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PAPER

Solution and mechanochemical syntheses, and spectroscopic and structural studies in the silver(I) (bi-)carbonate: triphenylphosphine system†

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Syntheses of a number of adducts of silver(I) (bi-)carbonate with triphenylphosphine, both mechanochemically, and from solution, are described, together with their infra-red spectra, ^{31}P CP MAS NMR and crystal structures. Ag(HCO$_3$):PPh$_3$ (1 : 4) has been isolated in the ionic form [Ag(PPh$_3$)$_4$](HCO$_3$)·2EtOH·3H$_2$O. Ag$_2$CO$_3$:PPh$_3$ (1 : 4) forms a binuclear neutral molecule [(Ph$_3$P)$_2$Ag(*O*,μ-*O*′·CO)Ag(PPh$_3$)$_2$](·2H$_2$O), while Ag(HCO$_3$):PPh$_3$ (1 : 2) has been isolated in both mononuclear and binuclear forms: [(Ph$_3$P)$_2$Ag(O$_2$COH)] and [(Ph$_3$P)$_2$Ag(μ-*O*·CO·OH)$_2$Ag(PPh$_3$)$_2$] (both unsolvated). A more convenient method for the preparation of the previously reported copper(I) complex [(Ph$_3$P)$_2$Cu(HCO$_3$)] is also reported.

Introduction

While adducts of univalent coinage metal carboxylates with Group 15 donor ligands have been widely studied, those of the parent carbonate species are much more limited and, in particular, for donors beyond the initial member nitrogen. Thus, for systems combining M/CO$_3$/ER$_3$ (M = Cu, Ag, Au; E = P, As, Sb), the only adducts for which crystal structure determinations have been hitherto recorded appear to be the complexes [{(Ph$_3$P)$_2$Cu}$_2$(CO$_3$)] and [{(Ph$_3$P)$_2$Cu}(μ-*O*·CO·OH)$_2$].[1] The ready accessibility of a number of novel species and/or forms by way of mechanochemical synthesis[2] has led us to explore the disilver(I) carbonate/tertiary phosphine system in this manner, resulting in a number of new and interesting complexes of this anion for which we record structural and spectroscopic characterization, and which extend those forms which we have accessed from solution.

Experimental

Synthesis

[{(Ph$_3$P)$_2$Ag}$_2$(CO$_3$)]·2H$_2$O. Disilver(I) carbonate (0.138 g, 0.5 mmol) was added to a solution of triphenylphosphine (0.787 g, 3.0 mmol) dissolved in warm acetonitrile (15 ml) and the mixture was stirred at ambient temperature in an open flask for 3 h, resulting in the formation of a voluminous off-white microcrystalline solid. Further acetonitrile (10 ml) was added and the mixture was gently heated to *ca.* 60 °C to dissolve the solid product. The resulting solution was filtered while hot to remove a small amount of black residue, and colourless crystals formed upon slow cooling of the filtrate in a covered flask. The product was collected by vacuum filtration. Yield 0.32 g (94%). Anal. Calcd for C$_{73}$H$_{64}$Ag$_2$O$_5$P$_4$: C, 64.43; H, 4.74. Found: C, 64.2; H, 4.7%.

[Ag(PPh$_3$)$_4$](HCO$_3$)·2EtOH·3H$_2$O. Disilver(I) carbonate (0.276 g, 1.0 mmol) was added to a solution of triphenylphosphine (1.128 g, 4.3 mmol) dissolved in warm ethanol (10 ml) and the mixture was stirred at ambient temperature in an open flask for 3 h, resulting in the formation of a colourless microcrystalline solid together with some black residue. The mixture was gently heated to dissolve the colourless product. The resulting solution was filtered while hot to remove the undissolved black residue (0.25 g), and colourless crystals formed upon slow cooling of the filtrate in a covered flask. A small sample of the product was removed, dried with filter paper, and examined under the microscope, revealing that the crystals slowly fragment to a white powder on standing in the air. Because of this instability, crystals for the X-ray work were taken directly from the reaction

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mixture and kept wet with mother liquor until transferred to the low-temperature stream of the diffractometer.

$[(\mathrm{Ph_3P})_2\mathrm{Ag(HCO_3)}]$. Method 1. To a boiling solution of triphenylphosphine (1.574 g, 6.0 mmol) in ethanol (30 ml) was added, with stirring, a hot solution of silver nitrate (0.510 g, 3.0 mmol) in water (5 ml). The resulting hot solution was immediately added, with rapid stirring, to a solution of sodium bicarbonate (1.05 g, 12.5 mmol) in water (30 ml) at ambient temperature. A white, flocculent precipitate formed immediately. The mixture was stirred until cool and the product was collected by vacuum filtration and washed with 1 : 1 EtOH/H$_2$O. Yield 2.013 g (97%). A portion of this product (1.0 g) was dissolved in acetonitrile by stirring and heating to 75 °C in a water bath. The resulting solution was filtered while hot to remove a small amount of black residue, and colourless crystals formed upon cooling of the filtrate in an open beaker and evaporation of about half of the solvent. Colourless crystals of the product were collected and dried on a piece of filter paper. Anal. Calcd for $C_{37}H_{31}AgO_3P_2$: C, 64.08; H, 4.51. Found: C, 63.9; H, 4.5%; N, < 0.2%. In view of the potential co-crystallization of nitrate with bicarbonate, we note specifically the absence of N in the elemental analysis, and the absence of nitrate bands in the IR spectrum of this and the corresponding copper(I) complex $[(\mathrm{Ph_3P})_2\mathrm{Cu(HCO_3)}]$ (see below). Method 2. Disilver carbonate (0.069 g, 0.25 mmol) and triphenylphosphine (0.262 g, 1.0 mmol) were ground together with a mortar and pestle, first dry and then after addition of ethanol (0.5 ml). As the grinding progressed the mixture formed an off-white paste, which was allowed to dry in the air before sampling for IR spectroscopy. This process was repeated six times with addition of ethanol (0.3 ml) each time. The IR spectrum of the final product was the same as that of the product obtained by Method 1 above.

$[(\mathrm{Ph_3P})_2\mathrm{Cu(HCO_3)}]$. A solution of $[(\mathrm{Ph_3P})_2\mathrm{Cu(NO_3)}]$ (0.650 g, 1.0 mmol) in acetonitrile (10 ml) at ambient temperature was slowly added dropwise to a rapidly stirred solution of sodium bicarbonate (2.135 g, 25.4 mmol) in water (50 ml) at ambient temperature. An initial white cloudy suspension partially coagulated upon further addition of the $[(\mathrm{Ph_3P})_2\mathrm{Cu(NO_3)}]$ solution, finally resulting in a white flocculent precipitate of product. This was collected and washed with water, followed by a small volume of ethanol (4 ml). Yield 0.496 g (76%). Anal. Calcd for $C_{37}H_{31}CuO_3P_2$: C, 68.46; H, 4.81. Found: C, 68.5; H, 4.9%; N, < 0.2%.

Structure determinations

Full spheres of CCD/area-detector diffractometer data were measured (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, ω-scans; T *ca.* 100 K) yielding $N_{\mathrm{t(otal)}}$ reflections, these merging to N unique after 'analytical'/face-indexed absorption correction (R_{int} cited), which were used in the full matrix least squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model. N_o reflections with $I > 2\sigma(I)$ were considered 'observed'; reflection weights were $(\sigma^2(F_o^2) + (aP)^2(+\,bP))^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$. Neutral atom complex scattering factors were employed within the SHELXL program.[3] Pertinent results are presented below and in the Tables and Figures, the latter showing the non-hydrogen atoms with 50% probability amplitude displacement ellipsoids, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å.

