1,2-Bis(diphenylphosphino)ethane bridged dinuclear copper (I) complexes: Investigations of solid state and solution structures by CP/MAS ^{31}P NMR spectroscopy, X-ray crystallography, IR spectroscopy and solution ^{31}P NMR and ^{63}Cu NMR spectroscopy

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Three different complexes of copper (I) with bridging 1, 2-bis(diphenylphosphino)ethane (dppe), namely [Cu$_2$ (μ-dppe) (CH$_3$CN)$_6$] (ClO$_4$)$_2$ (1), [Cu$_2$ (μ-dppe)$_2$ (CH$_3$CN)$_2$] (ClO$_4$)$_2$ (2), and [Cu$_2$ (μ-dppe) (dppe)$_2$ (CH$_3$CN)$_2$] (ClO$_4$)$_2$ (3) have been prepared. The structure of [Cu$_2$ (μ-dppe) (dppe)$_2$ (CH$_3$CH)$_2$] (ClO$_4$)$_2$ has been determined by X-ray crystallography. It crystallizes in the space group P$\bar{1}$ with $a = 12.984$ (6) Å, $b = 13.180$ (6) Å, $c = 14.001$ (3) Å, $\alpha = 105.23$ (3), $\beta = 105.60$ (2), $\gamma = 112.53$ (4), $V = 1944$ (3) Å^3, and $Z = 1$. The structure was refined by least-squares method with $R = 0.0365$; $R_w = 0.0451$ for 6321 reflections with $F_0 \geqslant 3 \ \sigma (F_0)$. The CP/MAS ^{31}P and IR spectra of the complexes have been analysed in the light of available crystallographic data. IR spectroscopy is particularly helpful in identifying the presence of chelating dppe. ^{31}P chemical shifts observed in solid state are very different from those observed in solution, and change significantly with slight changes in structure. In solution, complex 1 remains undissociated but complexes 2 and 3 undergo extensive dissociation. With a combination of room temperature ^{1}H, ^{63}Cu, and variable temperature ^{31}P NMR spectra, it is possible to understand the various processes occurring in solution.

1,2-BIS(DIPHENYLPHOSPHINO)ETHANE (dppe), an ubiquitous ligand in transition metal chemistry[1-3], prefers to chelate[4-6], rather than bridge[7,8]. Copper-dppe complexes have been extensively studied. A number of copper-dppe complexes with different ratios of copper and dppe (1:1, 1:2, 2:3 and 3:4), having a halide (X) as an additional ligand, have been reported[9,10]. Solid-state structures are known for the following mononuclear bis-chelated complexes [Cu(dppe)$_2$]$^+$ (CF$_3$COO)$^-$ (toluene)[11], [Cu(dppe)$_2$]$^+$ [Cu$_6$Fe$_4$(CO)$_{16}$]$^{-\ (ref.\ 12)}$, [Cu(dppe)$_2$]$^+$ [Cu(Mesityl)$_2$]$^-$ (ref. 13). Dinuclear complexes of the type [Cu$_2$(μ-dppe) (dppe)$_2$(X)$_2$], where X is a coordinating anion such as chloride[14], azide[15], and phenoxide[16], are also known. The latter complexes, in the solid state, have chelating as well as bridging dppe

units but undergo extensive dissociation in solution. Comprehensive studies on other copper–dppe complexes, without an additional bridging ligand, in which Cu/dppe ratios equal to 1:1, 2:1, etc. are forthcoming. In particular, the correlation of solid state ^{31}P NMR values and structural studies of these complexes would aid in better characterization of these complexes. Though the solid state CP/MAS ^{31}P NMR spectroscopy has been extensively used to study monophosphine and phosphole complexes of copper[17,18] and diphosphine complexes of nickel[19], there has been no report hitherto on the solid state spectra of copper–diphosphine complexes.

In this article, we report the preparation and characterization of dinuclear copper (I) complexes, with Cu(I) and dppe in the ratios 1:1, 2:1 and 2:3. Structures in the solid state and solution have been determined by CP/MAS ^{31}P and solution ^{31}P and ^{63}Cu NMR spectroscopy, respectively. X-ray crystallographic data have been used to interpret the solid-state ^{31}P spectra. A variety of species existing in solution whose number and nature depend on the ratio of Cu (I) to dppe, have been identified using the solution state ^{31}P NMR spectra. The complexes have different ^{31}P chemical shifts in solution and solid state. Further, the solid state CP/MAS chemical shifts are sensitive to small changes in structure. Surprisingly, dppe is sensitive to the coordination requirements of the metal and functions as a bridging ligand with ease when Cu/dppe ratio is greater than or equal to one.

Experimental

Measurements

Infrared spectra were recorded on a PE 503 ratio recording spectrophotometer as nujol mulls between

KBr plates. NMR spectra were recorded on a Bruker ACF 200 spectrometer at 200 MHz (^{1}H) and 81.1 MHz (^{31}P) using TMS and 85% H_3PO_4 as internal and external standards respectively. The ^{1}H NMR of the samples were recorded in $CDCl_3$, and ^{31}P$\{^1$H$\}$ spectra in acetone with D_2O lock. The variable temperature ^{31}P$\{^1$H$\}$ NMR spectra of the complex 2 were recorded on a 400 MHz instrument operating at a frequency of 161.98 MHz and the ^{63}Cu NMR of complexes 1–3 were recorded on the same instrument at 106.098 MHz. ^{63}Cu NMR chemical shifts were referenced to 0.1 M solution of [Cu(CH$_3$CN)$_4$]BF$_4$ in acetonitrile. Solid-state ^{31}P spectra were recorded at room temperature on a Bruker MSL-300 instrument at 121.49 MHz with high power proton-decoupling, cross polarization from protons and magic angle spinning (CP/MAS). Samples (500 mg) were packed into a delrin rotor, and spun at a speed of 2.5 to 3.5 kHz. Contact times were 1 ms and pulse recycle times were 5 ms. Chemical shifts were referenced to 85% H_3PO_4. The elemental analyses were carried out with a Heraeus CHN-O-rapid analyser. The crystallographic data were collected on an Enraf–Nonius CAD4 diffractometer equipped with a PDP11 computer.

Methods

The reactions were carried out with [Cu(CH$_3$CN)$_4$] (ClO$_4$) as the starting material. [Cu(CH$_3$CN)$_4$] (ClO$_4$) and dppe were prepared by reported procedures[20,21]. All reactions were performed under nitrogen atmosphere and the solvents were dried and distilled before use.

