



Chelating and bridging diphosphinoamine (PPh₂)₂N(ⁱPr) complexes of copper(I)

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ABSTRACT

The ligand *bis*(diphenylphosphino)isopropylamine (dppipa) has been shown to be a versatile ligand sporting different coordination modes and geometries dictated by copper(I). Most of the molecular structures were confirmed by X-ray crystallography. It is found in a chelating mode, in a monomeric complex when the ligand to copper ratio is 2:1. A tetrameric complex is formed when low ratios of ligand to metal (1:2) were used. But with increasing ratios of ligand to metal (1:1 and 2:1), a trimer or a dimer was obtained depending on the crystallization conditions. Variable temperature ³¹P{¹H} NMR spectra of these complexes in solution showed that the Cu–P bond was labile and the highly strained 4-membered structure chelate found in the solid state readily converted to a bridged structures. On the other hand, complexes with the ligand in a bridging mode in the solid state did not form chelated structures in solution. The effect of adding tetra-alkylammonium salts to solutions of various complexes of dppipa were probed by ³¹P{¹H} NMR and revealed the effect of counter ions on the stability of complexes in solution.

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1. Introduction

The study of transition metal complexes in low oxidation states depends to a large extent on the use of π -acceptor ligands such as carbon monoxide or tertiary phosphines [1]. Organometallic compounds containing diphosphine ligands having a P–C–P backbone have been the subject of numerous investigations [2], while interest in analogous diphosphinoamine ligands (Fig. 1) has been growing rapidly. The latter have proved very versatile catalysts [3] because substituents on both phosphorus and nitrogen atoms can be easily varied with attendant changes in both the P–N–P bond angle and the conformation around the phosphorus centers [4]. Furthermore, fairly small differences in these ligands can cause significant changes in their coordination behavior and the structural features in the resulting complexes [5]. In addition, heterofunctional diphosphazanes bearing P,O-, P,S- or P,N-functionalities at one or both phosphorus centers can be readily prepared. Unfortunately, these ligand systems have not proved versatile due to low thermal stability [6,7].

Though the monodentate mode of coordination of RN(PX₂)₂ is feasible in principle, the choice of substituents on nitrogen favors bidentate ligation through suitable orientation of the phosphorus lone pairs [7]. The planar geometry of nitrogen in diphosphazanes [8] permits facile incorporation of these ligands as chelates or

bridges in transition metal complexes. The PF₂ derivatives of these ligands have been shown by Johnson and Nixon [9], King [3a] and Cotton and his coworkers [10] to be quite versatile in coordination chemistry. The coordination and organometallic chemistry of these short bite diphosphazane ligands [11] have been reviewed extensively [12]. Interest in these ligands also stem from the formation of multinuclear transition metal complexes [13] where the metal atoms are held in close proximity to each other. A variety of complexes of dppipa, have been reported with various transition metals [14,15]. Complexes of (PPh₂)₂N(Ph) (dppan) with copper(I) hexafluorophosphate (NMR studies) [16], Ag(I) complexes of *bis*(diphenylphosphino)amine and those of *bis*(diphenylphosphino)methyl amine have been studied recently [17a,b]. With hydrogen as a substituent on the nitrogen of the PNP, the ligand forms a bridge whereas with a methyl group, it prefers to form a chelate. Recently chelating vs bridging bonding modes of these types of ligands have been reported in case of Pt as well as Co₂Pt clusters [17c].

The present investigation involves the complexation behavior of dppipa with copper(I). Unlike silver(I) which prefers low coordination numbers, copper(I) prefers four coordination. The diphosphinoamine to metal ratio has been found to control the nuclearity and the solid state structure of the copper complexes studied herein. Since the ligands are showing flexible binding modes in the presence of copper(I), we expect them to have good catalytic activities. Thus the utility of these complexes as catalysts in the cyclopropanation of olefins is the subject of a subsequent article [18].

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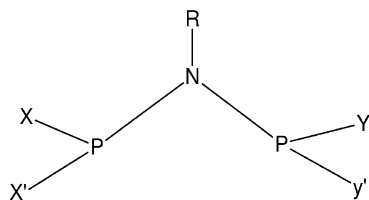


Fig. 1. P–N–P framework.

2. Results and discussion

The nature of the free ligand should be understood before discussing the metal complexes. The $^{31}\text{P}\{^1\text{H}\}$ NMR of the dppipa ligand in CDCl_3 gave a single resonance at δ 48.1 at RT, which split into two clear doublets at δ 52.9 and δ 39.8 at -60°C with $^2J_{\text{PP}} = 24$ Hz [4a]. Repulsion between the lone pairs on phosphorus and the anomeric effect stabilized the C_s conformer making the two phosphorus atoms inequivalent (Fig. 2). The greater stability of the C_s conformer was reflected in the solid state crystal structure of the free ligand [4a]. Single crystals contain well-separated molecules of the C_s conformer, with the lone pairs on phosphorus approximately *trans* and *cis* to the N–C (isopropyl) bond. The P–N bond lengths in the free ligand were 1.706(4) and 1.711(4) Å and the P–N–P bond angle was $122.8(3)^\circ$.

2.1. Copper(I) complexes of dppipa

Complexes of dppipa have been synthesized with various ligand to metal ratios ranging from 2:1 to 1:2 in CH_2Cl_2 . Depending on the copper(I) precursor and the ratio of ligand to metal, different complexes were formed and were isolated by crystallization or precipitation followed by recrystallization. Most of these complexes have been characterized by X-ray crystallography.

2.1.1. Complex 1: $[\text{Cu}(\text{dppipa})_2]\text{ClO}_4$

The first complex (Fig. 3) of dppipa was synthesized by the reaction carried out between the ligand (dppipa) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ in the ratio of 2:1. It was crystallographically characterized as a monomeric bischelate with the counter anion outside the coordination sphere of copper.

