FULL PAPER

# Structural and spectroscopic studies on three- and two-co-ordinate copper(I) halide tribenzylphosphine complexes

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# Introduction

Interest in two- and three-co-ordinate copper(I) complexes arises from their relative rarity, especially when compared with the extensive chemistry for four-co-ordinate copper(I).<sup>1</sup> Recently, it has been shown that the reaction of 1:1 stoichiometric ratios of copper(I) bromide and tribenzylphosphine (PBz<sub>3</sub>) yields the salt  $[Cu(PBz_3)_2][CuBr_2]^2$  rather than the expected dimeric or tetrameric complex  $[Cu(PBz_3)Br]_n$  (n = 2 or 4). With hexafluorophosphate as anion, and a 1:2 Cu:PBz<sub>3</sub> stoichiometric ratio, we were able to isolate the two-co-ordinate salt [Cu(PBz<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>.<sup>3</sup> Crystal structure determinations on both these compounds show the  $[Cu(PBz_3)_2]^+$  cation to be linear with the P-Cu-P angle equal to 180°. This was a somewhat unexpected result since similar two-co-ordinate copper phosphine complexes have been obtained previously only for very bulky phosphine ligands such as trimesitylphosphine.<sup>4</sup> This structural outcome been ascribed<sup>3</sup> to non-covalent bonding interactions between the phenyl groups on the two ligands which sweep back over the copper to generate an intramolecular form of the sixfold phenyl embrace (6PE).<sup>5</sup> In our current investigations of the reactions of copper(I) halides with tribenzylphosphine in 1:1 and 1:2 stoichiometric ratios we have isolated crystalline samples of the three-co-ordinate 1:2 complexes [Cu(PBz<sub>3</sub>)<sub>2</sub>X], for X = Cl, Br and I, the two-coordinate 1:1 complex [Cu(PBz<sub>3</sub>)<sub>2</sub>][CuCl<sub>2</sub>] and the three-coordinate dinuclear complex [Cu<sub>2</sub>(PBz<sub>3</sub>)Cl<sub>2</sub>]·3C<sub>6</sub>H<sub>6</sub>. These have been characterized by single crystal X-ray diffraction studies, solid state <sup>31</sup>P CPMAS NMR spectroscopy and by low frequency vibrational spectroscopy with the outcomes reported here.

#### Experimental

All chemicals were reagent grade or better and solvents were dried by the usual methods. Solvents were distilled before use and all reactions were carried out under a dinitrogen atmosphere. Tribenzylphosphine was obtained from the Aldrich Chemical Co. Copper(I) halides<sup>6</sup> and  $[Cu(PBz_3)_2][CuBr_2]^2$  were prepared according to literature preparations. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Mass spectra were obtained using a Varian VG70-250S double-focussing magnetic sector spectrometer by the method of liquid secondary ion mass spectroscopy (LSIMS) using *m*-nitrobenzyl alcohol as the matrix. Isotope abundance calculations were performed to identify the ions.

#### Preparation of the complexes

**[Cu(PBz<sub>3</sub>)<sub>2</sub>Cl].** CuCl (0.038 g, 0.383 mmol) and PBz<sub>3</sub> (0.34 g, 1.125 mmol) were refluxed in 10 mL of chloroform for 15 min and the resulting solution was cooled then filtered. The chloroform was removed using a rotary evaporator and the white solid recrystallised from 20:1 ethanol–acetone (*ca.* 10 mL) to give 0.21 g (77%) of colourless crystals, mp 147–155 °C (Found: C, 71.49; H, 5.97. Calc. for C<sub>42</sub>H<sub>42</sub>ClCuP<sub>2</sub>: C, 71.28; H, 5.96%).

**[Cu(PBz<sub>3</sub>)<sub>2</sub>Br].** CuBr (0.108 g, 0.75 mmol) and PBz<sub>3</sub> (0.685 g, 2.25 mmol) were refluxed in 15 mL acetonitrile for 3 h and the resulting solution was cooled then filtered. The filtrate was allowed to stand overnight to produce 0.324 g (57%) of colourless crystals of the product, which were filtered off and dried

*in vacuo*, mp 140–143 °C (Found: C, 67.33; H, 5.75; Br, 10.52. Calc. for C<sub>42</sub>H<sub>42</sub>BrCuP<sub>2</sub>: C, 67.07; H, 5.63; Br, 10.62%).

**[Cu(PBz<sub>3</sub>)<sub>2</sub>I].** CuI (0.143 g, 0.75 mmol) and PBz<sub>3</sub> (0.685 g, 2.25 mmol) were refluxed in 15 mL of acetonitrile for 3 h and on cooling crystals of the product formed, which were filtered off and dried *in vacuo*. The yield was 0.37 g (62%), mp 171–173 °C (Found: C, 62.85; H, 5.04. Calc. for C<sub>42</sub>H<sub>42</sub>ICuP<sub>2</sub>: C, 63.12; H, 5.30%). The above product was formed even if a 1:1 ratio of CuI to PBz<sub>3</sub> was used.

**[Cu(PBz<sub>3</sub>)<sub>2</sub>][CuCl<sub>2</sub>].** To a stirred suspension of CuCl (0.143 g, 1.5 mmol) in 10 mL of chloroform was added PBz<sub>3</sub> (0.463 g, 1.52 mmol) in 10 mL of the same solvent, and the mixture refluxed until the CuCl had dissolved (*ca.* 10 min). The solution was cooled, filtered and the volume reduced by half using a rotary evaporator. Hexane (45 mL) was added and the solution left to stand overnight. The resulting white powder was filtered off and recrystallized from 2:1 acetone–ethanol (about 50 mL) to yield 0.5 g (83%) of colourless crystals of the product, mp 199–202 °C (Found: C, 62.29; H, 5.20. Calc. for C<sub>21</sub>H<sub>21</sub>ClCuP: C, 62.53; H, 5.25%).

If the above reaction was carried out in refluxing acetonitrile (30 mL) for 3 h using the same reagents, colourless crystals of tribenzylphosphine oxide (0.3 g, 63% yield), mp 219–222 °C (lit.<sup>7</sup> 217 °C), were obtained on cooling (Found: C, 78.34; H, 6.40. Calc. for C<sub>21</sub>H<sub>21</sub>OP: C, 78.73; H, 6.61%). *m/z* 321 (MH<sup>+</sup>, 100) and 641 (M<sub>2</sub>H<sup>+</sup>, 7%).