Synthesis

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of the material should be prepared, and these complexes should be handled with great caution.

[Cu$_2$ (μ-dppe) (CH$_3$CN)$_6$] (ClO$_4$)$_2$ (1)
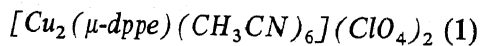
[Cu(CH$_3$CN)$_4$] (ClO$_4$) (327 mg, 1 mmole) and dppe (199 mg, 0.5 mmole) were mixed in 20 ml of dry, deaerated methylene chloride. The sparingly soluble [Cu(CH$_3$CN)$_4$] (ClO$_4$) dissolved completely on complex formation. The formation of a clear, homogeneous solution and the disappearance of free dppe (*vide* TLC) indicated the completion of the reaction. After stirring the mixture for an additional 2 h, the methylene chloride solution was concentrated to half its original volume and dry ether (10 ml) was added. Complex 1, was obtained as a white precipitate and was washed with ether to remove traces of unreacted dppe, if any. Yield: 95%.

[Cu$_2$ (μ-dppe)$_2$ (CH$_3$CN)$_2$] (ClO$_4$)$_2$ (2)
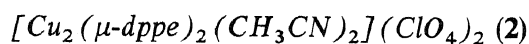
Complex 2 was prepared using [Cu(CH$_3$CN)$_4$] (ClO$_4$) (327 mg, 1 mmol) and dppe (398 mg, 1 mmol) by the same procedure as the one used for complex 1. Yield: 96%.

[Cu$_2$ (μ-dppe) (dppe)$_2$ (CH$_3$CN)$_2$] (ClO$_4$)$_2$ (3)
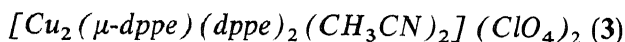
Complex 3 was prepared from [Cu(CH$_3$CN)$_4$] (ClO$_4$) (327 mg, 1 mmol) and dppe (600 mg, 1.5 mmol). The procedure was the same as that used for complex 1. Yield: 93%.

Crystal structure of complex [Cu$_2$ (μ-dppe) (dppe)$_2$ (CH$_3$CN)$_2$] (ClO$_4$)$_2$ (3):

Crystals of the complex 3 suitable for X-ray diffraction study were obtained by recrystallizing the compound from a mixture (1:1 v/v) of methylene chloride and petroleum ether.

Crystal data

$C_{82}H_{78}N_2O_8P_6Cl_2Cu_2$, $M = 1601.98$, triclinic, space group $P\bar{1}$, $a = 12.984(6)$, $b = 13.180(6)$, $c = 14.001(3)$ Å, $\alpha = 105.23(3)$, $\beta = 105.60(2)$, $\gamma = 112.53(4)$, volume, $V = 1944(3)$ Å^3, by least squares refinement from the θ values of 24 accurately measured reflections in the range $16.04 \leq \theta \leq 17.87$ Mo$-$K$_\alpha$ ($\lambda = 0.71069$ Å), $z = 1$, μ(Mo$-$K$_\alpha$) $= 7.42$ cm^{-1}.

Data collection and processing

A crystal suitable for X-ray diffraction study was mounted on a glass fibre. All reflections in the range $1 \leq \theta \leq 25$ were measured; $0 \leq h \leq 15$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$ (total number of reflections 7356), of the 6846 independent reflections, 6321 having $F_0 \geq 3\sigma(F_0)$ were considered observed and used in the analysis.

Structure solution and refinement

The structure has been solved using Patterson Heavy atom method and successive difference Fourier syntheses. The hydrogen atoms were located from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms, isotropically, using full-matrix least-squares methods with SHELX-76 (ref. 22), to final R factors, $R = 0.0365$; and $R_w = 0.0451$. An individual sigma weighting scheme based on counting statistics, where $w = 1.0000/(\sigma^2(F_0) + 0.000750 (F_0)^2)$ was used.

Results

Preparation and characterization of the complexes

The complexes 1–3 were prepared by mixing [Cu $(CH_3CN)_4$] (ClO_4) and dppe in the ratios 2:1, 1:1 and 2:3 respectively in methylene chloride. While acetonitrile could also be used as the reaction medium for complex 3, complexes 1 and 2 were formed only in methylene chloride. Complex 1, prepared from acetonitrile medium, had the composition corresponding to [Cu_2 (μ-dppe)$(CH_3CN)_5$]$(ClO_4)_2$ 1a, and the complex 2 had the composition corresponding to the formula [Cu_2 (μ-dppe)$_2$ $(CH_3CN)_4$]$(ClO_4)_2$ 2a. The complexes prepared from methylene chloride showed a decrease in solubility and an increase in melting point, on ageing. The complex resulting from the recrystallization of complex 2 was dependent on the solvent used for recrystallization. While recrystallization from methylene chloride yielded crystals of unchanged complex 2, that from acetonitrile led to a different complex [Cu_3 $(dppe)_2$ $(CH_3CN)_8$]$(ClO_4)_3$. In order to have the same complex before and after recrystallization, methylene chloride was chosen as the solvent. The characteristic data, (m.p., conductivity and analysis) of the complexes 1–3 are given in Table 1.

Solid-state studies

Infra-red spectroscopy

The IR spectra of all the three complexes 1–3 (Figure 1), exhibited a strong, broad band around 1090 cm^{-1}, due to perchlorate, indicating its ionic nature[23]. The acetonitrile bands were seen only in the case of complex 1 at 2276 and 2307 cm^{-1}; the shift of $\nu C \equiv N$ stretching frequency towards higher values in the complex with respect to the corresponding vibration in free acetonitrile (2240 cm^{-1}) was in agreement with the reported values[20, 24]. The band due to perchlorate obscures two bands expected at 1105 cm^{-1} and 1112 cm^{-1}, due to coordinated dppe[25]. However, the bands, in the region 760–680 cm^{-1} of the free ligand dppe were also sensitive to coordination, enabling the identification of
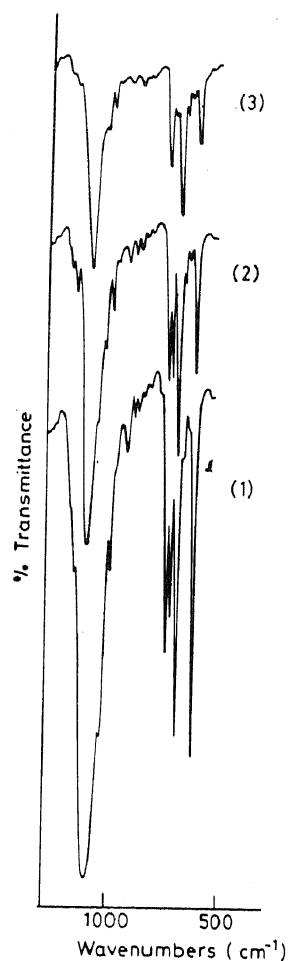