There was no significant change in P–N bond lengths on forming the complex whereas there was a definite change in the PNP bond angle (Table 1). A decrease of approx. 17° from the free ligand was observed. Correspondingly there was considerable decrease in the P...P distance from 3.00 Å in the free ligand to 2.71 Å required for the formation of a chelate. Interestingly, in the case of *cis*- $[\text{W}(\text{CO})_4]^i\text{PrN}(\text{PPh}_2)_2$, tungsten imposed a smaller P–N–P angle of $102.5(3)^\circ$ required by the *cis* coordination in an octahedral site [14a]. The solid state structure of **1** showed weak hydrogen bonds with the phenyl ring protons as well as the isopropyl CH proton. These interactions are listed in the Supplementary material (Table S1).

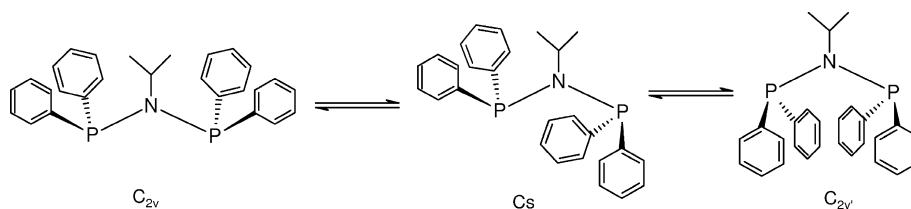


Fig. 2. Conformational changes in dppipa.

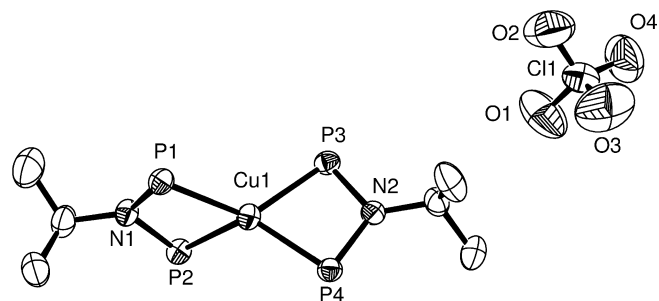
Fig. 3. ORTEP view of complex **1**; $[\text{Cu}(\text{dppipa})_2]\text{ClO}_4$ at 50% thermal ellipsoid probability. Phenyl rings on phosphorus and hydrogen atoms omitted for clarity.

Table 1

Selected bond lengths and bond angles in complex **1**.

Bond lengths (Å)			
Cu1–P1	2.283(1)	P1–N1	1.718(2)
Cu1–P2	2.275(1)	P2–N1	1.715(2)
Cu1–P3	2.295(1)	P3–N2	1.702(2)
Cu1–P4	2.282(1)	P4–N2	1.710(2)
Bond angles ($^\circ$)			
P1–Cu1–P2	73.16(3)	P2–Cu1–P4	122.28(3)
P1–Cu1–P4	143.38(3)	P1–N1–P2	104.62(12)
P2–Cu1–P3	129.80(3)	P3–N2–P4	105.39(12)

2.1.2. Complex 2: $[\text{Cu}_2(\text{dppipa})_2(\text{SCN})_2]$

The reaction of dppipa and CuSCN in a ratio of 1:1 in dichloromethane resulted in an insoluble material. When a similar reaction was carried out with L:M as 2:1, a clear bright yellow solution was obtained from which single crystals were obtained by layering with petroleum ether. The structure of the complex was found to be dimeric from a single crystal X-ray diffraction study. The ORTEP plot of the complex showed (Fig. 4) two dppipa ligands in the chelating mode. The ambidentate anion bridged the metal centers in a symmetrical fashion resulting in a centrosymmetric molecule. Important bond lengths and bond angles are listed in Table 2.

2.1.3. Complex 3: $[\text{Cu}_4(\text{dppipa})_2\text{Cl}_4]$

The tendency of dppipa to adopt a bridging mode was strongest when copper(I) halide precursors were used. However, the ligand exhibited different binding modes with copper(I) when the ratios of ligand to metal and crystallization conditions were changed.

The tetrameric complex (Fig. 5) was obtained by a reaction of dppipa and copper(I) chloride (1:2) in dichloromethane. The complex had all four copper atoms in almost the same plane and there were four μ_2 -chloride bridges. Here the ligand was bound to the metal in a bridging mode unlike the complexes discussed earlier. The PNP ligand bridging the two copper centers, forced the copper atoms to be close to each other (average distance 2.646 Å) as compared to those that were bridged by chloride (2.766 Å) (Table 3). Cl1 and Cl2 were more or less in the same plane as that of the four metal atoms. On the other hand, Cl4 was above and Cl3 below the Cu_4 plane. The phosphorus atoms of one ligand were found to be

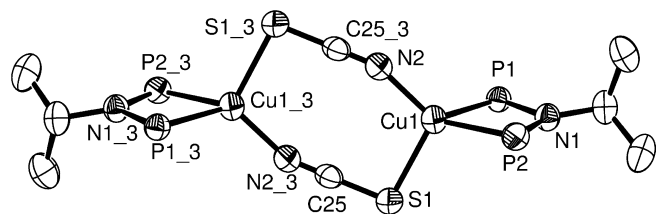


Fig. 4. ORTEP view of complex 2; $[\text{Cu}_2(\text{dppipa})_2(\text{SCN})_2]$ at 50% thermal ellipsoid probability. Phenyl rings on phosphorus and hydrogen atoms omitted for clarity.

above the Cu_4 plane and the other below the plane (Table S2 in Supplementary material). The Cu_4Cl_4 motif had been encountered earlier with *bis*(diphenylphosphino)methane(dppm): $[\text{Cu}_4(\text{dppm})_2(\text{Cl})_4]$ [19]. In this case, the Cu–Cu distances were 2.905 Å for the dppm bridged copper centers and 2.914 Å for the chloride bridged copper centers. The short Cu–Cu distance in the structure reported here were typical of the short bite nature of the diphosphinoamine ligand.

