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New structural features in triphenylphosphinesilver(I) sulfanylcarboxylates†

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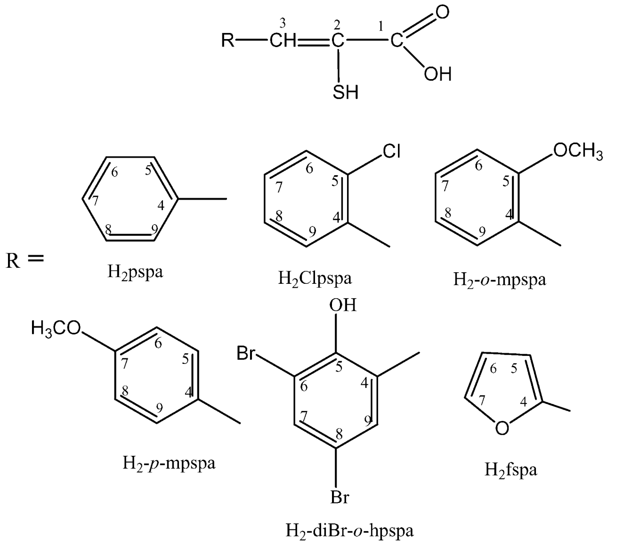
We investigated the reactions of 1.5 : 1 : 1 mole ratio mixtures of triphenylphosphine, silver nitrate and 3-(aryl)-2-sulfanylpropenoic acids H_2xspa in chloroform/water, where in the acid nomenclature, spa = 2-sulfanylpropenoato and x = p, Clp, mp, diBr-*o*-hp or f with p = 3-phenyl-, Clp = 3-(2-chlorophenyl)-, mp = 3-methoxyphenyl-, diBr-*o*-hp = 3-(3,5-dibromo-2-hydroxyphenyl)- and f = 3-(2-furyl)-. The compounds [Ag(PPh$_3$)(Hpspa)](**1**), [(AgPPh$_3$)$_2$(xspa)] [x = Clp (**2**), *o*-mp (**3**), *p*-mp (**4**), diBr-*o*-hp (**5**) and f (**6**)] and [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) were isolated and all except **7** were characterized by IR, Raman and FAB mass spectrometry and by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Compound **6** was also characterized by ^{13}C CP/MAS, and compounds **1** and **6** by ^{109}Ag NMR spectroscopy. The crystal structures of **1, 2, 3, 4**·(CH$_3$)$_2$CO, **5, 6**·(CH$_3$)$_2$CO and **7** were determined by X-ray diffraction. **1** has a supramolecular structure based on hydrogen bonding between dinuclear units, and all the other complexes adopt discrete structures. **2, 3, 4**·(CH$_3$)$_2$CO, **5**, and **6**·(CH$_3$)$_2$CO are tetranuclear, and **7** mononuclear. The tetranuclear complexes contain the eight-membered coordination ring $Ag_4S_2O_2$ (**2, 3, 4**·(CH$_3$)$_2$CO, **6**·(CH$_3$)$_2$CO) or the twelve-membered ring $Ag_4(CO_2)_2S_2$ (**5**).

Introduction

The biological and/or medicinal activities of the thiolate complexes of Ag(I) and Au(I) have increased interest in the coordination chemistry and structures of these compounds.[1–6] Au(I) thiolates can have antiarthritic,[1,7] antitumor[1,3,8,9] and antimicrobial activities,[4,5a–e] while the antibacterial effects of silver compounds have long been known, and silver nitrate and certain silver complexes are still used against local infections, Nomiya *et al.*[5f] have shown that the key factors determining the antimicrobial effects of silver complexes include the kind of atom co-ordinated to the silver(I) atom and the ease with which the ligand is exchanged with biologically relevant ligands.

A number of Au(I) complexes of types [Au(PPh$_3$)(Hxspa)], [HQ][Au(PPh$_3$)(xspa)] and [(AuPPh$_3$)$_2$(xspa)] [HQ = diisopropylammonium; spa = 2-sulfanylpropenoato; x = f, t, p, where f = 3-(2-furyl)-, t = 3-(2-thienyl)-, and p = 3-phenyl-] were recently studied in our laboratories,[10] and the structures of other triphenylphosphinegold(I) sulfanylcarboxylates have also received attention (see ref. 10). However, the only similar compounds of silver(I) to have had their structures elucidated are, as far as we know, [Ag(PPh$_3$)$_3$(Hmna)][11] (H$_2$mna = 2-sulfanylnicotinic acid), [Ag(PPh$_3$)$_3$ (Hmba)][12] (H$_2$mba = 2-sulfanylbenzoic acid) and [H$_4$Ag$_8$(2-mpa)$_6$(PPh$_3$)$_6$].EtOH (2-H$_2$mpa = racemic 2-sulfanylpropionic acid).[13] [Ag(PPh$_3$)$_3$(Hmna)][11] and [Ag(PPh$_3$)$_3$(Hmba)][12] are mononuclear, and [H$_4$Ag$_8$(2-mpa)$_6$(PPh$_3$)$_6$].EtOH[13] is octanuclear; all three have Ag–S and Ag–P bonds but no Ag-carboxylate bonds.

We have now prepared triphenylphosphinesilver(I) complexes of the 3-(aryl)-2-sulfanylpropenoic acids depicted in Scheme 1. The R groups of these acids were chosen partly to allow comparison of the structures of Ag(I) and Au(I) compounds with the same ligands, partly because of the possibility of their engaging in intra- or intermolecular interactions, and partly because of their likely influence on the hydrophilicity and lipophilicity of the complexes prepared, which are of great importance for their pharmaceutical activity.[1,14,15] This paper describes the structures of [(AgPPh$_3$)(Hpspa)] (**1**), [(AgPPh$_3$)$_2$(Clpspa)] (**2**), [(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**), [(AgPPh$_3$)$_2$(*p*-mpspa)]·(CH$_3$)$_2$CO (**4**·(CH$_3$)$_2$CO), [(AgPPh$_3$)$_2$(diBr-*o*-hpspa)] (**5**), [(AgPPh$_3$)$_2$-(fspa)]·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO) and [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) where Clp = 3-(2-chlorophenyl), mp = 3-methoxyphenyl, diBr-*o*-hp = 3-(3,5-dibromo-2-hydroxyphenyl) and f = 3-(2-furyl). **1** has a supramolecular structure, based on hydrogen bonding between dinuclear units, and all the other complexes adopt discrete structures; **2, 3, 4**·(CH$_3$)$_2$CO, **5**, and **6**·(CH$_3$)$_2$CO are tetranuclear and **7** mononuclear. The tetranuclear complexes contain the unprecedented eight-membered coordination



Scheme 1

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† Electronic supplementary information (ESI) available: Molecular structures of [(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**), [(AgPPh$_3$)$_2$(*p*-mpspa)] (**4**), [(AgPPh$_3$)$_2$(fspa)] (**6**). ^{109}Ag NMR spectra of **6** and **1** (Figs. S1–S4). See http://www.rsc.org/suppdata/dt/b5/b501309g/

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ring $Ag_4S_2O_2$ (**2, 3, 4**·$(CH_3)_2CO$, **6**·$(CH_3)_2CO$) or the twelve-membered ring $Ag_4(CO_2)_2S_2$ (**5**).

Experimental

Material and methods

2-Chlorobenzaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, 3,5-dibromo-2-hydroxybenzaldehyde and furfural-2-carboxaldehyde (all from Aldrich), benzaldehyde (Probus), triphenylphosphine (Riedel-de-Haën) and silver nitrate (Prolabo) were all used as supplied.

Elemental analyses were performed with a Fisons 1108 microanalyser. Melting points were determined with a Büchi apparatus and are uncorrected. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 system and operating in FAB mode (*m*-nitrobenzyl alcohol, Xe, 8 eV; *ca.* 1.28×10^{-15} J); ions were identified by DS90 software and the data characterizing the metallated peaks were calculated assuming the Ag isotope to be ^{107}Ag. IR spectra (KBr pellets or Nujol mulls) and Raman spectra (polycrystalline samples) were recorded on a Bruker IFS66V FT-IR spectrometer equipped with an FRA-106 Raman accessory, and are reported in the synthesis section using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. ^{1}H and ^{13}C NMR spectra in solution were recorded in dmso-d_6 or $CDCl_3$ at room temperature on a Bruker AMX 300 operating at 300.14 (^{1}H) and 75.40 MHz (^{13}C), using 5 mm o.d. tubes; chemical shifts are reported relative to TMS using the solvent signal (δ ^{1}H = 2.50 ppm; δ ^{13}C = 39.50 ppm or δ ^{1}H = 7.26 ppm; δ ^{13}C = 77.00 ppm) as reference. ^{1}H–^{1}H COSY NMR spectra were recorded, and ^{1}H–^{13}C HMBC (heteronuclear multiple bond correlation) and HMQC (heteronuclear multiple quantum coherence) experiments were performed, using a Varian Inova 400 spectrometer. ^{31}P NMR spectra were recorded at 202.46 MHz on a Bruker AMX 500 spectrometer using 5 mm od tubes, and are reported relative to external H_3PO_4 (85%). Since the ligands rapidly decompose in dmso-d_6, ^{1}H and ^{13}C NMR data were obtained from freshly prepared concentrated solutions.