Crystal/refinement data

$[\{(\mathrm{Ph_3P})_2\mathrm{Ag}\}_2(\mathrm{CO_3})]\cdot 2\mathrm{H_2O} \equiv \mathrm{C_{73}H_{64}Ag_2O_5P_4}$, M_r = 1360.9. Triclinic, space group $P\bar{1}$(C_i^1, No. 2), a = 12.1730(3), b = 13.1340(6), c = 21.6602(10) Å, α = 88.890(4), β = 82.094(3), γ = 62.430(4)°, V = 3036.7(2) Å^3. D_c (Z = 2) = 1.48$_8$ g cm^{-3}. μ_{Mo} = 0.80 mm^{-1}; specimen: = 0.17 × 0.11 × 0.06 mm; 'T'$_{\mathrm{min,max}}$ = 0.91, 0.97. $2\theta_{\mathrm{max}}$ = 59°; N_t = 28935, N = 12361 (R_{int} = 0.083), N_o = 8081. $R1$ = 0.064, $wR2$ = 0.158 (a = 0.075); S = 0.93. $|\Delta\rho_{\mathrm{max}}|$ = 2.4 e Å^{-3}.

Variata. Difference map residues were modelled as a pair of water molecule oxygen atoms, one of which was disordered over a pair of sites, occupancies refining to 0.73(1) and complement (O···O′ 1.36(2) Å); associated hydrogen atoms were not located.

$[\mathrm{Ag(PPh_3)_4}](\mathrm{HCO_3})\cdot 2\mathrm{EtOH}\cdot 3\mathrm{H_2O} \equiv \mathrm{C_{77}H_{79}AgO_8P_4}$, M_r = 1364.2. Monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a = 18.2112(5), b = 20.6996(12), c = 20.3860(13) Å, β = 108.315(5)°, V = 7295.5(7) Å^3. D_c (Z = 4) = 1.24$_1$ g cm^{-3}. μ_{Mo} = 0.42 mm^{-1}; specimen: = 0.50 × 0.31 × 0.21 mm; 'T'$_{\mathrm{min,max}}$ = 0.82, 0.95. $2\theta_{\mathrm{max}}$ = 80°; N_t = 158838, N = 22140 (R_{int} = 0.056), N_o = 15154. $R1$ = 0.051, $wR2$ = 0.149 (a = 0.089); S = 0.98. $|\Delta\rho_{\mathrm{max}}|$ = 2.4 e Å^{-3}.

Variata. The cation was well-defined; the remainder of the components were modelled as disordered about the crystallographic 2-axis, occupancies 0.5, attempted modelling in a lower symmetry space group being unfruitful. Associated OH hydrogen atoms were not located.

$[(\mathrm{Ph_3P})_2\mathrm{Ag(O_2COH)}] \equiv \mathrm{C_{37}H_{31}AgO_3P_2}$, M_r = 693.4. Triclinic, a = 10.2351(3), b = 11.9944(3), c = 13.8661(3) Å, α = 85.949(2), β = 87.989(2), γ = 65.093(3)°, V = 1540.05(7) Å^3. D_c (Z = 2) = 1.49$_5$ g cm^{-3}. μ_{Mo} = 0.80 mm^{-1}; specimen: = 0.23 × 0.09 × 0.08 mm; 'T'$_{\mathrm{min,max}}$ = 0.87, 0.95. $2\theta_{\mathrm{max}}$ = 75°; N_t = 52522, N = 15737 (R_{int} = 0.037), N_o = 12086. $R1$ = 0.028, $wR2$ = 0.056 (a = 0.024); S = 0.92. $|\Delta\rho_{\mathrm{max}}|$ = 0.63 e Å^{-3}.

Variata. The bicarbonate hydrogen atom was refined in (x, y, z, U_{iso}), consistent with (at the least) the bulk of the sample being the bicarbonate, rather than the unsolvated mononuclear form of the nitrate, which has rather similar cell dimensions.[4]

$[(\mathrm{Ph_3P})_2\mathrm{Ag}(\mathit{O}\mathrm{.CO.OH})_2\mathrm{Ag(PPh_3)_2}]$. $\mathrm{C_{74}H_{62}Ag_2O_6P_4}$, M = 1386.9. Orthorhombic, space group $P2_12_12$ (D_2^3, No. 18), a = 14.990(2) Å, b = 23.435(7) Å, c = 9.296(3) Å, V = 3266(2) Å^3. D_c (Z = 2 dimers) = 1.41$_0$ g cm^{-3}. μ_{Mo} = 0.75 mm^{-1}; specimen: 0.31 × 0.30 × 0.28 mm; $T_{\mathrm{min,max}}$ = 0.80, 0.84 (gaussian correction). $2\theta_{\mathrm{max}}$ = 50°; N = 3229, N_o = 2669; R_1 = 0.035, $wR2$ = 0.069 (a = 0.011, b = 0.69); S = 1.05 $|\Delta\rho_{\mathrm{max}}|$ = 0.32 e Å^{-3}. x_{abs} = 0.21(4)

Variata. A unique data set for this specimen was measured previous to the above using a single counter instrument operating at room temperature (*ca.* 296 K). $(x,y,z,U_{\mathrm{iso}})_{\mathrm{H}}$ were refined for the disordered anionic hydrogen atom, after location in a difference map; constrained *cf.* unconstrained refinement resulted in no significant differences in the model. The complex is isostructural with its copper(I) analogue[1] and with the unsolvated binuclear $P2_12_12$ nitrate.[4]

Infrared spectroscopy

IR spectra were recorded at 4 cm^{-1} resolution on dry powders using a Perkin Elmer Spectrum 400 FT-IR spectrometer equipped with a Universal ATR sampling accessory. Far-infrared spectra were recorded at 4 cm^{-1} resolution using a Perkin Elmer Spectrum 400 FT-IR spectrometer on petroleum jelly mulls between Polythene plates.

NMR spectroscopy

^{31}P cross-polarisation, magic-angle-spinning (CPMAS) NMR spectroscopic data were acquired at 9.4 T on a Bruker DSX-400 spectrometer operating at a ^{31}P frequency of 161.92 MHz. All spectra were obtained with conventional cross-polarisation (CP) methods and a MAS frequency of ~10 kHz using a Bruker 3.2 mm double-air-bearing probe. The typical pulse parameters employed were: a ^{1}H $\pi/2$ pulse time of 3.5 μs, a Hartmann–Hahn contact period of 10 ms, a recycle delay of 20 s, and a ^{1}H decoupling field strength during acquisition of *ca.* 80 kHz. All data were referenced to 85% H_3PO_4 *via* an external reference of $(NH_4)(H_2PO_4)$ (δ 1.0 ppm), which was also used to set the Hartmann–Hahn match condition.

Results and discussion

Syntheses

The compound $[(Ph_3P)_2Ag(HCO_3)]$ was initially prepared adventitiously in an experiment involving the reaction of Ag_2CO_3 with triphenylphosphine in contact with air. The formation of the bicarbonate implies incorporation of CO_2 and H_2O from the air during the course of the reaction:

$$Ag_2CO_3 + 4PPh_3 + H_2O + CO_2 \rightarrow 2[(Ph_3P)_2Ag(HCO_3)] \quad (1)$$

In order to investigate this question further, the Ag_2CO_3 + $4PPh_3$ reaction was investigated by the method of solvent-assisted mechanochemical synthesis, which has recently been shown to be applicable to the synthesis of a range of different types of coordination compound.[2,5] The IR spectrum of the initially formed product showed the presence of both a carbonate and a bicarbonate complex, with the proportion of bicarbonate increasing at the expense of carbonate with successive treatments (see Experimental and IR Spectroscopy sections). This implies that the reaction proceeds in two stages:

$$Ag_2CO_3 + 4PPh_3 \rightarrow [\{(Ph_3P)_2Ag\}_2(CO_3)] \quad (2)$$

$$[\{(Ph_3P)_2Ag\}_2(CO_3)] + H_2O + CO_2 \rightarrow 2[(Ph_3P)_2Ag(HCO_3)] \quad (3)$$

