Binuclear Copper(I) Complexes containing Two or Three 2-(Diphenylphosphine)pyridine (dppy) Bridging Ligands: *X*-Ray Crystal Structure of $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ and Variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ Nuclear Magnetic Resonance Studies †

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Treatment of $[Cu(MeCN)_4]BF_4$ with 2-(diphenylphosphino)pyridine (dppy) at room temperature in acetonitrile or dichloromethane gives $[Cu_2(\mu\text{-dppy})_2(MeCN)_x][BF_4]_2$, $x = 4$ or 2, respectively. Reaction with an excess of dppy in refluxing acetone leads to the formation of $[Cu_2(\mu\text{-dppy})_3][BF_4]_2$, which gives $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ upon recrystallization from acetonitrile. This complex can also be obtained from $[Cu(MeCN)_4]BF_4$ by reaction with an excess of dppy in refluxing acetonitrile. Substituted complexes $[Cu_2(\mu\text{-dppy})_3L_x][BF_4]_2$ [$x = 1$, L = 2-methylpyridine, $x = 2$, L = 4-methylpyridine, $P(OMe)_3$, or PMe_3] are also described. Variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. studies show that MeCN and dppy dissociation and rapid ligand-exchange processes take place in solution. The crystal structure of $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ has been determined by *X*-ray methods. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 21.424(7)$, $b = 13.186(6)$, $c = 18.232(6)$ Å, and $\beta = 99.77(2)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-matrix least squares to $R = 0.0657$ for 6 539 observed reflections [$I \geqslant 2\sigma(I)$]. The structure consists of $[Cu_2(\mu\text{-dppy})_3(MeCN)]^{2+}$ cations and of BF_4^- anions. In the cations the two copper atoms are held in close proximity [2.721(3) Å] by three dppy ligands acting as bridges through the P and N atoms. One copper atom is three-co-ordinate, being bonded to two N and one P atom from dppy ligands, the other is four-co-ordinate, being bonded to two P and one N atom from dppy ligands and to an additional N atom from an acetonitrile molecule. As expected, the Cu–P and Cu–N bonds for the three-co-ordinate copper are shorter than these of the four-co-ordinate copper.

Binuclear transition-metal complexes containing bidentate bridging ligands, L–L, have been the focus of much investigation in the last few years. Particularly, many examples with two bridges of the diphosphine $Ph_2PCH_2PPh_2$ (dppm)[1] or the aminophosphine 2-(diphenylphosphino)pyridine (dppy),[2] including a variety of metals, oxidation states, and stereochemistries, have been described. They are generally characterized by the presence of an eight-membered ring $M(\mu\text{-L-L})_2M'$, in different conformations. However, this is not the case for copper(I) for which, to the best of our knowledge, no dppy complexes have been reported, and dppm generally forms tri- and tetra-nuclear complexes having related diphosphine-bridged structures with additional bridging groups.[3]

We have recently reported[4] the preparation of binuclear dppm–copper(I) complexes of the type $[Cu_2(\mu\text{-dppm})_2(MeCN)_n]X_2$ and $[Cu_2(\mu\text{-dppm})_3]X_2$ ($n = 2$ or 4, X = BF_4 or ClO_4) in which the copper atoms are bridged only by dppm ligands. They were obtained from $[Cu(MeCN)_4]X$ by reaction with appropriate amounts of dppm in CH_2Cl_2, MeCN, or refluxing acetone.

In the present paper we report the preparation of the first copper(I) complexes containing dppy, where the aminophosphine, acting as a bridging ligand, forms binuclear complexes of the type $[Cu_2(\mu\text{-dppy})_2(MeCN)_n][BF_4]_2$ ($n = 2$ or 4) and $[Cu_2(\mu\text{-dppy})_3L_n][BF_4]_2$ ($n = 0$, 1, or 2; L = N- or P-unidentate ligand), in which the copper atoms, as in the analogous dppm complexes, are bridged only by dppy ligands. Variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. studies show that the ligands undergo facile dissociation and exchange processes in solution.

The structure of $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$, which has been determined by an *X*-ray single-crystal diffraction study, provides the first example of a new structural type of dppy-bridged bimetallic complexes. It comprises two copper(I) atoms linked by three dppy ligands, where the co-ordination geometry around each metal atom is different, one being three- and the other four-co-ordinate. In contrast to the extensively known binuclear complexes containing two bridging ligands, only a few cases with a higher number of bridging phosphines have been characterized, probably due to the extensive crowding around the metal centres. Examples of compounds with three or four bridging ligands are limited to the relatively small diphosphines $RN(PF_2)_2$ (PNP)[5,6] and $R_2PCH_2PR_2$ (P–P, R = Me or Ph),[7–9] *e.g.* $[Co_2(\mu\text{-PNP})_3(CO)_2]$, $[M_2(\mu\text{-PNP})_3(\mu\text{-CO})(CO)_4]$ (M = Cr, Mo or W), $[Mo_2(\mu\text{-PNP})_4Cl_2]$, $[M_2(\mu\text{-P-P})_3]$ (M = Pd or Pt), $[Pt_2(\mu\text{-P-P})_3(PPh_3)_n]$ ($n = 1$ or

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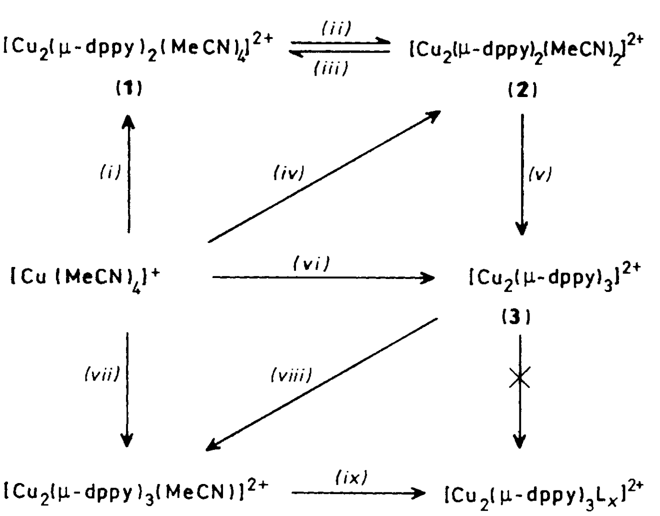
† 1-Acetonitrilebis[μ-2′-(diphenylphosphino)pyridine-*N*(Cu^2)*P*(Cu^1)]-μ-[2′-(diphenylphosphino)pyridine-*N*(Cu^1)*P*(Cu^2)]-dicopper(I) bis(tetrafluoroborate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. (*i*) + dppy [MeCN, room temperature (r.t)]; (*ii*) − 2MeCN (CH_2Cl_2, r.t.); (*iii*) MeCN solution; (*iv*) + dppy (CH_2Cl_2, r.t.); (*v*) refluxing $CHCl_3$; (*vi*) + dppy (excess) (refluxing acetone); (*vii*) + dppy (excess) (refluxing MeCN). (*viii*) MeCN solution; (*ix*) + L, −MeCN [x = 1, L = 2-Mepy (**8**); x = 2, L = $P(OMe)_3$ (**5**), PMe_3 (**6**), or 4-Mepy (**7**)] (CH_2Cl_2, r.t.)

