325$ Å³. D_c ($Z = 1$ dimer) = 1.55_3 g cm^{-3} . $\mu_{\text{Mo}} = 10.1 \text{ cm}^{-1}$; specimen: $0.20 \times 0.15 \times 0.54$ mm; $T_{\text{min/max}} = 0.92$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4672$, $N_o = 3892$; $R = 0.036$, $R_w = 0.045$. $|\Delta\rho_{\text{max}}| = 0.83(4) \text{ e Å}^{-3}$. ($x, y, z, U_{\text{iso}})_\text{H}$ refined. Single-counter instrument, T ca. 295 K.

β -Form. Triclinic, space group $P\bar{1}$, $a = 11.6034(8)$, $b = 13.0032(9)$, $c = 19.676(1)$ Å, $\alpha = 101.114(2)$, $\beta = 102.057(2)$, $\gamma = 111.188(2)^\circ$, $V = 2587$ Å³. D_c ($Z = 2$ dimers) = 1.59_1 g cm^{-3} . $\mu_{\text{Mo}} = 10.4 \text{ cm}^{-1}$; specimen: $0.32 \times 0.16 \times 0.08$ mm; $T_{\text{min/max}} = 0.83$. $2\theta_{\text{max}} = 75^\circ$; $N_t = 52828$, $N = 26405$ ($R_{\text{int}} = 0.027$), $N_o = 19359$; $R = 0.035$, $R_w = 0.040$. $|\Delta\rho_{\text{max}}| = 1.24(8) \text{ e Å}^{-3}$. ($x, y, z, U_{\text{iso}})_\text{H}$ refined. CCD instrument, T ca. 153 K.

2.3.1.4. Ag(ac):dppp (1:1)₂·2 MeCN (4). $\text{C}_{62}\text{H}_{64}\text{Ag}_2\text{N}_2\text{O}_4\text{P}_4$, $M = 1240.9$. Triclinic, space group $P\bar{1}$, $a = 13.134(5)$, $b = 11.783(11)$, $c = 11.644(6)$ Å, $\alpha = 64.39(5)$, $\beta = 84.52(4)$, $\gamma = 67.00(5)^\circ$, $V = 1490$ Å³. D_c ($Z = 1$ (solvated) dimer) = 1.38_3 g cm^{-3} . $\mu_{\text{Mo}} = 8.1 \text{ cm}^{-1}$; specimen: $0.24 \times 0.32 \times 0.22$ mm; $T_{\text{min/max}} = 0.95$

(Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 5179$, $N_o = 4153$; $R = 0.029$, $R_w = 0.031$. $|\Delta\rho_{\max}| = 0.34(3)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined (MeCN excepted). Single-counter instrument, T ca. 295 K.

2.3.1.5. *Ag(tfa):dppp (1:1)₂ · H₂O (5)*. $\text{C}_{58}\text{H}_{54}\text{Ag}_2\text{F}_6\text{O}_5\text{P}_4$, $M = 1284.7$. Monoclinic, space group $C2/c$ (C_{2h}^6 , No. 15), $a = 18.065(5)$, $b = 13.538(3)$, $c = 24.22(1)$ $\text{\AA}$, $\beta = 100.92(3)^\circ$, $V = 5816$ $\text{\AA}^3$. D_c ($Z = 4$ dimers) = 1.467 g cm^{-3} . $\mu_{\text{Mo}} = 8.5$ cm^{-1} ; specimen: $0.12 \times 0.29 \times 0.20$ mm; $T_{\min/\max} = 0.89$ (Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 5120$, $N_o = 2549$; $R = 0.041$, $R_w = 0.035$. $|\Delta\rho_{\max}| = 0.51(2)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined single-counter instrument, T ca. 295 K. (x , y , z , U_{iso})_H refined.

Variata. The fluorine atoms of the anion were modelled as rotationally disordered over two sets of sites, occupancies set at 0.5 after trial refinement.

2.3.1.6. *Ag(tfs):dppp (1:1)₂ (6)*. $\text{C}_{56}\text{H}_{52}\text{Ag}_2\text{F}_6\text{O}_6\text{P}_4\text{S}_2$, $M = 1338.8$. Triclinic, space group $P\bar{1}$, $a = 10.668(2)$, $b = 12.260(2)$, $c = 13.363(2)$ $\text{\AA}$, $\alpha = 62.907(2)$, $\beta = 86.390(2)$, $\gamma = 65.623(2)^\circ$, $V = 1400$ $\text{\AA}^3$. D_c ($Z = 1$ dimer) = 1.587 g cm^{-3} . $\mu_{\text{Mo}} = 9.6$ cm^{-1} ; specimen: $0.40 \times 0.30 \times 0.25$ mm; $T_{\min/\max} = 0.79$. $2\theta_{\max} = 58^\circ$; $N_t = 15964$, $N = 6720$ ($R_{\text{int}} = 0.019$), $N_o = 6201$; $R = 0.027$, $R_w = 0.040$. $|\Delta\rho_{\max}| = 0.69(3)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined. CCD instrument, T ca. 153 K.

Variata. The anion was modelled as disordered about the sulfur over two sets of sites, occupancies refining to 0.675(3) and complement.

2.3.1.7. *CuCl:dppp (1:1)₂ (7)*. $\text{C}_{54}\text{H}_{52}\text{Cl}_2\text{Cu}_2\text{P}_4$, $M = 1022.9$. Monoclinic, space group $P2_1/n$ (C_{2h}^5 , No. 14), $a = 10.0800(6)$, $b = 18.405(1)$, $c = 14.6089(8)$ $\text{\AA}$, $\beta = 104.380(1)^\circ$, $V = 2446$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.389 g cm^{-3} . $\mu_{\text{Mo}} = 11.5$ cm^{-1} ; specimen: $0.47 \times 0.26 \times 0.21$ mm; $T_{\min/\max} = 0.76$. $2\theta_{\max} = 58^\circ$; $N_t = 25175$, $N = 6169$ ($R_{\text{int}} = 0.019$), $N_o = 5110$; $R = 0.024$, $R_w = 0.032$. $|\Delta\rho_{\max}| = 0.31(5)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined. CCD instrument, T ca. 298 K.

2.3.1.8. *CuBr:dppp (1:1)₂ (8)*. $\text{C}_{54}\text{H}_{52}\text{Br}_2\text{Cu}_2\text{P}_4$, $M = 1111.8$. Monoclinic, space group $P2_1/n$, $a = 10.2272(7)$, $b = 18.445(1)$, $c = 13.5002(9)$ $\text{\AA}$, $\beta = 104.657(1)^\circ$, $V = 2464$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.499 g cm^{-3} . $\mu_{\text{Mo}} = 26.5$ cm^{-1} ; specimen: $0.38 \times 0.26 \times 0.16$ mm; $T_{\min/\max} = 0.67$. $2\theta_{\max} = 58^\circ$; $N_t = 27502$, $N = 6249$ ($R_{\text{int}} = 0.028$), $N_o = 4852$; $R = 0.024$, $R_w = 0.028$. $|\Delta\rho_{\max}| = 0.4(1)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined. CCD instrument, T ca. 298 K.

2.3.1.9. *CuI:dppp (1:1)₂ (9)*. $\text{C}_{54}\text{H}_{52}\text{Cu}_2\text{I}_2\text{P}_4$, $M = 1205.8$. Monoclinic, space group $P2_1/n$, $a = 10.482(4)$, $b = 18.541(6)$, $c = 13.373(2)$ $\text{\AA}$, $\beta = 104.43(2)^\circ$, $V = 2517$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.591 g cm^{-3} . $\mu_{\text{Mo}} = 22.3$ cm^{-1} ; specimen: $0.10 \times 1.0 \times 0.25$ mm; $T_{\min/$

$\max = 0.39$ (analytical correction). $2\theta_{\max} = 55^\circ$, $N = 5768$, $N_o = 4934$; $R = 0.049$, $R_w = 0.073$. $|\Delta\rho_{\max}| = 2.2(2)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined. Single-counter instrument, T ca. 295 K.

2.3.1.10. *AgBr:dppb (1:1)₂ (10)*. $\text{C}_{56}\text{H}_{56}\text{Ag}_2\text{Br}_2\text{P}_4$, $M = 1228.5$. Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14) $a = 10.303(2)$, $b = 18.429(2)$, $c = 15.836(4)$ $\text{\AA}$, $\beta = 120.87(2)^\circ$, $V = 2581$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.581 g cm^{-3} . $\mu_{\text{Mo}} = 24.7$ cm^{-1} ; specimen: $0.30 \times 0.18 \times 0.16$ mm; $T_{\min/\max} = 0.90$ (Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 4306$, $N_o = 2984$; $R = 0.057$, $R_w = 0.064$. $|\Delta\rho_{\max}| = 3.14(4)$ e $\text{\AA}^{-3}$. Single-counter instrument, T ca. 295 K. 11, 12 are isomorphous.

2.3.1.11. *AgI:dppb (1:1)₂ (11)*. $\text{C}_{56}\text{H}_{56}\text{Ag}_2\text{I}_2\text{P}_4$, $M = 1322.5$. Monoclinic, space group $P2_1/c$, $a = 10.305(2)$, $b = 18.881(4)$, $c = 15.801(2)$ $\text{\AA}$, $\beta = 120.53(1)^\circ$, $V = 2648$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.658 g cm^{-3} . $\mu_{\text{Mo}} = 20.6$ cm^{-1} ; specimen: $0.42 \times 0.20 \times 0.38$ mm; $T_{\min/\max} = 0.80$ (Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 4654$, $N_o = 3821$; $R = 0.027$, $R_w = 0.031$. $|\Delta\rho_{\max}| = 0.69(4)$ e $\text{\AA}^{-3}$. Single-counter instrument, T ca. 295 K.

2.3.1.12. *AgCN:dppb (1:1)₂ (12)*. $\text{C}_{58}\text{H}_{56}\text{Ag}_2\text{N}_2\text{P}_4$, $M = 1120.8$. Monoclinic, space group $P2_1/c$, $a = 10.196(1)$, $b = 18.749(9)$, $c = 15.757(8)$ $\text{\AA}$, $\beta = 120.55(3)^\circ$, $V = 2594$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.435 g cm^{-3} . $\mu_{\text{Mo}} = 9.2$ cm^{-1} ; specimen: $0.39 \times 0.25 \times 0.30$ mm; $T_{\min/\max} = 0.95$ (Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 4526$, $N_o = 3401$; $R = 0.032$, $R_w = 0.034$. $|\Delta\rho_{\max}| = 0.83(3)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined single-counter instrument, T ca. 295 K.

2.3.1.13. *AgClO₄:dppb (1:1)₂ (13)*. $\text{C}_{56}\text{H}_{56}\text{Ag}_2\text{Cl}_2\text{O}_8\text{P}_4$, $M = 1267.6$. Triclinic, space group $P\bar{1}$, $a = 12.596(5)$, $b = 11.851(4)$, $c = 10.593(4)$ $\text{\AA}$, $\alpha = 69.02(3)$, $\beta = 84.65(3)$, $\gamma = 66.30(3)^\circ$, $V = 1349$ $\text{\AA}^3$. D_c ($Z = 1$ dimer) = 1.559 g cm^{-3} . $\mu_{\text{Mo}} = 10.0$ cm^{-1} ; specimen: $0.10 \times 0.25 \times 0.10$ mm; $T_{\min/\max} = 0.98$ (Gaussian correction). $2\theta_{\max} = 50^\circ$; $N = 3977$, $N_o = 2767$; $R = 0.058$, $R_w = 0.063$. $|\Delta\rho_{\max}| = 1.14(4)$ e $\text{\AA}^{-3}$. Single-counter instrument, T ca. 295 K.

2.3.1.14. *AgNO₃:dppb (1:1)₂ (14)*. $\text{C}_{56}\text{H}_{56}\text{Ag}_2\text{N}_2\text{O}_6\text{P}_4$, $M = 1192.7$. Monoclinic, space group $P2_1/n$, $a = 12.6969(7)$, $b = 11.1607(6)$, $c = 19.198(1)$ $\text{\AA}$, $\beta = 105.351(1)^\circ$, $V = 2623$ $\text{\AA}^3$. D_c ($Z = 2$ dimers) = 1.510 g cm^{-3} . $\mu_{\text{Mo}} = 9.2$ cm^{-1} ; specimen: $0.25 \times 0.20 \times 0.16$ mm; $T_{\min/\max} = 0.84$. $2\theta_{\max} = 75^\circ$; $N_t = 54067$, $N = 13740$ ($R_{\text{int}} = 0.040$), $N_o = 8480$; $R = 0.041$, $R_w = 0.042$. $|\Delta\rho_{\max}| = 2.43(8)$ e $\text{\AA}^{-3}$. (x , y , z , U_{iso})_H refined. CCD instrument, T ca. 153 K.

Variata. A redetermination of a previously published structure [7,8]; quantitatively, the present results, of im-

proved precision, are essentially harmonious with the preceding. Ref. [7] however, describes the structure fairly explicitly as $[\text{Ag}(\text{dppb})_2(\text{NO}_3)_2]$, while the CCDC pictogram associates the nitrate with one silver only, i.e., $[(\text{O}_2\text{NO})\text{Ag}(\text{dppb})_2\text{Ag}(\text{ONO}_2)]$.

2.3.1.15. $\text{Ag}(\text{tfa}): \text{dppb} (1:1)_2$ (15). $\text{C}_{60}\text{H}_{56}\text{Ag}_2\text{F}_6\text{O}_4\text{P}_4$, $M = 1294.8$. Triclinic, space group $P\bar{1}$, $a = 13.513(5)$, $b = 12.333(5)$, $c = 10.280(7)$ Å, $\alpha = 106.69(5)$, $\beta = 95.25(5)$, $\gamma = 116.74(3)^\circ$, $V = 1416$ Å³. D_c ($Z = 1$ dimer) = 1.51_8 g cm⁻³. $\mu_{\text{Mo}} = 8.7$ cm⁻¹; specimen: $0.14 \times 0.24 \times 0.19$ mm; $T_{\text{min/max}} = 0.91$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4973$, $N_o = 3635$; $R = 0.048$, $R_w = 0.057$. $|\Delta\rho_{\text{max}}| = 1.03(4)$ e Å⁻³. Single-counter instrument, T ca. 295 K.

2.3.1.16. $\text{CuCl}: \text{dppb} (1:1)_2 \cdot 4\text{CHBr}_3$ (16). $\text{C}_{60}\text{H}_{60}\text{Br}_{12}\text{Cl}_2\text{Cu}_2\text{P}_4$, $M = 2061.0$. Triclinic, space group $P\bar{1}$, $a = 10.235(2)$, $b = 13.162(2)$, $c = 14.952(2)$ Å, $\alpha = 117.026(3)$, $\beta = 99.727(4)$, $\gamma = 93.607(4)^\circ$, $V = 1746$ Å³. D_c ($Z = 1$ (solvated) dimer) = 1.96_1 g cm⁻³. $\mu_{\text{Mo}} = 77$ cm⁻¹; specimen: $0.40 \times 0.30 \times 0.20$ mm; $T_{\text{min/max}} = 0.57$. $2\theta_{\text{max}} = 50^\circ$; $N_t = 35550$, $N = 5996$ ($R_{\text{int}} = 0.095$), $N_o = 4115$; $R = 0.050$, $R_w = 0.053$. $|\Delta\rho_{\text{max}}| = 1.8(3)$ e Å⁻³. CCD instrument, T ca. 153 K.

Variata. Two of the bromine atoms ($\text{Br}(012, 013)$) of solvent 1 were resolved and modelled as disordered over pairs of sites, occupancies refining to 0.75(4) and complement ($\text{Br} \dots \text{Br}$ 0.53(4), 0.47(4) Å). U_{eq} for bridging chloride appeared slightly low; the atom was refined as a Cl/Br composite with common (x, y, z, U_{ij}) and site occupancy as a variable; the latter refined to $p(\text{Cl}) = 0.901(6)$, $p(\text{Br}) = \text{complement}$, R being reduced to 0.048. Although the structure is recorded and discussed as a pure chloride adduct, it seems likely that crystallization has resulted in a small but significant bromide admixture. The hydrogens of solvents 1 contact the chloride atoms of the dimer at 2.37 Å.

2.3.1.17. $\text{CuBr}: \text{dppb} (1:1)_2 \cdot 4\text{CHBr}_3$ (17). $\text{C}_{60}\text{H}_{60}\text{Br}_{14}\text{Cu}_2\text{P}_4$, $M = 2150.8$. Triclinic, space group $P\bar{1}$, $a = 10.2680(4)$, $b = 13.2218(6)$, $c = 14.7525(6)$ Å, $\alpha = 115.257(1)$, $\beta = 99.411(1)$, $\gamma = 96.170(1)^\circ$, $V = 1751$ Å³. D_c ($Z = 1$ (solvated) dimer) = 2.03_9 g cm⁻³. $\mu_{\text{Mo}} = 8.7$ cm⁻¹; specimen: $0.25 \times 0.17 \times 0.12$ mm; $T_{\text{min/max}} = 0.43$. $2\theta_{\text{max}} = 58^\circ$, $N_t = 35926$, $N = 9220$ ($R_{\text{int}} = 0.059$), $N_o = 6791$; $R = 0.039$, $R_w = 0.040$. $|\Delta\rho_{\text{max}}| = 1.7(3)$ e Å⁻³. CCD instrument, T ca. 153 K.

Variata. Similar solvent disorder was modelled, cf. the isomorphous chloride, also in $\text{Br}(021)$ of solvent 2, seemingly concerted, occupancies 0.66(5), and complement ($\text{Br} \dots \text{Br}$ 0.30(2), 0.35(4), 0.31(4) Å); the solvent(1) $\text{H} \dots \text{Br}$ contacts are 2.6₃ Å. The iodide was also obtained crystalline in the present CHBr_3 solvate form, but with a much more substantial bromide occupancy than the chloride and we do not discuss it further.

2.3.1.18. $\text{AgCl}: \text{dppn} (1:1)_{(\infty/\infty)} \cdot \text{py} \cdot \text{H}_2\text{O}$ (18). $\text{C}_{58}\text{H}_{60}\text{Ag}_2\text{Cl}_2\text{P}_4 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$, $M = 1264.8$. Triclinic, space group $P\bar{1}$, $a = 21.717(7)$, $b = 14.380(4)$, $c = 9.640(4)$ Å, $\alpha = 100.67(3)$, $\beta = 94.96(3)$, $\gamma = 90.48(3)^\circ$, $V = 2948$ Å³. D_c ($Z = 2$ f.u.) = 1.42_5 g cm⁻³. $\mu_{\text{Mo}} = 9.1$ cm⁻¹; specimen: $0.32 \times 0.42 \times 0.58$ mm; $T_{\text{min/max}} = 0.91$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 10364$, $N_o = 6998$; $R = 0.042$, $R_w = 0.044$. $|\Delta\rho_{\text{max}}| = 0.90(3)$ e Å⁻³. Single-counter instrument, T ca. 295 K.