2.1.4. Complex 4: $[\text{Cu}_3(\text{dppipa})_3\text{Cl}_2][\text{CuCl}_2]$

When the ratio of ligand to metal was changed from 1:2 as above to 1:1, a trimeric complex was isolated. The structure was established by single crystal crystallography. The complex (Fig. 6) had three metal centers with three bridging ligands and two chloride ions in the core. Out of the three copper ions, Cu1 and Cu2 were four coordinate and Cu3 was three coordinate as the two chloride caps were unsymmetrical (Table 4). The counter anion in this case was a linear CuCl_2^- ion that showed weak hydrogen bonding contacts with phenyl hydrogen atoms (Table S3 in Supplementary material).

Similar trimeric structures are known with dppm [*bis*(diphenylphosphino)methane] [20] and dppa [*bis*(diphenylphosphino)amine] [21] with average Cu–Cu distance of 3.210(4) Å and 2.989(2) Å, respectively. The Cu–Cl distances varied from 2.407(7) Å to 2.678(6) Å in the former and range from 2.426(2) Å to 2.487(3) Å in the latter. Cu1–Cu3 distance was significantly longer than the

Table 2
Selected bond lengths and bond angles in complex 2.

Bond lengths (Å)			
Cu1–P1	2.318(1)	Cu1–S1	2.350(1)
Cu1–P2	2.277(1)	P1–N1	1.705(2)
Cu1–N2	1.938(2)	P2–N1	1.709(2)
Bond angles (°)			
P1–Cu1–P2	72.63(2)	P2–Cu1–S1	107.04(3)
P1–Cu1–N2	118.34(7)	N2–Cu1–S1	106.08(7)
P1–Cu1–S1	118.76(3)	P1–N1–P2	105.78(11)
P2–Cu1–N2	131.91(7)		

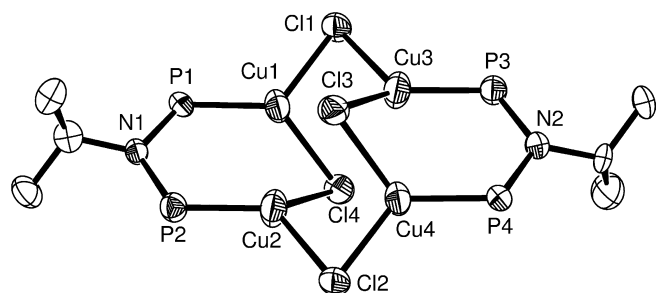


Fig. 5. ORTEP view of complex 3; $[\text{Cu}_4(\text{dppipa})_2(\text{Cl})_4]$ at 50% thermal ellipsoid probability. Phenyl rings on phosphorus and hydrogen atoms omitted for clarity.

Table 3
Selected bond lengths and bond angles in complex 3.

Bond lengths (Å)			
Cu1–Cu2	2.650(2) ^a	Cu3–P3	2.180(3)
Cu1–Cu3	2.748(2) ^b	Cu3–Cl1	2.287(2)
Cu2–Cu4	2.784(2) ^b	Cu3–Cl3	2.446(3)
Cu3–Cu4	2.641(2) ^a	Cu4–P4	2.178(2)
Cu1–P1	2.183(3)	Cu4–Cl2	2.283(2)
Cu1–Cl1	2.283(2)	Cu4–Cl3	2.408(3)
Cu1–Cl4	2.446(3)	P1–N1	1.707(7)
Cu2–P2	2.170(3)	P2–N1	1.71(1)
Cu2–Cl2	2.290(3)	P3–N2	1.71(1)
Cu2–Cl4	2.389(3)	P4–N2	1.714(6)
Bond angles (°)			
P1–Cu1–Cl1	124.95(10)	P3–Cu3–Cl3	132.29(10)
P1–Cu1–Cl4	121.53(10)	P3–Cu3–Cu1	161.62(10)
P1–Cu1–Cu2	91.88(8)	P3–Cu3–Cu4	93.62(8)
P1–Cu1–Cu3	174.03(11)	Cl1–Cu3–Cl3	97.96(9)
Cl1–Cu1–Cl4	100.59(9)	P4–Cu4–Cl2	123.41(10)
P2–Cu2–Cl2	121.19(10)	P4–Cu4–Cl3	124.85(10)
P2–Cu2–Cl4	132.74(11)	P4–Cu4–Cu2	167.33(10)
P2–Cu2–Cu1	93.71(8)	P4–Cu4–Cu3	92.63(8)
P2–Cu2–Cu4	157.48(10)	Cl2–Cu4–Cl3	103.15(9)
Cl2–Cu2–Cl4	100.19(9)	P1–N1–P2	116.1(4)
P3–Cu3–Cl1	122.03(10)	P3–N2–P4	116.0(4)

^a Phosphine bridged.

^b Chloride bridged.

other two. Unlike the analogous dppm bridged complex [20] where all the phosphorus atoms were almost in the same plane, two of the three dppipa ligands in this complex straddled the plane of the copper atoms. The third dppipa ligand retained both phosphorus atoms on one side of the plane.

2.1.5. Complex 6: $[\text{Cu}_3(\text{dppipa})_3\text{Br}_2][\text{CuBr}_2^-]$

Using a procedure similar to that used for the preparation of the chloride trimer, the analogous bromide trimer was isolated. It was characterized by single crystal X-ray crystallography. The complex was isostructural to the chloride complex with three bridging ligands, two bromide caps in the core and a linear CuBr_2^- as the counter anion. Cu1 was three coordinate and Cu2, Cu3 are four coordinate as the two bromine caps were unsymmetrical. The Cu–Br distances (see Fig. S1 and Table S5 in Supplementary material) varied from 2.529(1) Å to 2.651(1) Å. The Cu–Cu distances were in the range of 2.824(1) Å and 2.999(1) Å. The analogous bromide trimer with dppm bridging ligands had much longer Cu–Cu distances compared to those reported here [22]. The influence of the PNP ligand in bringing the copper centers closer together is obvious (see Table 5).