Subsequent experiments resulted in the synthesis of both of these compounds by conventional solution methods. $[\{(Ph_3P)_2Ag\}_2(CO_3)]$ was prepared as the dihydrate $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$ by reaction of Ag_2CO_3 and PPh_3 in a 1 : 6 mole ratio in acetonitrile. Carrying out the reaction in dry acetonitrile with exclusion of air resulted in no dissolution of the Ag_2CO_3 and no product formation, but the product formed rapidly in contact with ambient air, with incorporation of H_2O from the air. Removal of $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$ as a solid product prevented further reaction with CO_2 from the air to form a bicarbonate complex. Use of ethanol as a solvent, as in the mechanochemical experiment, prevented the formation of an insoluble carbonate complex, but the reaction was found to be very temperature sensitive. Heating was required to dissolve Ag_2CO_3 in the ethanolic PPh_3 solution, but such solutions began to decompose, with deposition of a silver mirror in the reaction flask, before all of the Ag_2CO_3 was dissolved. It was thus difficult to prepare solutions with a sufficiently high silver content to produce the target $[(Ph_3P)_2Ag(HCO_3)]$ complex. The formation of bicarbonate in these reactions was demonstrated in one case by the isolation of the complex $[Ag(PPh_3)_4](HCO_3)\cdot 2EtOH\cdot 3H_2O$, which, however, was unstable w.r.t. loss of at least some of the solvate ethanol or water molecules (see Experimental, Structure determinations and IR Spectroscopy sections). As a result of these difficulties, the target $[(Ph_3P)_2Ag(HCO_3)]$ complex was synthesised by a different route, involving metathesis of the corresponding nitrate complex with bicarbonate:

$$[(Ph_3P)_2Ag(NO_3)] + HCO_3^- \rightarrow [(Ph_3P)_2Ag(HCO_3)] + NO_3^- \quad (4)$$

This was characterized by X-ray crystallography, and shown by IR spectroscopy to be identical to the final product of the $Ag_2CO_3 + 4PPh_3$ mechanochemical reaction. Previously published examples of applications of solvent-assisted mechanochemical synthesis to the preparation of coordination compounds have all involved the use of solid- or liquid-phase reactants. The present example of the formation of $[(Ph_3P)_2Ag(HCO_3)]$ from Ag_2CO_3 + $4PPh_3$ demonstrates that gas phase reactants (CO_2 in this case; eqn (3)) can also be readily incorporated by this method.

An attempted synthesis of the copper(I) carbonate complex $[\{(Ph_3P)_2Cu\}_2(CO_3)]$ *via* redox reaction between basic copper(II) carbonate $CuCO_3\cdot Cu(OH)_2$ and triphenylphosphine:

$$CuCO_3\cdot Cu(OH)_2 + 5Ph_3P \rightarrow [\{(Ph_3P)_2Cu\}_2(CO_3)] + Ph_3PO + H_2O \quad (5)$$

was unsuccessful; no reaction at all was observed between the basic copper(II) carbonate and Ph_3P, *cf*. the synthesis of triphenylphosphine copper(I) halide complexes from copper(II) halide and triphenylphosphine. This precludes access to the copper(I) bicarbonate complex $[(Ph_3P)_2Cu(HCO_3)]$ *via* the potential route:

$$CuCO_3\cdot Cu(OH)_2 + 5Ph_3P + CO_2 \rightarrow 2[(Ph_3P)_2Cu(HCO_3)] + Ph_3PO \quad (6)$$

A previously reported synthesis of $[(Ph_3P)_2Cu(HCO_3)]$ used an indirect route, involving decarboxylation of the precursor complex bis(triphenylphosphine)copper(I) phenylmalonate benzyl ester.[1] In the present study we have prepared a compound of the same composition by a metathesis route analogous to that in eqn (4) for the corresponding silver(I) complex (see Experimental, Infrared, and ^{31}P CP MAS NMR sections).

Structure determinations

The results of the single crystal X-ray studies define the stoichiometries and forms of the above silver(I) (bi-)carbonate: triphenylphosphine complexes. The maximal stoichiometry of four triphenylphosphine ligands per silver atom is achieved in the salt formulated as $[Ag(PPh_3)_4](HCO_3)\cdot 2EtOH\cdot 3H_2O$, the anionic and solvent components being ill-defined in the context of very extensive data, despite expectations consequent on their appreciable charges and/or dipolar characteristics. One half of the formula unit comprises the asymmetric unit of the structure, the cation being disposed with the metal atom lying on a crystallographic 2-axis in space group $C2/c$ (Fig. 1; *cf.* a number of the other examples of $[M(EPh_3)_4]^+$ recorded in ref. [6] in salts which crystallize in space group $R\bar{3}$, with the cation disposed on (and, usually somewhat disordered about) the crystallographic 3-axis)). Here we find Ag–P precisely established to be almost identical (2.6037(4), 2.6168(4) Å) with P–Ag–P about the axis 108.97(2), and 110.69(2)°, and between the distinct phosphorus atoms 108.42(2) and 110.16(1)°, a closely regular tetrahedral array with Ag–P 2.61 Å, more in keeping with the trend expected for the sequence Ag–As 2.67, Ag–Sb 2.73 Å in $[Ag(EPh_3)_4]^+$ arrays than previously estimated.[6]

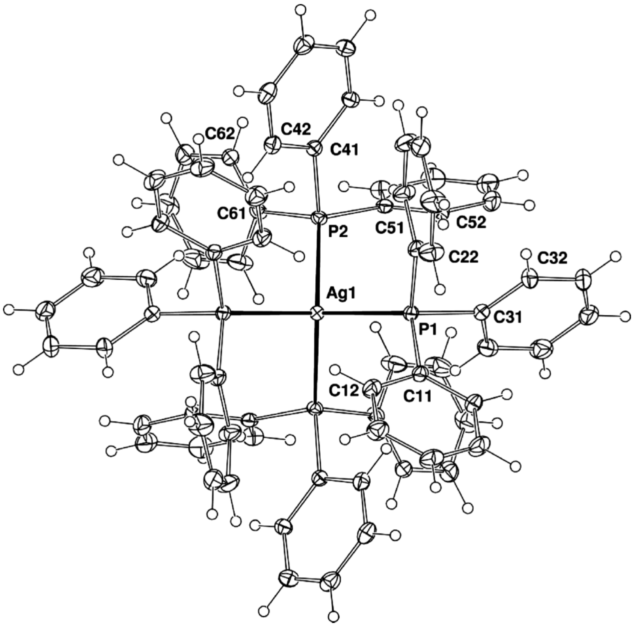

Fig. 1 Projection of the $[Ag(PPh_3)_4]^+$ cation in $[Ag(PPh_3)_4](HCO_3)\cdot 2EtOH\cdot 3H_2O$ down the/its (crystallographic) two-fold axis.

The remaining structurally characterized adducts all have two triphenylphosphine ligands per silver atom, all silver atoms being three- or four-coordinate with $P_2AgO_{1,2}$ environments. One of these incorporates the carbonate ion as a complex of disilver(I) carbonate, thus Ag_2CO_3:PPh_3 (1 : 4) $\cdot 2H_2O$. The complex is shown to be binuclear $[\{(Ph_3P)_2Ag\}_2(CO_3)]$, in a triclinic cell rather similar to that of the copper(I) analogue recorded in ref. [1]; a full neutral molecule devoid of crystallographic symmetry (together with solvent), comprises the asymmetric unit of the structure. The molecule is shown projected normal to the plane of the carbonate group which bridges the two silver atoms (Fig. 2). The structure, however, is subtly different from that of the copper atom, the linkage between the metal atoms being M(O·C(μ-*O*)·O)M in the case of the copper complex, the bridging array having *quasi*-C_{2v} symmetry, and the metal atoms both four-coordinate, P_2CuO,(μ-O), while in the silver complex, the array becomes unsymmetrical M(*O*·CO(μ-*O*))M (*m*-symmetry), Ag(1) being four-coordinate P_2AgO,(μ-O) and Ag(2) three-coordinate P_2Ag(μ-O), the distance Ag(2)···O(3) having now become long. Core geometries for both species are presented in Table 1, wherein we see that the geometry about Ag(2) may be considered trigonal planar. Although hydrogen atoms have not been defined, the residues assigned as probable water molecule components all lie at sensibly interacting distances with the carbonate oxygen atoms, thus O(4) (full component)···O(2,5) 2.702(6), 2.92(1); O(5)(fragment)···O(3) 2.88(1); O(6)(fragment)···O(3) 2.54(3) Å.