Solid-state ^{13}C (75.40 MHz) spectra were recorded at room temperature using a Bruker AMX 300 spectrometer equipped with a CP/MAS (cross-polarization magic angle spinning) accessory. Samples were packed in 7 mm Zirconia rotors and spun at 3.0 and 4.0 kHz at the "magic" angle. ^{109}Ag NMR spectra were acquired at 23.27 MHz from solutions in a 4 : 1 mixture of dmso and dmso-d_6 in 10 mm od tubes in a Bruker AMX500 apparatus, and were referenced by the substitution method using a 4M solution of $AgNO_3$ in D_2O ($\delta = 0$) as standard.

Synthesis

The 3-(Aryl)-2-sulfanylpropenoic acids H_2pspa, H_2Clpspa, H_2-*o*-mpspa, H_2-*p*-mpspa, H_2-diBr-*o*-hpspa and H_2fspa were prepared[16] by condensation of the appropriate aldehyde with rhodanine, subsequent alkaline hydrolysis of the 5-substituted rhodanines so obtained (Rod-pspa, Rod-Clpspa, Rod-*o*-mpspa, Rod-*p*-mpspa, Rod-diBr-*o*-hpspa and Rod-fspa), and acidification with aqueous HCl.

H_2pspa. Rod-pspa (2.21 g, 10 mmol), 1M NaOH (50 cm^3), 1 M HCl (50 cm^3), yellow solid. Yield: 70%. Mp: 123° C. Anal. found, C 59.4, H 4.4, S 17.5%; calc. for $C_9H_8O_2S$, C 60.0, H 4.4, S 17.8%. IR and Raman (R) (cm^{-1}): 1670vs, ν(C=O); 1416s, δ(OH); 1266vs, ν(C–O); 2567m 2570w (R), ν(S–H). NMR (dmso-d_6): ^{1}H, δ 12.6 (w, 1H, C(1)OH), 5.22 (vw, 1H, C(2)SH), 7.73 (s, 1H, C(3)H), 7.68 (d, 2H, C(5)H, C(9)H), 7.47 (t, 2H, C(6)H, C(8)H) and 7.39 (m, 1H, C(7)H); ^{13}C, δ 167.1 C(1), 129.5 C(2), 145.6 C(3), 134.4 C(4), 131.3 C(5), C(9), 129.4 C(6), C(8) and 130.8 C(7).

H_2Clpspa. Rod-Clpspa (2.55 g, 10 mmol), 2 M NaOH (50 cm^3), 2 M HCl (50 cm^3), beige solid. Yield: 81%. Mp: 110° C. Anal. found, C 50.4. H 3.2, S 14.7%; calc. for $C_9H_7O_2SCl$, C 50.4, H 3.3, S 14.9%. IR and Raman (R) (cm^{-1}): 1638vs, ν(C=O); 1437m, δ(OH); 1259s, ν(C–O); 2561m 2564m (R), ν(S–H). NMR (dmso-d_6): ^{1}H, δ 13.30 (w, 1H, C(1)OH), 7.933 (s, 1H, C(3)H) and 7.37 (m, 4H, C(6)H, C(7)H, C(8)H, C(9)H). NMR ($CDCl_3$): ^{1}H, δ 9.49 (w, 1H, C(1)OH), 4.46 (s, 1H, C(2)SH), 8.14 (s, 1H, C(3)H), 7.46 (d, 1H, C(6)H), 7.34 (m, 2H, C(7)H, C(8)H) and 7.82 (d, 1H, C(9)H); ^{13}C, δ 170.6 C(1), 125.5 C(2), 135.1 C(3), 134.6 C(4), 1343.5 C(5), 130.3 C(6), 130.8 C(7), 127.7 C(8) and 130.1 C(9).

H_2-*o*-mpspa. Rod-*o*-mpspa (2.51 g, 10 mmol), 1 M NaOH (50 cm^3), 1 M HCl (50 cm^3), yellow solid. Yield: 49%. Mp: 130° C. Anal. found, C 56.5, H 4.6, S 15.7%; calc. for $C_{10}H_{10}O_3S$, C 57.1, H 4.8, S 15.2%. IR and Raman (R) (cm^{-1}): 1664vs, ν(C=O); 1481s, δ(OH); 1282vs, ν(C–O); 2560m 2561w (R), ν(S–H). NMR (dmso-d_6): ^{1}H, δ 13.00 (w, 1H, C(1)OH), 7.92 (s, 1H, C(3)H), 7.70 (d, 1H, C(6)H), 7.02 (t, 1H, C(7)H) 7.40 (t, 1H, C(8)H) 7.08 (d, 1H, C(9)H) and 3.82 (s, 3H, OCH_3); ^{13}C, δ 166.2 C(1), 128.9 C(2), 139.5 C(3), 119.9 C(4), 157.6 C(5), 111.1 C(6), 131.6 C(7), 122.4 C(8), 130.4 C(9) and 55.6 C(OCH_3).

H_2-*p*-mpspa. Rod-*p*-mpspa (2.51 g, 10 mmol), 1 M NaOH (50 cm^3), 1 M HCl (50 cm^3), orange solid. Yield: 67%. Mp: 160° C. Anal. found, C 56.9, H 5.1, S 15.0%; calc. for $C_{10}H_{10}O_3S$: C 57.1, H 4.8, S 15.2%. IR and Raman (R) (cm^{-1}): 1662vs, ν(C=O); 1427m, δ(OH); 1259vs, ν(C–O); 2570m 2570w (R), ν(S–H). NMR (dmso-d_6): ^{1}H, δ 12.90 (w, 1H, C(1)OH), 7.90 (s, 1H, C(3)H), 7.82 (d, 2H, C(5)H, C(9)H), 6.94 (d, 2H, C(6)H, C(8)H) and 3.79 (s, 3H, OCH_3); ^{13}C, δ 166.7 C(1), 125.3 C(2), 145.0 C(3), 126.4 C(4), 133.2 C(5), C(9), 113.9 C(6), C(8), 160.8 C(7) and 55.4 C(OCH_3).

H_2-diBr-*o*-hpspa. Rod-diBr-*o*-hpspa (3.79 g, 10 mmol), 1 M NaOH (50 cm^3), 1M HCl (50 cm^3), beige solid. Yield: 95%. Mp: 120° C. Anal. found, C 30.7, H 1.5, S 8.8%; calc. for $C_9H_6O_3SBr_2$: C 31.9, H 1.8, S 9.4%. IR and Raman (R) (cm^{-1}): 1682vs, ν(C=O); 1449s, δ(OH); 1278vs, ν(C–O); 2565m 2565w (R), ν(S–H). NMR (dmso-d_6): ^{1}H, δ 11.39 (w, 1H, C(1)OH), 10.06 (s, 1H, C(3)H) 9.86 (w, 1H, C(5)OH), 8.07 (d, 1H, C(7)H) and 7.88 (d, 1H, C(9)H); ^{13}C, δ 169.3 C(1), – C(2), – C(3), 124.2 C(4), 155.9 C(5), 111.2 C(6), 140.4 C(7), 113.3 C(8) and 132.9 C(9). NMR ($CDCl_3$): ^{1}H, δ 9.81 (s, 1H, C(3)H), 11.51 (s, 1H, C(5)OH), 7.91 (d, 1H, C(7)H) and 7.67 (d, 1H, C(9)H); ^{13}C, δ – C(1), 118.3 C(2), – C(3), 121.9 C(4), 157.3 C(5), 112.5 C(6), 142.0 C(7), 111.4 C(8) and 134.9 C(9).

H_2fspa. Rod-fspa (2.11 g, 10 mmol), 1 M NaOH (50 cm^3), 1 M HCl (50 cm^3), light brown solid. Yield: 64%. Mp: 109° C. Anal. found, C 49.1, H 3.7, S 18.9%; calc. for $C_7H_6O_3S$: C 49.4, H 3.5, S 18.8%. IR (R) (cm^{-1}): 1673vs, ν(C=O); 1417s, δ(OH); 1266s, ν(C–O); 2568m, ν(S–H). NMR (dmso-d_6): ^{1}H, δ 12.82 (w, 1H, C(1)OH), 7.60 (s, 1H, C(3)H), 7.22 (d, 1H, C(5)H), 6.67 (t, 1H, C(6)H) and 7.87 (d, 1H, C(7)H); ^{13}C, δ 166.4 C(1), 124.5 C(2), 132.0 C(3), 149.9 C(4), 118.8 C(5), 113.4 C(6) and 146.8 C(7). NMR ($CDCl_3$): ^{1}H, δ 4.71 (s, 1H, C(2)SH), 7.75 (s, 1H, C(3)H), 6.90 (d, 1H, C(5)H), 6.58 (t, 1H, C(6)H) and 7.67 (d, 1H, C(7)H); ^{13}C, δ 170.5 C(1), 118.8 C(2), 124.3 C(3), 150.7 C(4), 116.4 C(5), 112.7 C(6) and 144.7 C(7).