Figure 1. IR spectra of the complexes 1–3.

coordinated dppe. Relevant IR data on the free ligand and complexes are given in Table 2. From the data it can be seen that the vibrations due to CH_2 rocking, P–CH_2 stretching, and out of plane gamma (CH) deformations of the phenyl ring hydrogens are sensitive to coordination. The band due to CH_2 rocking vibration was not discernible and the P–CH_2 stretching vibration appeared as a weak band at 675 cm^{-1} in the spectra of the complexes. The relative intensities of the two bands arising from gamma (CH) vibrations in the region 760–680 cm^{-1} were the same in the spectra of

Table 1. Analytical data for complexes 1–3

Complex	M.P. (°C)	Conductivity[a] (s. cm^{-2} mol^{-1})	C	Analysis[b] H	N
1 [$Cu_2(\mu$-dppe)$(CH_3CN)_6$]$(ClO_4)_2$	134	138	47.093 (47.0)	4.406 (4.33)	8.884 (8.66)
1a [$Cu_2(\mu$-dppe)$(CH_3CN)_5$]$(ClO_4)_2$	104–105	180	43.9996 (46.5)	4.1328 (4.198)	7.9509 (7.53)
2 [$Cu_2(\mu$-dppe)$_2(CH_3CN)_2$]$(ClO_4)_2$	168–170	190	58.06 (55.8)	4.63 (4.48)	2.813 (2.32)
2a [$Cu_2(\mu$-dppe)$_2(CH_3CN)_4$]$(ClO_4)_2$	138–139	190	53.82 (55.98)	4.56 (4.66)	4.195 (4.354)
3 [$Cu_2(\mu$-dppe)$(dppe)_2(CH_3CN)_2$]$(ClO_4)_2$	202–204	188	60.86 (61.42)	4.9 (4.86)	2.12 (1.747)

[a] Conductivity values of 10^{-3} M solutions in acetone of the complexes are given.
[b] Calculated percentages of C, H and N are given in parentheses.

Table 2. Characteristic IR bands for complexes 1–3

Band-position (cm^{-1}) dppe	complex 1	Assignments^S complex 2	complex 3
755(s)	—	—	CH$_2$ rock (trans)
745(s)	747(m)	747(m)	gamma (CH)*
730(vs)	728(m)	—	gamma (CH)*
710(s)	—	—	r X-sensitive
695(vs)	699(s)	699(s)	phenyl(CC)
680(m)	—	—	(P-CH$_2$)

^{S} Assignments of free dppe bands made by Bacci[26] are made use of in the present study.
*see text.

complexes 1 and 2 and different in the case of complex 3. In the light of the crystal structure of the complexes 2 and 3 (*vide infra*), it appears that the region 760–680 cm^{-1} can be used as a finger print region to identify the presence of chelating dppe. The presence of a chelating dppe leads to a weak band at 728 cm^{-1} (complex 3) whereas if only bridging dppe units are present (complexes 1 and 2) the two bands at 747 cm^{-1} and 728 cm^{-1} are of almost equal intensity.

Crystal structure of complex 2

The structure of complex 2 consists of [Cu$_2$(μ-dppe)$_2$ (CH$_3$CN)$_2$]$^{2+}$ cations and perchlorate anions[27]. The special feature of the structure is the presence of doubly bridging dppe units between the two copper atoms.

Crystal structure of complex 3

The structure of the complex 3 consists of [Cu$_2$ (μ-dppe) (dppe)$_2$ (CH$_3$CN)$_2$]$^{2+}$ cations and perchlorate anions. The structure of the cation is depicted in Figure 2, with the atom numbering scheme. The atomic coordinates of the non-hydrogen atoms are given in Table 3; selected
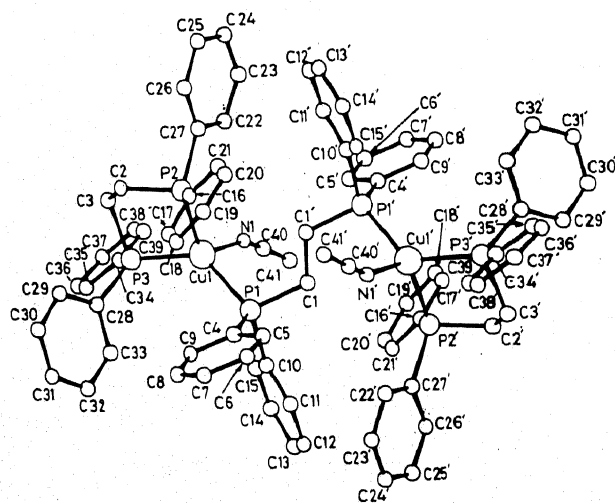

Figure 2. PLUTO diagram of the complex 3.

bond-distances and bond-angles are given in Table 4. In the complex, each copper atom is bound to one nitrogen and three phosphorus atoms. There are two types of dppe ligands in the molecule, two crystallographically equivalent bidentate dppe and a monodentate dppe, which bridges the two copper atoms. The molecule as a whole is centrosymmetric, with the centre of symmetry located between the methylene carbon atoms of the bridging dppe ligand. The co-ordination geometry around each copper atom is a distorted tetrahedron. The distortions from idealized tetrahedral geometry can be attributed, at least in part, to the 'bite' angle of dppe.

The structure of complex 3 is similar to the structures of many reported complexes of the type Cu$_2$ (μ-dppe) (dppe)$_2$ (X)$_2$ in which X is a uni-negative species such as Cl, OPh, and N$_3$, coordinated to copper. The uniqueness in the structure of complex 3 is that the fourth co-ordination site around copper is occupied by a neutral ligand, rather than an anion. A comparison of the bond-angles and the bond-distances of the complex 3, with those reported for the complexes mentioned above, shows that the presence of a neutral ligand in the place of an anion, does not cause drastic changes in the bond-distances and bond-angles around copper. This is in agreement with the observation of Baker and co-workers[28] that 'a 2:3 stoichiometry of copper to dppe must allow chelated and bridged dppe ligands to achieve minimum energy conformations and in doing so, create a cavity into which various anions, can be accommodated on co-ordination to copper'. In this case a neutral ligand, acetonitrile, is trapped in the cavity.

