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Why are the $\{Cu_4N_4\}$ rings in copper(I) phosphinimide clusters $[Cu\{\mu\text{-}N{=}PR_3\}]_4$ (R = NMe$_3$ or Ph) planar?†‡

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The copper phosphinimide complexes $[Cu\{\mu\text{-}N{=}PR_3\}]_4$ (**1**, R = NMe$_2$ and **2**, R = Ph) were obtained in good yields from the reactions of Cu[Mes] (Mes = mesityl, $C_6H_2Me_3$-2,4,6) with the corresponding iminophosphoranes, HNPR$_3$. The molecular structures of **1** and **2** reveal the presence of planar eight-membered $\{Cu_4N_4\}$ rings which contrasts with the saddle-shaped $\{M_4N_4\}$ rings found in related metal phosphinimide complexes. According to computations, there is negligible aromaticity in the planar $\{Cu_4N_4\}$ rings in **1** and **2** and the saddle shape observed in related $\{M_4N_4\}$ rings is due to steric factors.

Introduction

The significance of iminophosphoranes is well established in both organic synthesis[1] and organometallic chemistry,[2] with metal phosphinimide complexes (especially those of titanium and some rare earth elements) having been exploited in the development of highly efficient of '*non-metallocene*' based catalysts,[3] of the general form $(R'_3PN)_2MR_x$ and $(Cp)MR_x(NPR'_3)$ (R′ = alkyl or aryl, R = alkyl). In comparison, exploitation of metal phosphinimide complexes in organic synthesis is predominantly limited to the use of lithium phosphinimide systems, which find utility in a number of areas including, as an $[NH_2^-]$ synthon, in the preparation of non-ionic phosphazene bases, in dehydrocoupling of primary and secondary phosphines, in the synthesis of primary, secondary, cyclic or functional amines, as well as in the generation of heteroatomic linkages (P–N–P, P–N–As, P–N–S).[1a,b]

The chemistry of iminophosphoranes is intrinsically associated by an isolobal, isoelectronic and isoneutral relationship with phosphorus ylides and phosphine oxides. The P═E bonding (E = CH$_2$, NH and O) in these systems being viewed as a resonance hybrid between a double bonded neutral 'ylene' form and a zwitterionic 'ylide' form (Fig. 1).[4]

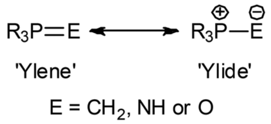

Fig. 1 Hybrid resonance structures of R$_3$P═E.

Given the developing utility of lithium phosphinamide complexes, it has been suggested that the preparation and development of potassium,[5] magnesium,[6] nickel, palladium and copper derivatives may lead to promising applications in organic synthesis.[1a] Indeed, the novel Co(I) and Ni(I) complexes $[Co(\mu_2\text{-}NP^tBu_3)]_4$ and $[Ni(\mu_2\text{-}NP^tBu_3)]_4$ have both been reported recently, along with their use as catalysts in the mild hydrogenation of alkenes and alkynes.[7]

Until now, the isolation and unambiguous characterisation of a neutral homoleptic *N*-Cu(I)-metallated iminophosphorane complexes has not, to our knowledge, been reported, although the related cationic systems, $[Cu_4(NHPEt_3)_4]^{4+}$,[8] and the cubic $[M_{12}(NPEt_3)_8]^{4+}$ (M = Cu(I) or Ag(I)) clusters[9] and $[M_3(\mu\text{-}NPR_3)(PR_3)_3]^{2+}$ (M = Ag(I) or Au(I); R = Me or Ph) systems[10] have been described. Other structurally characterised phosphinimide complexes of copper are limited to the Cu(II)–acetate systems $Cu(HNPPh_3)_2(OAc)_2$, $[Cu_2(HNPPh_3)_2(OAc)_4]$[11] and $[Cu_4(NPMe_3)_3(OAc)_5]$[12] and the mixed-valence species $[Cu_6Br_6(NPMe_3)_4]$, $[Cu_6Cl_7(NPMe_3)_4]$ and $[Cu_6Cl_6(NPMe_3)_4]^+$.[13] Continuing our ongoing research at Bath into the coordination chemistry of Group 11 metals with anionic nitrogen coordination ligands,[14] we report here the syntheses and structural characterisations, by single crystal X-ray diffraction, of the copper(I) phosphinimide complexes $[c\text{-}\{Cu[\mu\text{-}NP(NMe_2)_3]\}_4]$ (**1**) and $[c\text{-}\{Cu[\mu\text{-}NPPh_3]\}_4]$ (**2**).

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† Dedicated to the memory of Prof. Kenneth Wade FRS, an inspirational thinker, teacher, mentor and friend.

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Results and discussion

Syntheses and characterisation

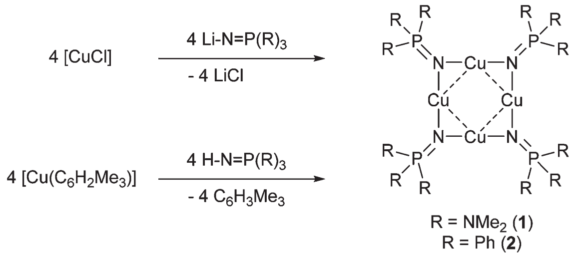
Initial reactions to prepare Cu(I) phosphinimide complexes **1** and **2** focussed on the reaction of CuCl with either $[LiNP(NMe_2)_3]$[15] or $[LiNPPh_3]$[16] in THF (Scheme 1). The $[LiNP(NR_2)_3]$ complexes were made *in situ* from *n*-butyllithium and $HNP(NR_2)_3$. While successful, these reactions were low yielding (17–21%), therefore an alternative synthetic procedure utilising the reagent [Cu(Mes)] (Mes = $C_6H_2Me_3$-2,4,6) was investigated.