Variata. (x, y, z, U_{iso})_H were refined for the complex substrate. The nitrogen atom of the pyridine seemingly scrambled, all constituent atoms were modelled as carbon with pendant hydrogen. A difference map residue was modelled as (water) oxygen, site occupancy constrained at unity after trial refinement.

2.3.1.19. $\text{AgBr}: \text{dppn} (1:1)_2$ (19). $\text{C}_{58}\text{H}_{60}\text{Ag}_2\text{Br}_2\text{P}_4$, $M = 1256.6$. Triclinic, space group $P\bar{1}$, $a = 12.049(6)$, $b = 11.664(6)$, $c = 10.0590(7)$ Å, $\alpha = 94.78(2)$, $\beta = 96.16(2)$, $\gamma = 101.73(4)^\circ$, $V = 1368$ Å³. D_c ($Z = 1$ dimer) = 1.52_5 g cm⁻³. $\mu_{\text{Mo}} = 23.3$ cm⁻¹; specimen: $0.30 \times 0.48 \times 0.39$ mm; $T_{\text{min/max}} = 0.62$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4809$, $N_o = 4110$; $R = 0.031$, $R_w = 0.040$. $|\Delta\rho_{\text{max}}| = 0.47(4)$ e Å⁻³. Single-counter instrument, T ca. 295 K.

Variata. The central hydrocarbon string of the ligand was modelled as disordered over two conformations, occupancies refining to 0.75 and complement.

2.3.1.20. $\text{AgI}: \text{dppn} (1:1)_2$ (20). $\text{C}_{58}\text{H}_{60}\text{Ag}_2\text{I}_2\text{P}_4$, $M = 1350.6$. Orthorhombic, space group $Fddd$ (D_{2h}^{24} , No. 70), $a = 25.333(5)$, $b = 25.572(5)$, $c = 34.244(9)$ Å, $V = 22184$ Å³. D_c ($Z = 16$ dimers) = 1.61_7 g cm⁻³. $\mu_{\text{Mo}} = 19.7$ cm⁻¹; specimen: $0.43 \times 0.10 \times 0.25$ mm; $T_{\text{min/max}} = 0.86$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4769$, $N_o = 3334$; $R = 0.071$, $R_w = 0.047$. $|\Delta\rho_{\text{max}}| = 1.0(1)$ e Å⁻³. Single-counter instrument, T ca. 295 K.

2.3.1.21. $\text{AgNCO}: \text{dppn} (1:1)_{2(\infty/\infty)} \cdot \text{py}$ (21). $\text{C}_{65}\text{H}_{65}\text{Ag}_2\text{N}_3\text{O}_2\text{P}_4$, $M = 1259.9$. Triclinic, space group $P\bar{1}$, $a = 13.505(4)$, $b = 12.603(5)$, $c = 10.049(2)$ Å, $\alpha = 90.01(2)$, $\beta = 109.90(2)$, $\gamma = 112.44(2)^\circ$, $V = 1470$ Å³. D_c ($Z = 1$ f.u.) = 1.42_3 g cm⁻³. $\mu_{\text{Mo}} = 8.2$ cm⁻¹; specimen: $0.20 \times 0.22 \times 0.46$ mm; $T_{\text{min/max}} = 0.92$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5143$, $N_o = 4170$; $R = 0.060$, $R_w = 0.067$. $|\Delta\rho_{\text{max}}| = 1.04(3)$ e Å⁻³. Single-counter instrument, T ca. 295 K.

Variata. Phenyl ring 12 was modelled as disordered over two sites of equal occupancy, as was the hydrocarbon string. The pyridine ring is disposed about a crystallographic inversion centre, the nitrogen atom not resolvable.

2.3.1.22. $\text{AgNCS}: \text{dppn} (1:1)_{2(\infty/\infty)} \cdot \text{py}$ (22). $\text{C}_{60}\text{H}_{60}\text{Ag}_2\text{N}_2\text{P}_4\text{S}_2 \cdot \text{C}_5\text{H}_5\text{N}$, $M = 1292.0$. Monoclinic, space group $P2_1/c$, $a = 13.770(2)$, $b = 9.467(7)$, $c = 26.745(4)$

$\text{\AA}$, $\beta = 120.51(1)^\circ$, $V = 3002 \text{ \AA}^3$. D_c ($Z = 2$ f.u.) = 1.42_8 g cm^{-3} . $\mu_{\text{Mo}} = 8.7 \text{ cm}^{-1}$; specimen: $0.14 \times 0.34 \times 0.04 \text{ mm}$; $T_{\text{min/max}} = 0.91$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5285$, $N_o = 1657$; $R = 0.056$, $R_w = 0.050$. $|\Delta\rho_{\text{max}}| = 0.69(3) \text{ e \AA}^{-3}$. Single-counter instrument, T ca. 295 K (see 18 for py treatment).

2.3.1.23. *Ag(ac):dppn (1:1)_(\infty/\infty) (23)*. $\text{C}_{31}\text{H}_{33}\text{AgO}_2\text{P}_2$, $M = 607.4$. Monoclinic, space group Cc (C_2^2 , No. 9), $a = 21.736(5)$, $b = 9.285(2)$, $c = 16.017(1) \text{ \AA}$, $\beta = 112.32(1)^\circ$, $V = 2990 \text{ \AA}^3$. D_c ($Z = 4$ f.u.) = 1.34_9 g cm^{-3} . $\mu_{\text{Mo}} = 8.1 \text{ cm}^{-1}$; specimen: $0.48 \times 0.38 \times 0.55 \text{ mm}$; $T_{\text{min/max}} = 0.91$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 2604$, $N_o = 2383$; $R = 0.038$, $R_w = 0.044$ (both chiralities). $|\Delta\rho_{\text{max}}| = 0.78(2) \text{ e \AA}^{-3}$. Single-counter instrument, T ca. 295 K.

2.3.1.24. *CuBr:dppn (1:1)₂·2MeCN (24)*. $\text{C}_{62}\text{H}_{66}\text{Br}_2\text{Cu}_2\text{N}_2\text{P}_4$, $M = 1250.0$. Monoclinic, space group $P2_1/n$, $a = 12.163(1)$, $b = 17.617(2)$, $c = 27.069(3) \text{ \AA}$, $\beta = 92.120(2)^\circ$, $V = 5796 \text{ \AA}^3$. D_c ($Z = 4$ dimers) = 1.43_2 g cm^{-3} . $\mu_{\text{Mo}} = 36 \text{ cm}^{-1}$; specimen: $0.15 \times 0.13 \times 0.12 \text{ mm}$; $T_{\text{min/max}} = 0.87$. $2\theta_{\text{max}} = 58^\circ$; $N_t = 57468$, $N = 14717$ ($R_{\text{int}} = 0.055$), $N_o = 9216$; $R = 0.040$, $R_w = 0.045$. $|\Delta\rho_{\text{max}}| = 1.0(3) \text{ e \AA}^{-3}$. CCD instrument, T ca. 153 K.

2.3.1.25. *CuI:dppn (1:1)₂ (25)*. $\text{C}_{58}\text{H}_{60}\text{Cu}_2\text{I}_2\text{P}_4$, $M = 1261.9$. Monoclinic, space group $C2/c$, $a = 18.691(8)$, $b = 14.811(7)$, $c = 20.822(7) \text{ \AA}$, $\beta = 103.07(3)^\circ$, $V = 5615 \text{ \AA}^3$. D_c ($Z = 4$ dimers) = 1.49_3 g cm^{-3} . $\mu_{\text{Mo}} = 20 \text{ cm}^{-1}$; specimen: $0.20 \times 0.15 \times 0.056 \text{ mm}$; $T_{\text{min/max}} = 0.86$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4942$, $N_o = 3603$; $R = 0.038$, $R_w = 0.056$. $|\Delta\rho_{\text{max}}| = 0.7(2) \text{ e \AA}^{-3}$. Single-counter instrument, T ca. 295 K.

2.3.1.26. *Cu(ac):dppn:(Hac) (1:1:1)_(\infty/\infty) (26)*. $\text{C}_{33}\text{H}_{37}\text{CuO}_4\text{P}_2$, $M = 623.1$. Orthorhombic, space group $Pna2_1$ (C_{2v}^2 , No. 33), $a = 17.822(2)$, $b = 8.2613(7)$, $c = 20.383(2) \text{ \AA}$, $V = 3001 \text{ \AA}^3$. D_c ($Z = 4$ f.u.) = 1.37_9 g cm^{-3} . $\mu_{\text{Mo}} = 8.7 \text{ cm}^{-1}$; specimen: $0.45 \times 0.03 \times 0.12 \text{ mm}$; $T_{\text{min/max}} = 0.81$. $2\theta_{\text{max}} = 68^\circ$; $N_t = 46092$, $N = 6052$ ($R_{\text{int}} = 0.043$), $N_o = 5014$; $R = 0.040$, $R_w = 0.045$. $|\Delta\rho_{\text{max}}| = 2.0(1) \text{ e \AA}^{-3}$. CCD instrument, T ca. 153 K.

Variata. 'Friedel' data being retained distinct, x_{abs} refined to 0.12(1).

2.3.1.27. *AgBr:dpph (1:1)₂ (27)*. $\text{C}_{60}\text{H}_{64}\text{Ag}_2\text{Br}_2\text{P}_4$, $M = 1284.6$. Triclinic, space group $P\bar{1}$ (the previously recorded perchlorate [5] is also isomorphous). $a = 12.473(2)$, $b = 11.742(2)$, $c = 10.067(4) \text{ \AA}$, $\alpha = 99.84(2)^\circ$, $\beta = 92.02(2)^\circ$, $\gamma = 101.63(1)^\circ$, $V = 1419 \text{ \AA}^3$. D_c ($Z = 1$ dimer) = 1.50_3 g cm^{-3} . $\mu_{\text{Mo}} = 22.5 \text{ cm}^{-1}$; specimen: $0.16 \times 0.18 \times 0.41 \text{ mm}$; $T_{\text{min/max}} = 0.89$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4976$, $N_o = 3375$;

$R = 0.043$, $R_w = 0.045$. $|\Delta\rho_{\text{max}}| = 0.83(4) \text{ e \AA}^{-3}$. (x , y , z , U_{iso})_H refined. Single-counter instrument, T ca. 295 K.

2.3.1.28. *AgI:dpph (1:1)₂ (28)*. $\text{C}_{60}\text{H}_{64}\text{Ag}_2\text{I}_2\text{P}_4$, $M = 1378.6$. Triclinic, space group $P\bar{1}$, $a = 12.535(2)$, $b = 12.028(2)$, $c = 10.064(1) \text{ \AA}$, $\alpha = 101.19(1)^\circ$, $\beta = 92.36(1)^\circ$, $\gamma = 101.94(1)^\circ$, $V = 1451 \text{ \AA}^3$. D_c ($Z = 1$ dimer) = 1.57_7 g cm^{-3} . $\mu_{\text{Mo}} = 18.8 \text{ cm}^{-1}$; specimen: $0.12 \times 0.12 \times 0.14 \text{ mm}$; $T_{\text{min/max}} = 0.92$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5097$, $N_o = 3081$; $R = 0.036$, $R_w = 0.033$. $|\Delta\rho_{\text{max}}| = 0.46(5) \text{ e \AA}^{-3}$. (x , y , z , U_{iso})_H refined. Single-counter instrument, T ca. 295 K.

2.3.1.29. *AgNCO:dpph (1:1)₂ (29)*. $\text{C}_{62}\text{H}_{64}\text{Ag}_2\text{N}_2\text{O}_2\text{P}_4$, $M = 1208.9$. Triclinic, space group $P\bar{1}$, $a = 12.228(4)$, $b = 11.372(8)$, $c = 10.282(3) \text{ \AA}$, $\alpha = 79.12(4)^\circ$, $\beta = 91.52(3)^\circ$, $\gamma = 96.62(4)^\circ$, $V = 1395 \text{ \AA}^3$. D_c ($Z = 1$ dimer) = 1.43_9 g cm^{-3} . $\mu_{\text{Mo}} = 8.6 \text{ cm}^{-1}$; specimen: $0.19 \times 0.22 \times 0.38 \text{ mm}$; $T_{\text{min/max}} = 0.97$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 4921$, $N_o = 3249$; $R = 0.038$, $R_w = 0.039$. $|\Delta\rho_{\text{max}}| = 0.37(3) \text{ e \AA}^{-3}$. (x , y , z , U_{iso})_H refined. Single-counter instrument, T ca. 295 K.

Variata. The silver atom was modelled as disordered over two sites, occupancies set at 0.875 and complement after refinement; $\text{Ag} \dots \text{Ag}'$ is $0.748(5) \text{ \AA}$. 30a is isomorphous.

2.3.1.30. *Ag(NCS):dpph (1:1)₂ (30)*. $\text{C}_{62}\text{H}_{64}\text{Ag}_2\text{N}_2\text{P}_4\text{S}_2$, $M = 1241.0$.

α -Form. Triclinic, space group $P\bar{1}$, $a = 12.2066(8)$, $b = 12.110(3)$, $c = 10.315(3) \text{ \AA}$, $\alpha = 75.49(2)^\circ$, $\beta = 91.10(1)^\circ$, $\gamma = 97.56(1)^\circ$, $V = 1463 \text{ \AA}^3$. D_c ($Z = 1$ dimer) = 1.40_8 g cm^{-3} . $\mu_{\text{Mo}} = 8.9 \text{ cm}^{-1}$; specimen: $0.23 \times 0.58 \times 0.51 \text{ mm}$; $T_{\text{min/max}} = 0.89$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5137$, $N_o = 4296$; $R = 0.032$, $R_w = 0.037$. $|\Delta\rho_{\text{max}}| = 0.51(3) \text{ e \AA}^{-3}$. (x , y , z , U_{iso})_H refined. Single-counter instrument, T ca. 295 K.

β -Form. Monoclinic, space group $P2_1/c$, $a = 10.321(3)$, $b = 18.001(7)$, $c = 16.471(9) \text{ \AA}$, $\beta = 105.51(4)^\circ$, $V = 2948 \text{ \AA}^3$. D_c ($Z = 2$ dimers) = 1.39_7 g cm^{-3} . $\mu_{\text{Mo}} = 8.8 \text{ cm}^{-1}$; specimen: $0.36 \times 0.20 \times 0.42 \text{ mm}$; $T_{\text{min/max}} = 0.90$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5182$, $N_o = 3682$; $R = 0.064$, $R_w = 0.079$. $|\Delta\rho_{\text{max}}| = 3.02(3) \text{ e \AA}^{-3}$. Single-counter instrument, T ca. 295 K.

2.3.1.31. *AgNO₃:dpph (1:1)₂ (31)*. $\text{C}_{60}\text{H}_{64}\text{Ag}_2\text{NO}_6\text{P}_4$, $M = 1248.8$. Triclinic, space group $P\bar{1}$, $a = 12.611(4)$, $b = 11.409(6)$, $c = 10.242(4) \text{ \AA}$, $\alpha = 97.33(4)^\circ$, $\beta = 92.46(3)^\circ$, $\gamma = 100.15(3)^\circ$, $V = 1436 \text{ \AA}^3$. D_c ($Z = 1$ dimer) = 1.44_4 g cm^{-3} . $\mu_{\text{Mo}} = 8.4 \text{ cm}^{-1}$; specimen: $0.24 \times 0.41 \times 0.24 \text{ mm}$; $T_{\text{min/max}} = 0.87$ (Gaussian correction). $2\theta_{\text{max}} = 50^\circ$; $N = 5045$, $N_o = 3921$; $R = 0.041$, $R_w = 0.048$. $|\Delta\rho_{\text{max}}| = 0.67(4) \text{ e \AA}^{-3}$. Single-counter instrument, T ca. 295 K.

Variata. The nitrate ion is disordered quasi-centro-symmetrically (corresponding to two types of bridging mode), the two components being modelled with site occupancies 0.5 the perchlorate [5] and 27 are isomorphous.

2.3.1.32. *CuCN:CuSCN:dppn (2:1:4) · MeCN (32)*. $C_{121}H_{123}Cu_3N_4P_8S$, $M = 2103.8$. Monoclinic, space group $P2_1/n$, $a = 18.184(1)$, $b = 15.2114(9)$, $c = 39.279(2)$ Å, $\beta = 102.684(1)^\circ$, $V = 10669$ Å³. D_c ($Z = 4$ f.u.) = 1.31_0 g cm⁻³. $\mu_{Mo} = 18.9$ cm⁻¹; specimen: $0.18 \times 0.17 \times 0.14$ mm; $T_{min/max} = 0.89$. $2\theta_{max} = 58^\circ$; $N_t = 118214$, $N = 26822$ ($R_{int} = 0.039$), $N_o = 19004$; $R = 0.042$, $R_w = 0.047$. $|\Delta\rho_{max}| = 1.4(1)$ e Å⁻³. CCD instrument, T ca. 153 K.

Variata. The result of an attempt to crystallize a CuSCN: dppn adduct from acetonitrile, the characterization of the small amount of sample obtained rests solely on the X-ray study. Solution and refinement was generally smooth, straightforward and seemingly unambiguous, the only ‘unusual’ feature being the modelling of the cyanide groups as ‘scrambled’ with atoms set as C/N composites, a common necessity in cyanide structures (x, y, z, U_{iso})_H refined (MeCN excepted).

In augmentation/completion of the structural characterization of relevant dpex ligands (for dpem, dpee, dppb see [1,3,12], respectively) determinations of dppp, dppn, dpbh are recorded:

2.3.1.33. *dppp (≡Ph₂P(CH₂)₃PPh₂) (33)*. $C_{27}H_{26}P_2$, $M = 412.5$. Monoclinic, space group $C2/c$, $a = 18.924(3)$, $b = 8.166(1)$, $c = 29.343(5)$ Å, $\beta = 90.622(3)^\circ$, $V = 4534$ Å³. D_c ($Z = 8$) = 1.20_8 g cm⁻³. $\mu_{Mo} = 20$ cm⁻¹; specimen: $0.4 \times 0.25 \times 0.12$ mm; $T_{min/max} = 0.67$. $2\theta_{max} = 58^\circ$; $N_t = 19250$, $N = 4013$ ($R_{int} = 0.071$), $N_o = 2331$; $R = 0.071$, $R_w = 0.075$. $|\Delta\rho|_{max} = 0.45(8)$ e Å⁻³. CCD instrument, T ca. 293 K.

Variata. One of the phosphorus atoms was modelled as disordered over a pair of sites P(2)...P(2') $1.793(4)$ Å, disorder also resolvable and refinable in the pendant methylene group and one phenyl ring, site occupancies of the two sets of components set at 0.5 after trial refinement.