 $[Cu_2(PBz_3)_2Cl_2]\cdot 3C_6H_6$ .  $[Cu(PBz_3)_2][CuCl_2]$  (0.457 g, 0.565 mmol) was dissolved in 20 mL of boiling benzene and left to stand overnight. The resulting crystals of the product were filtered off and quickly air-dried, since they readily lost benzene over a short time (3–4 h), reverting to the ionic form [Cu-(PBz\_3)\_2][CuCl\_2]. The pure dimeric product melted at 45–48 °C, solidified at *ca*. 75 °C and then melted again at 173–175 °C as the solvated benzene was removed. It was not possible to obtain analytical data corresponding to the trisolvate (*e.g.* Found: C 66.15; H 5.75% corresponds to *ca*. 0.75 mol of benzene per dimeric unit. Calc. 66.16; H 5.51%).

#### Crystallography

**Crystal data.**  $[Cu(PBz_3)_2Cl]$ .  $C_{42}H_{42}ClCuP_2$ , M = 707.69, monoclinic, space group C2/c, a = 25.4813(3), b = 12.2113(1), c = 25.1532(3) Å,  $\beta = 109.571(1)^\circ$ , U = 7374.5(1) Å<sup>3</sup>, T = 291 K, Z = 8,  $\mu$ (Mo-K $\alpha$ ) = 0.780 mm<sup>-1</sup>, 21077 reflections measured, 7955 unique ( $R_{int} = 0.0153$ ) which were used in all calculations. The final wR2 = 0.0906, R1 = 0.0410,  $R1[I > 2\sigma(I)] = 0.0328$ .

[ $Cu(PBz_3)_2Br$ ].  $C_{42}H_{42}BrCuP_2$ , M = 752.15, monoclinic, space group  $P2_1/n$ , a = 22.7747(4), b = 14.4082(2), c = 23.4308(5)Å,  $\beta = 100.986(1)^\circ$ , U = 7547.7(2) Å<sup>3</sup>, T = 291 K, Z = 8,  $\mu$ (Mo-K $\alpha$ ) = 1.750 mm<sup>-1</sup>, 43932 reflections measured, 16605 unique ( $R_{int} = 0.0205$ ) which were used in all calculations. The final wR2 = 0.0938, R1 = 0.0668,  $R1[I > 2\sigma(I)] = 0.0388$ .

[ $Cu(PBz_3)_2I$ ].  $C_{42}H_{42}ICuP_2$ , M = 799.14, monoclinic, space group  $P2_1/n$ , a = 10.001(2), b = 14.529(3), c = 26.330(5) Å,  $\beta = 94.68(3)^\circ$ , U = 3813(1) Å<sup>3</sup>, T = 291 K, Z = 4,  $\mu$ (Mo-K $\alpha$ ) = 1.494 mm<sup>-1</sup>, 13921 reflections measured, 6717 unique ( $R_{int} = 0.0377$ ) which were used in all calculations. The final wR2 = 0.1202, R1 = 0.0860,  $R1[I > 2\sigma(I)] = 0.0409$ .

 $[Cu(PBz_3)_2][CuCl_2]$ . C<sub>42</sub>H<sub>42</sub>Cl<sub>2</sub>Cu<sub>2</sub>P<sub>2</sub>, M = 806.68, triclinic, space group  $P\overline{1}$ , a = 9.7619(3), b = 9.7619(3), c = 9.7619(3) Å, a = 90.02(3),  $\beta = 90.02(3)$ ,  $\gamma = 90.02(3)^{\circ}$ , U = 930.26(5) Å<sup>3</sup>, T = 203 K, Z = 1,  $\mu$ (Mo-K $\alpha$ ) = 1.402 mm<sup>-1</sup>, 3522 reflections measured, 2429 unique ( $R_{int} = 0.0146$ ) which were used in all calculations. The final wR2 = 0.2428, R1 = 0.0924,  $R1[I > 2\sigma(I)] = 0.0894$ .

 $[Cu_2Cl_2(PBz_3)_2] \cdot 3C_6H_6$ . C<sub>33</sub>H<sub>33</sub>ClCuP, M = 559.55, triclinic, space group PI, a = 9.902(3), b = 10.432(4), c = 14.326(5) Å,

 $a = 94.710(5), \beta = 97.485(4), \gamma = 95.759(5)^\circ, U = 1453.1(8)$  Å<sup>3</sup>, T = 163 K,  $Z = 2, \mu$ (Mo-Kα) = 0.918 mm<sup>-1</sup>, 17080 reflections measured, 5107 unique ( $R_{int} = 0.0646$ ) which were used in all calculations. The final wR2 = 0.1187, R1 = 0.0933, $R1[I > 2\sigma(I)] = 0.0502.$ 

X-Ray analysis. Data collection, reduction, solution and refinement were performed as previously described.<sup>8,9</sup> However, refinement of [Cu(PBz<sub>3</sub>)<sub>2</sub>][CuCl<sub>2</sub>] presented several challenges. Refinement in rhombohedral space groups (R3,  $R\overline{3}$ , for which data merged poorly) and in triclinic space groups (P1 and  $P\overline{1}$ ) died with  $R1 \approx 0.28$ . Refinements assuming three-fold twinning (trilling) lead to improved values for R1. The penultimate model, with twin matrix 0 -1 0 0 0 1 1 0 0, led to values for wR2 and R1 (data for which  $F > 4\sigma(F)$ ) of 0.328 and 0.107. At this stage, (i) seven reflections for which  $F(\text{calc.}) \ll F(\text{obs.})$  were omitted, (ii) restraints on eccentricity of atomic displacement parameters were introduced, and (iii) two peaks 2.15 Å from each copper atom were assigned as alternative orientations of the  $[Cu(PBz_3)_2]^+$  and  $[CuCl_2]^-$  moieties with a fixed thermal parameter (U = 0.04 Å, similar to  $U_{equiv}$  of the major P and Cl atoms) and occupancy set to the complement of the occupancy of the major component, which was refined as a free variable. Final values for wR2 and R1 were 0.2428 and 0.0924. The occupancy of the major component is 0.945(7). No attempt was made to model the alternative orientation of the benzyl moieties of the tribenzylphosphine. Unit cell contents given are corrected to whole numbers for C and H atoms. Although modelled successfully as an alternative orientation, at least from the perspective of least-squares refinement and absence of residual electron density above the noise level of the final difference Fourier map, the peaks are probably artifacts arising from the alternative trigonal twin law.