Complexes **1–6** were prepared as follows. A solution of the appropriate sulfanylcarboxylic acid and a 56% excess of triphenylphosphine in chloroform was added to a solution of silver nitrate and NaOAc in water, and the mixture was shaken for 20 min. The organic phase was separated using a separation funnel, dried with $MgSO_4$, and the $CHCl_3$ was evaporated under vacuum. The crude oily product was treated with 1 : 1 hexane/ethanol, and the resulting solid was dried *in vacuo* and crystallized from acetone. Crystals of **7** were obtained from the mother liquor (hexane/ethanol) of **6**. Only in the case of the *p*-mpspa derivative did a molecule of $(CH_3)_2CO$ co-crystallize upon initial crystallization although this co-crystallization process also occurred with **6** upon recrystallization from the same solvent.

[(AgPPh$_3$)(Hpspa)] (1). H$_2$pspa (0.74 g, 4.2 mmol), PPh$_3$ (1.71 g, 6.5 mmol), AgNO$_3$ (0.71 g, 4.2 mmol), NaOAc (0.57 g, 6.9 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), yellow crystals. Yield: 45%. Mp: 155 °C. Anal. Found, C 58.8, H 4.1, S 5.6%; calc. for C$_{27}$H$_{22}$O$_2$SPAg, C 59.0, H 4.0, S 5.8%. MS (FAB): the main metallated signals are at m/z 918(14%), [(AgPPh$_3$)$_2$pspa]$^+$; 631(46), [(PPh$_3$)$_2$Ag]$^+$; 369(100), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}): 1637vs, ν(C=O); 1435s, δ(OH); 1252s, ν(C–O); 1479m, 1435s, ν(PPh$_3$). NMR (dmso-d$_6$): ^{1}H, δ 12.56 (w, 1H, C(1)OH), 7.54 (s, 1H, C(3)H), 8.20 (d, 2H, C(5)H, C(9)H), 7.25 (t, 2H, C(6)H, C(8)H), 7.19–7.41 (m, 16H, C(7)H, H(PPh$_3$)); ^{13}C, δ 171.0 C(1), – C(2), 136.5 C(3), 136.2 C(4), 130.2 C(5), 127.5 C(6), 127.3 C(7), 132.0 (d, C$_i$(Ph$_3$), J = 26.4), 133.2 (d, C$_o$(Ph$_3$), J = 17.3), 128.7 (d, C$_m$(Ph$_3$), J = 9.5), 130.1 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 11.3 (s). ^{109}Ag NMR (dmso/dmso-d$_6$): δ 936.3 (s).

[(AgPPh$_3$)$_2$(Clpspa)] (2). H$_2$Clpspa (0.71 g, 3.3 mmol), PPh$_3$ (1.36 g, 5.13 mmol), AgNO$_3$ (0.56 g, 3.3 mmol), NaOAc (0.90 g, 10.9 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), golden crystals. Yield: 45%. Mp: 200 °C. Anal. found, C 56.4, H 3.7, S 3.0%; calc. for C$_{45}$H$_{35}$O$_2$SP$_2$Ag$_2$Cl, C 56.6, H 3.7, S 3.4%. MS (FAB): the main metallated signals are at m/z 1322 (3%), [(AgPPh$_3$)$_3$Clpspa]$^+$; 953 (11), [M]$^+$; 631 (100), [(PPh$_3$)$_2$Ag]$^+$; 369 (91), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}):1533vs, ν_{as}(COO); 1354vs, ν_{sym}(COO); $\Delta\nu$ 179; 1475vs, 1433vs, ν(Ph$_3$P). NMR (dmso-d$_6$): ^{1}H, δ 7.85 (s, 1H, C(3)H), 7.54 (d, 1H, C(6)H), 7.15 (t, 1H, C(7)H), 7.61 (m, 1H, C(8)H), 9.42 (d, 1H, C(9)H), 7.19–7.42 (m, 30H, H(PPh$_3$));^{13}C, δ 171.4 C(1), 125.4 C(2), 135.5 C(3), 142.7 C(4), 132.7 C(5), 128.6 C(6), 131.4 C(7), 125.8 C(8), 127.7 C(9) 133.2 (d, C$_o$(Ph$_3$), J = 17.5), 128.8 (d, C$_m$(Ph$_3$), J = 8.2), 129.8 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 6.9(s), 29.5 (s). NMR (CDCl$_3$): ^{1}H, δ 8.10 (s, 1H, C(3)H), 7.67 (m, 1H, C(6)H), 6.95 (m, 1H, C(7)H), 6.66 (m, 1H, C(8)H), 9.10 (d, 1H, C(9)H), 7.17–7.34 (m, 30H, H(PPh$_3$));^{13}C, δ 168.6 C(1), 125.4 C(2), 133.2 C(3), 138.5 C(4), 135.7 C(5), 129.1 C(6), 130.1 C(7), 127.7 C(8), 128.3 C(9), 133.2 (d, C$_i$(Ph$_3$), J = 15.5), 133.6 (d, C$_o$(Ph$_3$), J = 17.0), 128.7 (d, C$_m$(Ph$_3$), J = 8.8), 129.7 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 3.7 (s), 28.4 (s).

[(AgPPh$_3$)$_2$(*o*-mpspa)] (3). H$_2$-*o*-mpspa (0.50 g, 2.4 mmol), PPh$_3$ (0.98 g, 3.7 mmol), AgNO$_3$ (0.41 g, 2.4 mmol), NaOAc (0.48 g, 3.9 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), orange crystals. Yield: 37%. Mp: 185 °C. Anal. found, C 59.6, H 4.0, S 3.8%; calc. for C$_{46}$H$_{38}$O$_3$SP$_2$Ag$_2$, C 58.2, H 4.0, S 3.4%. MS (FAB): the main metallated signals are at m/z 1317 (1%), [(AgPPh$_3$)$_3$-*o*-mpspa]$^+$; 948 (26), [M]$^+$; 631 (54), [(PPh$_3$)$_2$Ag]$^+$; 369 (100), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}): 1534vs, ν_{as}(COO); 1350vs, ν_{sym}(COO); $\Delta\nu$ 184; 1475m, 1433s, ν(Ph$_3$P). NMR (dmso-d$_6$): ^{1}H, δ 7.93 (s, 1H, C(3)H), 8.99 (d, 1H, C(6)H), 6.67 (t, 1H, C(7)H), 6.88 (d, 1H, C(9)H), 3.69 (s, 3H, OCH$_3$), 7.20–7.60 (m, 31H, C(8)H, H(PPh$_3$));^{13}C, δ 171.8 C(1), 128.2 C(2), 133.2 C(3), 125.8 C(4), 156.7 C(5), 110.2 C(6), 129.4 C(7), 119.1 C(8), 128.5 C(9), 55.3 C(OCH$_3$), 133.1 (d, C$_i$(Ph$_3$), J = 21.3), 133.1 (d, C$_o$(Ph$_3$), J = 17.2), 128.7 (d, C$_m$(Ph$_3$), J = 9.2), 130.1 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 11.0 (s), 29.6 (s).

[(AgPPh$_3$)$_2$(*p*-mpspa)]·(CH$_3$)$_2$CO (4·(CH$_3$)$_2$CO). H$_2$-*p*-mpspa (0.75 g, 3.6 mmol), PPh$_3$ (1.47 g, 5.6 mmol), AgNO$_3$ (0.61 g, 3.6 mmol), NaOAc (0.48 g, 5.9 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), yellow crystals. Yield: 38%. Mp: 195 °C. Anal. found, C 57.9, H 4.2, S 3.3%; calc. for C$_{49}$H$_{44}$O$_4$SP$_2$Ag$_2$, C 58.0, H 4.5, S 3.2%. MS (FAB): the main metallated signals are at m/z 948 (26%), [M]$^+$; 631 (54), [(PPh$_3$)$_2$Ag]$^+$; 369 (100), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}): 1534vs, ν_{as}(COO); 1354, ν_{sym}(COO); $\Delta\nu$ 182; 1479s, 1435vs, ν(Ph$_3$P). NMR (dmso-d$_6$): ^{1}H, δ 7.57 (s, 1H, C(3)H), 8.00 (d, 2H, C(5)H), 6.80 (d, 2H, C(6)H), 3.70 (s, 3H, OCH$_3$), 7.03–7.63 (m, 31H, C(3)H, H(PPh$_3$)).

