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Crystal structures and vibrational and solid-state (CPMAS) NMR spectroscopic studies in the tris(triphenylphosphine)-copper(I) and -silver(I) formate systems

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The complexes $[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$ (**1**), $[Cu(PPh_3)_3O_2CH]\cdot 0.5EtOH$ (**2**), $[Ag(PPh_3)_3O_2CH]\cdot HCO_2H$ (**3**) and $[Ag(PPh_3)_3O_2CH]$ (**4**) have been prepared and studied by infrared and solid-state ^{13}C and ^{31}P cross-polarization magic-angle-spinning (CPMAS) NMR spectroscopy. Crystal structures of **1**, **2** and **3** show increasing degrees of disorder, but all are shown to contain $[M(PPh_3)_3O_2CH]$ molecular units containing a four-coordinate metal centre with the three crystallographically independent PPh_3 ligands occupying three of the coordination sites and the formate anion coordinated through one oxygen atom to the fourth site. The formic acid molecule in $[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$ is hydrogen-bonded to the formate ion ($O\cdots O = 2.529(5)$ Å) to form an assembly that is best described as a biformate anion $[H(HCO_2)_2]^-$. Unlike the corresponding silver(I) complex, $[Cu(PPh_3)_3O_2CH]$ is not stable in its unsolvated form; the loss of the solvent of crystallization results in conversion of the complex to $[Cu(PPh_3)_2O_2CH]$ and PPh_3. Bands in the IR spectra due to the formate and formic acid groups are assigned, and these are consistent with the silver complexes having structures analogous to those of the corresponding copper complexes. The ^{13}C CPMAS NMR spectra clearly resolve resonances from the formate and formic acid carbon atoms, while the ^{31}P CPMAS NMR spectra exhibit complex, partially resolved multiplets arising from inequivalence of the phosphine ligands and the presence of $^1J(M,^{31}P)$ and $^2J(^{31}P,^{31}P)$ scalar (or spin–spin) coupling. These spectra were interpreted with the aid of the 2D ^{31}P CPCOSY technique.

Introduction

Simple copper(I) and silver(I) carboxylates have long been known,[1,2] and have proved useful as reagents in organic and inorganic synthesis.[3] These compounds are easily oxidised or disproportionate in the presence of moisture, and it is only relatively recently that they, and the complexes they form, have been studied in detail. Adducts of copper(I) and silver(I) carboxylates with neutral ligands have been documented,[4–15] with structures reported for some cases.[8–15]

As the simplest carboxylate ligand the formate ion is of particular importance in the study of these types of compounds. It is also of interest with respect to some important industrial reactions involving small organic molecules, such as in the synthesis and selective partial oxidation of methanol, which may be carried out over copper and silver catalysts.[16,17] There is spectroscopic evidence for the existence of surface formate species on these catalysts,[18,19] and there is considerable interest in the mode of bonding of the formate species to the catalyst surface. It may be possible to shed further light on this by studying model copper(I) and silver(I) complexes involving coordinated formate whose structures and spectroscopic properties can be readily determined.

The only such complexes that have had their structures determined to date are $[Cu(triphos)O_2CH]$ [triphos = $MeC(CH_2CH_2PPh_2)_3$],[14] $[Cu(PPh_3)_2O_2CH]$,[9] $[Ag(PPh_3)_2O_2CH]$[15] and $[Ag(PPh_3)_2O_2CH]\cdot 2HCO_2H$.[15] Vibrational spectroscopic data for $[Cu(PPh_3)_2O_2CH]$, and for $[Cu(PPh_3)_3O_2CH]$, have been reported,[4,7] but the reports are limited to the symmetric and antisymmetric O–C–O stretching modes, and there are discrepancies in band assignments between these different studies. There is also little in the way of corroborating evidence between the structural and vibrational reports, with each report employing a different preparative route, and there are inconsistencies in the analytical data. Vibrational, as well as solid-state cross-polarisation magic-angle-spinning (CPMAS) NMR, spectroscopic data have been previously reported for $[Ag(PPh_3)_2O_2CH]$ and $[Ag(PPh_3)_2O_2CH]\cdot 2HCO_2H$.[15]

The aim of this work was to investigate the properties of the 1 : 3 complexes $[M(PPh_3)_3O_2CH]$ (M = Cu, Ag) and to compare these with the previously characterized 1 : 2 compounds. The spectroscopic techniques employed in this study were IR and solid-state CPMAS NMR spectroscopy. Vibrational spectroscopy has been shown to be particularly useful in providing information about the nature of carboxylate coordination *via* the dependence of the symmetric and antisymmetric O–C–O stretching mode positions on the mode of coordination.[20] For the NMR analyses of these systems, ^{13}C and ^{31}P CPMAS NMR studies were undertaken. The 100% natural abundance of the $I = 1/2$, ^{31}P isotope makes ^{31}P CPMAS NMR a particularly useful technique. It can provide information about the coordination environment of the $I = 3/2$, $^{63,65}Cu$ and $I = 1/2$, $^{107,109}Ag$ metal nuclei within these complexes as a result of the dependence of the $^1J(M,P)$ scalar (or spin–spin) coupling constant

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and, in the case of the copper compounds, the ^{63,65}Cu nuclear quadrupole coupling constant C_q ($= e^2qQ$), on changes in coordination environment. Single-crystal X-ray studies have also been used, where possible, to obtain detailed structural information about these complexes.

Experimental

Preparation of compounds

(*O*,*O*′-Formato)bis(triphenylphosphine)copper(I), [Cu(PPh$_3$)$_2$O$_2$CH]. This complex was prepared by a modification of the literature method,[4] by adding a hot solution of copper(II) formate (1.90 g, 10 mmol) in water (30 ml) to a hot solution of triphenylphosphine (6.56 g, 25 mmol) in ethanol (30 ml) to which concentrated ammonium hydroxide solution (1 ml) had been added, and boiling the mixture for a few minutes until the colour was discharged. Upon cooling, colourless crystals of the complex formed. These were collected by filtration, washed with a small quantity of ethanol/water (1:1), and air-dried. Yield 6.27 g, mp 184–186 °C. Found: C 69.9, H 5.0; calc. for $C_{37}H_{31}CuO_2P_2$: C 70.2, H 4.6%.

(*O*-Formato)tris(triphenylphosphine)copper(I) formic acid monosolvate, [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H 1. This complex was initially prepared by addition of 1.12 g (17.6 mmol) of copper powder to a stirred solution of 13.9 g (53 mmol) triphenylphosphine and 2 ml formic acid in 50 ml acetonitrile. After stirring for several hours the copper powder began to dissolve and a fine white precipitate of the complex began to form. After 2 days stirring all the copper powder had dissolved. After 3 days no further reaction appeared to have occurred, and the product was collected by filtration and dried *in vacuo*. Yield 5.6 g, mp: discharge of vapour 130–138 °C, solid darkened in colour 158 °C, solid melted 198–201 °C. Found: C 71.5, H 5.3; calc. for $C_{56}H_{48}CuP_3O_4$: C 71.4, H 5.1%.

The complex was subsequently prepared by dissolution of [Cu(PPh$_3$)$_2$O$_2$CH] (0.112 g, 0.18 mmol) in a warm stirred solution of PPh$_3$ (0.050 g, 0.19 mmol) and HCO$_2$H (0.048 g, 1.0 mmol) in CH$_3$CN (30 ml). Slow evaporation of the solution yielded the complex in the form of a white microcrystalline solid.

Crystals for the X-ray structure determination were obtained by dissolution of the complex in neat formic acid, followed by slow evaporation to yield colourless crystals. [Cu(PPh$_3$)$_3$O$_2$CD]·DCO$_2$D was also prepared *via* this technique by recrystallisation of [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H from neat DCO$_2$D.