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See http://www.rsc.org/suppdata/dt/b0/b007698h/ for crystallographic files in .cif format.

#### Spectroscopy

Far-infrared spectra were recorded at  $4 \text{ cm}^{-1}$  resolution at room temperature as Polythene discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 line mm<sup>-1</sup> wire mesh beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector. Raman spectra were recorded at 4.5 cm<sup>-1</sup> resolution using a Jobin–Yvon V1000 spectrometer equipped with a cooled photomultipler (RCA C31034A) detector. The 514.5 nm exciting line from a Spectra physics Model 2016 argon–ion laser was used.

<sup>31</sup>P CPMAS solid state NMR spectra were acquired at room temperature operating at a field strength of  $B_0 = 9.40$  T and a <sup>31</sup>P Zeeman frequency ( $v_{\rm P}$ ) of 162.92 MHz. Conventional cross polarisation<sup>10</sup> and magic angle spinning techniques,<sup>11</sup> coupled with spin temperature alternation to eliminate spectral artifacts,12 were implemented using a Bruker 4 mm double air bearing probe in which MAS frequencies  $\geq 10$  kHz were achieved. A recycle delay of 20 s, a <sup>1</sup>H-<sup>31</sup>P contact period of 10 ms and a <sup>1</sup>H  $\pi/2$  pulse length of 3 µs were common to all spectra. No spectral smoothing was invoked prior to Fourier transformation. Two-dimensional correlation spectroscopy (COSY) experiments were implemented with the timeproportional phase incrementation (TPPI) method<sup>13</sup> for acquisition of phase-sensitive data in both F1 and F2 dimensions. The application of this technique has been discussed in detail elsewhere.<sup>14</sup> The recycle delay, contact period, <sup>1</sup>H  $\pi/2$ pulse length and MAS spinning rate were the same as those implemented for the one-dimensional experiments. A total of 256 F1 increments were acquired into 256 word F2 blocks, with both dimensions zero filled to 1 K words and weighted with sine bell apodization prior to Fourier transformation. The

 $^{31}$ P chemical shifts for all experiments were externally referenced to external solid triphenylphosphine which exhibits a chemical shift of -9.9 ppm with respect to 85% H<sub>3</sub>PO<sub>4</sub>.

#### **Results and discussion**

#### Synthesis

The reaction of CuX with  $PBz_3$  in a 1:2 mole ratio in chloroform (X = Cl) or acetonitrile (X = Br or I) yielded the 1:2 complexes [Cu(PBz<sub>3</sub>)<sub>2</sub>X], which have been shown by single crystal X-ray crystallography to contain three-co-ordinate copper(I) (see below). In the case of CuCl, if the reaction was carried out in a 1:1 mole ratio the ionic two-co-ordinate complex, [Cu-(PBz<sub>3</sub>)<sub>2</sub>][CuCl<sub>2</sub>], was isolated. Attempts to prepare this complex in acetonitrile following the literature method<sup>2</sup> for the bromo analogue, [Cu(PBz<sub>3</sub>)<sub>2</sub>][CuBr<sub>2</sub>], gave tribenzylphosphine oxide in good yield. Presumably the oxygen arise from traces in the solvent implying that CuCl acts as a reagent/catalyst in this solvent for the oxidation of PBz<sub>3</sub>. In contrast, under similar conditions in the presence of CuBr or CuI, this reaction does not occur to any significant extent. Attempts to prepare a 1:1 iodo complex failed regardless of the CuI:PBz<sub>3</sub> molar ratio used.

When  $[Cu(PBz_3)_2][CuCl_2]$  was recrystallized from hot benzene a product with a low melting point was obtained and this was shown by X-ray crystallography (see below) to be the benzene-solvated dimer  $[Cu_2(PBz_3)_2Cl_2] \cdot 3C_6H_6$ . This product rapidly loses its solvated benzene and reverts to the ionic form, suggesting the latter complex is obtained as a dissociation product of the initially formed dimeric isomer according to eqn. (1). Dimer species are also observed under the conditions

$$2CuCl + 2PBz_{3} \longrightarrow [Cu_{2}(PBz_{3})_{2}Cl_{2}] \longrightarrow [Cu(PBz_{3})_{2}][CuCl_{2}] \quad (1)$$

used to record the positive ion liquid secondary ionization mass spectra, although the most prominent peaks † for all the complexes reported in this study are assigned to the monomeric  $[Cu(PBz_3)_2]^+$  ion at m/z 671 (100%) and its derivatives,  $[Cu(PBz_3)_2]^+$  (367, 60–95%) and  $[Cu(PBz_2)]^+$  (185,  $\approx 20\%$ ). For the ionic 1 : 1 complexes,  $[Cu(PBz_3)_2][CuX_2]$  (X = Cl or Br), the dicopper ions,  $[Cu_2(PBz_3)_2X]^+$ , are seen with moderate intensity (X = Cl m/z 771; X = Br 815,  $\approx 20\%$ ) as well as weak peaks assignable to  $[Cu_2(PBz_3)_2X_2]^+$  (X = Cl 806; X = Br 896,  $\approx 3\%$ ) and  $[Cu_3(PBz_3)_2Cl_2]^+$  (869,  $\approx 3\%$ ). In contrast, in the mass spectra of the  $[Cu(PBz_3)_2X]$  1:2 complexes, the dicopper  $[Cu_2(PBz_3)_2X]^+$  peaks, although still observed, are much weaker (X = Cl m/z 771, 8%; X = Br 815, 3%; X = I 861, 3%). The mass spectrum of  $[Cu_2(PBz_3)_2Cl_2]\cdot 3C_6H_6$  is similar to that seen for the ionic isomer.

#### Structural determinations

The structure determinations of the 1:2 complexes of copper(I) halides for X = Cl, Br and I with PBz<sub>3</sub> are consistent with their formulation as monomeric three-co-ordinate  $[Cu(PBz_3)_2X]$  species. One, two and one molecules constitute the asymmetric units of the cells for X = Cl, Br and I, respectively. Representative views of the molecular structures are shown in Fig. 1 with relevant geometric parameters listed in Table 1. Comparison of these data with those of the two-co-ordinate  $[Cu(PBz_3)_2]X$  (X = PF<sub>6</sub> or CuBr<sub>2</sub>) complexes<sup>2,3</sup> and  $[Cu(PBz_3)_2][CuCl_2]$  (see below) show that co-ordination of the halide anion to the copper results in a lengthening of the Cu–P (see footnote *e* in Table 1) bond lengths from 2.19–2.20 to 2.21–2.25 Å and a decrease in the P–Cu–P angles from 180 to 136.53(2)–



Fig. 1 ORTEP<sup>15</sup> diagrams of (a)  $[Cu(PBz_3)_2Cl]$ , (b)  $[Cu(PBz_3)_2Br]$  (Molecule A), (c)  $[Cu(PBz_3)_2I]$ . Ellipsoids are drawn at the 40% probability level in all figures.

