Crystal Structures and Spectroscopic Studies of the Mononuclear Complex $[AgBr(PPh_3)_2]$ and Binuclear $[Ag_2X_2(PPh_3)_4]\cdot 2CHCl_3$ (X = Cl or Br)†

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The structures of the silver(I) complexes $[AgBr(PPh_3)_2]$ and $[Ag_2X_2(PPh_3)_4]\cdot 2CHCl_3$ (X = Cl or Br) have been determined by single-crystal X-ray diffraction. The complex $[AgBr(PPh_3)_2]$ crystallizes in the monoclinic space group *C*2/*c* and contains discrete monomeric $[AgBr(PPh_3)_2]$ units with essentially trigonal-planar $AgBrP_2$ co-ordination, and a crystallographic two-fold axis of symmetry coincident with the Ag–Br bond. The geometric parameters for the silver atom environment are: Ag–Br 2.568(1), Ag–P 2.458(2) Å, P–M–P 124.14(5), P–M–Br 117.93(3)°. The complexes $[Ag_2X_2(PPh_3)_4]\cdot 2CHCl_3$ (X = Cl or Br) are isomorphous, monoclinic, space group *C*2/*c*, and contain $[Ag_2X_2(PPh_3)_4]$ dimers. Each of the two silver atoms in the structure is four-co-ordinated by forming bonds with the P atoms of the two phosphine ligands and the two doubly bridging halide atoms. The Ag and X atoms lie in a plane, and each of the molecules in the unit cell has a C_2 axis which passes through the two X atoms. A chloroform molecule is hydrogen bonded to each X atom. The far-IR spectra of these complexes show bands which are assigned to ν(AgX) modes, and the spectra of these and the unsolvated dimer $[Ag_2Cl_2(PPh_3)_4]$ are analysed to yield information about the Ag–X bonding. The Raman spectrum of $[AgBr(PPh_3)_2]$ shows a band which is assigned to a ν(AgP) mode, an assignment which is confirmed by the observation of similar bands in the Raman spectra of the isostructural gold(I) complexes $[AuX(PPh_3)_2]$ (X = Cl, Br or I). The solid-state cross-polarization magic-angle spinning (CP MAS) ^{31}P NMR spectra of the silver complexes show multiplets due to $^1J(AgP)$ coupling. The spectra of the dimers show separate chemical shifts for the crystallographically inequivalent phosphorus atoms, and $^2J(PP)$ coupling between these atoms. The splitting patterns are interpreted in terms of the silver co-ordination environment.

Tertiary phosphine complexes of silver(I) of the type $[AgXL_n]$ (L = tertiary phosphine; n = 1–4; X = co-ordinating or non-co-ordinating anion) were first prepared in 1937 by Mann *et al.*[1] The general method of preparation involves the reaction of stoichiometric amounts of the phosphine ligand with the appropriate silver(I) salt. These complexes display a diversity of structural types, and several reviews on this topic have been published.[2–5] The established structural chemistry of the $[AgXL_n]$ complexes is quite similar to that of the copper(I) analogues, although the number of reported X-ray crystallographic studies is rather fewer in the case of silver(I). The similarities and differences between the silver(I) and copper(I) cases are well illustrated by the complexes with L = PPh_3 and X = Cl, Br or I. Thus, for n = 1, tetramers $[\{AgXL\}_4]$ with both the cubane and step structures have been characterized,[6–9] and this parallels closely the situation for the corresponding copper complexes.[10–15] However, complexes with n = 1.5 have been reported only in the case of copper and these have a binuclear halogen-bridged structure with one three-co-ordinate and one four-co-ordinate copper atom.[13,16,17] It has been reported that the n = 2 silver complexes have dimeric halogen-bridged structures $[\{AgXL_2\}_2]$,[8,18] whereas the corresponding copper complexes are all monomeric, with trigonal-planar co-ordination at the copper atom.[19] For n = 3, monomeric complexes $[AgXL_3]$ with four-co-ordinate silver are found,[20–22] and this again parallels the situation observed for the corresponding copper compounds.[23]

As well as X-ray diffraction techniques, there are several potentially useful spectroscopic techniques for characterizing compounds in the solid state. Thus, far-IR spectroscopy has proved to be a useful technique for the determination of structures in silver(I) halide complexes.[24–28] More recently, the technique of cross-polarization magic-angle spinning (CP MAS) ^{31}P NMR spectroscopy has been shown to yield useful information about the structure and bonding in silver(I) complexes with phosphine ligands.[28,29] A recent far-IR and ^{31}P CP MAS NMR study of some complexes of the silver(I) halides with phosphole ligands[28] revealed some anomalies in the previously published interpretation of the far-IR data for the corresponding 2:1 PPh_3–AgX complexes.[25] These anomalies have been resolved in the present study, which reveals that the unsolvated 2:1 PPh_3–AgBr complex contains the mononuclear species $[AgBr(PPh_3)_2]$, the first example of a complex with trigonal planar $AgXP_2$ co-ordination. This contrasts with the previously published structure for the unsolvated 2:1 PPh_3–AgCl complex, which reveals the presence of dimers, $[Ag_2Cl_2(PPh_3)_4]$, which contain bridging chloride and terminal PPh_3 ligands.[18] In this latter structure, however, the

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chloride bridging is quite unsymmetrical, so that the structure can also be regarded as one arising from the relatively weak interaction between two mononuclear $[AgCl(PPh_3)_2]$ units. Recrystallization of these complexes from $CHCl_3$ results in the formation of solvates $[Ag_2X_2(PPh_3)_4]\cdot 2CHCl_3$ which contain almost perfectly symmetrically halogen-bridged dimers. We report here the crystal structures of these complexes and their characterization by far-IR and solid-state ^{31}P CP MAS NMR spectroscopy.

Experimental

Preparation of Compounds.—Bis[(μ*-chloro*)*bis*(*triphenylphosphine*)*silver*(I)], $[Ag_2Cl_2(PPh_3)_4]$. Triphenylphosphine (1.65 g, 6.30 mmol) and silver(I) chloride (0.45 g, 3.14 mmol) were added to acetonitrile (10 cm^3) and the mixture was stirred under reflux overnight. The white microcrystalline product was collected by filtration, washed with acetonitrile and dried in air. M.p. 180–187 °C (Found: C, 64.7; H, 4.6. Calc. for $C_{72}H_{60}Ag_2Cl_2P_4$: C, 64.7; H, 4.6%).

Bis[(μ*-chloro*)*bis*(*triphenylphosphine*)*silver*(I)]*-chloroform* (1/2), $[Ag_2Cl_2(PPh_3)_4]\cdot 2CHCl_3$. This was obtained by slow evaporation of a solution of the unsolvated 2:1 complex $[Ag_2Cl_2(PPh_3)_4]$ (0.25 g) in chloroform (5 cm^3). The large, colourless crystals which formed overnight were collected by vacuum filtration. M.p. 170–180 °C (Found: C, 56.5; H, 3.7. Calc. for $C_{74}H_{62}Ag_2Cl_8P_4$: C, 56.5; H, 4.0%).

Bromobis(*triphenylphosphine*)*silver*(I), $[AgBr(PPh_3)_2]$. This was prepared by a method similar to that described above by using triphenylphosphine (1.73 g, 6.60 mmol) and silver(I) bromide (0.62 g, 3.30 mmol). The white microcrystalline product was collected by filtration, washed with acetonitrile, and dried in air. M.p. 188–190 °C (Found: C, 60.4; H, 4.5. Calc. for $C_{36}H_{30}AgBrP_2$: C, 60.7; H, 4.3%). This compound was also obtained by the reaction of PPh_3 (10.0 mmol) and $AgNO_3$ (5.0 mmol)–NMe_4Br (5.0 mmol) solutions in acetonitrile, a method analogous to that previously reported for the preparation of unsolvated $[Ag_2Cl_2(PPh_3)_4]$.[18] Crystals for the structure determination were obtained by recrystallizing a 2:1 PPh_3–AgBr mixture from 2,4,6-trimethylpyridine. The products from all three preparations were shown to be identical by means of far-IR spectroscopy and/or an X-ray unit-cell check.

Bis[(μ*-bromo*)*bis*(*triphenylphosphine*)*silver*(I)]*-chloroform* (1/2), $[Ag_2Br_2(PPh_3)_4]\cdot 2CHCl_3$. This was obtained by dissolution of the unsolvated 2:1 complex (0.25 g) in chloroform (3 cm^3) and careful addition of a layer of diethyl ether (2 cm^3) to the resulting solution in a small test tube. The large, colourless crystals which formed overnight were collected by vacuum filtration. M.p. 180–186 °C (Found: C, 53.5; H, 3.6. Calc. for $C_{74}H_{62}Ag_2Br_2Cl_6P_4$: C, 53.4; H, 3.8%).

Attempted Preparations of $[\{AgI(PPh_3)_2\}_n]$ *Complexes.*—Attempts to prepare the 2:1 PPh_3–AgI complexes by the methods described above for the corresponding AgCl and AgBr complexes were unsuccessful, yielding mixtures of the 3:1 and 1:1 complexes, with the relative proportions of each of these components being dependent on the conditions of recrystallization.