2.3.1.34. *dppn (≡Ph₂P(CH₂)₅PPh₂) (34)*. $C_{29}H_{30}P_2$, $M = 440.5$. Orthorhombic, space group $Pbcn$ (D_{2h}^{14} , N_o 60), $a = 7.9297(9)$, $b = 12.340(1)$, $c = 25.676(3)$ Å, $V = 2512$ Å³. D_c ($Z = 4$) = 1.16_4 g cm⁻³. $\mu_{Mo} = 1.9$ cm⁻¹; specimen: $0.25 \times 0.22 \times 0.20$ mm; $T_{min/max} = 0.71$. $2\theta_{max} = 58^\circ$; $N_t = 23047$, $N = 3337$ ($R_{int} = 0.064$), $N_o = 2608$; $R = 0.043$, $R_w = 0.052$. $|\Delta\rho_{max}| = 0.40(3)$ e Å⁻³. (x, y, z, U_{iso})_H refined. CCD instrument, T ca. 153 K. Source: Aldrich, as supplied.

2.3.1.35. *dpph (≡Ph₂P(CH₂)₆PPh₂) (35)*. $C_{30}H_{32}P_2$, $M = 454.3$. Monoclinic, space group $P2_1/c$,

$a = 12.296(1)$, $b = 5.6687(6)$, $c = 17.994(2)$ Å, $\beta = 101.008(3)^\circ$, $V = 1231$ Å³. D_c ($Z = 2$) = 1.22_6 g cm⁻³. $\mu_{Mo} = 1.9$ cm⁻¹; specimen: $0.4 \times 0.22 \times 0.20$ mm; $T_{min/max} = 0.61$. $2\theta_{max} = 75^\circ$; $N_t = 10632$, $N = 6501$ ($R_{int} = 0.047$), $N_o = 4502$; $R = 0.043$, $R_w = 0.048$. $|\Delta\rho_{max}| = 0.55(4)$ e Å⁻³. (x, y, z, U_{iso})_H refined. CCD instrument, T ca. 153 K. Source: Aldrich, as supplied.

3. Results and discussion

3.1. Syntheses

The reaction of MX ($M = Cu$ or Ag , $X = Cl, Br, I, NO_3, tfa, ac, tfs, ClO_4, CN, SCN$ or CNO) with equimolar bis(diphenylphosphino)alkane (in general dppx; in detail dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; dppn = 1,5-bis(diphenylphosphino)pentane; dpbh = 1,2-bis(diphenylphosphino)hexane) at room temperature gave rise to compounds **1–32** (Charts 1–3). The choice of solvent and the slow crystallisation are determinants not only of the formation of compounds (for example, pyridine-type solvents are often required for the silver-halide species), but also in determining their structures. The ligand to metal ratio and the nature of the diphosphine employed may also be important factors: e.g., if an excess of dppp is used in reaction with silver halide AgX acceptors, compounds of the form $[Ag(dppp)_2]X$ are immediately formed [13,14], whereas under the same conditions dppb and dpbh do not form analogous compounds. The derivative $Cu(ac):dppn:(Hac)$ (1:1:1)_(∞|∞) **26** has been obtained from the reaction of the copper(II) salt $Cu(ac)_2$ with an excess of the P₂-donor ligand.

The compounds **1–32** are generally air-stable, colorless materials, soluble in polar solvents such as acetonitrile, dimethylformamide and dimethylsulfoxide. They are, however, insoluble in water, diethyl ether and tetrahydrofuran but, with the exception of the silver(I) halide species and of the polymeric complexes **22** and **23** they exhibit good solubility in the chlorinated hydrocarbons CH_2Cl_2 and $CHCl_3$. Solid samples of these compounds show generally no sensitivity to light, but they are unstable in solution, their chlorinated solvent solutions often darkening after 24h. The solubilities of the perchlorate derivatives are generally lower than those found for all trifluoroacetate and trifluoromethanesulfonate species. Similarly the solubilities of chloride and bromide species are lower than those of their iodide counterparts. Conductivity measurements, as expected, indicate that the trifluoromethanesulfonate and the perchlorate complexes **6** and **13** are 2:1 electrolytes in dichloromethane solution, the values of Λ_M for both compounds being $40 \Omega^{-1}cm^2mol^{-1}$. The nitrates **14** and **31**, the perchlorate **3** and the acetate **4** exhibit values typical of a 1:1 electro-

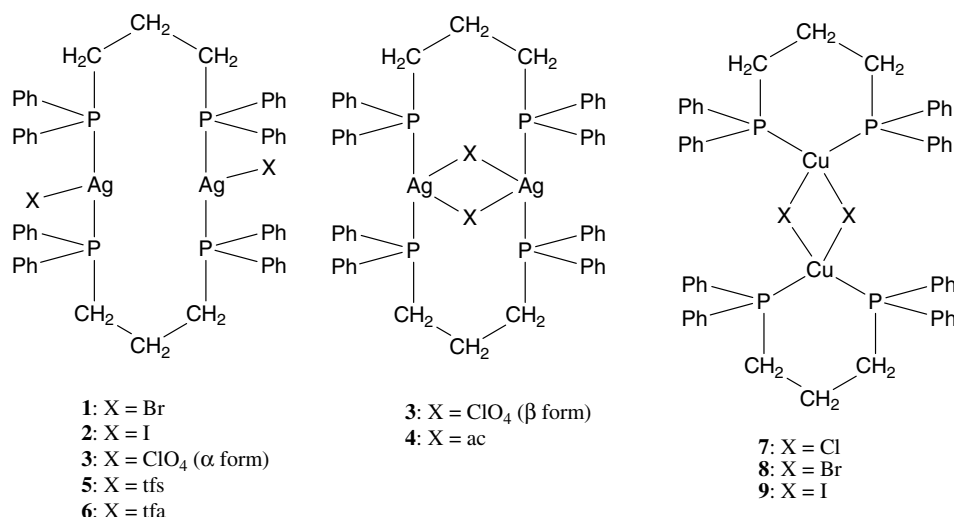
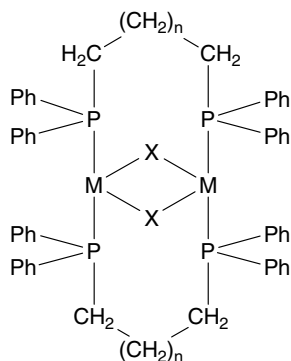


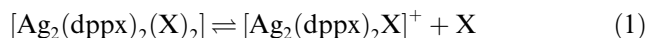
Chart 1.



- | | |
|---|---|
| 10: n = 2, M = Ag, X = Br | 20: n = 3, M = Ag, X = I |
| 11: n = 2, M = Ag, X = I | 24: n = 3, M = Cu, X = Br |
| 12: n = 2, M = Ag, X = CN | 25: n = 3, M = Cu, X = I |
| 13: n = 2, M = Ag, X = OClO ₃ | 27: n = 4, M = Ag, X = Br |
| 14: n = 2, M = Ag, X = ONO ₂ | 28: n = 4, M = Ag, X = I |
| 15: n = 2, M = Ag, X = OCOCF ₃ | 29: n = 4, M = Ag, X = NCO |
| 16: n = 2, M = Cu, X = Cl | 30: n = 4, M = Ag, X = NCS |
| 17: n = 2, M = Cu, X = Br | 31: n = 4, M = Ag, X = ONO ₂ |
| 19: n = 3, M = Ag, X = Br | |

Chart 2.

lyte in CH₂Cl₂ solution in accordance with Eq. (1), suggesting dissociation only of an X counter-ion. This partial ionic dissociation is also supported from the ESI MS data (see below).



The conductivity values found for the dppp derivatives **7**, **8** and **9**, all halide-containing species, are higher than those found for the halide and pseudohalide derivatives of dppb, dppn and dppe and suggestive of partial dissociation. Also, although we cannot exclude the occurrence of an equilibrium such as Eq. (1) for

this species, on the basis of the NMR and ESI MS results we hypothesize in solution the dissociation Eq. (2).



This is also consistent with the fact that slow crystallisation of dichloromethane solutions of **1** and **2** yielded derivatives of formula $[\text{Ag}(\text{dppp})_2]^+[\text{X}]^-$ in ca. 50% yield [13], together with an equimolar quantity of the silver halide salt.

All the other species are non-electrolytes, not only in dichloromethane but also in acetonitrile solution.

3.2. Spectroscopy

The infrared spectra of **1–32** (see Experimental section) are consistent with the formulations proposed, showing all of the bands required by the presence of the counter-ion and of the phosphorus donor [15]. The bands due to the phosphine and ligands are only slightly shifted with respect to those of the free donors. In the far-IR spectra of derivatives **1–4** we assign, on the basis of previous report on phosphino silver(I) derivatives [16,17], the broad absorptions near 500 cm⁻¹ and those at 450–400 cm⁻¹ to Whiffen's y and t vibrations, respectively. Some bands in the region 300–200 cm⁻¹, similar to those described in the literature for other silver(I)-oxanyan derivatives [18], may be tentatively assigned to ν(Ag–O).

The spectroscopic behaviour of the counter-ion in compound **3** is typical of an ionic outer-sphere group: in the case of ionic ClO₄⁻ (T_d geometry) only two vibrations (ν₃ and ν₄) are expected to be IR active [19], as in fact is found in **3**, at ca. 1100 and 620 cm⁻¹ in good accordance with the results found in the solid state that suggest the existence of a weak perturbation of ClO₄⁻.

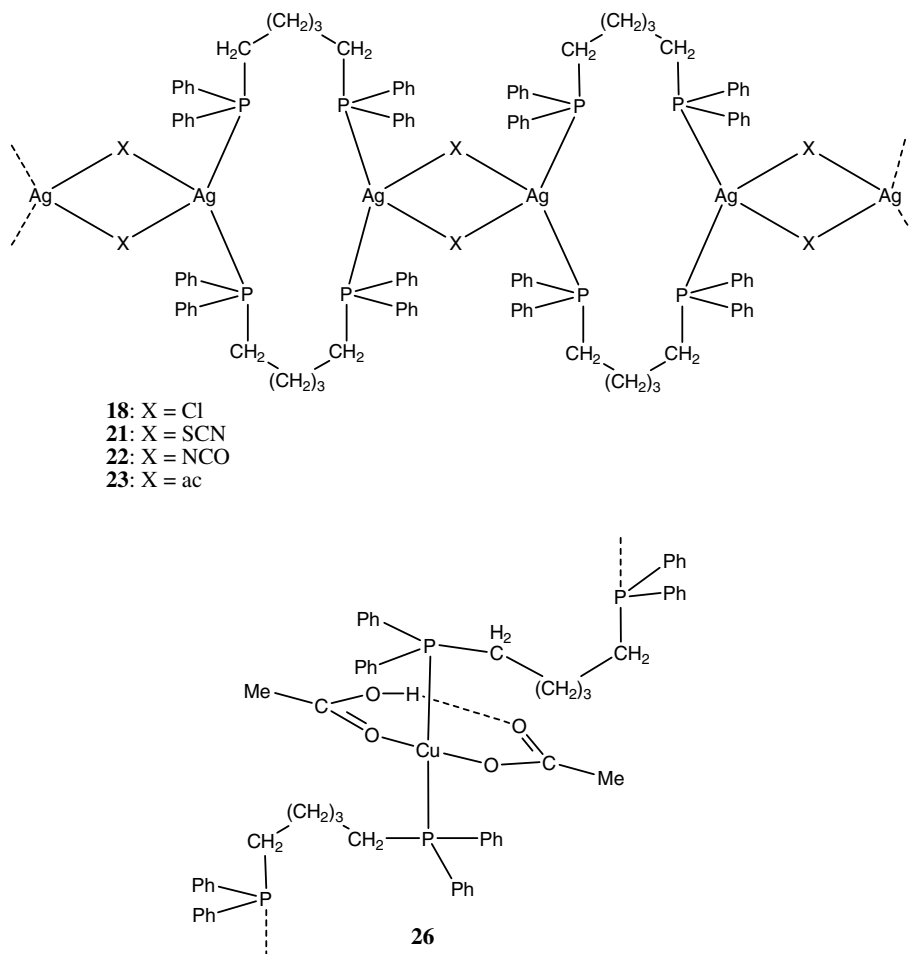


Chart 3.

On the other hand different absorptions have been found in the case of derivatives **3** and **13**, a number of broad bands being observed between 1120 and 1000 cm^{-1} and two strong bands at 620 and 580 cm^{-1} , in accordance with a coordinated unidentate or bidentate ClO_4^- groups.

In the case of carboxylate derivatives it is generally accepted [20] that it is possible to distinguish between ionic, unidentate, chelating bidentate or bridging bidentate groups on the basis of Δ values (where $\Delta = \nu_a(\text{COO}) - \nu_s(\text{COO})$), the trend generally accepted being:

$$\Delta_{\text{unidentate}} > \Delta_{\text{ionic}} > \Delta_{\text{bridgingbidentate}} > \Delta_{\text{chelatingbidentate}}$$

In compounds **5**, **15** and **26** the Δ is ca. 230, 200 and 230 cm^{-1} , respectively, consistent with unidentate coordination, of the carboxylate group, whereas the Δ is ca. 130 for **4** in accordance with bridging bidentate coordination as also supported by the X-ray data (see below).

Unambiguous assignment of the vibrational modes of CF_3SO_3^- in **6** is not possible due to mixing of CF_3 , SO_3 and organic ligand vibrational modes. On the basis of

literature reports on silver triflate complexes and on the Ag^+ salt [21–23], we assign the bands at 1270, 1040 cm^{-1} to $\nu[\text{SO}_3(\text{E})]$ and $\nu[\text{SO}_3(\text{A}_1)]$ and those at ca. 1240 and 1170 cm^{-1} to $\nu[\text{CF}_3(\text{A}_1)]$ and $\nu[\text{CF}_3(\text{E})]$, respectively, consistent with an ionic formulation or a weakly interacting CF_3SO_3^- group.

The absorptions in the region 2140–2040 cm^{-1} due to CN, SCN and CNO groups in complexes **12**, **21**, **22**, **29** and **30** are in agreement with those reported in literature for bridging pseudohalide groups [24,25]. No band that can be assigned unequivocally to M-halide stretching vibration has been detected at low frequencies, as expected for strongly bonded bridging halide groups.

In the ^1H NMR spectra of **1–32** in CDCl_3 (see the Experimental section), the signals due to the diphosphine ligand show different pattern with respect to those found for the free donors, confirming the existence of the complexes in solution. The bridging methylene resonances in **1–32** appear as broad singlets or resolved multiplets between 1.40 and 2.60 ppm, generally shifted downfield with respect to those of the free donors.

^{31}P chemical shifts (CDCl_3 solution) and ^{31}P –Ag coupling-constants for all derivatives are reported in the Experimental section. Our experiments have been carried out at a concentration of 0.005 mol/L.

The room temperature ^{31}P NMR spectra of compounds **6**, **12–15**, **20**, and **28–31** support the occurrence of dinuclear structures, also stable in solution. One or two broad doublets have been found at room temperature, the magnitude of the ^{31}P –Ag coupling constants being in the range typical of $[\text{Ag}(\text{P}_2\text{-donor})]_2\text{X}_2$ or $[\text{Ag}(\mu\text{-X})_2(\text{P}_2\text{-donor})]_2$ systems [1–3,26]. The low temperature ^{31}P spectra of these species consists of a sharper, more intense double doublet (Fig. 1), often flanked by less intense double doublets characterized by similar coupling constants. This could be due to the existence of two forms of the same species in solution. The magnitude of the coupling constants and the chem-

ical shift values indicated also that the counter-ion has an effect on the strength of the Ag–P bond [26]: in fact greater $^1J(^{31}\text{P},\text{Ag})$ coupling constants (420–580 Hz) and greater $\Delta [= \delta(^{31}\text{P}_{\text{complex}}) - \delta(^{31}\text{P}_{\text{free donor}})]$ values have been found for the perchlorato and trifluoromethanesulfonate derivatives which probably exist as ionic species in solution, containing a pair of two-coordinate silver atoms, whereas the halide and pseudohalide species, which presumably contain three- or four-coordinate silver centers, exhibit coupling constant values in the range 350–450 Hz. Compounds **1**, **2**, **4**, **10**, **11**, **19**, **21** and **23** are fluxional species at room temperature, a broad signal being always detected (Fig. 2a) which resolves at low temperature into one or more double doublets (Fig. 2b).

The spectra of the dppp:silver adducts **1–3** are peculiar: in all cases an intense signal has been found -5.2

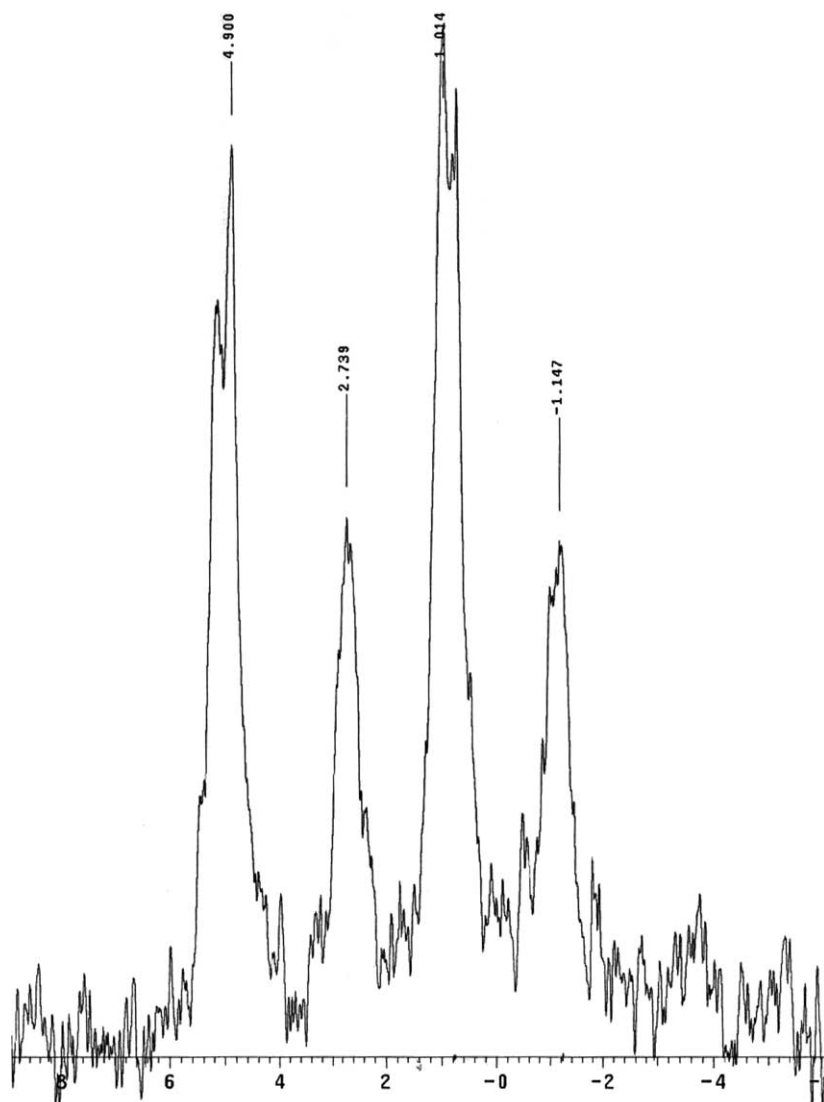


Fig. 1. ^{31}P NMR spectrum (218 K) of compound **8**.