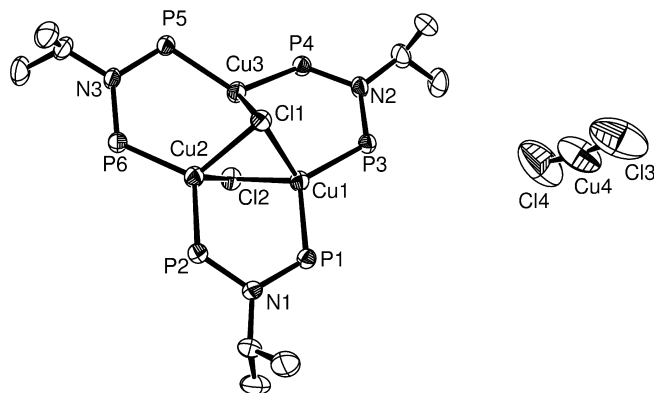


Fig. 6. ORTEP view of complex 4; $[\text{Cu}_3(\text{dppipa})_3(\text{Cl})_2][\text{CuCl}_2]$ at 50% thermal ellipsoid probability. Phenyl rings on phosphorus and hydrogen atoms omitted for clarity.

Table 4
Selected bond lengths and bond angles in complex **4**.

Bond lengths (Å)			
Cu1–Cu2	2.863(1)	Cu2–Cl2	2.440(1)
Cu1–Cu3	2.972(1)	Cu3–Cl1	2.440(1)
Cu2–Cu3	2.822(1)	Cu3–Cl2	2.536(1)
Cu1–P1	2.254(1)	Cu4–Cl3	2.047(3)
Cu1–P3	2.251(1)	Cu4–Cl4	2.015(3)
Cu2–P2	2.252(1)	P1–N1	1.714(4)
Cu2–P6	2.261(1)	P2–N1	1.715(4)
Cu3–P4	2.271(14)	P3–N2	1.720(4)
Cu3–P5	2.271(1)	P4–N2	1.702(4)
Cu1–Cl1	2.481(1)	P5–N3	1.703(4)
Cu1–Cl2	2.409(1)	P6–N3	1.712(4)
Cu2–Cl1	2.463(1)		
Bond angles (°)			
P1–Cu1–P3	119.74(5)	P4–Cu3–P5	122.92(5)
P1–Cu1–Cl1	107.83(5)	P4–Cu3–Cl1	111.85(5)
P1–Cu1–Cl2	111.08(5)	P4–Cu3–Cl2	99.04(5)
P3–Cu1–Cl1	106.76(5)	P5–Cu3–Cl1	105.65(5)
P3–Cu1–Cl2	112.83(5)	P5–Cu3–Cl2	120.28(5)
P2–Cu2–P6	119.26(5)	Cl3–Cu4–Cl4	174.84(18)
P2–Cu2–Cl1	106.46(5)	P1–N1–P2	117.2(2)
P2–Cu2–Cl2	114.24(5)	P3–N2–P4	117.6(2)
P6–Cu2–Cl1	117.96(5)	P4–N3–P6	117.9(2)
P6–Cu2–Cl2	101.16(5)		

2.1.6. Complexes **7** and **8**

Complexes **7** and **8** based on iodide, similar to **3** and **6**, were isolated but were not structurally characterizable.

2.1.7. Complex **9**: [Cu₂(dppipa)₂Cl₂] and complex **10**: [Cu₂(dppipa)₂Br₂]

We recently reported two dimeric complexes of dppipa [23]. These complexes had two Cu(I) centers with one bridging dppipa ligand and one bridging halide. One of the metal centers had one chelating ligand and the other one had one terminal halide ion. The formation of these complexes depended on the crystallization conditions employed and are discussed below.

Different complexes were obtained with L:CuX (X = Cl, Br, I) ratios of 1:1 or 2:1, because of differences in the polarity of the sol-

vent used and the time taken for crystallization. The trimer (**4**) crystallized out in about four to five days from the reaction mixture dissolved in 7 ml of CH₂Cl₂ and 14 ml of petroleum ether. Whereas, when the same reaction mixture was concentrated up to 2 ml and around 7 ml of petroleum ether was allowed to diffuse through the solution, a different complex [Cu₂(dppipa)₂Cl₂] (**9**) having a dimeric core crystallized out in 10–12 h [23]. This suggested that the trimer was thermodynamically more stable and that the dimeric complex was an intermediate species. Similar behavior was observed in the case of the bromide trimer (**6**) and the corresponding dimeric compound [Cu₂(dppipa)₂Br₂] (**10**) [23]. A similar motif had been found in the case of ((Dimethylamino)methyl)phenylphosphine-N,N',N'',P ligand that bridged as well as chelated copper(I) [24].

2.2. Variable temperature ³¹P{¹H} NMR studies

The relative stability of chelating and bridging modes could be gauged by examining the nature of these complexes in solution using variable temperature ³¹P{¹H} NMR experiments. This was important since the structures seen in the solid state could be attributed to selective crystallization of one of the forms.

The Cu–P bond was labile in the case of dppipa complexes and in solution it generated a set of two doublets similar to that observed for the C_s conformer of dppipa with different chemical shifts and coupling constants depending upon the chemical environment around phosphorus atoms in the corresponding complex. The chelating phosphorus atoms appeared in the range of 79–82 ppm and bridging ones fell in the range of 55–64 ppm. Invariably the complexes having a chelating phosphine, were unstable in solution and tended to go to the more stable bridging geometry. However, complexes with a bridging ligand retained their structure in solution and did not equilibrate with structures having a chelated ligand so easily.