(*O*-Formato)tris(triphenylphosphine)copper(I) ethanol hemisolvate, [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH 2. Hot water (25 ml) was added to a solution of [Cu(PPh$_3$)$_2$O$_2$CH] (1.90 g, 3 mmol) and triphenylphosphine (0.79 g, 3 mmol) in boiling ethanol (50 ml). Cooling and slow evaporation of the resulting solution (*ca.* 20 ml of solvent removed) yielded the complex as a white microcrystalline solid. The product was collected, washed with ethanol/water (1:1), and air-dried. Yield 2.23 g, mp 174–178 °C (see Discussion). Found: C 72.3, H 5.5; calc. for $C_{56}H_{49}CuO_{2.5}P_3$: C 73.2, H 5.4%.

(*O*,*O*′-Formato)bis(triphenylphosphine)silver(I), [Ag(PPh$_3$)$_2$O$_2$CH]. This complex was prepared by a modification of the literature method.[15] A solution of sodium formate (3.4 g, 50 mmol) in water (20 ml) was added to a solution of silver nitrate (1.70 g, 10 mmol) in water (10 ml) to yield a white slurry of silver formate. To this was added, with stirring, a hot solution of triphenylphosphine (5.25 g, 20 mmol) in ethanol (50 ml). The product formed immediately as an off-white precipitate, which was collected, washed with ethanol/water (1:1) and air dried. Yield 6.40 g.

(*O*-Formato)tris(triphenylphosphine)silver(I) formic acid monosolvate, [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H 3. This compound was originally obtained in crystalline form as a by-product in an attempted electrochemical synthesis of [Ag(PPh$_3$)$_2$O$_2$CH].[15] It was subsequently prepared as a pure product by the following method. Formic acid (3.0 g, 65 mmol) was added to a mixture of silver(I) oxide (0.58 g, 2.5 mmol) and triphenylphosphine (3.93 g, 15 mmol) in acetonitrile (10 ml). The silver oxide dissolved almost completely upon warming the mixture. The hot solution was filtered, and the filter was rinsed with warm acetonitrile (5 ml). The filtrate was allowed to stand, and the white solid that formed after most of the solvent had evaporated was treated with diethyl ether (20 ml), collected and washed with diethyl ether. Yield 4.49 g. Found: C 68.2, H 4.7; calc. for $C_{56}H_{48}AgO_4P_3$: C 68.2, H 4.9%.

(*O*-Formato)tris(triphenylphosphine)silver(I), [Ag(PPh$_3$)$_3$O$_2$CH] 4. A mixture of [Ag(PPh$_3$)$_2$O$_2$CH] (2.03 g, 3 mmol) and triphenylphosphine (0.89 g, 3.4 mmol) was dissolved in boiling ethanol (30 ml), and the resulting solution was filtered. The filtrate was heated, and water (30 ml) was added slowly with heating so that the solution just boiled. The product, which separated as a white microcrystalline solid upon cooling, was collected, washed with ethanol/water (1:2), and air-dried. Yield 2.85 g. Found: C 70.2, H 4.9; calc. for $C_{55}H_{46}AgO_2P_3$: C 70.3, H 4.9%.

Structure determinations

Spheres of X-ray data were collected for [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H, (**1**) and [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH, (**2**) using a Siemens SMART diffractometer with a CCD area detector system at 293 K. For [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H, (**3**), a unique single counter diffractometer data set was originally obtained at room temperature ($2\theta/\theta$ scan mode; T *ca.* 295 K) yielding N independent reflections, N_o being considered 'observed' according to the specified criterion and used in the least squares refinement after Gaussian absorption correction. Unlike the above copper complexes and related isomorphous structures,[2,3] disorder was extensive and the result regarded as unsatisfactory and shelved for some years. With the advent of an area detector (Bruker AXS CCD) instrument operating at lower temperature (*ca.* 153 K), the problem was exhumed and re-examined, a full sphere of data (N_t total reflections) being measured on a crystal obtained from a new preparation of the complex (see above), and merged after 'empirical' absorption correction (proprietary software 'SAINT'/'SADABS'/'XPREP')[53] (R_{int} quoted).

Monochromatic Mo-Kα radiation ($\lambda = 0.7107_3$ Å) was employed in all cases. The structures were solved by direct methods and refined by full matrix least squares refinement on F^2 after absorption corrections. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. 'Thermal' parameters of the minor anion fragments in the silver structure were refined with isotropic forms. Neutral atom complex scattering factors were used. Conventional residuals R on $|F|$ and R_w on $|F|^2$ are quoted at convergence. Computation used SHELX 97 or XTAL 3.4 software.[21,22] The three structures are isomorphous with those of other [(Ph$_3$E)$_3$MX]·solv arrays previously studied[23–25] (*e.g.* [(PPh$_3$)$_3$CuNO$_3$]·EtOH)[24] and the structures have been refined in the cell and coordinate setting of the latter. The carbon atoms of the PPh$_3$ ligands are labelled C(*lmn*) where *l* is the ligand number 1, 2 or 3, *m* is the ring number 1, 2 or 3 and *n* is the atom number 1–6 with the carbon bound to the phosphorus labelled C(*lm*1).

Crystal/refinement data. (1). [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H ≡ $C_{56}H_{48}CuO_4P_3$, $M = 941.4$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), $a = 15.716(2)$, $b = 22.220(4)$, $c = 13.616(2)$ Å, $\beta = 95.69(1)°$, $V = 4731$ Å^3, $Z = 4$, $D_c = 1.32_7$ g cm^{-3}. $\mu = 6.1$ cm^{-1}; crystal size = 0.37 × 0.30 × 0.20 mm;

$T_{\mathrm{max,min}} = 0.89,\ 0.81$: $2\theta_{\mathrm{max}} = 52.8°$, $N = 9607$, N_o ($I > 2\sigma(I)$) = 7460, $R = 0.064$, $R_\mathrm{w} = 0.139$; $|\Delta\rho_{\mathrm{max}}| = 0.93$ e Å^{-3}.

(**2**) [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH ≡ $C_{56}H_{49}CuO_{2.5}P_3$, $M = 918.4$. Monoclinic, space group $P2_1/n$, $a = 15.675(1)$, $b = 22.454(1)$, $c = 13.935(1)$ Å, $\beta = 93.57(1)°$, $V = 4895$ Å^3, $Z = 4$, $D_\mathrm{c} = 1.25_6$ g cm^{-3}. $\mu = 5.9$ cm^{-1}; crystal size = 0.5 × 0.5 × 0.2 mm; $T_{\mathrm{max,min}} = 0.89,\ 0.76$; $2\theta_{\mathrm{max}} = 55.8°$, $N_\mathrm{t} = 93602$, $N = 11651$ ($R_{\mathrm{int}} = 0.027$), N_o ($I > 2\sigma(I)$) = 8871, $R = 0.075$, $R_\mathrm{w} = 0.216$; $|\Delta\rho_{\mathrm{max}}| = 1.30$ e Å^{-3}.

The results for the two copper structures show evidence for disorder in the carbon atoms of rings (11*n*) and (32*n*) in (**1**) and phenyl rings (11*n*), (21*n*), (32*n*) in (**2**), each being modelled as disordered. In the structure of (**2**), the solvent site was modeled as half an ethanol molecule on the basis of solid-state ^{13}C NMR evidence, which showed the presence of ethanol in the crystalline sample. However, the possibility of inclusion of water molecules in this site can not be discounted, and this could explain the low carbon value in the elemental analysis. Disorder in the silver structure (**3**) is more extensive (see below).

(**3**) [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H ≡ $C_{56}H_{48}AgO_4P_3$, $M = 985.8$. Monoclinic, space group $P2_1/n$, $Z = 4$, $F(000) = 2032$. (a) *T ca.* 295 K, single counter instrument study: $a = 15.96(1)$, $b = 22.24(2)$, $c = 13.881(6)$ Å, $\beta = 94.93(4)°$, $V = 4908$ Å^3, $D_\mathrm{c} = 1.33_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 5.5$ cm^{-1}; specimen: 0.24 × 0.20 × 0.38 mm; $T_{\mathrm{max,min}} = 0.91,\ 0.84$. $2\theta_{\mathrm{max}} = 55°$; $N = 11244$, N_o ($I > 3\sigma(I)$) = 4612; $R = 0.058$, $R_\mathrm{w} = 0.058$; $n_\mathrm{v} = 669$, $|\Delta\rho_{\mathrm{max}}| = 0.67$ e Å^{-3}. (b) *T ca.* 153 K, CCD instrument study: $a = 15.894(2)$, $b = 22.028(3)$, $c = 13.715(2)$ Å, $\beta = 94.906(2)°$, $V = 4784$ Å^3. $D_\mathrm{c} = 1.36_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 5.7$ cm^{-1}; specimen: 0.35 × 0.24 × 0.08 mm; $T_{\mathrm{max,min}} = 0.91,\ 0.76$. $2\theta_{\mathrm{max}} = 58°$; $N_\mathrm{t} = 55747$, $N = 12118$ ($R_{\mathrm{int}} = 0.025$), N_o ($F > 4\sigma(F)$) = 9315; $R = 0.039$, $R_\mathrm{w} = 0.049$; $|\Delta\rho_{\mathrm{max}}| = 1.01$ e Å^{-3}.