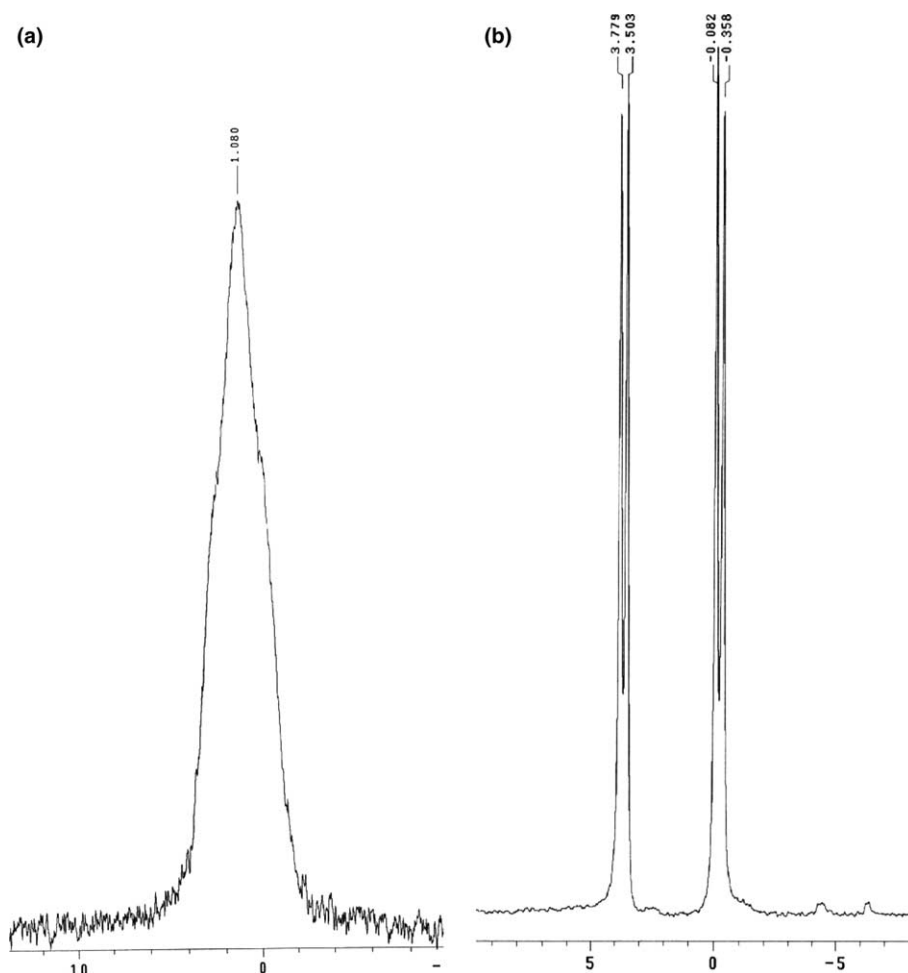


Fig. 2. ^{31}P NMR spectrum r.t. (a) and 218 K (b) of compound **3**.

ppm with $^1J(^{31}\text{P}, ^{107}\text{Ag})$ and $^1J(^{31}\text{P}, ^{109}\text{Ag})$ coupling constant values of ca. 220 and 250 Hz, which are typical of a species of formula $[\text{Ag}(\text{dppp})_2]^+$ containing an AgP_4 silver environment [14].

The copper species appear to widely dissociate in solution, most likely yielding, in a statistical redistribution, species of different stoichiometry such as $[\text{Cu}_2(\text{dppx})_3\text{X}_2]$, $[\text{Cu}_3(\text{dppx})_2\text{X}_2]$, $[\text{Cu}(\text{dppx})_2]\text{X}$, and $[\text{Cu}_2(\text{dppx})\text{X}_2]$ due to labile-bond formation and breakage, as emerges from the ^{31}P variable temperature spectra which exhibit a single broad signal at room temperature and at least six broad signals at low temperature. This has been confirmed also by ESI MS spectroscopy investigations.

The positive electrospray mass spectra of **1–32** (the most relevant data are reported in the Experimental section, with two typical spectra shown in Fig. 3) further support the existence of dinuclear species also in solution, the isotopic distribution always being in accordance with the calculated composition. It is noteworthy that the major peaks in the positive spectra

of the perchlorate and trifluoromethanesulfonate species are always those due to the dicationic species $[\text{Ag}_2(\text{dppx})_2]^{2+}$ formed upon loss of both X counterions. A different situation obtains for the trifluoroacetate, halide and pseudohalide species where the dominant aggregate is generally the $[\text{Ag}_2(\text{tfa})(\text{dppx})_2]^+$ species, consequent upon the loss of only one tfa group. These data are in good accordance with those derived from the conductivity studies and are further consistent with stronger interaction between tfa, halide and pseudohalide groups and the silver center, relative to NO_3 , ClO_4 and tfs. However it should be mentioned that in the case of the cyanate species no signals due to $[\text{Ag}_2(\text{NCO})(\text{dppx})_2]^+$ can be easily detected, whereas signals due to $[\text{Ag}_2(\text{Cl})(\text{dppx})_2]^+$ and $[\text{Ag}_2(\text{CN})(\text{dppx})_2]^+$ have been identified, respectively, arising from substitution of NCO^- with the Cl^- present in the solvent, and decomposition of the NCO^- to CN^- .

Another relevant feature observed in the ESI MS spectra of the silver:dppp adducts is the presence of the $[\text{Ag}(\text{dppp})_2]^+$ cation. It appears that a determinant

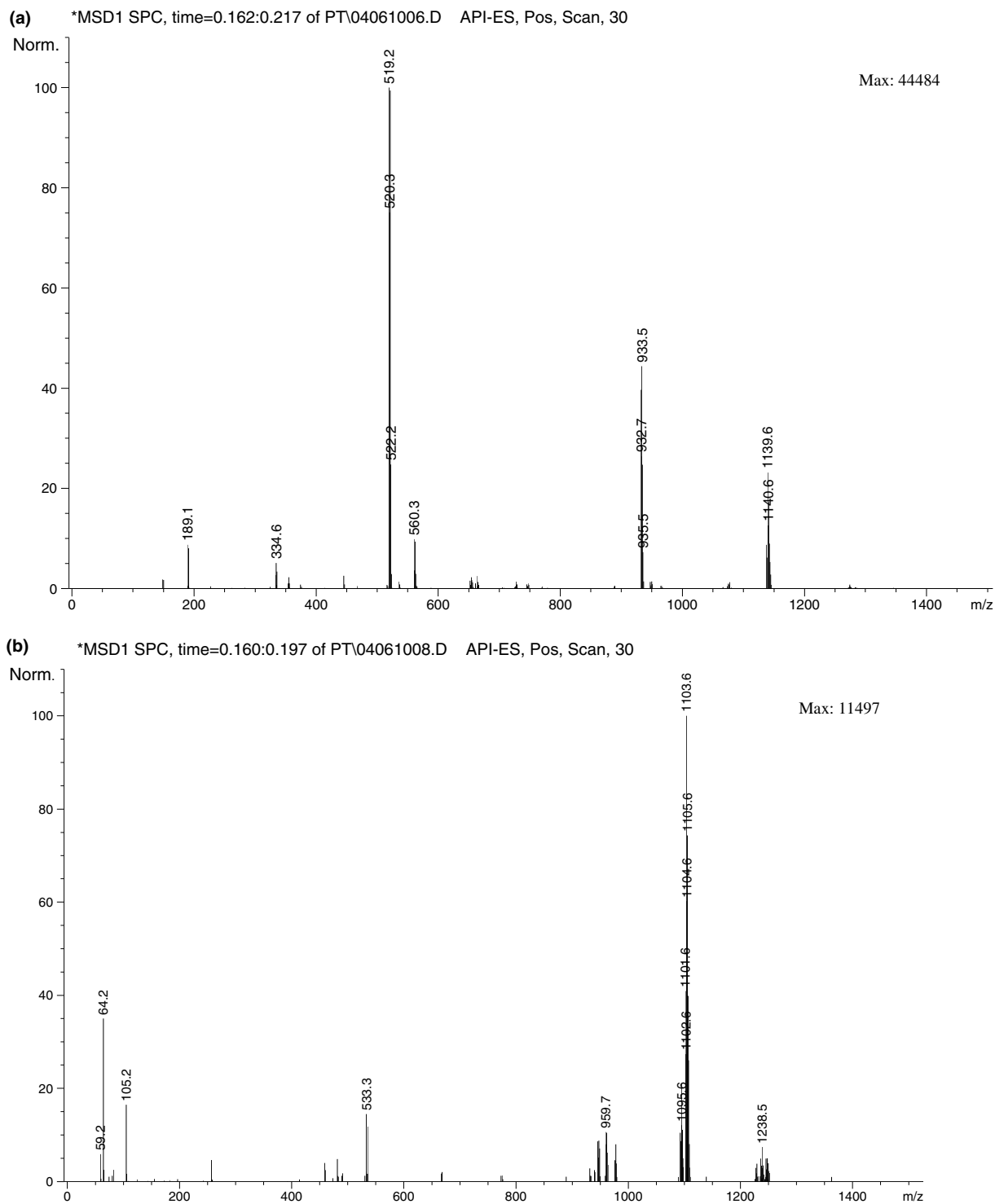


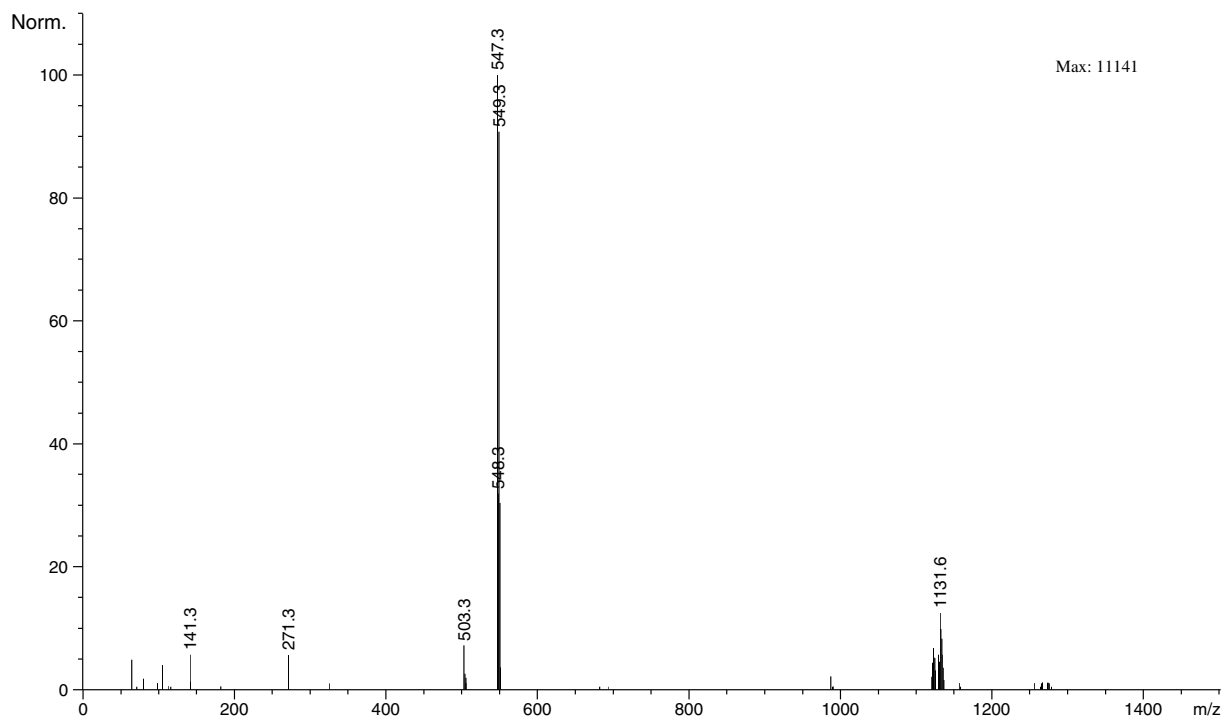
Fig. 3. ESI MS (ion positive) spectra of compounds **3** (a), **12** (b), **23** (c), and **25** (d).

in the formation of the bis(chelate) complex $[\text{Ag}(\text{dppp})_2]^+$ is the bite angle (steric constraint) of the P_2 -donor dppp which is smaller than those offered by dppb, dppn and dpph: with the other ligands in fact formation of the bis(chelate) is not evident. It is notable that the presence of cationic species containing coordi-

nated solvent molecules, is evident only in the spectra of those derivatives which are also solvated in the solid state, and in the polymeric compounds.

The negative electrospray spectra are always dominated by the presence of molecular peaks due to X and AgX_2^- .

(c) *MSD1 SPC, time=0.181:0.218 of PT\04061800.D API-ES, Pos, Scan, 30



*MSD1 SPC, time=0.181:0.218 of PT\04061800.D API-ES, Pos, Scan, 30

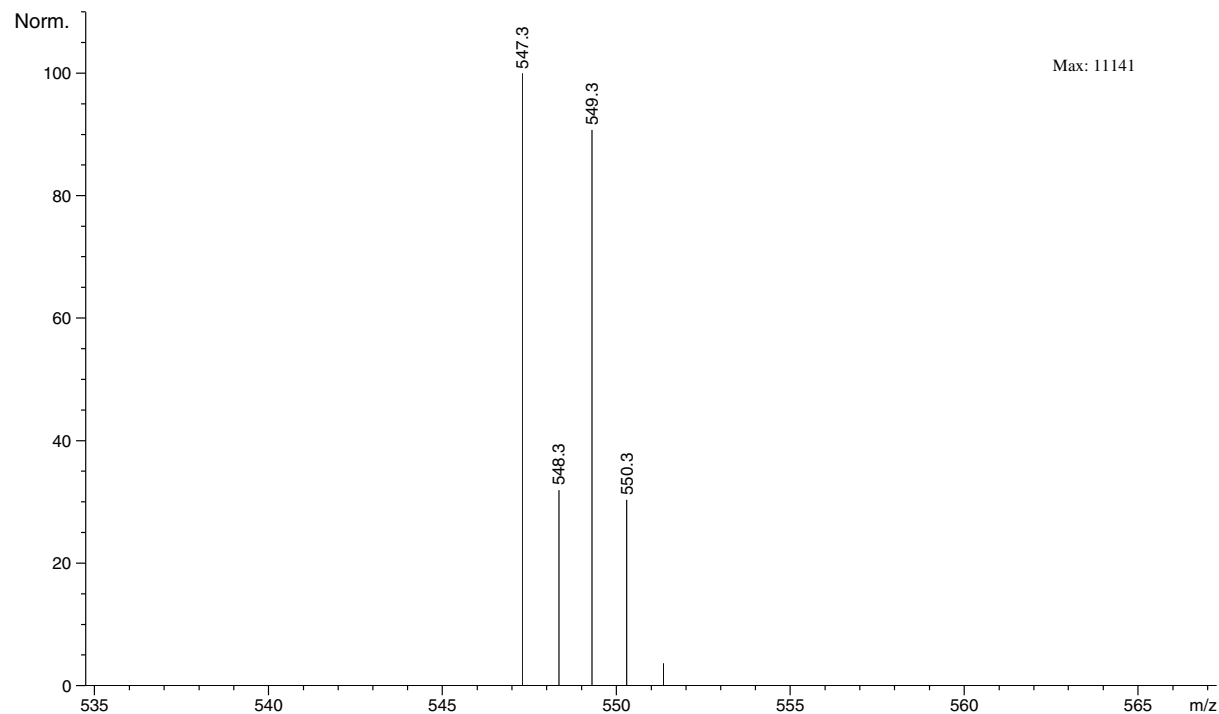


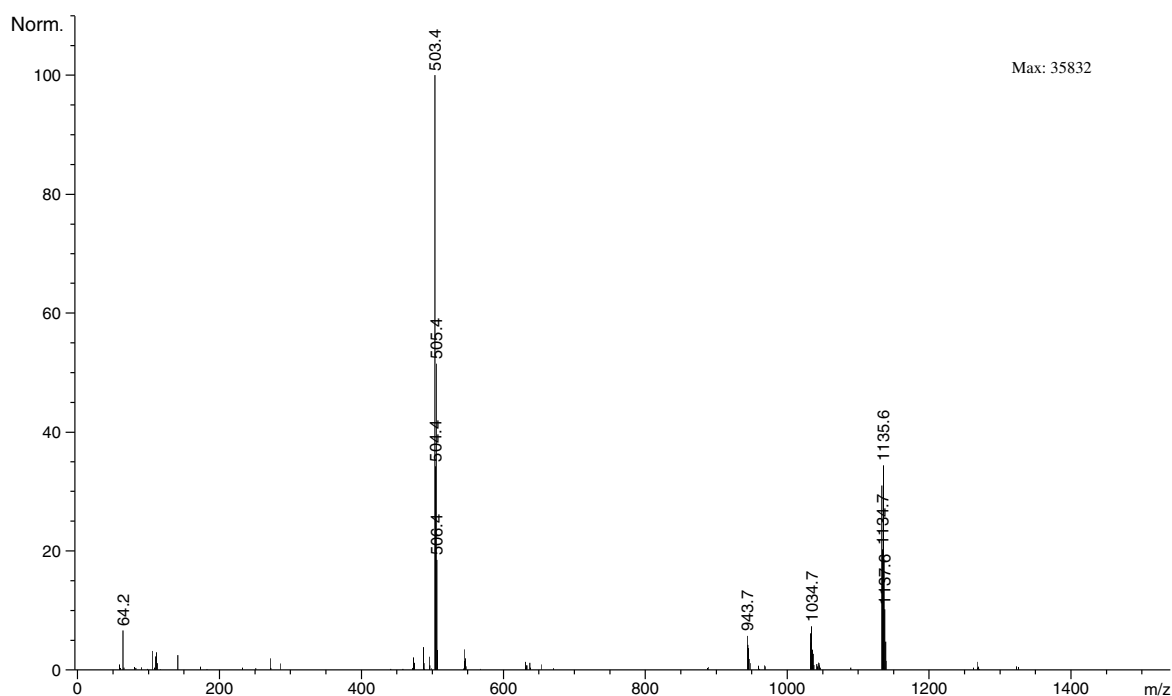
Fig. 3 (continued)