Structure Determinations.—Unique diffractometer data sets were measured at ≈295 K within the limit $2\theta_{max} = 50°$ on specimens mounted in capillaries (2θ–θ scan mode; monochromated Mo-Kα radiation, $\lambda = 0.7107_3$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered observed and used in the full-matrix least-squares refinements after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R,R' on $|F|$ at convergence are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system[30] implemented by S. R. Hall; neutral-atom complex scattering factors were employed.[31] Pertinent results are given in Figs. 1 and 2, and in Tables 1 and 2.

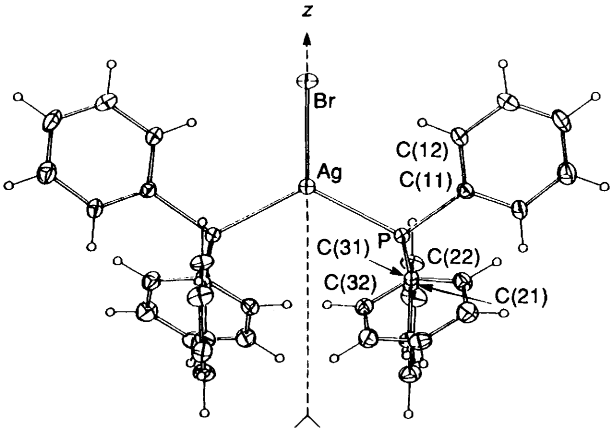

Fig. 1 Structure of $[AgBr(PPh_3)_2]$; 20% thermal ellipsoids are shown for the non-hydrogen atoms and hydrogen atoms have arbitrary radii of 0.1 Å

Table 1 Non-hydrogen atom coordinates for $[AgBr(PPh_3)_2]$

Atom	*x*	*y*	*z*
Ag	0	0.122 28(6)	1/4
Br	0	0.405 53(8)	1/4
P	0.094 77(6)	−0.004 7(1)	0.291 7(1)
C(11)	0.158 7(2)	0.112 9(5)	0.315 6(3)
C(12)	0.157 2(2)	0.256 7(6)	0.344 3(4)
C(13)	0.205 8(3)	0.348 7(6)	0.368 1(5)
C(14)	0.255 8(3)	0.298 9(7)	0.362 8(5)
C(15)	0.256 5(3)	0.158 9(7)	0.332 4(4)
C(16)	0.208 1(2)	0.064 5(6)	0.308 3(4)
C(21)	0.089 9(2)	−0.133 7(5)	0.196 9(3)
C(22)	0.078 2(3)	−0.077 0(6)	0.106 2(4)
C(23)	0.068 5(3)	−0.168 9(7)	0.028 0(4)
C(24)	0.068 5(3)	−0.319 0(7)	0.039 4(5)
C(25)	0.079 4(2)	−0.376 1(6)	0.129 2(5)
C(26)	0.089 8(2)	−0.284 5(5)	0.207 6(4)
C(31)	0.120 1(2)	−0.117 9(5)	0.402 9(3)
C(32)	0.077 5(2)	−0.195 9(5)	0.415 8(4)
C(33)	0.093 3(2)	−0.280 4(6)	0.498 8(4)
C(34)	0.152 6(3)	−0.288 4(6)	0.571 2(4)
C(35)	0.195 4(2)	−0.210 1(6)	0.559 4(4)
C(36)	0.178 9(2)	−0.126 3(6)	0.475 3(4)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Crystal/refinement data. $[AgBr(PPh_3)_2]$, $C_{36}H_{30}AgBrP_2$, $M = 712.4$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 25.329(6)$, $b = 9.065(3)$, $c = 15.342(4)$ Å, $\beta = 118.31(2)°$, $U = 3101.3$ Å^3. $D_c(Z = 4) = 1.53$ g cm^{-3}; $F(000) = 1432$, $\mu_{Mo} = 19.6$ cm^{-1}, specimen 0.18 × 0.17 × 0.27 mm, $A^*_{min,max} = 1.32, 1.39$, $N = 2734$, $N_o = 1798$, $R = 0.035$, $R' = 0.032$, $n_v = 182$.

Abnormal features/variations in procedure. This compound is isomorphous with various other $[MX(PPh_3)_2]$ complexes reported elsewhere;[19] it was refined in the same setting.

$[Ag_2Cl_2(PPh_3)_4]\cdot 2CHCl_3$, $C_{72}H_{60}Ag_2Cl_2P_4\cdot 2CHCl_3$, $M = 1574.6$, monoclinic, space group $C2/c$, $a = 19.449(9)$, $b = 17.56(1)$, $c = 21.601(4)$ Å, $\beta = 92.19(3)°$, $U = 7370$ Å^3, $D_c(Z = 4) = 1.42$ g cm^{-3}; $F(000) = 3184$, $\mu_{Mo} = 8.6$ cm^{-1}, specimen 0.33 × 0.29 × 0.14 mm, $A^*_{min,max} = 1.11, 1.30$, $N = 5730$, $N_o = 2645$, $R = 0.047$, $R' = 0.046$, $n_v = 427$.

$[Ag_2Br_2(PPh_3)_4]\cdot 2CHCl_3$, $C_{72}H_{60}Ag_2Br_2P_4\cdot 2CHCl_3$, $M = 1663.5$, monoclinic, space group $C2/c$, $a = 19.497(6)$, $b = 17.617(8)$, $c = 21.84(1)$ Å, $\beta = 92.55(3)°$, $U = 7494$ Å^3, $D_c(Z =$

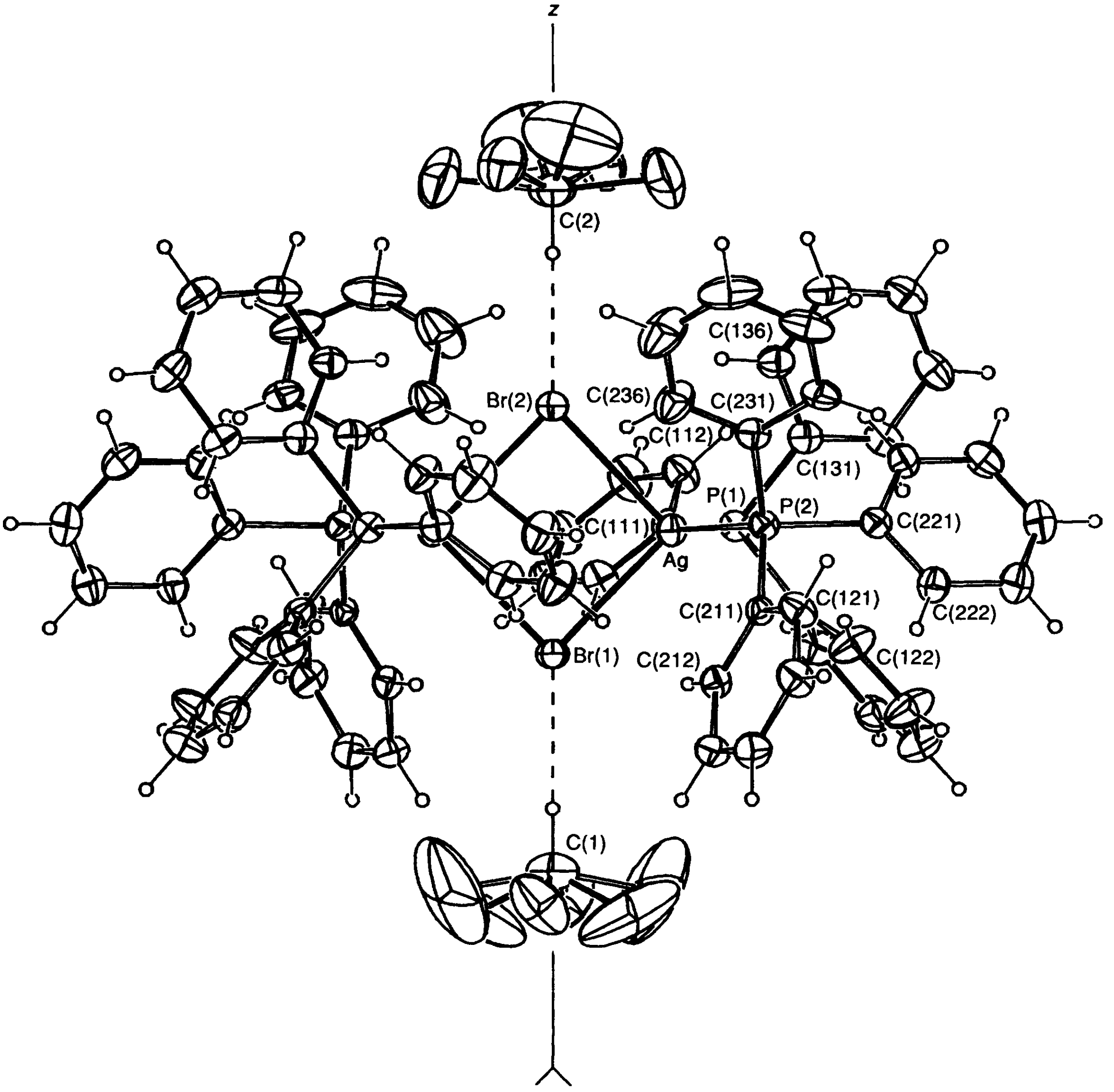

Fig. 2 Structure of $[Ag_2Br_2(PPh_3)_4]\cdot 2CHCl_3$, projected normal to the $AgBr_2Ag$ plane

4) = 1.47 g cm^{-3}; $F(000) = 3328$, $\mu_{Mo} = 18.2$ cm^{-1}, specimen 0.42 × 0.17 × 0.40 mm, $A^*_{min,max} = 1.36, 1.74$, $N = 6637$, $N_o = 3299$, $R = 0.043$, $R' = 0.044$, $n_v = 427$.