The reaction of [Cu(Mes)] with $HNP(NMe_2)_3$ in toluene (Scheme 1) at low temperature (−78 °C) produced an immediate reaction with the solution turning from pale yellow to colourless. Warming of the solution to ambient temperature followed by filtration, *via* cannula, and cooling gave a crop of pale yellow crystals (**1**) in 78% isolated yield. A similar reaction of $HNPPh_3$ with [Cu(Mes)] followed by filtration and cooling afforded pale yellow crystalline material (**2**), in 70% isolated yield.

For both complexes **1** and **2**, NMR spectroscopic data reveal the absence of resonances associated with phosphinamide hydrogen atoms.[17] In the case of **1**, the ^1H NMR spectrum (in C_6D_6) shows resonances for the NMe_2 moieties at $\delta = 2.72$ ppm and a single resonance in the ^{31}P NMR spectrum at $\delta = 32.9$ ppm. Correspondingly, the ^1H NMR spectrum of **2** (in CD_2Cl_2) shows the presence of the aromatic CH groups on the phosphinimide ligand and the ^{31}P NMR spectrum shows a single resonance at $\delta = 15.9$ ppm.

X-ray crystallography

Single-crystal X-ray diffraction studies were carried out on crystals of **1** and **2** to determine their solid-state structures. Complex **1** crystallises in the space group $P2_1/n$ with the molecule sitting on a centre of symmetry such that only half of complex **1** is present in the asymmetric unit. Complex **2** crystallises in the space group $P2_1/c$ and one molecule of the complex is present in the asymmetric unit cell (along with half of a disordered toluene molecule residing on a centre of crystallographic symmetry such that one toluene molecule is present for two molecules of **2**). The molecular structures of complexes **1** and **2** are shown in Fig. 2 and selected structural parameters listed in Table 1. Complexes **1** and **2** are amongst only a relatively small number of known homoleptic planar, tetranuclear coinage metal(I) clusters singly bridged by monoanionic ligands, and represent the first examples of homoleptic Group 11 phosphinimide complexes. The planar core contrasts with other reported $\{M_4N_4\}$ phosphinimide complexes where the $\{M_4N_4\}$ cores are either cubic[18] or saddled (approx. D_{2d} symmetry, Fig. 3).[7]

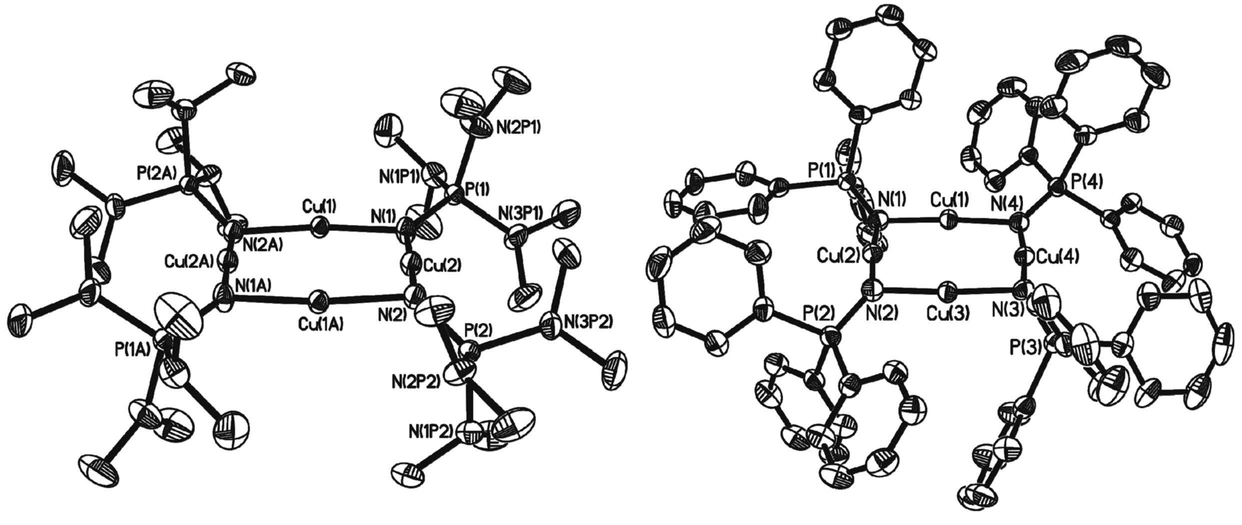


Scheme 1

The structural element of interest in both **1** and **2** is the presence of a square-planar centro-symmetric eight-membered $(CuN)_4$ ring with N–Cu–N angles close to 180° [N–Cu–$N_{(Ave)}$; (**1**) 174.95(8)°, (**2**) 175.46(15)°: Cu–N; (**1**) 1.854(2)Å, (**2**) 1.854(3)Å] which are comparable to those of other two-coordinate or quasi-two-coordinate Cu(I) complexes in a nitrogen coordination environment[14a,d,19] and Cu–N–Cu angles close to 90° (av. 93.62(8)°). The planar $\{Cu_4\}$ cores of **1** and **2** (with approx. D_{4h} symmetry, Fig. 3) have each Cu atom bonded to two doubly bridging phosphinimide ligands (μ^2-N=PR_3) *via* the nitrogen atom creating a two-coordinate geometry about the copper atoms. While the average Cu⋯Cu distances [(**1**): 2.702(3)Å, (**2**): 2.705(6)Å] are shorter than the sum of the van der Waals radii of Cu (1.40 Å)[20] and within the range for potential d^{10}–d^{10} closed shell interactions as observed for unsupported Cu(I)–Cu(I) interactions, the Cu–Cu distances in **1** and **2** are at the longer end of the scale observed for ligand-supported cuprophilic interactions.[14a]