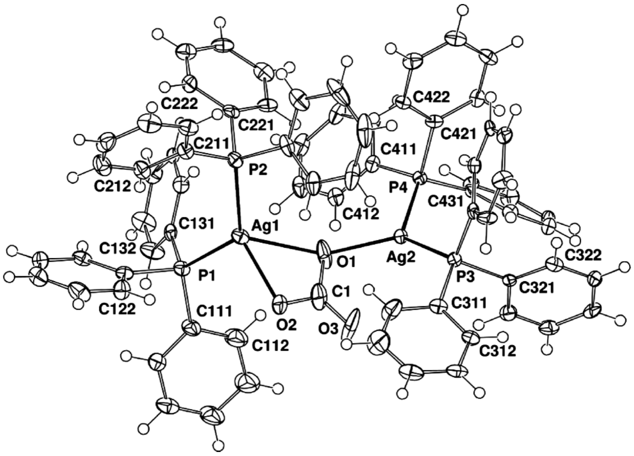

Fig. 2 Projection of a single molecule of $[\{(Ph_3P)_2Ag\}_2(CO_3)]$, normal to the carbonate plane.

With the bicarbonate two forms have been obtained, both crystallized from acetonitrile and both unsolvated, with neutral molecules of quite different nuclearities. The asymmetric unit of the mononuclear, triclinic 'α' phase contains a single molecule of the form $[(Ph_3P)_2Ag(O_2COH)]$, devoid of crystallographic symmetry; it is depicted in Fig. 3. Ag–P;O are 2.4323(3), 2.4345(3); 2.4128(7), 2.5951(9) Å, with P–Ag–P, O–Ag–O 132.882(9), 52.47(3), and P–Ag–O 100.47(2)–116.33(2)°. C–O;OH are 1.274(1), 1.241(1); 1.347(1) Å, with O–C–O; O–C–OH 123.9(1); 118.2(1), 117.9(1)°; the silver atom lies 0.071(2) Å out of the CO_3 plane. The molecule lies close to its inversion image, as shown in Fig. 3, by virtue of hydrogen bonding between their bicarbonate OH components (O,H(3)···O(1′) 2.624(1), 1.75(2) Å).

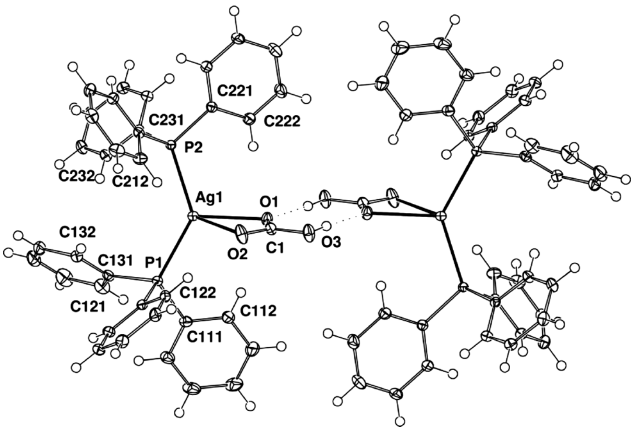

Fig. 3 Projection of mononuclear $[(Ph_3P)_2Ag(O_2COH)]$, through the (bi)carbonate plane, together with its hydrogen-bonded inversion image.

The second form was obtained adventitiously on only one occasion, and there was no obvious difference in the experimental conditions that led to this product. It takes a binuclear form

Table 1 Comparative core geometries of $[\{(Ph_3P)_2M\}_2(CO_3)]$, M = Cu, Ag

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
M(1)–O(1)	2.20(1), 2.438(4)	M(2)–O(1)	2.11(1), 2.232(4)
M(1)–O(2)	2.12(1), 2.376(4)	M(2)–O(3)	2.18(1), 2.914(6)
M(1)–P(1)	2.23(1), 2.438(1)	M(2)–P(3)	2.24(1), 2.434(1)
M(1)–P(2)	2.21(1), 2.426(2)	M(2)–P(4)	2.27(1), 2.455(1)
C(1)–O(1)	1.32(5), 1.314(7)	C(1)–O(3)	1.24(5), 1.231(8)
C(1)–O(2)	1.29(1), 1.277(7)		
Angles (degrees)			
P(1)–M(1)–P(2)	127.0(6), 125.15(5)	P(3)–M(2)–P(4)	119.1(6), 124.09(5)
P(1)–M(1)–O(1)	109.3(8), 121.2(1)	P(3)–M(2)–O(1)	112.7(8), 129.0(1)
P(2)–M(1)–O(1)	114.4(8), 106.8(1)	P(4)–M(2)–O(1)	125.8(8), 106.4(1)
P(1)–M(1)–O(2)	115.3(8), 103.7(1)	P(3)–M(2)–O(3)	118.6(7), —
P(2)–M(1)–O(2)	110.5(8), 126.3(1)	P(4)–M(2)–O(3)	104.4(7), —
O(1)–M(1)–O(2)	63(1), 54.3(1)	O(1)–M(2)–O(3)	60(1), —
M(1)–O(1)–C(1)	87(1), 92.0(3)	M(2)–O(3)–C(1)	91(1), —
M(2)–O(1)–C(1)	92(1), 105.8(3)	O(1)–C(1)–O(2)	119(1), 116.1(6)
M(1)–O(1)–M(2)	174(1), 151.9(2)	O(1)–C(1)–O(3)	115(1), 120.4(6)
M(1)–O(2)–C(1)	91(1), 95.8(4)	O(2)–C(1)–O(3)	126(1), 123.5(6)

In the copper complex,[1] Cu(1,2) lie 0.16(4), −0.35(4) Å out of the carbonate plane; counterpart values in the silver complex are 0.56(1), −1.24(1) Å. In the silver complex, the angle sum about Ag(2) is $359._5$°.

$[(Ph_3P)_2Ag(\mu\text{-}O\cdot COOH)_2Ag(PPh_3)_2]$, also unsolvated, one half of the dimer comprising the asymmetric unit of the structure. It is isomorphous with its copper(I) counterpart of ref. [1], and also the nitrate of ref. [4]; the dimer is depicted in Fig. 4(a). The silver atoms have $P_2Ag(\mu\text{-}O)_2$ coordination environments and are linked by a four-membered $Ag(\mu\text{-}O)_2Ag$ ring; comparative geometries which, apart from differing metal radii, are remarkably similar, but very different from those of the mononuclear form, are presented in Table 2. The generator of the dimer is the two-fold axis of the rather unusual space group $P2_12_12$ which passes through the (μ-O)-C bonds of each of the two bicarbonate components. The molecules are linked into columns along the 2-axis by hydrogen-bonds (O(12)···O(22) 2.591(5) Å; Fig. 4(b)), a feature not possible in the isomorphous nitrate.

