

Structural and ^{31}P CP MAS NMR spectroscopic studies of the P_2CuN_2 copper(I) complexes $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$ for $\text{X} = \text{PF}_6$, BF_4 and ClO_4

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The mixed ligand P_2CuN_2 copper(I) complexes $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$ have been studied by one- and two-dimensional ^{31}P CP MAS NMR spectroscopy for $\text{X} = \text{PF}_6$, BF_4 or ClO_4 and single crystal X-ray diffraction for $\text{X} = \text{PF}_6$ and ClO_4 , completing availability of precise structural data for this isomorphous series. The compounds crystallise as discrete cations and anions in space group $P2_1/n$ with $a \approx 15$, $b \approx 27$, $c \approx 9$ Å, $\beta = 95^\circ$, $Z = 4$. The anion is located *ca.* 6 Å from the copper atom and adjacent to a cleft formed between the acetonitrile ligands and phosphine ligand 2 while the crystallographically independent PPh_3 ligands adopt staggered three-bladed propeller-type conformations of opposite chirality. The geometric symmetry of the P_2CuN_2 co-ordination sphere is low with Cu–P(1) 2.276(4)–2.287(2), Cu–P(2) 2.258(4)–2.269(1) Å, Cu–N 2.023(9)–2.053(3) Å, P–Cu–P 126.82(4)–127.73(5), N–Cu–N 99.5(4)–100.3(1), P(1)–Cu–N 100.87(8)–102.34(9) and P(2)–Cu–N 110.4(1)–111.9(3)°. One- and two-dimensional solid state ^{31}P CP MAS NMR spectra of the compounds at 9.40 T show chemical shift differences of 6 ppm between the signals arising from the two P sites which form part of an ABX spin system with $^1J(^{31}\text{P}(1)\text{--}^{63}\text{Cu})$ 1.13–1.14 kHz, $^1J(^{31}\text{P}(2)\text{--}^{63}\text{Cu})$ 1.30 kHz and $^2J(^{31}\text{P}\text{--}^{31}\text{P})$ 75 Hz. The copper quadrupolar induced distortion of the line spacings is different for the two sites and is postulated to be a consequence of variation in the angle between the Cu–P vectors and the z axis of the electric field gradient tensor. The magnitude of the distortion is relatively small and consistent with small copper quadrupolar coupling constants for the compounds and a balanced electronic charge distribution about the copper(I) site in spite of the low geometric symmetry of the P_2CuN_2 co-ordination sphere.

Bis(triphenylphosphine)copper(I) compounds with monovalent anions, $\text{Cu}(\text{PPh}_3)_2\text{X}$, have been shown by single crystal structure determinations to crystallize from polar organic solvents as discrete monomeric $[\text{Cu}(\text{PPh}_3)_2\text{X}]$ or dimeric $[\{\text{Cu}(\text{PPh}_3)_2\text{X}\}_2]$ molecules with X acting as monodentate, bidentate or bridging ligands and the copper site(s) three- or four-co-ordinate, depending on the donor and steric properties of the anion.^{1–9} For the weakly co-ordinating anions PF_6^- , BF_4^- and ClO_4^- , however, recrystallization from acetonitrile results instead in the formation of mixed ligand ionic compounds $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$ in which the anion is displaced from the copper co-ordination sphere by a pair of solvent molecules.^{10–13} Single crystal structure determinations for the ClO_4 ¹⁰ and BF_4 ¹² compounds show the overall structure of the P_2CuN_2 copper co-ordination sphere to be similar and considerably distorted from tetrahedral symmetry. However, line spacing distortions in the solid state ^{31}P CP MAS NMR spectra of the perchlorate compound¹⁰ arising from perturbation of the spectra by copper quadrupolar interactions^{14–18} were found to be unusually small and consistent with a relatively balanced charge distribution about the copper site. In order to improve the quality of the NMR data for these compounds, and because the cation has been shown to be an active catalyst in cyclopropanation reactions,¹² we recorded one- and two-dimensional (COSY) solid state ^{31}P CP MAS NMR parameters at 9.40 T for all three compounds, together with a determination of the structure of the PF_6 compound, completing the availability of structural data for the series. As part of this work we also redetermined the structure of the ClO_4 compound as the initial structure determination was completed on a crystal of marginal quality. The results of this work form the basis of the present report.