2), and $[Au_2(P–P)_3]^{2+}$. *X*-Ray single-crystal analysis of $[Cu_2(\mu\text{-dppy})_3(MeCN)]^{2+}$ and $[Pt_2(Me_2PCH_2PMe_2)_3(PPh_3)]$[7] showed them to have comparable structures.

Results and Discussion

Syntheses and transformations of the cationic copper(I) derivatives are summarized in the Scheme. Table 1 collects microanalytical, conductance, and room-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. data for all the novel compounds. They have been isolated as tetrafluoroborate salts and are air-stable white solids, but slow decomposition is observed in solution.

Treatment of an acetonitrile solution of the salt $[Cu(MeCN)_4]BF_4$[10] with 1 equivalent of dppy at room temperature gives $[Cu_2(\mu\text{-dppy})_2(MeCN)_4][BF_4]_2$ (**1**). Recrystallization of (**1**) in dichloromethane leads to the dissociation of two MeCN ligands to give $[Cu_2(\mu\text{-dppy})_2(MeCN)_2][BF_4]_2$ (**2**) which can be obtained directly from $[Cu(MeCN)_4]BF_4$ by reaction with 1 equivalent of dppy in CH_2Cl_2. I.r. spectra (Nujol mulls) show two very weak ν(C≡N) absorptions characteristic of the co-ordinated acetonitrile ligands, as well as a broad ν(B–F) absorption at *ca.* 1 060 cm^{-1} (see Experimental section).

Conductance data for acetone solutions of complexes (**1**) and (**2**) show that they are 2:1 electrolytes. Conductivity measurements in nitromethane at different concentrations (10^{-4}—10^{-3} mol dm^{-3}) on complex (**2**) give a value of K = 412 in Onsager's equation ($\Lambda_e = \Lambda_0 - Kc^{\frac{1}{2}}$) whilst K = 390 is obtained for the previously described[4] complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (used as standard). This value of K confirms the proposed binuclear nature and the bridging character of the dppy ligand.

Recrystallization of complex (**2**) from acetonitrile, or addition of MeCN to a dichloromethane solution of (**2**), gives (**1**) quantitatively, showing that the dissociation equilibrium (**1**) $\rightleftharpoons$ (**2**) + 2MeCN is dependent upon the solvent. Proton n.m.r. spectra (in CD_2Cl_2) show that a rapid acetonitrile ligand exchange is taking place at room temperature, in a similar way to that reported[4] for the analogous complexes $[Cu_2(\mu\text{-dppm})_2(MeCN)_x][BF_4]_2$ (x = 2 or 4). Thus, at 22 °C, single methyl resonances are observed at δ 2.00 and 1.99 for (**1**) and (**2**), respectively, which are shifted to higher fields by addition of acetonitrile, almost reaching the corresponding resonance for free acetonitrile (δ 1.93) (see Table 2).

Proton n.m.r. measurements for complex (**2**) have also been recorded at lower temperatures showing a single methyl resonance, δ 1.88 at −30 °C and two peaks, δ 2.00 and 1.79 p.p.m., at −60 °C. However, the spectrum in the presence of stoicheiometric amounts of MeCN at −60 °C again shows a single methyl resonance which is shifted in a similar way as discussed above for the room-temperature experiments, almost reaching the chemical shift for free MeCN at −60 °C (δ 1.95). A similar behaviour is observed at −80 °C. So, the rapid ligand-exchange process is operating even at these temperatures although, apparently, different species may exist in solution; this is also consistent with the $^{31}P\text{-}\{^1H\}$ spectra (see below and Figure 1).

Similarly, when a solution of $[Cu(MeCN)_4]BF_4$ in acetone is heated under reflux with an excess of dppy, $[Cu_2(\mu\text{-dppy})_3][BF_4]_2$ (**3**) is isolated as a white-yellow solid and characterized by elemental analysis and i.r. spectroscopy. Complex (**3**) is also formed when a solution of (**2**) in $CHCl_3$ is heated under reflux, but in much lower yield and contaminated with other unidentified products. Recrystallization of (**3**) from acetonitrile or, alternatively, addition of an equimolar amount of MeCN to (**3**) affords $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ (**4**). The presence of only one acetonitrile ligand is confirmed by the ^1H n.m.r. spectrum in CD_2Cl_2 which exhibits a single methyl resonance at δ 1.79 at room temperature. The spectrum of (**4**) in the presence of acetonitrile (see Table 2) also shows the expected shift of the methyl resonance, indicating a rapid ligand exchange as described above for (**1**) and (**2**). The spectra registered at lower temperatures reveal a similar behaviour to that discussed above for (**2**).

Variable-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. studies indicate that dppy exchange processes also take place (Figure 1). Thus, the spectrum of complex (**2**) exhibits two broad resonances at δ 5.28 and 2.82 (1,2-dichloroethane solution, 22 °C), which gradually approach each other as the temperature increases to give a single broad signal at 60 °C (δ 4.59).

By cooling CD_2Cl_2 solutions of (**2**) (δ 7.44 and 4.68, 22 °C) to −30 and −60 °C several phosphorus resonances are observed (Figure 1). These data seem to indicate the existence of equilibria between different species, *i.e.* isomers with ligand orientations 'head to head' or 'head to tail', which are rapidly interconvertible.

These processes probably involve phosphine dissociation, which is in fact observed in the spectra when stoicheiometric amounts of the ligand are added (Figure 2). Thus, the addition of further ligand to the solution of complex (**2**) at 22 °C gradually shifts the corresponding resonance to values closer to that of the free ligand (δ −1.72) indicating a rapid exchange of dppy on the n.m.r. time-scale.

However, the dissociation processes can be frozen at −60 °C, when, for molar ratios of compound (**2**):dppy greater than 1:4, the signal for the free ligand appears (δ −4.36). These spectra show a single phosphorus resonance at approximately δ 1.78 p.p.m., in the presence of excess of ligand, in a similar way to that discussed below for compound (**3**) (Figure 4) (δ 1.36 p.p.m.). Under these conditions mononuclear species of the type $[CuL_3]^+$ and/or $[CuL_4]^+$ are probably present in solution.