[(AgPPh$_3$)$_2$(diBr-*o*-hpspa)] (5). H$_2$-diBr-*o*-hpspa (0.50 g, 1.5 mmol), PPh$_3$ (1.25 g,4.8 mmol), AgNO$_3$ (0.25 g, 1.5 mmol), NaOAc (0.0.40 g, 4.9 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), white crystals. Yield: 50%. Mp: 190 °C. Anal. found, C 50.7, H 3.6, S 2.4%; calc. for C$_{45}$H$_{34}$O$_3$SP$_2$Ag$_2$Br$_2$, C 50.1, H 3.2, S 3.0%. MS (FAB): the main metallated signals are at m/z 1462 (3%), [(AgPPh$_3$)$_3$-diBr-*o*-hpspa]$^+$; 1092 (12), [M]$^+$; 631 (84), [(PPh$_3$)$_2$Ag]$^+$; 369 (100), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}): 1556s, ν_{as}(COO); 1349s, ν_{sym}(COO); $\Delta\nu$ 207; 1480m, 1434vs, ν(Ph$_3$P). NMR (dmso-d$_6$): ^{1}H, δ 9.98 (s, 1H, C(3)H), 8.73 (w, 1H, C(5)OH), 7.79 (s, 1H, C(7)H), 7.14–7.61 (m, 31H, C(9)H, H(PPh$_3$));^{13}C, δ – C(1), – C(2), – C(3), 122.0 C(4), 159.6 C(5), 112.6 C(6), 138.4 C(7), 109.8 C(8), 135.5 C(9), 133.3 (d, C$_o$(Ph$_3$), J = 16.8), 128.8 (d, C$_m$(Ph$_3$), J = 9.2), 130.1 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 7.0 (s), 29.6 (s). NMR (CDCl$_3$): ^{1}H, δ 9.87 (s, 1H, C(3)H), 6.78 (w, 1H, C(5)OH), 7.84 (d, 1H, C(7)H), 7.10 (d, 1H, C(9)H), 7.19–7.79 (m, 30H, H(PPh$_3$));^{31}P {^{1}H}: δ 2.4 (s), 28.4 (s).

[(AgPPh$_3$)$_2$(fspa)] (6). H$_2$fspa (0.76 g, 4.5 mmol), PPh$_3$ (1.85 g, 7.0 mmol), AgNO$_3$ (0.76 g, 4.5 mmol), NaOAc (0.60 g, 7.3 mmol), CHCl$_3$ (33 cm^3), H$_2$O (66 cm^3), orange crystals. Yield: 43%. Mp: 170° C. Anal. found, C 55.4, H 3.8, S 3.8%; calc. for C$_{43}$H$_{34}$O$_3$SP$_2$Ag$_2$, C 56.8, H 3.7, S 3.5%. MS (FAB): the main metallated signals are at m/z 1278 (2%), [(AgPPh$_3$)$_3$fspa]$^+$; 909 (18), [M]$^+$; 631 (100), [(PPh$_3$)$_2$Ag]$^+$; 369 (65), [(PPh$_3$)Ag]$^+$. IR (cm^{-1}): 1562m, ν_{as}(COO); 1479s, 1435s, ν(Ph$_3$P). NMR (dmso-d$_6$): ^{1}H, δ 7.44 (s, 1H, C(3)H), 7.59 (d, 1H, C(5)H), 6.42 (m, 1H, C(6)H), 7.61 (d, 1H, C(7)H), 7.20–7.43 (m, 30H, H(PPh$_3$));^{13}C, δ 170.2 C(1), 122.2 C(2), 128.6 C(3), 153.4 C(4), 112.9 C(5), 111.9 C(6), 142.0 C(7), 132.5 (d, C$_i$(Ph$_3$), J = 20.7), 133.2 (d, C$_o$(Ph$_3$), J = 17.2), 128.7 (d, C$_m$(Ph$_3$), J = 9.2), 129.9 C$_p$(Ph$_3$); ^{31}P {^{1}H}: δ 10.2 (s), 29.8 (s). NMR (CDCl$_3$): ^{1}H, δ 7.62 (s, 1H, C(3)H), 7.44 (d, 1H, C(5)H), 6.14 (t, 1H, C(6)H), 7.58 (d, 1H, C(7)H), 7), 7.16–7.54 (m, 30H, H(PPh$_3$));^{13}C, δ 169.2 C(1), 123.7 C(2), 128.4 C(3), 154.8 C(4), 112.6 C(5), 111.5 C(6), 141.7 C(7), 132.9 (d, C$_i$(Ph$_3$), J = 18.2), 133.5 (d, C$_o$(Ph$_3$), J = 18.4), 128.8 (d, C$_m$(Ph$_3$), J = 9.2), 129.7 C$_p$(Ph$_3$), ^{31}P {^{1}H}: δ 5.2 (s), 28.5 (s). Solid NMR ^{13}C, δ 167.9 C(1), 123.3 C(2), – C(3), 155.2 C(4), 112.8 C(5), 112.0 C(6), 139.8 C(7), 136.4, 133.6, 132.6, 129.7 C(Ph$_3$). ^{109}Ag NMR (dmso/dmso-d$_6$): δ 1033.4 (s). After separating the initial batch of **6** a small number of single crystals of [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) were obtained at room temperature from the mother liquor (ethanol/hexane). Crystals of **6**·(CH$_3$)$_2$CO suitable for X-ray diffractometry were obtained upon recrystallization of **6** from acetone.

Crystallography

X-Ray data collection and reduction. Single crystals of [(AgPPh$_3$)(Hpspa)] (**1**), [(AgPPh$_3$)$_2$(Clpspa)] (**2**), [(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**), [(AgPPh$_3$)$_2$(*p*-mpspa)]·(CH$_3$)$_2$CO (**4**·(CH$_3$)$_2$CO), [(AgPPh$_3$)$_2$(diBr-*o*-hpspa)] (**5**), [(AgPPh$_3$)$_2$(fspa)]·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO) and [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) were mounted on glass fibres in a Bruker Smart CCD automatic diffractometer. Data were collected at 293 K using Mo Kα radiation (λ = 0.71073 Å). Corrections for Lorentz effects, polarization[17a] and absorption[17b] were made. Table 1 summarizes the crystal data, experimental details and refinement results.

Structure analyses were carried out by direct methods.[17c] Least-squares full-matrix refinements on F^2 were performed using the program SHELXL97. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref. 17*d*. Reflection data for **4**·(CH$_3$)$_2$CO and **6**·(CH$_3$)$_2$CO were corrected for the diffuse scattering due to disordered solvent molecules by means of the program SQUEEZE.[17e] All non-hydrogen atoms were refined anisotropically, although in **4**·(CH$_3$)$_2$CO the same anisotropic factor was used for all the carbon atoms of one of the triphenylphosphine phenyl rings (C121–C126). Hydrogen atoms were refined as riders. Graphics were obtained with PLATON.[18]

CCDC reference numbers 261747–261753.

Table 1 Crystal data for [Ag(PPh$_3$)(Hpspa)] (**1**), [Ag(PPh$_3$)$_2$Clpspa] (**2**), [(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**), [(AgPPh$_3$)$_2$(*p*-mpspa)]·(CH$_3$)$_2$CO (**4**·(CH$_3$)$_2$CO), [(AgPPh$_3$)$_2$(diBr-*o*-hpspa)] (**5**), [(AgPPh$_3$)$_2$(fspa)]·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO), and [Ag(PPh$_3$)$_3$(Hfspa)] (**7**)

Compound	[Ag(PPh$_3$)(Hpspa)] (**1**)	[(AgPPh$_3$)$_2$(Clpspa)] (**2**)	[(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**)	[(AgPPh$_3$)$_2$(*p*-mpspa)]·(CH$_3$)$_2$CO (**4**·(CH$_3$)$_2$CO)	[(AgPPh$_3$)$_2$(diBr-*o*-hpspa)] (**5**)	[(AgPPh$_3$)$_2$(fspa)]·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO)	[Ag(PPh$_3$)$_3$(Hfspa)] (**7**)
Empirical formula	$C_{27}H_{22}AgO_2PS$	$C_{45}H_{35}Ag_2O_2P_2SCl$	$C_{46}H_{38}Ag_2O_3P_2S$	$C_{48}H_{43}Ag_2O_4P_2S$	$C_{45}H_{34}Ag_2O_3P_2SBr_2$	$C_{46}H_{40}Ag_2O_4P_2S$	$C_{61}H_{50}AgO_3P_3S$
M	549.35	952.92	948.50	993.56	1092.28	966.52	1063.85
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$	$P2(1)/n$
a/Å	14.056(4)	11.7866(10)	13.4962(9)	12.6832(13)	15.7725(9))	17.5325(12)	12.2174(16)
b/Å	9.356(3)	13.2797(12)	17.1129(11)	13.5698(14)	17.2472(10)	13.1244(9)	20.525(3)
c/Å	19.162(5)	14.8441(13)	18.6400(11)	15.7147(17)	17.4361(9)	18.6677(12)	20.943(3)
α/°		113.369(2)		107.707(2)			
β/°	109.806(6)	104.383(2)	107.1740(10)	98.165(2)	116.0150(10)	100.0680(10)	95.790(3)
γ/°		96.518(2)		113.460(2)			
U/Å^3	2370.7(11)	2006.4(3)	4113.1(5)	2253.8(4)	4262.6(4)	4229.4(5)	5224.9(12)
Z	4	2	4	2	4	4	4
D_c/Mg M^{-3}	1.539	1.577	1.532	1.464	1.702	1.518	1.352
μ/mm^{-1}	1.028	1.212	1.121	1.028	2.957	1.093	0.563
Crystal size/mm	0.19 × 0.11 × 0.03	0.19 × 0.13 × 0.09	0.21 × 0.20 × 0.19	0.26 × 0.24 × 0.22	0.28 × 0.26 × 0.12	0.14 × 0.18 × 0.36	0.15 × 0.20 × 0.25
θ Range for data collection/°	1.57–28.03	1.58–28.05	1.58–28.01	1.43–28.08	1.44–28.03	1.75–28.05	1.85–28.03
Index ranges	$-18\le h\le 10$, $-12\le k\le 12$, $-19\le l\le 25$	$-15\le h\le 15$, $-12\le$ k ≤ 17, $-19\le l\le 15$	$-17\le h\le 15$, $-22\le k\le 22$, $-24\le l\le 22$	$-16\le h\le 15$, $-17\le k\le 17$, $-20\le l\le 14$	$-19\le h\le 20$, $-14\le k\le 22$, $-22\le l\le 23$	$-23\le h\le 22$, $-17\le k\le 14$, $-22\le l\le 24$	$-10\le h\le 16$, $-25\le k\le 27$, $-26\le l\le 27$
Reflections collect.	11160	12024	22070	12975	23200	22434	29034
Unique reflections,	0.1239	0.0527	0.0737	0.0494	0.0527	0.0605	0.0416
R(int)	5082	8436	9136	9092	9513	9378	11647
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0498, 0.0633	0.0486, 0.0702	0.0414, 0.0767	0.0518,0.1198	0.0359, 0.0469	0.0411, 0.0755	0.0554, 0.0880
All data	0.3461, 0.1041	0.1285, 0.0853	0.1714, 0.0993	0.1257, 0.1198	0.1341, 0.0572	0.1552, 0.0901	0.1029, 0.0996