Experimental

Synthesis

The compounds $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$, for $\text{X} = \text{PF}_6$, BF_4 , ClO_4 , were prepared according to established procedures.^{10–13} Dissolution of $[\text{Cu}(\text{MeCN})_4]\text{X}$ (2 mmol) and PPh_3 (4 mmol) in warm acetonitrile (20 ml) followed by slow cooling and partial evaporation of the solvent gave well formed air stable crystals of the desired complex. Melting points: $\text{X} = \text{PF}_6$, 168–172; BF_4 , 171–176; ClO_4 , 182–186 °C (decomp.).

Crystallography

Unique diffractometer data sets were measured at *ca.* 293 K (2 θ – θ scan mode, monochromatic Mo–K α radiation, $\lambda = 0.71073$ Å) for $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$, $\text{X} = \text{PF}_6$ or ClO_4 . N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered ‘observed’ and used in the full matrix least squares refinements after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x , y , z , $U_{\text{iso}}(\text{H})$) were included, constrained at estimated values. Conventional residuals at convergence, R , R' on $|F|$ are recorded, statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Neutral atom complex scattering factors were used, computation with the XTAL 3.2 program system implemented by S. R. Hall.¹⁹ The phenyl rings of the PPh_3 ligands are labelled nm where n is the ligand number 1 or 2 and m is the ring number 1, 2 or 3. Phenyl carbons are labelled $C(nml)$, $l = 1\text{--}6$ where 1 is the *ipso*- and 2 the *ortho*-carbon that points towards the P atom.

Crystal/refinement data. $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{PF}_6 \equiv \text{C}_{40}\text{H}_{36}\text{CuF}_6\text{N}_2\text{P}_3$, $M = 814.9$, monoclinic, space group $P2_1/n$, (C_{2h}^5 , no. 14, variant), $a = 15.616(3)$, $b = 27.38(1)$, $c = 9.194(7)$ Å, $\beta =$

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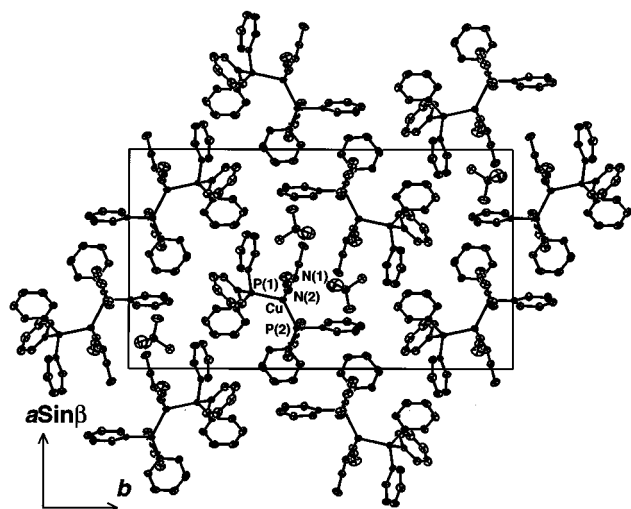


Fig. 1 Molecular packing of $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{ClO}_4$ viewed down the c axis

95.32(5), $U = 3913 \text{ \AA}^3$, $D_c (Z = 4) = 1.38 \text{ g cm}^{-3}$, $F(000) = 1672$, $\mu_{\text{Mo}} = 7.7 \text{ cm}^{-1}$, specimen $0.40 \times 0.37 \times 0.32 \text{ mm}$, $2\theta_{\text{max}} = 50^\circ$, $A^*_{\text{min,max}} = 1.23, 1.30$, $N = 6830$, $N_o = 4039$, $R = 0.047$, $R' = 0.045$.

$[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{ClO}_4 = \text{C}_{40}\text{H}_{36}\text{ClCuN}_2\text{O}_4\text{P}_2$, $M = 769.7$, monoclinic, space group $P2_1/n$, $a = 15.434(2)$, $b = 26.958(3)$, $c = 9.199(2) \text{ \AA}$, $\beta = 94.68(5)$, $U = 3815 \text{ \AA}^3$, $D_c (Z = 4) = 1.34 \text{ g cm}^{-3}$, $F(000) = 1592$, $\mu_{\text{Mo}} = 7.4 \text{ cm}^{-1}$, specimen $0.62 \times 0.45 \times 0.60 \text{ mm}$, $2\theta_{\text{max}} = 50^\circ$, $A^*_{\text{min,max}} = 1.17, 1.37$, $N = 6692$, $N_o = 4669$, $R = 0.039$, $R' = 0.044$.

CCDC reference number 186/1013.

See <http://www.rsc.org/suppdata/dt/1998/2321/> for crystallographic files in .cif format.