In both determinations for this complex, phenyl rings 11 and 32 were modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement; this disorder is presumably concerted, since there are otherwise unreasonably close contacts between certain of the adjacent ring atoms. The oxygen atoms of the coordinated formate were also modelled as disordered over two sets of sites, occupancies refining to 0.762(6) (295 K) and 0.833(3) (153 K) and complements.

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See http://www.rsc.org/suppdata/dt/a9/a908427d/ for crystallographic files in .cif format.

Spectroscopy

Infrared spectra were recorded at 4 cm^{-1} resolution as KBr or CsI pressed discs or Nujol mulls on a Digilab FTS-60 Fourier transform infrared spectrometer employing an uncooled DTGS 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 infrared spectrometer employing an FTS-60 vacuum optical bench with a 6.25 µm Mylar film beam splitter, a mercury lamp source and a TGS detector.

Solid-state ^{31}P CPMAS 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[26] and magic-angle-spinning[27] techniques, coupled with spin temperature alternation[28] to eliminate spectral artifacts, were implemented using a Bruker 4 mm double-air-bearing probe in which MAS frequencies of ≥10 kHz were achieved. A recycle delay of 15 s, Hartmann–Hahn contact period of 10 ms and an initial ^{1}H $\pi/2$ pulse width of 3 µs were common to all ^{31}P spectra. No spectral smoothing was employed prior to Fourier transformation. The 2D ^{31}P CP COSY experiment was implemented with the TPPI (time proportional phase incrementation) method[29] for acquisition of phase-sensitive data in both the F1 and F2 dimensions. The application of this technique has been discussed in detail elsewhere.[30] The recycle delay, contact period, ^{1}H $\pi/2$ pulse width and MAS rate were the same as those implemented in the above 1D ^{31}P CPMAS experiments. A total of 256 F1 increments were acquired into 256 word blocks, with both dimensions zero-filled to 1 K words and weighted with Gaussian multiplication prior to Fourier transformation. All ^{31}P chemical shifts were externally referenced to triphenylphosphine which has a shift of δ −9.9 with respect to 85% H$_3$PO$_4$. Solid-state ^{13}C CPMAS NMR spectra were obtained at ambient temperature on a Bruker CXP-90 spectrometer operating at a ^{13}C frequency of 22.63 MHz. The cross-polarization methods outlined above were implemented on a Doty 7 mm probe in which MAS frequencies of 4 kHz were achieved. A recycle delay of 10 s, contact period of 5 ms and initial ^{1}H $\pi/2$ pulse width of 3.5 µs were common to all ^{13}C spectra. No spectral smoothing was employed prior to Fourier transformation, and ^{13}C chemical shifts were referenced to SiMe$_4$ *via* an external sample of solid hexamethylbenzene.

Results and discussion

The 1 : 3 copper(I) formate/triphenylphosphine complex could only be prepared in solvated forms. The previously reported unsolvated complex [Cu(PPh$_3$)$_3$O$_2$CH][4] is probably the ethanol hemisolvate reported in the present study; the analytical figures reported in the previous study agree well with those expected for [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH. When this complex desolvates (by heating to 50 °C or upon standing for a long period in the air), it undergoes a solid-state transformation to [Cu(PPh$_3$)$_2$O$_2$CH] + PPh$_3$, which can be followed by IR and ^{31}P CP MAS NMR spectroscopy. Thermal analysis showed an endotherm at about 80 °C followed by another at 180 °C. The first of these corresponds to the melting point of triphenylphosphine and the second to the melting point of the 1 : 2 complex [Cu(PPh$_3$)$_2$O$_2$CH], showing that the transformation referred to above occurs below 80 °C, in agreement with the spectroscopic measurements. The 1 : 3 copper(I) formate/triphenylphosphine complex was also prepared as the formic acid adduct [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H. Attempts to prepare a copper analogue of the previously reported complex [Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H[15] by reaction of the 1 : 2 compound [Cu(PPh$_3$)$_2$O$_2$CH] with formic acid resulted in the formation of [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H, the formic acid adduct of the 1 : 3 complex. This also forms as a minor component in the preparation of [Cu(PPh$_3$)$_2$O$_2$CH] from copper(II) formate and triphenylphosphine, since this reaction, involving the oxidation of triphenylphosphine to triphenylphosphine oxide by copper(II), also produces formic acid. This can be prevented by the addition of a suitable base, such as ammonium hydroxide, to the reaction mixture (see Experimental section). In contrast to the situation for the corresponding copper(I) complex, the 1 : 3 silver formate/triphenylphosphine complex [Ag(PPh$_3$)$_3$O$_2$CH] is stable in the unsolvated form, but like the copper(I) analogue, it also forms the formic acid monosolvate adduct [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H.

Crystal structure determinations

The X-ray structure determinations on the 1 : 3 copper complexes [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H, **1** and [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH, **2** show both structures to be isomorphous with [Cu(PPh$_3$)$_3$NO$_3$]·EtOH[24] and [Cu(AsPh$_3$)$_3$NO$_3$]·MeOH,[25] crystallizing in space group $P2_1/n$ with $a \approx 15$, $b \approx 23$, $c \approx 14$ Å, $\beta \approx 90°$. The [Cu(PPh$_3$)$_3$O$_2$CH] molecular unit in **1** comprises a four-coordinate copper centre with the crystallographically independent PPh$_3$ ligands occupying three of the coordination sites and the formate anion cordinated through one oxygen atom to the fourth site. The conformational structures of the PPh$_3$ ligands fall into two distinct categories. Ligand 1 possesses approximate mirror symmetry with phenyl group 2 perpendicular to the plane defined by Cu–P–C(121). Rings 1 and 3 are disposed to either side of that plane. Ligands 2 and 3 possess approximate three-fold symmetry axes to give distorted three-

Table 1 P_3MX core geometries for isomorphous $[M(PPh_3)_3X]{\cdot}solv$ complexes, M = Cu/Ag, X = O_2CH/NO_3, solv = HO_2CH/EtOH

	$Cu/NO_3/EtOH$ [a]	$Cu/O_2CH/HO_2CH$ [a]	$Cu/O_2CH/0.5EtOH$ [b]	$Ag/O_2CH/HO_2CH$ (153/295 K) [b,c]	
M–P(1)	2.312(2)	2.315(1)	2.332(1)	2.5199(7)	2.527(2)
M–P(2)	2.337(2)	2.329(1)	2.332(1)	2.5237(6)	2.533(2)
M–P(3)	2.339(2)	2.332(1)	2.341(1)	2.4953(7)	2.510(3)
M–O	2.174(4)	2.085(3)	2.042(4)	2.509(2), *2.15(1)*	2.507(9), *2.21(2)*
P(1)–M–P(2)	114.15(7)	112.72(4)	112.29(4)	110.70(2)	111.32(8)
P(2)–M–P(3)	121.37(6)	115.42(4)	116.09(4)	119.75(2)	119.95(7)
P(3)–M–P(1)	113.42(6)	119.45(4)	117.98(4)	116.53(2)	116.41(8)
P(1)–M–O(1)	109.5(1)	109.77(9)	106.4(2)	89.90(7), *113.5(4)*	88.1(2), *113.3(6)*
P(2)–M–O(1)	95.4(1)	98.36(9)	101.3(1)	99.05(6), *98.3(4)*	99.7(2), *99.2(6)*
P(3)–M–O(1)	97.9(1)	97.35(8)	99.8(2)	116.10(6), *94.7(4)*	116.2(2), *93.0(6)*