See http://www.rsc.org/suppdata/dt/b5/b501309g/ for crystallographic data in CIF or other electronic format.

Results and discussion

We initially attempted to prepare the complexes by reacting $AgPh_3NO_3$ and alkaline H_2xspa in 1 : 1 or 2 : 1 mole ratio, *i.e.* by the same procedure as previously described[10] for analogous Au(I) complexes. Hovewer, even after tedious purification steps, this method only afforded pure compounds in the case of the 2 : 1 complexes, and even these were non-crystalline. We therefore tried reacting silver nitrate, phosphine and sulfanylcarboxylate under heterogeneous conditions, as described by Becker *et al.*[19] This afforded the 1 : 1 : 1 silver–phosphine–sulfanylcarboxylate complex **1** and the 2 : 2 : 1 complexes **2–6**, and the mother liquor of **6** also afforded the 1 : 3 : 1 complex **7**. This stoichiometric variety suggests that several species are present in the reaction media, the species isolated being determined by their relative solubilities. The coexistence of several species with a different PPh_3 contents has previously been observed by Nomiya *et al.*[11] in solutions of the Ag(I) compounds of 2-sulfanylnicotinic acid.

The presence in the FAB$^+$ mass spectra of signals for both the [M]$^+$ peak and fragments with different PPh_3 contents suggests easy cleavage of Ag–P bonds, and cleavage of Ag–S bonds is also evident.

Solid state studies

$[Ag(PPh_3)(Hspa)]$ (1). Single crystals obtained by slow concentration of an acetone solution of $[Ag(PPh_3)(Hspa)]$ were composed of $[Ag(PPh_3)(Hspa)]_2$ units which can be seen as formed by $Ag(PPh_3)$(Hspa) monomers connected by Ag–S bonds, the metal atom in each monomer being O,S-chelated. Fig. 1 shows this structure, and the most significant structural parameters are listed in Table 2.

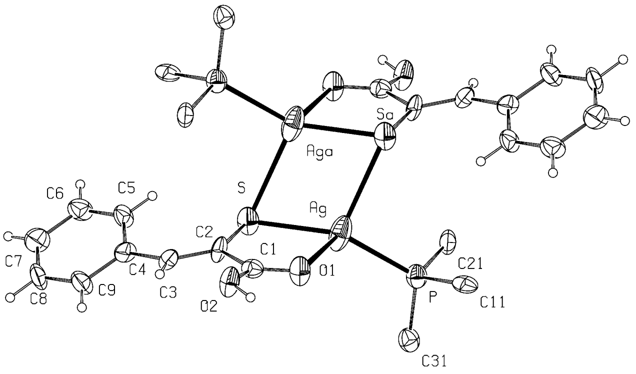


Fig. 1 Molecular structure of $[Ag(PPh_3)(Hspa)]$ (**1**) (for clarity, triphenylphosphine phenyl rings are represented by their P-bound *ipso* carbons).

Table 2 Selected interatomic distances (Å) and angles (°) in $[Ag(PPh_3)(Hspa)]$ (**1**)

(a) Ag environment			
Ag–P	2.369(3)	P–Ag–S	149.83(9)
Ag–S	2.429(2)	P–Ag–O(1)	112.97(16)
Ag–O(1)	2.599(6)	S–Ag–O(1)	74.12(15)
Ag–S#1	2.849(3)	P–Ag–S#1	97.73(9)
Ag–Ag#1	3.1283(19)	S–Ag–S#1	107.80(7)
		O(1)–Ag–S#1	108.69(16)
		Ag–S–Ag#1	72.19(7)
(b) Hspa			
O(1)–C(1)	1.241(9)	O(1)–C(1)–O(2)	121.0(10)
O(2)–C(1)	1.302(9)	O(1)–C(1)–C(2)	121.9(9)
C(1)–C(2)	1.496(11)	O(2)–C(1)–C(2)	117.1(9)
C(2)–C(3)	1.349(10)	C(3)–C(2)–C(1)	115.6(9)
C(3)–C(4)	1.442(10)	C(3)–C(2)–S	125.5(7)
		C(1)–C(2)–S	118.7(7)

The S atoms both bridge asymmetrically between the two silver(I) ions [Ag–S = 2.429(2) Å, Ag–S#1 = 2.849(3) Å], forming a planar Ag_2S_2 core. Each silver(I) is four-coordinated in a distorted tetrahedral AgS_2OP environment, being bound to the two S atoms, the triphenylphosphine P atom [Ag–P = 2.369(3) Å] and one of the carboxylate O atoms [Ag–O(1) = 2.599(6) Å]. The Ag–O(1) distance is at the upper end of the range of Ag–O distances in tetrahedral environments,[20] and is thus indicative of a weak interaction. The coordination of this O atom leads to the formation of an essentially planar AgC_2SO five-membered chelate ring. The Ag1 ··· Ag#1 distance, 3.1283(19) Å, although longer than in metallic silver [2.889(6) Å] is shorter than twice the van der Waals radius of this metal (3.44 Å),[21] and shorter than the 3.1300(3) Å found in $\{[Ag(PPh_3)(SPh)]_4\}$,[22] in which it has been argued that there is a significant bonding interaction between the Ag(I) centres.

The dinuclear units are associated in chains by hydrogen bonds between their carboxy groups (Fig. 2), and the weakness of the Ag–O bond is corroborated by the geometric parameters of both these bonds [0.872(5), 1.789(6), 2.661(8) Å, 177.6(5)° for O(2)–H(2)...O(1)#2] and the CO_2H group (C=O = 1.21–1.25 Å, C–OH = 1.31–1.35 Å) being within their normal ranges.[23]

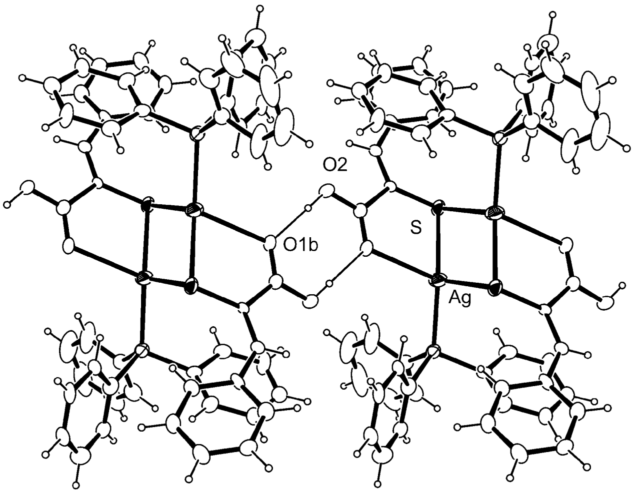


Fig. 2 Hydrogen bonding in $[Ag(PPh_3)(Hspa)]$ (**1**).

Both the structure of **1** and that of $[Ag(pyOS)(PPh_3)]_2$[24] (H_2pyOS = 1-hydroxypyridine-2-thione) are based on an Ag_2S_2 core in which each Ag atom acquires a distorted tetrahedral geometry by co-ordinating to one oxygen, two sulfurs and one phosphorus. The Ag_2S_2 core of **1** is slightly broader and slightly less skewed than that of $[Ag(pyOS)(PPh_3)]_2$, in which the Ag–S distances are 2.057(1) and 2.822(1) Å, Ag–S–Ag 74.8(1)° and S–Ag–S 105.2(1)°. Like **1**, however, $[Ag(pyOS)(PPh_3)]_2$ has a weak interaction between the two silver ions [Ag ··· Ag 3.248(1) Å]. Perhaps the most significant difference between the two compounds is that whereas the dinuclear units of the 1-hydroxypyridine-2-thione derivative are isolated, those of **1** are linked in chains by hydrogen bonds.