2.2.1. Complex **1**, [Cu(dppipa)₂]ClO₄

The RT spectrum (Fig. 7) was deceptively simple with one peak at δ 81.3 and the other at δ 55.8. At lower temperatures, the peak at δ 81.3 became sharper (FWHM: 174 Hz at RT to 92 Hz at –60 °C).

Table 5
Crystallographic data for copper(I) dppipa complexes.

	1	2	3	4	6
Empirical formula	C ₅₄ H ₅₄ ClCuN ₂ O ₄ P ₄	C ₅₆ H ₅₄ Cu ₂ N ₄ P ₄ S ₂	C ₆₂ H ₇₂ Cl ₄ Cu ₄ N ₂ P ₄	C ₈₈ H ₉₇ Cl ₄ Cu ₄ N ₃ P ₆	C ₈₇ H ₉₅ Br ₄ Cu ₄ N ₃ P ₆
Formula weight	1017.86	1098.11	1365.06	1778.47	1943.29
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P1	P1
a (Å)	12.855(2)	10.283(3)	16.026(4)	14.330(3)	14.3941(15)
b (Å)	21.396(4)	16.669(4)	16.213(3)	15.146(3)	15.1690(16)
c (Å)	18.629(3)	16.217(4)	23.880(10)	19.785(4)	19.948(2)
α (°)	90	90	90	67.875(3)	67.935(2)
β (°)	98.217(3)	98.47(2)	100.024(10)	87.712(3)	87.494(2)
γ (°)	90	90	90	83.105(3)	81.945(2)
Volume (Å ³)	5071.5(16)	2749.4	6110(3)	3949.3(13)	3996.5(7)
Z	4	2	4	2	2
Density (calculated) (mg/m ³)	1.333	1.326	1.484	1.496	1.615
Crystal size (mm ³)	0.30 × 0.2 × 0.15	0.4 × 0.22 × 0.20	0.30 × 0.16 × 0.10	0.48 × 0.32 × 0.20	0.28 × 0.20 × 0.18
Reflections collected	38723	5147	10735	41734	1970
Independent reflections	9947 [0.1056]	4831 [0.0137]	10735 [0.0602]	15552 [0.0585]	18470 [0.0826]
[R _{int}]					
Final R ₁ ^a , wR ₂ ^b [I > 2σ(I)]	R ₁ = 0.0507, wR ₂ = 0.1135	R ₁ = 0.0328, wR ₂ = 0.0743	R ₁ = 0.0761, wR ₂ = 0.2032	R ₁ = 0.0595, wR ₂ = 0.1456	R ₁ = 0.0616, wR ₂ = 0.1212
Final R ₁ ^a , wR ₂ ^b (all data)	R ₁ = 0.0774, wR ₂ = 0.1252	R ₁ = 0.0535, wR ₂ = 0.0822	R ₁ = 0.1700, wR ₂ = 0.2420	R ₁ = 0.0963, wR ₂ = 0.1634	R ₁ = 0.1474, wR ₂ = 0.1505
Goodness-of-fit (GOF) on F ₂ ^c	0.959	1.064	1.046	0.950	0.928

^a R₁ = (∑||F_o – |F_c||) / (∑|F_o|).^b wR₂ = [∑(w|F_o – |F_c|)² / ∑w|F_o|²]^{1/2}.^c GOF = [w(F_o² – F_c²)² / (n – p)]^{1/2}.

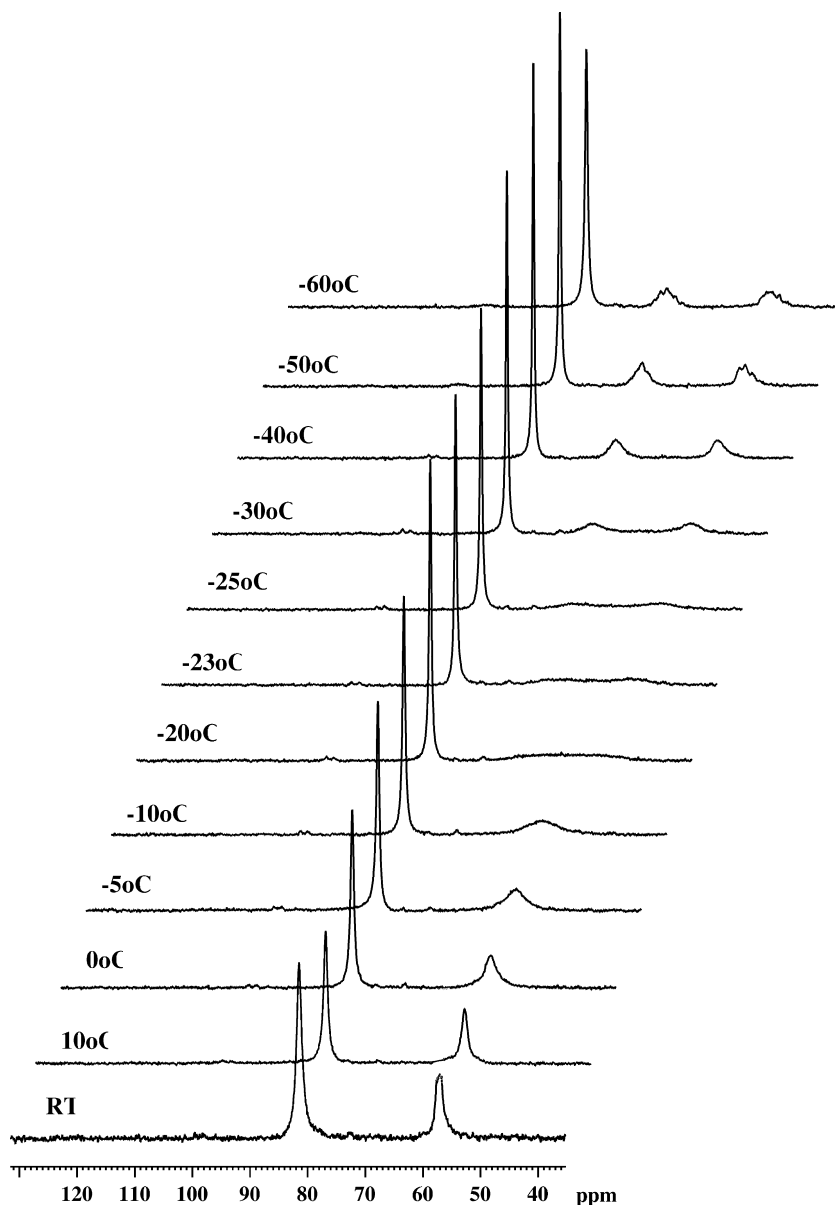


Fig. 7. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex 1.