Abnormal features/variations in procedure. The two compounds above are isomorphous. They may also be isomorphous with the bromide dimer, recorded as a chloroform monosolvate, in an early communication form.[8] We have not identified any other chloroform solvates of either of these two complexes in the course of our studies. Moreover, we note that the alleged monosolvate crystallizes in the space group *I2/m* with cell dimensions $a = 14.311(2)$, $b = 17.624(3)$, $c = 14.961(3)$ Å, $\beta = 96.56(1)°$, $Z = 2$; the final residual was 0.08 for 1526 independent reflections. The volume of this cell is almost identically half that of the present cell, with a comparable *b* axial length. The space group *C2/m* (*I2/m*) is a common missetting of doubled cells more accurately describable as *C2/c* or $P2_1/c$ in situations where pseudo-symmetry generating a weak superlattice obtains,[32] and it seems likely that the present bromide is the same as that previously studied for which the residual was somewhat high. The chloroform solvent molecules of the present study are hydrogen bonded to the two halide atoms of the dimer which is disposed with a crystallographic two-fold axis passing through the two halide atoms *and* the C(H?) component of each solvent molecule (the two hydrogen atoms have been assumed to be also disposed on the axis); in each solvent molecule, the chlorine atoms form a tolerable quasi-tetrahedrally disposed set, modelled as disordered about the two-fold axis, but with very high chlorine thermal motion possibly indicative of further disorder. Site populations were allowed to vary in refinement, but the results suggested no better model than that in which all chlorine sites were half-occupied and site occupancies were constrained to that value in the final cycles.

Spectroscopy.—Infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as Nujol mulls between KBr plates on a Digilab FTS-60 Fourier-transform spectrometer employing an uncooled DTGS (denteriotriglycine sulfate) detector. Far-IR spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed Polythene discs on a Digilab FTS-60 Fourier-transform spectrometer employing an FTS-60V vacuum optical bench with a 6.25 μm mylar film beam splitter, a mercury lamp source and a TGS (triglycine sulfate) detector. Raman spectra were excited with 100 mW of Ar^+ 514.5 mm radiation using a Coherent model 52 argon ion laser, and were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer. Phosphorus-31 CP MAS NMR spectra were obtained at ambient temperature on a Bruker MSL 400 spectrometer operating at a ^{31}P frequency of 161.92 MHz.

Conventional cross-polarization[33] and magic-angle spinning[34] techniques, coupled with spin temperature alternation[35] to eliminate spectral artifacts, were implemented using a Bruker

Table 2 Non-hydrogen atom coordinates for $[(Ph_3P)_2AgX_2Ag(PPh_3)_2]\cdot 2CHCl_3$[a]

	X = Cl			X = Br		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ag	0.508 62(3)	0.744 10(4)	0.666 76(3)	0.510 40(2)	0.744 61(3)	0.665 77(2)
X(1)	0.5	0.635 8(2)	0.75	0.5	0.630 27(6)	0.75
X(2)	0.5	0.852 8(2)	0.75	0.5	0.858 36(6)	0.75
P(1)	0.397 1(1)	0.747 2(2)	0.605 68(9)	0.398 81(8)	0.747 8(1)	0.604 05(8)
C(111)	0.316 0(4)	0.748 5(5)	0.644 7(3)	0.317 5(3)	0.749 2(4)	0.642 0(3)
C(112)	0.305 1(4)	0.699 0(5)	0.691 6(4)	0.308 0(3)	0.698 4(5)	0.689 5(3)
C(113)	0.243 5(5)	0.695 6(6)	0.720 4(4)	0.245 8(4)	0.694 9(5)	0.717 9(3)
C(114)	0.190 6(4)	0.742 3(6)	0.701 7(4)	0.194 0(4)	0.742 2(5)	0.699 5(3)
C(115)	0.199 8(5)	0.792 8(6)	0.654 1(5)	0.201 5(4)	0.792 5(5)	0.653 6(4)
C(116)	0.262 4(5)	0.796 9(5)	0.625 9(4)	0.264 0(4)	0.796 6(5)	0.625 2(3)
C(121)	0.386 3(4)	0.667 6(4)	0.553 4(4)	0.388 0(3)	0.667 7(4)	0.552 5(3)
C(122)	0.444 8(5)	0.639 1(5)	0.526 9(5)	0.446 4(4)	0.638 5(4)	0.526 5(4)
C(123)	0.441 5(5)	0.579 9(6)	0.485 4(5)	0.441 9(4)	0.580 7(5)	0.485 2(4)
C(124)	0.378 1(6)	0.547 9(6)	0.468 9(5)	0.379 7(5)	0.549 2(5)	0.469 1(4)
C(125)	0.321 7(5)	0.575 8(5)	0.493 8(4)	0.322 8(4)	0.576 2(4)	0.494 4(3)
C(126)	0.323 6(4)	0.634 3(5)	0.535 7(4)	0.325 4(4)	0.635 5(4)	0.534 7(3)
C(131)	0.393 0(4)	0.829 8(4)	0.555 1(4)	0.393 4(3)	0.829 6(4)	0.552 9(3)
C(132)	0.416 2(4)	0.898 6(5)	0.578 8(4)	0.417 1(4)	0.898 4(4)	0.577 1(3)
C(133)	0.414 9(5)	0.963 0(5)	0.541 8(5)	0.415 2(4)	0.963 0(4)	0.540 1(4)
C(134)	0.390 4(5)	0.959 9(5)	0.481 5(4)	0.390 2(4)	0.958 7(4)	0.480 0(4)
C(135)	0.366 8(5)	0.892 0(6)	0.457 3(4)	0.366 6(4)	0.891 0(5)	0.456 7(4)
C(136)	0.367 8(4)	0.827 9(5)	0.493 6(4)	0.367 8(3)	0.827 2(4)	0.493 3(3)
P(2)	0.618 3(1)	0.749 0(2)	0.613 20(8)	0.620 86(8)	0.748 7(1)	0.613 61(7)
C(211)	0.678 0(4)	0.669 7(4)	0.625 3(4)	0.679 9(3)	0.668 9(3)	0.624 8(3)
C(212)	0.655 7(4)	0.605 7(5)	0.655 4(3)	0.657 5(3)	0.604 6(4)	0.653 7(3)
C(213)	0.697 9(5)	0.543 0(5)	0.664 0(4)	0.700 1(3)	0.542 9(4)	0.662 1(3)
C(214)	0.763 6(4)	0.544 4(5)	0.640 6(4)	0.765 7(4)	0.543 2(4)	0.641 7(3)
C(215)	0.786 5(4)	0.607 8(5)	0.611 7(4)	0.788 5(3)	0.608 0(4)	0.613 9(3)
C(216)	0.744 2(4)	0.670 3(5)	0.604 4(4)	0.746 7(3)	0.670 2(4)	0.606 3(3)
C(221)	0.602 8(3)	0.750 2(5)	0.529 6(3)	0.604 7(3)	0.750 5(4)	0.531 0(3)
C(222)	0.562 9(4)	0.808 8(5)	0.504 4(4)	0.564 4(3)	0.808 1(4)	0.505 9(3)
C(223)	0.543 5(4)	0.809 0(5)	0.442 1(4)	0.544 2(3)	0.808 9(4)	0.445 2(3)
C(224)	0.563 7(4)	0.751 6(6)	0.404 5(4)	0.563 7(4)	0.751 3(5)	0.407 8(3)
C(225)	0.602 7(5)	0.693 7(6)	0.428 3(4)	0.603 1(4)	0.694 1(5)	0.430 3(3)
C(226)	0.622 5(4)	0.694 1(5)	0.490 8(4)	0.624 2(3)	0.692 8(4)	0.492 8(3)
C(231)	0.671 0(4)	0.833 6(5)	0.627 1(3)	0.673 1(3)	0.832 6(4)	0.628 9(3)
C(232)	0.710 0(5)	0.868 2(5)	0.584 3(4)	0.710 0(4)	0.868 4(4)	0.584 7(3)
C(233)	0.749 5(5)	0.931 1(5)	0.600 3(5)	0.749 1(4)	0.931 0(4)	0.600 2(4)
C(234)	0.747 6(5)	0.960 8(5)	0.658 1(6)	0.751 9(5)	0.961 2(5)	0.656 4(5)
C(235)	0.709 6(6)	0.927 5(7)	0.701 5(6)	0.714 6(5)	0.925 3(6)	0.699 8(5)
C(236)	0.671 0(5)	0.863 4(6)	0.685 5(5)	0.675 4(4)	0.862 0(5)	0.686 3(4)
C(1)	0.5	0.443 7(9)	0.75	0.5	0.434 9(7)	0.75
Cl(1A)[b]	0.585 9(4)	0.415 1(5)	0.771 7(4)	0.588 0(3)	0.405 2(4)	0.771 0(3)
Cl(1B)[b]	0.450 4(4)	0.404 9(5)	0.794 7(6)	0.454 5(4)	0.397 0(5)	0.798 9(6)
Cl(1C)[b]	0.492 2(9)	0.439(1)	0.670 1(6)	0.496 5(8)	0.417 7(9)	0.677 6(5)
C(2)	0.5	1.040 9(8)	0.75	0.5	1.054 3(6)	0.75
Cl(2A)[b]	0.430 0(5)	1.087 0(6)	0.750 9(8)	0.435 5(5)	1.104 1(6)	0.755 4(6)
Cl(2B)[b]	0.536 1(5)	1.056 4(5)	0.674 0(3)	0.533 8(5)	1.065 8(5)	0.674 5(3)
Cl(2C)[b]	0.564 7(5)	1.072 0(5)	0.796 6(3)	0.570 6(4)	1.078 5(4)	0.795 1(3)