The average P–N bond lengths observed in both **1** and **2** [**1**: 1.545(2)Å; **2**: 1.556(4)Å] are both marginally shorter than those found in the parent iminophosphorane systems (1.557(1) Å and 1.582(2) Å respectively)[21] suggesting retention of similar P–N bond character to that the parent ligand with some electrostatic shortening. Pyramidalisation of the nitrogen atoms of the ligands is indicated by the sum of angles about each nitrogen atom [for **1** N1: $\Sigma_N = 355.33(10)°$, N2: $\Sigma_N = 343.64(10)°$; for **2** N1: $\Sigma_N = 351.9(2)°$, N2: $\Sigma_N = 342.4(2)°$, N3: $\Sigma_N = 341.4(2)°$, N4: $\Sigma_N = 352.3(2)°$], such that the P–N vectors are at an angle to the $\{Cu_4\}$ planes in both **1** and **2** [For **1**: P(1)–N(1)–X = 162.56(3)°; P(2)–N(2)–X = 147.58(3)°, For **2**: P(1)–N(1)–X = 155.95(3)°; P(2)–N(2)–X = 146.32(3)°, P(3)–N(3)–X = 143.27(3)°; P(4)–N(4)–X = 157.85(3)° (where X is the midpoint between two Cu atoms)]. Similar bonding geometries have been reported previously for magnesium phosphinimide complexes and are proposed to originate from the ylidic character of the P–N bonding with a lone pair of electrons residing on the N atom in a predominantly p-type orbital (Fig. 1).[6] The distortion of the ligands away from co-planarity with the $\{Cu_4\}$ cores result in a *cis*, *trans*, *cis*, *trans* (*c*,*t*,*c* *t*) orientation with respect to each Cu–Cu interaction around the $\{Cu_4\}$ ring (conformer A, Fig. 4).

In a more general context, the planar $\{Cu_4N_4\}$ cores of **1** and **2** contrast to the saddle shaped geometries observed for other copper imido complexes (Fig. 5) such as $[Cu(\mu_2\text{-}N{=}C^tBu_2)]_4$ (saddle angles, θ = 95.2,94.1°),[22] $[Cu(\mu_2\text{-}N{=}C^tBuPh)]_4$ [23] (θ = 130.9,131.2°) and $[Cu(\mu_2\text{-}N{=}CPh_2)]_4$, ($\theta$ = 141.9°)[22] which contain $\{Cu_4N_4\}$ rings with bridging imino ligands, in which each imino nitrogen atom has a planar coordination geometry at the nitrogen (conformer D, Fig. 4). The structurally related copper(I) amide complexes $[Cu_4(NR_2)_4]$ (NR_2 = NMe_2, NEt_2, and N{*c*-$(CH_2)_4$}), also form tetrameric clusters with a central 8 membered $\{Cu_4N_4\}$ core; while both



(1) (2)

Fig. 2 Molecular structures of the complexes **1** and **2** (50% probability ellipsoids). Hydrogen atoms in **1** and **2** have been omitted for clarity. Symmetry transformations used to generate equivalent atoms in **1**: −*X*, −*Y* + 1, −*Z* + 1.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2** from experimental (X-ray) and optimised (DFT) geometries

	$\mathbf{1}^a$	$\mathbf{1}^a$ (calc)	$\mathbf{2}^a$	$\mathbf{2}^b$ (calc)
Cu(1)–Cu(2)	2.7484(3)	2.854	2.7479(7)	2.830
Cu(2)–Cu(1A/3)	2.6556(3)	2.760	2.6436(6)	2.825
Cu(3)–Cu(4)			2.7508(7)	2.830
Cu(4)–Cu(1)			2.6762(6)	2.825
Cu(1)–N(1)	1.8454(17)	1.860	1.861(4)	1.860
Cu(1)–N(2A/4)	1.8550(17)	1.863	1.855(3)	1.864
Cu(2)–N(1)	1.8561(17)	1.864	1.854(3)	1.861
Cu(2)–N(2/3)	1.8576(17)	1.869	1.861(3)	1.864
Cu(3)–N(2)			1.848(3)	1.861
Cu(3)–N(3)			1.861(3)	1.864
Cu(4)–N(3)			1.850(3)	1.860
Cu(4)–N(4)			1.846(3)	1.864
N(1)–P(1)	1.5413(17)	1.554	1.551(3)	1.568
N(2)–P(2)	1.5480(17)	1.558	1.559(4)	1.568
N(3)–P(3)			1.557(3)	1.569
N(4)–P(4)			1.555(4)	1.568
Cu(2)–Cu(1)–Cu(2A/4)	85.518(10)	89.73	91.30(2)	90.018
Cu(1)–Cu(2)–Cu(1A/3)	92.482(10)	90.27	88.74(2)	89.956
Cu(2)–Cu(3)–Cu(4)			91.94(2)	90.020
Cu(3)–Cu(4)–Cu(1)			88.02(2)	89.961
N(1)–Cu(1)–N(2A/4)	172.91(8)	171.66	176.11(15)	170.14
N(1)–Cu(2)–N(2)	176.98(8)	172.24	175.38(15)	170.11
N(2)–Cu(3)–N(3)			176.65(16)	170.17
N(3)–Cu(4)–N(4)			173.69(15)	170.09

[a] Conformer A. [b] Conformer B (see Fig. 4).