Spectroscopy

Solid state ^{31}P CP MAS NMR spectra were acquired at room temperature on a Bruker MSL-400 high field ($B_0 = 9.40 \text{ T}$) spectrometer operating at a ^{31}P frequency of 161.92 MHz. Conventional cross-polarization and magic-angle-spinning techniques, coupled with spin temperature alternation to eliminate spectral artefacts 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, contact period of 10 ms and ^1H $\pi/2$ pulse length of 3 μs were common to all spectra. No spectral smoothing was employed prior to Fourier transformation. Two-dimensional ^{31}P CP MAS correlation spectroscopy (COSY) experiments were implemented at high field with the time proportional phase incrementation (TPPI) method for acquisition of phase sensitive data in both F1 and F2 dimensions. The recycle delay, contact period, ^1H $\pi/2$ pulse length and MAS spinning rate were the same as those implemented for the one-dimensional experiments. The ^{31}P chemical shifts were externally referenced to solid triphenylphosphine which has a chemical shift of $\delta -9.9$ with respect to 85% H_3PO_4 .

Results and Discussion

Structural data

The isomorphous series of compounds $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$ for $\text{X} = \text{PF}_6$, BF_4 or ClO_4 crystallize in space group $P2_1/n$ with $a \approx 15$, $b \approx 27$, $c \approx 9 \text{ \AA}$, $\beta = 95^\circ$ and $Z = 4$. The molecular packing viewed down the c axis is shown in Fig. 1 while a representative view of the cation and an associated anion is shown in Fig. 2. Relevant geometric parameters are listed in Table 1. The anion is located *ca.* 6 \AA from the nearest copper site and adjacent to a cleft formed between the acetonitrile ligands and phosphine ligand 2 with $\text{H} \cdots \text{F/O}$ contact distances of 2.8–3.0 \AA between

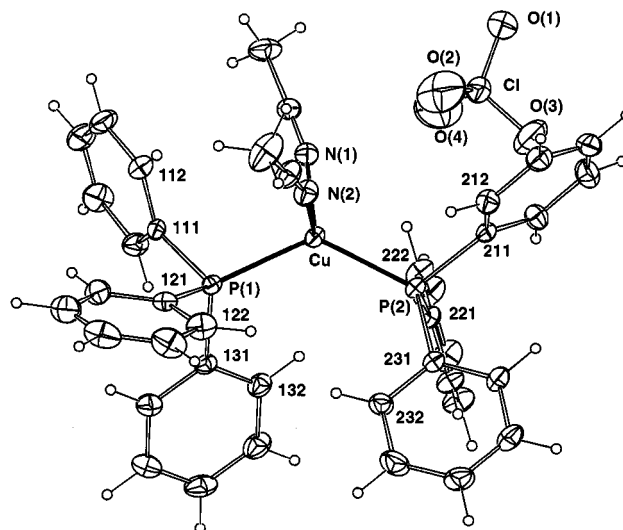


Fig. 2 Molecular structure of $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]^+$ with its associated perchlorate anion; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 \AA

Table 1 Core geometries (distances in \AA , angles in $^\circ$) for $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$, $\text{X} = \text{PF}_6$, BF_4 or ClO_4

	X		
	PF_6	BF_4^*	ClO_4
Cu–P(1)	2.287(2)	2.276(4)	2.284(1)
Cu–P(2)	2.269(1)	2.258(4)	2.265(1)
Cu–N(1)	2.049(4)	2.032(9)	2.053(3)
Cu–N(2)	2.039(4)	2.023(9)	2.037(3)
P(1)–Cu–P(2)	127.73(5)	127.1(1)	126.82(4)
N(1)–Cu–N(2)	100.1(2)	99.5(4)	100.3(1)
P(1)–Cu–N(1)	101.5(1)	101.1(3)	100.87(8)
P(1)–Cu–N(2)	101.7(1)	102.3(3)	102.34(9)
P(2)–Cu–N(1)	110.4(1)	111.0(3)	111.42(8)
P(2)–Cu–N(2)	111.7(1)	111.9(3)	111.60(9)
Cu–N(1)–C(1)	167.8(4)	165.3(9)	166.2(3)
Cu–N(2)–C(2)	166.4(4)	168.0(10)	165.7(3)
Cu–P(1)–C(111)–C(112)	–59.6(4)	–61.9(9)	–62.2(3)
Cu–P(1)–C(121)–C(122)	–41.7(5)	–41(1)	–40.9(3)
Cu–P(1)–C(131)–C(132)	–16.9(5)	–16(1)	–17.2(3)
Cu–P(2)–C(211)–C(212)	55.4(4)	55.7(8)	56.3(3)
Cu–P(2)–C(221)–C(222)	48.5(4)	48.2(6)	49.7(3)
Cu–P(2)–C(231)–C(232)	35.4(5)	32(1)	32.3(3)