CP/MAS ^{31}P NMR spectra of complexes 1–3

The solid-state spectra of complexes 1–3 are shown in Figures 3–5 respectively. The spectrum of complex 1 consists of one asymmetric quartet and the spectra of complexes 2 and 3 consist of two asymmetric quartets each, the asymmetry arising from the copper quadrupole moment interacting with phosphorus[29]. The chemical shift values and line spacings are given in

Table 3. Atomic co-ordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of the complex 3 with the estimated standard deviations in parentheses

Atom	X/A	Y/B	Z/C	$U^*_{eq} (\text{Å})^2 \times 10^4$
Cu1	0.27570(2)	0.11608(2)	0.20862(2)	309(2)
P1	0.15706(5)	0.18330(4)	0.12450(4)	285(3)
P2	0.32374(5)	−0.00069(5)	0.09516(4)	324(3)
P3	0.47291(5)	0.21468(5)	0.33823(4)	333(2)
C1	0.1059(1)	0.77320(1)	0.4358(1)	643(4)
N1	0.1635(2)	0.03590(2)	0.2766(2)	425(9)
C1	0.0013(2)	0.05480(2)	0.0381(2)	332(9)
C2	0.4922(2)	0.06920(2)	0.1670(2)	424(12)
C3	0.5303(2)	0.11270(2)	0.2897(2)	416(10)
C4	0.2030(2)	0.25590(2)	0.0378(2)	345(10)
C5	0.1276(2)	0.22590(2)	−0.0681(2)	486(12)
C6	0.1717(3)	0.29010(3)	−0.1260(2)	630(18)
C7	0.2876(3)	0.38260(3)	−0.0810(3)	652(19)
C8	0.3626(3)	0.41470(3)	0.0252(3)	654(16)
C9	0.3223(2)	0.35160(2)	0.0834(2)	489(13)
C10	0.1226(2)	0.28730(2)	0.2074(2)	322(9)
C11	0.0638(2)	0.34450(2)	0.1636(2)	430(11)
C12	0.0329(2)	0.41700(2)	0.2270(2)	547(14)
C13	0.0589(3)	0.43350(2)	0.3333(2)	608(13)
C14	0.1173(3)	0.37780(3)	0.3779(2)	656(17)
C15	0.1502(3)	0.30600(2)	0.3154(2)	501(13)
C16	0.3028(2)	0.00180(2)	−0.0389(2)	371(10)
C17	0.3652(2)	0.11270(2)	−0.0431(2)	477(12)
C18	0.3467(3)	0.12050(3)	−0.1422(3)	649(20)
C19	0.2665(3)	0.01970(3)	−0.2378(2)	678(20)
C20	0.2029(3)	−0.08840(3)	−0.2344(2)	608(15)
C21	0.2208(2)	−0.09780(2)	−0.1360(2)	460(12)
C22	0.2698(2)	−0.15810(2)	0.0733(2)	384(10)
C23	0.1966(2)	−0.20620(2)	0.1230(2)	474(12)
C24	0.1543(3)	−0.32550(3)	0.1081(3)	645(16)
C25	0.1854(3)	−0.39640(2)	0.0446(3)	671(17)
C26	0.2595(3)	−0.34970(3)	−0.0054(3)	660(16)
C27	0.3019(3)	−0.23100(2)	0.0097(2)	507(13)
C28	0.5756(2)	0.35900(2)	0.3444(2)	402(11)
C29	0.6794(2)	0.38150(3)	0.3233(2)	571(13)
C30	0.7478(3)	0.49190(3)	0.3221(3)	735(17)
C31	0.7158(3)	0.57930(3)	0.3435(3)	764(17)
C32	0.6149(3)	0.56000(3)	0.3662(3)	697(16)
C33	0.5451(2)	0.45020(2)	0.3652(2)	544(14)
C34	0.5081(2)	0.23230(2)	0.4785(2)	391(10)
C35	0.6039(2)	0.33450(2)	0.5673(2)	582(13)
C36	0.6260(3)	0.34090(3)	0.6720(2)	763(17)
C37	0.5537(3)	0.24560(3)	0.6880(2)	755(19)
C38	0.4585(3)	0.14410(3)	0.6012(3)	671(17)
C39	0.4353(2)	0.13730(2)	0.4967(2)	539(12)
C40	0.1144(3)	0.03180(3)	0.3305(2)	576(17)
C41	0.0462(5)	0.02670(5)	0.3983(4)	1294(45)
01	0.0176(4)	0.79660(4)	0.4608(4)	1632(38)
02	0.0462(4)	0.69090(4)	0.3285(3)	1533(31)
03	0.1448(4)	0.71730(3)	0.4993(3)	1542(31)
04	0.2005(4)	0.87830(4)	0.4584(5)	2314(40)

$$U_{eq} = \frac{1}{3}\sum_i \sum_j a^*_i a^*_j \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

Table 5. The distance between the centre lines of each quartet can be approximated to the scalar copper–phosphorus coupling constant (a/h)[30]. From the value of a/h, using an empirical formula derived by Nelson et al.[31], copper–phosphorus bond-lengths r(Cu–P) were calculated (Table 5). The calculated values agree well with those obtained from the crystal structure data vide infra for the complexes 2 and 3.

The CP/MAS ^{31}P NMR spectra of complexes 2 and 3 can be interpreted on the basis of the structural data given in Table 6. The two phosphorus atoms in complex 2 are equidistant from the copper atom. However, the angles subtended by these two phosphorus atoms at Cu with N are different, making them crystallographically inequivalent. This accounts for the presence of two quartets in the spectrum[32]. The substantial difference in the chemical shifts of the two P atoms, in spite of their chemical equivalence, reflects the sensitivity of the solid state ^{31}P NMR chemical shift to subtle changes in structure.

Table 4. Selected bond-distances (Å) and bond-angles (°) for $[Cu_2(\mu\text{-dppe})(dppe)_2(CH_3CN)_2](ClO_4)_2$ complex 3.