The structural differences between **1** and the stoichiometrically similar triphenylphosphinegold(I) sulfanylpropenoato $[Au(PPh_3)(Hfspa)]$[10] are more marked. Although both have similar M–S and M–P bond lengths, the monomers of the gold compound are not linked in dimers by M–S coordinate bonds but by π-stacking between triphenylphosphine phenyl rings and by hydrogen bonds between the CO_2H groups, which are, accordingly, not available for polymerizing interactions. Additionally, the M–O bond is shorter in Ag(I), which narrows the S–M–P angle.

In keeping with deprotonation of S and with the CO_2H group hydrogen bonding shown by the X-ray study, the IR and Raman spectra of $[Ag(PPh_3)(Hspa)]$ do not show the ν(SH)

Table 3 Selected interatomic distances (Å) and angles (°) in [Ag(PPh$_3$)$_3$(Hfspa)] (**7**)

(a) Ag environment			
Ag–P(2)	2.5505(9)	P(2)–Ag–P(1)	110.52(3)
Ag–P(1)	2.5597(8)	P(2)–Ag–P(3)	114.96(3)
Ag–P(3)	2.6120(9)	P(1)–Ag–P(3)	104.76(3)
Ag–S	2.6179(9)	P(2)–Ag–S	116.23(3)
Ag–O(1)	3.997(3)	P(1)–Ag–S	103.68(3)
Ag–O(2)	5.140(3)	P(3)–Ag–S	105.50(3)
(b) Hfspa			
O(1)–C(1)	1.318(5)	O(1)–C(1)–O(2)	120.6(5)
O(2)–C(1)	1.203(5)	O(1)–C(1)–C(2)	115.9(4)
C(1)–C(3)	1.506(6)	O(2)–C(1)–C(2)	123.5(5)
C(2)–C(3)	1.339(5)	C(3)–C(2)–C(1)	117.2(4)
C(3)–C(4)	1.435(6)	C(3)–C(2)–S	126.9(3)
		C(1)–C(2)–S	115.9(3)

band located at 2567 cm^{-1} in the spectrum of H$_2$pspa, and the vibrations of the CO$_2$H group are slightly shifted from their positions in the latter spectrum [1670, ν(C=O); 1416, δ(OH); 1266, ν(C–O)].

[Ag(PPh$_3$)$_3$(Hfspa)] (7). Single crystals of [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) obtained from the mother liquor of **6** are formed of isolated Ag(PPh$_3$)$_3$(Hfspa) units. Fig. 3 shows the molecular structure, and the most significant structural parameters are listed in Table 3. The Ag atom is coordinated to three PPh$_3$ ligands and to the deprotonated S atom of the Hfspa fragment. The angles around the silver atom are those of a very slightly distorted tetrahedron. The Ag–P distances [2.5597(8), 2.5505(9) and 2.6120(9) Å] and the Ag–S distance [2.6179(9) Å] are significantly longer than those found previously in the similar near-tetrahedral complexes [Ag(PPh$_3$)$_3$(Hmna)][11] (H$_2$mna = 2-sulfanylnicotinic acid) and [Ag(PPh$_3$)$_3$(Hmba)][12] (H$_2$mba = 2-sulfanylbenzoic acid) both of which, like **7**, have an AgSP$_3$ core.

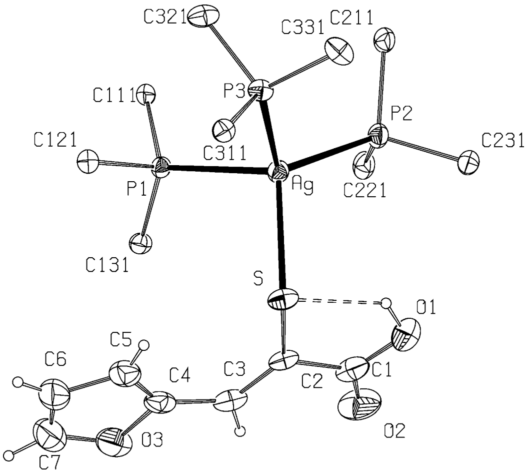


Fig. 3 Molecular structure of [Ag(PPh$_3$)$_3$(Hfspa)] (**7**) (for clarity, triphenylphosphine phenyl rings are represented by their P-bound carbons).

Interestingly, the free CO$_2$H group does not form intermolecular hydrogen bonds as in **1** and [Au(PPh$_3$)(Hfspa)],[10] but a single intramolecular hydrogen bond with the S atom [O(1)–H(1)...S 0.946(3) 2.1590(11) 2.876(3) Å, 131.7(2)°]. As a result, the C(1)–O(2) bond is shorter than in **1** and [Au(PPh$_3$)(Hfspa)], showing greater π-bond character.

[(AgPPh$_3$)$_2$(xspa)] (2, 3, 4·(CH$_3$)$_2$CO and 6·(CH$_3$)$_2$CO). Fig. 4 shows the structure and numbering scheme of the complex [(AgPPh$_3$)$_2$(Clpspa)] (**2**) and Table 4 lists the most significant structural parameters for this complex and for [(AgPPh$_3$)$_2$(*o*-mpspa)] (**3**), [(AgPPh$_3$)$_2$(*p*-mpspa)] (**4**) and [(AgPPh$_3$)$_2$(fspa)] (**6**) (Figs. S1–S3, ESI†). All four complexes are formed by tetranuclear [(AgPPh$_3$)$_2$(xspa)]$_2$ units in which most of the coordinate bonds (shown schematically in Scheme 2) create the eight-membered ring Ag$_4$O$_2$S$_2$. In addition to the bonds forming this ring, there is an Ag–P bond on each Ag atom, and the O(2) atoms form highly asymmetric Ag–O···Ag bridges supplementing the Ag–S–Ag bridges.

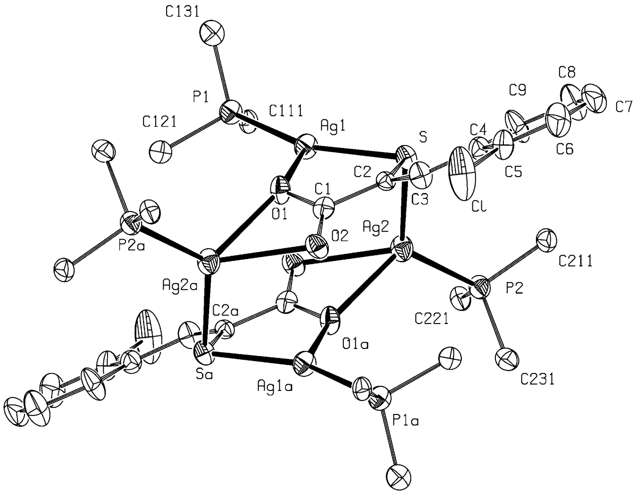
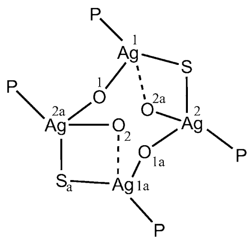


Fig. 4 Molecular structure of [(AgPPh$_3$)$_2$(Clpspa)] (**2**) (for clarity, hydrogen atoms have been omitted and triphenylphosphine phenyl rings are represented by their P-bound carbons).



Scheme 2

Each tetranuclear unit has two types of silver atom with different environments. Ag(1) is essentially three-coordinated, to P(1), S and one of the carboxylate O atoms of the same xspa as the S belongs to [Ag(1)–O(1) = 2.347(4)–2.414(3) Å], although it is also bound weakly[20] by the other carboxylate O atom of the other xspa (xspa#1) [Ag(1)–O(2)#1 = 2.736(4)–2.808(3) Å], the weakness of this bond being confirmed by P(1), Ag(1), S and O(1) being almost coplanar. Ag(2) is four-coordinated to P(2), to the S coordinated to Ag(1), and to both the carboxylate O atoms of xspa#1 [Ag(2)–O(1)#1 = 2.365(4)–2.624(4) Å; Ag(2)–O(2)#1 = 2.470(4)–2.590(5) Å]. In all four compounds the Ag(1)–Ag(2) distance [3.1429(7)–3.3839(8) Å] is shorter than twice the van der Waals radius of this metal (3.44 Å).[21]

Other characteristics common to these four compounds include: (i) the asymmetry of the Ag–S–Ag and Ag–O–Ag bridges; (ii) the almost rectangular Ag–S–Ag angles [79–86°] and much wider main Ag–O–Ag angles [138–147°]; and (iii) the shortness of the Ag–P bond on essentially three-coordinated Ag(1) in comparison with the bond on the four-coordinated Ag(2). It is also worth noting that whereas the Ag(1)–O(1) distance is practically constant (though just a little longer in **6**), O(1)–Ag(2)#1 bond varies in length from 2.365(4) Å in **4** (in which the Ag–O–Ag bridge is practically symmetrical) to 2.624(4) Å in **3** (which has the most asymmetrical bridge). This latter value is at the upper end of the range for Ag–O bonds in tetrahedral Ag environments[20]; a longer O(1)–Ag(2)#1 distance would make the xspa carboxylate group bridge between Ag(1) and Ag(2) in bis-monodentate fashion, as in **5** (see below), instead of being monodentate for Ag(1) and chelating Ag(2).