139.86(3)°. The Cu-P distances in the three-co-ordinate molecules vary, with Cu-P(1) being longer in each case [2.2399(5)-2.2509(7) Å] and Cu-P(2) shorter [2.2127(8)-2.2396(7) Å]. As well, significant changes in the conformational structure of the  $PBz_3$  ligands occur with co-ordination of the halides. The P(2) ligand adopts approximately  $C_3$  symmetry, similar to that observed for the two-co-ordinate complexes with the three phenyl groups oriented towards the copper site (torsion angles  $Cu-P(2)-C(2n)-C(2n1) < 90^{\circ}$ , Table 2). However, in the P(1) ligand, one phenyl ring is rotated away from the copper atom such that the torsion angle  $Cu-P(1)-C(12)-C(121) > 90^\circ$ . For the chloride complex this ring is trans to the Cu-Cl bond, while for the iodide complex and both molecules in the bromide complex it is *cis* to the Cu-X bond. The P(2)-Cu-X angle is consistently larger than the P(1)-Cu-X angle, reflecting a movement of the halide towards the less sterically hindered P(1) ligand.

<sup>&</sup>lt;sup>†</sup> Peaks quoted are for the most abundant isotopomer. Percentages are relative intensities.

**Table 1** Geometric parameters (bond lengths in Å and angles in °) for two-co-ordinate,  $[Cu(PBz_3)_2]X (X = PF_6, CuCl_2 \text{ or } CuBr_2)$ , and three-co-ordinate,  $[Cu(PBz_3)_2X] (X = Cl, Br \text{ or } I)$ , complexes

Х	Cu–P(1)	Cu–P(2)	Cu–X	P(1)–Cu–P(2)	P(1)–Cu–X	P(2)–Cu–X
Two-co-ord	inate					
$PF_6^{a}$	2.191(1)	$2.191(1)^{b}$		$180.0(-)^{c}$		
CuČl <sub>2</sub>	2.205(3)	$2.205(3)^{b}$	2.079(4)	$180.0(-)^{c}$		
CuBr <sub>2</sub> <sup>d</sup>	2.196(1)	$2.196(1)^{b}$	2.2076(8)	$180.0(-)^{c}$		
			2.2077(8)			
Three-co-or	dinate					
Cl	2.2399(5)	2.2275(5)	2.2521(6)	136.53(2)	105.34(2)	117.76(2)
Br <sub>A</sub> <sup>e</sup>	2.2436(7)	2.2127(8)	2.4034(4)	138.92(3)	100.76(2)	119.83(2)
Br <sub>B</sub> <sup>e</sup>	2.2509(7)	2.2396(7)	2.3995(4)	139.86(3)	106.92(2)	113.09(2)
Ι	2.239(1)	2.234(1)	2.5865(8)	139.78(5)	105.11(4)	115.07(4)

<sup>*a*</sup> Ref. 3. <sup>*b*</sup> Identical due to crystallographically imposed symmetry. <sup>*c*</sup> Precisely 180° because Cu sits at a centre of symmetry. <sup>*d*</sup> Ref. 2. <sup>*e*</sup> Br<sub>A</sub> and Br<sub>B</sub> refer to the two different molecules in the asymmetric unit. Hence for Molecule A, to facilitate comparison with the other compounds, the atoms labelled as Cu(1), P(11) and P(12) in Fig. 1 are referred to as Cu, P(1) and P(2) respectively.

Table 2Torsion angles (°) for two-co-ordinate,  $[Cu(PBz_3)_2][CuCl_2]$ , and three-co-ordinate,  $[Cu(PBz_3)_2X]$  (X = Cl, Br or I), complexes

	CuCl <sub>2</sub>	Cl	Br <sub>A</sub> <sup><i>a</i></sup>	Br <sub>B</sub> <sup><i>a</i></sup>	Ι
Cu–P(1)–C(11)–C(111)	-50(1)	49.8(1)	-58.1(2)	50.7(3)	-54.8(5)
Cu-P(1)-C(12)-C(121)	-53(1)	174.3(1)	-142.7(2)	162.6(2)	-152.9(4)
Cu-P(1)-C(13)-C(131)	-49(1)	-49.79(1)	-56.2(2)	55.1(2)	-51.2(4)
Cu–P(2)–C(21)–C(211)	50(1)	70.1(1)	84.9(3)	-69.2(2)	75.3(4)
Cu–P(2)–C(22)–C(221)	53(1)	59.2(1)	46.0(2)	-54.7(2)	52.5(4)
Cu-P(2)-C(23)-C(231)	49(1)	55.5(2)	53.7(3)	-60.3(2)	61.9(4)

" See footnote e in Table 1.



Fig. 2 ORTEP diagram of [Cu(PBz<sub>3</sub>)<sub>2</sub>][CuCl<sub>2</sub>].

The single crystal structure of  $[Cu(PBz_3)_2][CuCl_2]$  (Fig. 2 and Tables 1 and 2) confirms that the complex contains discrete  $[Cu(PBz_3)_2]^+$  cations with a linear P–Cu–P co-ordination, as also observed when the anion is  $[PF_6]^-$  or  $[CuBr_2]^{-,2,3}$  As in the other two structures, the phenyl groups of the PBz<sub>3</sub> swing back over the copper atom to generate a sixfold phenyl embrace  $(6PE)^5$  as the hydrogen atoms of each phenyl group are directed towards the plane of the phenyl group on the opposite ligand.