[a] (*x*, *y*, *z*) (estimated) for the chloroform hydrogens are: X = Cl, H(1) ($\frac{1}{2}$, 0.498, $\frac{3}{4}$), H(2) ($\frac{1}{2}$, 0.988, $\frac{3}{4}$); X = Br, H(1) ($\frac{1}{2}$, 0.492, $\frac{3}{4}$), H(2) ($\frac{1}{2}$, 0.997, $\frac{3}{4}$).
[b] Population = 0.5.

4 mm double-air-bearing probe in which MAS frequencies of 12 kHz were achieved. A recycle delay of 30 s, contact period of 10 ms and ^{1}H $\frac{\pi}{2}$ pulse length of 3 μs were common to all spectra. No spectral smoothing was employed prior to Fourier transformation. The ^{31}P CP MAS two-dimensional correlation spectroscopy (COSY) experiment was implemented with the TPPI (time proportional phase incrementation) method[36–38] for acquisition of phase-sensitive data in both the F1 and F2 dimensions. The application of this technique has been discussed in detail elsewhere.[39] The recycle delay, contact period, ^{1}H $\frac{\pi}{2}$ pulse length and MAS rate were the same as those implemented in the one-dimensional experiments above. A total of 256 F1 increments were acquired into 256 word F2 blocks, with both dimensions zero-filled to 1 K words and weighted with sine bell apodization prior to Fourier transformation. All ^{31}P chemical shifts were externally referenced to solid triphenylphosphine which has a shift of δ −9.9 with respect to 85% H_3PO_4.

Results and Discussion

Syntheses.—Reaction of triphenylphosphine and silver(I) chloride or bromide in a 2:1 mole ratio in acetonitrile yields unsolvated 2:1 complexes of empirical formula $[AgX(PPh_3)_2]$ (X = Cl or Br). The chloride complex appears to correspond to the one which results from the reaction between PPh_3 and $AgNO_3$–NMe_4Cl solutions in acetonitrile, and for which an unsymmetrically chloride-bridged dimer structure was found.[18] This is supported by the far-IR results (see below). The bromide complex corresponds to one which was reported previously (prepared by the same method as that used in the present study), and which was assumed to have a dimer structure.[25] However, the only 2:1 PPh_3–AgBr complex for which a crystal structure has been reported is one which was obtained by recrystallization of the complex from chloroform, and which was formulated as $[Ag_2Br_2(PPh_3)_4]\cdot CHCl_3$.[8] In the present study, recrystallization of the unsolvated 2:1 PPh_3–AgX

Table 3 Comparison of metal atom environments in [$MBr(PPh_3)_2$]; distances (Å), angles (°)

	M = Cu*	M = Ag	M = Au*
M–Br	2.346(2)	2.568(1)	2.625(1)
M–P	2.282(3) 2.263(2)	2.458(2)	2.323(2)
P–M–P	126.0(1)	124.14(5)	132.45(8)
P–M–Br	112.8(1) 121.0(1)	117.93(3)	113.78(5)

* Ref. 19.

Table 4 Silver atom environments in [$Ag_2X_2(PPh_3)_4$]·$2CHCl_3$; distances (Å), angles (°) (primed atoms are related by the two-fold symmetry axis)

	X = Cl	X = Br
Ag–X(1)	2.625(3)	2.742(1)
Ag–X(2)	2.630(3)	2.734(1)
Ag–P(1)	2.516(2)	2.509(2)
Ag–P(2)	2.448(2)	2.482(2)
X(1)–Ag–X(2)	92.95(8)	94.43(5)
X(1)–Ag–P(1)	107.94(7)	106.78(5)
X(1)–Ag–P(2)	114.68(7)	114.90(5)
X(2)–Ag–P(1)	106.05(7)	104.87(5)
X(2)–Ag–P(2)	111.50(7)	112.29(5)
P(1)–Ag–P(2)	120.09(7)	120.15(6)
Ag–X(1)–Ag′	87.1(1)	85.43(5)
Ag–X(2)–Ag′	87.0(1)	85.72(5)
Out-of-plane deviations*		
ΔP(1)	−2.278(3)	−2.297(2)
ΔP(2)	2.011(3)	2.004(2)

* ΔP(*i*) is the deviation (Å) of P(*i*) from the Ag_2X_2 plane.

complexes from chloroform resulted in the isolation of [$Ag_2X_2(PPh_3)_4$]·$2CHCl_3$ (X = Cl or Br), with two molecules of $CHCl_3$ per dimer rather than one.

In contrast to the syntheses of the above complexes, no 2:1 complexes (solvated or unsolvated) of PPh_3 with AgI could be prepared and both far-IR and solid-state ^{31}P NMR spectra of the products obtained were indicative of the presence of the 3:1 and 1:1 complexes only, with the relative amounts of each component being dependent on the conditions of recrystallization. Although an earlier reference to the unsolvated complex exists in the literature,[25] the analytical data were apparently not in good agreement with this formulation, and the far-IR data given there are consistent with the presence of a mixture of the 3:1 and 1:1 complexes.

Crystal Structure of [$AgBr(PPh_3)_2$].—This complex crystallizes as discrete monomeric [$AgBr(PPh_3)_2$] units (Fig. 1). A crystallographic two-fold axis of symmetry lies coincident with the Ag–Br bond, rendering the two PPh_3 ligands crystallographically equivalent. Each ligand adopts pseudo C_3 symmetry with M–P(1)–C(1*m*1)–C(1*m*2) torsion angles of 23, 65 and 40° for rings 1, 2 and 3. A Newman projection of the molecule down the P–P vector shows that the two ligands adopt an eclipsed conformation as required by symmetry, with phenyl rings 2 and 3 of each ligand orthogonal to each other and projecting above and below the $AgBrP_2$ plane. Phenyl rings 1 lie approximately in this plane with a Br··· H(112) distance of 2.81 Å. This *C*2/*c* lattice is commonly observed for [$MX(PPh_3)_2$] complexes, having previously been reported for M = Cu, X = I,[19] BH_4,[40] NO_3[41] or O_2CH,[42] and for M = Au, X = Br or I.[19]

Comparison of the $MBrP_2$ core geometries for the benzene solvate of the copper(I) complex and the isomorphous unsolvated silver and gold complexes is provided in Table 3. As has been observed for [$M(dppe)_2$]$^+$ [dppe = 1,2-bis(diphenylphosphine)ethane] complexes,[43] the M–P distances increase in the order Cu < Au < Ag. The M–Br distances in the present complexes increase in the order Cu < Ag < Au, however, reflecting the greater tendency of the gold(I) system towards linear co-ordination.

The structural parameters of the present complex are remarkably similar to those of the asymmetric [$AgCl(PPh_3)_2$] unit in the unsolvated chloride dimer;[18] this latter structure might be more appropriately considered to be an aggregate of two independent [$AgCl(PPh_3)_2$] units, as evidenced by the significant differences in the Ag–Cl bond lengths of 2.596(2) and 2.741(2) Å.