3.3. Single crystal X-ray studies

Single crystal X-ray structural characterisations are recorded for a variety of adducts of MX:dppx (1:1)

stoichiometry, for univalent $M = \text{Cu}, \text{Ag}$, various (pseudo-) halide and oxyanion X , and $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ligands ($x = 3\text{--}6$). The characterization, although not exhaustive, is more complete for the more readily

(d) *MSD1 SPC, time=0.162:0.199 of PT\04061805.D API-ES, Pos, Scan, 30



*MSD1 SPC, time=0.162:0.199 of PT\04061805.D API-ES, Pos, Scan, 30

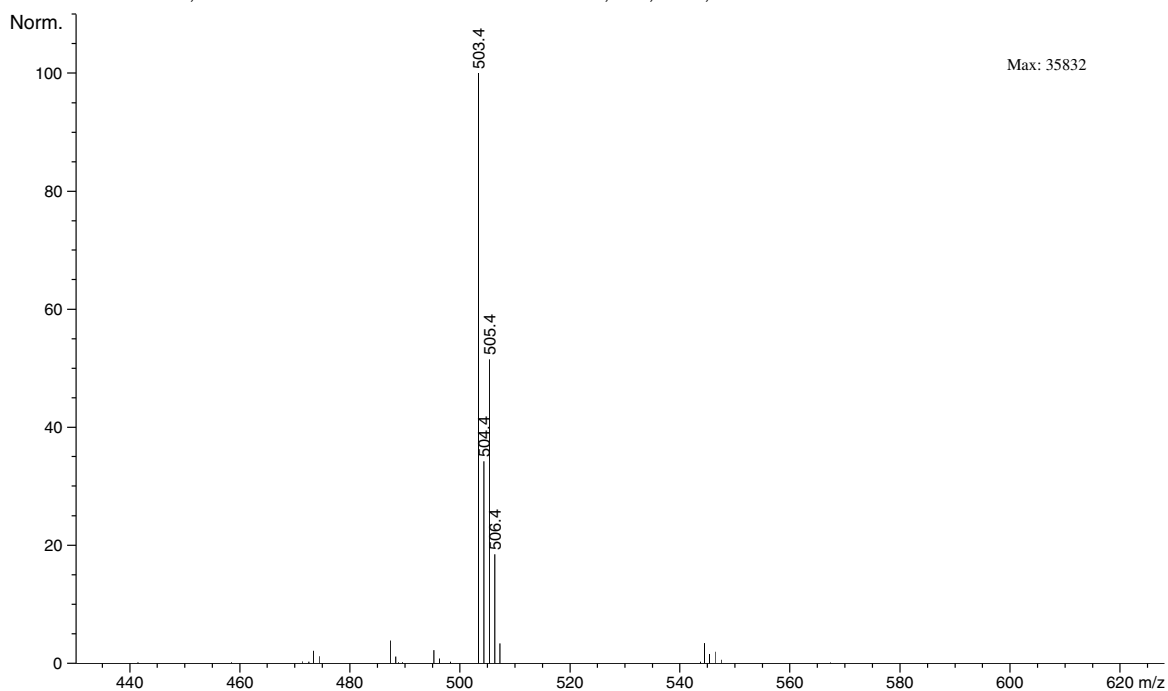


Fig. 3 (continued)

accessible complexes of $M = Ag$; the bulk of the arrays are centrosymmetric dimers, but some diversity of interesting forms and variants is found within and beyond these, within an aggregate of arrays where isomorphisms or similarities of lattice arrays are widespread. The anions in the systems studied encompass Cl, Br, I, SCN, NCO, CN, together with ClO_4 ,

NO_3 , carboxylate as an oxyanion array of increasing basicity.

With the dppp ligand, the only adduct of this stoichiometry to have been structurally characterized previously is for the Ag/NO_3 combination [6]; the present work defines a number of adducts for both $M = Cu$, Ag , the arrays for the two series being of different types,

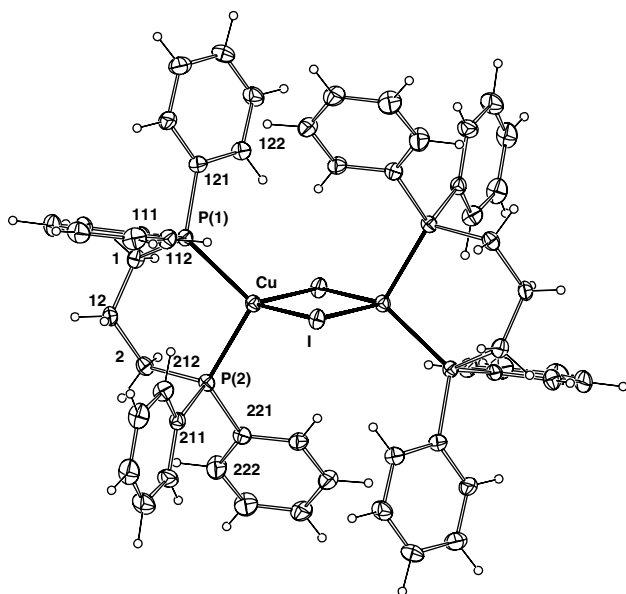


Fig. 4. A dimer of centrosymmetric $[(\text{dppp})\text{Cu}(\mu\text{-I})_2\text{Cu}(\text{dppp})]$ (**9**) projected through the central Cu_2I_2 plane.

Table 1

Selected geometries, $\text{P}_2\text{M}(\mu\text{-X})_2\text{MP}_2$ arrays Italicized atoms belong to the alternate fragment of the molecule; **C** is the central dppn carbon

X (Compound)	(a) $\text{CuX} : \text{dppp} (1:1)_2^*$			(b) $\text{AgX} : \text{dppn} (1:1)$			(c) $\text{CuX}:\text{dppn}(1:1)$	
	$[(\text{dppp-}P,P')\text{Cu}(\mu\text{-X})_2\text{Cu}(P,P'\text{-dppp})]$			$[(P\text{-dppn-}P)_{2/2}\text{Ag}(\mu\text{-X})_2\text{Ag}(P\text{-dppn-}P)_{2/2}](\infty)(\infty)$			<i>O,O'</i> -ac (27)	<i>O</i> -ac/ <i>O</i> -Hac (26) ^c
Symmetry	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\text{Cl}(\mathbf{18}\beta)(2 \text{ 'mols'})$	$\text{SCN}(\mathbf{22})^a$	$\text{NCO}(\mathbf{21})^b$		
<i>Distances (Å)</i>								
M-X	2.3726(4)	2.4937(3)	2.6491(7)	2.583(2), 2.581(2)	2.732(5) (S)	2.408(6)	2.379(6)	2.113(3)
M-X	2.3908(5)	2.5180(3)	2.675(1)	2.692(2), 2.805(2)	2.32(2) (N)	2.400(7)	2.545(6)	2.076(3)
M...M	3.0314(3)	3.0664(3)	3.1017(9)	3.530(1), 3.691(1)		3.405(1)		
X...X	3.6744(6)	3.9642(4)	4.328(1)	3.922(2), 3.939(2)		3.395(8)		
M-P	2.2509(4)	2.2571(5)	2.272(1)	2.477(2), 2.459(2)	2.514(4)	2.459(2)	2.419(2)	2.256(1)
M-P'	2.2568(4)	2.2635(5)	2.272(1)	2.506(2), 2.467(1)	2.462(5)	2.459(2)	2.426(2)	2.261(1)
<i>Angles (°)</i>								
X-M-X	100.95(2)	104.56(1)	108.74(3)	96.03(6), 93.60(5)	97.7(4)	89.8(2)	52.7(3)	101.8(1)
M-X-M	79.05(1)	75.44(1)	71.26(2)	83.97(6), 86.40(5)	-90.2(2)			
X-M-P	119.34(1)	119.34(1)	119.37(3)	120.99(6), 114.18(6)	96.2(1)	113.1(1)	110.4(2)	119.0(1)
X-M-P	112.23(2)	111.66(2)	110.94(4)	112.80(5), 109.29(6)	112.7(2)	99.4(1)	118.2(2)	100.22(9)
X-M-P	112.71(2)	111.38(2)	110.36(3)	107.35(6), 95.48(6)	102.4(3)	106.5(1)	119.1(2)	113.9(1)
X-M-P	107.86(2)	105.35(1)	102.51(3)	108.45(5), 104.26(5)	113.2(3)	113.2(1)	106.7(2)	110.65(9)
P-M-P	103.55(2)	103.86(2)	103.55(4)	109.67(5), 130.58(5)	129.3(1)	128.01(8)	127.07(6)	110.27(4)
<i>Torsion angles (°)</i>								
M-P-C-C	60.5(1)	59.8(2)	59.8(3)	82.6(6), 51.6(5)	-58(1)	-66(1)/-178(1)	62.8(7)	60.9(3)
P-C-C-C	-82.9(2)	-83.1(2)	-83.7(4)	-161.3(5), -178.8(5)	-165(1)	175.4(8)/177(1)	175.8(6)	-177.1(3)
C-C-C-C'				-41.5(9), -63.4(8)	-53(2)	159.1(9)/-102(2)	-176.7(8)	178.2(3)
C-C-C'-C'				-178.9(6), -167.0(5)	-63(2)	57(1), 95(1)	177.7(8)	175.5(3)
C-C-C'-P'	70.4(2)	70.8(2)	72.2(5)	-167.3(5), 178.4(5)	-174(1)	178(1)	178.1(6)	-174.1(3)
C-C'-P'-M	-42.9(2)	-42.9(2)	-44.0(4)	57(1), 65(1)	-56.7(7)	-56.7(7)	53.2(7)	55.6(3)

Italicized atoms belong to the alternate fragment of the molecule; **C** is the central dppn carbon.

Torsion angles in the string P-C-(C_n)-C'-P' are denoted $\alpha, \beta, \dots, \beta', \alpha'$, here and subsequently.

^a In the Ag/SCN adduct, **22**, C-S, N are 1.64(2), 1.14(2) Å; Ag-S-C, S-C-N, C-N-Ag are 97.4(7), 176(2), 161(1)°. The (AgSCN)₂ ring is planar (χ^2 8.4). In the Ag/NCO adduct, C-N, O are 1.132(9), 1.19(1) Å. Ag, Ag-N-C are 143.2(7), 120.4(6); N-C-O 179(1)°.

^b The NCO line makes a dihedral angle of 71.3(1)° with the Ag₂N₂ plane. C(11a)...C(11b), C(12a)...C(12b) are 1.00(2), 1.09(2) Å. P...

^c The ac adduct, **27**, is of a single stranded form (P-dppn-P){Ag(*O,O'*-ac)}(P-dppn-P){Ag... tabulated here for convenience, together with its acetic acid solvated copper(I) counterpart: (-P)Cu(*O*-ac)(*O*-Hac)(P-dppn-P)Cu(*O*...), (**26**).

* In the Cu/Cl, Br, I adducts, **7–9**, H(122)...X are 2.80(2), 2.91(2), 2.97 Å. P...P' is the ligand 'bite', being 3.5411(6), 3.5590(6), 3.570(2)° for Cl, Br, I, respectively.

which we discuss separately. The three copper(I) complexes, **7–9**, discussed are isomorphous, all dimeric with one half of the dimer crystallographically independent; all take the form $[(\text{dppp-}P,P')\text{Cu}(\mu\text{-X})_2\text{Cu}(P,P'\text{-dppp})]$, each dppp ligand associated with only one copper atom via chelation, the two four-coordinate copper atoms being bridged by a pair of halogens, and a common ligand conformation. The iodide, **9**, (which has been characterized previously in a different polymorph [27]) is depicted as representative in Fig. 4; geometries are presented comparatively in Table 1. The bite angles of the symmetrical coordinated six-membered chelate rings are large, effectively constant from Cl to I despite the bite of the $(\mu\text{-X})_2$ core, also large, increasing, with a slight but appreciable concomitant increase in Cu-P and in P...P. As might be expected Cu...Cu increase relatively slowly cf. X...X, the two Cu-X distances being essentially equivalent. The symmetry of the molecular array is essentially $2/m$; this symmetry is broken by the phenyl dispositions which, nevertheless, divide into axial and equatorial sets vis-à-vis the six-membered

rings, the prowl carbons lying to the same side as the axial substituents; close substituent phenyl-H...X contacts are noted. This less common form of the (1:1) MX:dppx dimer has been recorded previously only for a number of adducts with dppf (bis(diphenylphosphino)ferrocene), a ligand of similar P...P distance for $M = \text{Cu}$, $X = \text{I}$, ONO_2 , OCHO [28], further discussed in the following paper [29]; in those complexes the chelate ring is also effectively six-membered, with the ferrocene disposition skewed across the $\text{P}_2\text{C}_2\text{P}_2$ plane.

The majority of the remaining complexes discussed in this paper are of the form (ligands only) $[\text{M}(\text{P-dppx-P})_2\text{M}]$; exceptions are found for a number of AgX:dppn

adducts which are polymeric, resembling the present arrays, in as much as the persistent motif comprises the two metal atoms linked closely by the bridging halogens. However, unlike the present arrays, the ligands, although bridging those units into polymers, may be, by virtue of their length, considered as imposing no constraint on the manner of coordination of the phosphorus atoms, phenyl hindrances aside. Data for these compounds are also presented in Table 1.

Previous work has described a 1:1 (dimeric) adduct of AgNO_3 with dppp [6] (Fig. 5 (a)). The present AgX/dppp arrays are also of this general form, but, here again, variants are possible, depending on whether the

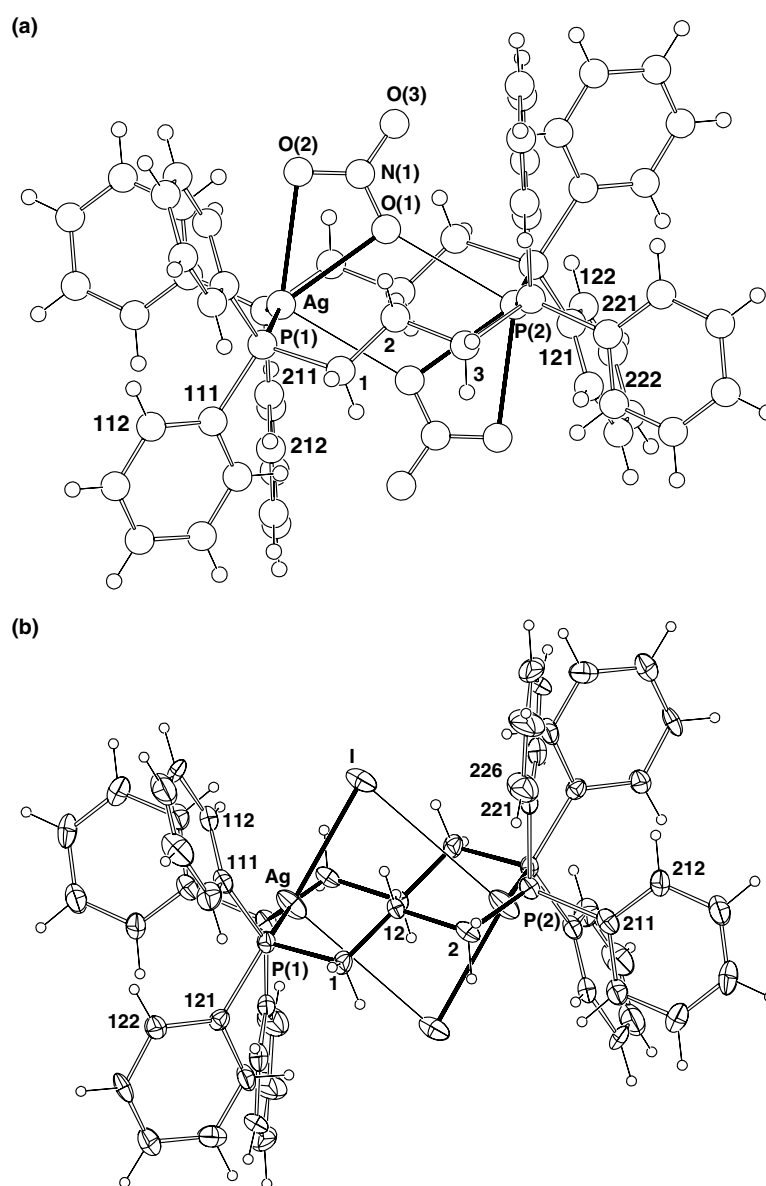


Fig. 5. (a) A projection of centrosymmetric $\text{AgNO}_3:\text{dppp}$ (1:1)₂, constructed from the published data [6], projected normal to the incipient Ag_2X_2 core plane. (b) (Centrosymmetric) AgI:dppp (1:1)₂ (2) (α -form), projected normal to the P_4 plane. (The two molecules of the β -form are similar (both centrosymmetric) but with non-bonded Ag–I of molecule 2 much shorter (Table 2)).

Table 2
Selected geometries, Ag(*P*-dppp-*P'*)₂Ag arrays

X (Compound)	O ₂ NO ^{a,b}	Br (1)	I(2α)	I(2β)(2xAg) ^c	tfs ^d (6)	OClO ₃ (3α) ^b	OClO ₃ (3β)(2xAg) ^c	O-ac ^e (4)	O-tfa- ^f (5)
Symmetry	$\bar{1}$	$\bar{1}$	$\bar{1}$	$2 \times \bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	2
<i>Distances (Å)</i>									
M-X	2.581(3)/2.674(3)	2.704(2)	2.841(3)	2.8095(3), 2.8985(4)	2.606(3)/2.564(7)	2.835(7), 2.885(5)	2.813(2), 2.765(2)	2.497(3)	2.418(6)
M-X	(2.9757(6))	(3.428(2))	(3.771(3))	(4.3232(5), 3.2538(4))			3.013(2), 2.956(2)	2.383(2)	
M...M	4.6614(5)	(4.155(2))	4.238(3)	(4.6930(6), 3.9099(6))		4.878(2)	4.7254(3), 4.7871(3)	3.867(2)	5.874(2)
X...X		(4.567(2))	(5.160(3))	5.5805(6), 4.7635(5)			3.413(3), 3.138(2)	2.979(4)	
M-P	2.403(1)	2.433(2)	2.422(6)	2.4249(8), 2.4510(8)	2.4078(8)	2.394(2)	2.4012(4), 2.3914(4)	2.427(2)	2.413(2)
M-P	2.426(1)	2.449(2)	2.441(5)	2.4410(8), 2.4601(8)	2.4146(8)	2.405(2)	2.4027(3), 2.4010(3)	2.420(2)	2.415(2)
<i>Angles (°)</i>									
X-M-X							71.63(5), 66.44(5)	75.20(8)	
M-X-M							108.37(6), 113.56(6)	104.80(9)	
X-M-P	108.6(1)/92.9(1)	111.55(5)	111.8(1)	113.93(2), 109.82(2)	108.8(1), 97.9(2)	110.6(1), 105.24(9)	100.33(3), 106.16(3)	105.60(8)	106.8(1)
X-M-P'	97.8(1)/111.2(1)	103.11(6)	102.6(2)	102.50(2), 100.95(2)	90.1(1)/102.9(2)	88.6(1), 95.7(1)	99.03(3), 95.53(3)	97.86(8)	110.0(1)
X-M-P							94.00(3), 88.25(3)	101.45(7)	
X-M-P'							94.11(3), 94.81(3)	109.66(8)	
P-M-P'	152.2(1)	144.30(7)	144.6(2)	143.55(2), 144.37(3)	159.19(2)	157.96(5)	160.53(2), 157.40(2)	144.90(3)	142.63(6)
<i>Torsion angles (°)</i>									
M-P-C-C (α)	50.2(2)	48.3(4)	46(1)	40.8(2), -50.4(2)	45.6(2)	48.5(4)	46.6(1), -51.6(1)	-53.6(3)	65.9(5)
P-C-C-C (β)	-165.3(2)	-160.7(4)	-162(1)	-171.9(2), 153.6(2)	-174.1(2)	-167.4(3)	-165.2(1), 164.5(9)	151.3(3)	-173.5(4)
C-C-C'-P'(β')	152.2(3)	147.6(5)	149(1)	153.3(2), -148.2(2)	164.0(2)	156.3(3)	162.9(1), -154.3(1)	147.5(3)	-167.9(3)
C-C'-P'-M(α')	-58.9(2)	-54.8(4)	-56(1)	-53.9(2), 57.3(2)	-53.4(2)	-56.3(3)	-53.9(1), 59.5(1)	-45.6(4)	-49.4(5)

^a Ref. [6] (all other data in the Table originate in the present work).