The structure of the benzene-solvated dimeric complex,  $[Cu_2(PBz_3)_2Cl_2]\cdot 3C_6H_6$ , consists of discrete centrosymmetric dimers separated by co-crystallized benzene molecules (Fig. 3). However, there are several close contacts between these benzene molecules and the complex. This is most evident with the benzene that effectively caps the tribenzylphosphine ligands (see Fig. 3). Several of the H atoms on the phosphine have close (3.0–3.5 Å) contacts with the benzene which clearly stabilize the dimeric nature of the complex. The 'PCuCl\_2CuP' unit is essentially planar, closely approximating  $D_{2h}$  symmetry with insignificant differences in the Cu–Cl distances or P–Cu–Cl angles (Table 3). The Cu–P bond length of 2.185(1) Å is similar



**Fig. 3** ORTEP diagram of  $[Cu_2(PBz_3)_2Cl_2] \cdot 3C_6H_6$ . One  $C_6H_6$  molecule of solvation is included.

to those observed for other 1:1 dimeric complexes (Table 3) and slightly shorter than the distances of 2.19–2.20 Å observed for the two-co-ordinate 1:2 complexes and of 2.21–2.25 Å for the three-co-ordinate 1:2 complexes. The PBz<sub>3</sub> ligand adopts the  $C_3$ conformation observed for the two-co-ordinate complexes, with the phenyl groups oriented towards the 'CuCl<sub>2</sub>Cu' core [torsion angles Cu–P–C(*n*)–C(*n*1): 57.9(3), 64.4(3), 70.2(3)°], although the two ligands are not close enough to interact.

# Solid state <sup>31</sup>P CPMAS NMR spectroscopy

The 1-D <sup>31</sup>P CPMAS NMR spectra for the complexes studied in this work are shown in Fig. 4 with the 2-D spectra for the chloride and bromide 1:2 complexes in Fig. 5. The NMR parameters derived from these spectra are listed in Table 4. The results obtained are similar to those reported for other copper(I) phosphine complexes under high magnetic field

**Table 3** Geometric parameters (bond lengths in Å and angles in °) for dimeric  $[Cu_2(PR_3)_2Cl_2]$  complexes

PR <sub>3</sub>	Cu–P	Cu–Cl	Cl···Cl	$Cu \cdots Cu$	Cu–Cl–Cu	P-Cu-Cl	Cl–Cu–Cl
PBz <sub>3</sub>	2.185(1)	2.305(1) 2 302(1)	3.439(1)	3.065(1)	83.41(4)	131.14(4) 132.07(4)	96.59(4)
$P(o-Tol)_3^a$	2.191(1)	2.302(1) 2.289(2) 2.316(2)	3.402(2)	3.103(1)	84.74(6)	132.47(6)	95.26(5)
PCy <sub>3</sub> <sup>b</sup>	2.183(2)	2.285(2) 2.322(2)	3.439(3)	3.066(1)	83.44(7)	127.40(7) 136.05(7)	95.56(7)

<sup>*a*</sup> Ref. 16,  $P(o-Tol)_3 = tris(2-methylphenyl)phosphine.$  <sup>*b*</sup> Ref. 17,  $PCy_3 = tris(cyclohexyl)phosphine.$ 

**Table 4** <sup>31</sup>P CP-MAS NMR data for two-co-ordinate,  $[Cu(PBz_3)_2]X$ , and three-co-ordinate,  $[Cu(PBz_3)_2X]$ , complexes at  $B_0 = 9.40$  T

		$\delta_{\rm iso}{}^a$	⊿ <sub>21</sub> /kHz	$\Delta_{32}/kHz$	$\varDelta_{43}/\mathrm{kHz}$	<sup>1</sup> J/kHz	d/kHz	<i>d</i> <sub>1</sub> /kHz	$dv_{\rm Cu}/10^9~{\rm Hz^2}$	
Two	o-co-ordinate									
[Cu	(PBz <sub>3</sub> ) <sub>2</sub> ][CuCl <sub>2</sub> ]	29.6	1.00	1.63	1.92	1.54	0.23	0.05	24.3	
[Cu	$(PBz_3)_2 [CuBr_2]^b$	30.9	1.03	1.58	1.91	1.52	0.22	0.03	23.3	
[Cu	$(PBz_3)_2]PF_6^{b}$	29.9	0.98	1.66	1.93	1.56	0.24	0.05	25.4	
Thr	ree-co-ordinate									
ſCu	(PBz <sub>2</sub> ) <sub>2</sub> Cl]	6.8	1.15	1.41	1.64	1.41	0.12	0.01	13	
	3/2 - 1	-3.5	1.00	1.23	1.37	1.23	0.09	0.02	10	
[Cu	$(PBz_3)_2Br](A)^c$	6.3	1.30	1.46	1.60	1.46	0.08	0.00	8	
•		1.8	1.03	1.26	1.50	1.26	0.12	0.00	12	
[Cu	$(PBz_3)_2Br](B)^c$	4.2	1.09	1.39	1.58	1.36	0.12	0.02	13	
[Cu	I(PBz <sub>3</sub> ) <sub>2</sub> I]	6.0	1.09	1.37	1.56	1.34	0.12	0.02	12	

<sup>*a*</sup> The average chemical shift, with respect to free PPh<sub>3</sub>, of the centre points of the four lines of the quartet  $(\delta_1 + \delta_2 + \delta_3 + \delta_4)/4$ . The values can be transformed to chemical shifts with respect to 85% H<sub>3</sub>PO<sub>4</sub> by subtraction of 9.9 ppm. <sup>*b*</sup> Ref. 3. <sup>*c*</sup> See footnote *e* in Table 1.



 $\label{eq:Fig.4} \begin{array}{ll} \mbox{I-D Solid state $^{31}$P CPMAS NMR spectra of (a) [Cu(PBz_3)_2Cl],} \\ \mbox{(b) [Cu(PBz_3)_2Br], (c) [Cu(PBz_3)_2l], (d) [Cu(PBz_3)_2][CuCl_2].} \end{array}$ 

 $(B_0 > \approx 7 \text{ T})$  and slow <sup>63,65</sup>Cu relaxation conditions<sup>14,18-20</sup> in that they consist of asymmetric quartets arising from quadrupolar perturbed scalar (*J*) and dipolar coupling between the spin 1/2 <sup>31</sup>P and spin 3/2 <sup>63,65</sup>Cu nuclei. The linewidths are too broad to resolve the *J*-coupled multiplets attributed to each copper isotope and the spectra are dominated by <sup>31</sup>P resonances associated with the more abundant <sup>63</sup>Cu nuclei. The linewidth is too broad also to resolve geminal <sup>2</sup>*J*(<sup>31</sup>P–<sup>31</sup>P) coupling. The overlap of the peaks in each quartet precludes accurate



Fig. 5 2-D Solid state  ${}^{31}$ P CPMAS COSY NMR spectra of (a) [Cu-(PBz\_3)\_2Cl], (b) [Cu(PBz\_3)\_2Br].