* Ref. 12.

the anion and phenyl ring (21) and 3.0–3.2 \AA between the anion and the methyl group of acetonitrile ligand 2. Weak $\text{H}_{\text{Ph}} \cdots \text{O/F}$ interactions with contact distances of *ca.* 2.8 \AA also exist between the anion and the cation located at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. The cations related by the crystallographic centre of symmetry are linked through $\text{N} \cdots \text{H}_{\text{Me}}$ interactions between acetonitrile ligands with contact distances of *ca.* 2.8 \AA (Fig. 1).

Accommodation of these crystal packing forces results in considerable angular distortion of the P_2CuN_2 copper coordination sphere of the cation away from C_{2v} symmetry. In particular, the two acetonitrile ligands bend by 10° or more out of the plane orthogonal to the CuP_2 plane and towards phenyl rings 11 and 12. The two PPh_3 ligands are staggered with respect to each other and adopt three-bladed propeller conformations of opposite chirality with $\text{Cu–P(1)–C(1n1)–C(1n2)} \approx -60, -40$ and -15° and $\text{Cu–P(2)–C(2n1)–C(2n2)} \approx +55, +50$ and $+30^\circ$. This conformational structure differs from that found for the majority of $[\text{Cu}(\text{PPh}_3)_2\text{X}]$ complexes in which $\text{X} \cdots \text{H}_{\text{Ph}}$ interactions between the co-ordinated anion and one phenyl ring of each phosphine ligand lock the structure into an

Table 2 P_2Cu Geometries (distances in Å, angles in °) for selected $[Cu(PPh_3)_2X_2]$ species

Compound	Cu–P(1)	Cu–P(2)	P–Cu–P	Ref.
$[Cu(PPh_3)_2(O_2CCF_3)]$	2.235(2)	2.228(2)	136.7(1)	6
$[Cu(PPh_3)_2(NO_3)]$	2.249(1)	2.249(1)	130.87(7)	7
$[Cu(PPh_3)_2(O_2CPh)]$	2.238(1)	2.228(1)	126.78(4)	7
$[Cu(PPh_3)_2(S_2CPh)]$	2.267(2)	2.257(2)	125.6(1)	20
$[Cu(PPh_3)_2(bpy)]ClO_4$	2.256(3)	2.246(3)	125.4(1)	21
$[Cu(PPh_3)_2(BH_4)]$	2.276(1)	2.276(1)	123.26(6)	22
$\{[Cu(PPh_3)_2(4-Me-pc)]_2\}$	2.284(1)	2.257(1)	121.7(1)	1
$[Cu(PPh_3)_2(py)_2]NO_3$	2.295(3)	2.271(4)	115.85(9)	21
$[Cu(PPh_3)_2(phen)]NO_3$	2.271(1)	2.245(10)	115.44(4)	23

py = Pyridine, bpy = 2,2'-bipyridyl, phen = 1,10-phenanthroline.

eclipsed conformation with the same chirality for both ligands.⁷ For each compound, Cu–P(1) is found to be consistently *ca.* 0.02 Å longer than Cu–P(2) in accord with the differences in steric crowding observed about the Cu–P(1) and Cu–P(2) bonds. Comparison of the geometry of the P_2Cu molecular core with those of other four-co-ordinate $Cu(PPh_3)_2X$ compounds (Table 2^{1,6,7,20–23}) shows that the Cu–P distances of 2.258(4)–2.287(2) Å lie at the upper end of the range and similar to values found for other $Cu(PPh_3)_2N_2$ compounds (Table 2) while the P–Cu–P angles of 126.82(4)–127.73(5)° are significantly greater than these, reflecting the smaller steric profile of the acetonitrile ligands. Despite the angular distortion of the P_2CuN_2 core, the Cu–N bond lengths of 2.023(9)–2.053(3) Å are short and indicative of relatively strong co-ordination of the acetonitrile ligands to the copper.