Table 2 Comparative $[(Ph_3P)_2M(\mu\text{-}OX)_2M(PPh_3)_2]$ core geometries

M/OX	Cu/μ-OCOOH	Ag/μ-OCOOH	Ag/μ-ONO_2
Distances (Å)			
M–P(1)	2.272(3)	2.457(2)	2.448(1)
M–P(2)	2.283(3)	2.441(2)	2.425(1)
M–O(11)	2.150(7)	2.353(3)	2.341(3)
M–O(21)	2.154(7)	2.351(3)	2.340(3)
N,C(1)–O(11)	1.22(2)	1.251(9)	1.248(8)
N,C(2)–O(21)	1.27(2)	1.269(9)	1.288(7)
N,C(1)–O(12)	1.29(1)	1.295(5)	1.295(5)
N,C(2)–O(22)	1.27(2)	1.277(5)	1.290(4)
Angles (degrees)			
P(1)–M–P(2)	116.9(1)	120.55(5)	120.6(1)
P(1)–M–O(11)	104.5(2)	101.63(6)	101.2(1)
P(1)–M–O(21)	119.6(1)	117.87(4)	117.0(1)
P(2)–M–O(11)	121.9(1)	121.37(5)	122.1(1)
P(2)–M–O(21)	110.1(2)	111.24(6)	111.9(1)
O(11)–M–O(21)	78.6(3)	76.19(14)	75.7(1)
M–O(11)–C(1)	129.2(1)	128.13(10)	127.9(1)
M–O(21)–C(2)	129.4(2)	128.06(10)	127.8(1)
O(11)–C(1)–O(12)	122.1(7)	120.3(4)	120.8(3)
O(21)–C(2)–O(22)	119.4(8)	119.7(4)	119.4(3)
O(12)–C(1)–O(12′)	116(1)	119.5(7)	118.3(6)
O(22)–C(2)–O(22′)	121(2)	120.6(7)	121.2(5)
M–O(11)–M′	101.5(4)	103.7(2)	104.3(2)
M–O(21)–M′	101.3(2)	103.9(2)	104.4(2)
Metal atom deviations (δÅ) from the μ-O(C/N)O_2 plane			
δM/plane 1	0.18(2)	0.05(1)	0.19(1)
δM/plane 2	0.10(2)	0.22(1)	0.05(1)

Infrared spectroscopy

The IR spectra of the air-stable complexes in the range 800–1800 cm^{-1} are shown in Fig. 5. The bands of coordinated CO_3^{2-} arising from the E' ν(CO) (ν_3) mode of CO_3^{2-} normally occur in the range 1260–1580 cm^{-1};[7] in the IR spectrum of $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$ the bands at 1308, 1460 cm^{-1} are thus assigned, with possible additional absorption around 1400 cm^{-1} partially obscured by a strong Ph_3P band at 1433 cm^{-1} (Fig. 5(a)). The corresponding ν_3 absorption in pure solid Ag_2CO_3 occurs at 1410 cm^{-1}.[8] The splitting Δν of this band in $[\{(Ph_3P)_2Ag\}_2(CO_3)]$ (*ca.* 150 cm^{-1}) is at the lower end of the range 0–440 cm^{-1} that has been reported for a wide range of carbonato complexes.[9] It is also small compared with the range 200–300 cm^{-1} calculated on the basis of a linear correlation that has been proposed between Δν and Δα (the difference between the largest and the smallest O–C–O angle in the coordinated carbonate ion;[9] in the present case Δα = 11 ± 2°; Table 1). The A_1 ν(CO) (ν_1) mode of CO_3^{2-} in Ag_2CO_3 occurs at 1020 cm^{-1},[8] but unfortunately this is close to a strong Ph_3P band at 1069 cm^{-1}, so that unambiguous assignment of this mode in $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$ cannot be made. The A_2'' out-of plane bending (ν_2) mode of CO_3^{2-} in Ag_2CO_3 occurs at 880 cm^{-1},[8] and the band at 854 cm^{-1} in $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$ (Fig. 5(a)) is assigned to this mode. The ν_2 band has been reported to occur in the range 820–890 cm^{-1} in a wide range of carbonato complexes.[7,10]

The uncomplexed bicarbonate ion HCO_3^- shows asymmetric and symmetric CO stretching vibrations $\nu_{as}(CO)$ = 1697, $\nu_s(CO)$ = 1338 cm^{-1}, as well as a stretching vibration of the C–OH

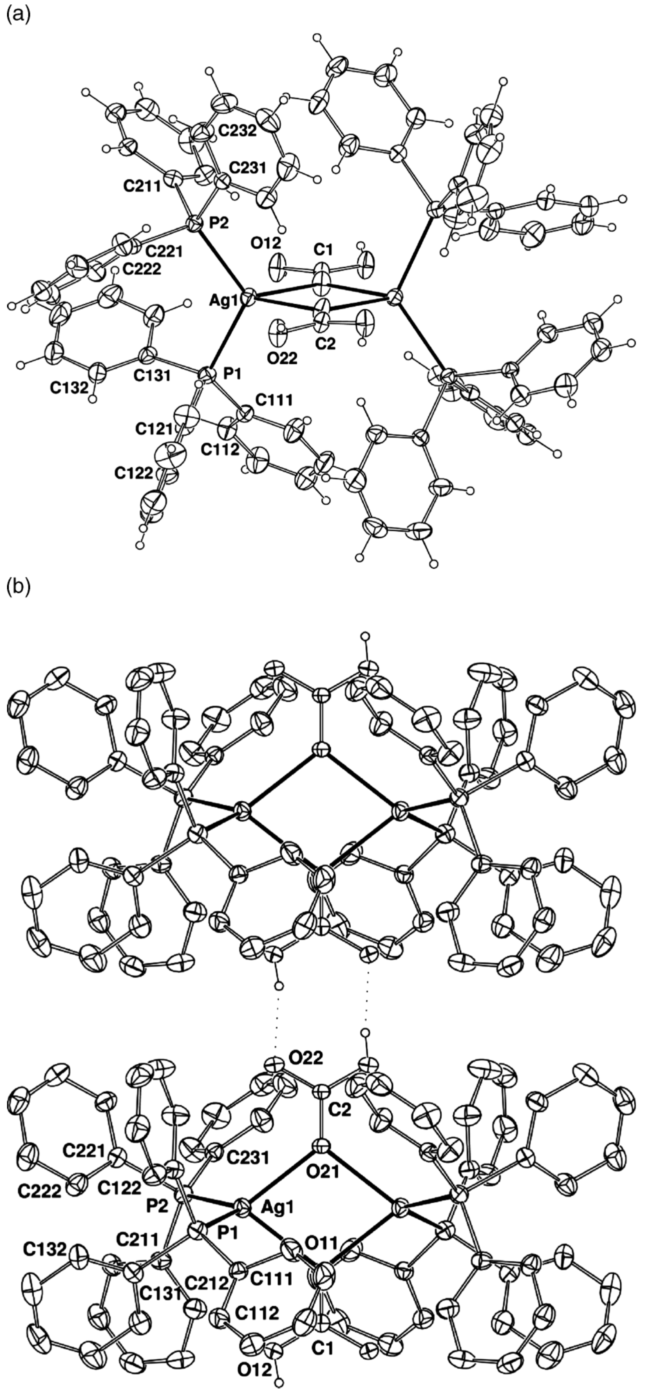

Fig. 4 (a) Projection of binuclear $[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$, through the central bis(bicarbonate) plane; (b) Projection normal to the central bis(bicarbonate) plane, showing the hydrogen-bonded columnar formation.