Crystal Structures of [$Ag_2X_2(PPh_3)_4$]·$2CHCl_3$ (X = Cl *or* Br).—These two compounds are isomorphous, and contain [$Ag_2X_2(PPh_3)_4$] dimers. The structure of the bromide is shown in Fig. 2. In this structure each of the two silver atoms is four-co-ordinated by forming bonds with the P atoms of the two phosphine ligands and the two doubly bridging halide atoms. Each of the molecules in the unit cell has a C_2 axis which passes through the two X atoms, so that the AgX_2Ag core is strictly planar. These compounds are not isomorphous with the unsolvated dimeric chloride complex [$Ag_2Cl_2(PPh_3)_4$] which crystallizes in a triclinic unit cell in which the molecules have an inversion centre as well as a two-fold symmetry axis perpendicular to the Ag_2Cl_2 plane.[18] In each case, however, the molecules have two different phosphorus environments P(1) and P(2). The relationship between the present structure for the bromide and that reported previously for a purported chloroform monosolvate of the same compound[8] is discussed above (see Experimental section), and it is likely that the earlier incompletely reported structure is that of the chloroform disolvate reported here. The important structural parameters for the chloroform disolvates investigated in the present study are listed in Table 4. The two structures are obviously very similar in many respects. Thus, they both contain a nearly square Ag_2X_2 arrangement, the X–Ag–X and Ag–X–Ag angles being close to 90°. In this respect the structures are similar to that of the unsolvated chloride.[18] However, this latter structure has two symmetrically inequivalent Ag–Cl bond lengths which differ by nearly 0.15 Å, whereas these bond lengths are essentially identical (difference less than 0.01 Å) in the present compounds. The Ag–P bond lengths in the two complexes are quite similar, although the difference between the two symmetrically inequivalent Ag–P is significantly greater for the chloride. The Ag–Br and Ag–P bond lengths in the bromide are significantly longer than those in the unsolvated trigonal monomer (see above), as expected on the basis of the different co-ordination environments involved. There is a slight decrease of about 4° in the P–Ag–P angle from the monomer to the dimer, but this is considerably less than the decrease of about 10° which would obtain if the silver co-ordination environment changed from perfectly trigonal to perfectly tetrahedral.

In these structures, a Newman projection along the P–P axis shows that, unlike the unsolvated complexes, the two ligands are of opposite chirality and are staggered with respect to each other. Ligand 1 has approximate C_3 symmetry with Ag–P(1)–C(1*n*1)–C(1*n*2) = 47, 33 and 42° for X = Cl and Br. In ligand 2, however, the analogous angles are 9, 56 and 38°. Rings 1 and 3 are oriented such that the *ortho*-phenyl hydrogen atoms H(212) and H(232) are directed towards the bridging halide with X··· H distances ranging from 2.8 to 3.0 Å. By comparison, the X··· H($CHCl_3$) distance is estimated to be 2.2 Å.

Infrared Spectra.—The mid-IR spectra of this series of complexes show no major differences in the frequencies assignable to vibrations of the PPh_3 ligands. For the chloroform solvated complexes, bands due to the hydrogen-bonded $CHCl_3$

Table 5 Infrared wavenumbers (cm^{-1}) for CH(D)Cl$_3$ in [Ag$_2$X$_2$(PPh$_3$)$_4$]·2CH(D)Cl$_3$ (shifts relative to values for vapour phase CH(D)Cl$_3$[a] are given in parentheses)

Compound	ν(CH/D) (A$_1$)	δ(CH/D) (E)	ν(CCl) (A$_1$)
[Ag$_2$Cl$_2$(PPh$_3$)$_4$]·2CHCl$_3$	*b*	1242 (+20)	*b*
[Ag$_2$Cl$_2$(PPh$_3$)$_4$]·2CDCl$_3$	2209 (−56)	922 (+7)	644 (−14)
[Ag$_2$Br$_2$(PPh$_3$)$_4$]·2CHCl$_3$	*b*	1235 (+13)	*b*
[Ag$_2$Br$_2$(PPh$_3$)$_4$]·2CDCl$_3$	2215 (−50)	918 (+3)	646 (−12)

[a] Ref. 44. [b] Obscured by PPh$_3$ bands.

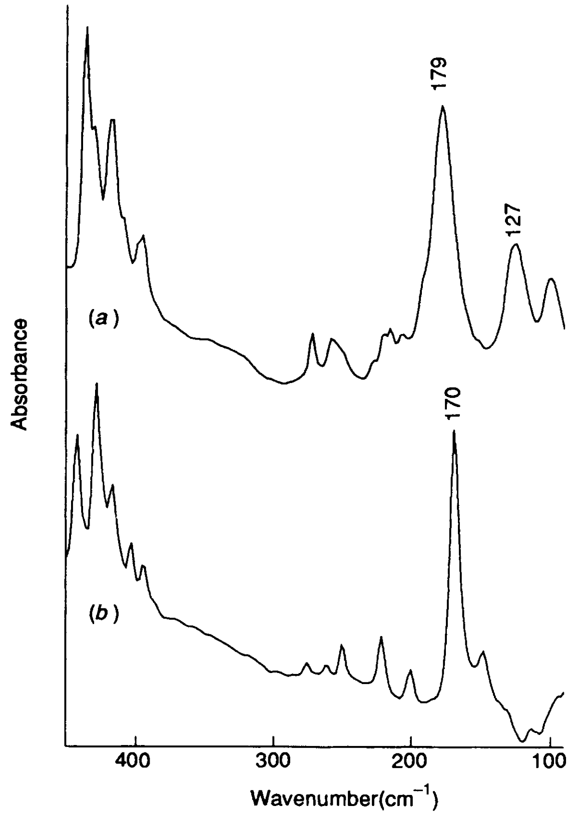

Fig. 3 Far-IR spectra of (*a*) [Ag$_2$Cl$_2$(PPh$_3$)$_4$] and (*b*) [AgBr(PPh$_3$)$_2$]. Bands due to vibrations of the AgX or Ag$_2$X$_2$ units are labelled with their wavenumbers

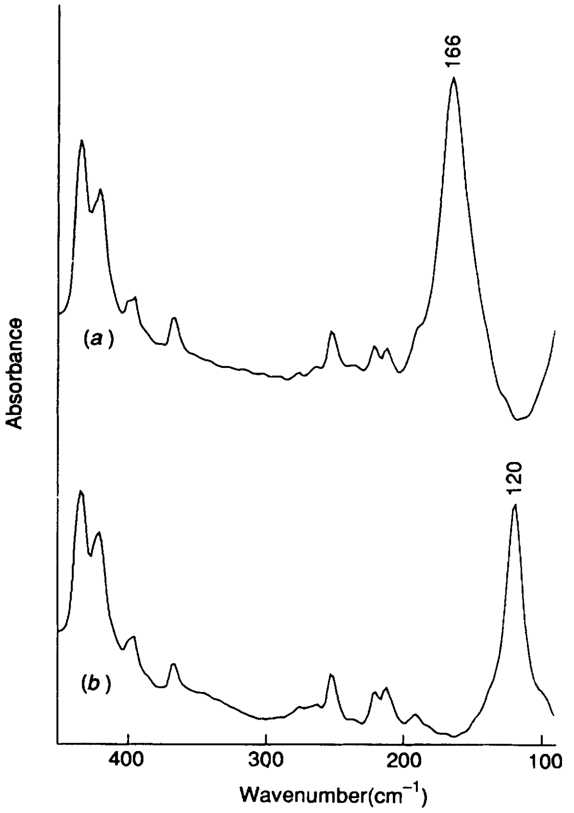

Fig. 4 Far-IR spectra of [Ag$_2$X$_2$(PPh$_3$)$_4$]·2CHCl$_3$; (*a*) X = Cl, (*b*) X = Br. Bands due to vibrations of the Ag$_2$X$_2$ units are labelled with their wavenumbers

molecule are observed and these are listed in Table 5, together with those of the corresponding CDCl$_3$ solvates. The shifts in the wavenumbers of these bands relative to the values for vapour phase CH(D)Cl$_3$[44] are also listed. These shifts are mainly a consequence of the hydrogen-bonding interaction of the chloroform molecule with the bridging halogen atom. Previous studies have shown that the ν(CH) mode shows a decrease, while the δ(CH) mode shows an increase in wavenumber on hydrogen-bond formation.[45,46] An increase is observed for the δ(CH) mode in the present complexes, but the ν(CH) bands of the chloroform are obscured by those of the PPh$_3$ ligand. Bands due to both the ν(CD) and the δ(CD) modes are observed in the CDCl$_3$ complexes, however, and these show shifts of the type described above. The magnitudes of these shifts give an indication of the strength of the hydrogen-bonding interaction. Thus, the decrease in ν(CD) due to hydrogen-bond formation with covalently bonded O in acetone is about 20 cm^{-1}, whereas a decrease of about 100 cm^{-1} is observed with covalently bonded N in aliphatic amines.[45,46] The shift of about 50 cm^{-1} observed in the present examples, where the chloroform is hydrogen-bonded to ionic halide, lies within this range. A greater shift is observed for X = Cl than for X = Br, which is consistent with the expectation that the hydrogen bonding should be stronger in the former case. The ν(CCl) bands are mostly obscured by the strong phenyl deformation modes which occur in the same region. In the case of the CDCl$_3$ complexes, however, the A$_1$ ν(CCl) band is observable and this shows a downward shift on complex formation.