But the other peak broadened and then split into two peaks at δ 65.9 and δ 48.6. These could be assigned to the ligand bound in a monodentate fashion (species **B** in Scheme 1), *vide infra*. Chelation with Cu(I) induced a lot of strain on the ligand with a significant drop in the PNP angle. Hence it led to dissociation of the coordinated phosphorus in solution. This hypothesis was supported by VT $^{31}\text{P}\{^1\text{H}\}$ NMR and the equilibria in solution is illustrated in Scheme 1.

2.2.2. Complex 2, $[\text{Cu}_2(\text{dppipa})_2(\text{SCN})_2]$

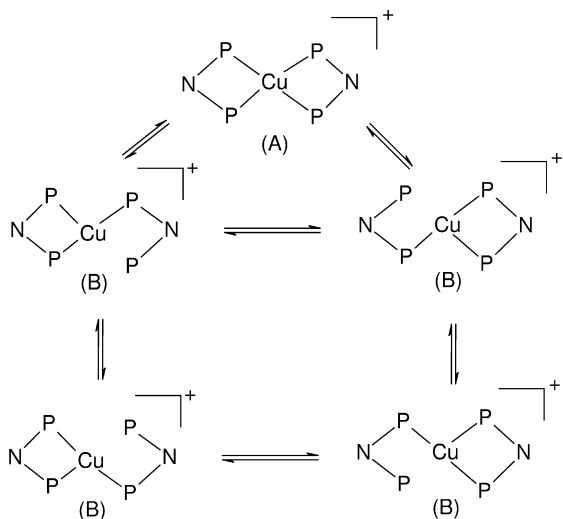
Due to poor solubility in chlorinated solvents at low temperatures, the spectra were not very clear, although the presence of dissociated dppipa was discernible (Supplementary material, Fig. S2).

2.2.3. Complex 3, $[\text{Cu}_4(\text{dppipa})_2\text{Cl}_4]$

A singlet at δ 63.3 was obtained in ^{31}P NMR at room temperature due to rapid flipping of the phosphorus atoms above and below the plane. At -60°C , two clear doublets at δ 69.7 and δ 55.9 were obtained due to magnetically different phosphorus atoms

on each ligand (coupling constant $^2J_{\text{PP}} = 228$ Hz). All the species having a bridging PNP ligand appeared as doublets (Fig. 8). Line shape analyses were carried out using WINDNMR software [25] (for simulated spectra see Supplementary material, Fig. S3). Activation parameters were calculated using the Eyring equation $\ln(K/T) = -(\Delta H/R) \cdot (1/T) + \ln(K_b/h) + \Delta S/R$ (where K = rate constant, ΔH = enthalpy of activation, ΔS = entropy of activation, ΔG = free energy of activation, R = gas constant ($1.9872 \text{ cal K}^{-1} \text{ mol}^{-1}$), T = temperature (K), K_b = Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$) and h = Planck constant ($6.626 \times 10^{-34} \text{ J s}$). A plot of $\ln(K/T)$ versus $1/T$ is shown in Fig. 9 in Supplementary material (Fig. S4). From slope as $-\Delta H/R$, ΔH was found to be 14.46 kcal/mol and from the intercept, $\ln(K_b)/h + \Delta S/R$, ΔS was found to be 21.009 cal/mol/K. ΔG of the process were calculated (from $\Delta G = \Delta H - T\Delta S$) to be 8.20 kcal/mol.

The single crystals of the analogous tetrameric bromide complex **5** could not be obtained. Nevertheless, it exhibited a solution behavior (Supplementary material) similar to what was seen in the case of the chloride tetramer in the variable temperature NMR experiment. So a similar structure is expected for the bromide complex.



Scheme 1. Dynamic equilibrium in solution for complex 1.

2.2.4. Complex 4, $[\text{Cu}_3(\text{dppipa})_3\text{Cl}_2][\text{CuCl}_2]$

The ^{31}P NMR resonance for the trimer was at δ 55.9 where all six phosphorus were equivalent (Fig. S5 in Supplementary material). The δ 55.9 peak started broadening with fall in temperature. The

positional differences of the phosphorus atoms as discussed in the solid state structure resulted in two sets of overlapping doublets emerging at -40 °C at δ 65.8 and δ 47.5. Even at -60 °C, they exchanged rapidly resulting in large line widths of approximately 800 Hz. Given the small difference in the environments of the phosphorus, the appearance of two peaks was probably due to dissociation and exchange of bound and free dppipa. Similar observations were made in the case of the bromide complex **6**, $[\text{Cu}_3(\text{dppipa})_3\text{Br}_2][\text{CuBr}_2]$.

2.2.5. Complex 7, $[\text{Cu}_4(\text{dppipa})_2\text{I}_4]$ and complex 8, $[\text{Cu}_3(\text{dppipa})_3\text{I}_2]$

Complexes were sparingly soluble in chlorinated solvents, hence variable temperature NMR were not recorded.