[a] Ref. 24. [b] This work. [c] Where there are two values in each entry, they are for the major and *minor* X components respectively.

bladed propeller conformations of opposite chirality that are staggered with respect to each other. The geometric parameters of the P_3CuO copper coordination sphere are listed in Table 1 together with analogous data for the isomorphous nitrate complex. The Cu–P bond lengths range from 2.315(1) to 2.341(1) Å and are similar to values recorded for a range of other $[Cu(PPh_3)_3X]$ complexes.[31] The P–Cu–P angles range from 112 to 121° with average values of *ca.* 116°, indicative of a coordination geometry mid way between tetrahedral and trigonal planar. The Cu–O bond lengths for the formic acid and ethanol solvated complexes differ slightly with values of 2.085(3) Å and 2.042(4) Å respectively. Both distances are considerably shorter than the distance of 2.174(4) Å recorded for the nitrate complex. The P(2)–Cu–O(1) and P(3)–Cu–O(1) angles range from 95–101° and this increases to 106–110° for P(1)–Cu–O(1), reflecting movement of the coordinated anion away from ligand 1 and towards the solvated molecules which are located adjacent to ligands 2 and 3.

Comparison of these 1 : 3 structures with those of the unsolvated 1 : 2 formate[9] and nitrate[32] complexes show that the Cu–P bond lengths increase by *ca.* 0.07 Å with coordination of the third PPh_3 ligand, while the Cu–O distances decrease from 2.226(3) Å for the bidentate coordinated anion to 2.04–2.08 Å for the unidentate coordinated formate anion, with a corresponding change in the Cu–O bond length from 2.297(3) to 2.174(4) Å for the nitrate complex.

The formic acid solvate molecule in **1** is hydrogen-bonded to the formate anion to form an assembly that is best described as a biformate anion $[H(HCO_2)_2]^-$. This anion is the simplest member of a class of H-bonded complexes involving carboxylic acids and carboxylate anions,[33] and has been the subject of numerous theoretical studies.[34] Hydrogen bonds display an almost continuous distribution of O ··· O bond lengths between 2.36 and 3.69 Å, and have been subdivided into classes which are referred to as 'very strong' (<2.5 Å), 'strong' (2.50 to 2.65 Å), 'medium' (2.65 to 2.80 Å), and 'weak' (>2.80 Å).[35] For **1** the hydrogen bond of the $[H(HCO_2)_2]^-$ ion, with *d*(O(2) ··· O(4)) = 2.529(5) Å, falls in the 'strong' category. This can be compared with the hydrogen bond length observed for $K[H(HCO_2)_2]$ (*d*(O ··· O) = 2.45 Å) which is in the 'very strong' class,[36] and the hydrogen bond lengths observed for $[Ag(PPh_3)_2O_2CH]{\cdot}2CHO_2H$ (*d*(O ··· O) = 2.50, 2.56 Å) which are in the 'strong' class.[15] The apparent reduction in hydrogen bond strength compared to the free biformate ion could be due, in part, to the competition for formate ion electron density between the copper atom and the formic acid molecule.

The solvated ethanol molecule in **2** is less well defined. However, it occupies a similar site in the crystal lattice to the formic acid in **1** and shows significant hydrogen bonding with the formate anion with an O(2) ··· O(3) distance of 2.75 Å indicative of weaker hydrogen bonding effects by comparison with the formic acid solvated complex.

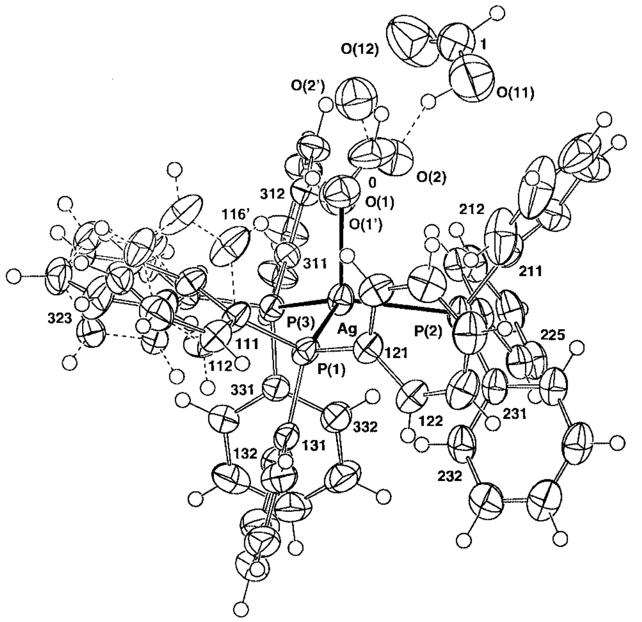

Fig. 1 Molecular structure of $[Ag(PPh_3)_3O_2CH]{\cdot}HCO_2H$ (153 K determination) showing all non-hydrogen atoms and the atom numbering scheme, inclusive of disordered components excepting those for the minor components of the solvate molecule. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

The results of the single crystal X-ray studies of the silver compound **3** (Fig. 1) show that it is of the form described above for the analogous copper compound **1**. As in the copper(I) nitrate and formate adducts, the three M–P distances are similar (and similar to values found in numerous other P_3AgX arrays[23]), with similar divergence in the P–M–P angles (Table 1). The present data, measured at room, and in particular at low temperature, are of good quality, enabling resolution of some interesting features. Disorder is more extensive than in the two isomorphous copper(I) formate complexes; it is unlikely that this is contingent upon the use of low temperature, since it is also observed in the room temperature determination. As in the copper(I) compound, disorder is displayed in two of the phenyl groups of the triphenylphosphine ligands, assigned site occupancies of 0.5 in both orientations of both rings. However, further disorder is evident, associated with the ligated formate entity, seemingly independent of, rather than concerted with, the phenyl disorder, and dependent only slightly, if at all, on temperature, resolving with major and minor components similarly distributed at either 'low' or 'room' temperature; consequent discussion is therefore conducted in terms of the results of the more precise low temperature study. Here, we find the ligated formate moiety, as modelled, to be comprised of two components, defined by the associated oxygen atoms, disposed in different conformations about an unresolved common carbon atom site, with occupancies 0.833(3) and complement. The geometries of the two individual components, as far as precision permits, are sensible: for the major component, C–O(1,2) are 1.187(5), 1.280(5) Å with O–C–O 128.7(3)°; for the minor component 1.22(1), 1.23(1) Å, 128(1), 128(1)°, all very reasonable, except that associated Ag–O(1,1′) are 2.509(2), 2.15(1) Å, widely disparate, with Ag–O(1,1′)–C(0) 111.1(2), 136(1)°, associated disorder in the $[(Ph_3P)_3Ag]$ array being unresolvable (but see below). Interestingly, the minor component corresponds more nearly with counterpart atoms of the nitrate moieties in previously studied counterpart structures. The C–O(1′) distances, in combination with associated Ag–O(1′), associate long Ag–O with short O–C and *vice versa*, with C–O(2′) disposed conversely, raising the possibility that the two components represent different coordinated entities. The two major difference map residues (*ca.* 1 e $Å^{-3}$) are disposed close to the silver atom and opposed to the oxygen atom and may be indicative of a displaced but unresolved minor metal atom component with a more sensible Ag–O distance. It may be that one of the formate moieties approximates to coordinated formate and the other, formic acid, or, alternatively, that the formate may coordinate in definitively uni-dentate or unsymmetrically bi-dentate mode, Ag···O(2) being 3.204(3) Å.