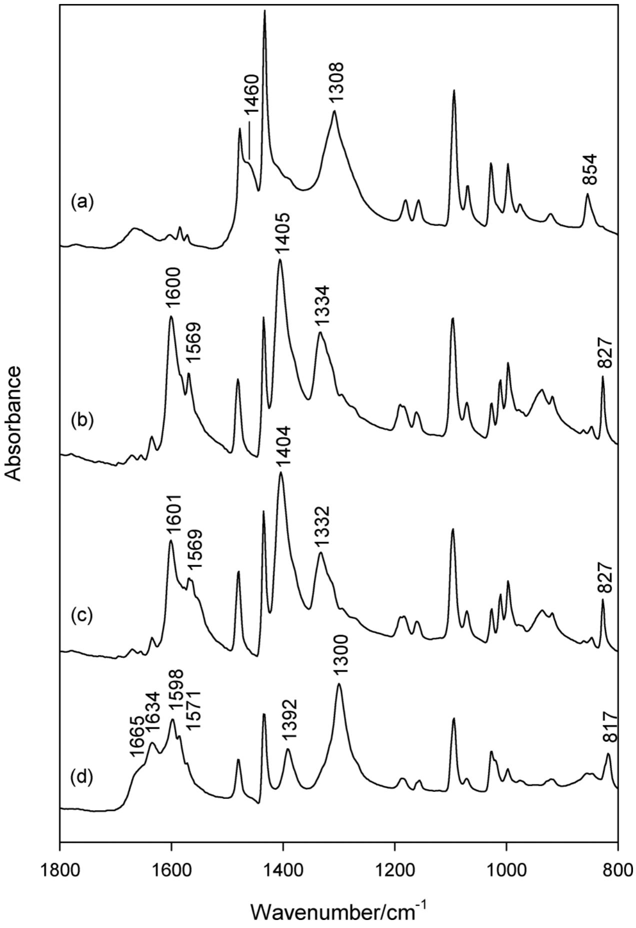

Fig. 5 Mid-IR spectra of (a) $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$; (b) $[(Ph_3P)_2Ag(O_2COH)]$; (c) $[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$; (d) $[(Ph_3P)_2Cu(HCO_3)]$.

bond ν(COH) = 960 cm^{-1}.[11] The corresponding absorptions in $[(Ph_3P)_2Ag(O_2COH)]$ are assigned at 1600, 1334, 936 cm^{-1} (Fig. 5(b)). An additional strong band is present at 1405 cm^{-1}, which does not appear to correspond to any of the ν(CO) modes in uncomplexed HCO_3^-. Although there are some reports of the existence of uncomplexed $AgHCO_3$ in the literature, with IR spectra reported in some cases, the material concerned has not been characterized to the extent that confident assignments of bands in its IR spectrum can be made.[12] However, the stoichiometric mixed valence silver(I, II, III) oxide bicarbonate $Ag_7O_8HCO_3$ has been reported and its IR spectrum assigned.[13] Assignments of $\nu_{as}(CO)$ = 1632, $\nu_s(CO)$ = 1314 cm^{-1} are in good agreement with those discussed above for uncomplexed HCO_3^- and $[(Ph_3P)_2Ag(O_2COH)]$. In addition, a band at 1448 cm^{-1} is assigned as δ(OHO) associated with the O–H···O hydrogen bonding between the bicarbonate ions in the compound, which agrees exactly with the value 1448 cm^{-1} calculated for the isolated $[HCO_3^-]_2$ dimer.[13] In the present $[(Ph_3P)_2Ag(O_2COH)]$ complex, the band at 1405 cm^{-1} is therefore assigned as δ(OHO) for the $2\times(Ph_3P)_2Ag^+$ complexed $[HCO_3^-]_2$ dimer present in this complex (Fig. 3). Rather surprisingly, the IR spectrum of the O-bridged dimer polymorph $[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$ is almost identical with that of the "monomer" form $[(Ph_3P)_2Ag(O_2COH)]$ (Fig. 5(c)), so the same assignments can be made. In the case of the O-bridged dimer, the presence of a δ(OHO) band at 1404 cm^{-1} is due to association of the dimers in a hydrogen-bonded columnar formation Fig. 4(b). While the IR spectra of the two polymorphs of $[(Ph_3P)_2Ag(HCO_3)]$ are almost identical, the ^{31}P CPMAS NMR spectra are more distinctly different (see NMR Spectroscopy section below). The uncomplexed bicarbonate ion HCO_3^- shows an out-of-plane bending mode (corresponding to the A_2'' out-of plane bending (ν_2) mode of CO_3^{2-}) at 835 cm^{-1},[11] and the band at 827 cm^{-1} in both polymorphs of [$(Ph_3P)_2Ag(HCO_3)$] (Fig. 5(b,c)) is assigned to this mode.

The IR spectrum of [$(Ph_3P)_2Cu(HCO_3)$] (Fig. 5(d)) is similar to those of the two corresponding [$(Ph_3P)_2Ag(HCO_3)$] polymorphs (Fig. 5(b,c)) so that similar assignments can be made: ν_{as}(CO) = 1598, ν_s(CO) = 1300, δ(OHO) = 1392 cm^{-1} (the expected ν(COH) band is not obvious in this case). There is some evidence of splitting of the ν_{as}(CO) band at *ca.* 1600 cm^{-1} in the two [$(Ph_3P)_2Ag(HCO_3)$] polymorphs (Fig. 5(b,c)), and this is more pronounced in the spectrum of [$(Ph_3P)_2Cu(HCO_3)$], with partially resolved bands at 1665, 1634, 1598, 1584, 1571 cm^{-1} (Fig. 5(d)). The crystal structure of a complex of this composition has been reported previously, and shows the O-bridged dimer structure [$(Ph_3P)_2Cu(\mu$-*O*.CO.OH$)_2Cu(PPh_3)_2$], with association of the dimers in a hydrogen-bonded columnar formation.[1] It is likely that the complex prepared in the present study has the same structure, although the fact that both “monomer” and O-bridged dimer forms have been found for the corresponding silver(I) complex leaves room for some ambiguity on this point. The band due to the out-of-plane bending mode of the bicarbonate ion HCO_3^- that corresponds to the A_2'' out-of plane bending (ν_2) mode of CO_3^{2-} occurs at 817 cm^{-1} in [$(Ph_3P)_2Cu(HCO_3)$] (Fig. 5(d)), shifted to lower wavenumber relative to the corresponding band at 827 cm^{-1} in both polymorphs of [$(Ph_3P)_2Ag(HCO_3)$] (Fig. 5(b,c)).

The IR spectra of the dry products from the solvent (ethanol) assisted mechanochemical reaction of Ag_2CO_3 + $2Ph_3P$ after 1–6 mechanochemical treatments (see Experimental section) are shown in Fig. 6. Initially the *E′* ν(CO) (ν_3) mode of CO_3^{2-} gives a single broad band centred at 1378 cm^{-1}, and there is no evidence of the bicarbonate ν_{as}(CO) band at 1600 cm^{-1} (Fig. 6(a)). Upon further mechanochemical treatments, the band at 1378 cm^{-1} splits, and a band at *ca.* 1600 cm^{-1} begins to appear (Fig. 6(b,c)). Finally, after six successive treatments, the spectrum (Fig. 6(d)) is essentially identical with those of the two [$(Ph_3P)_2Ag(HCO_3)$] polymorphs (Fig. 5(b,c)). This is consistent with the reaction (3) above, although the band at 1308 cm^{-1} corresponding to [$\{(Ph_3P)_2Ag\}_2(CO_3)$]·$2H_2O$ does not gain much intensity before the bicarbonate band begins to build, suggesting that the formation of the bicarbonate complex occurs almost as rapidly as the reaction between Ag_2CO_3 and Ph_3P. The A_2'' out-of plane bending (ν_2) mode of CO_3^{2-} in the initial product of the mechanochemical synthesis occurs at 845 cm^{-1} (Fig. 6(a)), significantly lower than the values for Ag_2CO_3 (880 cm^{-1})[8] and [$\{(Ph_3P)_2Ag\}_2(CO_3)$]·$2H_2O$ (854 cm^{-1}; Fig. 5(a)). This band shifts to lower wavenumber upon further mechanochemical treatment (Fig. 6(b–d)), approaching the value 827 cm^{-1} found for both polymorphs of [$(Ph_3P)_2Ag(HCO_3)$] (Fig. 5(b,c)), and in accordance with the reaction (3) above.