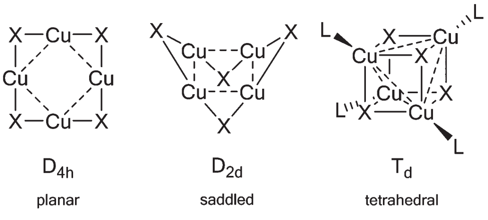


Fig. 3 Geometries for Cu_4X_4 and $Cu_4X_4L_4$ clusters.

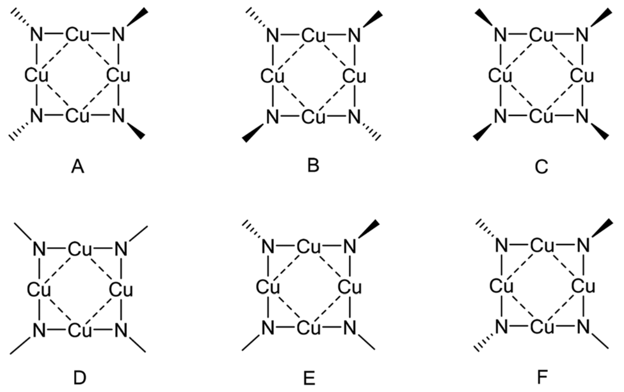


Fig. 4 Conformers for $\{Cu_4N_4\}$ complexes with N atoms in pyramidal and/or planar coordinations.

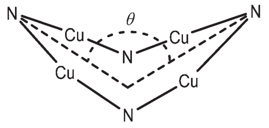


Fig. 5 One saddle angle (θ) shown of two possible within the $\{Cu_4N_4\}$ ring.

$[Cu_4(NMe_2)_4]$ and $[Cu_4(N\{c\text{-}(CH_2)_4\})_4]$[24] display planar geometries, the more sterically encumbered ethyl system $[Cu_4(NEt_2)_4]$ displays a saddle shaped geometry ($\theta = 141.87°$).[19c]

A survey of the Cambridge Structural Database[25] shows a number of complexes with $\{Cu_4X_4\}$ cores (X = 1st row element, *i.e.* B, C, N or O as part of an anionic ligand) which can similarly be categorised as having either an approximate D_{4h} or D_{2d} core arrangement. Computational studies have attributed this preference for Group 11 transition metals tetramers to form clusters with D_{4h}/D_{2d} geometry to a significant electrostatic stabilisation and a dominant effect of the Pauli repulsion between metal atoms.[26] This is in contrast to alkali metal tetramers, for which cubic geometries dominate and attractive electrostatic and orbital interaction terms compensate for large Pauli repulsion energies.[26] This is supported by the fact that while tetrahedral/cubic $\{M_4(NPR_3)_4\}$ systems (M = Li, K, Cs and Rb)[27] are known structurally, copper(I) based clusters with a central tetrahedral $\{Cu_4X_4\}$ core are not known in the literature in the absence of ancillary groups coordinating to the metal centre *i.e.* $[(L)CuX]_4$ systems (T_d symmetry, Fig. 3).

It has been suggested that the steric demands of the anionic ligand play a dominant role in the solid state conformation of the cluster rather than a saddle-like geometry being indicative of strong metallophilic interactions.[19a,c,d,24] However, the planarity of the $\{Cu_4\}$ rings in related clusters (and analogous Ag and Au systems) has also been attributed to a contribution from transition metal based σ-aromatic stabilisation resulting from a degree of cyclic electron conjugation within the cluster bonding (*vide infra*).[28]

In the cobalt and nickel phosphinimide complexes recently reported by Stryker *et al.*,[7] and related to **1** and **2**, saddled $\{Co_4N_4\}$ (saddle angle, $\theta = 112.5°$) and $\{Ni_4N_4\}$ ($\theta = 117.7°$) ring conformations are observed. The structures include two planar imido nitrogen atoms and two pyramidalised imido nitrogen atoms (Fig. 4, conformer E, for $\{Co_4N_4\}$ $\Sigma_N = 359.6°, 347.5°$; for $\{Ni_4N_4\}$ $\Sigma_N = 359.7°, 347.4°$). This geometry is suggested to result from repulsion between the bulky $\{NP^tBu_3\}$ groups. However, it is worth noting that the different planar and pyramidal environments at the imido nitrogen have no significant influence on the corresponding bond lengths involving these imido nitrogens.[7]