measurement of the chemical shift and line spacing data from the 1-D spectra, but reasonable values of these parameters have been estimated from the two-dimensional <sup>31</sup>P CPMAS COSY spectra which separate the two  ${}^{1}J(P-Cu)$  coupled quartets above and below the main diagonal (Fig. 5). For the three-coordinate  $[Cu(PBz_3)_2X]$  (X = Cl, Br or I) complexes, the average chemical shifts of  $\delta$  2–7 represent a significant upfield shift from the value of  $\delta$  ca. 30 observed for the ionic two-co-ordinate  $[Cu(PBz_3)_2]X$  (X = PF<sub>6</sub>, CuCl<sub>2</sub> or CuBr<sub>2</sub>) complexes. For [Cu-(PBz<sub>3</sub>)<sub>2</sub>Cl], the quartets centred at  $\delta$  6.8 and -3.5 [Fig. 5(a)] are assigned to P(2) and P(1) respectively on the basis of correlation of the  ${}^{1}J({}^{31}P-{}^{63}Cu)$  coupling constants of 1.41 and 1.23 kHz with the shorter and longer Cu-P bond lengths. For [Cu-(PBz<sub>3</sub>)<sub>2</sub>Br], two distinct AB patterns are expected for each of the two crystallographically independent molecules in the crystal lattice. However, only three quartets can be identified in the spectra of the complex (Fig. 4). The 2-D spectra show two multiplets (at  $\delta$  6.3 and 1.8) to be  ${}^{2}J({}^{31}P-{}^{31}P)$  coupled with  ${}^{1}J({}^{31}P-{}^{63}Cu)$  values of 1.46 and 1.26 kHz which are assigned to P(2) and P(1) of molecule A on the basis of the significant differences in the Cu-P(1,2) bond lengths. The third, more intense quartet at  $\delta$  4.2, is assigned as an unresolved but strongly AB-coupled pair of quartets from the two P atoms of molecule B, the similar chemical shifts values being consistent with the small differences in the Cu-P bond lengths found for this molecule. For [Cu(PBz<sub>3</sub>)<sub>2</sub>I], one quartet only is observed and, as for molecule B of the bromide complex, is assigned as an unresolved but strongly AB coupled pair of quartets, consistent with the similar Cu-P distances in this complex. The values of  ${}^{1}J({}^{31}P-{}^{63}Cu)$  of 1.2–1.4 kHz for these three-coordinate complexes are significantly smaller than the 1.52-1.56 kHz recorded for the two-co-ordinate complexes,3,18 reflecting transfer of electron density away from the Cu-P bonds with coordination of the halide.

The spacings between the lines of each quartet are not symmetric but show a significant increase in the upfield direction. This phenomenon arises from perturbation of the simple J spectrum by dipolar interactions between the phosphorus and the quadrupolar copper nuclei. First order analysis<sup>21</sup> predicts a field dependent shift of the outer two lines upfield and the inner two lines  $(\delta_2, \delta_3)$  downfield by a magnitude d such that  $(\Delta_{32} - \Delta_{21}) = (\Delta_{43} - \Delta_{32}) = 2d$ , from which  $d = (\Delta_{43} - \Delta_{21})/4$ . Multiplication of d by the <sup>63</sup>Cu Zeeman frequency yields a field-independent parameter  $dv_{Cu}$  that is suitable for comparison of results obtained from spectra recorded at different field strengths.

The first-order analysis also generates eqn. (2) for  $dv_{cu}$  where  $\chi_{cu} = e^2 q Q/h$  is the <sup>63</sup>Cu quadrupolar coupling constant,

$$dv_{\rm Cu} = (3\chi_{\rm Cu}D_{\rm eff}/20)(3\cos^2\beta^{\rm D} - 1 + \eta\sin^2\beta^{\rm D}\cos 2a^{\rm D}) \quad (2)$$

 $\begin{array}{l} D_{\rm eff} = (D - \Delta J/3) \ (D = (\mu_0/4\pi)\gamma_{\rm P}\gamma_{\rm Cu}h/4\pi^2r^3 \ {\rm is} \ {\rm the} \ {\rm Cu-P} \ {\rm dipolar} \ {\rm coupling} \ {\rm constant} \ {\rm and} \ \Delta J \ {\rm is} \ {\rm the} \ {\rm anisotropy} \ {\rm in} \ {\rm the} \ J \ {\rm tensor}), \ \eta \ {\rm is} \ {\rm the} \ {\rm asymmetry} \ {\rm parameter} \ {\rm of} \ {\rm the} \ {\rm electric} \ {\rm field} \ {\rm gradient} \ ({\rm EFG}) \ {\rm tensor}, \ {\rm and} \ \alpha^{\rm D} \ {\rm and} \ \beta^{\rm D} \ {\rm are} \ {\rm the} \ {\rm polar} \ {\rm angles} \ {\rm defining} \ {\rm the} \ {\rm direction} \ {\rm of} \ {\rm the} \ {\rm Cu-P} \ {\rm internuclear} \ {\rm vector} \ {\rm with} \ {\rm respect} \ {\rm to} \ {\rm the} \ {\rm principal} \ {\rm axial} \ {\rm system} \ ({\rm PAS}) \ {\rm of} \ {\rm the} \ {\rm EFG} \ {\rm tensor}. \ {\rm In} \ {\rm practice}, \ {\rm higher} \ {\rm order} \ {\rm quadrupole} \ {\rm effects}^{22,23} \ {\rm result} \ {\rm in} \ {\rm the} \ {\rm line} \ {\rm spacings} \ {\rm deviating} \ {\rm from} \ {\rm this} \ {\rm first} \ {\rm order} \ {\rm model} \ {\rm with} \ (\varDelta_{32} - \varDelta_{21}) > \ 2d > (\varDelta_{43} - \varDelta_{32}). \ {\rm These} \ {\rm effects} \ {\rm are} \ {\rm generally} \ {\rm small} \ {\rm and} \ {\rm are} \ {\rm recorded} \ {\rm for} \ {\rm the} \ {\rm practice} \ {\rm downfield} \ {\rm shifts} \ {\rm of} \ {\rm peaks} \ 1 \ {\rm and} \ 3 \ {\rm and} \ {\rm a downfield} \ {\rm shift} \ {\rm of} \ {\rm peaks} \ 2 \ {\rm and} \ 4 \ {\rm by} \ {\rm a correction} \ {\rm term} \ {\rm term} \ {\rm of} \ {\rm magnitude} \ {\rm d}_1 \ {\rm such} \ {\rm that} \ {\rm d}_{21} = J - 2d - 2d_1, \ {\rm d}_{32} = \ J + 2d_1 \ {\rm and} \ {\rm d}_{43} = J + 2d - 2d_1; \ {\rm from} \ {\rm which} \ {\rm d} = (\varDelta_{43} - \varDelta_{21})/4 \ {\rm as} \ {\rm before}, \ {\rm d}_{1} = (\varDelta_{32} - J)/2 \ {\rm while} \ J = (\varDelta_{21} + 2\varDelta_{32} + \varDelta_{43})/4. \ {\rm d} \ {\rm d} \ {\rm d}_{1} \ {\rm d}_{21} \ {\rm d}_{1} \ {\rm d}_{21} \ {\rm d}_{1} \ {\rm d}_{$ 