Table 4 Selected interatomic distances (Å) and angles (°) in the 2 : 1 triphenylphosphinesilver(I) sulfanylcarboxylate complexes **2, 3, 4**·$(CH_3)_2CO$, and **6**·$(CH_3)_2CO$

	2	**3**	**4**·$(CH_3)_2CO$	**6**·$(CH_3)_2CO$
(a) Ag environment				
Ag(1)–P(1)	2.3504(16)	2.3547(17)	2.3503(19)	2.3629(14)
Ag(1)–S	2.4300(15)	2.4577(16)	2.4489(18)	2.4539(13)
Ag(1)–O(1)	2.359(3)	2.356(4)	2.347(4)	2.414(3)
Ag(1)–O(2)#1	2.808(3)	2.736(4)	2.748(4)	2.791(3)
Ag(1)–Ag(2)	3.1429(7)	3.2519(6)	3.3839(8)	3.3111(6)
Ag(2)–P(2)	2.3905(15)	2.3812(15)	2.3784(17)	2.3856(15)
Ag(2)–S	2.5072(14)	2.4593(16)	2.5267(18)	2.5173(14)
Ag(2)–O(1)#1	2.519(3)	2.624(4)	2.365(4)	2.457(3)
Ag(2)–O(2)#1	2.470(4)	2.502(4)	2.590(5)	2.509(3)
P(1)–Ag(1)–S	158.11(5)	151.12(6)	155.62(6)	157.56(5)
P(1)–Ag(1)–O(1)	120.91(10)	124.37(10)	118.29(11)	118.38(8)
P(1)–Ag(1)–O(2)#1	90.37(8)	104.98(9)	101.16(11)	100.18(7)
O(1)–Ag(1)–S	80.11(10)	78.77(10)	78.88(11)	79.01(8)
Ag(1)–O(1)–Ag(2)#1	143.75(17)	146.51(17)	137.49(19)	143.84(14)
Ag(1)–S–Ag(2)	79.06(4)	82.81(5)	85.69(6)	83.52(4)
P(2)–Ag(2)–S	127.75(5)	149.72(6)	130.63(6)	128.36(5)
P(2)–Ag(2)–O(1)#1	119.67(9)	110.62(9)	126.91(11)	128.47(9)
P(2)–Ag(2)–O(2)#1	122.01(19)	106.53(10)	117.23(11)	120.76(8)
O(2)#1–Ag(2)–S	105.52(9)	100.68(9)	98.26(10)	100.63(8)
O(1)#1–Ag(2)–S	105.46(9)	96.65(9)	101.61(11)	100.26(8)
O(1)#1–Ag(2)–O(2)#1	52.49(11)	51.21(12)	52.19(14)	53.00(10)
(b) Ligand				
S–C(2)	1.764(5)	1.770(6)	1.772(6)	1.764(5)
O(1)–C(1)	1.271(6)	1.259(6)	1.243(7)	1.270(5)
O(2)–C(1)	1.245(6)	1.260(7)	1.257(7)	1.255(5)
C(1)–C(2)	1.516(7)	1.538(8)	1.536(8)	1.510(6)
C(2)–C(3)	1.335(7)	1.329(7)	1.324(8)	1.337(6)
C(3)–C(4)	1.451(7)	1.469(8)	1.476(9)	1.451(7)
O(2)–C(1)–O(1)	122.5(5)	123.4(6)	122.2(6)	122.8(5)
O(2)–C(1)–C(2)	118.9(5)	117.4(6)	117.6(6)	117.6(5)
O(1)–C(1)–C(2)	118.6(5)	119.2(6)	120.2(6)	119.6(5)
C(3)–C(2)–C(1)	116.5(5)	116.7(6)	117.2(6)	117.7(5)
C(3)–C(2)–S	124.9(4)	123.7(5)	125.2(5)	121.8(4)
C(1)–C(2)–S	118.5(4)	119.4(4)	117.6(5)	120.4(4)
C(2)–C(3)–C(4)	133.7(5)	129.5(6)	132.5(6)	129.4(5)

Although, as far as we know, the $Ag_4O_2S_2$ ring of these complexes has not previously been reported, it can be compared with the similarly eight-membered ring Ag_4S_4 that is found, for example, in the triphenylphosphine silver(I) thiocarboxylate $[(AgPPh_3)_4(\mu\text{-SC}\{O\}Me\text{–}S)_4]\cdot C_6H_5CH_3$,[25] in which two of the Ag–S–Ag angles are 76.42(3)° (similar to the values of 79.06(4)-85.69(6)° in **2, 3, 4**·$(CH_3)_2CO$ and **6**·$(CH_3)_2CO$) and two are 123.46(5)° (137.49(19)–146.51(17)° for Ag(1)–O(1)–Ag(2)#1 in the new compounds).

In the dinuclear monomeric molecules of gold complexes of type $[(AuPPh_3)_2(xspa)]$,[10] each gold atom is strongly bound to a P atom and to the thiolate S atom and a bond with a carboxylate O atom gives Au(I) an environment similar to that of Ag(I) in **2, 3, 4**·$(CH_3)_2CO$ and **6**·$(CH_3)_2CO$. The silver compounds can be seen as formed by two mutually inverted $(AgPPh_3)_2(xspa)$ monomers similar to the Au(I) compounds, each of which chelates the less coordinated M atom of the other through its carboxylate group. In both silver and gold complexes, the M(1)–M(2) distance is shorter than twice the corresponding van der Waals radius.

In keeping with their crystallographically demonstrated dideprotonation and coordination the 2 : 1 silver complexes have IR and Raman spectra in which there are no SH bands and the IR bands due to the carboxylate group being strongly modified with respect to those of the free ligands at least in the cases of **2**, **3** and **4** in which the asymmetric carboxylate band appears around 1534 cm^{-1} and the symmetric band around 1354 cm^{-1}, making $\nu_{as}(CO_2^-)$–$\nu_{sym}(CO_2^-)$ around 180 cm^{-1}.

$[(AgPPh_3)_2$(diBr-*o*-hpspa)] (5). Single crystals obtained by slow concentration of an acetone solution of $[(AgPPh_3)_2$(diBr-*o*-hpspa)] are composed of tetranuclear dimers of formula $[(AgPPh_3)_2$(diBr-*o*-hpspa)$]_2$ (Fig. 5), the most significant structural parameters of which are listed in Table 5. Each tetranuclear unit features a twelve-membered $Ag_4(CO_2)_2S_2$ ring in which each Ag is linked indirectly to two others: to one *via* the S atom of the monomer to which these two silver atoms may be considered to belong, and to the other *via* a bis-monodentate carboxylate group that for Ag(1) belongs to its own monomer (by which it is thus O,S-chelated) and for Ag(2) to the other. The only other atoms to which the Ag atoms are coordinated are the P atoms of their PPh_3 ligands, so both types of Ag atom are three-coordinated. The Ag–S, Ag–P and Ag–O distances are, respectively, 2.4033(10), 2.3442(11) and 2.402(3) Å for Ag(1) and 2.4331(10), 2.3719(11) and 2.445(3) Å for Ag(2), *i.e.* all the bonds of Ag(2) are 0.03–0.05 Å longer than those of Ag(1). The angles around Ag(1) and Ag(2) are also different, Ag(2) having the more perfect trigonal environment. The Ag(1)···Ag(2) distance, 3.2208(4) Å, is again shorter than twice the van der Waals radius of this metal (3.44 Å).[21]

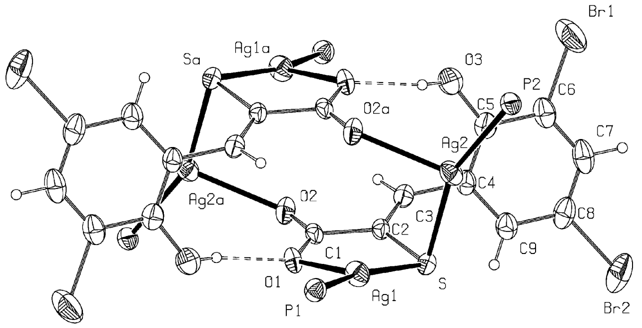


Fig. 5 Molecular structure of $[(AgPPh_3)_2$(diBr-*o*-hpspa)] (**5**) (triphenylphosphine phenyl rings have been omitted for clarity).