^b Dual entries correspond to the two oxygens of the chelating, non-bridging anion, O-Ag-O being 46.9(1) (nitrate), 46.8(1)° (perchlorate).

^c Dual entries correspond to the two halves of the molecule which are crystallographically independent.

^d Dual entries correspond to the two disordered components of O(1) of the anion.

^e Ag,Ag'-O-C are 134.7(2), 118.7(2)°; the Ag₂O₂/C₂O₂ interplanar dihedral angle is 12.0(1)°.

^f Ag..O(2) is 3.01(1) Å. In the bromide and iodide (α,β) counterparts, the angle sums about the metal are 359.0, 358.2, 360.0 and 355.1 (mols. 1,2); for the tfa adduct the value is 359.4.°

array takes the form $[XM(P\text{-dppe-}P)_2MX]$ with each anionic X associated solely with one (three-coordinate) metal atom, or $[M(\mu\text{-}X)_2(P\text{-dppx-}P)_2M]$, with the anions bridging. With few exceptions, those of one form (β) of the Ag/ClO_4 , **3**, and of the Ag/ac adducts, **4** all of the present, **1–6**, and the published nitrate, are of the former type, although whether the anion is totally devoid of interaction with the other metal may be considered a moot point. Nevertheless, this type is not found with the dppx adducts of the more extended ($x > 3$) ligands; presumably the determinants of the form of the present dppp adducts with both CuX and AgX are largely a consequence of constraints determined by the relatively small chain length of the ligand and the size of the metal atom (see below). In the published $\text{AgNO}_3\text{:dppp}$ adduct,

the shortest *trans*-annular $\text{AgNO}_3\cdots\text{Ag}$ distance is 2.976(2) Å; the anion, if not actually active in the dimerisation process, is nevertheless ‘pre-positioned’ for such an interaction (Fig. 4). Such is also the case with the crystallographically similar bromide (**1**) and iodide (3α -form), (Fig. 5 (b)); the iodide is found in a second β form), in which there are two independent centrosymmetric dimers, the first closely resembling the α -iodide (etc.), as does molecule 1 of the β -form. Molecule 2 of the β -form is subtly different; without gross changes in core conformation, the $\text{AgI}\cdots\text{Ag}$ approach is much closer, as is the $M\cdots M$ distance, with the incipient bridging much more immediate (Table 2), and the silver environment less precisely planar, and Ag-P concomitantly lengthened.

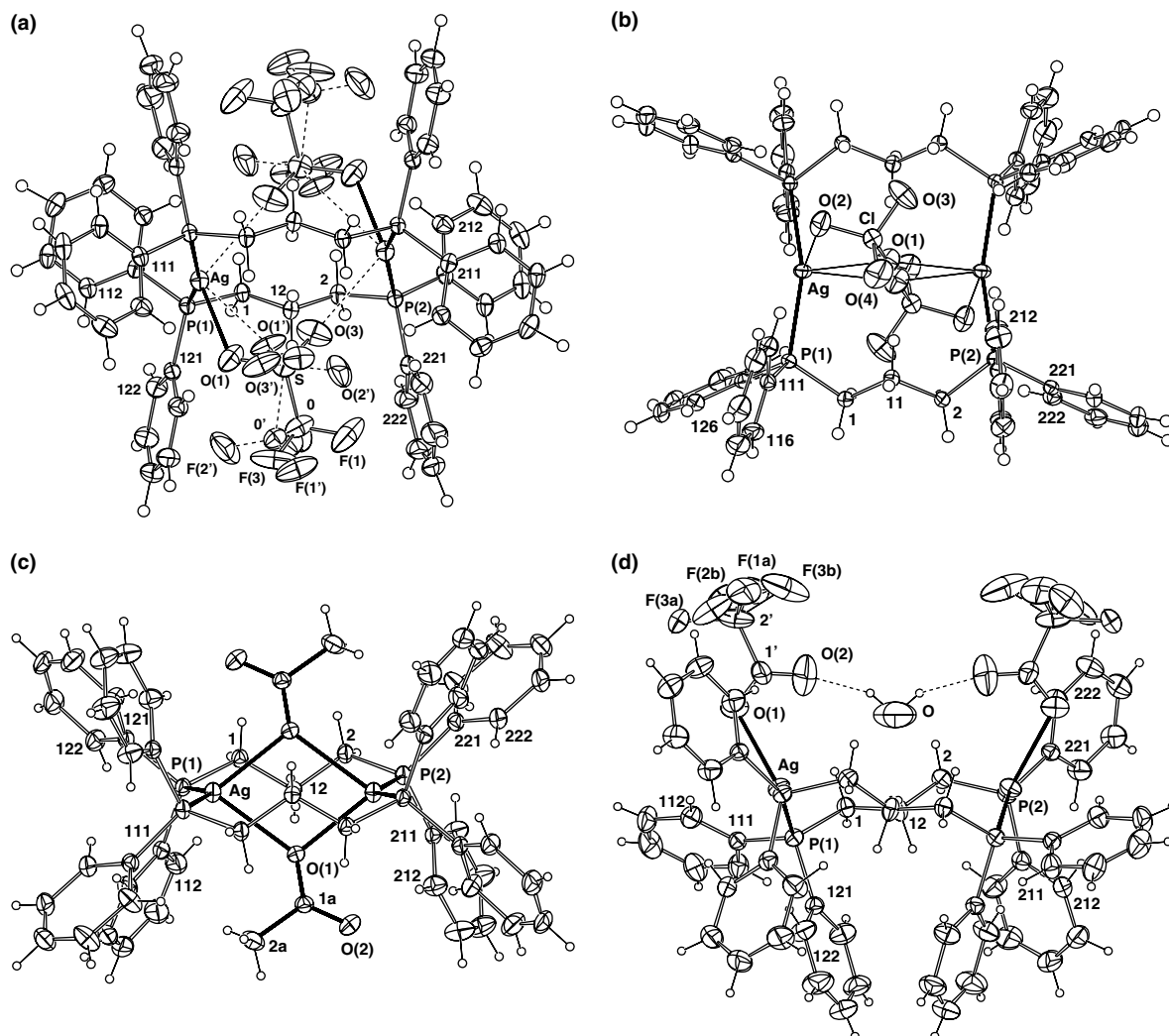


Fig. 6. (a) The (centrosymmetric) dimer of Agtfs:dppp (1:1)₂ (**6**). (b) The (centrosymmetric) dimer of $\text{AgClO}_4\text{:dppp}$ (1:1)₂ (3β) (150 K; molecule 1), projected through the (incipient) Ag_2O_2 core plane. (c) Centrosymmetric Agac:dppp (1:1)₂ (**4**), projected normal to the Ag_2O_2 core plane. (d) Agtfa:dppp (1:1)₂ · H_2O , **5**, projected *quasi*-normal to the crystallographic 2-axis (which lies vertical in the page, passing through the water molecule oxygen).

Table 3

Selected geometries, $[M(\mu-X)_2(P\text{-dppx-}P')_2M]$, $x = b, n, h$

M	Cu			Ag					
X (Compound)	OCIO ₃ ^a	Cl (16)	Br (17)	Br (10)	I (11)	CN (12)	OCIO ₃ ^b (13)	ONO ₂ ^c (14)	O-tfa ^d (15)
(a) dppb complexes; all are centrosymmetric dimers									
Distances (Å)									
M-X	2.435(8)	2.421(3)	2.5323(9)	2.801(2)	2.9314(6)	2.420(5)	2.791(6)	2.490(2)	2.441(5)
M-X'	(3.110(8))	2.467(2)	2.5726(7)	2.817(1)	2.9330(5)	2.363(4)	2.715(6)	2.699(1)	2.568(7)
M...M	4.631(3)	3.112(2)	3.1405(9)	3.557(1)	3.4453(6)	2.975(2)	4.483(2)	4.2616(3)	3.817(2)
X...X	3.13(1)	3.770(3)	4.0249(7)	4.348(2)	4.7457(9)	3.746(7)	3.20(1)	2.969(2)	3.246(8)
M-P	2.239(3)	2.255(2)	2.258(1)	2.458(4)	2.474(2)	2.501(1)	2.409(3)	2.4192(6)	2.413(2)
M-P'	2.241(3)	2.235(2)	2.246(1)	2.447(3)	2.469(1)	2.481(1)	2.402(8)	2.4301(5)	2.439(2)
P...P									
Angles (°)									
X-M-X		100.92(8)	104.07(3)	101.42(4)	108.04(2)	103.1(2)	71.0(2)	69.65(5)	80.7(2)
M-X-M		79.08(7)	75.93(2)	78.58(4)	71.96(2)	76.9(1)	109.0(3)	110.35(6)	99.3(2)
X-M-P'	97.2(3)	111.11(9)	110.29(4)	108.28(8)	106.03(3)	110.1(1)	108.3(2)	119.50(4)	110.2(1)
X-M-P'	118.8(3)	104.49(9)	102.47(4)	99.19(8)	98.93(3)	102.4(1)	99.4(2)	99.17(4)	103.0(1)
X-M-P		98.62(7)	98.36(4)	94.94(7)	96.60(3)	98.3(2)	115.2(2)	105.24(4)	118.1(1)
X-M-P'		115.10(7)	115.14(3)	118.43(8)	116.02(3)	119.6(1)	94.9(2)	99.66(4)	92.2(1)
P-M-P'	142.8(1)	124.4(1)	125.03(5)	131.24(9)	129.90(4)	121.98(5)	114.19(8)	139.23(2)	137.62(9)
Torsion angles (°)									
α	-59.8(8)	-65.2(4)	-63.2(3)	56.7(8)	56.3(4)	58.9(4)	56.0(8)	-62.2(2)	-67.1(4)
β	-176.3(7)	167.4(4)	166.7(3)	-173.2(8)	-170.7(4)	-168.4(4)	-73(1)	74.1(2)	67.3(7)
γ	-179.5(9)	-68.1(9)	-69.8(5)	75(1)	74.9(7)	70.1(6)	-179(1)	-174.9(2)	70.7(9)
β'	71.4(9)	-63.5(10)	-64.3(6)	71(1)	70.8(5)	68.6(5)	175.0(8)	177.0(2)	-178.0(6)
α'	-62.4(7)	77.2(7)	76.7(4)	-69.7(7)	-70.1(3)	-68.8(3)	55.8(9)	-56.7(2)	61.0(6)
Sequence	gaagg	gaggg	gaggg	gaggg	gaggg	gaggg	gaggg	gaggg	gaggg

M	Cu		Ag		
X (Compound)	Br (24)	I (25)	Cl ^e	Br (19)	I (20)
Symmetry	1	2	$\bar{1}$	$\bar{1}$	2 × 222
(b) dppn complexes					
Distances (Å)					
M-X	2.5892(6), 2.5258(6)	2.725(1), 2.732(1)	2.664(4), 2.663(3)	2.759(1)	2.975(1), 2.920(1)
M-X'	2.5492(6), 2.6283(6)	(2.725(1), 2.732(1))	2.797(1)	2.797(1)	
M...M	3.6635(7)	2.718(3), 2.678(3)	3.812(1)	3.814(1)	4.122(2)
X...X	3.6132(7)	4.079(2)	3.769(4)	4.040(1)	4.292(2)
M-P	2.255(1), 2.251(1)	2.274(1), 2.270(1)	2.472(3), 2.493(4)	2.464(1)	2.478(2), 2.503(2)
M-P'	2.277(1), 2.271(1)	(2.274(1), 2.770(1))	2.492(3), 2.499(4)	2.471(1)	(2.478(2), 2.503(2))
Angles (°)					
X-M-X	89.36(2), 89.00(2)	96.90(4), 96.58(4)	88.9(1), 89.7(1)	93.30(2)	92.30(4), 94.55(4)
M-X-M	89.20(2), 92.42(2)	83.26(4)	91.1(1), 90.2(1)	86.70(2)	87.70(3), 85.45(3)
X-M-P'	102.96(3), 119.32(3)	108.88(4), 106.84(4)	124.7(1), 94.1(1)	101.41(4)	100.94(6), 105.05(5)
X-M-P'	123.26(3), 99.06(3)	(111.63(4), 113.01(4))	97.1(1), 126.6(1)	119.66(3)	116.29(6), 113.12(5)
X-M-P	119.88(3), 101.08(3)	111.63(4), 113.01(4)	97.6(1), 119.0(1)	121.39(3)	
X-M-P'	99.16(3), 123.02(3)	(108.88(4), 106.84(4))	120.4(1), 94.0(1)	99.24(4)	
P-M-P ^b)	119.40(4), 121.78(4)	117.09(6), 118.48(6)	124.4(1), 128.6(1)	119.92(4)	125.66(9), 122.53(9)
Torsion angles (°)					
α	78.7(3), 76.8(3)	-79.5(4)	-66.3(9), -88(1)	82.6(4)/43.3(7)	-71.5(6), -68.0(7)
β	-155.1(8), -166.2(3)	157.2(4)	163.4(9), 49(4)	-138.6(4)/171.6(8)	165.0(6), 163.0(6)
γ	79.3(4), 78.1(4)	-80.5(7)	-85(1), 87(3)	79.3(6)/150.3(10)	-82.4(7), -85.4(7)
γ'	73.8(4), 76.7(4)	-76.5(7)	-78(1), 177(2)	-140.2(5)/-73(1)	
β'	-166.8(2), -156.4(3)	161.4(4)	167(1), 144(2)	-177.5(5)/143.2(6)	
α'	71.5(3), 69.4(3)	-75.2(4)	-69(1), -60(1)	-49.2(4)/-89.7(6)	
Sequence	2 × gaggag	gaggag	gaggag, gaggag	gaggag	gaggag

Table 3 (continued)

M	Cu		Ag						
X (Compound)	O ₂ NO ^f	O,O'-ClO ₄ ^f	Br (27)	I (28)	NCO ^g (29)	SCN(30α)	SCN (30β)	O,O'-ClO ₄ ^f	O,O'-NO ₃ (31)
(c) <i>dpph</i> complexes									
Distances (Å)									
M-X	2.245(7), 2.097(5)	2.236(6)	2.7129(9)	2.8632(7)	2.625(5)/2.063(7)	2.336(4)	2.429(8)	2.639(4)	2.435(8)
M-X	2.089(6), 2.345(6)		2.904(1)	2.9954(8)	2.245(5)/2.817(7)	2.677(1)	2.614(3)	2.712(6)	2.53(1)
M...M	4.985(2)	5.213(3)	4.0341(8)	4.0909(8)	5.274(2)/5.438(6)	5.4385(7)		5.318(2)	5.116(2)
X...X			3.913(1)	4.1958(8)					
M-P	2.241(2), 2.267(2)	2.234(2)	2.496(2)	2.485(2)	2.460(1)/2.438(4)	2.458(1)	2.372(3)	2.419(2)	2.433(2)
M-P'	2.242(2), 2.244(2)	2.238(2)	2.487(2)	2.481(2)	2.426(1), 2.513(5)	2.437(1)	2.529(2)	2.416(2)	2.428(1)
Angles (°)									
X-M-X	90.3(3), 86.3(2)		88.24(3)	91.45(2)	98.8(2)/97.6(2)	108.04(9)	103.9(2)	110.5(2)	101.8(3)
M-X-M			91.76(3)	88.55(2)					
X-M-P'	99.0(3), 105.6(1)	108.5(2)	103.74(5)	105.05(4)	90.5(1)/106.5(2)	95.31(8)	91.6(2)	103.6(1)	104.6(3)
X-M-P'	110.9(2), 119.3(2)		126.99(5)	124.19(5)	109.7(1)/128.8(2)	118.72(9)	120.2(2)	107.2(2)	112.3(3)
X-M-P	112.8(2), 101.0(2)	107.1(2)	120.01(5)	117.09(5)	115.6(1)/98.3(2)	111.35(4)	110.2(1)	95.0(2)	110.4(3)
X-M-P'	112.1(3), 105.4(2)		100.45(5)	102.09(5)	112.0(1)/93.1(2)	96.99(4)	101.17(9)	104.6(2)	94.0(3)
P-M-P'	125.31(8), 128.53(7)	130.92(8)	115.55(6)	115.21(6)	122.0(5)/121.2(2)	126.13(3)	120.2(2)	134.33(5)	130.07(5)
Torsion angles (°)									
α	-68.4(5), 67.3(5)	64.1(5)	62.1(6)	60.4(7)	55.7(4)/74.3(4)	58.1(3)	56.4(8)	-63.4(4)	60.9(4)
β	177.9(4), -174.3(4)	-175.7(5)	179.3(6)	-179.5(6)	-169.5(3)	-171.1(2)	-169.6(7)	177.1(3)	178.5(3)
γ	-64.0(7), 63.1(7)	175.3(6)	175.0(7)	176.0(8)	-174.6(4)	-176.0(3)	-178.1(8)	-176.1(4)	-179.4(4)
δ	-62.7(8), 63.9(7)	-63.6(8)	-54.3(10)	-57.6(10)	-176.9(4)	-176.9(3)	178.2(2)	65.0(4)	-62.0(5)
γ'	177.0(6), -179.0(5)	-62.6(7)	-61.4(8)	-60.9(8)	65.3(6)	65.5(4)	65(1)	65.1(4)	-65.8(5)
β'	-176.6(5), 176.1(4)	177.6(4)	174.0(5)	174.4(5)	60.0(6)	64.2(4)	62(7)	-178.4(3)	176.4(3)
α'	-61.7(5), 59.5(5)	65.6(5)	-71.8(5)	-70.6(5)	-81.6(4)/-61.9(5)	-75.1(3)	-70.7(7)	-62.2(3)	-62.0(4)
Sequence	2 × <i>gaggag</i>	<i>gaaggag</i>	<i>gaaggag</i>	<i>gaaggag</i>	<i>gaaaggg</i>	<i>gaaaggg</i>	<i>gaaaggg</i>	<i>gaaggag</i>	<i>gaaggag</i>

^a Ref. [5] (other entries: this work); the oxygen is positioned as incipiently bridging, even though the contact is long.