Phosphine-exchange processes in solution are also present in complexes (**3**) and (**4**), as is shown by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. Although the presence of three unsymmetrical bridges in each complex should give rise to two non-equivalent phosphorus atoms providing that a 'head to tail' configuration is adopted for the framework '$Cu_2(\mu\text{-dppy})_3$' (see below), only

Table 1. Microanalytical,[a] conductance,[b] and n.m.r.[c,d] data

	Analysis (%)			^{1}H N.m.r.		^{31}P-{^{1}H} N.m.r.	Λ_M
Complex	C	N	H	δ(Me)	δ(Ph)	δ(dppy)	(ohm^{-1} cm^2 mol^{-1})
(**1**) $[Cu_2(\mu\text{-dppy})_2(MeCN)_4][BF_4]_2$	49.85	7.85	4.10	2.00(s)[d]	7.43(m)[d]	7.69, 4.77[d]	190
	(50.85)	(8.50)	(4.45)				
(**2**) $[Cu_2(\mu\text{-dppy})_2(MeCN)_2][BF_4]_2$	50.95	6.10	3.65	1.99(s)[d]	7.30(m)[d]	7.44, 4.68[d]	196
	(50.20)	(6.15)	(4.45)				
(**3**) $[Cu_2(\mu\text{-dppy})_3][BF_4]_2$	56.60	3.65	4.10		7.15(m)[d]	4.63[d]	221
	(56.15)	(3.85)	(3.90)				
(**4**) $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$	55.15	4.75	3.90	1.79(s)[d]	7.20(m)[d]	5.45[d]	220
	(56.25)	(4.95)	(4.00)				
(**5**) $[Cu_2(\mu\text{-dppy})_3\{P(OMe)_3\}_2][BF_4]_2$	50.35	3.05	4.25	3.59(s)[c]	7.27(m)[c]	1.70[c]	220
	(51.15)	(3.15)	(4.50)				
(**6**) $[Cu_2(\mu\text{-dppy})_3(PMe_3)_2][BF_4]_2$	55.40	3.15	5.15	1.06(s)[c]	7.37(m)[c]	1.46[c,e]	218
	(55.10)	(3.40)	(4.85)				
(**7**) $[Cu_2(\mu\text{-dppy})_3(4\text{-Mepy})_2][BF_4]_2$	61.10	5.25	4.60	2.40(s)[c]	7.70(m)[c]	1.82[c]	220
	(59.30)	(5.50)	(4.40)				
(**8**) $[Cu_2(\mu\text{-dppy})_3(2\text{-Mepy})][BF_4]_2$	58.50	4.55	4.20	2.54(s)[c]	7.08(m)[c]	4.79[c]	214
	(57.85)	(4.75)	(4.15)				

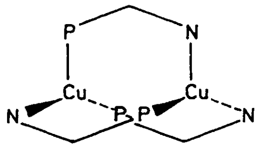
[a] Calculated values are given in parentheses. [b] In acetone solution at 20 °C. [c] Proton (79.54 MHz) and ^{31}P-{^{1}H} n.m.r. (32.20 MHz). Values in p.p.m. to high frequency of $SiMe_4$ or 85% H_3PO_4 measured in $CDCl_3$ at *ca.* 20 °C. [d] Proton (300 MHz) and ^{31}P-{^{1}H} n.m.r. (121.5 MHz). Values measured in CD_2Cl_2 at *ca.* 22 °C. [e] δ(PMe_3) −43.11 p.p.m.

Table 2. Variable-temperature ^{1}H n.m.r. studies (300 MHz) of compounds (**2**) and (**4**) in CD_2Cl_2 in the presence of MeCN

	δ(Me)	
Molar ratio	22 °C	−60 °C
(**2**):MeCN		
1:0	1.99(s)	2.00, 1.79[a]
1:1.5	1.98(s)	1.89(s)
1:3	1.97(s)	1.92(s)
1:6	1.95(s)	
0:1	1.93(s)	1.95(s)[b]
(**4**):MeCN	1.79(s)	2.00, 1.59[c]
1:0	1.88(s)	1.89(s)
1:1.5	1.90(s)	1.90(s)
1:3	1.93(s)	1.95(s)[b]
0:1		

[a] At −30 °C, δ(Me) 1.88. [b] Free MeCN at −30 °C, δ(Me) 1.94. [c] At −30 °C, δ(Me) 1.69.

a single resonance at δ 4.63 and 5.45 p.p.m. (22 °C) appears in the spectra of (**3**) and (**4**), respectively.



Variable-temperature ^{31}P-{^{1}H} n.m.r. studies for complex (**3**) (Figure 3) confirm the existence of exchange processes. As discussed above for (**2**), the increasing addition of phosphine to solutions of (**3**) gives rise to a rapid exchange of the ligand at 22 °C, which can be slowed down at −60 °C (Figure 4).

In order to obtain more information about these unusual complexes a single-crystal *X*-ray structure determination was undertaken for complex (**4**). In the solid state two different phosphorus types are found (see crystal structure below).

The lability of the MeCN ligand in complex (**4**) as well as the presence of one co-ordinatively unsaturated copper atom

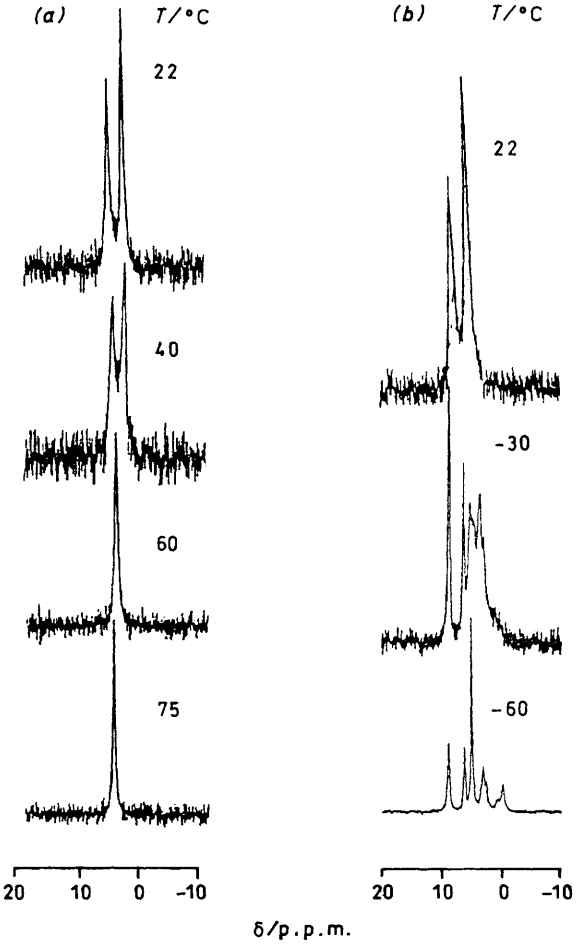


Figure 1. Variable-temperature ^{31}P-{^{1}H} n.m.r. spectra (121.5 MHz) of compound (**2**) in (*a*) 1,2-dichloroethane solutions with 10% C_7D_8 added, (*b*) CD_2Cl_2 solutions

allows the synthesis of the substituted complexes $[Cu_2(\mu\text{-dppy})_3L_x][BF_4]_2$ [x = 2, L = $P(OMe)_3$ (**5**), PMe_3 (**6**), or 4-methylpyridine (4-Mepy) (**7**)] by addition of the appropriate