2.2.6. Complex 9, $[\text{Cu}_2(\text{dppipa})_2\text{Cl}_2]$

The RT spectrum showed two peaks (81.3 and 55.9) assigned to chelating (δ 81.3) and bridging (δ 55.9) phosphorus. At low temperature, the 81.3 ppm peak disappeared and the one at higher field (bridging) split into two multiplets centered at δ 66.4 and δ 48.2. The low temperature spectra (-60 °C) of **4** and **9** were similar (Fig. S6 in Supplementary material). The similarity presumably resulted from the formation of an intermediate chloride bridged species with pendant PNP ligands in solution. Similarly the bromide dimer **10**, $[\text{Cu}_2(\text{dppipa})_2\text{Br}_2]$ exhibited two sets of multiplets at low temperature.

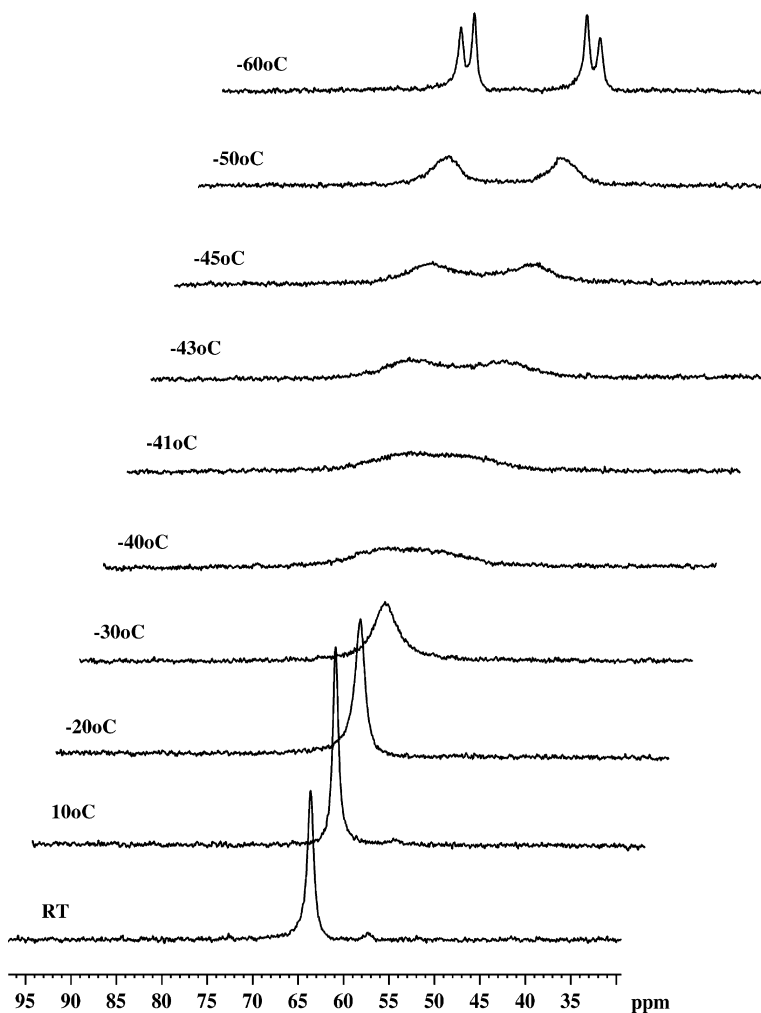


Fig. 8. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex 3.

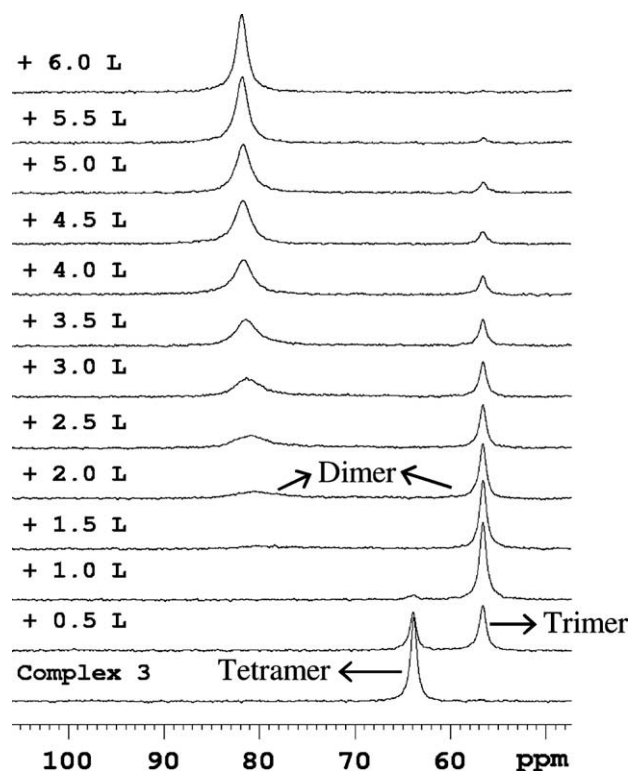
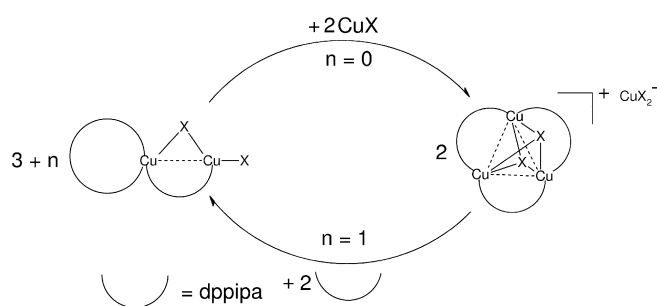
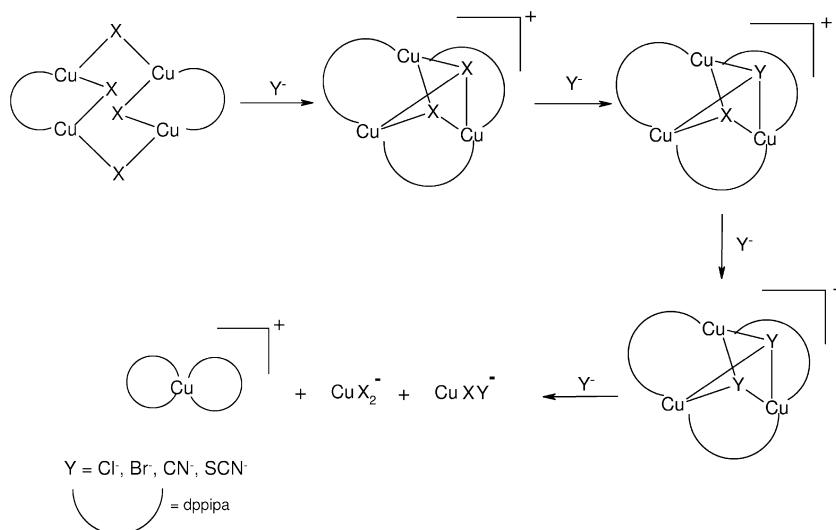