^b Ag,Ag'-O-Cl are 143.7(4), 106.1(3)°.

^c cf. Ref. [7,8]; the NO₃/Ag₂O₂ interplanar dihedral angle is 10.58(8)°.

^d The C₂O₂/Ag₂O₂ interplanar dihedral angle is 61.8(4)°.

^e Ref. [8]; the author notes some dissatisfaction with resolution of certain carbon atoms in the second ligand hydrocarbon string, suggesting the possibility of unresolved disorder, reflected in the large s.u.'s for derivative data, notably the torsion angles here. Data for other compounds are derivative of present work.

^f Ref. [5].

^g Dual entries correspond to the alternative silver atom sites.

The oxyanion complexes display a sequence which encompass the transition from non-bridging to bridging anion, broadly correlating with increase in basicity; the tfa example is an interesting diversion. For X = tfs, **6**, the closest 'bridging' Ag...O contact is Ag...O(3) 3.065(3) Å; the situation here is confused by disorder of the anion over two sets of sites, occupancies 0.675(3) and complement (Fig. 6 (a)). In the α-phase of the perchlorate **3**, determined at 295 K, the anion symmetrically chelates the associated silver, with a longer *trans*-annular contact (Ag...O(2) 3.104(4) Å), while in the β-form (Fig. 6 (b)), determined at ca. 153 K, where there are two independent centrosymmetric similar dimers in the structure, in each case one oxygen atom clearly bridges both metal atoms reasonably symmetrically, although the chelate interaction persists (Ag-O(n22) 3.133(2), 2.881(2) Å (n = 1,2)); Ag...Ag are rather shorter in the latter than in the α-form. Finally, with the most strongly basic anion, X = ac, **4**, one oxy-

gen atom of each anion bridges the two metals (Fig. 6 (c)), some slight asymmetry possibly consequent on the asymmetry of the CH₃O peripheral atom dispositions, and the Ag...O(2) interaction (3.273(3) Å). In this latter complex, Ag...Ag is much shorter than in the others.

Given the above trend, it is remarkable that the X = tfa complex, **5**, is not also of the above type. Indeed it is dimeric, but with decidedly non-bridging X which are unidentate to the silver. The explanation is to be found in the association of one water molecule of hydration with the dimer (Fig. 6 (d)), which, having 2 rather than $\bar{1}$ symmetry presents the uncoordinated oxygen atoms to the water molecule hydrogens, the oxygen well drawn into the molecular core. H...O(2) is 2.01(5) Å. Ag...Ag is long in this complex, in keeping with a more extended hydrocarbon chain conformation in the ligand (Table 2).

With the exception of a limited number of dppn adducts, the structurally defined dppx arrays for x = b, n,

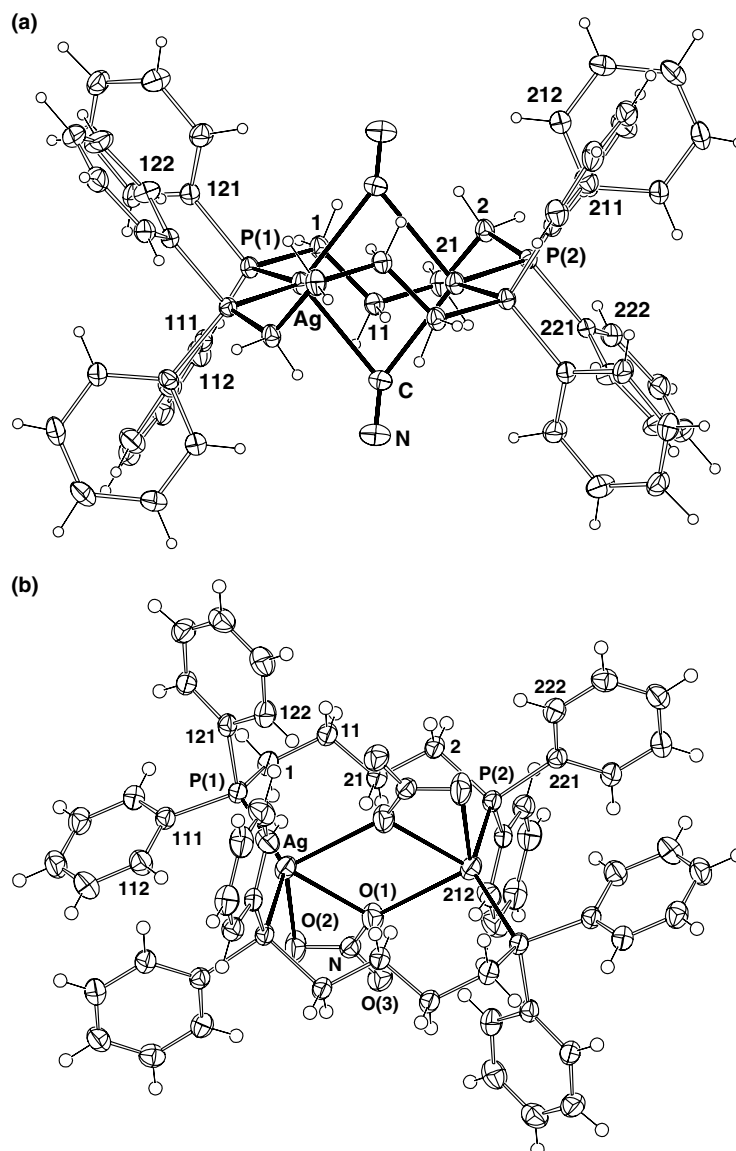


Fig. 7. (a), (b) Projections of the centrosymmetric dimers of AgX:dppb (1:2)_2 $\text{X} = \text{CN}$, **12**, NO_3 , **14**, normal to the central Ag_2X_2 core planes, showing the two types of ligand hydrocarbon chain conformation.

h, $\text{M} = \text{Cu}$, Ag , are all binuclear and all of the $[\text{M}(\mu\text{-X})_2(\text{P-dppx-P}')_2\text{M}]$ form, the two metal atoms being bridged by both phosphine and halide ligands.¹ Interestingly, no oxanion adducts have been crystallized with dppn; for the remainder, we find that, regardless

¹ In this form, as in most of those remaining to be discussed, with dppx, $x = 4, 5, 6$ ligands, the two phosphine ligands bridge the two metal atoms, $[\text{M}(\text{P-dppx-P}')_2\text{M}]$, in a manner described for the more extended ligands as an 'anion trap' by other workers [5]. Given the almost ubiquitous persistence of the $\text{M}(\mu\text{-X})_2\text{M}$ motif throughout these complexes of dppx ($x \geq 3$), this appears to us a misnomer; the $\text{M}(\mu\text{-X})_2\text{M}$ kernel is 'wrapped' or enveloped by the pair of dppx ligands and we suggest the alternative terminology of 'parcel' compound.

of metal, the M_2X_2 cores for the dppp, dppb adducts in the oxanion arrays are four-membered rings, one oxygen only of the anion serving to bridge the two metal atoms (although other oxygens may be involved in coordination by (partial) chelation) (Table 3). With dpph, in those adducts which have been structurally characterized (Table 3), the anion coordinates in extended fashion as O-X-O' rather than $\mu\text{-O-X}$, although the evidence of the halide complexes suggests the latter mode is not precluded by considerations such as strain associated with different hydrocarbon conformations. For a given dppx, the latter are widely constant for diverse arrays of bridging X anions and metals M (Table 3); for complexes containing hydrocarbon chains with odd numbers of

carbon atoms (dppp, dppn), torsion angles exhibit symmetry about the central atom of the chain, the sign unchanged for dppn but reversed for dppp, while for the chains of the dppb, dpph complexes no such symmetry is found. The conformations of the ligands within the arrays of largest P–Ag–P angle are different to those with smaller angle (Table 3). In the majority of structures, where the dimer is disposed about a crystallographic inversion centre, the conformation of one ligand is the obligate inverse of the other, an arrangement tending to persist in the absence of the crystallographic inversion, but there are a couple of examples where the dimer is disposed about a 2-axis. Specifically, for the dppp ad-

ducts it is of interest to note the different conformation adopted by the ligands in the copper(I) complexes where the ligand is a compact chelate, cf. the silver(I) counterparts, where the ligands are extended to encompass the $M(\mu-X)_2$ core of the dimer. In the dppb adducts, two conformations are found (Fig. 7), defined by whether the torsion about the central bond is *anti* or *gauche*, the former being found with the oxyanion adducts and the latter the (pseudo-) halides thus far defined for both Cu(I) and Ag(I) (Table 3(a)). Of the dppn dimers (see above), the ligand conformation in the silver bromide adduct is aberrant, a new unsymmetrical type, disordered over its two possible orientations,

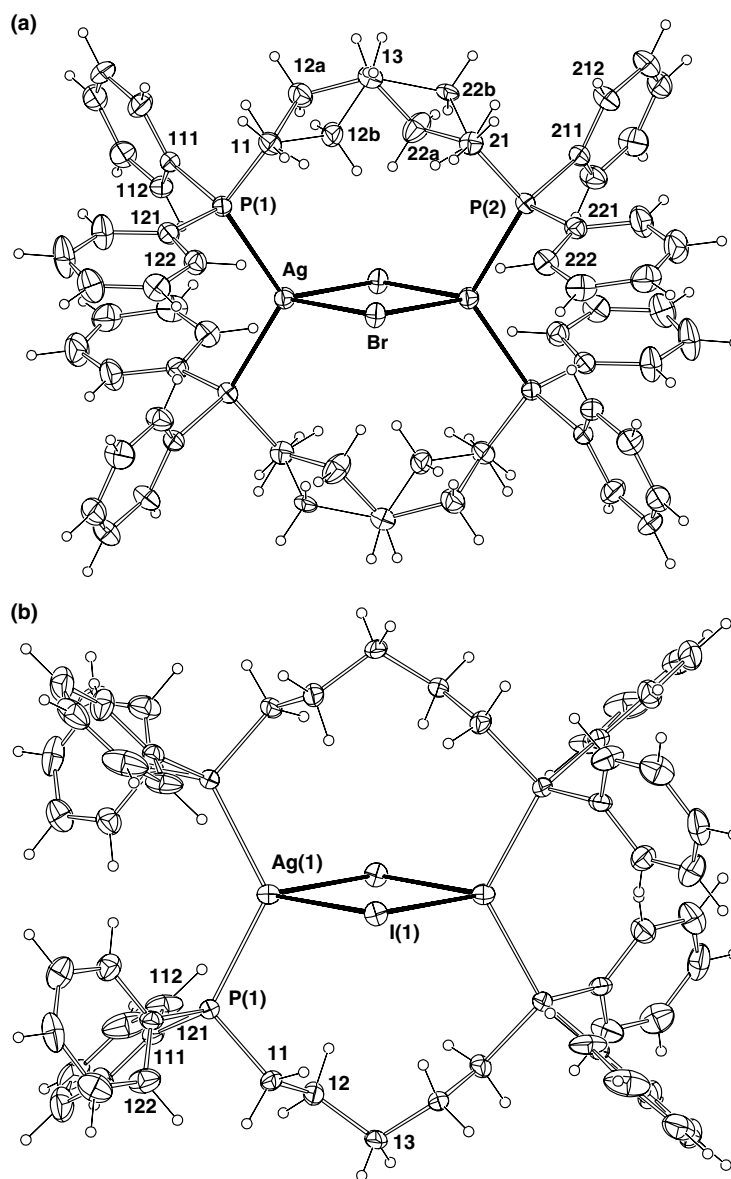


Fig. 8. (a), (b) Projections of the dimers of $AgX:dppn$ (1:1)₂, X = Br (**19**; centrosymmetric), I (**20**; molecule 1 (222 symmetry)), through the central Ag_2X_2 core planes.

being found (see also comment above on the chloride analogue) (Fig. 8).

The flexible and extended hydrocarbon chain of the dpnh ligand has an increased adaptability vis-à-vis accommodation of different combinations of M, X – as uni- or ambi-dentate bridge, and conformation, and here we find a greater variety of conformational possibilities realized than in the complexes of the ‘shorter’ ligands. All arrays contain three *anti* torsions in their string, but with variations in location – the (thio)cyanates have these sequentially to one end of the ligand, beginning at the centre (e.g. Fig. 9), while in the remainder, the central one becomes *gauche*, being relocated to the other side, so that in the bonds between the phosphorus atoms, the (‘normalized’) sequence is transformed from *gaaggg* to *gaaggag*. In the latter, the peripheral *gauche* bonds may have various sign combinations relative to the central *gg* pair. We finally note the recording of examples of ‘parcel’ type compounds with related ligands, e.g., AgX:*o,m*-PP (1:1)₂ (*o,m*-P,P'≡1,2/1,3-bis[(diphenylphosphino)methyl]benzene) [30], AgBF₄:^tBu₂P(CH₂)₃P^tBu (1:1)₂ [31].

A number of adducts of MX:dpnh (1:1) stoichiometry are not of dimeric form. As noted above, a number of adducts of AgX with the dpnh ligand adopt a polymeric form-P₂Ag(μ-X)₂Ag(P-dppn-P)₂Ag(μ-...), propagated by inversion centres between the silver atoms, their geometries being conveniently given in Table 1, where the [(dppp-P,P)Cu(μ-X)₂Cu(P,P-dppp)] arrays with similar cores are also listed, differing from the silver(I) adducts in that the constraint of the dppp chelate might be expected to be demanding, more so than the bridging dpnh pair. The latter are defined for X = Cl, NCO, SCN

(Fig. 10); interestingly the cyanate bridges solely through the nitrogen atom, so that an Ag(μ-NCO)₂Ag four-membered ring results, whereas the thiocyanate linked is extended, bonding through both ends, yielding the familiar Ag $\begin{pmatrix} \text{SCN} \\ \text{NCS} \end{pmatrix}$ Ag eight-membered ring, result-

ing in the (μ-NCO)₂ bidentate array subtending an appreciably smaller ‘bite’ angle at the metal, with concomitant flow-on effects to the other geometrical parameters about the metal. Direct comparison of the silver environment is possible with the (1:1)₂ dpnh:AgSCN complex, **30**, showing significant differences, suggesting that even with these extended ligands, conformational considerations may not be benign in impact. Such is also the case in making comparison of the present AgCl/dppn structure with the different polymorph previously recorded, wherein significant differences again are found between the two silver environments; more remarkable is the difference in the two independent P–Ag–P angles of the polymer, suggesting that even in this situation, conformational constraints may be significant, a point made particularly pertinently in the fact that there are two independent and quite different polymer structures, the existence of the two isomers showing that it is not solely factors associated with the anion that determine its inclusion or otherwise within the Ag(dppx)₂Ag array. Unsurprisingly, in the present arrays, different ligand conformations may be found, the cyanate, **21**, being a disordered composite. In the present AgX: dpnh (1:1)_{2(∞|∞)} one-dimensional polymers, the Ag(μ-X)₂Ag four- or eight-membered rings alternate within sixteen-membered macrocycles, similar to the manner found in the array recorded for Agtfa:*trans*-Ph₂PCH:CHPh₂(1:

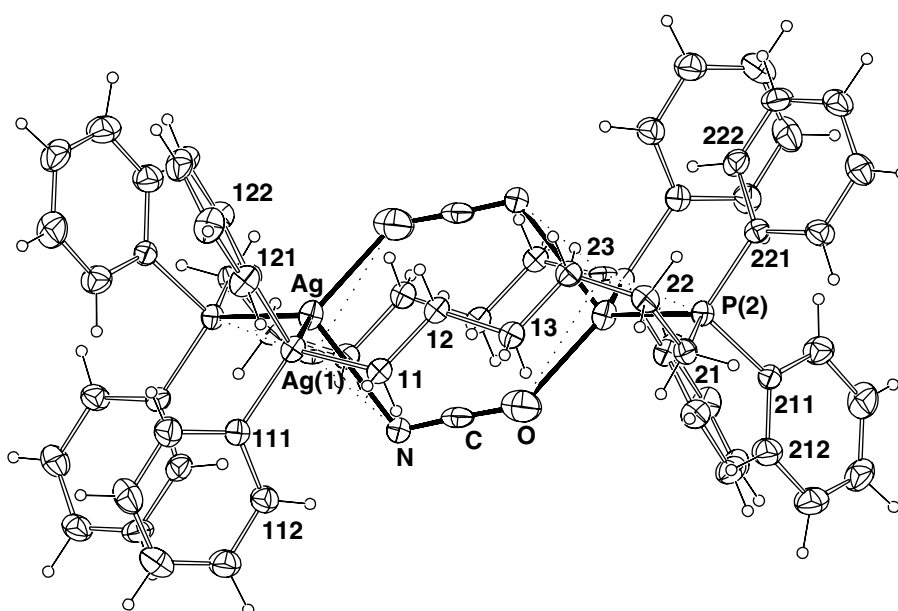


Fig. 9. The centrosymmetric dimer of AgNCO:dpnh (1:1)₂ projected normal to the central core plane showing the silver atom disorder.