Hybrid-DFT studies

In order to provide further insight as to whether the planarity of the $\{Cu_4N_4\}$ ring present in the X-ray geometries of **1** and **2** is due to steric and/or electronic factors, geometry optimisations at the B3LYP/6-311G(d,p) level were carried out on **1** and **2**. Using the molecular geometries obtained from single crystal X-ray diffraction experiments as starting geometries, a *cis*, *trans*, *cis*, *trans*- (*c*,*t*,*c*,*t*-) orientation (conformer A, Fig. 4) and planarity was retained for complex **1**, but for complex **2** molecular rearrangement to a *trans*, *trans*, *trans*, *trans*- (*t*,*t*,*t*,*t*-) configuration (conformer B, Fig. 4) was observed upon optimisation with an average saddle angle of 159.4°. Selected parameters, for comparison between the experimental and computed geometries, are listed in Table 1 and reveal that bond lengths are consistently longer by 0.1 Å in the computed values giving some confidence in the accuracy of B3LYP/6-311G(d,p) for copper phosphinimides. Table 2 lists the sum of angles at the ring nitrogen atoms and the saddle angles for optimised geometries of $Cu_4(NR_2)_4$ systems investigated here. The sum of angles at the ring nitrogen atoms are all similar at 350.4–350.8° for the optimised and rearranged geometry of **2** and are close to the sum of angles of 342.4–352.3° found for nitrogen atoms in the experimental data. The barrier between these two conformers, A and B, in **2** must be small reflecting little steric influence of the PPh_3 groups.

Geometry optimisation of complex **1** starting with a *t*,*t*,*t*,*t*-conformer (B, Fig. 4), however, gave a minimum with a $\{Cu_4N_4\}$ ring containing a more acute saddle angle of $\theta = 132.6°$ compared to 159.4° for the optimised geometry of **2**. There are two planar imido nitrogens ($\Sigma_N = 353.9°, 360.0°$) and two pyramidal imido nitrogens ($\Sigma_N = 339.3°, 348.0°$) resulting in conformer E (Fig. 4). This shows significant steric repulsion

Table 2 Relative energies (in kcal mol^{-1}), saddle angle (θ in degrees°) of $\{Cu_4N_4\}$ rings, sum (∑) of angles (°) at N in $\{Cu_4N_4\}$ rings and nucleus-independent chemical shifts (NICS) in ppm for selected cyclic $Cu_4(NR_2)_4$ systems

R_2	Geometry	Rel. E.	Ring	Θ_1	Θ_2	∑N1	∑N2	∑N3	∑N4	NICS	Ref.
H_2			Planar	180.0	180.0					1.0	
Me_2			Planar	179.1	179.1					0.0	
Me_2 *(Expt)*			*Planar*	*180.0*	*180.0*						24
Et_2		0.00	Saddled	132.8	132.7					−1.7	
Et_2		1.11	Saddled	144.6	144.6					−2.0	
Et_2 *(Expt)*			*Saddled*	*141.9*	*141.9*						19*c*
$H(PH_3)^+$	*A*	1.20	Planar	180.0	180.0					−0.7	
$H(PH_3)^+$	*B*	0.00	Saddled	156.5	156.5					−0.8	
$H(PEt_3)^+$ *(Expt)*	*B*		*Saddled*	*125.8*	*125.8*						8
$H(PH_3)^+$	*C*	2.65	Planar	180.0	180.0					−0.7	
PH_3	A	0.06	Planar	179.9	179.9	356.7	356.5	356.6	356.5	1.2	
PH_3	B	0.00	Planar	179.1	179.1	356.0	356.1	356.1	356.0	1.3	
PH_3	C	0.16	Planar	180.0	180.0	357.5	357.5	357.5	357.5	1.3	
PH_3	D	1.17	Planar	180.0	180.0	360.0	360.0	360.0	360.0	1.4	
PMe_3	E		Saddled	166.3	166.3	358.9	347.7	349.7	356.8	1.0	
PEt_3	F		Saddled	151.1	149.9	359.9	347.9	331.6	350.9	0.1	
$P(NMe_2)_3$	A	3.06	Planar	180.0	180.0	356.6	346.3	356.5	346.3	0.2	
$P(NMe_2)_3$ **1** *(Expt)*	A		*Planar*	*180.0*	*180.0*	*355.3*	*343.6*	*355.3*	*343.6*		*ibid*
$P(NMe_2)_3$	E	0.00	Saddled	134.0	132.6	360.0	339.3	348.0	359.9	−0.2	
PPh_3	B		Saddled	159.4	159.3	350.4	350.8	350.6	350.7	1.6	
PPh_3 **2** *(Expt)*	A		*Planar*	*179.0*	*179.0*	*351.9*	*342.4*	*341.4*	*352.3*		*ibid*
CH_2	D		Planar	179.9	179.9	360.0	360.0	360.0	360.0	3.8	
CPh_2 *(Expt)*	D		*Saddled*	*138.1*	*138.6*	359.8	360.0	360.0	360.0		22

in accord with the higher Tolman cone angle for the bulky $P(NMe_2)_3$ groups compared to the PPh_3 groups,[29] thus resulting in a non-planar $\{Cu_4N_4\}$ ring containing planar imido nitrogens (conformer E).