Atoms	Distance	Atoms	Distance
Cu1–P1	2.2717(7)	Cu1–P2	2.2939(8)
Cu1–P3	2.2915 (14)	Cu1–N1	2.0592 (30)
P1–C1	1.8457 (23)	P1–C4	1.8183 (31)
P1–C10	1.8278 (30)	P2–C2	1.8527 (25)
P2–C16	1.8345 (30)	P2–C22	1.8236 (28)
P3–C3	1.8396 (31)	P3–C28	1.8194 (27)
P3–C34	1.8216 (29)	N1–C40	1.1102 (48)
C1–C1'	1.5361 (39)	C2–C3	1.5274 (38)
C40–C41	1.4593 (78)		

Atoms	Angle	Atoms	Angle
P3–Cu1–N1	107.0(1)	P2–Cu1–N1	118.3 (1)
P2–Cu1–P3	90.2(1)	P1–Cu1–N1	96.9 (1)
P1–Cu1–P3	132.1(1)	P1–Cu1–P2	114.3 (1)
Cu1–P1–C10	118.6(1)	Cu1–P1–C4	118.7 (2)
Cu1–P1–C1	108.7(2)	C4–P1–C10	102.2 (2)
C1–P1–C10	100.4(2)	C1–P1–C4	106.1 (1)
Cu1–P2–C22	112.0(1)	Cu1–P2–C16	119.1 (2)
Cu1–P2–C2	103.3(1)	C16–P2–C22	105.7 (2)
C2–P2–C22	103.2(2)	C2–P2–C16	102.9 (2)
Cu1–P3–C34	122.2(2)	Cu1–P3–C28	116.6 (1)
Cu1–P3–C3	101.7(1)	C28–P3–C34	106.3 (2)
C3–P3–C34	102.3(2)	C3–P3–C28	105.3 (2)
Cu1–N1–C40	156.6(3)	P1–C1–C1'	113.7 (3)
P2–C2–C3	110.1(3)	P3–C3–C2	111.3 (3)
P1–C4–C9	116.8(2)	P1–C4–C5	125.1 (3)
P1–C10–C15	119.2(3)	P1–C10–C11	121.8 (2)
P2–C16–C21	123.5(3)	P2–C16–C17	118.0 (2)
P2–C22–C27	122.1(3)	P2–C22–C23	119.0 (3)
P3–C28–C33	118.1(3)	P3–C28–C29	124.0 (3)
P3–C34–C39	117.9(2)	P3–C34–C35	123.7 (3)
N1–C40–C41	177.8(4)		

Figure 4. Solid state CP/MAS ^{31}P NMR spectrum of complex 2.
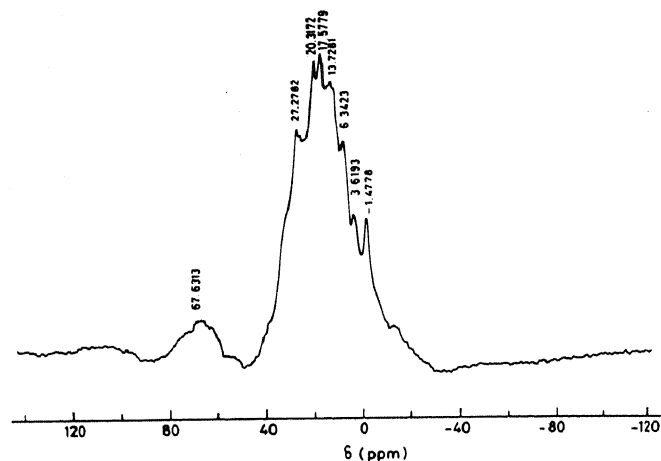
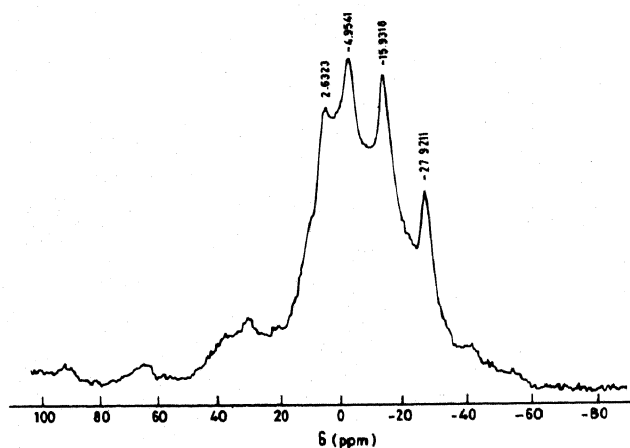**Figure 5.** Solid state CP/MAS ^{31}P NMR spectrum of complex 3.

Figure 3. Solid state CP/MAS ^{31}P NMR spectrum of complex 1.

There are three different P atoms in the complex 3, two chelating, and one bridging. The chelating phosphorus atoms are at a longer distance from copper compared to bridging atom. As a result, the quartets arising from them are subjected to smaller splitting and considerable overlap, as opposed to the larger splitting observed in the quartet due to the bridging phosphorus atom.

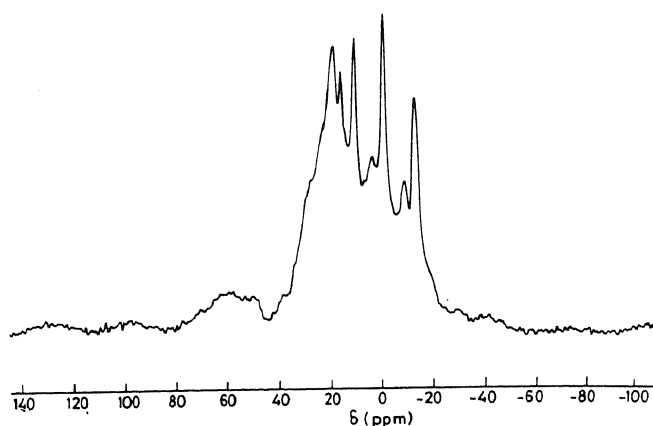Though the crystal structure is not available for complex 1, a comparison of the CP/MAS spectra of the complexes 1–3, throws some light on the solid state structure of complex 1. A single asymmetric quartet, observed in the spectrum of complex 1 shows that the two phosphorus atoms of coordinated dppe are in the same chemical and crystallographic environment. The large negative value of the observed chemical shift almost close to the chemical shift of free dppe (− 12.3 ppm)[33] rules out the possibility of a chelating dppe in the molecule. It is likely that the changes in the principal components of chemical shift anisotropy tensor, (σ_{11}, σ_{22}, and σ_{33}) are appreciable[34], but they cancel each other such that the observed isotropic chemical shift is close to that of the free ligand. Since this complex has only bridging dppe units in solution, it is highly likely that the very different chemical shift observed for this dppe unit is probably due to difference in the conformation of the dppe ligand in 1. In complexes 2 and 3, the conformation of bridging dppe is dictated by another bridging or chelating dppe respectively. However, in complex 1, the conformation