The far-IR spectra of the PPh$_3$–AgX complexes prepared in this study all showed halogen-sensitive bands which could be assigned to silver–halogen stretching modes ν(AgX). The spectra are shown in Figs. 3 and 4, and the wavenumbers and assignments of the bands are given in Table 6. The spectra of the unsolvated 2:1 complexes have been reported previously,[25] but there are now reasons to question the assignments made in this earlier work. The materials used in that study were prepared in a manner similar to that used here to prepare the unsolvated compounds, so the compounds obtained should be the same, and this can be checked by comparing their far-IR spectra.

In the case of the unsolvated 2:1 PPh$_3$–AgBr complex, a single strong band was observed at 170 cm^{-1}, in agreement with the previously reported value.[25] This complex was previously assigned a dimeric structure by analogy with the known structure of the complex obtained by recrystallization from chloroform,[8] and the 170 cm^{-1} band was assigned to ν(AgBr) of the bridged Ag$_2$Br$_2$ units in the dimer. However, the present study shows that the unsolvated complex is the trigonal monomer [AgBr(PPh$_3$)$_2$], so the observed band is assigned to ν(AgBr) of the terminal AgBr bond in this structure. This assignment fits well with assignments for related species, *e.g.* ν(CuBr) 218 cm^{-1} in [CuBr(PPh$_3$)$_2$];[50,51] the ratio of the wavenumbers for these corresponding copper and silver complexes (1.28) is the same as that for the diatomic CuBr and AgBr molecules, whose wavenumbers in the vapour phase have been determined.[47]

The unsolvated 2:1 PPh$_3$–AgCl complex shows two bands which are assigned to ν(AgCl) at 179 and 127 cm^{-1}. These are considerably lower in wavenumber than the single band

Table 6 Vibrational wavenumbers ν(AgX), Ag–X force constants f_r, and bond lengths d(Ag–X) for AgX (X = Cl or Br) and their complexes with PPh_3 and related ligands

Complex	ν(AgX)/cm^{-1}	f_r/N m^{-1}	Ref.	d(Ag–X)/Å	Ref.
AgCl (vapour)	341	183	47	2.281	49
[AgCl(tmpp)]^a	282	125	48	2.342	48
[$AgCl(PPh_3)_3$]	192	58	25	2.54	20
[$Ag_2Cl_2(PPh_3)_4$]	179	44		2.596	18
	127	19	*b*	2.741	
[$Ag_2Cl_2(PPh_3)_4$]·$2CHCl_3$	166	37	*b*	2.63	*b*
AgBr (vapour)	246	164	47	2.393	49
[AgBr(tmpp)]	215	125	48	2.45	48
[$AgBr(PPh_3)_3$]	138	52	25	2.69	20
[$AgBr(PPh_3)_2$]	170	78	*b*	2.568	*b*
[$Ag_2Br_2(PPh_3)_4$]·$2CHCl_3$	120	33	*b*	2.74	*b*

^{a} tmpp = Tris (2,4,6-trimethoxyphenyl)phosphine. ^{b} This work.

previously reported for this compound (208 cm^{-1}).[25] The present result fits better with the previously reported structure of this complex, as discussed below.

The ideal point group symmetry of an isolated dimer of the type [$Ag_2X_2(PPh_3)_4$] is D_{2h}, and two IR-active ν(AgX) modes of B_{2u} and B_{3u} symmetry are predicted for this structure. For a perfectly square Ag_2X_2 unit (x parallel to the Ag···Ag diagonal, y parallel to the X···X diagonal) the two IR-active normal modes involve displacement of X and Ag along the positive and negative x directions respectively (B_{3u}) or a similar vibration in the y direction (B_{2u}). For an isolated square Ag_2X_2 unit, these two modes would have the same frequency. A distortion in which two bonds on opposite sides of the square are shortened and the other two are lengthened results in a lowering of the symmetry from D_{2h} to C_{2h}, and the two IR-active ν(AgX) modes both have B_u symmetry. The forms of these modes are such that one mainly involves stretching of the two short Ag–X bonds, while the other mainly involves stretching of the two long Ag–X bonds, so that the two modes should give rise to bands at significantly different wavenumbers. This situation apparently obtains for unsolvated [$Ag_2Cl_2(PPh_3)_4$], whose crystal structure shows a distorted Ag_2Cl_2 core with two sets of Ag–Cl bond lengths which differ by 0.15 Å.[18] Elsewhere we have shown that the dependence of ν(AgCl) on the Ag–Cl bond length is such that a difference of 0.15 Å in the bond length corresponds to a difference in the vibrational frequency of up to 50 cm^{-1}.[48] Thus, the splitting observed for [$Ag_2Cl_2(PPh_3)_4$] is of the right order of magnitude for the observed bond length difference. In the previously reported IR study,[25] only a single ν(AgCl) band was reported and this was assigned to the B_{2u} and/or B_{3u} modes, thus leaving open the question of whether these two modes are coincident or whether only one of the two possible bands had been observed. In the present study the two bands which are expected for the observed unsymmetrically bridged structure are assigned. Similar effects have been reported previously for complexes containing unsymmetrically bridged Hg_2X_2 units.[52]

The reason for the discrepancy between the present and previously reported far-IR results for the unsolvated 2:1 PPh_3–AgCl complex is not known at present. The possibility that the previous result was obtained for a sample containing a trigonal monomeric form of the complex seems unlikely; on the basis of the wavenumbers for the vapour phase diatomic AgCl and CuCl molecules,[47] and using ν(CuCl) 298 cm^{-1} for [$CuCl(PPh_3)_2$][50,51] (see discussion above for the trigonal monomeric bromo complex) ν(AgCl) for the trigonal monomeric chloro complex would be expected to lie at about 246 cm^{-1}, which is considerably higher than the previously reported value of 208 cm^{-1}.[25]

As discussed above, a 2:1 PPh_3–AgI complex could not be prepared in pure form, in agreement with a statement in the original report.[25] We note that the ν(AgI) wavenumbers (130, 107 cm^{-1}) reported in that work are the same as those for [$Ag_4I_4(PPh_3)_4$] (step isomer) and [$AgI(PPh_3)_3$] respectively, suggesting that the product is a mixture of the 1:1 and 3:1 compounds, with an approximate overall average PPh_3–AgI ratio of 2:1.

The far-IR spectra of the chloroform disolvate dimers [$Ag_2X_2(PPh_3)_4$]·$2CHCl_3$ show single strong ν(AgX) bands at 166 and 120 cm^{-1} for X = Cl or Br respectively (Fig. 4). These are assigned as the B_{2u} and B_{3u} modes of the Ag_2X_2 core which are expected to be coincident for a D_{2h} structure with internal 90° angles (see above). This expectation is supported by the results of several previous studies, which suggest that the separation between the two IR active ν(MX) modes of planar MX_2M bridges is small when the bond lengths are nearly equal, and the bridge angles are close to 90°.[52–55] In order to investigate this point further, we have carried out approximate normal coordinate calculations.

We have shown previously that the metal–halogen vibrational frequencies of the metal–halogen core in phosphine–metal halide complexes can be calculated with reasonable accuracy by carrying out a normal coordinate analysis on the metal–halogen core only.[56–58] We have used this approach here to calculate the frequencies of D_{2h} Ag_2X_2 units, and to investigate the effects of a distortion of this unit from D_{2h} to C_{2h} symmetry. A simple diagonal force field was used which involves an Ag–X bond stretching force constant f_r and X–Ag–X, Ag–X–Ag angle bending force constant f_α, with $f_\alpha = 0.1 f_r$. The Ag–X bond lengths for the D_{2h} Ag_2X_2 units were taken as the average of the Ag–X bond lengths in the chloroform disolvates [$Ag_2X_2(PPh_3)_4$]·$2CHCl_3$, and all of the internal bond angles were set equal to 90°. In agreement with the expectations discussed above, these yield identical values for the wavenumbers of the IR-active B_{2u} and B_{3u} modes. The values of the bond stretching force constants f_r which give exact agreement between the calculated wavenumber of these modes and the wavenumber of the single observed ν(AgX) band in the chloroform disolvates are given in Table 6. Distortion of the Ag_2Cl_2 unit to the C_{2h} structure observed in unsolvated [$Ag_2Cl_2(PPh_3)_4$] while maintaining equal force constants for all of the Ag–Cl bonds results in a difference of only 1 cm^{-1} between the wavenumbers of the two IR-active ν(AgCl) modes. In order to produce the much greater difference between the wavenumbers of the two bands assigned as ν(AgCl) in this complex, different values of the force constants for the two inequivalent sets of Ag–Cl bonds must be used. The values which reproduce the wavenumbers of the two bands at 179 and 127 cm^{-1} in unsolvated [$Ag_2Cl_2(PPh_3)_4$] are given in Table 6. The force constant for the shorter bond is about a factor of two greater than that for the longer bond. In order to determine whether this is reasonable for the bond lengths concerned, a