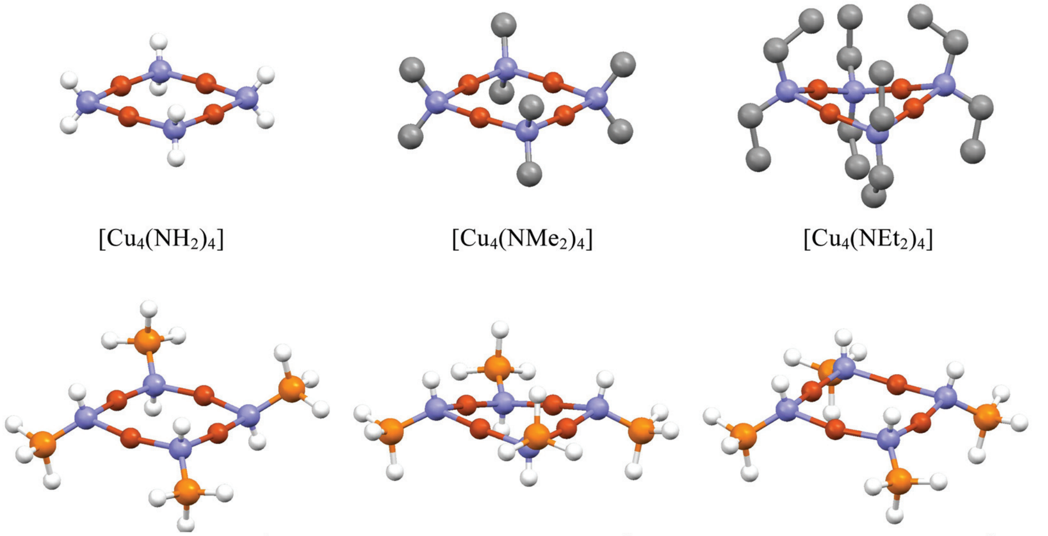
To our knowledge, there is only one comparable computational study[30] on $\{Cu_4N_4\}$ ring systems reported in the literature. The parent molecule $Cu_4(NH_2)_4$ at BP86/cc-pVDZ-PP was identified as saddled not planar. Several $\{Cu_4N_4\}$-containing structures with tetrahedral nitrogen atoms, such as $Cu_4(NMe_2)_4$, have been shown by X-ray crystallographic studies to be planar so the reported saddled form is surprising.

As B3LYP/6-311G(d,p) optimisations on the much more complex molecule **1** gave geometries in good agreement with experimental data (Table 1), B3LYP/6-311G(d,p) was used on simpler models with tetrahedral ring nitrogens to predict whether planar or saddled forms are in accord with experimental data. The results of $Cu_4(NR_2)_4$ are summarised in Table 2 where R is H, Me and Et and the optimised molecular geometries ae shown in Fig. 6.

With B3LYP/6-311G(d,p), the parent molecule $Cu_4(NH_2)_4$ is planar and attempts to locate the saddled form by starting with saddled geometries all resulted in the planar form. While this parent molecule has not been structurally determined experimentally, the methyl and ethyl analogues have been determined by X-ray crystallography. As already noted, the ethyl analogue $Cu_4(NEt_2)_4$ is saddled while the methyl analogue $Cu_4(NEt_2)_4$ is planar. Geometry optimisations of $Cu_4(NMe_2)_4$ and $Cu_4(NEt_2)_4$ only succeeded in locating planar and saddled minima respectively in total agreement with observed data. The presence of bulkier ethyl groups is clearly responsible for steric interactions between ligands leading to the saddled form being favoured over the planar form. The only structurally determined $\{Cu_4N_4\}$ system from copper and iminophosphorane prior to our work is the tetracation $[Cu_4(NHPEt_3)_4]^{4+}$ which is found in the saddled form.[8] The simpler model system $[Cu_4(NHPH_3)_4]^{4+}$ was looked at computationally to establish whether the saddled form can be attributed to the steric bulk of the ethyl groups or not. There are four possible conformers based on the positions of the PH_3 and H at the nitrogens – three based on conformers A–C were looked at (see Fig. 6). Conformer B was found to be the most stable conformer and saddled whereas the other two are planar. This suggests that the sterics of the ethyl groups are not a determining factor in this case.

Since our experimental results concern $\{Cu_4N_4\}$ systems with three-coordinate ring nitrogens (complexes **1** and **2**), several systems containing three-coordinate ring nitrogens (Table 2), including the parent system $[Cu_4(NPH_3)_4]$, were looked at in detail (see Fig. 7). Optimised geometries of $[Cu_4(NPH_3)_4]$ based on conformers A, B, C and D were obtained with C and D requiring symmetry constraints to avoid rearrangements to the more stable forms A and B. All contained planar $\{Cu_4N_4\}$ rings with near-planar nitrogen atoms for A, B and C. However, replacing hydrogens with methyl and ethyl groups gave optimised geometries with saddle angles of 166.3° (av) and 150.5° (av) respectively. Their planar forms could not be located from various starting planar geometries. It seems that even the less bulky PMe_3 groups are responsible for steric interactions leading to saddled $\{Cu_4N_4\}$ rings (Fig. 7). The planar forms observed experimentally for **1** and **2** seem to occur due to favourable packing of the PR_3 groups leading to planar $\{Cu_4N_4\}$ geometries.