Table 5. ^{31}P CP-MAS NMR data and computed Cu-P distances for complexes 1–3

Complex	Chemical shift (ppm)					Line spacing (Hz)			a/h* (kHz)	r(Cu-P)* (Å)
	$\delta 1$	$\delta 2$	$\delta 3$	$\delta 4$	$\langle \delta \rangle$					
1	2.6	−5.0	−16.0	−28.0	−11.6	921	1333	1457	1.3	2.27
2										
(Quartet 1)	18.8	10.0	−1.0	−13.2	3.7	1060	1339	1485	1.3	2.27
(Quartet 2)	30.0	15.6	3.0	−9.4	9.8	1748	1534	1508	1.5	2.24
3										
(Quartet 1)	17.6	8.3	−1.5	−15.1	2.3	1122	1193	1655	1.2	2.29
(Quartet 2)	27.3	20.3	13.7	3.6	16.2	846	801	1228	0.8	2.34

*See text.

Table 6. Selected bond distances and bond angles for complexes 2 and 3

Complex	Bond distances (Å)		Bond angles (°)	
	Atoms	Distance	Atoms	Angle
2	Cul–P1	2.267 (2)	P2–Cul–N1	125.0 (3)
	Cul–P2	2.264 (2)	P1–Cul–N1	120.2 (2)
			P1–Cul–P2	112.1 (2)
			Pl′–Cul′–P2′	112.1 (2)
3	Cul–P1	2.272 (1)	P3–Cul–N1	107.0 (1)
	Cul–P2	2.294 (1)	P2–Cul–N1	118.3 (1)
	Cul–P3	2.292 (1)	P2–Cul–P3	90.2 (1)
			P1–Cul–N1	96.9 (1)
			P1–Cul–P3	132.1 (1)
			P1–Cul–P2	114.3 (1)

adopted by dppe is not influenced by any other ligand, as the other ligands present are sterically accommodating acetonitriles. This would result in very different M–P–C angles, in complex 1 compared to 2 and 3. It has recently been demonstrated that changes in the M–P–C bond angle could cause chemical shift anisotropy tensors to change by 25–27 ppm/deg (ref. 34). However, in the absence of crystallographic data it would not be possible to confirm this hypothesis.

Solution studies on the complexes

The conductivity values of the complexes lie in the range expected for 1:2 electrolytes[35].

^1H and ^{31}P NMR studies on complexes 1–3

The results of room-temperature NMR experiments are given in Table 7. The ^{1}H NMR spectra of the complexes 1–3 showed the presence of coordinated acetonitrile ($\triangle \delta = 0.2$ ppm) and dppe ($\triangle \delta = 0.16$ to 0.25 ppm). The peak at 2.36 ppm in the spectra of the complexes 1 and 2 and the peak at 2.43 ppm in complex 3 was assigned to the methylene resonance of bridging dppe, and the peaks at 2.46 ppm and 2.45 ppm in the spectra of complexes 2 and 3 respectively to the corresponding resonance of chelating dppe. The coupling between methylene protons and phosphorus atoms was not resolved and the signals were broad.

Room temperature ^{31}P NMR

The peaks around −4 ppm in complexes 1 and 2 and the peak at −0.7 ppm in complex 3 were assigned to bridging dppe and the broad peaks between 0 and 30 ppm in complexes 2 and 3 to chelating dppe. Copper-phosphorus coupling was not resolved due to the bulky phenyl groups attached to phosphorus[36]. The appearance of a broad peak due to chelating dppe in the spectrum of complex 2, which was shown to have only bridging dppe in the solid state, indicated dissociation of the complexes in solution. Hence a variable temperature ^{31}P NMR study was carried out on complexes 2 and 3. The spectra are presented in Figures 6 and 7. There was no change in the spectra of complex 1 recorded at room temperature, 296 K and at 233 K. This showed that unlike the other two complexes, complex 1 remained intact in solution.

Variable temperature ^{31}P NMR spectra of complex 2

On lowering the temperature, the peak corresponding

Table 7. ^{1}H and ^{31}P NMR data of the complexes

Complex	^{1}H NMR (δ ppm)			^{31}P (ppm)
	CH$_3$(CH$_3$CN)	CH$_2$ (dppe)	ϕ (dppe)	
1	2.19 (s, 18H)	2.36 (s, 4H)	7.4 (m, 20H)	−4.44
2	2.16 (s, 3H)	2.36 (s, b, 24)	7.31	−4.33, 0–20 ppm
	2.17 (<1H)	2.45 (b, 2H)	7.19	
3	2.16 (s, 3H)	2.43	7.19 (m, 20H)	−0.7, 0–30 ppm
	2.18 (s, 3H)	2.46	7.30	

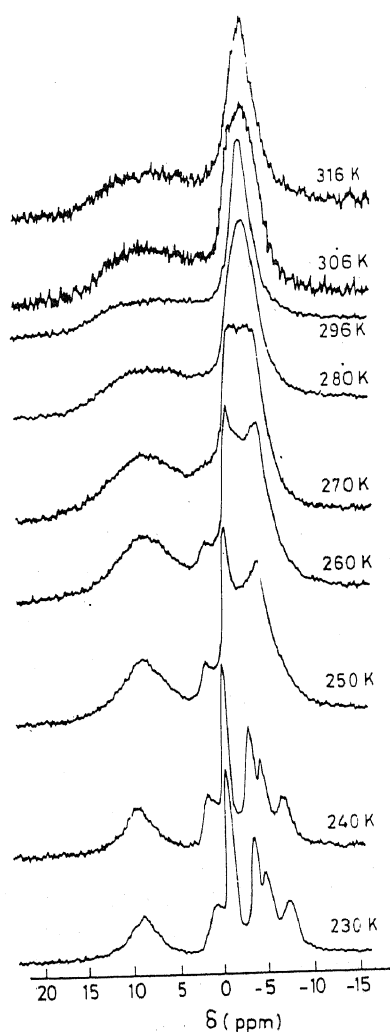**Figure 6.** Variable temperature solution ^{31}P NMR spectra of complex 2.