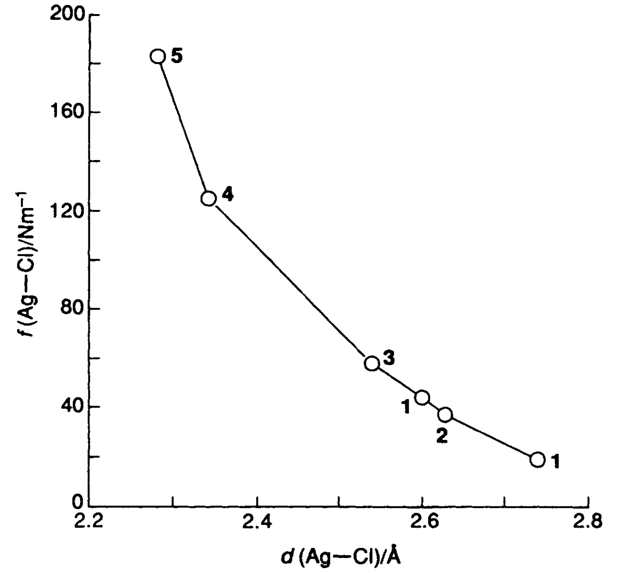

Fig. 5 Dependence of the AgCl force constant on bond length in some AgCl complexes; $[\{AgCl(PPh_3)_2\}_2]$ **1**, $[\{AgCl(PPh_3)_2\}_2]\cdot 2CHCl_3$ **2**, $[AgCl(PPh_3)_3]$ **3**, [AgCl(tmpp)] **4** and AgCl **5**

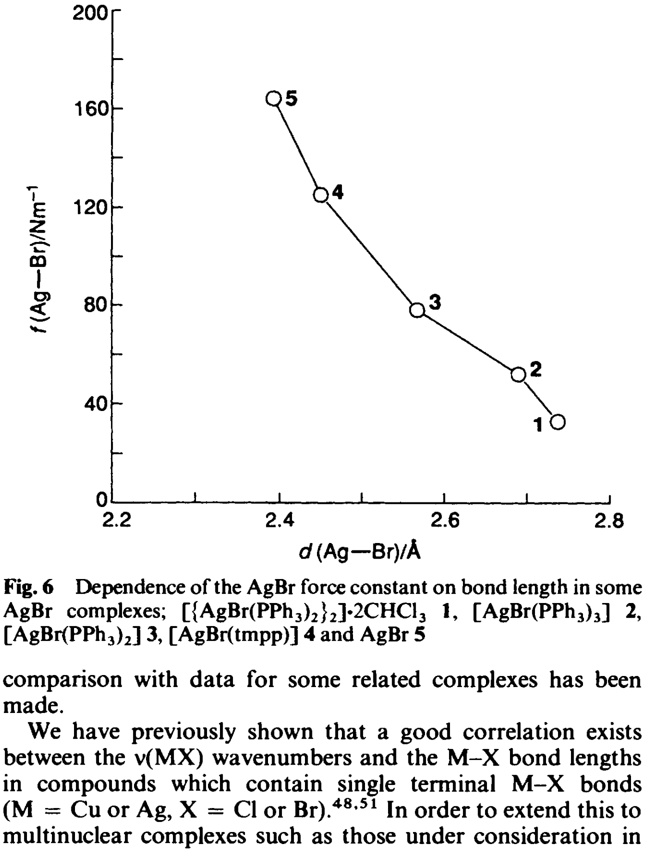

Fig. 6 Dependence of the AgBr force constant on bond length in some AgBr complexes; $[\{AgBr(PPh_3)_2\}_2]\cdot 2CHCl_3$ **1**, $[AgBr(PPh_3)_3]$ **2**, $[AgBr(PPh_3)_2]$ **3**, [AgBr(tmpp)] **4** and AgBr **5**

comparison with data for some related complexes has been made.

Table 7 Vibrational wavenumbers (cm⁻¹) for the MXP_n core in $[MX(PPh_3)_n]$ (n = 1 or 2)

Complex	ν(MP) Raman	ν(MX) IR	ν(MX) Raman	Ref.
$[AgBr(PPh_3)_2]$	132	170	169	*
$[AuCl(PPh_3)_2]$	164	221	211	50*
$[AuBr(PPh_3)_2]$	160	139	138	50*
$[AuI(PPh_3)_2]$	158	119	118	50*
$[AuCl(PPh_3)]$	182	329	329	59
$[AuBr(PPh_3)]$	173	234	234	59
$[AuI(PPh_3)]$	159	189	189	60

* This work.

We have previously shown that a good correlation exists between the ν(MX) wavenumbers and the M–X bond lengths in compounds which contain single terminal M–X bonds (M = Cu or Ag, X = Cl or Br).[48,51] In order to extend this to multinuclear complexes such as those under consideration in this work, force constants must be considered instead of the vibrational frequencies. The Ag–X force constants and bond lengths for diatomic AgX (X = Cl or Br) and a number of mononuclear complexes of AgX with phosphine ligands are given in Table 6 for comparison with the results obtained from the normal coordinate treatment for the dinuclear complexes. The data for the mononuclear complexes were obtained by using a diatomic approximation, which is consistent with the approach of considering only the Ag_2X_2 core in the dinuclear case. The relationship between the force constants and the bond lengths is shown graphically in Figs. 5 and 6. In both cases good monotonic relationships are observed. For the X = Cl case, this provides good support for the interpretation of the spectrum of the unsolvated $[Ag_2Cl_2(PPh_3)_4]$, and confirms that the splitting of the ν(AgCl) bridging mode is due to the presence of the two different kinds of Ag–Cl bonds of different strength. For the X = Br case, the present results for three-co-ordinate $[AgBr(PPh_3)_2]$ are seen to fit in very well with those obtained previously for one-, two- and four-co-ordinate species.

The Raman spectra of the complexes were recorded, but these yielded no new information except in the case of $[AgBr(PPh_3)_2]$. Bands assigned to the $AgBrP_2$ group in this complex are listed in Table 7. In addition to a ν(AgBr) band at 169 cm⁻¹ which is almost coincident with the band due to the same mode at 170 cm⁻¹ in the IR spectrum, there is a band at 132 cm⁻¹ in the Raman spectrum which is assigned to a ν(AgP) mode. For the C_{2v} $AgBrP_2$ unit, two IR and Raman active ν(AgP) modes are expected, but only a single band is observed in the Raman spectrum. In order to provide further data to support this assignment, we have recorded the Raman spectra of the series $[AuX(PPh_3)_2]$ (X = Cl, Br or I), and the bands assigned to the $AuXP_2$ group are listed in Table 7. The pattern of bands was similar to that of the corresponding AgBr complex. For the gold complexes, ν(AuP) appears as a single band at about 160 cm⁻¹, the wavenumber decreasing slightly from the AuCl to the AuI complex. The Raman spectra of $[AuX(PPh_3)]$ show strong bands at 182 or 173 cm⁻¹ (X = Cl or Br) which have been assigned as ν(AuP),[59] and we have measured the Raman spectrum of $[AuI(PPh_3)]$ and find ν(AuP) 159 cm⁻¹ in this case.[60] The decrease in the ν(AuP) frequency from the 1 : 1 to the 2 : 1 complexes is consistent with the expected weakening of the bond as the co-ordination number increases from two to three, and correlates well with an increase in the Au–P bond length; Au–P 2.23 Å in $[AuCl(PPh_3)]$, 2.33 Å in $[AuCl(PPh_3)_2]$.[19] As discussed above, the Ag–P bond length in $[AgBr(PPh_3)_2]$ is greater than the Au–P bond length in $[AuBr(PPh_3)_2]$ (Table 3), despite the fact that Au has a greater atomic radius than Ag. This is a clear indication that the Ag–P bond is weaker than the Au–P bond, and this correlates well with the lower ν(MP) value found for the silver complex (Table 7). The difference must be considerable; if the bond strengths were equal, difference in the metal atomic mass would result in a higher ν(MP) frequency for the silver complex.