Fig. 9. Changes in ^{31}P NMR of complex **3** on addition of ligand ($L = \text{dppipa}$).



Scheme 2. Proposed interconversion of dimer and trimer.



Scheme 3. Pathway for exchange of anion in case of dppipa tetrameric complexes.

The above mentioned results indicated that the chelated structures were not stable in solution and tend to open up in solution to form bridged structures. In the case of the dimer and trimer, the ^{31}P NMR was actually similar at $-60\text{ }^\circ\text{C}$, and matched with the one obtained for the bis chelate perchlorate complex. This degeneracy at $-60\text{ }^\circ\text{C}$ supports the hypothesis that the chelated complex after opening up in solution forms more stable bridged species.

2.3. Interconversion of complexes

The conversion of dimer into a trimer could be realized when two of the dimeric species $[\text{Cu}_2(\text{dppipa})_2\text{X}_2]$ released one free ligand and one CuX_2^- species to form a $[\text{Cu}_3(\text{dppipa})_3\text{X}_2]$ species. Addition of CuX to a solution of dimer led to the formation of trimer and addition of dppipa to a solution of the trimer resulted in the formation of the dimer ($^{31}\text{P}\{^1\text{H}\}$ NMR) (Scheme 2).

The chloride and bromide complexes showed three diverse structures with different nuclearity and modes of ligand binding. All three clusters had different L:M ratios. On addition of ligand, the tetramer converted to the trimeric species, and then the dimeric species and ultimately to a chelated species. This could be achieved by changing L:M ratio starting from 1:2 in tetramer to 3:4 in trimer to 1:1 in dimer and then 2:1 in the chelated species (Fig. 9).

In order to find the possibility of converting complexes having the same ratio of ligands/metal, we carried out $^{31}\text{P}\{^1\text{H}\}$ NMR experiments with different anions (see Supplementary material; Fig. S7–S11). A known concentration of the complex was titrated with an appropriate tetra-alkylammonium salt of the anion in CDCl_3 .

The halide exchange observed in the case of the chloride and bromide tetramers could be explained by Scheme 3 (also Fig. S8). Addition of any halide anion to the tetramer (^{31}P NMR: 57 ppm) first led to the formation a trimer (^{31}P NMR: 56 ppm for hetero-capped trimer and 54 ppm for homo-capped trimer), from which the halide caps were exchanged. Excess of anion scavenged the metal as CuX_2^- and depleted the concentration of copper, thus leading to the formation of a trimer with a M:L ratio of 4:3 and eventually leading to a 1:2 species (^{31}P NMR: 81 ppm).

Addition of chloride ions to the tetrameric chloride complex of dppipa (**3**) gave similar results indicating that the formation of a trimeric species was a must before they eventually form the 1:2 species in the presence of excess anion. The trimeric complexes **4** and **6** also formed the chelate species on addition of halide as well as cyanide ions.

The above results showed that even though the chelated species were not favored in solution, their formation could be forced by having a large ligand to metal ratio making the chelated species favorable.

3. Summary and conclusions

Diphosphinoamines are quite flexible ligands and capable of bridging and chelating copper with equal ease. But their solution behavior at low temperatures gives away the preference of the ligand for non-chelated structures. Chelation of the ligand results in a 4-membered ring with the PNP bond angle close to 105° that induces a lot of strain on the ligand. Hence in solution, the ligands tend to dissociate and stay in sterically less demanding, monodentate or bridging modes. That the ligand adopts a comfortable conformation in the bridging mode was confirmed by the fact that the tetramer and the trimer retain the bridging mode in solution. Although bridging dppipa is also labile, Cu–P bonds are shorter in bridges than in the chelate structures showing that the bonding of copper(I) with dppipa is clearly stronger in its bridging mode.

The variety of structures found in these complexes was orchestrated by ligand to metal ratio. In the absence of other coordinating ligands, the ligand was forced to form a bis chelate. Structural diversity is at its peak in the case of halide complexes, wherein three different complexes: dimer, trimer and tetramer are obtained. The structure of the tetramer is forced by low ligand to metal ratio. The dimer (where one dppipa was forced into the chelating mode) is an intermediate species, providing a snapshot of how the trimer is formed. Even though the trimer is thermodynamically favored, the slow rate of conversion of the dimer to the trimer permits isolation of the dimer (in the case of chloride and bromide) when crystallization is accelerated.

The present work brings out the ability of diphosphinoamines to adopt various binding modes. By just tuning the ligand to metal ratio, a variety of Cu(I) complexes with different nuclearity can be synthesized. The structures formed by the ligand with copper(I) are similar to formed by the ligand where H and Ph are replaced by ⁱPr on the nitrogen. In solution, the electronic differences are clearly manifested as the dppipa complexes were labile due to its poorer π -accepting character.

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Appendix A. Supplementary material

CCDC 191475, 191472, 191474, 191473 and 254021 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.028.

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