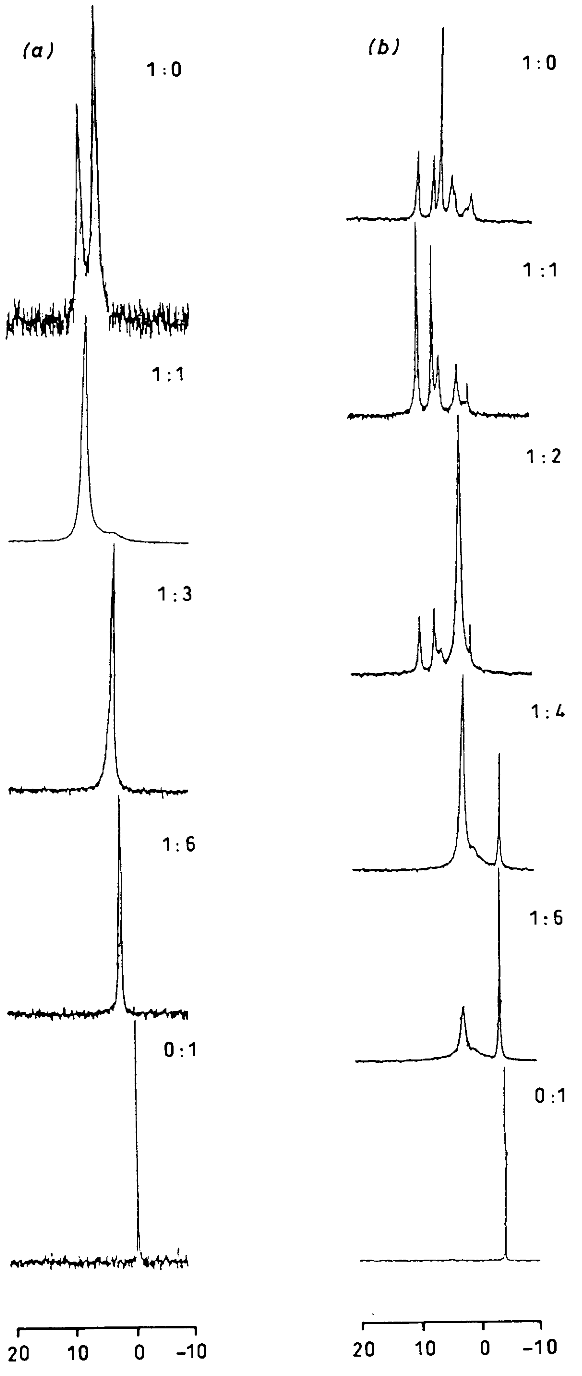


Figure 2. $^{31}P-\{^1H\}$ N.m.r. spectra (121.5 MHz) of compound (**2**) at different (**2**): dppy molar ratios, at (*a*) 22°, (*b*) -60 °C

unidentate ligand to a solution of (**4**) in dichloromethane. These complexes are air-stable white solids and have been characterized by elemental analyses, conductivity measurements, and n.m.r. spectra (see Table 1). The $^{31}P-\{^1H\}$ n.m.r. spectra also exhibit single resonances for the bridging ligand and unidentate P ligands; this seems to indicate that dissociation processes involving rapid unidentate ligand exchange are also operating. Thus, for complex (**6**) the $^{31}P-\{^1H\}$ n.m.r. spectrum shows a single signal at δ -43.11 p.p.m.; the addition of further PMe_3 ligand leads to a shift in the corresponding phosphorus resonance to higher field [molar

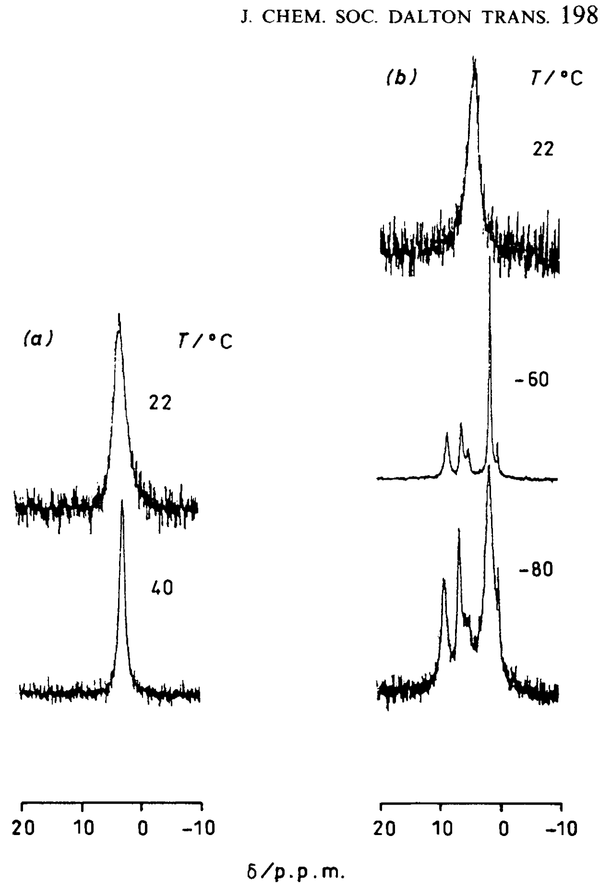


Figure 3. Variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectra (121.5 MHz) of compound (**3**) in (*a*) 1,2-dichloroethane solutions with 10% C_7D_8 added, (*b*) CD_2Cl_2 solutions

ratio of complex (**6**):PMe_3 = 1:0, -43.11; 1:1, -54.53; 0:1, -60.83 p.p.m.].

On the other hand, complex (**8**) [$x = 1$, L = 2-methylpyridine (2-Mepy)] is the sole product formed even when 2 molar equivalents of ligand are used. Steric as well as electronic properties of methyl-substituted pyridine ligands are known to determine tri- or tetra-co-ordination geometries of copper(I) complexes,[11] *e.g.* $[Cu(2\text{-}Mepy)_3]^+$ and $[Cu(py)_4]^+$. When complex (**3**) is used as starting material instead of (**4**) or, alternatively, an excess of ligand is added, a mixture of different derivatives is obtained probably due to partial substitution of the labile bridging ligand dppy by the entering ligand. No reaction is observed with carbon monoxide and 1-phenyl-1-propyne.