*Phosphorus-*31 *CP MAS NMR Spectra.*—The naturally occurring isotopes of silver (^{107}Ag, 51.82% natural abundance; ^{109}Ag, 48.18%) both have nuclear spin $I = \frac{1}{2}$, and their magnetogyric ratios are similar in magnitude $[\gamma(^{109}Ag)/\gamma(^{107}Ag) = 1.15]$. Thus, the ^{31}P NMR spectra of complexes of silver(I) with phosphorus donor ligands may show splitting due to $^{1}J(Ag-P)$ coupling, and such splitting has been observed in several studies of such complexes in solution.[28,48] The resulting spectra normally show two doublets in which the separate couplings of ^{31}P to the ^{107}Ag and ^{109}Ag nuclei are resolved. Despite the large number of ^{31}P NMR studies of silver(I) complexes of phosphorus donor ligands in solution, only three solid-state

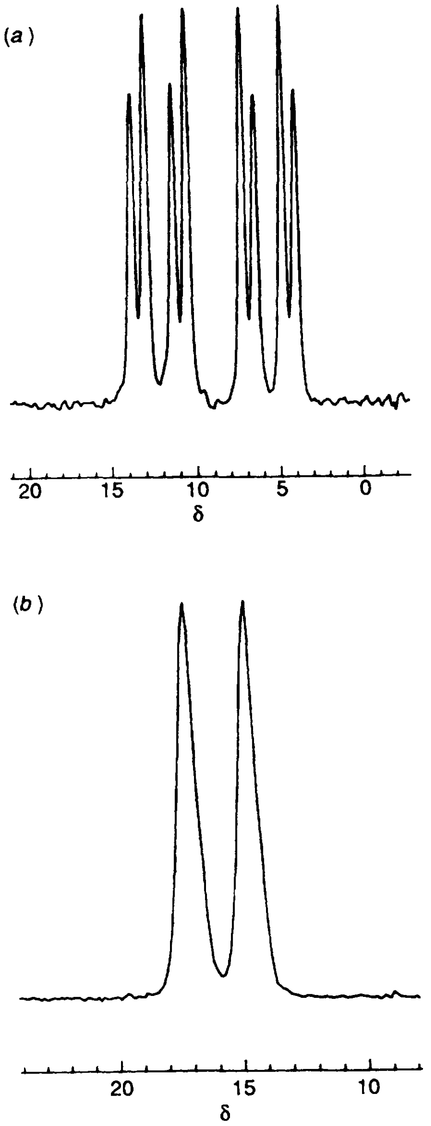

Fig. 7 Phosphorus-31 CP MAS NMR spectra of (*a*) $[Ag_2Cl_2(PPh_3)_4]$ and (*b*) $[AgBr(PPh_3)_2]$

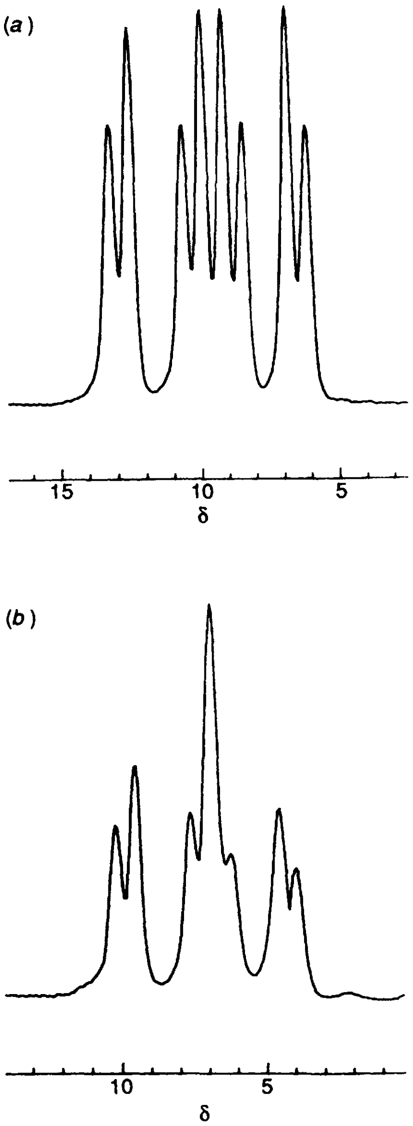

Fig. 8 Phosphorus-31 CP MAS NMR spectra of $[Ag_2X_2(PPh_3)_4]\cdot2CHCl_3$; (*a*) X = Cl, (*b*) X = Br

Table 8 Phosphorus-31 CP MAS NMR parameters

Complex	δ	^1J(AgP)/Hz	^2J(PP)/Hz
$[Ag_2Cl_2(PPh_3)_4]$	12.2, 5.7	394, 394	131
$[Ag_2Cl_2(PPh_3)_4]\cdot2CHCl_3$	11.6, 7.7	423, 376	113
$[AgBr(PPh_3)_2]$	16.0	394	—
$[Ag_2Br_2(PPh_3)_4]\cdot2CHCl_3$	8.6, 5.4	410, 360	102

studies have been reported to date.[28,29,48] The ^{31}P CP MAS NMR spectra of these complexes normally show splitting due to ^1J(Ag–P) coupling, but the separate splittings due to the ^{107}Ag and ^{109}Ag nuclei are not normally resolved due to the greater linewidths ($\Delta\nu_{\frac{1}{2}} \approx 40$ Hz) which are observed in the solid-state spectra. However, it has recently been shown that this isotopic splitting can be resolved in some cases.[48]

The ^{31}P CP MAS NMR spectra of the unsolvated $[AgBr(PPh_3)_2]$ and $[Ag_2Cl_2(PPh_3)_4]$ comprise Fig. 7 whilst those of $[Ag_2X_2(PPh_3)_4]\cdot2CHCl_3$ (X = Cl or Br) are shown in Fig. 8. The chemical shifts and coupling constants determined from these spectra are listed in Table 8. The monomeric AgBr complex exhibits a simple doublet due to ^1J(Ag–P) coupling arising from the A_2 part of an A_2X spin system, where A_2 represents the two crystallographically equivalent P nuclei and X represents the Ag nucleus. The observed resonances for the dimers arise from the superposition of two quartets emanating from two inequivalent P sites associated with each Ag nucleus. These additional resonances identify the AM portion of a total AMX spin system (X again representing the Ag nucleus), with evident further splittings assigned to (*a*) two potentially different ^1J(AgP) couplings for the two chemically and magnetically inequivalent P atoms, and (*b*) a smaller ^2J(PP) coupling between these P sites. This AMX coupling scheme is further illustrated by the two-dimensional ^{31}P CP MAS COSY result of $[Ag_2Cl_2(PPh_3)_4]$ given in Fig. 9, where the selective association of each doublet is described. As observed, each doublet is not correlated to all other doublets, but rather for each passive ^1J(AgP) coupling (and associated chemical shift) there exists active homonuclear ^2J(PP) correlation only between doublets possessing the same ^1J(AgP) spin label. This result is analogous to previously reported ^{31}P CP MAS COSY experiments for the ^{31}P–^{199}Hg ABX system of $[Hg\{P(C_6H_{11})_3\}_2(ClO_4)_2]$,[38] and the more complicated ^{31}P–$^{63/65}Cu$ ABX system of $[\{Cu(PPh_3)_2(4\text{-}RC_6H_4NCN)\}_2]$ (R = H, Cl or Me).[39] Both cases of chloroform disolvates at the field strength of 9.4 T exhibit a reduced chemical shift difference between the P sites in comparison to $[Ag_2Cl_2(PPh_3)_4]$, with the $[Ag_2Br_2(PPh_3)_4]\cdot2CHCl_3$ complex showing substantial overlap of the

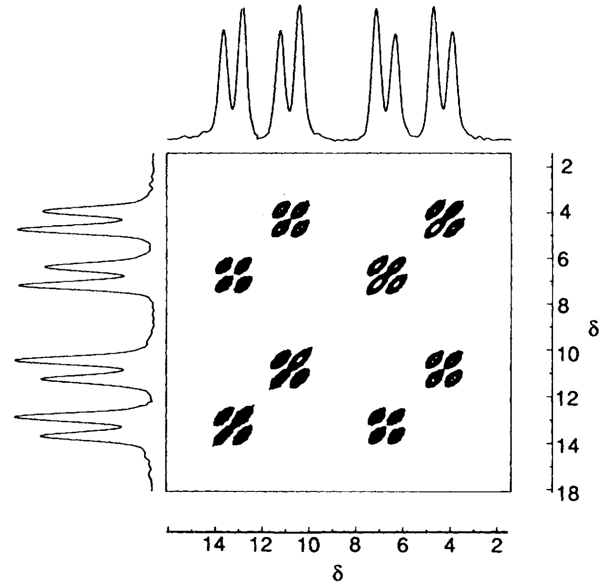

Fig. 9 Phosphorus-31 CP MAS COSY spectrum of $[Ag_2Cl_2(PPh_3)_4]$

high-field component of the low-field $^1J(AgP)$ doublet with the low-field component of its high-field counterpart. Similar spectra have been previously reported for $[Ag_2X_2L_4]$ (L = 3,4-dimethyl-1-phenylphosphole or 5-phenyldibenzophosphole),[28] with the NMR parameters for these complexes being similar to those reported for the dimers in Table 8. This interpretation of these spectra implies that the two AgP_2 units of each dimer behave identically and independently, with no observable coupling being translated across the halogeno bridges. The inequivalence of the two P sites in the AgP_2 units is consistent with the crystal structures which suggest that the dimer molecules possess a two-fold symmetry axis, and as outlined in Table 4, the differences between the two Ag–P bond lengths are greater in the chloroform disolvate dimers than in the unsolvated $[Ag_2Cl_2(PPh_3)_4]$.[18] This is also reflected by the $^1J(AgP)$ values of Table 8. However, in contrast, the chemical shift difference between the two inequivalent P sites is greatest for this latter complex.

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