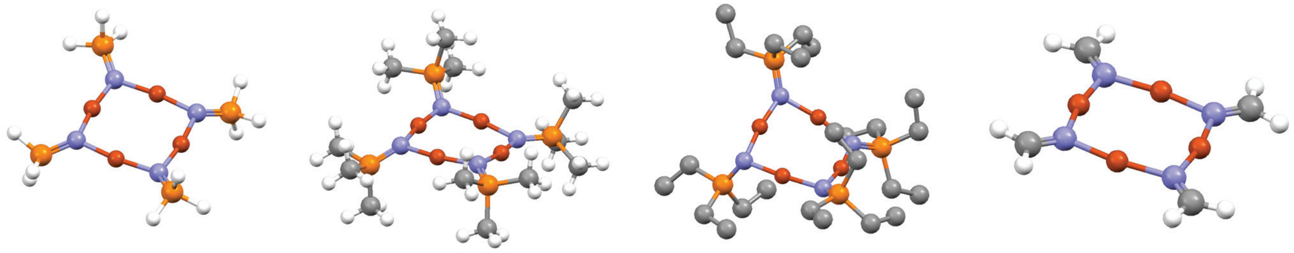
The $Cu_4(NCR_2)_4$ systems with $\{\mu\text{-}N{=}CR_2\}$ moieties resemble the $Cu_4(NPR_3)_4$ systems in that the ring nitrogen atoms are three-coordinate. The parent $Cu_4(NCH_2)_4$ is shown to be planar like $Cu_4(NPH_3)_4$ at B3LYP/6-311G(d,p), but inevi-



$[Cu_4(NH_2)_4]$ $[Cu_4(NMe_2)_4]$ $[Cu_4(NEt_2)_4]$

c,t,c,t-$[Cu_4(N(H)PH_3)_4]^{4+}$ (A) *t,t,t,t*-$[Cu_4(N(H)PH_3)_4]^{4+}$ (B) *c,c,c,c*-$[Cu_4(N(H)PH_3)_4]^{4+}$ (C)

Fig. 6 Diagrams showing the optimised molecular geometries of selected complexes containing 4-coordinate nitrogen ligands in $\{Cu_4N_4\}$ clusters. In the case of $[Cu_4(NMe_2)_4]$ and $[Cu_4(NEt_2)_4]$ hydrogen atoms have been omitted for clarity.



$[Cu_4(NPH_3)_4]$ (B) $[Cu_4(NPMe_3)_4]$ (E) $[Cu_4(NPEt_3)_4]$ (F) $[Cu_4(NCH_2)_4]$ (D)

Fig. 7 Diagrams showing the optimised molecular geometries of selected complexes containing 3-coordinate nitrogen ligands in $\{Cu_4N_4\}$ clusters. In the case of $[Cu_4(NPEt_3)_4]$ hydrogen atoms have been omitted for clarity.

tably replacing the hydrogens with bulkier substituents will cause steric repulsions resulting in saddled forms as found experimentally.

As noted above, there have been theoretical studies on $\{Cu_4\}$ ring systems that suggest aromatic stabilisation resulting from cyclic electron conjugation within the planar ring.[28] Here, the nucleus-independent chemical shift (NICS)[31] calculations were carried out as a measure of (anti)aromaticity in **1**, **2** and the related $\{Cu_4N_4\}$ systems listed in Table 2. At the B3LYP/6-311G(d,p) level, benzene has a NICS value of −8.9 ppm and cyclobutadiene of 25.4 ppm which reflect aromatic and antiaromatic character respectively. The optimised geometries of **1** and **2** have values close to zero (0.2 and 1.6 ppm, respectively) indicative of have negligible aromaticity or antiaromaticity. The saddled form of **1** has a NICS value of −0.2 ppm which shows that the saddled form is slightly more aromatic than the planar form of **1** (0.2 ppm). Any degree of aromaticity as a result of the planarity in the $\{Cu_4N_4\}$ ring is not supported here. While different functionals and basis sets have been used, the reported NICS value for the saddled $Cu_4(NH_2)_4$ geometry is −1.7 ppm compared to 1.3 ppm here for the planar form *i.e.* again, the saddled form is more 'aromatic'. Our computations suggest that the preference for planarity in the parent systems, where there are no steric effects from the ligand substituents, is very unlikely to be due to ring aromaticity based on the NICS data.

In conclusion, the planar geometries observed in the solid state structures of **1** and **2** arise from the 'tuned' steric demands of the phosphinimide ligands rather than on the basis of either strong Cu⋯Cu interactions and σ-bond delocalisation.[32] Sterics are clearly important in determining the planarity of the $\{Cu_4N_4\}$ ring in $\{Cu_4N_4\}$ systems while according to computations here the planar forms are favoured in neutral parent $\{Cu_4N_4\}$ systems.

Experimental section

General remarks

All manipulations were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk and glove-box techniques. Toluene and hexane were dried using an Innovative Technology Inc. solvent purification system (SPS) system and degassed under dinitrogen or argon prior to use. The starting materials, CuMes[33] and $HNPPh_3$[34] were prepared using literature procedures. $HP(NMe_2)_3$, was purchased from Sigma-Aldrich and used as received. NMR spectra were recorded at 298 K on Bruker Avance 500 and 400 MHz NMR spectrometers and referenced as follows for ^1H and $^{13}C\{^1H\}$ spectra: benzene (^1H, δ = 7.16 ppm; ^{13}C, δ = 128.0 ppm) d^2-dichloromethane (^1H, δ = 5.32 ppm; ^{13}C, δ = 53.84 ppm). $^{31}P\{^1H\}$ NMR chemical shifts were referenced to 85% H_3PO_4 (δ = 0.0 ppm). Elemental analyses were performed externally by the London Metropolitan University Microanalysis Service.