Solid state CP MAS ^{31}P NMR spectroscopy

Under high field ($B_0 > \approx 5$ T) and slow $^{63,65}Cu$ relaxation conditions, solid state CP MAS ^{31}P NMR spectroscopy of copper(i) phosphine complexes yields signals for each crystallographically independent phosphorus atom which are split into pairs of closely spaced asymmetric quartets in an intensity ratio of $\approx 2:1$ as a result of scalar spin–spin coupling and quadrupolar interactions between the phosphorus and the spin $\frac{3}{2}$ ^{63}Cu ($\gamma = 7.0965 \times 10^7$ rad $T^{-1} s^{-1}$, natural abundance 69.09%) and ^{65}Cu ($\gamma = 7.6018 \times 10^7$ rad $T^{-1} s^{-1}$, natural abundance 30.91%) isotopes. The linewidths of the peaks are such that the two quartets are not generally resolved and observed spectra are dominated by the ^{63}Cu spectrum, with the ^{65}Cu spectrum identified (when the linewidth is sufficiently narrow) as a splitting of the outer peaks of the quartet.^{14–18} Spectra recorded for the present series of complexes at 9.40 T are reproduced in Fig. 3 and consist of overlapping quartets of doublets representing the AB portion of a total ABX spin system arising from spin–spin coupling between the ^{31}P and ^{63}Cu nuclei and smaller geminal $^2J(^{31}P-^{31}P)$ coupling, with satellite signals from the ^{65}Cu spectrum also observable. The overlap of the peaks in each quartet precludes accurate measurement of the chemical shift and line spacing data from these spectra, but these may be extracted from the two-dimensional ^{31}P CP MAS COSY spectra which separate the two $^1J(P-Cu)$ coupled quartets above and below the main diagonal (Fig. 4). These parameters are in Table 3. The average chemical shift for each P site is located at δ 13–14 and 7–8 [$\delta(PPh_3)$ 0] and assigned to P(1) and P(2) on the basis of the values of the $^1J(^{31}P-^{63}Cu)$ coupling constants 1.14(1) kHz for the signals centred at δ 13–14 and 1.30(1) kHz for the signals centred at δ 7–8 corresponding to the longer and shorter Cu–P bond lengths respectively. These coupling constants are comparable to values of 1.08(1) and 1.25(2) kHz for $\{[Cu(PPh_3)_2(4-Me-pc)]_2\}$ (pc = phenylcyanamide),^{1,16} 1.15 kHz for $[Cu(PPh_3)_2(BH_4)]$ ³ and 1.17 kHz for $[Cu(PPh_3)_2(S_2CPh)]$,²⁴ but smaller than the 1.40 kHz found for $[Cu(PPh_3)_2(NO_3)]$ ^{3,25,26} reflecting relatively weaker covalent bonding character for the copper–oxygen bonds in this compound.

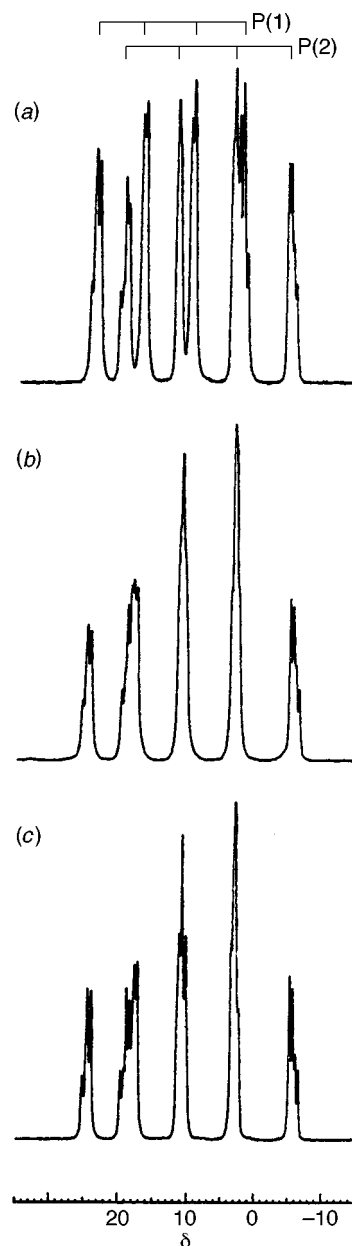


Fig. 3 One-dimensional ^{31}P CP MAS NMR spectra of $[Cu(PPh_3)_2(MeCN)_2]X$ at 9.40 T for $X = PF_6$ (a), BF_4 (b) and ClO_4 (c). Resolution of the outer components of the ^{65}Cu multiplet is apparent for each quartet