Crystal Structure of $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ (**4**).—The crystal structure of complex (**4**) consists of binuclear $[Cu_2(\mu\text{-dppy})_3(MeCN)]^{2+}$ cations and of BF_4^- anions. The structure of the cation is depicted in Figure 5 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 3. In the binuclear cation the two copper atoms are held in close proximity by three dppy ligands acting as bridges through the P and N atoms. To the best of our knowledge, this is the first example of a copper complex with dppy ligands and the first example of a binuclear complex with three dppy ligands.

Two N atoms, N(2) and N(3), and one P atom, P(1), are bonded to the Cu(1) atom, whereas two P atoms, P(2) and P(3), and one N atom, N(1), are bonded to the Cu(2) atom. The CuP_3 and CuN_3 co-ordination environments, with the three ligands bonded to one copper through only P or only N atoms, are avoided, probably through steric hindrance of the bulky phenyl

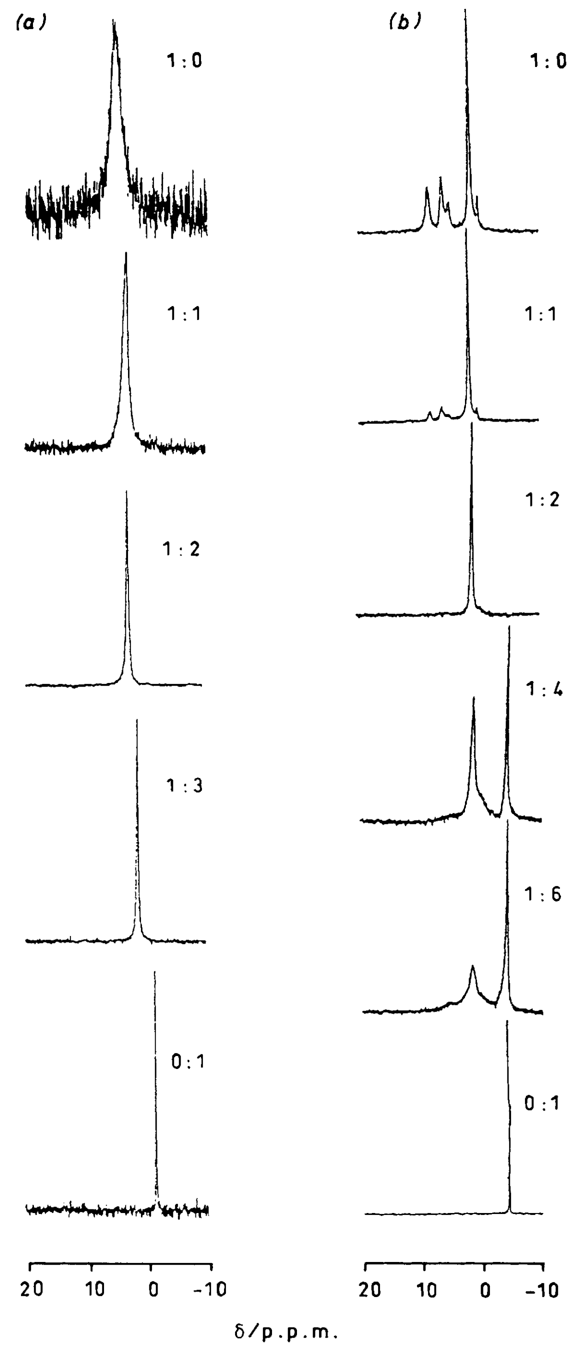


Figure 4. $^{31}P-\{^{1}H\}$ N.m.r. spectra (121.5 MHz) of compound (**3**) at different (**3**):dppy molar ratios at (*a*) 22, (*b*) −60 °C

groups on the P atoms, which must be forced in order to lie in the co-ordination plane. If the mean plane through Cu(1),P(1),C(11),N(1), and Cu(2) is indicated as bridge 1, that through Cu(1),N(2),C(12),P(2), and Cu(2) as bridge 2, and that through Cu(1),N(3),C(13),P(3), and Cu(2) as bridge 3, the dihedral angles between bridges 1 and 2, 1 and 3, and 2 and 3 are 116.3(1), 117.6(1), and 125.9(1)° respectively. The largest angle corresponds to the two bridges carrying two P atoms co-ordinated to the same copper atom and the steric demand of two P atoms in the co-ordination plane is indicated by the very large P(2)–Cu(2)–P(3) angle [129.4(1)°]. The conformation of all three bridges is roughly 'envelope' with four atoms approximately co-planar and one 'out of the plane' [C(11) in bridge 1, by 0.45(1) Å, Cu(1) in the other two bridges, by 0.71(1) and 0.69(1) Å respectively].

The Cu ··· Cu separation, 2.721(3) Å, can be considered indicative of a weak bonding interaction, even though three bulky bridging dppy ligands should produce severe geometric constraints in a binuclear complex to hold the two metals in close proximity.[12]

The two copper atoms show different co-ordination environments: Cu(1) forms a distorted trigonal array with two N and one P atoms, to which it is bonded. The trigonal planar co-ordination is distorted by the displacement of the metal atom from the plane of its donor atoms by 0.171(2) Å towards Cu(2). The other copper atom, Cu(2), is four-co-ordinate being bonded to two N and one P atoms from dppy ligands and to an additional N atom from an acetonitrile ligand. This co-ordination can be described alternatively as distorted tetrahedral or as trigonal pyramidal with N(1),P(2), and P(3) in the equatorial plane [P(2)–Cu(2)–P(3) 129.4(1), P(2)–Cu(2)–N(1) 108.5(1), and P(3)–Cu(2)–N(1) 116.6(1)°] and N(4) (from acetonitrile) at the apex of the pyramid [N(4)–Cu(2)–P(2) 97.7(2), N(4)–Cu(2)–P(3) 97.8(2), and N(4)–Cu(2)–N(1) 98.0(2)°], the metal being displaced from the equatorial plane by 0.303(2) Å towards the apex.

The two trigonal planar arrays about the two copper atoms are nearly parallel, the dihedral angle being 3.7(1)°. A rather short Cu(1) ··· F(1) distance of 2.755(6) Å, involving one of the BF_4^- anions, can be observed. The Cu(1)–F(1) vector is almost perpendicular to the equatorial co-ordination plane of Cu(1), the angle with the normal to the plane being 5.8(1)°; also the Cu(1)–Cu(2) vector is almost perpendicular to the same plane, the angle with the normal being 9.5(1)°. By considering also the Cu(1)–Cu(2) and Cu(1)–F(1) contacts, the co-ordination around Cu(1) can be seen as elongated trigonal bipyramidal. Taking into account that the Cu(1)–Cu(2) vector is almost perpendicular to the equatorial co-ordination plane of Cu(2) [angle with the normal to the plane 12.3(1)°], the co-ordination around Cu(2) can also be considered as distorted trigonal bipyramidal. With these introductory statements, it is easy to understand how the complex can add an additional ligand to Cu(1) in a direction perpendicular to the N(2)N(3)P(1) plane. Thus, in practice the non-bulky donor atom must substitute the F(1) atom and approach the metal atom along the Cu(1)–F(1) direction with consequent movement of the metal out of the equatorial plane towards the new donor atom. The co-ordination environments of the two metal atoms become, in this case, similar. Also the loss of the acetonitrile ligand in the complex can be predicted with the Cu(2) atom reaching a co-ordination environment similar to that of Cu(1) with little changes in the positions of the co-ordinated atoms and little movement of the metal towards the other copper atom, along the Cu(1)–Cu(2) direction.