The solvent molecule in these structures is formic acid. In the room temperature determination, only a simplistic refinement model is supported, describing the moiety as a bent O–C–O triatomic with very high thermal motion, 'chelating' O(2) of the coordinated formate (O(2)···O(11,12) 2.75(2), 2.86(2) Å). In the low temperature model, associated displacement parameters are more sensible but at the expense of resolution into a number of fragments, some substantial, others less so, commensurate with their modelling as carbon or oxygen with site occupancies corresponding to those associated with the coordinated moieties, but insusceptible of deconvolution into/description in terms of, a sensible pair of discrete formate entities: a major component, modelled as a bent O–C–O triatomic, one oxygen refining to unit site occupancy, and the remaining CO as 0.83, is sensible, and suggestive of a pivoting of the disordered components about the unit oxygen (which lies nearest the coordinated array), but the associated minor fragments are less convincing as any sort of coherent moiety. A plausible acid hydrogen atom may be discerned in association with the larger fragment, contacting O(2), but not O(2′), which presumably interacts with some appropriate description of the minor fragment (H,O(11)···O(2) 1.5, 2.505(4) Å).

Infrared spectroscopy

The mid-range IR spectra (4000–400 cm^{-1}) of $[Cu(PPh_3)_2O_2CH]$, $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$, and $[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$ are shown in Fig. 2. Wavenumbers of the bands that can be assigned to vibrations of the formate and formic acid moieties in the Cu complexes are compared with those for a number of related species in Table 2.

The frequencies $\nu_s(CO_2)$ and $\nu_a(CO_2)$ of the symmetric and antisymmetric O–C–O stretching modes of the coordinated formate ion in $[Cu(PPh_3)_2O_2CH]$ are assigned at 1346 and 1577, 1564 cm^{-1} respectively. As with $[Ag(PPh_3)_2O_2CH]$,[15] the $\nu_a(CO_2)$ band appears as a sharp doublet for $[Cu(PPh_3)_2O_2CH]$. The IR spectrum of $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$ shows bands at 1335 and 1607 cm^{-1} that are assigned respectively to the $\nu_s(CO_2)$ and $\nu_a(CO_2)$ modes of the coordinated formate. The separation, Δ (272 cm^{-1}), is significantly larger than that observed for $[Cu(PPh_3)_2O_2CH]$. The latter compound contains a symmetrically bound bidentate formate group, with two equivalent oxygen atoms.[9] A study by Deacon and Phillips[20] found that for bidentate carboxylates the Δ value is similar to, or less than, that found in the free formate, taken as those for the sodium ($\Delta = 241$ cm^{-1})[37] or potassium ($\Delta = 233$ cm^{-1})[41] salts, and this is what is observed experimentally for $[Cu(PPh_3)_2O_2CH]$ ($\Delta = 231$ cm^{-1}). The same study found that unidentate carboxylate coordination, which removes the equivalence of the two oxygen atoms, leads to an increase in the separation between the $\nu_a(CO_2)$ and $\nu_s(CO_2)$ modes, relative to the value for the free formate.[20] Therefore, unidentate coordination should yield larger Δ values than bidentate coordination. Hence the increased Δ values for $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$, as compared to $[Cu(PPh_3)_2O_2CH]$, indicate unidentate coordination. This agrees with the observed structures for these types of compound (see above). For $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$, $\nu_a(CO_2)$ appears as a sharp singlet, but this becomes a broad band in the formic acid adduct. The splitting ($\Delta = 194$ cm^{-1}) in this compound is well below the range expected for unidentate coordination, despite the fact that only one of the formate oxygen atoms is bound to the copper. Apparently the H-bonding interaction with the non-coordinating oxygen has the effect of generating an effective bridging bidentate coordination situation for the formate ion in this complex.

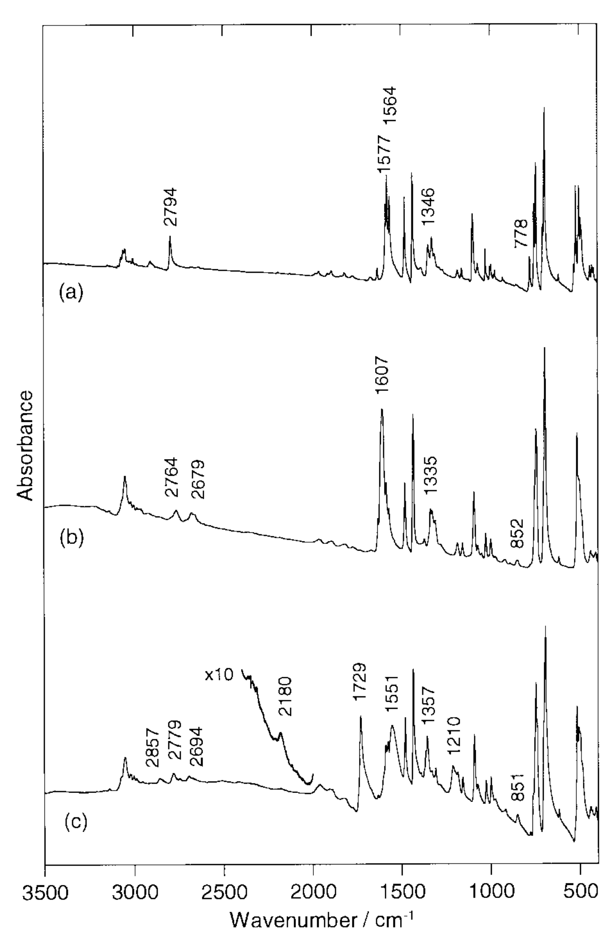

Fig. 2 Mid-range infrared spectra of (a) $[Cu(PPh_3)_2O_2CH]$, (b) $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$, and (c) $[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$.

The frequencies of the ν(C=O) and ν(C–O) modes of the formic acid molecule in $[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$ are assigned to 1729 and 1210 cm^{-1} respectively. The difference between these values (519 cm^{-1}) lies between the values for the formic acid monomer (671 cm^{-1})[38] and $Na[H(HCO_2)_2]$ (439 cm^{-1}),[40] similar to the value observed for the H-bonded formic acid dimer $[HCO_2H]_2$ (524 cm^{-1}),[39] and also within the range found for $[Ag(PPh_3)_2O_2CH]\cdot2HCO_2H$ (520–550 cm^{-1}).[15]

The ν(CH) mode of the coordinated formate in $[Cu(PPh_3)_2O_2CH]$ is assigned at 2794 cm^{-1}. This is similar to that of $[Ag(PPh_3)_2O_2CH]$. For $[Cu(PPh_3)_3O_2CH]\cdot0.5EtOH$ two bands of similar intensity are observed at 2764, 2679 cm^{-1}. Two bands of similar intensity are also observed in this region for sodium formate (2832, 2718 cm^{-1})[37] and for potassium formate (2808, 2715 cm^{-1}).[41] The higher wavenumber band has been assigned

Table 2 Wavenumbers (cm^{-1}) of IR bands associated with the formate/formic acid moieties

	Formate				Formic acid			
Compound	ν(CH)	ν_a(CO$_2$)	ν_s(CO$_2$)	δ(OCO)	ν(CH)	ν(C=O)	ν(C–O)	δ(OCO)
Na[O$_2$CH][a]	2832	1609	1368	774				
HCO$_2$H[b]					2944	1776	1105	625
[HCO$_2$H]$_2$[c]					2938	1746, 1736	1217	699
Na[H(HCO$_2$)$_2$][d]	2778	1626	1366	768	2902	1755	1316	730
[Cu(PPh$_3$)$_2$O$_2$CH]	2794	1577, 1564	1346	778				
[Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH	2764, 2679	1607	1335	852				
[Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H	2779, 2694	1551	1357	851	2857	1729	1210	
[Cu(PPh$_3$)$_3$O$_2$CD]·DCO$_2$D	2094, 2072	1548	1330		2133	1701		
[Ag(O$_2$CH)][e]	2185	1631, 1603	1351					
[Ag(PPh$_3$)$_2$O$_2$CH][e]	2777	1576, 1562	1343	772				
[Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H[e]		1554	1364	800	2838	1730	1210, 1179	
[Ag(PPh$_3$)$_3$O$_2$CH]	2740, 2648	1595	1340	850				
[Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H	2784, 2694	1586, 1576, 1562	1344	849	2869	1720	1214	

[a] Ref. 37. [b] Ref. 38. [c] Ref. 39. [d] Ref. 40. [e] Ref. 15.