Geminal $^2J(^{31}P-^{31}P)$ coupling constants for $[Cu(PPh_3)_2X(X')]$ compounds have been previously determined only for $\{[Cu(PPh_3)_2(4-Me-pc)]_2\}$ ¹⁶ (122 Hz), $[Cu(PPh_3)_2(BH_4)]$ ²⁶ (140 Hz) and $[Cu(PPh_3)_2(NO_3)]$ ²⁶ (157 Hz). The value of 75 Hz recorded for each of the present compounds is, therefore, by far the smallest value yet measured. The reasons for this large decrease in magnitude are not readily apparent. Studies on the effect of change in the donor ligand X on $^2J(^{31}P-^{31}P)$ for a series of mercury complexes $[Hg(PPh_3)_2X_2]$ complexes^{27,28} show a correlation between the co-ordinating ability of X and decreasing $^2J(^{31}P-^{31}P)$ which would suggest an expectation of comparable values of $^2J(^{31}P-^{31}P)$ for the acetonitrile, phenylcyanamide and tetrahydroborate complexes.

A characteristic feature of the quartets observed in the spectra of all copper(i) phosphine complexes under high field conditions ($B_0 > \approx 5$ T) is that the chemical shifts δ_1 , δ_2 , δ_3 and δ_4 of the peaks of the J quartet show differential chemical shifts as a result of perturbation of the spectra by copper quadrupolar interactions. Analysis of this interaction as a first order perturbation of the J spectrum¹⁷ predicts the outer two lines

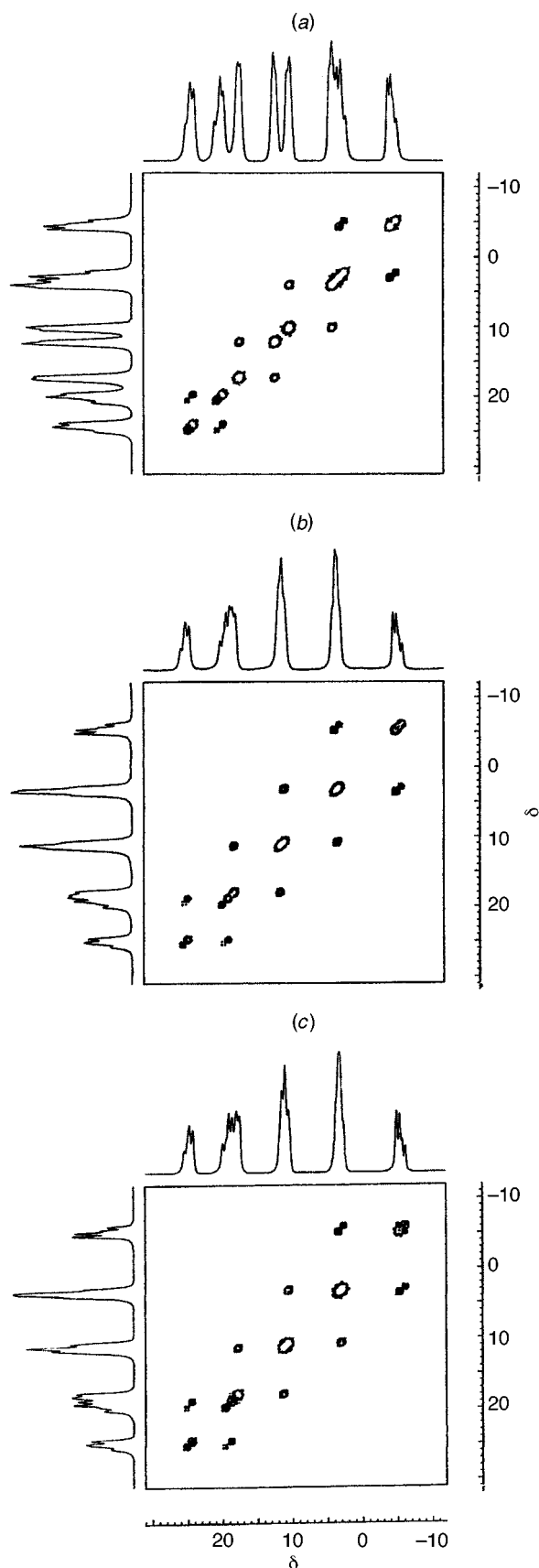


Fig. 4 Two-dimensional ^{31}P CP MAS COSY NMR spectra of $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$ at 9.40 T for X = PF_6 (a), BF_4 (b) and ClO_4 (c)

(δ_1 , δ_4) to shift to more negative ppm (upfield) and the inner two lines (δ_2 , δ_3) to more positive ppm (downfield) by a parameter d such that $(\Delta_{32} - \Delta_{21}) = (\Delta_{43} - \Delta_{32}) = 2d$, from which $d = (\Delta_{43} - \Delta_{21})/4$; d is found to be inversely dependent on the field strength and multiplication by the ^{63}Cu Zeeman frequency, ν_{Cu} , yields a

field independent parameter $d\nu_{\text{Cu}}$ that is suitable for comparison of results obtained from spectra recorded at different field strengths.