Further IR spectroscopic evidence for this reaction can be seen in changes in the spectra in the ν(OH) region, shown in Fig. 7. Broad bands due to H_2O in the 3200–3400 cm^{-1} region in the early stages of the mechanochemical process (Fig. 7(a,b)) decrease in intensity upon further mechanochemical treatment (Fig. 7(c,d) and are replaced by bands at 2670, 2615 cm^{-1} (Fig. 7(c,d)). These latter bands are assigned to ν(OH) of the H-bonded bicarbonate dimer groups in [$(Ph_3P)_2Ag(HCO_3)$], and may be compared with the values 2935, 2615 cm^{-1} in the H-bonded bicarbonate dimers in $KHCO_3$.[11] There is essentially no difference in the ν(OH) bands in the two polymorphs of [$(Ph_3P)_2Ag(HCO_3)$]; in [$(Ph_3P)_2Cu(HCO_3)$] ν(OH) is observed as a single band at 2615 cm^{-1}.

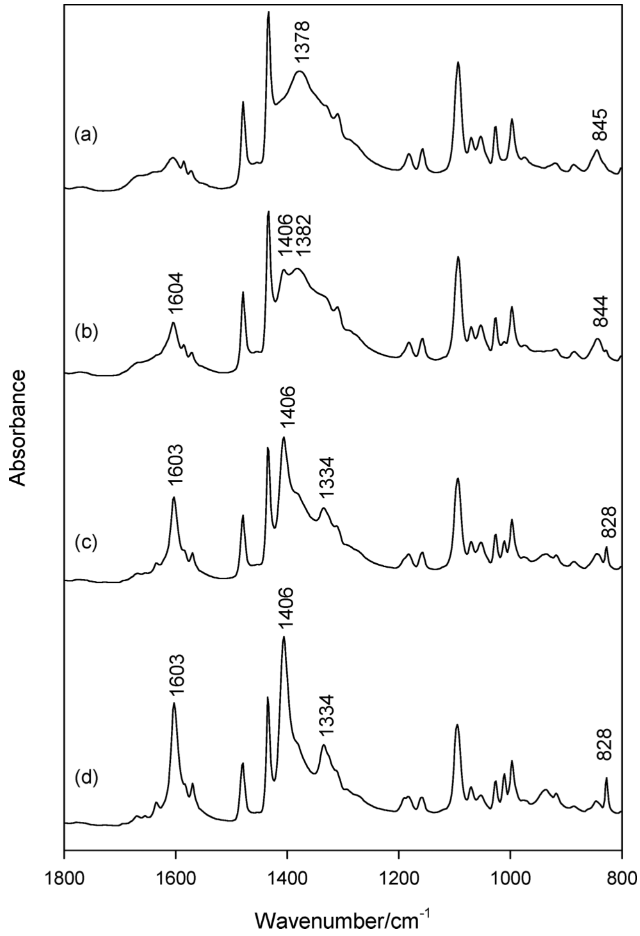

Fig. 6 Mid-IR spectra (800–1800 cm^{-1}) of the dry products from the solvent (ethanol) assisted mechanochemical reaction of Ag_2CO_3 + $2Ph_3P$ after (a) one; (b) two; (c) four; (d) six mechanochemical treatments.

Solid State ^{31}P MAS NMR Spectroscopy

The ^{31}P CPMAS NMR spectra of the air-stable complexes are shown in Fig. 8, and the derived NMR parameters are listed in Table 3. In general, the spectra of the silver complexes are expected to consist of partially resolved multiplets due to the individual ^{31}P chemical shifts emanating from the chemically inequivalent P nuclei bound to each Ag centre. Each resonance displays $^1J(^{107,109}Ag,^{31}P)$ scalar coupling between the ^{31}P ($I = 1/2$) and ^{107,109}Ag nuclei ($I = 1/2$), and further splitting of these doublets can occur *via* $^2J(^{31}P,^{31}P)$ coupling.[14,15] For the present compounds, this is well illustrated by the case of [$(Ph_3P)_2Ag(O_2COH)$], which contains two inequivalent P atoms bound to the same Ag atom, resulting in an ABX spin system (A, B = ^{31}P; X = ^{107,109}Ag) for each Ag isotope. The ^{31}P spectrum shows the AB part of the ABX spectra, which in general consists of two overlapping sets of AB quartets,[16] the separate patterns for coupling to the ^{107,109}Ag isotopes normally remaining unresolved. In the case of [$(Ph_3P)_2Ag(O_2COH)$] the spectrum consists of two non-overlapping, nearly identical AB quartets (Fig. 8(b)). This occurs in the special case for which the J_{AX}, J_{BX} coupling constants are

Table 3 ^{31}P CPMAS NMR parameters

Compound	$\delta(^{31}P)$/ppm	$^1J(^{107,109}Ag,^{31}P)$ or $^1J(^{63,65}Cu,^{31}P)$/Hz
$[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$	6.8	421
$[(Ph_3P)_2Ag(O_2COH)]$	6.1, 7.2	475, 469 (^2J(PP) = 147 Hz)
$[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$	5.4	432
$[(Ph_3P)_2Cu(HCO_3)]$	−7.7	1340

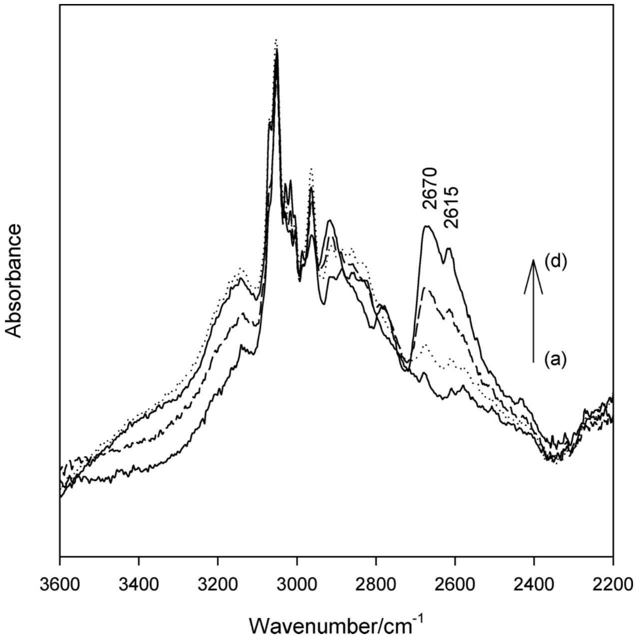

Fig. 7 Mid-IR spectra (2200–3600 cm^{-1}) of the dry products from the solvent (ethanol) assisted mechanochemical reaction of Ag_2CO_3 + $2Ph_3P$ after (a) one; (b) two; (c) four; (d) six mechanochemical treatments.