Syntheses of complexes

$[Cu(\mu_2\text{-}NP(NMe_2)_3)]_4$ (1). $HNP(NMe_2)_3$ (2 mmol, 0.34 g), was added to a toluene solution (10 ml) of [CuMes] (2 mmol, 0.37 g), at ambient temperature. The reaction mixture was allowed to stir for 2 hr. The solvent was removed under reduced pressure. The residue was re-dissolved in a minimum of fresh toluene (10 ml) with gentle heating. The solution was filtered hot to remove insoluble residues. A colourless crystalline solid was obtained on standing for 24 h at −20 °C. The solid was collected by filtration, washed with cold hexane, and dried *in vacuo*. Yield: 0.38 g, 78%. Anal. Calcd for $C_{24}H_{72}Cu_4N_{16}P_4$: C, 29.93; H, 7.54; N, 23.27: Found: C, 30.04; H, 7.59; N, 23.31; ^1H NMR, C_6D_6 (ppm): δ 2.72 (d, $^3J_{P-H}$ = 9.6 Hz); $^{31}P\{^1H\}$: δ 32.9 (s); $^{13}C\{^1H\}$ NMR: δ 38.4 (br,s). Calculated GIAO-NMR: ^{31}P: δ 35.0 (conformer A), 33.9 (conformer B); ^{13}C: 38.7 (conformer A), 37.8 (conformer B).

$[Cu(\mu_2\text{-}NPPh_3)]_4$ (2). Complex **2** was synthesised in an analogous fashion to complex **1** using $HNPPh_3$ (2 mmol, 0.55 g) to afford **3** as pale yellow crystals. Yield: 1.74 g, 70%. Anal. Calc. for $C_{72}H_{60}Cu_4N_4P_4\cdot(C_7H_8)_{0.5}$: C, 64.52, H, 4.59, N, 3.99, found: C, 64.26, H, 4.61, N, 4.02%. ^1H NMR, CD_2Cl_2 (ppm): δ 6.94–7.05 (m, 6H, *meta*-Ar–C*H*), 7.15–7.25 (m, 3H, *para*-Ar–C*H*), 7.14–7.52 (m, 6H, *ortho*-Ar–C*H*); $^{31}P\{^1H\}$: δ 15.9 (s); $^{13}C\{^1H\}$ NMR: δ 128.4 (d, $^2J_{C-P}$ = 12.1 Hz, *meta*-CH), 130.6 (s, *para*-CH), 132.6 (d, $^3J_{C-P}$ = 9 Hz, *ortho*-CH), 138.4 (d, $^1J_{C-P}$ = 94.4 Hz, *ipso*-CH). Calculated GIAO-NMR: ^{31}P: δ 16.4; ^{13}C: 129.6 (*meta*), 133.5 (*para*), 136.5 (*ortho*), 145.6 (*ipso*).

Table 3 Crystal data and structure refinement for compounds **1** and **2**

Compound	**1**	**2**
Chemical formula	$C_{12}H_{36}Cu_2N_8P_2$	$C_{75\cdot 50}H_{64}Cu_4N_4P_4$
Formula mass	481.51	1405.35
Crystal system	Monoclinic	Monoclinic
a/Å	13.2320(1)	9.1310(4)
b/Å	13.9940(2)	24.407(1)
c/Å	13.3030(2)	29.4590(7)
α/°	90.00	90.00
β/°	117.240(2)	98.382(2)
γ/°	90.00	90.00
Unit cell volume/Å^3	2190.11(5)	6495.1(4)
Temperature/K	150(2)	150(2)
Space group	$P21/n$	$P21/c$
No. of formula units per unit cell, Z	4	4
Absorption coefficient, μ/mm^{-1}	2.100	1.438
No. of reflections measured	17 527	24 762
No. of independent reflections	4667	10 711
R_{int}	0.0475	0.0645
Final R_1 values ($I > 2\sigma(I)$)	0.0289	0.0490
Final wR (F^2) values ($I > 2\sigma(I)$)	0.0760	0.1073
Final R_1 values (all data)	0.0329	0.0951
Final wR (F^2) values (all data)	0.0793	0.1280
Goodness-of-fit on F^2	1.064	1.081
Largest diff. peak and hole/e Å^{-3}	0.702, −0.530	0.959, −0.436
CCDC reference number	955629	955630

Single crystal X-ray crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 3. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-Kα radiation (λ = 0.71073 Å). Structure solution and refinements were performed using SHELX86[35] and SHELX97[36] software, respectively. Corrections for absorption were made in all cases. Data were processed using the Nonius Software.[37] Structure solution,[38] followed by full-matrix least squares refinement[36b] was performed using the WINGX-1.80 suite of programs throughout.[39] For all complexes, hydrogen atoms were included at calculated positions. Crystals of the complex **2** were both small and weakly diffracting, with intensity loss at higher 2-theta angle. Hence a data completeness of >93.5% (max 2θ = 25.0 °) could not be met. The CCDC reference numbers for **1** and **2** are 955629 and 955630 respectively.

Computational studies

Calculations were carried out using the Gaussian09 package.[40] All starting geometries of **1**, **2** and related systems were optimised without symmetry constraints at B3LYP/6-311G(d,p) level of theory.[41] No imaginary frequencies were found from frequency calculations on these optimised geometries and indicate that the geometries are true minima. Symmetry constraints were however applied to conformers C (C_{4v}) and D (C_{4h}) of $Cu_4(NPH_3)_4$. NICS values were obtained from dummy atoms placed in the centre of the {Cu_4} rings using the GIAO[42]-NMR method at B3LYP/6-311G(d,p). Calculated ^{31} GIAO-NMR chemical shifts were obtained using the $\delta(^{31}P) = 310.0 - \sigma(^{31}P)$ scale while the ^{13}C shifts were calculated using the $\delta(^{13}C) = 182.5 - \sigma(^{31}C)$ scale.

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