The first order theory allows $d\nu_{\text{Cu}}$ to be calculated according to expression (1) where $\chi_{\text{Cu}} = e^2qQ/h$ is the ^{63}Cu quadrupolar

$$d\nu_{\text{Cu}} = (3\chi_{\text{Cu}}D_{\text{eff}}/20)(3\cos^2\beta^{\text{D}} - 1 + \eta\sin^2\beta^{\text{D}}\cos 2\alpha^{\text{D}}) \quad (1)$$

coupling constant, $D_{\text{eff}} = (D - \Delta J/3)$ [where $D = (\mu_0/4\pi)\gamma_{\text{P}}\gamma_{\text{Cu}}h/4\pi^2r^3$ is the Cu–P dipolar coupling constant and ΔJ is the anisotropy in the J tensor], η is the asymmetry parameter of the electric field gradient (EFG) tensor, and α^{D} , β^{D} are the polar angles defining the direction of the Cu–P internuclear vector with respect to the principal axial system (PAS) of the EFG tensor. In practice, the observed spectra are found to deviate from this first order model with $(\Delta_{32} - \Delta_{21}) > 2d > (\Delta_{43} - \Delta_{32})$. This result has been ascribed to higher order quadrupole effects with the sense of the distortion indicative of a positive sign for J .^{14,18} These latter effects, however, are generally quite small and are recorded for the present compounds as an upfield shift of peaks 1 and 3 and a downfield shift of peaks 2 and 4 by a correction term of magnitude d_1 such that $\Delta_{21} = J - 2d - 2d_1$, $\Delta_{32} = J + 2d_1$ and $\Delta_{43} = J + 2d - 2d_1$, from which $d = (\Delta_{43} - \Delta_{21})/4$ as before, $d_1 = (\Delta_{32} - J)/2$ while $J = (\Delta_{21} + 2\Delta_{32} + \Delta_{43})/4$.

For the present complexes, the measured values of $d\nu_{\text{Cu}}$ for each phosphorus site differ by ca. 50%, ranging from $(2.2\text{--}2.5) \times 10^9$ Hz² for P(1) and $(3.3\text{--}4.0) \times 10^9$ Hz² for P(2). As the contribution of the copper quadrupolar coupling constant, χ_{Cu} , to the determination of the value of $d\nu_{\text{Cu}}$ is the same for both sites, these different values must arise from differences in other factors such as D_{eff} , the orientation of the Cu–P vectors with respect to the PAS of the EFG tensor and/or higher order effects. While the relative contributions of these effects await measurement of further data from (for example) single crystal NMR studies, it is interesting that the observed differences can be accounted for by a decrease in the angle between Cu–P(2) and the z axis of the EFG tensor [and an increase in the angle between Cu–P(1) and the same z axis] by ca. 5° , corresponding to a shift of the z axis towards the bond of greater electron density.

Comparison of these values of $d\nu_{\text{Cu}}$ with those calculated from published NMR data for other four-co-ordinate $[\text{Cu}(\text{PPh}_3)_2\text{X}(\text{X}')]_2$ compounds shows this parameter to increase from $(1.5\text{--}2.0) \times 10^9$ Hz² for $\{[\text{Cu}(\text{PPh}_3)_2(4\text{-Mepc})]_2\}$ ¹⁶ to $(2.2\text{--}4.0) \times 10^9$ Hz² for the present series to 4.5×10^9 Hz² for $[\text{Cu}(\text{PPh}_3)_2(\text{S}_4\text{CPh})]$,²⁴ 6.0×10^9 Hz² for $(\text{Ph}_3\text{P})_2\text{CuBr}_2\text{Cu}(\text{PPh}_3)$,²⁹ 7.0×10^9 Hz² for $[\text{Cu}(\text{PPh}_3)_2(\text{BH}_4)]$ ³ and 10.0×10^9 Hz² for $[\text{Cu}(\text{PPh}_3)_2(\text{NO}_3)]$.³ Rearrangement of equation (1) to the expression (2) where $G = (3\cos^2\beta^{\text{D}} - 1 + \eta\sin^2\beta^{\text{D}}\cos 2\alpha^{\text{D}})$