to the ν(CH) mode and the lower wavenumber band has been assigned to the first overtone of the in-plane C–H bending vibration.[37] Two bands have also been observed for surface formate on copper, at 2910 and 2840 cm^{-1}.[18] The similarity in intensities of the fundamental and combination bands is a result of the Fermi resonance effect.[42] It is interesting to note the absence of this effect in [Cu(PPh$_3$)$_2$O$_2$CH]. This is presumably a result of the conditions required for Fermi resonance no longer being fulfilled in this complex due to changes in the metal–formate interaction. The Fermi resonance effect is also observed for [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H, with bands at 2779, 2694 cm^{-1} attributed to the coordinated formate. These values may be compared to that for Na[H(HCO$_2$)$_2$] where a sharp band at 2778 cm^{-1} has been assigned to the ν(CH) mode of the formate.[40] In the IR spectrum of [Cu(PPh$_3$)$_3$O$_2$CD]·DCO$_2$D these two bands disappear and are replaced by bands at 2094, 2072 cm^{-1}. A band at 2857 cm^{-1} for [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H is assigned to the ν(CH) mode of the formic acid molecule. This value lies between the value of the formic acid ν(CH) mode for [Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H (2838 cm^{-1}),[15] and for Na[H(HCO$_2$)$_2$] (2902 cm^{-1}).[40] This band also disappears in the spectrum of [Cu(PPh$_3$)$_3$O$_2$CD]·DCO$_2$D, being replaced by a band at 2133 cm^{-1}.

The vibrational spectra of H-bonded complexes have been studied in considerable detail, and relationships between vibrational frequencies and the strength of the H-bond interaction are well established.[43,44] In the case of 'weak' to 'medium' H-bonding of the type A–H···B ν(AH) occurs in the range 2000–3500 cm^{-1}, while for 'strong' to 'very strong' H-bonding, very broad bands are observed below 1600 cm^{-1} (the criteria for the different classes of H-bond strength in terms of bond length are those of ref. 34). This is illustrated by the following species which involve H-bonded formic acid: in the formic acid dimer, which has an H-bonded O···O distance of 2.703 Å,[45] ν(OH) = 2570–3490 cm^{-1}, with a maximum at about 3100 cm^{-1};[39] K[H(O$_2$CH)$_2$], which has an H-bonded O···O bond length of 2.45 Å,[36] shows a broad ν(OH) band with a maximum at 1400 cm^{-1};[40] while for [Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H, which has H-bonded O···O bond lengths of 2.50 and 2.56 Å, ν(OH) modes are assigned at 1921 cm^{-1} for d(O···O) = 2.50 Å and at 2360 cm^{-1} for d(O···O) = 2.56 Å.[15] A correlation of the ν(OH) frequencies and the O···O bond lengths, based on the above results, gives a predicted position of the ν(OH) mode in [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H at 2140 cm^{-1}. A very weak band at 2180 cm^{-1} is therefore assigned to the ν(OH) mode. This band is absent in the spectrum of [Cu(PPh$_3$)$_3$O$_2$CD]·DCO$_2$D; the expected isotopic shift of ν(OH) on deuteration would put the ν(OD) band at about 1540 cm^{-1}, in a very crowded region of the spectrum, so this band is not observed.

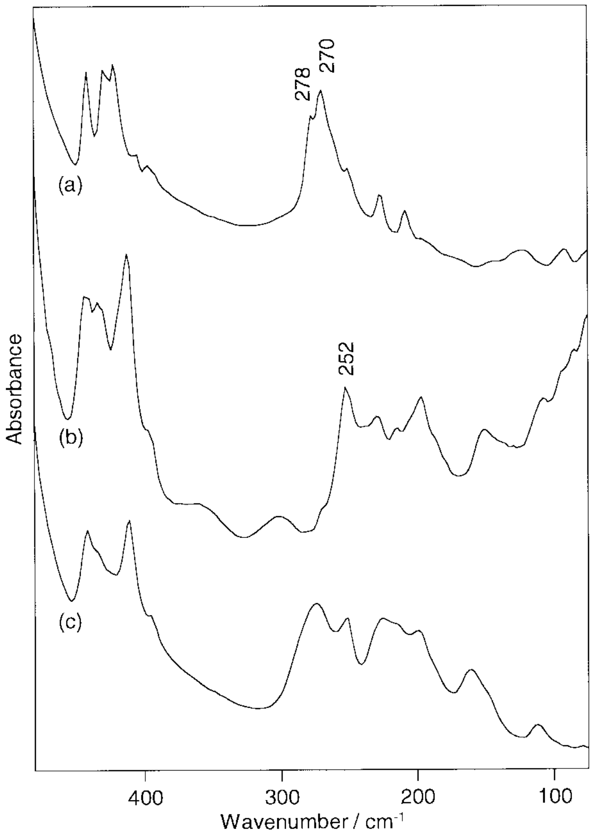

Fig. 3 Far-IR spectra of (a) [Cu(PPh$_3$)$_2$O$_2$CH], (b) [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH, and (c) [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H.

The far-IR spectra of [Cu(PPh$_3$)$_2$O$_2$CH], [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH and [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H are shown in Fig. 3. The far-IR spectrum of [Cu(PPh$_3$)$_2$O$_2$CH] shows a partially resolved doublet at 278, 270 cm^{-1}, which is assigned to the ν(CuO) modes. These values can be compared with the assignment of the ν(AgO) modes in [Ag(PPh$_3$)$_2$O$_2$CH] at 259, 250 cm^{-1},[15] and with surface formate on copper where ν(CuO) has been observed at 340 cm^{-1}.[18] The increase in wavenumber of the ν(CuO) modes for [Cu(PPh$_3$)$_2$O$_2$CH] compared to [Ag(PPh$_3$)$_2$O$_2$CH] is consistent with the smaller mass of copper.

For [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH a band at 252 cm^{-1} is assigned to the ν(CuO) mode. The observation of a single band is consistent with a unidentate formate ion that is suggested by the separation between ν_s(CO) and ν_a(CO). The dependence of ν(CuX) on the number of coordinated PPh$_3$ ligands in compounds of the type CuX(PPh$_3$)$_n$ (n = 2, 3; X = Cl, Br, I) has been previously demonstrated.[46,47] On increasing the number of PPh$_3$

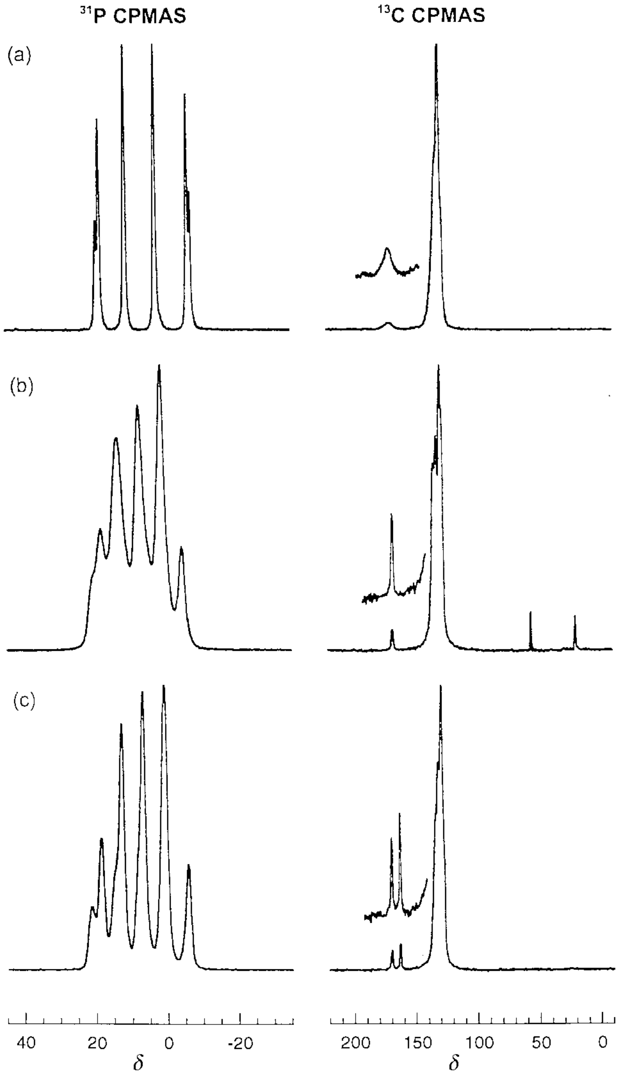

Fig. 4 Solid-state ^{31}P (left) and ^{13}C (right) CP MAS NMR spectra of (a) [Cu(PPh$_3$)$_2$O$_2$CH], (b) [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH, and (c) [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H.