The structure of the cation of (**4**) is comparable to that of $[Pt_2(\mu\text{-dmpm})_3(PPh_3)]$ (dmpm = $Me_2PCH_2PMe_2$),[7] in which a trigonal planar co-ordination of one Pt atom and a distorted tetrahedral co-ordination of the other Pt atom are observed. Also, in this case, complexes such as $[Pt_2(\mu\text{-dmpm})_3]$ or $[Pt_2(\mu\text{-dmpm})_3(PPh_3)_2]$ can be obtained.

It is noteworthy that the Cu–P and Cu–N bond distances in (**4**) involving the three-co-ordinate copper are shorter than those involving the four-co-ordinate one [Cu(1)–P(1) 2.196(2), Cu(2)–P(2) 2.301(3), and Cu(2)–P(3) 2.274(2); Cu(1)–N(2) 2.056(6), Cu(1)–N(3) 2.048(4), and Cu(2)–N(1) 2.114(4) Å], as already pointed out by Engelhardt *et al.*[11] for the $[Cu(py)_4]^+$ and $[Cu(2\text{-Mepy})_3]^+$ cations.

The acetonitrile in complex (**4**) is co-ordinated to Cu(2) in a bent fashion, as indicated by the Cu(2)–N(4)–C(18) angle of 164.5(5)°, with a Cu(2)–N(4) distance of 2.089(5) Å. A comparison of these values with the ones found in the structure of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ [Cu–N 1.999(9) and 2.161(3) Å, Cu–N–C 173.1(9) and 157.4(9)°] allows us to point out that for the bonding of copper with an acetonitrile ligand the shorter the Cu–N distance the larger the Cu–N–C angle.[4]

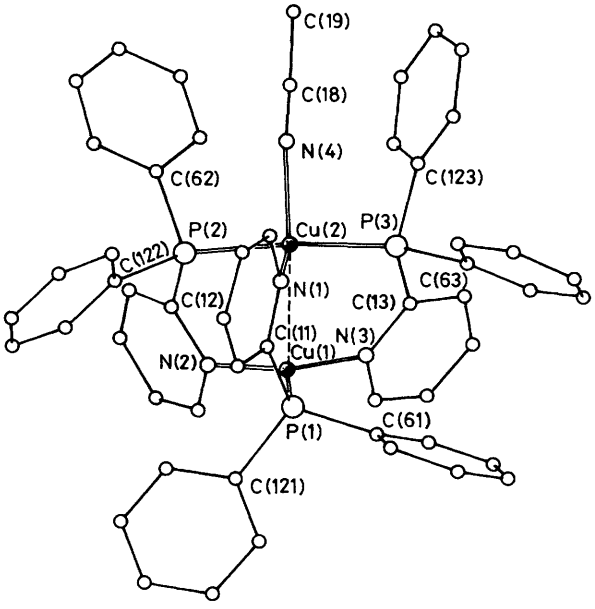


Figure 5. View of the $[Cu_2(\mu\text{-dppy})_3(MeCN)]^{2+}$ cation showing the different co-ordination around the two copper atoms and the atomic numbering scheme

Conclusions

Binuclear copper(I) complexes containing the bridging ligand 2-(diphenylphosphino)pyridine have been obtained and belong to complexes of the types: '$Cu_2(\mu\text{-dppy})_2$' (**1**) and (**2**) and '$Cu_2(\mu\text{-dppy})_3$' (**3**)—(**8**).

Variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. studies reveal that complexes are labile and undergo MeCN and/or dppy dissociation involving ligand-exchange processes in solution.

Characteristic n.m.r. features are: (*i*) MeCN dissociation with rapid exchange processes on the n.m.r. time-scale (at 22, −30, and −60 °C), which are shown by addition of MeCN to solutions of complexes (**1**), (**2**), and (**4**); the single proton methyl resonance of acetonitrile is shifted, reaching values close to that of the free ligand; Similar behaviour has been found for the analogous copper complexes with dppm,[4] namely, $[Cu_2(\mu\text{-dppm})_2(MeCN)_n]^{2+}$ (n = 2 or 4). (*ii*) dppy dissociation with exchange processes are shown. At 22 °C or higher temperatures, for compounds (**3**) and (**4**), or 60 °C for (**2**), a single phosphorus resonance is observed, showing a rapid exchange of the ligand that allows the phosphorus atoms in complex (4) to be effectively equivalent (the *X*-ray single-crystal structure determination shows to structurally different phosphorus atoms around the copper atoms in the solid state). $^{31}P\text{-}\{^1H\}$ N.m.r. spectra of solutions of complexes (**2**) and (**3**) in the presence of stoicheiometric amounts of free ligand measured at low temperatures (−60 and −80 °C) show that the ligand-exchange processes can be frozen.

These dissociation processes of 2-(diphenylphosphino)-pyridine in copper(I) complexes are further examples showing the ability of this bridging ligand to undergo rupture, probably involving mononuclear species, and realignment in binuclear

Table 3. Selected interatomic bond distances (Å) and angles (°) for compound (**4**)