Figure 7. Variable temperature solution ^{31}P NMR spectra of complex 3.

to chelating dppe sharpened and became less intense relative to that at room temperature, while the other peak broadened and split, resulting in five peaks at 240 K. Further decrease in temperature did not alter the spectrum. The coalescence temperature for the 5 peaks was 280 K. The number of peaks at 240 K could be accounted for if one assumes that the various species involved in the conversion of the dinuclear structure with bridging dppe to a mononuclear structure are frozen out. A plausible scheme is shown in Scheme 1.

Based on the room temperature ^{31}P NMR spectrum of complex 1, the peak at −5 ppm could be assigned to the parent, annular, dibridged structure (I). The cleavage of a single copper–phosphorus bond would result in a system consisting of four different phosphorus atoms (II). For instance, in IIa, highly shielded uncoordinated phosphorus P2′, and a strongly coordinated and hence the most deshielded phosphorus PI′ exist. In between these two extremes, P1 and P2
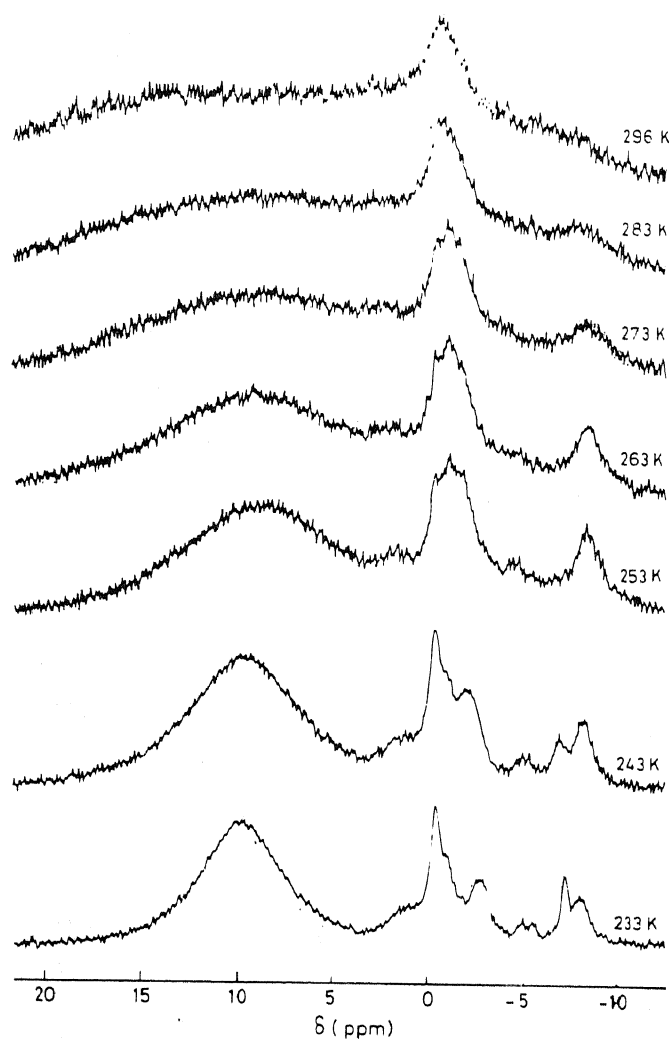
would be present. II would be converted to IV through III.

The peak around 7.7 ppm could be assigned to the chelating dppe in IV and the peak at −8.7 ppm to the uncoordinated end of dppe. The increase in intensity of the peaks around −5 ppm and the sharpening of the peak due to chelating dppe with decrease in temperature indicate the greater stability of structures with bridging dppe relative to chelated dppe and the slower rates of interconversion at lower temperature. At room temperature species I, IIa–IId, IIIa–IIId, and IV would be in equilibrium in solution, resulting in two broad peaks.

Variable temperature ^{31}P NMR spectra of the complex 3

The ^{31}P NMR spectra of the complex 3 showed a temperature dependence similar to the one observed in
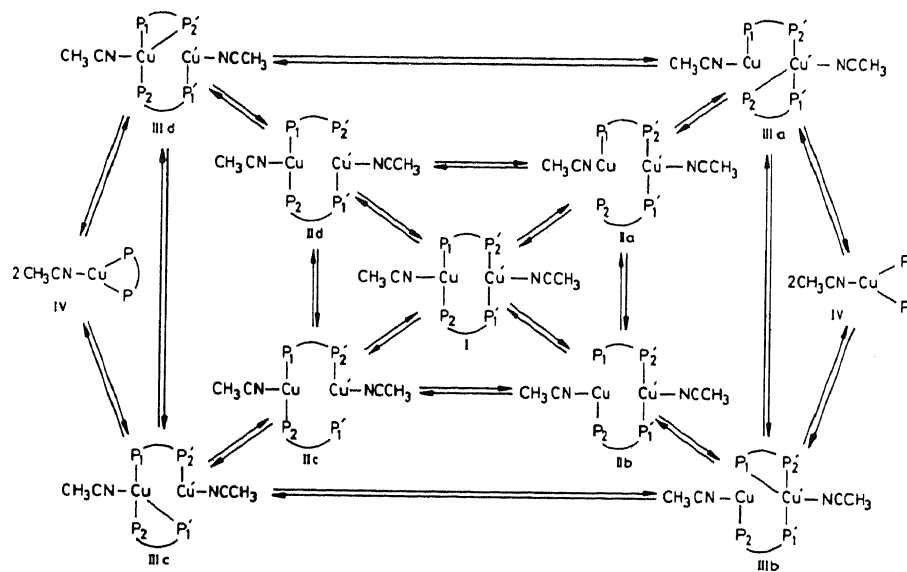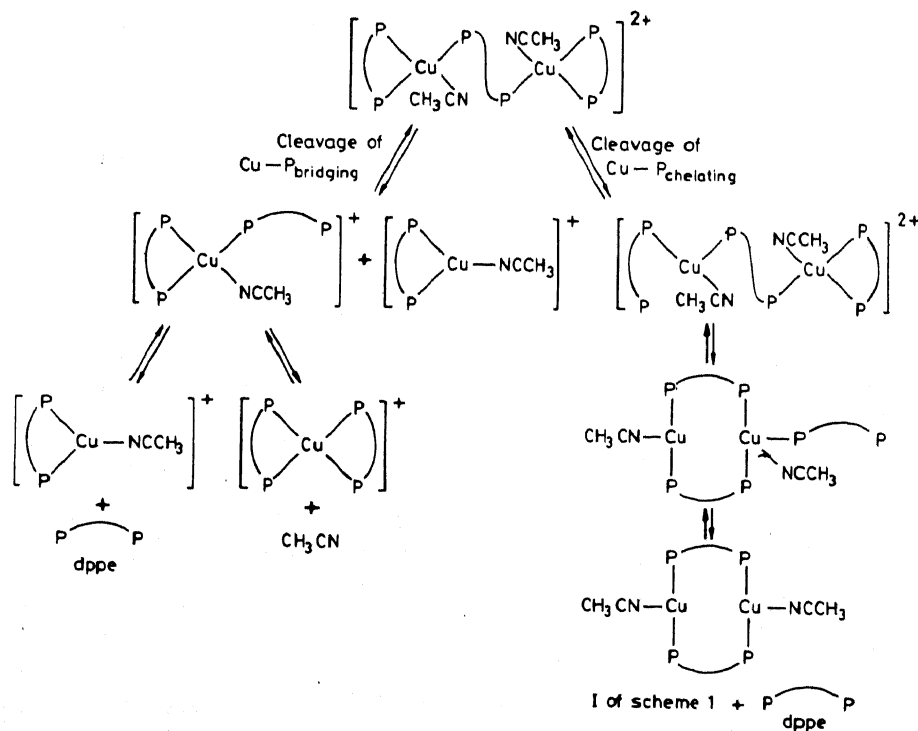
Scheme 1.