Table 5 Selected interatomic distances (Å) and angles (°) in the 2 : 1 triphenylphosphinesilver(I) sulfanylcarboxylate complex **5**

(a) Ag environment			
Ag(1)–P(1)	2.3442(11)	P(1)–Ag(1)–S	162.55(4)
Ag(1)–S	2.4033(10)	P(1)–Ag(1)–O(1)	118.19(7)
Ag(1)–O(1)	2.402(3)	S–Ag(1)–O(1)	79.12(7)
Ag(1)–Ag(2)	3.2208(4)	Ag(1)–S–Ag(2)	83.51(3)
Ag(2)–P(2)	2.3719(11)	P(2)–Ag(2)–S	157.64(4)
Ag(2)–S	2.4331(10)	P(2)–Ag(2)–O(2)#1	105.60(7)
Ag(2)–O(2)#1	2.445(3)	S–Ag(2)–O(2)#1	96.75(7)
		C(2)–S–Ag(1)	98.75(12)
		C(2)–S–Ag(2)	94.00(12)
		C(1)–O(2)–Ag(2)#1	130.6(3)
		C(1)–O(1)–Ag(1)	116.2(3)
(b) Ligand			
S–C(2)	1.779(4)	O(2)–C(1)–O(1)	125.7(4)
O(1)–C(1)	1.260(4)	O(2)–C(1)–C(2)	115.9(4)
O(2)–C(1)	1.251(5)	O(1)–C(1)–C(2)	118.4(4)
C(1)–C(2)	1.532(5)	C(3)–C(2)–C(1)	119.3(4)
C(2)–C(3)	1.324(4)	C(3)–C(2)–S	120.2(3)
C(3)–C(4)	1.473(5)	C(1)–C(2)–S	120.4(3)
		C(2)–C(3)–C(4)	126.6(4)

The two monomers are linked not only by the Ag(1)–OCO–Ag(2)#1 bridge, but also by hydrogen bonds between the diBr-*o*-hpspa OH groups and the carboxylate oxygen involved in chelation of Ag(1) [O(3)–H(3)...O(1)#1: 0.74(4), 1.91(4), 2.639(4) Å, 170(5)°]. This hydrogen bond may be responsible for the inability of O(1) to coordinate to Ag(2)#1 as it does in **2, 3, 4**·$(CH_3)_2CO$ and **6**·$(CH_3)_2CO$ (*vide supra*), and suggests that a molecule with an XH group able to form hydrogen bonds might be able to cleave the O(1)–Ag(2)#1 bond of these latter complexes.

The IR and Raman spectra of **5** show no SH bands and the bands due to the bis-monodentate bridging COO^- group are strongly modified with respect to the free ligand, the asymmetric band lying at 1556 cm^{-1} and the symmetric band at 1349 cm^{-1}, so that $\nu_{as}(CO_2^-)–\nu_{sym}(CO_2^-) = 207$ cm^{-1}.

Solution studies

Attempts were made to record ^1H and ^{13}C NMR spectra of the ligands and complexes in both dmso-d_6 and $CDCl_3$, but poor solubility prevented the recording of some of these spectra. Signals were identified on the basis of our previous data for similar compounds[10,26] and, when necessary, by means of two-dimensional ^1H–^{13}C NMR (HMQC and HMBC) and DEPT methods. The aromatic region of these spectra is complicated by the large number of hydrogen and carbon atoms of the triphenylphosphine ligand. Although several compounds were subjected to solid state ^{13}C CP/MAS spectrometry only for $[(AgPPh_3)_2fspa]$ was it possible to identify any of the signals.

All the ^1H NMR spectra of the ligands exhibited a very broad peak at low field that was attributed to the COOH proton. The thiol proton signal was only identified in the spectra of H_2pspa and H_2Clspa, in which it is located near 5.00 ppm. The ^{13}C spectra of all the ligands show the CO_2H signal near 167 ppm, the C(3) signal of H_2-diBr-*o*-hpspa was not located and those of H_2pspa, H_2Clspa, H_2-*o*-mpspa, H_2-*p*-mpspa and H_2fspa were located between 132.0 and 145.6 ppm.

$[Ag(PPh_3)(Hpspa)]$ (1). In keeping with the non-deprotonation of the CO_2H group in crystals of **1** the broad signal at 12.60 ppm in the ^1H NMR spectrum of the ligand persists in that of the complex, in which the absence of any SH signal and the shift of the C(3)H signal to higher field (from 7.73 ppm for H_2pspa) are in keeping with the S-coordination found in the solid state.[10,26,27] Although it is not clear whether both the Ag–S bonds persist (*i.e.* whether the dimers of **1** remain intact), S-coordination is further corroborated by the ^{13}C NMR spectrum, in which the C(3) signal has shifted to higher field (from 145.6 ppm in H_2pspa) and the C(1) signal to lower field (from 167.1 in H_2pspa). However, the fact that the C(1) signal is practically in the same position as in the spectrum of $[Au(PPh_3)(Hpspa)]$[10] suggests that the weak Ag–O bond is lost in solution. The *ipso* carbons of the PPh_3 phenyl rings are more shielded in the complexes than in free PPh_3 (for which their signal lies at 136.4[28]) and the value $^1J(^{13}C–^{31}P)$ increases from 11.5 Hz to 26.4 Hz. Also, the complex has a $^{31}P\{^1H\}$ NMR signal at 11.36 ppm, close to those of other 1 : 1 silver–triphenylphosphine complexes with S–Ag–P fragments,[29] which together with the foregoing suggests that the PPh_3 ligand is still coordinated in solution.

The ^{109}Ag NMR spectrum, in dmso/dmso-d_6 solution at room temperature shows just a single signal, which indicates that there is only one Ag species present in solution. Its position, 936.3 ppm, is compatible with the incorporation of a P atom in an Ag–S_2 environment,[5a,30,31] but also with other environments, such as $AgPS_2O$ (the result of coordination of a dmso molecule) or, more probably, AgPSO (the result of coordination of a dmso molecule and cleavage of the weaker Ag–S bond).

$[(AgPPh_3)_2(xspa)]$ (2, 3, 4·$(CH_3)_2CO$ and 6. In the ^1H NMR spectra of these complexes the dideprotonation of the ligand is reflected by there being no signals for either the thiol or the CO_2H group. Also, the C(3)H signals are shifted to higher field than in the spectra of the free ligands, which as in the case of **1** suggests that the S-coordination detected in the solid state is also present in solution. The ^{13}C NMR spectra show C(3) to be more shielded in the complexes than in the free ligands, which corroborates the persistence of S–Ag bonds in solution. The fact that the C(1) signal of **6** in solution is close to its position in the ^{13}C CP/MAS spectrum may perhaps be an indication that the Ag–O bonds detected in the solid state also persist in solution, and hence that the dimers of the solid remain intact, but the apparently contradictory though inconclusive ^{109}Ag results (*vide infra*) make it impossible to draw a definite conclusion in this regard.

As in **1**, the *ipso* carbons of the triphenylphosphine phenyl rings, are more shielded than in free PPh_3, in the spectrum of which they appear at 136.4 ppm in dmso and 137.4 ppm in $CDCl_3$,[29] and the value of $^1J(^{13}C–^{31}P)$ increases from 11.5 Hz (dmso) or 12,5 Hz ($CDCl_3$)[29] to around 20 Hz for the complexes. The ^{31}P NMR spectra of the complexes, all show a single peak attributable to coordinated PPh_3 at 6.9–11.0 ppm in dmso and 3.7–5.2 ppm in $CDCl_3$ (*cf.* −3.64 and −5.33 ppm, respectively, for free PPh_3). These chemical shifts are similar to those found in other triphenylphosphinesilver(I) derivatives.[5b,11,12]

The ^{109}Ag NMR spectrum of **6** in dmso/dmso-d_6 at room temperature showed just a single signal (at 1033.4 ppm), suggesting that all the Ag(I) atoms are equivalent in solution (and hence that the dimers of the solid do not remain intact, in apparent contradiction with the ^{13}C NMR results). Furthermore, the halfwidth of the peak, 217 Hz, (Fig. S4, ESI†), is half that of compound **1**, 535 Hz, which appears to rule out the possibility of equilibrium between the two types of Ag(I) coordination found in the solid state (or if there is an equilibrium it is very fast on the NMR experiment timescale). However as in the case of **1**, diagnosis of the Ag environment from the position of the signal is impossible because of the lack of systematic data for similar systems.

$[(AgPPh_3)_2(diBr\text{-}o\text{-}hpspa)]$ (5). As expected, the ^1H NMR spectrum of this complex showed no signals for either the thiol proton or the CO_2H group. Unfortunately, rigorous interpretation of the ^{13}C NMR spectrum was prevented by the poor solubility of the complex and the complexity of the spectrum; in particular, it was not possible to identify the C(1) and the C(3) signals, which prevented the coordination mode of the sulfanyl and carboxylate groups from being inferred.

The ^{31}P NMR spectra in dmso-d_6 and $CDCl_3$, both show a single peak attributable to coordinated PPh_3 (at 7.0 ppm in dmso and 2.4 ppm in $CDCl_3$).

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