Cu(1)–Cu(2)	2.721(3)	Cu(2)–N(4)	2.089(5)		
Cu(1)–P(1)	2.196(2)	Cu(2)–P(2)	2.301(3)	Cu(2)–P(3)	2.274(2)
Cu(2)–N(1)	2.114(4)	Cu(1)–N(2)	2.056(6)	Cu(1)–N(3)	2.048(4)
P(1)–C(11)	1.842(6)	P(2)–C(12)	1.838(7)	P(3)–C(13)	1.832(7)
P(1)–C(61)	1.809(6)	P(2)–C(62)	1.820(6)	P(3)–C(63)	1.824(6)
P(1)–C(121)	1.826(6)	P(2)–C(122)	1.825(6)	P(3)–C(123)	1.821(6)
N(1)–C(11)	1.358(7)	N(2)–C(12)	1.338(7)	N(3)–C(13)	1.351(7)
N(1)–C(51)	1.356(8)	N(2)–C(52)	1.342(9)	N(3)–C(53)	1.338(8)
C(11)–C(21)	1.378(8)	C(12)–C(22)	1.381(9)	C(13)–C(23)	1.398(8)
C(21)–C(31)	1.380(10)	C(22)–C(32)	1.416(11)	C(23)–C(33)	1.395(10)
C(31)–C(41)	1.387(9)	C(32)–C(42)	1.384(10)	C(33)–C(43)	1.355(10)
C(41)–C(51)	1.381(9)	C(42)–C(52)	1.370(10)	C(43)–C(53)	1.379(9)
N(4)–C(18)	1.127(8)	C(18)–C(19)	1.463(11)		
B(1)–F(1)	1.362(10)	B(2)–F(5)	1.358(9)		
B(1)–F(2)	1.363(10)	B(2)–F(6)	1.360(13)		
B(1)–F(3)	1.332(11)	B(2)–F(7)	1.306(15)		
B(1)–F(4)	1.343(11)	B(2)–F(8)	1.291(13)		
P(1)–Cu(1)–N(2)	132.3(2)	P(3)–Cu(2)–N(1)	116.6(1)	F(1)–B(1)–F(2)	109.9(7)
P(1)–Cu(1)–N(3)	127.7(2)	Cu(1)–Cu(2)–P(2)	74.7(1)	F(1)–B(1)–F(3)	109.4(7)
N(2)–Cu(1)–N(3)	97.9(2)	Cu(1)–Cu(2)–P(3)	80.8(1)	F(1)–B(1)–F(4)	109.1(7)
Cu(2)–Cu(1)–P(1)	85.9(1)	Cu(1)–Cu(2)–N(1)	93.3(2)	F(2)–B(1)–F(3)	106.5(8)
Cu(2)–Cu(1)–N(2)	103.6(2)	N(4)–Cu(2)–P(2)	97.7(2)	F(2)–B(1)–F(4)	107.0(7)
Cu(2)–Cu(1)–N(3)	96.8(2)	N(4)–Cu(2)–P(3)	97.8(2)	F(3)–B(1)–F(4)	114.9(8)
P(2)–Cu(2)–P(3)	129.4(1)	N(4)–Cu(2)–N(1)	98.0(2)	F(5)–B(2)–F(6)	108.0(8)
P(2)–Cu(2)–N(1)	108.5(1)	N(4)–Cu(2)–Cu(1)	168.0(2)	F(5)–B(2)–F(7)	113.4(7)
Cu(2)–N(4)–C(18)	164.5(5)	N(4)–C(18)–C(19)	176.1(8)	F(5)–B(2)–F(8)	111.4(7)
Cu(1)–P(1)–C(11)	115.7(2)	Cu(2)–P(3)–C(13)	117.3(2)	F(6)–B(2)–F(7)	102.8(8)
Cu(1)–P(1)–C(61)	115.8(2)	Cu(2)–P(3)–C(63)	116.2(2)	F(6)–B(2)–F(8)	108.5(8)
Cu(1)–P(1)–C(121)	114.5(2)	Cu(2)–P(3)–C(123)	110.2(2)	F(7)–B(2)–F(8)	112.3(9)
Cu(2)–P(2)–C(12)	121.1(2)	Cu(2)–N(1)–C(11)	123.7(4)		
Cu(2)–P(2)–C(62)	111.6(2)	Cu(1)–N(2)–C(12)	117.0(4)		
Cu(2)–P(2)–C(122)	114.7(2)	Cu(1)–N(3)–C(13)	123.3(4)		
P(1)–C(11)–N(1)	114.2(4)	P(3)–C(13)–N(3)	115.2(4)		
P(2)–C(12)–N(2)	113.9(4)				

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms

Atom	*x*	*y*	*z*
Cu(1)	3 243(1)	−378(1)	1 215(1)
Cu(2)	2 091(1)	263(1)	1 467(1)
P(1)	3 158(1)	−1 579(1)	2 027(1)
P(2)	1 934(1)	−227(1)	238(1)
P(3)	2 702(1)	1 537(1)	2 043(1)
F(1)	4 385(2)	−1 346(4)	1 231(4)
F(2)	5 409(3)	−1 188(5)	1 714(3)
F(3)	5 058(3)	−2 596(5)	1 196(6)
F(4)	5 109(2)	−1 182(6)	513(3)
F(5)	129(2)	−622(3)	3 098(3)
F(6)	−145(5)	943(5)	2 775(6)
F(7)	29(4)	606(6)	3 908(5)
F(8)	811(3)	625(5)	3 303(5)
N(1)	1 963(2)	−1 016(3)	2 125(2)
N(2)	3 148(2)	−387(4)	74(3)
N(3)	3 698(2)	987(3)	1 404(2)
N(4)	1 209(2)	940(4)	1 463(3)
C(11)	2 349(3)	−1 840(4)	2 194(3)
C(21)	2 152(3)	−2 783(4)	2 387(4)
C(31)	1 551(3)	−2 908(4)	2 550(4)
C(41)	1 169(3)	−2 057(5)	2 537(4)
C(51)	1 384(3)	−1 136(4)	2 319(3)
C(61)	3 586(3)	−1 368(4)	2 958(3)
C(71)	4 036(3)	−591(5)	3 077(3)
C(81)	4 386(4)	−416(5)	3 781(4)
C(91)	4 299(4)	−1 019(6)	4 369(4)
C(101)	3 867(4)	−1 797(6)	4 279(4)
C(111)	3 492(3)	−1 974(5)	3 571(4)
C(121)	3 405(3)	−2 833(4)	1 763(3)
C(131)	3 095(3)	−3 219(5)	1 088(4)
C(141)	3 278(4)	−4 139(6)	839(4)
C(151)	3 768(3)	−4 658(5)	1 241(4)
C(161)	4 080(4)	−4 302(6)	1 902(4)
C(171)	3 904(3)	−3 365(5)	2 173(4)
C(12)	2 577(3)	−155(4)	−311(3)
C(22)	2 479(3)	97(5)	−1 057(4)
C(32)	3 004(4)	71(6)	−1 435(4)
C(42)	3 589(3)	−197(6)	−1 036(4)
C(52)	3 638(3)	−430(5)	−296(4)
C(62)	1 329(3)	540(4)	−328(3)
C(72)	819(4)	150(6)	−785(4)
C(82)	380(4)	808(7)	−1 208(5)
C(92)	458(4)	1 811(7)	−1 176(5)
C(102)	978(4)	2 230(7)	−745(5)
C(112)	1 407(4)	1 589(6)	−302(4)
C(122)	1 669(3)	−1 535(4)	71(3)
C(132)	1 900(3)	−2 185(5)	−424(4)
C(142)	1 660(4)	−3 178(6)	−526(4)
C(152)	1 208(4)	−3 502(6)	−139(5)
C(162)	980(4)	−2 897(6)	343(4)
C(172)	1 205(3)	−1 889(5)	456(4)
C(13)	3 461(3)	1 777(4)	1 740(3)
C(23)	3 793(3)	2 691(4)	1 861(4)
C(33)	4 383(3)	2 787(5)	1 641(4)
C(43)	4 610(3)	1 991(5)	1 297(4)
C(53)	4 262(3)	1 107(5)	1 193(4)
C(63)	2 897(3)	1 461(4)	3 055(3)
C(73)	3 424(3)	1 916(5)	3 474(4)
C(83)	3 514(4)	1 891(6)	4 238(4)
C(93)	3 087(4)	1 395(6)	4 602(4)
C(103)	2 561(4)	941(7)	4 196(5)
C(113)	2 454(3)	966(5)	3 415(4)
C(123)	2 284(3)	2 741(4)	1 893(3)
C(133)	2 273(4)	3 263(6)	1 241(4)
C(143)	1 879(4)	4 113(7)	1 059(5)
C(153)	1 515(4)	4 459(6)	1 540(4)
C(163)	1 527(4)	3 954(6)	2 218(4)
C(173)	1 915(3)	3 100(5)	2 396(4)
C(18)	801(3)	1 489(5)	1 411(4)
C(19)	281(4)	2 222(7)	1 294(7)
B(1)	4 986(4)	−1 594(7)	1 147(5)
B(2)	228(5)	367(6)	3 292(6)