ligands from $n = 2$ to $n = 3$ there is a decrease in the frequency of ν(CuX) observed for these compounds (*ca.* 60 cm^{-1}). In this study, where X = O$_2$CH, a similar decrease in ν(CuX) is observed changing from the 2 : 1 formate to the 3 : 1 formate, but the decrease is not as great (*ca.* 20 cm^{-1}). Unlike the X = Cl, Br, I cases where there is an increase in the coordination number of the copper centre from 3 to 4, for the X = O$_2$CH the coordination number of the copper is 4 for both the 2 : 1 formate and the 3 : 1 formate. Therefore the effect of increasing the number of coordinated PPh$_3$ ligands should be reduced. This will be offset somewhat since an O-donor group is being replaced by a stronger P-donor group, leading to some weakening of the Cu–O bond and a reduction in ν(CuO).

The far-IR spectrum of [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H shows a number of broad unresolved bands in the 150–300 cm^{-1} region. A detailed assignment of these bands is not possible, but the bands in this region are attributed to ν(CuO) and to ν(O···H), the vibration of the O···H part of the strong O–H···O bond. The situation is further complicated by possible coupling of the ν(CuO) and ν(O···H) modes. Assignments for ν(O···H) modes have been made at 262 cm^{-1} in the formic acid dimer,[39] 177, 232 cm^{-1} in crystalline formic acid,[48] and 465 cm^{-1} in Na[H(O$_2$CH)$_2$].[40]

The IR spectra of [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H and [Ag(PPh$_3$)$_3$O$_2$CH] show features similar to those discussed above for the better structurally characterized copper complexes. However, the formate ν_a(CO$_2$) band in [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H shows a particularly complex structure (Table 2), which can be attributed to the disorder observed for the formate group in the crystal structure of this compound (see above).

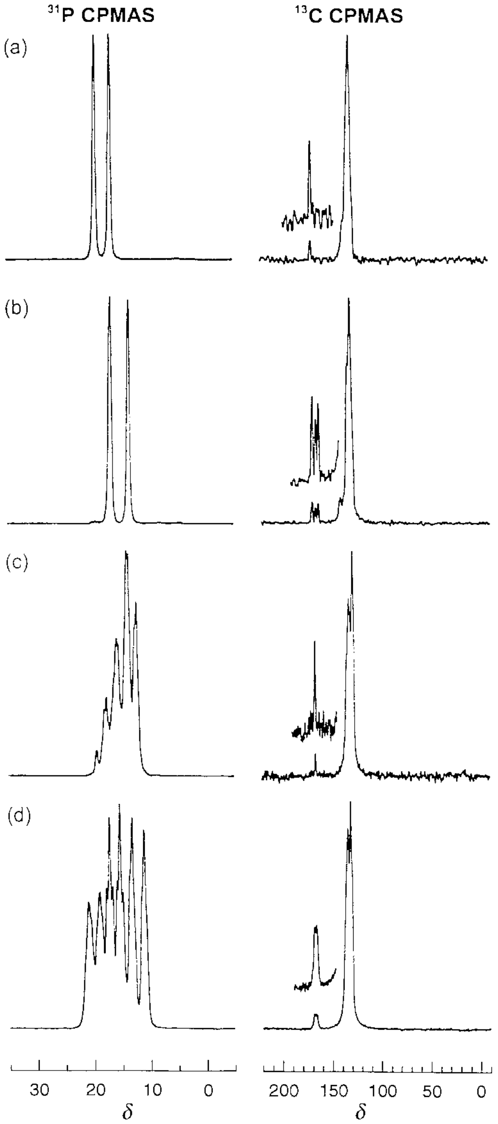

Fig. 5 Solid-state ^{31}P (left) and ^{13}C (right) CP MAS NMR spectra of (a) [Ag(PPh$_3$)$_2$O$_2$CH], (b) [Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H, (c) [Ag(PPh$_3$)$_3$O$_2$CH] and (d) [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H. Chemical shifts relative to solid PPh$_3$.

Solid-state NMR spectroscopy

The solid-state ^{13}C CPMAS NMR spectra of complexes **1**–**4** are shown in Figs. 4 and 5, and selected assignments for these and some related compounds are given in Table 3. The spectrum of [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H shows two distinct resonances at δ 163.2 and 169.7 which are assigned to the formic acid and coordinated formate carbon moieties, respectively. The spectrum of the ethanol solvate shows a formate resonance at δ 168.1 and additional resonances at δ 20.3 and 56.3 due to the ethanol molecule. In contrast to the corresponding copper complex, an unambiguous assignment of the ^{13}C formate and formic acid resonances in [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H is not possible as the chemical shifts of these moieties are very similar. However, if previous trends of the higher shift being attributed to the coordinated formate carbon are reliable, then the resonance at δ 168.1 is tentatively assigned to this species.

The ^{31}P CPMAS NMR spectra of both 1 : 3 copper complexes [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH and [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H (Fig. 4) are similar, consisting of relatively broad overlapping quartets with noticeably better resolution for the latter

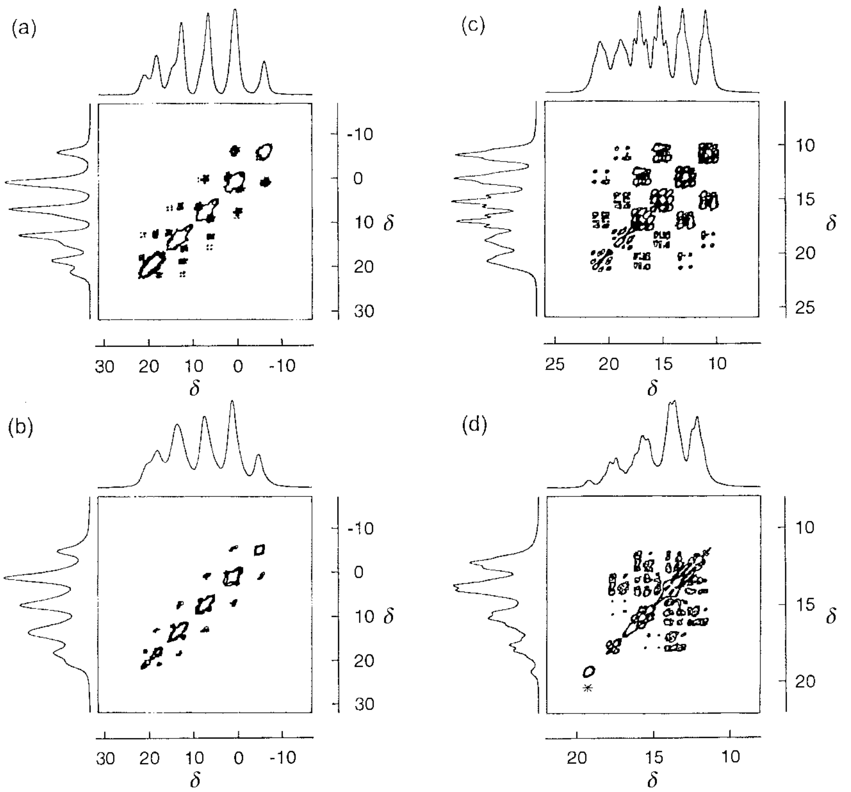

Fig. 6 Solid-state 2D ^{31}P CP COSY spectra of (a) [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H (b) [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH, (c) [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H and (d) [Ag(PPh$_3$)$_3$O$_2$CH]. Chemical shifts relative to solid PPh$_3$. The resonance in (d) marked with an asterisk is due to an impurity.