For the present three-co-ordinate complexes,  $dv_{\rm Cu}$  values range from  $8 \times 10^{-9}$  to  $13 \times 10^{9}$  Hz<sup>2</sup> and are very similar to the values of  $(10-11) \times 10^{9}$  Hz<sup>2</sup> found for [Cu(PPh<sub>3</sub>)<sub>2</sub>X] complexes<sup>24</sup> and (6–10) × 10<sup>9</sup> Hz<sup>2</sup> found for [Cu{PPh<sub>2</sub>(o-Tol)})<sub>2</sub>X] complexes.<sup>25</sup> These results suggest that for these



**Fig. 6** Far-IR spectra of the 1:1 complexes: (a)  $[Cu_2(PBz_3)_2Cl_2]$ ·  $3C_6H_6$ ; (b)  $[Cu_2(PBz_3)_2Cl_2]$ ·  $3C_6H_6$  during its conversion into  $[Cu_1(PBz_3)_2][CuCl_2]$ ; (c)  $[Cu(PBz_3)_2][CuCl_2]$  formed from  $[Cu_2Cl_2(PBz_3)_2]$ ·  $3C_6H_6$  by complete removal of  $C_6H_6$ ; (d)  $[Cu(PBz_3)_2][CuBr_2]$ . The  $\nu(CuCl)$  bands in (a) and the bands due to  $[CuX_2]^-$  in (c) and (d) are labeled with their wavenumbers.



**Fig.** 7 Far-IR spectra of the 1:2 complexes: (a)  $[Cu(PBz_3)_2Cl]$ , (b)  $[Cu(PBz_3)_2Br]$ , (c)  $[Cu(PBz_3)_2I]$ , (d)  $[Cu(PBz_3)_2]PF_6$ . The v(CuX) bands are labeled with their wavenumbers.

structurally related complexes the  ${}^{63}$ Cu NQR frequencies are likely to be comparable to the values of 33.17 and 33.93 MHz recorded for [Cu(PPh<sub>3</sub>)<sub>2</sub>Cl] and [Cu(PPh<sub>3</sub>)<sub>2</sub>Br].<sup>26</sup>

#### Vibrational spectroscopy

The far-IR spectra of the 1:1 and 1:2 complexes are shown in Figs. 6 and 7 respectively. The spectra contain a number of bands due to the co-ordinated PBz<sub>3</sub>, but comparison with the spectrum of uncomplexed PBz<sub>3</sub> allows assignments of the bands due to the v(CuX) modes of the neutral complexes and those of the [CuX<sub>2</sub>]<sup>-</sup> ions in the ionic complexes. These assignments are compared with those for some related compounds in Table 5.

The spectra in Fig. 6(a)-6(c) show the conversion from  $[Cu_2(PBz_3)_2Cl_2]\cdot 3C_6H_6$  into  $[Cu(PBz_3)_2][CuCl_2]$  that occurs with loss of benzene of solvation during recording of the spectrum

**Table 5** Bond lengths d(CuX) and vibrational frequencies v(CuX) for two-co-ordinate  $[Cu(PBz_3)_2]X$ , three-co-ordinate  $[Cu(PBz_3)_2X]$  and related complexes

Compound	d(CuX)/Å	v(CuX)/cm <sup>-1</sup>				
$[Cu_2(PBz_3)_2Cl_2]$	2.302(1), 2.305(1)	230, 208				
$[Cu_2 \{P(o-Tol)_3\}, Cl_2]^a$	2.289(2), 2.316(2)	237, 207				
[Cu(PBz <sub>3</sub> ) <sub>2</sub> ][CuCl <sub>2</sub> ]	2.079(4)	409 (IR)				
[NBu <sup>n</sup> <sub>4</sub> ][CuCl <sub>2</sub> ] <sup>b</sup>	2.107(1)	404 (IR), 304 (Raman)				
[Cu(PBz <sub>3</sub> ) <sub>2</sub> ][CuBr <sub>2</sub> ]	2.2076(8), 2.2027(8)	326 (IR), 196 (Raman)				
$[NBu_{4}^{n}][CuBr_{2}]^{b}$	2.226(1)	321 (IR), 191 (Raman)				
[Cu(PBz <sub>3</sub> ) <sub>2</sub> Cl]	2.2521(6)	262				
[Cu(PPh <sub>3</sub> ) <sub>2</sub> Cl] <sup>c</sup>	2.208(2)	298				
[Cu(PBz <sub>3</sub> ) <sub>2</sub> Br]	2.3995(4), 2.4034(4)	183				
$[Cu(PPh_3)_2Br]^c$	2.346(2)	218				
[Cu(PBz <sub>3</sub> ) <sub>2</sub> I]	2.5865(8)	153				
$[Cu(PPh_3)_2I]^d$	2.524(2)	184				
<sup>a</sup> Ref. 16. <sup>b</sup> Refs. 27 and 28. <sup>c</sup> Refs. 24 and 29. <sup>d</sup> Ref. 24.						