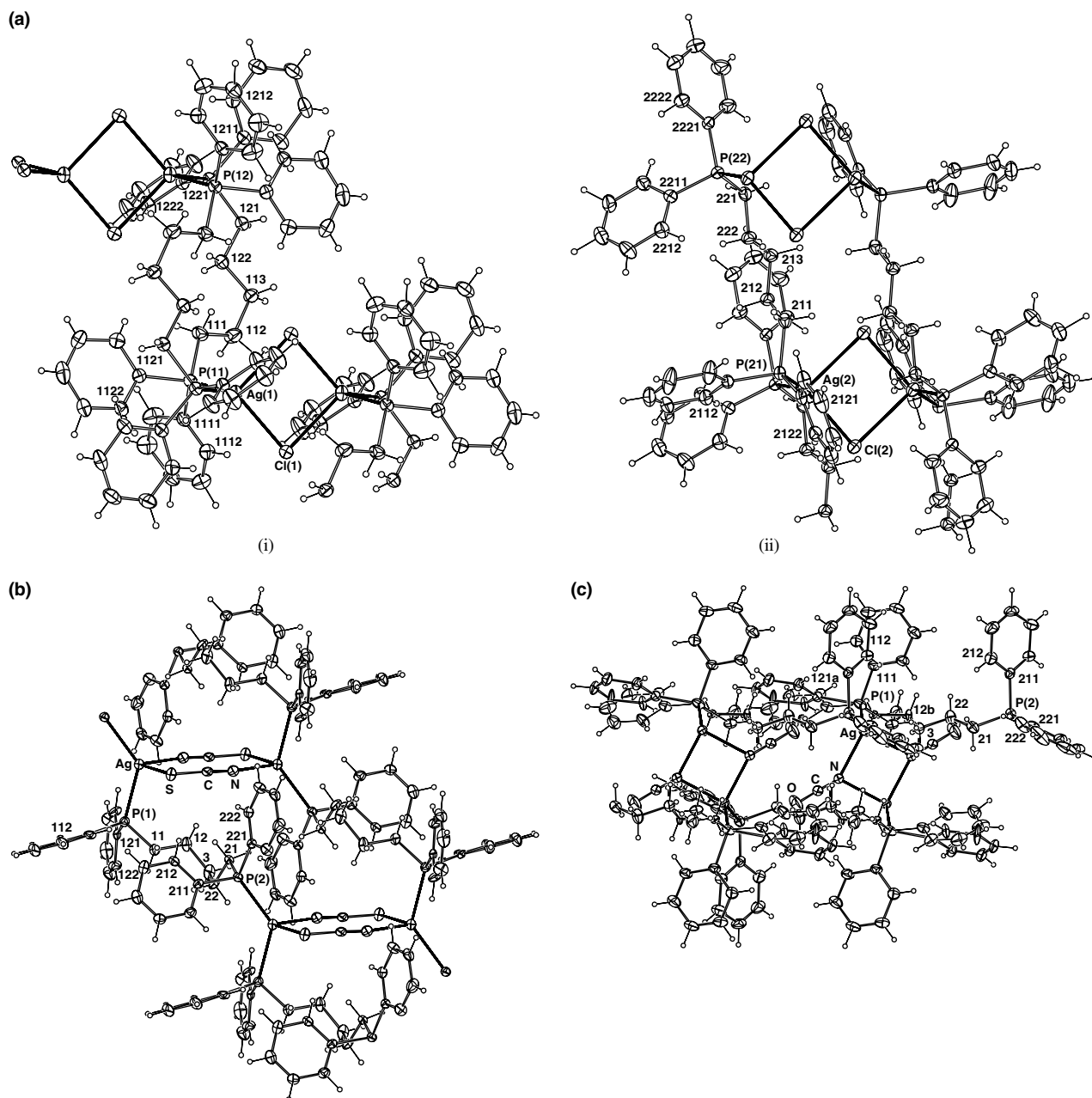


Fig. 10. (a) Projections of the two polymer strands of $\text{AgCl:dppn (1:1)}_{2(\infty|\infty)}$, **18**, normal to the propagation axis, and (i) normal to and (ii) through the Ag_2Cl_2 planes. (b) Projection of $\text{AgSCN:dppn (1:1)}_{2(\infty|\infty)}$, **22**, normal to the propagation axis, through the $\text{Ag}\left(\begin{smallmatrix} \text{SCN} \\ \text{NCS} \end{smallmatrix}\right)\text{Ag}$ 'planes'. (c) Projection of $\text{AgNCO:dppn (1:1)}_{2(\infty|\infty)}$, **21**, normal to the propagation axis, but normal to the AgN_2Ag planes.

$1)_{2(\infty|\infty)}$ [32]. The Agac:dppn (1:1) adduct, **23**, is also an extended polymer (Fig. 11); here, however, the $\text{Ag}(\mu\text{-X})_2$ linkages, defined for the carboxylate as four-membered $\text{Ag}(\mu\text{-O})_2\text{Ag}$ rings in the 1:1 Agac/dppp and Agtf/dppb adducts, are not found, these two coordination sites about the silver being occupied by O, O' -ac as chelate, single $P\text{-dppn-}P'$ linkages connecting these units in a single stranded polymer: $-\text{Agac}(P\text{-dppn-}P)\text{Agac}(P\text{-dppn-}P)$. Related to this adduct is an adventitious cop-

per(I) species with an acetic acid of solvation; $\text{Cuac.Hac:dppn (1:1)}_{(\infty|\infty)}$, **26** (Fig. 11 (b)), in which the acetate is unidentate, the other 'anion' site being occupied by O -acetic acid. Unsurprisingly, over and above the different metals, replacement of the small 'bite' O, O' -bidentate ligand by a pair of unidentate ligands results in quite different geometries for the two species. In the copper complex Cu-O for $O\text{-ac}$ and $O\text{-Hac}$ differ significantly, the anionic form presumably the more tightly

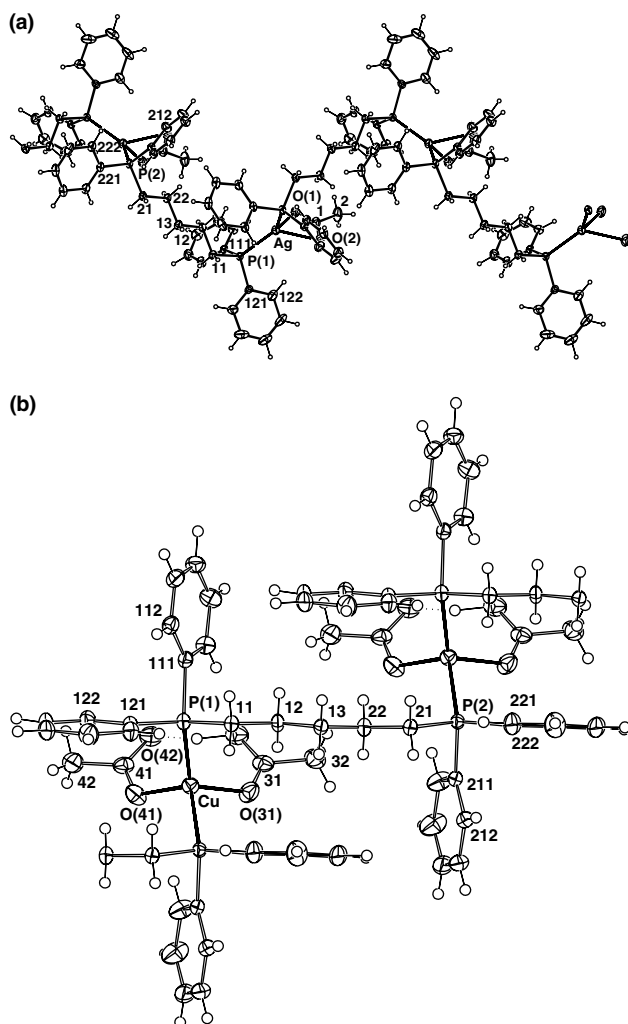
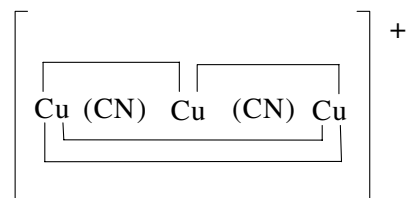


Fig. 11. (a) Projection of Agac:dppn (1:1) $_{\infty}$, normal to the polymer axis. (b) Projection of Cuac:Hac:dppn (1:1) $_{\infty}$, normal to the polymer axis.

bound as might be expected. However, the array is stabilized by a hydrogen bond between the two uncoordinated oxygen atoms of the two species, this constraint possibly also impinging on the copper-environment. H(032) ... O(32,42) are 1.1 $_{6}$, 1.3 $_{2}$ Å (est.), with associated C–O distances 1.293(6), 1.276(6) Å. The dppx arrays in this are the only fully *trans* conformations in the present series of complexes.

Finally, we record the definition of a product obtained adventitiously in small quantity from an attempted crystallization of a CuSCN:dppn adduct on one occasion from acetonitrile. Although obscure in its mode of formation, although SCN $^{-}$ is known to degrade to CN $^{-}$ and SO $_{4}^{2-}$ [33], the components as defined by the X-ray study appear well defined, unambiguous and plausible; it appears unlikely that attempts at ‘rational synthesis’ will be successful and we present the result as an interesting artefact of the above study. The complex in question is CuCN:CuSCN:dppn (2:1:4) acetonitrile

monosolvate, viz. [Cu $_{3}$ (CN) $_{2}$ (dppn) $_{4}$] $^{+}$ (SCN) $^{-}$ · MeCN, **32** one formula unit of which, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. Schematically (Fig. 12, Table 4), the cation is trinuclear, the CN moieties modelled with C, N scrambled.



The environments of all copper atoms are four-coordinate, the outer ones being P $_{3}$ Cu(C/N) and the central P $_{2}$ Cu(C/N) $_{2}$, with geometries similar to those recorded in recent studies [34] and the array overall having quasi-3 symmetry, and all ligands bridging pairs of copper atoms.

Above, and in accompanying papers, we have conjectured on the role of the polymethylene chain (descriptor ‘*x*’ in dppx) as a determinant of the nature of the array obtained. Although in no case is the form of the material obtained clearcut, nevertheless, it appears that one factor may be the bite capable of being adopted by the ligand as a chelate and the feasibility of that, cf. others such as may be found in bridging roles; with extended ligands in particular, we have drawn attention to the multiplicity of hydrocarbon string conformations which may be found. In a related study of the structures of ligands of the form R $_{2}$ P(CH $_{2}$) $_{2}$ PR $_{2}$, R aliphatic [12], attention has been drawn to the difficulty of crystallizing ligands for which *x* is odd. In the present context, we note that, for *x* > 1, structures have been previously defined for *x* = 2, 4, (augmented herein by *x* = 6 (35)), but *not* previously *x* = 3 or 5. These latter are now added (Fig. 13) (33, 34). It is noteworthy that the *x* = 2, 4, 6 ligands crystallise in centrosymmetric lattices with crystallographic inversion centres at the midpoints of (the central C–C bond of) the ligands, a situation not possible with the *x* = 3, 5 systems, one consequence of which is a face-to-face disposition of phenyl rings related by other inversion centres between them and assisting an auspicious crystal packing. Ref. [12] comments further, drawing attention to quasicoplanarity of the hydrocarbon chain with one of the pair of phenyl rings in dppb, a feature continued in dppn, dppb, with one of the disordered pairs in dppp precursive; further comment is made on phosphorus lone-pair ... phenyl interactions, but these appears to be of a tenuous nature in the present – e.g., for ‘dummy’ hydrogen atoms positioned at the phosphorus atoms of non-disordered dppn, dpph, in dppn, H ... H(13,14)C(13,14) (1 $\frac{1}{2}$ – *x*, *y* – $\frac{1}{2}$, *z*) are 2.33(2), 2.12(2), 2.811(2), 2.703(2) Å whereas in dpph there are no H ... H, C(Ph) < 2.6, 3.0 Å (respectively).

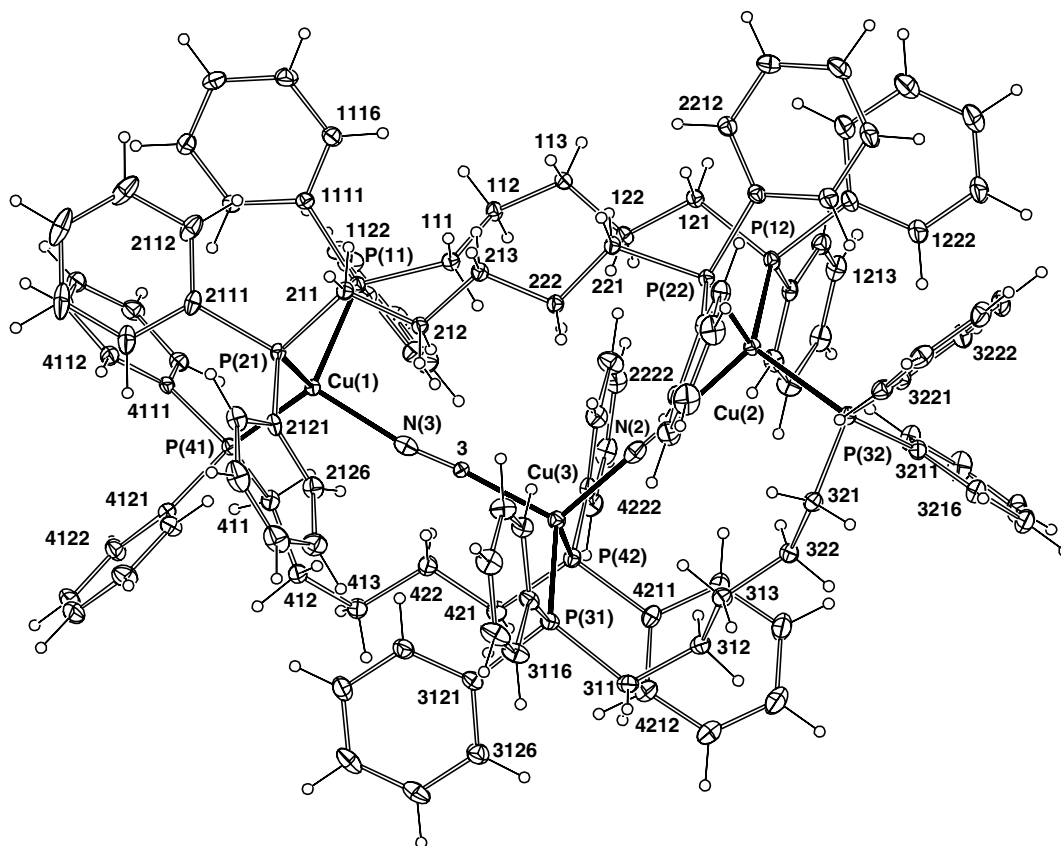
Fig. 12. The $[\text{Cu}_3(\text{CN})_2(\text{dppn})_4]^+$ cation of **32**, projected normal to its quasi-2 axis.

Table 4

Selected geometries, $[\text{Cu}_3(\text{CN})_2(\text{dppn})_4]^+$ (in **32**)

Atoms	Parameter	Atoms	Parameter
<i>Distances ($\text{\AA}$)</i>			
Cu(1)–C/N(3)	2.009(3)	Cu(2)–C/N(2)	2.001(2)
Cu(1)–P(41)	2.2918(7)	Cu(2)–P(32)	2.3197(8)
Cu(1)–P(11)	2.3176(7)	Cu(2)–P(12)	2.2960(8)
Cu(1)–P(21)	2.2915(8)	Cu(2)–P(12)	2.3047(8)
Cu(3)–C/N(2')	1.997(2)	Cu(3)–P(31)	2.2917(8)
Cu(3)–C/N(3')	2.008(3)	Cu(3)–P(42)	2.2721(8)
<i>Angles ($^\circ$)</i>			
C/N–Cu(1)–P(41)	109.75(7)	C/N(2)–Cu(2)–P(32)	107.27(8)
C/N(3)–Cu(1)–P(11)	98.71(7)	C/N–Cu(2)–P(12)	107.70(8)
C/N(3)–Cu(1)–P(21)	109.93(7)	C/N(2)–Cu(2)–P(22)	110.81(8)
P(41)–Cu(1)–P(11)	111.60(3)	P(42)–Cu(2)–P(32)	107.96(3)
P(41)–Cu(1)–P(21)	118.37(3)	P(32)–Cu(2)–P(12)	120.38(3)
P(11)–Cu(1)–P(21)	106.66(3)	P(12)–Cu(2)–P(22)	102.56(3)
C/N(2')–Cu(3)–C/N(3')	108.7(1)	P(31)–Cu(3)–P(42)	107.45(3)
C/N(2')–Cu(3)–P(31)	111.11(8)	C/N(3')–Cu(3)–P(31)	106.81(7)
C/N(2')–Cu(3)–P(42)	113.74(8)	C/N(3')–Cu(3)–P(42)	108.75(7)
<i>Torsion angles ($^\circ$)</i>			
(a) Ligands 1, 2			
α	160.8(2), –58.4(2)	α'	–60.5(2), 58.9(2)
β	166.6(2), 167.8(2)	β'	–179.2(2), 173.6(2)
γ	70.6(3), –174.0(3)	γ'	171.6(2), 172.4(2)
(b) Ligands 3, 4			
α	72.6(2), 63.1(3)	α'	32.4(3), 80.4(2)
β	–142.5(2), –159.6(3)	β'	70.1(3), –156.6(2)
γ	178.1(3), 141.0(3)	γ'	–172.7(3), 68.2(4)

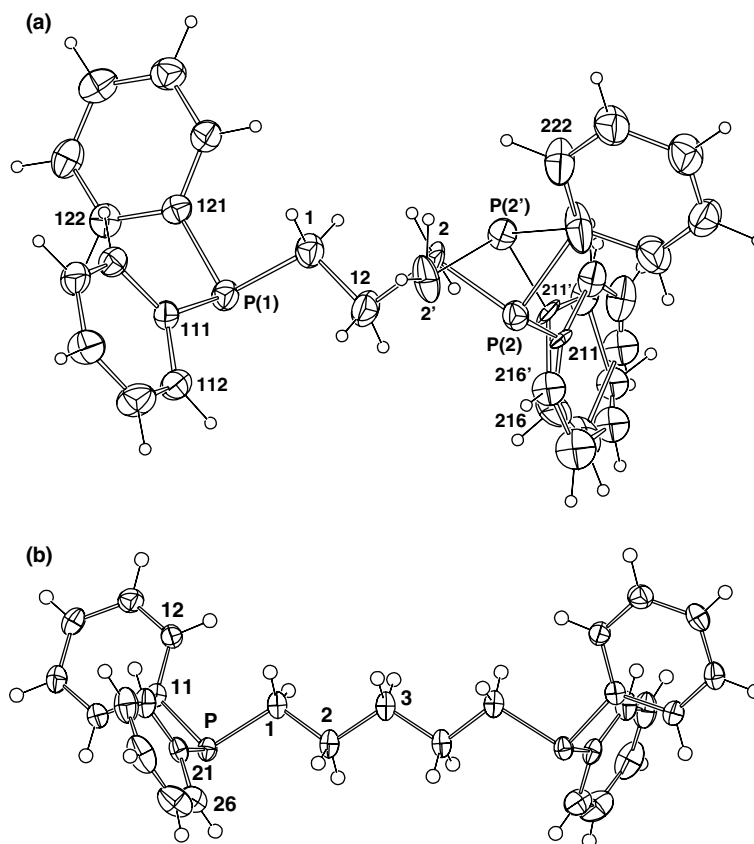


Fig. 13. (a) A single molecule of 'dppp', **33**, showing the disorder present in the structure. (b) A single molecules of 'dppn', **34**, a crystallographic 2-axis passing through the central bond.

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