complex **2**. The peak due to chelating dppe sharpened while the peak due to bridging dppe split into many peaks, at low temperatures. The main differences between the two spectra were the high intensity of chelating dppe and the presence of free dppe in the spectrum of complex **3**. These observations could be explained by invoking the equilibria given in Scheme 2.

Presence of a large number of intermediates with a chelating dppe ring would account for the high intensity of the peak due to chelating dppe. *Mono*- as

well as *bis*-chelated copper–dppe species are probable. Observed high field resonances could arise from the dinuclear annular complex **2** and the different species arising from this (Scheme 1). The peak at -8.75 ppm, at the negative end of the spectrum could be assigned to free dppe, exchanging with any of the copper–dppe species present. At 296 K, the fast exchange between free dppe with the species with bridged dppe results in a single broad peak.
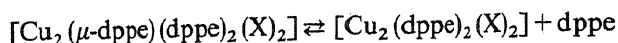
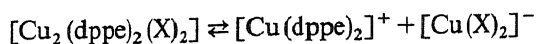Earlier solution state studies on the copper–dppe

Scheme 2.

complexes $[Cu_2(\mu\text{-dppe})(dppe)_2(X)_2]$ for $X=Cl$ (ref. 37) and OAc (ref. 38) have been explained by the following equilibria in solution, involving species A–D.

$$[Cu_2(\mu\text{-dppe})(dppe)_2(X)_2] \rightleftarrows [Cu_2(dppe)_2(X)_2] + dppe$$

$$\quad\quad\quad A \quad\quad\quad\quad\quad\quad B$$

$$[Cu_2(dppe)_2(X)_2] \rightleftarrows [Cu(dppe)_2]^+ + [Cu(X)_2]^-$$

$$\quad B \quad\quad\quad\quad C \quad\quad\quad\quad D$$

Presence of free dppe and the *bis*-chelated species (C) are the key features of the above equilibria. Free dppe is identified in the present study also. However, it appears from schemes 1 and 2 that the dissociation of B need not be restricted to the formation of the *bis*-chelated species (C) alone. The variable temperature ^{31}P NMR spectra of complexes 2 and 3 provide sufficient evidence for the presence of other possibilities such as the *mono*-chelated species in solution.

Another important point to be mentioned here is that the change in line-width of the peaks, as a function of temperature is determined not only by the chemical exchange but also by the copper quadrupolar coupling. These operate in opposite directions[39]. On lowering the temperature, chemical exchange processes would be slowed down which would result in the sharpening of peaks. On the other hand, the effect of copper quadrupole moment would increasingly manifest itself with a fall in temperature, which in turn would result in the broadening of phosphorus resonances. In the present study only the sharpening of the peaks was observed with a decrease in temperature, indicating that the broadening of the peaks was primarily determined by the rate of chemical exchange processes rather than the copper quadrupolar relaxation, in the temperature range studied.

The chemical shifts observed in the solution are very different from those in the solid state. The absence of chemical exchange and the possibility of having different fixed conformations of dppe in different complexes in solid state are probably responsible for the observed differences.

^{63}Cu NMR

The spectra of all the three complexes were similar, with a single, broad resonance around 132 ppm. Complex 1: $\delta = 131.5$ ppm; FWHM $= 3800$ Hz.; Complex 2 : $\delta = 131.6$ ppm; FWHM $= 3800$ Hz.; Complex 3 : $\delta = 132.1$ ppm; FWHM $= 3432$ Hz. All the species identified by ^{31}P NMR were not differentiated or observed in ^{63}Cu NMR due to the quadrupolar broadening. The most important feature of ^{63}Cu NMR is the absence of a peak corresponding to free
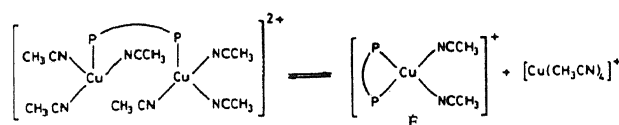
Equation 1.

$[Cu(CH_3CN)_4]$ cation in the spectrum of complex 1. One would have expected a peak corresponding to this cation if the equilibrium shown in equation (1) to give the chelated complex E and free cation existed. This also supported the inferences made from the ^{31}P NMR as it showed that the complex 1 remained undissociated in solution, while complexes 2 and 3 dissociated to give a *mono*-chelated dppe complex of copper.

Conclusions

The results obtained in the present study show that contrary to what is generally believed about dppe, the ligand can function as a bridging ligand even in the absence of metal–metal bonds. However the lability of the ligand and the chelate effect promote the formation of chelated species in solution. Combining various NMR spectroscopic investigations, schemes which would explain the solution behaviour of bridged and chelated dppe complexes of copper, have been proposed. The range of CP/MAS chemical shifts in bridging dppe complexes and their sensitivity to the conformation of dppe have been highlighted. The presence of a chelating dppe ligand changes the relative intensities of the bands observed in the 760 cm^{-1} to 680 cm^{-1} region allowing quick identification of the presence of chelating dppe.

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