of the former compound. This series of spectra allows the unambiguous assignment of the two bands at 230 and 208 cm<sup>-1</sup> in the spectrum of  $[Cu_2(PBz_3)_2Cl_2]$ ·3C<sub>6</sub>H<sub>6</sub> to the v(CuCl) modes of the 'Cu<sub>2</sub>Cl<sub>2</sub>' moiety in this complex. These are very similar to the values 237 and 207 cm<sup>-1</sup> reported previously <sup>16</sup> for the structurally related complex, [Cu<sub>2</sub>{P(o-Tol)<sub>3</sub>}<sub>2</sub>Cl<sub>2</sub>] (see Table 5). The ideal point group symmetry of the isolated dimer  $[Cu_2L_2X_2]$  is  $D_{2h}$ . The symmetry types and activities of the fundamentals due to vibrations of the  $D_{2h}$  Cu<sub>2</sub>X<sub>2</sub> core (x parallel to the Cu  $\cdots$  Cu diagonal, y parallel to the X  $\cdots$  X diagonal) are  $2A_g(R) + B_{1g}(R) + B_{1u}(IR) + B_{2u}(IR) + B_{3u}(IR)$ . These involve contributions from CuX bond stretching v(CuX) $(A_g + B_{1g} + B_{2u} + B_{3u})$  and in-plane  $(A_g)$  and out-of-plane  $(B_{1u})$  deformation. Thus two IR-active v(CuX) modes of  $B_{2u}$ and  $B_{3u}$  symmetry are predicted for this structure. For a perfectly square 'Cu<sub>2</sub>X<sub>2</sub>' unit the two IR-active normal modes involve displacement of X and Cu along the positive and negative x directions respectively  $(B_{3u})$  or a similar vibration in the y direction  $(B_{2u})$ . For an isolated square 'Cu<sub>2</sub>X<sub>2</sub>' unit these two modes would have the same frequency. A distortion in which two angles on opposite corners of the square are decreased and the other two are increased results in no change of symmetry, but leads to a separation in frequency of the two v(CuX) IR modes. This is possibly part of the reason for the splitting of the two v(CuCl) bands in  $[Cu_2L_2Cl_2]$  for which the Cu–Cl–Cu and Cl–Cu–Cl angles are 83.41(4),  $96.59(4)^{\circ}$ (L = PBz<sub>3</sub>) and 84.74(6),  $95.26(5)^{\circ}$  [L = P(o-Tol)<sub>3</sub>].<sup>16</sup> Another possible cause of the splitting is the inequality of the strengths of the two inequivalent Cu-Cl bonds in the 'Cu<sub>2</sub>Cl<sub>2</sub>' units, which is reflected in the different Cu-Cl bond lengths (Table 5). This inequivalence is less for the  $L = PBz_3$  than for the L = P-(o-Tol)<sub>3</sub> complex, which is consistent with the greater difference in the two v(CuCl) frequencies observed for the latter (Table 5).

For the ionic complexes  $[Cu(PBz_3)_2][CuX_2]$  (X = Cl or Br) three vibrational bands are expected for the  $[CuX_2]^-$  ion: two v(CuX) modes  $[v_1(R); v_3(IR)]$  and one  $\delta(XCuX)$  mode  $[v_2(IR)]$ . All three of these are observed for the X = Br case, but the  $v_1$ mode is obscured by ligand bands in the Raman spectrum of the X = Cl compound. The v(CuX) values are about 5 cm<sup>-1</sup> higher than those previously reported for  $[NBu_4^n][CuX_2]$ , which is consistent with the slightly shorter Cu–X bond lengths in the former complexes (Table 5). The  $\delta(XCuX)$  frequencies (107 and 79 cm<sup>-1</sup> for X = Cl and Br respectively) are slightly lower than those in  $[NBu_4^n][CuX_2]$  (111 and 81 cm<sup>-1</sup>).<sup>28</sup>

The 1:2 complexes  $[Cu(PBz_3)_2X]$  (X = Cl, Br or I) show halogen-sensitive bands at 262, 183 and 153 cm<sup>-1</sup> respectively, which are readily assigned as the v(CuX) modes (Fig. 7). The frequencies of these modes are significantly lower than those of the corresponding PPh<sub>3</sub> complexes,<sup>24,29</sup> which is consistent with the trend in the Cu–X bond lengths (Table 5). The observed frequencies agree reasonably well with those predicted from the bond lengths by the previously reported empirical relationship between these quantities.<sup>30</sup> The ionic complex  $[Cu(PBz_3)_2]PF_6$ shows a partially split band at 555 and 557 cm<sup>-1</sup> due to the  $v_4(T_{1u})$  mode of  $PF_6^{-,31}$  together with bands due to the coordinated  $PBz_3$  (Fig. 7). These latter bands show essentially the same frequencies and relative intensities as those of the 1:1 complexes  $[Cu(PBz_3)_2][CuX_2]$  (Fig. 6), confirming the ionic nature of these complexes.

In addition to the v(CuX) and anion bands, these complexes should in principle show bands due to the v(CuP) vibrations, but these are more difficult to assign. Previous v(MP) assignments for Group 11 metal phosphine complexes (132 cm<sup>-1</sup> in [Ag(PPh<sub>3</sub>)<sub>2</sub>Br]; 160 cm<sup>-1</sup> in [Au(PPh<sub>3</sub>)<sub>2</sub>Br]; 107, 121 cm<sup>-1</sup> in [Cu(PPh<sub>3</sub>)<sub>3</sub>Cl]; 174 cm<sup>-1</sup> in [Cu<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub>Cl<sub>4</sub>])<sup>32-34</sup> suggest that these occur in the range 100–180 cm<sup>-1</sup>. The only evidence of a possible v(CuP) band in this region for the present complexes is the band at 170 cm<sup>-1</sup> in the far-IR spectrum of [Cu(PBz<sub>3</sub>)<sub>2</sub>Br] (Fig. 7). The v(MP) modes are normally only observed in the Raman spectra,<sup>32-34</sup> but they can also occur in the IR when the frequencies of the v(MP) and v(MX) are similar, so that mixing of these two vibrations can occur. This possibly occurs in [Cu(PBz<sub>3</sub>)<sub>2</sub>Br], in a situation similar to that previously observed for [Au(PMe<sub>3</sub>)Br].<sup>35</sup>

### Conclusion

The present study shows that the reaction of copper(1) halides with tribenzylphosphine in a 1:2 stoichiometric ratio results in the formation of crystalline three-co-ordinate  $[Cu(PBz_3)_2X]$ complexes with co-ordination of the halide disrupting the intramolecular sixfold phenyl embrace observed between the two ligands for ionic  $[Cu(PBz_3)_2]^+$  with non-co-ordinating anions. It has also provided good evidence that the formation of  $[Cu(PBz_3)_2][CuX_2]$  salts for X = Cl or Br is likely to proceed through a dimeric intermediate,  $[Cu_2(PBz_3)_2X_2]$ , but that for X = I only the 1:2 complex is formed under all stoichiometric ratios.

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