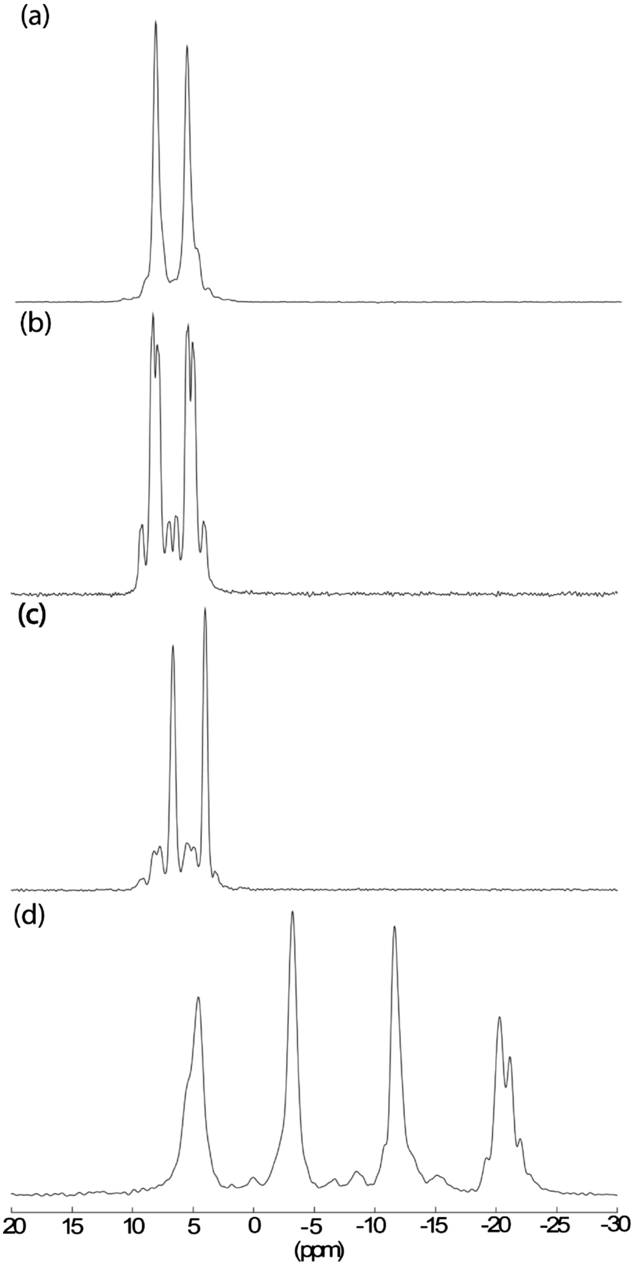

Fig. 8 ^{31}P CP MAS NMR spectra of (a) $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$; (b) $[(Ph_3P)_2Ag(O_2COH)]$; (c) $[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$; (d) $[(Ph_3P)_2Cu(HCO_3)]$.

nearly equal and the difference between the two ^{31}P chemical shifts δ_A, δ_B is small, as is evident from the values of the NMR parameters for $[(Ph_3P)_2Ag(O_2COH)]$ in Table 3. Expansion of this spectrum reveals that each line is an incompletely resolved doublet and this is attributed to resolution of the $^1J(^{107,109}Ag,^{31}P)$ coupling for the two silver isotopes, as evidenced by the good fit of the observed spectrum to that simulated with distinct $^1J(^{109}Ag,^{31}P)$, $^1J(^{107}Ag,^{31}P)$ values in the ratio 1.1496 corresponding to the ratio of the ^{109}Ag, ^{107}Ag magnetic moments (Fig. 9).

The spectrum of the sample from which crystals of the O-bridged dimer $[(Ph_3P)_2Ag(\mu\text{-}O.CO.OH)_2Ag(PPh_3)_2]$ were obtained shows a dominant intense doublet and a set of weaker signals (Fig. 8(c)), the latter being identical to those of the "monomer" polymorph $[(Ph_3P)_2Ag(O_2COH)]$ (Fig. 8(b)). This implies that the sample is a mixture consisting predominantly of the O-bridged dimer, but containing a smaller amount of the "monomer" form as well. The dominant doublet assigned to the dimer implies that the two P atoms are effectively equivalent in this case, although this is not required crystallographically (see Structure determination section and Fig. 3), resulting in a single ^{31}P chemical shift and $^1J(^{107,109}Ag,^{31}P)$ coupling constant (Table 3). A similar situation is found for the carbonate complex $[\{(Ph_3P)_2Ag\}_2(CO_3)]\cdot 2H_2O$, which shows essentially a simple doublet, despite the presence of four inequivalent P atoms in the molecule (see Structure determination section and Fig. 2).

The spectrum of $[(Ph_3P)_2Cu(HCO_3)]$ is shown in Fig. 8(d). The ^{31}P CP MAS NMR spectra of copper(I) phosphine complexes consist of quartets due to the $2I + 1 = 4$ splitting arising from $^1J(^{63,65}Cu,^{31}P)$ coupling (^{63}Cu, ^{65}Cu, $I = 3/2$). Multiplet peaks arising from ^{31}P coupling to ^{65}Cu are seen just outside of those

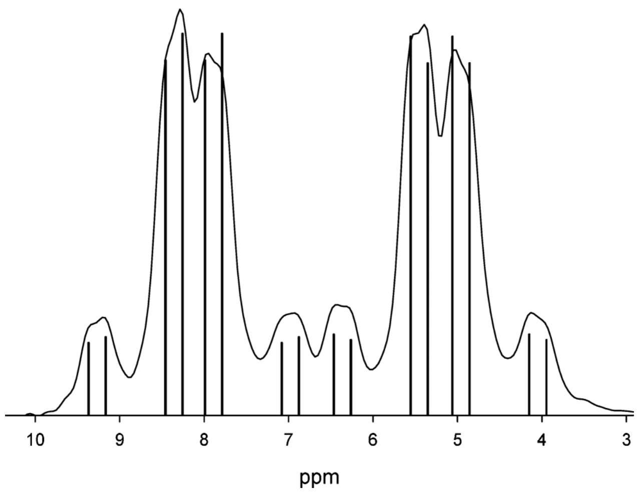

Fig. 9 Expansion of the ^{31}P CP MAS NMR spectrum of [(Ph$_3$P)$_2$Ag(O$_2$COH)] and stick diagram of the spectrum simulated as the AB part of an ABX system with $\delta_A = 6.14$, $\delta_B = 7.19$, $J_{AX}^{107} = 442$ Hz, $J_{AX}^{109} = 508$ Hz, $J_{BX}^{107} = 437$ Hz, $J_{BX}^{109} = 502$ Hz, $J_{AB} = 147$ Hz.

arising from coupling to ^{63}Cu, due to the slightly larger magnetic moment of the former. The peaks due to $^1J(^{63}\mathrm{Cu}, ^{31}\mathrm{P})$ are more than double the intensity of those arising from $^1J(^{65}\mathrm{Cu}, ^{31}\mathrm{P})$, due to the different natural abundances of the copper isotopes (69.1 and 30.9%, respectively). The spacings between the quartet peaks increase from high to low frequency due to the presence of residual dipolar coupling (*i.e.* from incomplete MAS averaging) between the ($I = 1/2$) ^{31}P and the quadrupolar ($I = 3/2$) ^{63,65}Cu nuclei.[14,17–21] These features are evident in the spectrum of [(Ph$_3$P)$_2$Cu(HCO$_3$)] (see Fig. 8(d)). If the structure of this complex is the same as that of the previously published O-bridged dimer [(Ph$_3$P)$_2$Cu(μ-*O*.CO.OH)$_2$Cu(PPh$_3$)$_2$][1] then the two P atoms bound to each Cu atom should be inequivalent. However, no evidence of $^2J(^{31}\mathrm{P}, ^{31}\mathrm{P})$ coupling is observed in this data and hence there is no suggestion of any inequivalence between these P positions. The NMR parameters, derived from a first order analysis of the spectrum,[20] for a single P site in the complex are given in Table 3. In this respect, the implied result for this particular copper complex is similar to that for [(Ph$_3$P)$_2$Ag(μ-*O*.CO.OH)$_2$Ag(PPh$_3$)$_2$].

Conclusion

Solution and mechanochemical methods involving incorporation of gaseous reactants have been used in the study of triphenylphosphine complexes of silver(I) carbonate and bicarbonate. In the case of the mechanochemical syntheses, this demonstrates an additional aspect of this type of synthesis, which potentially increases its versatility. The study further demonstrates the value of ATR IR and CPMAS NMR spectroscopy for monitoring the progress of mechanochemical syntheses.

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