complexes giving different bridge orientations. Such processes lead in some cases to the formation of 'head to head' and 'head to tail' isomers, as has been described[13] for homo- and hetero-binuclear rhodium and palladium complexes.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—600 cm^{-1}) using Nujol mulls between NaCl plates. Conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^3 acetone solutions, with a Metrohm AG E382 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. N.m.r. spectra were recorded on a Varian FT80A spectrometer at 79.54 MHz (^{1}H) or 32.20 MHz (^{31}P) and a Bruker AC300 at 300 MHz (^{1}H) or 121.5 MHz (^{31}P) using SiMe_4 and 85% H_3PO_4 as internal or external standards, respectively.

Preparation of Bis[2-(diphenylphosphino)pyridine] Complexes $[\text{Cu}_2(\mu\text{-dppy})_2(\text{MeCN})_n][\text{BF}_4]_2$ [$n = 4$(**1**) *or* 2(**2**)].—*Complex* (**1**) ($n = 4$). To a solution of $[\text{Cu(MeCN)}_4]\text{BF}_4$ (0.94 g, 3 mmol) in MeCN (30 cm^3), dppy (0.79 g, 3 mmol) was added and the mixture was stirred at room temperature for 12 h. Concentration of the resulting solution and addition of diethyl ether (20 cm^3) resulted in the precipitation of a white solid. Yield: 80%. I.r.: ν(C≡N) 2 280vw, 2 255vw, ν(B–F); 1 060s br cm^{-1}.

Complex (**2**) ($n = 2$). This compound was similarly isolated from a solution of dichloromethane or by recrystallization of (**1**) from a mixture of CH_2Cl_2–hexane (1:3). Yield: 75%. I.r.: ν(C≡N) 2 280vw, 2 260vw; ν(B–F) 1 055s br cm^{-1}.

Preparation of $[\text{Cu}_2(\mu\text{-dppy})_3][\text{BF}_4]_2$ (**3**).—A mixture of $[\text{Cu(MeCN)}_4]\text{BF}_4$ (0.314 g, 1 mmol) and dppy (0.657 g, 2.5 mmol) was heated in acetone under reflux (30 cm^3) for 24 h. The resulting cloudy solution was evaporated to dryness and the residue extracted with CH_2Cl_2 (20 cm^3). Concentration of the resulting solution and addition of diethyl ether (20 cm^3) gave a white solid (**3**) which was washed with diethyl ether (3 × 20 cm^3) and vacuum dried. Yield: 70%. I.r.: ν(B–F) 1 065s br cm^{-1}.

Preparation of $[\text{Cu}_2(\mu\text{-dppy})_3(\text{MeCN})][\text{BF}_4]_2$ (**4**).—A mixture of $[\text{Cu(MeCN)}_4]\text{BF}_4$ and dppy (in a molar ratio of *ca.* 1:3) was heated in acetonitrile under reflux for 24 h. The resulting cooled solution was concentrated under reduced pressure and diethyl ether (20 cm^3) was added yielding the required product as a white solid. Yield: 57%. I.r.: ν(C≡N) 2 290vw, 2 260vw; ν(B–F) 1 050s br cm^{-1}. Compound (**4**) was also obtained by recrystallization of (**3**) from a mixture of acetonitrile–diethyl ether (1:3).

Preparation of $[\text{Cu}_2(\mu\text{-dppy})_3\text{L}_n][\text{BF}_4]_2$ [$n = 2$, L = P(OMe)_3 (**5**), PMe_3 (**6**), or 4-Mepy (**7**); $n = 1$, L = 2-Mepy (**8**)].—A mixture of $[\text{Cu}_2(\mu\text{-dppy})_3(\text{MeCN})][\text{BF}_4]_2$ and the required ligand (1:2 mol ratio) was stirred in dichloromethane (20 cm^3) at room temperature for 1.5 h. Concentration of the resulting solution and addition of diethyl ether (20 cm^3) led to the precipitation of white solid complexes, (**5**)—(**7**), which were washed with diethyl ether (3 × 10 cm^3) and vacuum dried. Yields (**5**)—(**7**): 65—70%. I.r.: ν(B–F), 1 055s br, (**5**), 1 060s br (**6**), and 1 065s br cm^{-1} (**7**).

In the case of L = 2-Mepy, the complex (**8**) was isolated. Yield: 65%. I.r.: ν(B–F) 1 060s br cm^{-1}.

Crystal Structure of $[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ (**4**).—A white pyramidal crystal of approximate dimensions 0.26 × 0.34 × 0.37 mm was used for the *X*-ray analysis.

Crystal data. $C_{53}H_{45}B_2Cu_2F_8N_4P_3$, M = 1 131.59, monoclinic, space group $P2_1/c$, a = 21.424(7), b = 13.186(6), c = 18.232(6) Å, β = 99.77(2)°, U = 5 076(3) Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections, λ = 1.541 78 Å), Z = 4, D_c = 1.481 g cm^{-3}, $F(000)$ = 2 304, μ(Cu-K_α) = 25.26 cm^{-1}.

Data collection and processing. A Siemens AED single-crystal diffractometer (θ—2θ scan mode, nickel-filtered Cu-K_α radiation) was employed. All reflections with θ in the range 3—70° were measured; of 9 642 independent reflections, 6 539 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. Absorption was ignored because of the low absorbance of the sample.

Structure solution and refinement. Patterson and Fourier methods, block-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all the atoms except the carbons of the phenyl rings. The hydrogen atoms, clearly localized in a Fourier difference map, were not refined but introduced in the final structure-factor calculation with fixed isotropic thermal parameters. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, with K = 1.3094 and g = 0.004, was used in the last cycles of the refinement. Final R and R' values were 0.0657 and 0.0955 respectively.

Programs and sources of scattering factors are given in refs. 14 and 15. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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