Table 3 Solid-state CP/MAS ^{13}C NMR chemical shifts (ppm) for [M(PPh$_3$)$_n$O$_2$CH] (M = Cu, Ag; n = 2, 3) and related compounds

Complex	δ(HCO$_2^-$)	δ(HCO$_2$H)
[Cu(PPh$_3$)$_2$O$_2$CH]	170.0	
[Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH	168.1	
[Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H	169.7	163.2
[Ag(PPh$_3$)$_2$O$_2$CH][a]	170.0	
[Ag(PPh$_3$)$_2$O$_2$CH]·2HCO$_2$H[a]	169.4	163.3, 166.1
[Ag(PPh$_3$)$_3$O$_2$CH]	166.4	
[Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H	168.1	166.1
[NH$_4^+$][HCO$_2^-$][b]	171.4	
HCO$_2$H (0.5 M in H$_2$O)[c]		166.3

[a] Ref. 15. [b] Ref. 49; reported data converted to reference to SiMe$_4$ using δ(CS$_2$) = 192.8. [c] Ref. 50.

complex. These spin systems are of the ABCX type, where the quartet structure arises from $^1J(^{63,65}\mathrm{Cu},^{31}\mathrm{P})$ scalar coupling, and each ^{31}P quartet is further correlated to all other quartets *via* strong $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ coupling. The overlap of these resonances comprising each quartet from the three PPh$_3$ ligands bound to each Cu site preclude any measurement of the individual line spacings Δ_{12}, Δ_{23} and Δ_{34} from the 1D ^{31}P CPMAS spectra. However, the 2D ^{31}P CPCOSY spectra for these complexes (see Fig. 6) allow unambiguous identification of the 3 quartets in each case, and yield estimates for these line spacings subject to the linewidth and signal/noise constraints of the correlations that are observed. The results of these measurements are given in Table 4. For the [Cu(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H complex (Fig. 4(a)) all correlations describing the 3 quartets are observed, but for the [Cu(PPh$_3$)$_3$O$_2$CH]·0.5EtOH complex (Fig. 4(b)) the reduced resolution has rendered only the most prominent correlations (*i.e.* those closest to the main diagonal) observable and these are not well defined. The estimated values for ^1J(Cu,P) of ≈1000 Hz for these complexes (Table 4) are consistent with the ^1J(Cu,P) range of 900–1000 Hz measured for other [Cu(PPh$_3$)$_3$X] complexes.[51] Similarly, the quartet spacings show that the asymmetry expected from the quadrupolar perturbed scalar/dipolar couplings between the I = 1/2 ^{31}P nuclei and the I = 3/2 ^{63,65}Cu nucleus[30,52] is small and of the same order as found for other [Cu(PPh$_3$)$_3$X] complexes.[51] The large ^{31}P linewidths and diffuse lineshapes of all correlations in the 2D CPCOSY spectra are such that an accurate analysis of the quartet asymmetry is not possible. The spectra of these 1 : 3 complexes are clearly distinct from that for the 1 : 2 complex, [Cu(PPh$_3$)$_2$O$_2$CH] (Fig. 4, Table 4) which consists of a single sharp asymmetric quartet with ^1J(Cu,P) of the order of 1300 Hz, providing a convenient way of identifying the presence of the 1 : 2 complex (from decomposition for example) in the products obtained.

The ^{31}P CPMAS spectra of the 1 : 3 silver complexes [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H and [Ag(PPh$_3$)$_3$O$_2$CH] (see Fig. 5) also represent those of ABCX type spin systems, and consist of partially resolved multiplets due to the 3 individual ^{31}P chemical shifts emanating from the inequivalent phosphorus nuclei near each Ag metal site. Each resonance displays $^1J(^{107,109}\mathrm{Ag},^{31}\mathrm{P})$ scalar coupling between the I = 1/2 ^{31}P nuclei and the I = 1/2 ^{107,109}Ag nuclei, and further correlation between these doublets is established *via* strong $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ in which each doublet is scalar coupled to all other doublets, thus yielding complicated fine structure. Unlike the ^{31}P CPMAS spectra of the 1 : 3 Cu systems shown in Figs. 4(b) and 4(c), some evidence of this $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ coupling in the corresponding Ag systems can be observed from the 1D CPMAS spectra shown in Figs. 5(c) and 5(d). From the 2D ^{31}P CPCOSY spectra of Figs. 6(c) and 6(d) a more detailed and complete analysis of the coupling is observed, and approximate values of the ^1J(Ag,P) coupling constants can be ascertained. In Fig. 6(c) it can be verified that the multiplet structure from each P site in [Ag(PPh$_3$)$_3$O$_2$CH]·HCO$_2$H is sufficiently chemically shifted to be almost completely resolved, while Fig. 6(d) shows that the P sites in [Ag(PPh$_3$)$_3$O$_2$CH] exhibit much less chemical shift dispersion which results in a largely overlapping and unresolved 1D spectrum. The coupling constants given in Table 5 show that a significant reduction in ^1J(Ag,P) can be observed when comparing the values from the formic acid solvate to the unsolvated

Table 4 Solid-state CPMAS ^{31}P NMR parameters for $[Cu(PPh_3)_nO_2CH]$ ($n = 2, 3$)

Complex	$\delta(^{31}P)^a$	Δ_{12}/Hz	Δ_{23}/Hz	Δ_{34}/Hz	$^1J(Cu, P)^b$/Hz
$[Cu(PPh_3)_2O_2CH]$	6.4 ± 0.1	1160 ± 5	1390 ± 5	1460 ± 5	1340 ± 5
$[Cu(PPh_3)_3O_2CH]\cdot 0.5EtOH$	4.7 ± 0.4	996 ± 30	896 ± 30	937 ± 30	910 ± 30
	10.3 ± 0.4	918 ± 30	996 ± 30	937 ± 30	950 ± 30
	11.4 ± 0.4	996 ± 30	1074 ± 30	996 ± 30	1022 ± 30
$[Cu(PPh_3)_3O_2CH]\cdot HCO_2H$	3.5 ± 0.2	1016 ± 15	1016 ± 15	1015 ± 15	1016 ± 15
	10.2 ± 0.2	918 ± 15	957 ± 15	1035 ± 15	970 ± 15
	13.3 ± 0.2	996 ± 30	1094 ± 30	1172 ± 30	1087 ± 30

[a] Relative to solid PPh_3; calculated as the average of the chemical shifts of the resonance positions for each line in the quartet. [b] Calculated as the average of the three line spacings Δ_{12}, Δ_{23}, Δ_{34} of the quartet.

Table 5 Solid-state CPMAS ^{31}P NMR parameters for $[Ag(PPh_3)_nO_2CH]$ ($n = 2, 3$)

Complex	$\delta(^{31}P)^a$	$^1J(Ag, P)$/Hz
$[Ag(PPh_3)_2O_2CH]$	18.0 ± 0.1	432 ± 5
$[Ag(PPh_3)_2O_2CH]\cdot 2HCO_2H$	15.2 ± 0.1	517 ± 5
$[Ag(PPh_3)_3O_2CH]$	12.9 ± 0.4	224 ± 30
	14.5 ± 0.4	211 ± 30
	16.7 ± 0.4	275 ± 30
$[Ag(PPh_3)_3O_2CH]\cdot HCO_2H$	12.0 ± 0.2	352 ± 15
	16.2 ± 0.2	303 ± 15
	19.9 ± 0.2	313 ± 15

[a] Relative to solid PPh_3.

complex. This is similar to the phenomenon observed for the previously reported 1:2 complexes.[15] In the 1:2 case, this correlated with an increase in the P–Ag–P bond angle upon formation of the formic acid adduct, and the explanation in the case of 1:3 complexes is presumably the same. A possible rationalization of this is that the H-bonding of the formic acid with the coordinated formate reduces the strength of the Ag–formate bond. This would cause a change in coordination from tetrahedral (sp^3) towards trigonal planar (sp^2), where the resulting increase in the s character of the Ag–P bonds causes an increase in ^1J(Ag,P).

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