$$\chi_{\text{Cu}}/d\nu_{\text{Cu}} = (20G/3D_{\text{eff}}) \quad (2)$$

shows the ratio between χ_{Cu} and $d\nu_{\text{Cu}}$ to be dependent on a number of unknown factors including the magnitude of ΔJ and η , and the orientation of the EFG tensor in the molecular frame and, as well as higher order quadrupolar effects, precluding direct estimation of χ_{Cu} from the measured values of $d\nu_{\text{Cu}}$. However, for the present series of complexes, the ^{63}Cu nuclear quadrupolar resonance frequency for tetrahedral copper in $[(\text{Ph}_3\text{P})_2\text{CuBr}_2\text{Cu}(\text{PPh}_3)]$ has been found to be 14.31 MHz,³⁰ yielding χ_{Cu} of the order of 30 MHz and $\chi_{\text{Cu}}/d\nu_{\text{Cu}} \approx 5$. Using this ratio, and assuming an uncertainty of the order of 20%, yields estimates of χ_{Cu} of the order of 5–10 MHz for $\{[\text{Cu}(\text{PPh}_3)_2(4\text{-Mepc})]_2\}$, 10–20 MHz for the present series of complexes, 20–30 MHz for $[\text{Cu}(\text{PPh}_3)_2(\text{S}_4\text{CPh})]$, 30–40 MHz for $[\text{Cu}(\text{PPh}_3)_2(\text{BH}_4)]$ and 45–55 MHz for $[\text{Cu}(\text{PPh}_3)_2(\text{NO}_3)]$. While these estimates are very approximate in absolute terms, the trend that is observed is likely to be maintained as more accurate data become available from, for example, NQR or solid state $^{63,65}\text{Cu}$ NMR experiments, and supports the notion that even

Table 3 ^{31}P CP MAS NMR data for $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{X}$, X = PF_6 , BF_4 or ClO_4

	X = PF_6		BF_4		ClO_4	
	P(1)	P(2)	P(1)	P(2)	P(1)	P(2)
Cu–P/Å	2.287	2.269	2.276	2.258	2.284	2.265
$\langle\delta\rangle$	13.4	7.8	14.2	7.0	14.0	6.9
Δ_{21}/Hz	1080	1230	1094	1217	1080	1217
Δ_{32}/Hz	1136	1305	1149	1313	1136	1327
Δ_{43}/Hz	1174	1362	1176	1368	1163	1341
$^1J(^{31}\text{P}-^{63}\text{Cu})/\text{kHz}$	1.13	1.30	1.14	1.30	1.13	1.30
$^2J(^{31}\text{P}-^{31}\text{P})/\text{Hz}$		75		75		75
d/Hz	23	33	20	38	21	31
d_1/Hz	2.5	2.5	3.5	5.0	3.5	12.0
$d\nu_{\text{Cu}}/10^9 \text{ Hz}^2$	2.5	3.5	2.2	4.0	2.2	3.3

$\langle\delta\rangle$ = Average chemical shift of the four lines of each quartet with respect to PPh_3 ; $^1J(^{31}\text{P}-^{63}\text{Cu}) = (\Delta_{21} + 2\Delta_{32} + \Delta_{43})/4$; $d = (\Delta_{43} - \Delta_{21})/4$, $d_1 = (\Delta_{32} - ^1J)/2$; ν_{Cu} (9.40 T) = 106.1 MHz. Estimated errors in Δ_{ij} = 20 Hz, d 5 Hz, d_1 = 5 Hz and $d\nu_{\text{Cu}} = 1 \times 10^9 \text{ Hz}^2$.

quite small changes in the nature of the ligands or anions coordinated to $[\text{Cu}(\text{PPh}_3)_2]^+$ can have a significant influence on the distribution of charge about the copper site. For the present acetonitrile complexes, the results suggest this distribution to be relatively symmetric, despite the low geometric symmetry of the copper co-ordination sphere.

Finally, we note that in terms of the catalytic properties of these compounds¹² the results of this study are of interest in that they illustrate, first, the conformational flexibility of the $[\text{Cu}(\text{PPh}_3)_2]^+$ cation in interacting with co-ordinating bases and, secondly, the capacity of the cation to redistribute electron density about the copper site in response to changing donor properties of these bases.

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